

# High Temperature Corrosion in Molten Salts

*Edited by:*

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## PREFACE

Numerous commercial processes operate at temperatures exceeding 500 °C. In industry these processes include refinery plants (~500 °C), pulp and paper production (~700 °C), nitric acid production (~900 °C), heat-treatment (~1000 °C), and ethylene pyrolysis (~1000 °C). In the power sector they include waste incinerators (~500 °C), coal gasification systems (~600 °C), fluidised-bed combustion systems (~800 °C), fuel cells (~800 °C), and gas turbines (~1000 °C). Materials used in high-temperature structures have design constraints additional to those of materials used at or near room temperature. Three important additional constraints are time-dependent inelastic strain (creep), thermal stability of microstructure, and high-temperature corrosion. The inclusion of these constraints with the constraints of low cost, strength, toughness, machinability, formability, weldability, or some combination of these, has led to the intensive development over the past 50 years of a large group of metallic materials generally referred to as 'high-temperature alloys'. Included in this group are iron-, nickel- or cobalt-based alloys containing >20% chromium (or 30% for cobalt), metallic glasses or rapidly solidified materials, metal matrix composites, ceramic materials and various coatings used for protection against high-temperature corrosion.

There are certain distinguishing features about the morphology of high-temperature corrosion that aid in deciding upon the cause of damage. Some typical indications include thick scales, grossly thinned metal, burnt (blackened) or charred surfaces, molten phases, deposits of various colours, distortion and cracking, and magnetism in what was first a non-magnetic (e.g., austenitic) matrix.

Damage varies significantly based upon the environment, and will be most severe when a material's oxidation limits are exceeded, notably when an alloy sustains breakaway attack by oxygen/sulphur, halogen/oxygen, low-melting fluxing salts, molten glasses, or molten metals, especially after fires.

Oxidation, sulphidation, halogenation, carburisation, and nitriding are modes of corrosion found in many industrial processes. These corrosion problems are discussed in many excellent review papers and books.

Deposits are a common product in the metallurgical industry (steel reheating furnaces), in waste incineration (municipal wastes), in the manufacture of glass (fiberglass), in the pulp and paper industry (recovery boilers), and in many power and energy sectors (coal, oil and fluidised-bed systems, gas turbine and diesel engine systems, nuclear power systems). A whole series of reactions is possible should deposits become molten or semi-molten and no single mechanism can be applied generally to characterize such damage.

The mechanisms of molten product corrosion are complex. The types of damage include fuel-ash corrosion (sulphates, including acid and basic fluxing reactions, and vanadic slag attack), molten salt corrosion (chlorides, nitrates, and carbonates), and molten glass corrosion. Liquid metal attack is yet another special category.

Fuel-ash or ash/salt-deposit corrosion stems from high-temperature corrosion processes associated with fuel combustion products in boilers, waste incinerators, and gas turbines. Thus, products can include various deposits (oxidizing or reducing) with active contributions from oxygen, sulphur, halogens, carbon, and nitrogen. Typically, alloy matrices display intergranular attack (oxides and chlorides) beneath disturbed oxide layers possibly fused with molten deposits and internal sulphides within the alloy-affected zone.

Hot corrosion is generally regarded as attack in the joint presence of sulphur and oxygen. Typically, attack is considered to be triggered by molten alkali metal salts that melt above 700 °C.

Sodium sulphate, with a melting point of 884 °C, derived from sodium chloride and sulphur from the fuel, is considered to be closely involved in the mechanism of hot corrosion. This mechanism is considered to have four stages: oxidation (incubation); mild sulphidation; oxide failure; and catastrophic attack (internal sulphides via a porous voluminous complex oxide/deposit layer). Hot corrosion is an irreversible autocatalytic process.

Vanadic slag corrosion occurs following combustion of certain low-grade or residual fuel oils that are of high vanadium, sulphur, and alkali metals. The molten sodium vanadyl vanadates typically flux away protective oxides and then rapidly dissolve the metal. Many high-temperature alloys cannot survive 100 h at 900 °C in vanadic slags.

Molten glass typically induces intergranular attack with voids (from volatile halides) and sulphides. Oxides are generally fused into the glass. Attack is commonly rapid, and high chromium-nickel-based alloys are usually employed.

Molten salts, used for heat treating applications, nuclear engineering, solar cells, and metal extraction, generally promote intergranular attack in alloys, often with voids and internal low-melting products (halides).

The purpose of this book is to provide chemical, metallurgical and materials scientists and engineers with up-to-date corrosion data pertinent to academic studies and industrial problems found in pure molten salts and ash/salt deposit environments. Essentially the book covers some key aspects of corrosion reactions in molten deposits and provides engineering data to help in making a choice of candidate materials for high-temperature service in such process conditions.

The editor would like to acknowledge the review articles, research articles, and mixed review-research articles of the many talented contributors to this book which, it is believed, would make it interesting and timely to high-temperature corrosion specialists in industry as well as academia. Appreciation is also expressed to his wife, Maria Elisa, for her understanding, encouragement, and support during the course of this work.

César Sequeira

Lisbon, January 2003



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## **FIRST PART**

### **FUNDAMENTALS**

# Fundamentals of Molten Salt Corrosion

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**Keywords:** Carbonates, Chlorides, Commercial Alloys, Corrosion, Electrochemistry, Fluorides, Hydroxides, Kinetics, Molten Salts, Nitrates, Nitrites, Sulphates, Thermodynamics, Vanadates

**Abstract** The processes of high temperature corrosion in molten salts are reviewed to reveal the progress in understanding the reaction mechanisms proposed in the last three decades. Thermodynamic and kinetic analyses of the corrosion processes are outlined. The results of numerous investigations concerning the corrosion of metals and alloys in fused salts are also summarized.

## 1. Introduction

Interest in the use of molten or fused salts in industrial processes is continually increasing and these media are gradually becoming accepted as a normal field of chemical engineering. The change is being accelerated by the increasing demand for the production of refractory metals, actinides, lanthanides, transition, and light metals by processes involving fused salts, the use of molten salts in high-temperature batteries and fuel cells, and also by the novel chemical engineering techniques which have been developed in the nuclear-energy industry [1]. For example, a nuclear reactor using molten fluorides as a fluid fuel has operated, and this has involved the use of pumps, heat exchangers and similar equipment to circulate the high temperature melt [2].

In certain applications it has not always been easy to find suitable metallic container materials, particularly in the nuclear-energy industry, where, for certain applications, corrosion resistance of the same order as that required by the fine chemical industry has to be achieved in order to prevent contamination of the process stream. Such difficulties have stimulated the study of corrosion in fused salts and have led to a fairly high degree of understanding of corrosion reactions in these media.

The subject is also closely related to fuel-ash corrosion observed in oil fired refinery boilers, hot corrosion observed in gas turbines, and other molten or semi-molten deposit corrosion observed in waste incineration systems, etc. [3,4]. Attention has been focused on the electrochemistry of these types of deposit corrosion [5-8] and the relevant thermodynamic data summarised in the form of diagrams [9-15]. Fluxing and descaling reactions also resemble, in some aspects, reactions occurring during the corrosion of metals in fused salts.

There are two cases in which a metal can be attacked by a salt melt: if it is soluble in the melt, or if it is oxidised to metal ions. In the first case, attack occurs by direct dissolution without oxidation of the metal and the mechanism is likely to be closely similar to attack by liquid metals.

If the solubility is appreciable, excessive corrosion can be expected, but with few exceptions metals appear to be appreciably soluble only in their own salts. Most of the metals of the first and second groups of the periodic table are soluble in their own halides, and, in certain cases, there is complete miscibility at high temperatures [16-18].

Many hundreds of molten salt-metal corrosion studies have been documented. Helpful publications are those of Janz and Tompkins [19], Inman and Lovering [20], Allen and Janz [21], Gale and Lovering [22], Kofstad [23], Lai [24], Rahmel and Schwenk [25], Birks and Meier [26], Rapp [27,28], Schütze [29], Rahmel [30], Numata [31], and Rameau et al. [32]. Although the literature related to studies of corrosion in molten salts is extensive, there is still a strong need for intensive research in this field. The present article focuses on key aspects of molten salt corrosion processes, and on corrosion data useful in selecting high temperature materials. Of course, since little information on corrosion involving only metal solubility effects is available, the present study will be confined to corrosion arising as a result of oxidation of the metallic material to ions.

## 2. Corrosion Process

Molten salts are a class of high-temperature liquids which range from the low melting systems such as the  $\text{LiNO}_3\text{-KNO}_3$  eutectic (m.p.  $120^\circ\text{C}$ ) and molten organic salts to the high melting systems of molten metal oxides some of which have melting points in excess of  $1400^\circ\text{C}$ . Three broad classes of molten salts may be distinguished. These are the simple ionic liquids such as molten halides and halide mixtures, the simple oxyanionic liquids such as molten nitrates, sulphates and carbonates, and the complex polymeric oxyanionic liquids such as molten phosphates, borates and silicates. Molten halides and oxysalts are the most interesting melts with regard to their occurrence in molten salt corrosion processes.

Molten salts are liquids with some characteristics that are different from those of liquids at room temperature. Molten salt studies are very important for understanding the liquid state because molten salts consist of ions, and the principal forces between particles are coulombic interactions. The existence of coulombic interactions in molten salts are demonstrated by very high melting and boiling points, surface tensions and electrical conductivities, in comparison with these properties of other liquids. Other properties of the pure molten salts, or ionic liquids, or molten electrolytes, are of the same order of magnitude as for nonpolar liquids, although the ionic liquids exist only at high temperatures. These properties are density, viscosity, refractive index, compressibility, vapour pressure, heat of vaporization, heat of fusion, heat capacity, etc. [33-37].

In general, the ionic character of the solid crystalline form persists in the molten state, although local association reactions may take place. The range of co-existence of metal-molten salt systems depends on two simple factors namely the relative electronation-deelectronation potentials of the various constituents and their relative basicities. A measure of the basic or acidic strength of the system is given by

$$\text{pO}^{2-} = -\log \{\text{O}^{2-}\} \quad (1)$$

$\text{pO}^{2-}$  is equivalent to the pH for protolytic solvents. A high value of  $\text{pO}^{2-}$  indicates an acidic (and corrosive to metals) melt and a low value a basic melt. The self-dissociation constants of pure oxyanionic melts indicate the acidic strengths of the liquids.  $\text{pO}^{2-}$  for  $\text{CO}_3^{2-} < \text{SO}_4^{2-} < \text{NO}_3^-$ . This shows that molten nitrates are more acidic than molten carbonates (at comparable temperatures).  $\text{pO}^{2-}$  values for oxyanionic species in dilute solution provide a useful means for predicting acid-base reactions between different species. The numerical value of the term  $\text{pO}^{2-}$  will depend upon the units of concentration employed: convenient ones are molarities, molalities, mole fractions or mole ratios.

Trémillon [38] has reviewed acid-base reactions in fused salts. Bombara et al. [10], Burrows and Hills [5,39], Cutler et al. [40], Inman and Wrench [11], and Lewis [41] have discussed corrosion in fused salts in terms of acid-base properties of the melts. There have been many different methods used in the determination of  $\text{pO}^{2-}$  values. Most of the measurements have been

restricted to the low temperature systems of molten nitrates and chlorides. Acid-base reactions in molten sulphates are not so well documented.

The high electrical conductivity of many molten salts makes them particularly suitable as media for electrochemical investigation [37].

Electrochemical studies in oxyanion melts have been initially confined to nitrate and carbonate systems. Nitrates, being low melting, are convenient media to work with and carbonates have considerable technological importance as electrolytes for high temperature fuel cells. Molten sulphates have low vapour pressure and high melting points and their thermal stability depends on the nature of cations, alkali sulphates being the more stable. They appear to be convenient media for electrochemical studies [42] and they have received much attention due to their practical importance. For example, the sulphate-chloride provides a molten salt system over a wide range of temperatures relevant to gas turbine conditions, thus promoting many studies [43]. It follows from what has been said that effects analogous to "electrochemical" or "oxygen-concentration" corrosion in aqueous systems can occur in salt melts. Accordingly, in metal/melt systems one possible way of ensuring adequate corrosion resistance is to choose conditions such that the metal is passive, which requires that it should become covered with an adherent, compact, insoluble film or deposit, preventing direct contact of the metal with its environment. Any melt that reacts with a metal to give a corrosion product insoluble in the melt is in principle capable of passivating the metal, e.g. passivity can be expected to occur in oxidising salts in which metal oxides are sparingly soluble. Thus, iron is highly resistant to alkali nitrate melts because it becomes passive, and passivity has also been observed by electrode potential measurements of an iron electrode in chloride melts containing nitrates [44], although in this case the oxide corrosion product is not particularly protective. In general, fused salts are "good" solvents for inorganic compounds so that passivity is not likely to be a widely encountered phenomenon.

"Wash-line" attack is also a common feature of corrosion by molten salts in contact with air, because the anodic and cathodic reactions will not necessarily occur at the same metal site, and "anodic" and "cathodic" areas can develop as in aqueous solutions.

When a temperature gradient exists in a system containing metal in contact with molten salt, thermal potentials are set up, causing removal of metal at high-temperature points and deposition of metal at cooler places [45,46]. This mass transfer is essentially different in nature from that met in liquid-metal corrosion, which is simply a temperature-solubility effect. In fused salts, both the corrosion and deposition reactions are electrolytic, and it has been shown that an electrical path is necessary between the hot and cold regions of the metal. Edeleanu and Gibson suggest that this type of mass transfer be called "*Faradaic mass transfer*" to indicate that it requires an electrolytic current [47].

Mass-transfer deposits can lead to blockages in non-isothermal circulating systems, as in the case of liquid-metal corrosion. In fused salts, the effect can be reduced by keeping contamination of the melt by metal ions to a minimum; e.g. by eliminating oxidising impurities or by maintaining reducing conditions over the melt [46].

Corrosion of alloys at high temperatures is complicated by effects due to diffusion, particularly where the alloy components have different affinities for the environment, and corrosion of an alloy in a fused salt at high temperature often exhibits features similar to those of internal oxidation. Selective removal of the less noble component occurs, and as it diffuses outwards, vacancies move inwards and segregate to form visible voids (Kirkendall effect). Since diffusion rates are faster at grain boundaries than in the grains, voids tend to form at the grain boundaries and specimens often have the appearance of having undergone ordinary intercrystalline corrosion. More careful examination has shown, however, that in the case of Fe-18Cr-8Ni corroding in a fused 50-50 NaCl/KCl melt at 800°C in the presence of air, the attack is not continuous at the boundaries, and the voids formed are not in communication with each other [48]. In high-nickel alloys, a greater proportion of voids is formed within the grains and the appearance of intercrystalline attack is less marked [48-51]. When Inconel is exposed to fused sodium hydroxide, a two-phase corrosion-

product layer is formed, resulting from growth of the reaction product – a mixture of oxides and oxysalts – into the network of channels [50].

Selective removal of the less noble constituent has been demonstrated by chemical analysis in the case of nickel-rich alloys in fused caustic soda [49-51] or fused fluorides, and by etching effects and X-ray microanalysis for Fe-18Cr-8Ni steels in fused alkali chlorides [48]. This type of excessive damage can occur with quite small total amounts of corrosion, and in this sense its effect on the mechanical properties of the alloy is comparable with the notorious effect of intercrystalline disintegration in the stainless steels.

### 3. Thermodynamic Diagrams

The thermodynamic diagrams of Pourbaix [52] have been particularly useful in understanding the behaviour of metals in contact with aqueous solutions. Pourbaix plots equilibrium potential against pH, and the diagrams divide themselves into regions of stability of different solid phases (compounds of the metal in question).

In molten salts also, free energies can be expressed as equilibrium potentials, and there are a number of functions of composition that might be used as the other variable. The oxygen ions are generally quite important in matters of molten salt corrosion, so the function  $pO^{2-}$  (defined by the expression 1) is often used as the equivalent to the pH in aqueous environments [53]. A typical E versus  $pO^{2-}$  diagram for iron in molten sodium sulphate at 900°C is shown in Fig. 1 [14]. Areas of corrosion, immunity, and passivation are evident.

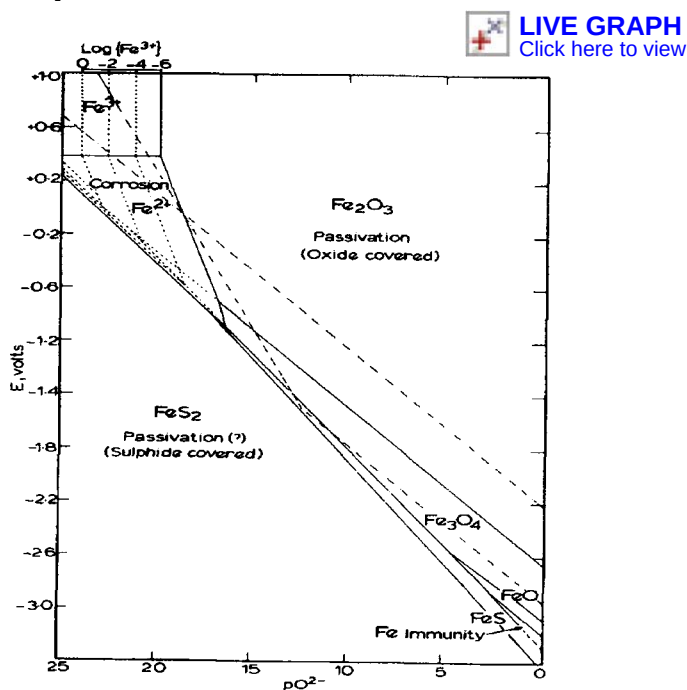


Fig. 1 Typical E versus  $pO^{2-}$  diagram for iron in molten sodium sulphate at 900°C [14]

In the construction of E/ $pO^{2-}$  diagrams there are two basic requirements, a reference scale of potential and a suitable standard state for oxidation activity. The first requirement has been satisfied by setting  $E^{\circ} = 0$  and  $dE^{\circ}/dT = 0$  for an appropriate reference electrode in the melt under

consideration. For example, for nitrate and sulphate melts the following electrode processes were assumed as basis for corresponding reference electrodes in these melts [14,54]:



The second requirement is rather more difficult to fulfil since a satisfactory and unambiguous oxygen electrode of the type



is not yet experimentally established in oxyanionic melts. In fact, apart from other difficulties, peroxide and superoxide ions have been identified in the melts [18,55,56], which enhances the problem.

Actually, the E versus  $\text{pO}^{2-}$  diagram is probably more useful than the Pourbaix diagram because of the absence of kinetic limitations at elevated temperatures. The following problems, however, do exist:

- Molten salt electrode reactions and the concomitant thermodynamic data are not readily available.
- Products from the reactions are often lost by vaporization.
- Diagrams based on pure component thermodynamic data are unrealistic because of departure from ideality.
- Lack of passivity even where predictions would show passive behaviour.
- The stable existence of oxides other than the  $\text{O}^{2-}$  species.

#### 4. Corrosion Rate Measurements

From what has been said already, it is clear that determinations of “corrosion rates” from small-scale experiments must be treated with great caution. If the metal cannot passivate, it will corrode until it becomes immune, at which point the corrosion rate will fall to zero; between initial exposure and the attainment of immunity the corrosion rate will be continually changing. If on the other hand, it is impossible for the metal to come to equilibrium with the melt, then the rate of corrosion, although probably constant, will be primarily controlled by diffusion and interphase mass transfer rates, and the geometry of the system will be an overriding factor. For this reason, it is not always possible to correlate the results of different workers under apparently similar conditions, nor can such results be expected to correspond particularly closely to the amount of corrosion encountered in larger-scale apparatus.

It is not worthwhile, therefore, to give a digest of experimentally determined corrosion rates, but the reader is referred to typical data [19,46,48-51,57-67] for further information on this topic.

One interesting feature of comparative experiments with a series of salts having a common anion is that the aggressiveness of the salts towards metals is dependent on the nature of the cation. The aggressiveness of chloride melts in contact with air is in the order [58,62]:



In the case of  $\text{CaCl}_2$  and  $\text{NaCl}$ , the order corresponds with the corrosion behaviour expected from cathodic polarization curves [58]. The order of aggressiveness of chlorides can also be explained on the basis of redox potentials of the melts, calculated on thermodynamic grounds from the free energies of formation of the appropriate oxides and chlorides [53]. The order of aggressiveness of nitrates is complicated by passivity effects [68], while that of alkalis in contact with air is [69]:





This is the reverse order of the aggressiveness of chlorides and indicates that the mechanism of corrosion in the two systems is different, i.e. in the latter case it involves the discharge of hydrogen as in acid aqueous solutions.

## 5. Test Methods

A number of kinetic and thermodynamic studies have been carried out in capsule-type containers. These studies can determine the nature of the corroding species and the corrosion products under static isothermal conditions and do provide some much-needed information. However, to provide the information needed for an actual flowing system, corrosion studies must be conducted in thermal convection loops or forced convection loops, which will include the effects of thermal gradients, flow, chemistry changes, and surface area effects. These loops can also include electrochemical probes and gas monitors [70].

The corrosion process is mainly electrochemical in nature because of the excellent ionic conductivity of most molten salts. Therefore, the techniques and processes used in the electrochemical area to study processes in molten electrolytes also apply to studies of molten salt corrosion. Furnaces, cells, electrodes and purification are particularly important aspects and deserve the following information.

Furnace and controls: The general experimental procedures in molten salt electrochemistry are common to most high-temperature measurements and have been extensively reviewed by Bockris, White and MacKenzie [71].

The most common type of high-temperature apparatus is based on the conventional vertical wire-wound furnace, which is cheap to build, and simple and safe to operate up to 1600°C. The heating element of Nichrome, Kanthal, or molybdenum strip, etc., is wound on a refractory tube, and embedded in thermal insulant.

Metallic shields should be placed inside the refractory tube primarily to reduce electrical noise and also to smooth out temperature gradients within the hot zone of the furnace. Temperatures are measured by chromel-alumel or platinum-platinum 13 per cent rhodium thermocouples sheathed in pyrex, supremax or alumina depending on temperature. Proportional or high-low controllers usually control furnace temperatures.

Electrochemical cell: Molten salt systems are normally contained in sealed envelopes of glass, silica or alumina, depending on the temperature. Electrodes can be introduced through ground glass joints placed on the cold side of the cell, without losing the controlled atmosphere in the envelope. The choice of materials directly in contact with the melt is particularly important since "acidic" materials like silica can modify the  $\text{pO}_2$  of the melt through their buffering action: hence metallic (platinum, gold) containers are preferable. However, non-metallic containers (especially of recrystallised alumina) have been widely used [37,39,43,72,73]. A typical high temperature cell assembly is shown in Fig. 2 [74].

Electrodes: Gold, silver, and most commonly, platinum, as foil or wire, are employed for redox (electronation-deelectronation) electrodes as well as for counterelectrodes. When the melt container is metallic it may also act as the counterelectrode. The working metal electrodes may be in form of rod, foil or wire; their adequate insulation, at lower temperatures, can be obtained with a refractory insulator (e.g. boron nitride insulating shield) [72], and, above 800°C, it is thought that the use of cordierite will avoid the triple contact metal-melt-atmosphere, suppress possible crevices on the edges of the metal electrode and would keep constant the exposed area of the specimen. Cordierite

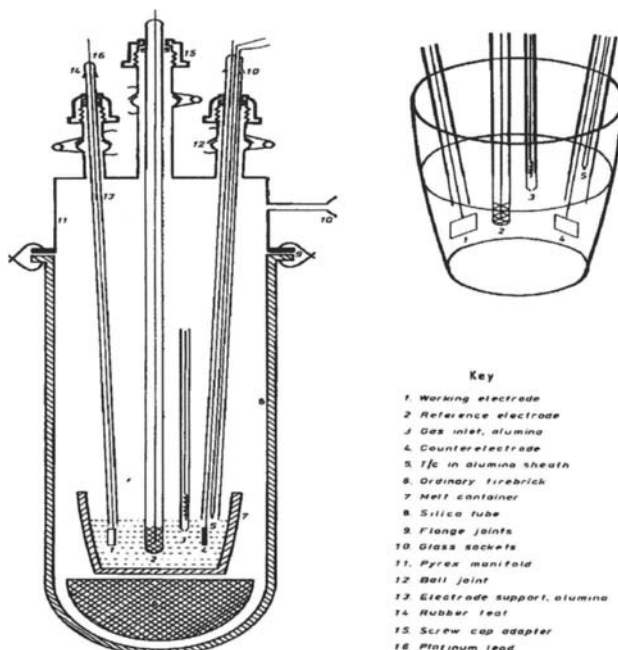


Fig. 2 Typical high temperature cell assembly [74]

bodies of general formula  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$  in addition to imperviousness to moisture, high surface resistance, high mechanical strength and high puncture strength, are characterised by a low glassy content and a low amount of alkali so as to ensure negligible ionic conductivity. In our laboratory, cordierite specimens were tested for sulphate attack at  $T > 800^\circ\text{C}$ , crucible experiments still being used. These tests showed cordierite to be completely insoluble and highly thermal-shock resistant in  $\text{Na}_2\text{SO}_4$ - $\text{NaCl}$  melts, so the production of a cordierite gasket was developed and a specimen holder was proposed as illustrated in Fig. 3.

**Reference electrodes:** The behaviour of a working electrode, either anode or cathode, is usually studied by measuring its potential with reference to a third electrode at constant potential, and the main problem in carrying out such electrochemical measurements in molten salts has been the development of a suitable reference electrode.

Minh and Redey [75] have published an extensive chapter on molten-salt reference electrodes. The commonest type of reference electrode in fused salts is a silver wire in contact with a solution of silver ions of known concentration in the solvent and separated from the bulk melt by a conductive barrier [76].

A paper by Danner and Rey [77] describes a silver-silver sulphate reference electrode system useful to  $1300^\circ\text{C}$ . Above the melting point of silver, a liquid silver pool was employed. This electrode was found to be the most satisfactory reference electrode for use in sulphate melts at temperatures up to  $1000^\circ\text{C}$  [39,42,78,79].

It consists of a silver wire dipped into a solution of silver sulphate in  $\text{Li}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$  eutectic (m.p.  $535^\circ\text{C}$ ) in concentration ranging from 1 to 10 mol. % and isolated from the melt by a pythagoras sheath:

Ag | 1-10% solution of  $\text{Ag}_2\text{SO}_4$  in  $\text{Li}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$  eutectic | pythagoras sheath |

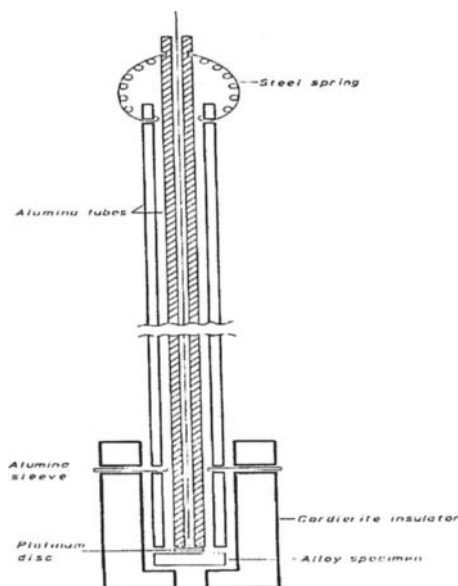


Fig. 3 Proposed specimen holder for corrosion studies in sulphate melts

The pythagoras porcelain acts as a solid  $K^+$ -ion conducting membrane. Pythagoras may be replaced by mullite ( $2Al_2O_3 \cdot SiO_2$ ), pyrex or suprema glass at lower temperatures. The mullite sheath is conductive to sodium ions and it was verified that it stood up well to the melt [73,80]. Pyrex or suprema glass rapidly develops a brown colouration and corresponding reference electrode potentials drift with time [42]. Dissolved silver sulphate may be obtained either through anodic dissolution of a silver wire (which sometimes is difficult because no satisfactory container for the cathode compartment can be found) or by simple dissolution of silver sulphate. A white precipitate of silver sulphate may be prepared by the addition of Analar sulphuric acid to an aqueous solution of Analar silver nitrate. Addition of silver ions to the solution by dissolution of silver oxide must be avoided because it decomposes thermally at  $340^\circ C$ . The concentration of  $Ag_2SO_4$  must be large enough to buffer the system but not so large as to cause a significant liquid junction potential.

For measurements over the longer periods of time, Rahmel [79] recommends use of electrodes with more than 1 mol. %  $Ag_2SO_4$  because of their higher potential stability. The atmosphere inside the reference half-cell may or may not be controlled and maintained in static or dynamic (slow bubbling) conditions. A criterion of the thermodynamically reversible e.m.f. properties of such reference electrodes are the micro-polarization test [81]. The relatively poor performance of these electrodes may be discerned in the local recrystallizations of the silver wire [39] as well as in the decrease of the resistivity of the diaphragm over a period of days.

A reference electrode (Fig. 4) has been developed by Sequeira and Hocking [74] which is similar to that described by Danner and Rey [77], but differs in that the pythagoras capsule used by them is replaced by a mullite capsule conductive to sodium cations. Mullite has relatively poor thermal shock resistance and the capsules fractured if brought from  $900^\circ C$  to room temperature in much less than 1 hour, with  $Na_2SO_4$ . Crucible tests showed that mullite is slightly dissolved in molten  $Na_2SO_4$  (see Table I) but the weight loss decreases strongly with time (as it is shown in Table 2) so that the mullite sheaths are useful, after ageing, as membrane junctions for the reference half-cells. Therefore, the main advantages of the mullite electrode are that it is not so reactive with the molten  $Na_2SO_4$  as the pythagoras electrode, and it is reversible to sodium ions in the melt under

study. In common with the Danner electrodes, it also has the advantage that salts in the sheath cannot intermix with those outside the sheath.

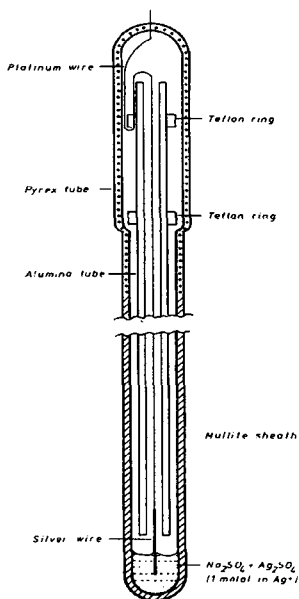


Fig. 4 Reference electrode for molten sulphates [74]

**Table 1**

Weight change and visual evidence of attack in  $\text{Na}_2\text{SO}_4$  immersed ceramics. (3 hour tests at  $900^\circ\text{C}$ , in air)

| Type of material                           | Weight change (mg/sq. cm) and observed corrosion |                              |                            |                  |                                |                     |
|--------------------------------------------|--------------------------------------------------|------------------------------|----------------------------|------------------|--------------------------------|---------------------|
|                                            | Sample 1                                         | Repeat Sample 1              | Sample 2                   | Repeat Sample 2  | Sample 3                       | Repeat Sample 3     |
| Pythagoras (sillimanite) (Anderman Ltd.)   | -1.86<br>surface roughened                       | severely cracked             | -2.24<br>surface roughened | severely cracked | -1.04<br>slightly rough        | few small fragments |
| Alsint (sintered alumina 99.7%) (Anderman) | -0.48                                            | -0.64<br>two large fragments | -0.18                      | -0.28            | -0.22<br>three large fragments |                     |
| Morgan puxox alumina                       | -0.24                                            | -0.24                        | -0.20                      |                  | -0.24                          |                     |
| Pythagoras 1800 (Anderman Ltd.)            | -0.12                                            | severely cracked             | -0.38                      |                  | severely cracked               | severely cracked    |
| Degussit AL 23 alumina                     | -0.46                                            | -0.40                        | -0.20                      | -0.36            | -0.24                          |                     |
| Silica (Thermal Syndicate)                 | -2.66<br>extremely rough                         | -3.06<br>severely dissolved  | -3.14<br>extremely rough   |                  |                                |                     |
| Mullite (Morgan Ref. Ltd.)                 | large fragments                                  |                              | -0.30                      | -0.24            | large fragments                | large fragments     |

**Table 2**  
Weight versus time of mullite in molten  $\text{Na}_2\text{SO}_4$  at  $900^\circ\text{C}$ , in air (a mullite fragment was used)

| Time<br>(hrs.) | Weight (g) |          |
|----------------|------------|----------|
|                | Sample 1   | Sample 2 |
| 0              | 1.0658     | 0.8086   |
| 24             | 1.0637     | 0.8031   |
| 48             | 1.0634     | 0.8020   |
| 72             | 1.0632     | 0.8014   |
| 96             | 1.0631     | 0.8010   |

The potential of this reference electrode is the same whether evacuated or merely closed at the top by a pvc bulb through which the wire passes; closing is essential to prevent  $\text{SO}_3$  escape from  $\text{Ag}_2\text{SO}_4$  ( $P_{\text{SO}_3} = 0.012$  atm at  $900^\circ\text{C}$ ). Reference electrodes are best stored at a red heat; long cooling times to ambient are necessary to prevent cracking. Against an Au wire electrode at  $900^\circ\text{C}$ , and “ideal” Fig. 4 reference electrode has a potential of  $-160$  mV. Its reproducibility, stability, reversibility and unpolarizability was tested by Sequeira [82] and found satisfactory for corrosion studies.

**Purification:** Molten salts, whether used for experimental purposes or in actual systems, must be kept free of contaminants. This task, which includes initial makeup, transfer, and operation, is specific for each type of molten salt. For example, for nitrates with a melting point of approximately  $220^\circ\text{C}$  purging with argon flowing above and through the salt at  $250$  to  $300^\circ\text{C}$  removes significant amounts of water vapour [83]. Another purification method used for this same type of salt consisted on bubbling pure dry oxygen gas through the  $350^\circ\text{C}$  melt for 2 hours and then bubbling pure dry nitrogen for 30 minutes to remove the oxygen [84]. All metals that contact the molten salt during purification must be carefully selected to avoid contamination from transfer tubes, thermocouple wells, the makeup vessel, and the container itself. This selection process may be an experiment in itself [85-87].

## 6. Molten Fluorides

Interest in molten fluorides stems from their importance in nuclear technology and their use in the production of fluorine, electrodeposition of refractory metals, formation of corrosion-resistant diffusion coatings, and fluorination by electrochemical techniques. Most studies in alkali metal fluorides and other fluorides are rather recent and in connection with the development of molten salt reactors [88] and electrodeposition of silicon and the refractory metals [89, 90]. Corrosion in many fluoride molten-salt melts is accelerated because protective surface films are not formed. In fact, the fluoride salts act as excellent fluxes and dissolve the various corrosion products. The design of a practicable system using molten fluoride salts, therefore, demands the selection of salt constituents, such as lithium fluoride ( $\text{LiF}$ ), beryllium fluoride ( $\text{BeF}_2$ ), uranium tetrafluoride ( $\text{UF}_4$ ) and thorium fluoride ( $\text{ThF}_4$ ), that are not appreciably reduced by available structural metals and alloys [70].

Corrosion data reveal clearly that in reactions with structural metals, M:



chromium is much more readily attacked than iron, nickel, or molybdenum [91, 92].

Nickel-base alloys, more specifically Hastelloy N ( $\text{Ni-6.5Mo-6.9Cr-4.5Fe}$ ) and its modifications, are considered the most promising for use in molten salts and have received the most

attention [92-94]. Stainless steels, having more chromium than Hastelloy N, are more susceptible to corrosion by fluoride melts, but can be considered for some applications [91,95].

Corrosion can become more aggressive as temperature increases. It is particularly severe for stainless steels because of tube plugging problems due to mass transfer. Adamson et al. [96] conducted corrosion tests in a thermal convection loop involving 43.5KF-10.9NaF-44.5LiF-1.1UF<sub>4</sub> (mol. %) with an 815°C hot leg and a 704°C cold leg. Types 410, 430, 316, 310 and 347 suffered severe tube plugging problems at the cold leg within short test durations. Nickel and nickel-base alloys, on the other hand, showed no plugging even after 500 hours of testing. However, these alloys suffered corrosion at the hot leg after 500 hours of exposure. Alloy 600 suffered internal attack consisting of voids about 0.30 to 0.38 mm deep. NIMONIC alloy 75 suffered intergranular pitting about 0.20 to 0.33 mm deep, and nickel suffered even metal removal of about 0.23 mm.

Misra and Whittenberger [97] reported corrosion data for a variety of commercial alloys in molten LiF-19.5CaF<sub>2</sub>, which was being considered for a heat-storage medium in an advanced solar space power system, at 797°C for 500 hours. The tests were conducted in alumina crucibles with argon as a cover gas.

For nickel-base alloys, chromium was detrimental. No influence of chromium, however, was noted in iron-base alloys.

Moisture, a common impurity in fluoride salts, can produce gaseous HF and increase corrosion attack [97,98]. Therefore, it is important to reduce its level in the salt, resulting in decreased corrosion rates.

Recently, corrosion of Cu and Mg was also investigated in HF-KF mixtures [99-101] because of their use as conducting busbars in fluorine electrowinning. Copper busbars are preferred in low acidic mixtures while magnesium is a more corrosion resistant material in high acidic and low temperature mixtures.

## 7. Chloride Salts

Molten chlorides are widely used for electrowinning of metals, alloys, and gases, for annealing and normalizing of steels in high-temperature batteries [37,61,99].

Jackson and LaChance [61] performed an extensive study on the corrosion of cast Fe-Ni-Cr alloys in the NaCl-KCl-BaCl<sub>2</sub> salt bath. They found that the alloys suffered intergranular attack significantly more than metal loss. HW alloy (12Cr-60Ni) was consistently the best performer among the four commercial cast alloys (HW, HT, HK and HH alloys) studied. These authors further noted that intergranular attack generally followed grain boundary carbides. Thus, lowering carbon content from 0.4% to about 0.07% resulted in a threefold improvement. Decreasing grain size also improved alloy resistance to intergranular attack. Five different neutral salt baths were compared for HW, HT and three Fe-Cr alloys. In general, the four chloride salt baths were quite similar. The KCl-Na<sub>2</sub>CO<sub>3</sub> salt bath was significantly less aggressive than the chloride baths. It is also interesting to note that Fe-17Cr alloy was better than HW (Fe-12Cr-60Ni) and HT (Fe-15Cr-35Ni) alloys in NaCl-KCl, NaCl-KCl-BaCl<sub>2</sub>, and NaCl-BaCl<sub>2</sub>-CaCl<sub>2</sub> salt baths.

Colom and Bodalo have investigated the corrosion of mild steel [102] and Armco iron [103] in molten LiCl-KCl eutectic as a function of the water content of the melt and of the temperature. Corrosion rates fell rapidly to a constant value with time (i.e. a passivating film is formed) and increased with rising temperature between 400 and 800°C. The oxidation kinetics followed first a parabolic, then a linear rate-law. The corrosion rate seemed to be scarcely affected by traces of water in the melt in the case of mild steel (it was enhanced by traces of water in the case of Armco iron) but, whereas the corrosion product in the dry melt was found to be Fe<sub>2</sub>O<sub>4</sub>, in the humid bath both Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>4</sub> were formed. Cathodic polarization waves indicate that the corrosion reaction is diffusion-controlled and the diffusing species is Fe<sup>3+</sup>. This interpretation requires further

support in view of the known electrochemistry of iron in LiCl-KCl eutectic mixture [104, 105]. The rate of corrosion is lowered by cathodic protection.

Hoff [106] has developed the theory for the corrosion of metals in molten salts under a temperature gradient. Dissolution of a metal on hot parts and recrystallization on the colder parts are caused by the thermoelectric effect. The equations of electrode kinetics can be used to obtain the theoretical relations. The temperature dependence of diffusion and of complex formation lead to a current distribution along the surface of the metal, showing a distinct maximum at the point where recrystallization occurs. The theory is tested using an aluminium wire in  $\text{AlCl}_3\text{-NaCl-KCl}$  in the temperature range 215-420°C.

Feng et al. [107] have shown that Fe, Co, Ni, Cu and Mo are considerably less corroded in molten LiCl-KCl eutectic when this melt contains lithium oxide which is due to oxide film formation.

Lai et al. [108] evaluated various wrought iron-, nickel-, and cobalt-base alloys in a NaCl-KCl-BaCl<sub>2</sub> salt bath at 840°C for 1 month. Surprisingly, two high-nickel alloys (alloys 600 and 601) suffered more corrosion attack than stainless steels such as Types 304 and 310. Co-Ni-Cr-W, Fe-Ni-Co-Cr, and Ni-Cr-Fe-Mo alloys performed best. Laboratory testing in a simple salt bath failed to reveal the correlation between alloying elements and performance. Tests were conducted at 840°C for 100 hours in a NaCl salt bath with fresh salt for each test run.

Similar to the field test results, Co-Ni-Cr-W and Fe-Ni-Co-Cr alloys performed best.

Smyrl and Blackburn [109] have been concerned with the stress corrosion cracking phenomena of the Ti-8Al-1Mo-1V alloy in molten LiCl-KCl at 350°C.

More recently, Atmani and Rameau [110-112] have described a tensile apparatus suitable for corrosion tests in molten salts. The behaviour of 304L stainless steel was studied in molten NaCl-CaCl<sub>2</sub> at 570°C using either a constant strain rate or a constant load technique. Intergranular corrosion fracture was shown and the role of  $\text{M}_{23}\text{C}_6$  precipitation in the crack propagation was evidenced.

Coyle et al. [113] conducted corrosion tests on various commercial alloys at 900°C in the molten 33NaCl-21.5KCl-45.5MgCl<sub>2</sub> eutectic. After 144 hours of exposure, eight of the fifteen Fe-, Ni-, Co-based alloys evaluated, were consumed. The remaining seven alloys disintegrated after a total of 456 hours of exposure.

The authors concluded that the chloride salt was too aggressive to be used at 900°C for a solar thermal energy system. In the same eutectic at 450 to 500°C, Susskind et al. [114] found much lower corrosion rates. Investigating the corrosion behaviour of alloys at 400 and 500°C in the LiCl-KCl eutectic, which was being considered as an electrolyte for lithium-sulphur fuel cells, Battles et al. [115] also found negligible corrosion rates. Aluminium in the aluminium-clad type 434 stainless steel sample corroded at a higher rate due to the galvanic couple between aluminium and stainless steel [115].

Takehara and Ueshiba [116] investigated the corrosion behaviour of steel, Fe-Cr, Fe-Ni, and Fe-Cr-Ni alloys in molten 20NaCl-30BaCl<sub>2</sub>-50CaCl<sub>2</sub> and molten 25LiCl-25ZnCl<sub>2</sub>-16BaCl<sub>2</sub>-24CaCl<sub>2</sub>-10NaCl at 500 and 600°C. Steels and Fe-Cr alloys suffered severe corrosion in both types of salts. Chromium in Fe-Cr alloys and nickel in Fe-Ni alloys improved performance. Fe-Cr-Ni alloys performed significantly better than steels and Fe-Cr alloys.

An overview of experimental observations and results of liquid Li and LiCl corrosion at 725°C of engineering nonferrous materials have been explained by Olson et al. [11]. It has been observed that oxygen contamination is particularly harmful for the tantalum and niobium-based refractory metal alloys where as nitrogen is deleterious to iron-based alloys. Materials tested included RA333, Hastelloy X, Airesist 213, Ta-2.5W and Nb-1Zr. The corrosion and protection mechanism of molten salt electrodeposited chromium coatings in a LiCl-KCl eutectic at 450°C has been studied by Emsley and Hill [118]. Factors influencing the optimum coating thickness on 20Cr-25Ni-Nb-stabilized stainless steel to achieve a satisfactory lifetime were discussed.

The corrosion behaviour of Mo-Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> cermets in BaCl<sub>2</sub> molten salt has been shown to be mainly due to the electrochemical corrosion of the component Mo [119]. It was also found that the other component (Cr<sub>2</sub>O<sub>3</sub>) is beneficial to the corrosion-resistance of the cermets investigated.

The corrosion behaviour of mild steel (St35.8), boiler steel 13Cr-Mo44 and stainless steel X 10Cr-Ni-Mo18 in contact with the eutectic salt mixtures AlCl<sub>3</sub>-NaCl, LiCl-LiNO<sub>3</sub>-NaCl, NaCl-NaNO<sub>3</sub> and KCl-LiCl has been investigated by Heine [120]. The test conditions were adapted to the operating conditions of latent heat storage systems. Only pure salts were used. Good corrosion resistance was observed.

Intergranular corrosion is the major corrosion morphology by molten chloride salts.

Another frequently observed corrosion morphology is internal attack by void formation [121]. Voids tend to form at grain boundaries as well as in the grain interior. The continuing formation and growth of chromium compounds at the metal surface causes outward migration of chromium and inward migration of vacancies, thus leading to internal void formation [121].

## 8. Molten Nitrates/Nitrites

Molten nitrates are commonly used for heat treatment baths; therefore, a great deal of material compatibility information exists. Plain carbon and low-alloy steels form protective iron oxide films that effectively protect the metal surface to approximately 500°C. Chromium additions to the melt further increase the corrosion resistance of the steel, and hydroxide additions to the melt further increase the resistance of chromium containing steels. Aluminium and aluminium alloys should never be used to contain nitrate melts, because of the danger of explosion.

Nitrate-nitrite mixtures are also widely used for heat treat salt baths at temperatures ranging from 160 to 590°C, as well as a medium for heat transfer or energy storage.

Marchiano and Arvia have constructed electrode-potential oxygen partial pressure diagrams for the iron-molten NaNO<sub>3</sub> system at 600 and 700K [122], and for iron, cobalt and nickel in molten sodium nitrite [123]. In both cases, four well-defined regions, corresponding to metal corrosion, immunity, passivity, and passivity breakdown, are observed.

Notoya and Midorikawa [124] have investigated the oxidation kinetics of iron in molten alkali-metal nitrates between 350 and 470°C. The parabolic rate law, with a temperature-dependent constant, appears to be followed. The activation energy for corrosion is found to be greater in KNO<sub>3</sub> than in NaNO<sub>3</sub>. X-ray studies show that the oxidation product is Fe<sub>3</sub>O<sub>4</sub>. The results are comparable with the oxidation kinetics of iron in air or oxygen. Notoya et al. [125] have studied the effects of alkali-metal and alkaline-earth halides on the oxidation kinetics of iron and low-carbon steels in molten KNO<sub>3</sub>-NaNO<sub>3</sub> at 400°C. The corrosion of iron in these melts appears to begin with pitting corrosion which eventually spreads to the entire surface. The rate of attack increases with halide concentration and seems to depend on both the anion and the cation, aggressiveness increasing in the order KCl < KBr < KI for the anion, and CaCl<sub>2</sub> < BaCl<sub>2</sub> < LiCl < NaCl < KCl for the cation; halide is found to be incorporated in the oxide film formed. It is found that low-carbon steels are more resistant to corrosion than pure iron. It is suggested that the corrosion behaviour is similar to that in atmospheres containing halogens at high temperatures.

Ishikawa and Sasaki [126] have carried out immersion and electrical resistance tests in alkali nitrate melts of 350 to 450°C, to elucidate the corrosion behaviour of iron wire specimens. A parabolic law was verified for the iron specimens. Moreover, the sensitive resistometry has been shown to be a useful technique for the continuous determination of the corrosion behaviour in various salt systems. Nitrate-nitrite mixtures and corrosion of iron and stainless steels by these melts were extensively studied (as a function of temperature and oxoacidity) in relation with their use as a coolant and storage fluid in solar thermal electric power plants [127-131]. In particular, passivation of iron is observed only in a narrow acidity domain where NaFeO<sub>2</sub> can be formed. It



was also demonstrated that a nitriding process appears only as a consequence of the oxidation process [127].

The corrosion resistance of Al, Ni, Ti, Ta, Nb, carbon steel and stainless steel was studied in molten  $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$  eutectic for the chemical open-circuit oxidation and for conditions of cathodic polarization [132]. Experiments were carried out at 632K under an argon atmosphere during 100 hours. By using XRD, ESCA, SIMS, SEM and gravimetric method, the metals under study show relatively high corrosion resistance in nitrate melts. Oxide films of predominantly higher oxidation state were formed on their surfaces. The effect of cathodic polarization on their corrosion behaviour was insignificant. Only in the case of Ni, a decrease in oxidation rate was observed under the conditions of cathodic polarization [132].

Molten salt corrosion behaviour of heat transfer plant materials, SS41, 2.25Cr-1Mo steel, SUS304 and Inconel 625, was studied in temperatures of 450 and 550°C [133]. The corrosion rate in the molten salt decreased in the decreasing order of SS41, 2.25Cr-1Mo steel, SUS304, Inconel 625. And the corrosion resistance of SS41, 2.25Cr-1Mo steel and SUS304 strongly depended on the temperature and Cl-exp content of the molten salt, while Inconel 625 showed high corrosion resistance in the molten salt environment. The morphology of corrosion products was examined by electron probe microanalysis (EPMA), X-ray diffraction, scanning electron microscopy (SEM) and Auger electron spectroscopy (AES). Corrosion products of SS41 and 2.25Cr-1Mo steel consisted of porous and easy-pearling multilayer films of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{KFeO}_2$ ,  $\text{NO}_2\text{O-Fe}_2\text{O}_3$ , and  $\text{Fe}_3\text{O}_4$ , while the corrosion products of SUS304 and Inconel 625 consisted of compact and well-sticked iron oxide films which contain Ni and Cr. The materials containing much more than 10 wt. % Cr showed high corrosion resistance against the molten salt [133].

Electropolished iron spontaneously passivates in molten sodium nitrate-potassium nitrite in the temperature range of 230 to 310°C at certain potentials [134]. A magnetite ( $\text{Fe}_3\text{O}_4$ ) film is formed, along with a reduction of nitrite or any trace of oxygen gas dissolved in the melt. At higher potentials, all reactions occur on the passivated iron. Above the passivation potentials, dissolution occurs with ferric ion soluble in the melt. At even higher potentials, nitrogen oxides are evolved, and nitrate ions dissolve in the nitrite melt. At higher currents, hematite ( $\text{Fe}_2\text{O}_3$ ) is formed as a suspension, and  $\text{NO}_2$  is detected. Carbon steel in molten sodium nitrate-potassium nitrate ( $\text{NaNO}_3\text{-KNO}_3$ ) at temperatures ranging from 250 to 450°C forms a passivating film consisting mainly of  $\text{Fe}_3\text{O}_4$  [84].

Iron anodes in molten alkali nitrates and nitrites at temperatures ranging from 240 to 320°C acquire a passive state in both melts. In nitrate melts, the protective  $\text{Fe}_3\text{O}_4$  oxidizes to  $\text{Fe}_2\text{O}_3$ , and the gaseous products differ for each melt [135].

An interesting study was conducted on the corrosion characteristics of several eutectic molten salt mixtures on such materials as carbon steel, stainless steel, and Inconel in the temperature range of 250 to 400°C in a nonflowing system [136]. As expected, the corrosion rate was much higher for carbon steel than for stainless steel in the same mixture. Low corrosion rates were found for both steels in mixtures containing large amounts of alkaline nitrate. The nitrate ions had a passivating effect.

Electrochemical studies showed high resistance to corrosion by Inconel. Again, the sulphate-containing mixture caused less corrosion because of passivating property of the nitrate as well as the preferential adsorption of sulphate ions.

Surface analysis by Auger electron spectroscopy indicated varying thicknesses of iron oxide layers and nickel and chromium layers. The Auger analysis showed that an annealed and air-cooled stainless steel specimen exposed to molten lithium chloride ( $\text{LiCl}$ )-potassium chloride ( $\text{KCl}$ ) salt had corrosion to a depth five times greater than that of an unannealed stainless steel specimen. Chromium carbide precipitation developed during slow cooling and was responsible for the increased corrosion. The mechanism of corrosion of iron and steel by these molten eutectic salts can be described by the following reactions:



In an actual flowing operating system of  $\text{KNO}_3$ - $\text{NaO}_2$ - $\text{NaO}_3$  (53, 40, and 7 mol %, respectively) at temperatures to 450°C, carbon or chromium-molybdenum steels have been used [137].

For higher temperatures and longer times, nickel or austenitic stainless steel are used. Weld joints are still a problem in both cases.

Alloy 800 and types 304, 304L, and 316 stainless steels were exposed to thermally convective  $\text{NaNO}_3$ - $\text{KNO}_3$  salt (draw salt) under argon at 375 to 600°C for more than 4500 hours. The exposure resulted in the growth of thin oxide films on all alloys and the dissolution of chromium by the salt. The weight change data for the alloys indicated that the metal in the oxide film constituted most of the metal loss, that the corrosion rate, in general, increased with temperature, and that, although the greatest metal loss corresponded to a penetration rate of 25  $\mu\text{m}/\text{year}$ , the rate was less than 13  $\mu\text{m}/\text{year}$  in most cases. These latter rates are somewhat smaller than those reported for similar loops operated with the salt exposed to the atmosphere [138,139] but are within a factor of two to five. Spalling had a significant effect on metal loss at intermediate temperatures in the type 304L stainless steel loop. Metallographic examinations showed no evidence of intergranular attack or of significant cold-leg deposits. Weight change data further confirmed the absence of thermal gradient mass transport processes in these draw salt systems [140].

Slusser et al. [141] evaluated the corrosion behaviour of a variety of alloys in molten  $\text{NaNO}_3$ - $\text{KNO}_3$  (equimolar volume) salt with an equilibrium nitrite concentration (about 6 to 12 wt.%) at 675°C for 336 hours. A constant purge of air in the melt was maintained during testing. Nickel-base alloys were generally much more resistant than iron-base alloys. Increasing nickel content improved alloy corrosion resistance to molten nitrate-nitrite salt. However, pure nickel suffered rapid corrosion attack.

Silicon-containing alloys, such as RA330 and NICROFER 3718, performed poorly. A long-term test (1920 hours exposure) at 675°C [141] was performed on selected alloys, showing corrosion rates similar to those obtained from 336-hour exposure tests. Alloy 800, however, exhibited a higher corrosion rate in the 1920-hour test than in the 336-hour test. As the temperature was increased to 700°C, corrosion rates became much higher, particularly for iron-base alloy 800, which suffered an unacceptably high rate [141]. Boehme and Bradshaw [142] attributed the increased corrosion rate with increasing temperature to higher alkali oxide concentration. Slusser et al. [141] found that adding sodium peroxide ( $\text{Na}_2\text{O}_2$ ) to the salt increased the salt corrosivity.

## 9. Hydroxide Melts

The reaction of metals with molten sodium hydroxide ( $\text{NaOH}$ ) leads to metal oxide, sodium oxide, and hydrogen [143]. Nickel is most resistant to molten  $\text{NaOH}$  [144-146], particularly low-carbon nickel such as Ni 201 [147,148]. Gregory et al. [149] reported corrosion rates of several nickel-base alloys obtained from static tests at 400 to 680°C. Molybdenum and silicon appear to be detrimental alloying elements in molten  $\text{NaOH}$  salt. Iron may also be detrimental. Molybdenum

## Electrochemistry of Corrosion in Molten Salts

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**Keywords:** Cobalt/Molten Sodium Sulphate, Corrosion Potential/ $pO^{2-}$  Relationship, Electrochemical Kinetics, Equilibrium Diagrams

### ABSTRACT

After pointing out the electrochemical nature of corrosion reactions in molten salts, an account of the essential parameters concerning the electrochemical corrosion phenomena is presented. Emphasis is given to the electrothermodynamics of corrosion; based on the «Erdey-Gruz-Volmer» theory and on the «acid-base concept» of Lux and Flood a relationship between the corrosion potential and the function  $pO^{2-}$  is derived. Diagrams in which the equilibrium potential  $E$  in the metal-fused salt system is plotted against the activity of oxide ion in the melt are developed, using the Pourbaix method of data presentation; as an example, an  $E$ - $pO^{2-}$  diagram is constructed for cobalt at  $900^{\circ}C$ , in contact with molten sodium sulphate, and its limited nature as an aid to corrosion control is summarized. The need for study of metal corrosion in terms of electrochemical kinetics is indicated. Further, it is suggested to apply the newer electrochemical techniques to the study of corrosion kinetics in high-temperature media.

### ELECTROCHEMICAL NATURE OF ATTACK

Theoretical considerations of the corrosion phenomena have often been considered inaccessible, mainly due to the great complexity of the corrosion processes. It is generally agreed today that several factors with different physicochemical characteristics can play an important role in the mechanisms of corrosion. However, despite these difficulties, corrosion problems have been successfully interpreted in recent years.

Particularly over the last fifty years, corrosion studies have demonstrated that the primary process between the corroding metal and corrodent is electrochemical in nature; attack is basically a chemical reaction accompanied by the transfer or displacement of electrons [1]. Electrochemical theory today rests secure in its application to corrosion phenomena in aqueous media [2].

If molten salts are regarded as infinitely concentrated aqueous solutions it is a natural step to try to formulate a description of corrosion in them on the basis of concepts like those which have been developed for aqueous solutions. The main difficulty here is that the problem is not completely similar to an aqueous system, and it is therefore necessary to assess other electrochemical parameters. Besides, whilst in aqueous solutions metals are virtually insoluble in the electronated state, in fused salts they can be appreciably soluble, corrosion occurring, in such cases, without the de-electronation of the metal. In spite of this the electrochemical approach for molten salt systems was put forward about forty years ago and is finding general acceptance. Experiments carried out by Baudo et al. [3], Burrows and Hills [4,5], Cutler [6], Janz and Conte [7], Littlewood and Argent [8], Sequeira [9], et al. have contributed considerably in this respect.

There have been some objections concerning electrochemical interpretations of corrosion based in the thermodynamics and kinetics of electrochemistry. In fact, these theories are restricted to cases well defined and checked by experience. They cannot, however, include all the simultaneous corrosion processes. Following these essential considerations, some basic concepts of electrochemistry are discussed; modern electrochemical views of corrosion in molten salts are also included and a synthesis of all the miscellaneous aspects considered have been put together.

## THE SINGLE POTENTIAL OF AN ELECTRODE

In the most general sense of the word, an electrode is a system consisting of two phases in contact with each other, which can be the seat of an electrode reaction, i.e. a reaction in which certain constituents of the two phases participate and by which a transfer of charge takes place from the bulk of one phase to the bulk of the other. In a more restricted sense an electrode is defined as a system metal/electrolyte or metal/solution of one or several electrolytes.

It has been shown over the last 90 years that at the interface of two phases one finds an electrical double layer with a characteristic potential [10,11].

The origin as well as the characterisation of the electrochemical double layer on a metal immersed in an aqueous electrolyte have been extensively studied. Similar studies in melts have been carried out only recently. This paper is not intended to deal with this aspect in detail but the subject is mentioned because of its importance. Very good reviews on the subject have been published by Devanathan and Tilak [12], Graves et al. [13] and Ukshe et al. [14].

Returning to the subject of this section, let the inner electric potential of the metal be  $\Phi_M$  and that at a remote point in the molten electrolyte be  $\Phi_S$ . Moreover, let  $\Delta\Phi$  represent the Galvani electric potential across the electrochemical double layer, i.e.  $\Delta\Phi = \Phi_M - \Phi_S$ . When a dynamic equilibrium across the double layer is set up, the electrochemical free energy of one mole of metal in the surface will be equal to the electrochemical free energy of one mole of ions on the melt side of the double layer:—

$$\tilde{\mu}_M = \tilde{\mu}_S$$

$$\text{or} \quad \mu_M + n F \Phi_M = \mu_S + n F \Phi_S \quad (1)$$

$$\text{and} \quad \mu_M - \mu_S = - n F \Delta \Phi \quad (2)$$

$\mu_M - \mu_S$  is the chemical energy balanced by the electrical energy liberated as the ions  $M^{n+}$  traverse the double layer;  $F$  is Faraday's constant and  $n$  is the number of free electrons exchanged at the  $M^{n+}/M$  interface. It is impossible to measure  $\Delta\Phi$  directly but if the metal/melt electrode system is coupled «back-to-back» with a second arbitrarily chosen electrode system, it is possible to obtain a relative potential difference. If a zero potential and a convenient reference scale of potentials is defined, the combined system acts as a cell between whose electrodes there exists an e.m.f. given by

$$E_{0,1} = \Delta\Phi - \Delta\Phi_R \quad (3)$$

(assumed zero)

$E_{0,1}$  is called the single potential of the  $M^{n+}/M$  electrode on the chosen standard reference scale. Considering now a more concise electrode reaction



where  $M_i$  represents the constituents of the electrode taking part in the reaction and  $e^-$  represents the electron; the corresponding conditions of dynamic equilibrium can be expressed in the general form

$$\sum_i v_i \mu_i - n F E_{0,4} = 0 \quad (5)$$

Relating the chemical potentials,  $\mu_i$ , to the standard chemical potential  $\mu_i^0$ , equation (5) can be put into the form

$$R T \sum v_i \log \{M_i\} = -\sum_i v_i \mu_i^0 + n F E_{0,4} \quad (6)$$

Changing from natural to Briggsian logarithms, the last relation can be rewritten in the form

$$E_{0,4} = E_{0,4}^0 + \frac{2.3026 R T}{n F} \sum_i v_i \log \{M_i\} \quad (7)$$

in which  $E_{0,4}^0$  has the following value in terms of the standard chemical potentials of the reactants

$$E_{0,4}^0 = \frac{\sum_i v_i \mu_i^0}{n F} \quad (8)$$

Equation (7) is the Nernst equation.  $E_{0,4}^0$  is the single potential of the electrode measured when the activity of every constituent of the system is equal to unity and is known as the normal or standard potential. Once the normal electrode potential on the standard reference scale is known, the Nernst equation permits a calculation of what the equilibrium electrode potential will be when the system has any  $\{M_i\} \neq 1$ . Extensive analytical treatments of this subject are given by Conway [15], De Groot [16], Grahame [17], Guggenheim [18], Parsons [19], Prigogine [20], et al.. Experimental proof of the validity of the Nernst equation in molten media is given by Blander et al. [21], Duke and Garfinkel [22], Gordon [23], Ranford and Flengas [24], and many other workers.

## THE TAFEL RELATIONSHIP

Considering now the dynamic side of the phenomenon, particular importance will be attached to electrochemical kinetic studies. A classic relationship precisely relating a characteristic parameter of the electrode, its electrode potential, and the current density traversing it, is that found by Tafel in 1905. Thereby this semi-empirical law enables us to establish a connection between the «thermodynamic electrode potential» and the current density which defines the kinetic character of the phenomenon.

The Tafel equation may be written

$$E = a + b \log i \quad (9)$$

where  $E$  is the relative electric potential of the electrode at a current density  $i$  (also called «reaction electrode potential»),  $a$  is a constant characteristic of the electrode, and  $b$  is the Tafel slope, which is one of the parameters indicating the mechanism of the electrode reaction.

Thus, a definition of overpotential for the reaction can be introduced by the expression:

$$\eta = E - E_0 \quad (10)$$

where  $E_0$  is the reversible or equilibrium electric potential possessed by the electrode at electrochemical equilibrium (i.e. at zero imposed current) or, more generally, the equilibrium potential of the electrochemical reaction of the type (4). Equation (10) defines the overpotential and

considering (9) it is seen that Tafel's equation is itself closely related to the overpotential ( $\eta$ ). These problems of electrochemical kinetics are discussed in more detail later.

The brief discussion given above is significant enough for the present purpose of showing that the Tafel relationship leads to the experimental polarization curves. Figures 1 and 2 represent the anodic and cathodic potential-current curves for two typical electrochemical reactions, with either an arithmetic scale for the reaction-current (Figs. 1-a and 2-a) or with a logarithmic one (Figs. 1-b and 2-b). The exchange current density ( $i_0$ ), which is defined as the exchange rate per unit area of the potential-determining electrode process at equilibrium, is represented in Figs. 1-b and 2-b. The aspect of the polarization curves is very important because it gives an account of the degree of irreversibility of the reactions. In fact, in the case of a reversible reaction (Fig. 1), the application of very small polarizing potentials is sufficient for producing significant densities of current. In the case of irreversibility (Fig. 2), on the contrary, the existence of high overpotentials is a measure of the extent of the irreversibility. The reversible or fast electrode processes exhibit high exchange current densities; on the other hand, the irreversible or slow ones exhibit low exchange current densities. Thus, if an electrode is more likely to behave reversibly the higher is its intrinsic exchange current density.

The Tafel curves giving  $E$  as the function of  $\log i$ , also provide interesting results about the kinetics of the phenomena. In fact, the plot of  $E$  against  $\log i$  is not usually a straight line, i.e. the kinetics of the reaction does not obey the Tafel law. The experimental curves obtained can be considered as built up of rectilinear portions or, on the contrary, as showing systematic departures from the linear Tafel law for certain current densities reached. It is well established in electrochemistry that the Tafel law does not apply precisely for small and large current densities. One reason for this is that the Tafel equation is derived purely by considering the overvoltage due to polarization caused by activation energy requirements, which assumes that a cation moves away from the metal-fused electrolyte interface as soon as it is dissolved. This is generally not the case. The removal of the anodic product does not increase in the same proportion as the current density and the concentration of these products will increase and cause a back e.m.f. This effect is particularly relevant in the case of fast electrode processes as observation of the Figures 1 and 2 shows:— The difficulty in obtaining a pure Tafel slope, i.e. unaffected by double layer and mass transfer effects, increases with the kinetics of the electrode processes (i.e. with high  $i_0$ ) due to increasing overlapping of the diffusion zones over the Tafel one. Polarization measurements also include ohmic overpotential which arises from an  $iR$  drop through a portion of the electrolyte and between the test electrode and the reference one, but this term is not significant in molten media as compared with an aqueous system. The validity of Tafel's equation has been verified by Laitinen and Gaur [25], Randles and White [26], et al. for many fused systems.

The facts mentioned above are very important especially due to their repercussion on the interpretation of electrochemical phenomena. So it is seen, by this simple enumeration, that it is possible to connect thermodynamic considerations to kinetic ones.

## GENERAL CONSIDERATIONS OF ELECTRODICS OF CORROSION

In the section above, where some concepts of electrode kinetics were discussed, a quantity of crucial importance to electrodics was defined: the overpotential ( $\eta$ ). In electrochemical kinetics the only reaction directly affected by the potential is the charge-transfer reaction, i.e. the reaction in which charge carriers are transferred across the electrochemical double layer at a phase boundary. The rate of the charge-transfer reaction determines the charge-transfer, or activation overpotential. This kind of overpotential has been treated in detail by Audubert [27], Bard and Faulkner [28], Bockris [29], Butler [30], Conway [15], Erdey-Gruz and Volmer [31], Gerischer [32], et al.

Prior to discussion, it is noted that only the basic electrodic equations will be considered.

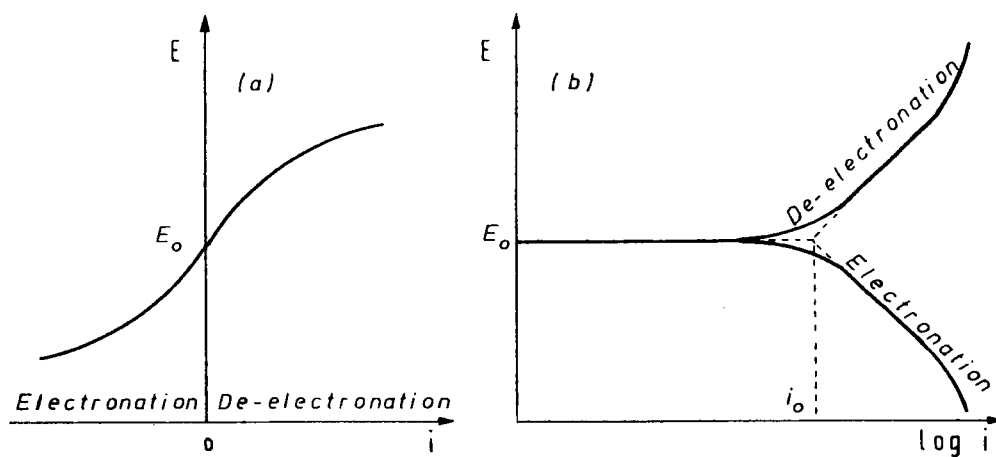


Fig. 1 - Polarization curves of a fast electrochemical reaction

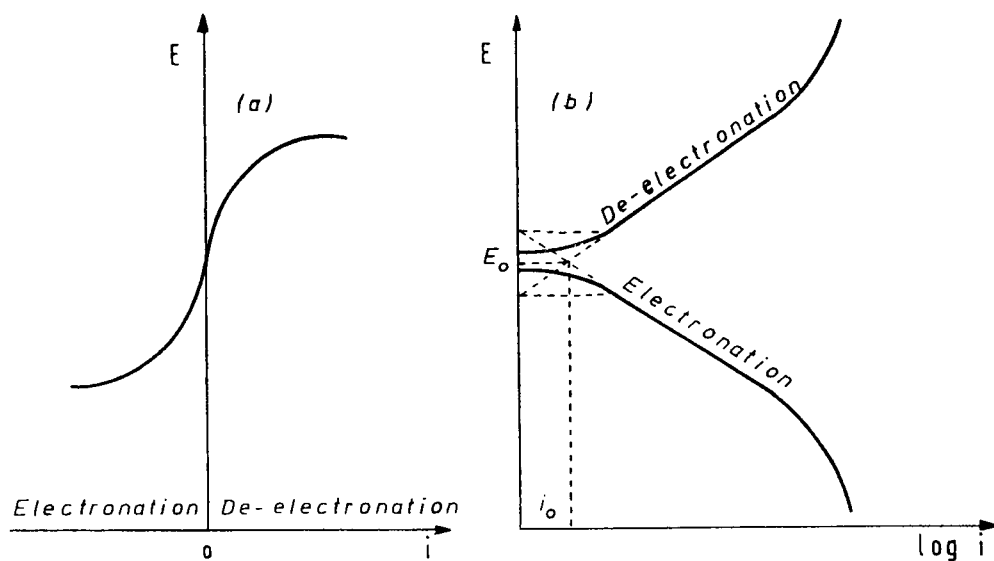
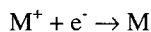


Fig. 2 - Polarization curves of a slow electrochemical reaction

Considering that the conversion of  $M^+$  ions into metallic  $M$ , the number of moles of positive ions reacting per second by crossing unit area of the melt/metal interface is proportional to the electronation-current density  $i_-$  and as a first approximation [31]:

$$\begin{aligned} i_- &= -K'_- \{M^+\} \exp(-\Delta\tilde{G}^* / RT) \\ &= -K'_- \{M^+\} \exp(-\Delta G^* / RT) \exp[-(1 - \alpha) F E / RT] \\ &= -K_- \{M^+\} \exp[-(1 - \alpha) F E / RT] \end{aligned} \quad (11)$$

$\Delta\tilde{G}^*$  is the activation energy required for the electronation process at the potential  $E$ ,  $K'_-$  and  $K_-$  are constants,  $\{M^+\}$  is the activity of cations  $M^+$  on the metal side of the interface,  $\Delta G^*$  is the chemical activation free energy barrier when there is zero electric field acting on the ion, and  $\alpha$  is the transfer coefficient for the de-electronation reaction introduced by Erdey-Gruz and Volmer [31] which has values ranging from zero to unity ( $0 < \alpha < 1$ ) [33].  $K_-$  is dependant on the reference potential chosen since  $K_- = K'_- \exp(\Delta G^* / RT)$ . Moreover, positive ions can move from the melt to the electrode and also in the opposite direction. Thus, there is an electronation reaction



and also a de-electronation reaction



In this case, the total current density passing through the double layer is

$$\begin{aligned} i &= i_+ + i_- \\ &= K_+ \{M\} \exp(\alpha F E / RT) - K_- \{M^+\} \exp[-(1 - \alpha) F E / RT] \end{aligned} \quad (12)$$

$\{M\}$  is the activity of the metallic atoms immediately at the electrode surface (unity). If the metal-melt interface reaches its equilibrium state there is no net current ( $i = 0$ ) but there is an exchange current. The electronation and de-electronation reactions continue to occur but at the same rate. The current densities corresponding to these individual reactions become the exchange current density  $i_0$  ( $i_0 = i_+ = |i_-|$ ). Hence,

$$\begin{aligned} i_0 &= i_+ = K_+ \{M\} \exp(\alpha F E_0 / RT) \\ &= i_- = K_- \{M^+\} \exp[-(1 - \alpha) F E_0 / RT] \end{aligned} \quad (13)$$

where  $E_0$  is the potential difference across the interface at equilibrium. On dividing equation (12) by the corresponding expressions in equation (13) and taking into consideration the definition for overpotential  $\eta$ , the following important relationship is obtained [31]:

$$i = i_0 \{ \exp(\alpha F \eta / RT) - \exp[-(1 - \alpha) F \eta / RT] \} \quad (14)$$

For higher charge-transfer overpotentials,  $| \eta | \gg RT / F$ , the first or second term on the r.h.s. of equation (14) can be neglected depending on the sign of the current so that if this equation (14) is put into a logarithmic form a linear relationship results between  $\eta$  and  $\log |i|$  similar to the Tafel equation:



$$\eta_+ = -\frac{2.3026 R T}{\alpha F} \log i_0 + \frac{2.3026 R T}{\alpha F} \log i_+ \quad (15)$$

or

$$\eta_- = +\frac{2.3026 R T}{(1-\alpha) F} \log i_0 - \frac{2.3026 R T}{(1-\alpha) F} \log |i_-|$$

Here the subscripts «+» and «-» to the overpotential denote anodic and cathodic polarization, respectively.

## APPLICATION TO MOLTEN SULPHATES

Let us now consider the following reaction of a metal M in a molten sulphate [4]:



This overall reaction can be considered as the sum of the two half reactions:



For these two processes to take place simultaneously, it is necessary and sufficient that the potential difference across the interface be more positive than the equilibrium potential for the reaction (17)

$$E_{0,17} = E_{0,17}^0 + \frac{2.3 R T}{F} \log \{M^+\}$$

and more negative than the equilibrium potential of the electronation reaction (18) involving electron acceptors (such as  $SO_3$ ) contained in the melt

$$E_{0,18} = E_{0,18}^0 + \frac{2.3 R T}{2 F} \log P_{SO_3} / P_{SO_2} - \frac{2.3 R T}{2 F} \log \{O^{2-}\}$$

The behaviour for the potential-current curve  $E(I)$  which can be envisaged for the process (16) is illustrated in Fig. 3 by the continuous thick line.  $I(E)$  is composed additively of the metal-dissolution current  $I_{17}(E)$  and the electronation current  $I_{18}(E)$ , and the two are independent of each other at the same potential value. This principle of additive combination of all partial processes at an electrode surface to obtain the total potential-current curve was first formulated by Wagner and Traud [34]. The potential  $E$  at zero current is neither  $E_{0,17}$  nor  $E_{0,18}$ , but a so-called mixed potential ( $E_M$ ) for which the total potential-current curve gives  $I(E_M) = 0$ . The total metal-dissolution current  $I_{17}$  and electronation current  $I_{18}$  are then equal in magnitude but opposite in sign, i.e.

$$I_{17} = -I_{18}$$

The rate of corrosion of the metal is obviously given directly by the rate of metal dissolution; hence, the free corrosion current  $I_c$  (i.e. the rate at which a metal destroys itself) is given by

$$I_c = I_{17} = -I_{18}$$

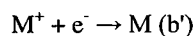
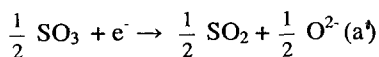
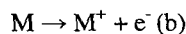
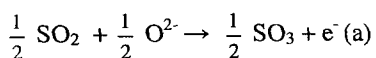
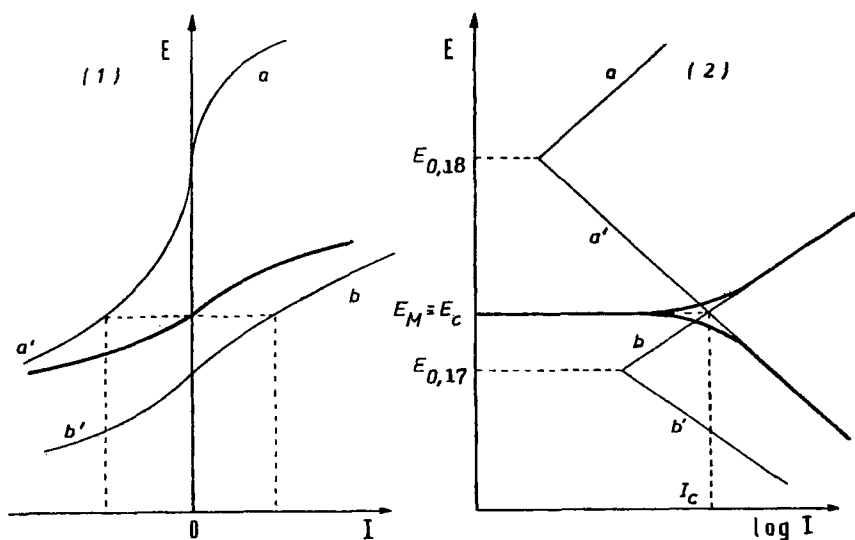


Fig. 3 Corrosion of a metal M in a molten sulphate with SO<sub>2</sub> evolution. Anodic and cathodic polarization curves. Corrosion-potential and corrosion-current.

(1) Representation with an arithmetic scale for the reaction-current.

(2) Representation with a logarithmic scale for the reaction-current.

Considering the electrode kinetics, we can thus write

$$\begin{aligned} I_c = I_{17} &= A_{17} i_{17} = A_{17} (i_{+,17} + i_{-,17}) \\ &= A_{17} K_{+,17} \{M\} \exp(\alpha_{17} F E_c / R T) - \\ &\quad - A K_{-,17} \{M^+\} \exp[-(1 - \alpha_{17}) F E_c / R T] \end{aligned} \quad (19)$$

$$\begin{aligned} I_c = -I_{18} &= -A_{18} K_{+,18} P_{\text{SO}_2}^2 \{O^{2-}\}^{\frac{1}{2}} \exp(\alpha F E_c / R T) + \\ &\quad + A_{18} K_{-,18} P_{\text{SO}_3}^{\frac{1}{2}} \exp[-(1 - \alpha_{18}) F E_c / R T] \end{aligned} \quad (20)$$

where  $A_{17}$  is the sink area and  $A_{18}$  is the electron-source area (at the interface metal-electrolyte). Assuming that overpotentials are sufficiently large, equations (19) and (20) become

$$I_c = I_{17} = A_{17} K_{+,17} \{M\} \exp (\alpha_{17} F E_c / R T)$$

$$I_c = -I_{18} = A_{18} K_{-,18} P_{SO_3}^{\frac{1}{2}} \exp [-(1 - \alpha_{18}) F E_c / R T]$$

The free corrosion potential,  $E_c$ , i.e. the uniform potential difference over the surface of the corroding metal can be evaluated from the expressions above. It follows that:

$$E_c = \frac{2.3 R T}{[\alpha_{17} + (1 - \alpha_{18})] F} \log \frac{A_{18} K_{-,18}}{A_{17} K_{+,17} \{M\}} + \frac{2.3 R T}{[\alpha_{17} + (1 - \alpha_{18})] F} \log P_{SO_3}^{\frac{1}{2}} \quad (21)$$

It is clear from this that the free corrosion potential and the mixed potential are identical.

In accordance with the theory of Lux [35] and Flood et al. [36] who assign a definite acid-base equilibrium to all oxyanionic melts, the acid-base equilibria for sulphates can be expressed by the equation



and by the equilibrium constant

$$K_{22} = P_{SO_3} \{O^{2-}\} \{SO_4^{2-}\}^{-1} \quad (23)$$

Assuming  $\{SO_4^{2-}\} = 1$ , it follows that

$$\log P_{SO_3}^{\frac{1}{2}} = \frac{1}{2} \log K_{22} + \frac{1}{2} pO^{2-} \quad (24)$$

where  $pO^{2-} = -\log \{O^{2-}\}$  is a nonprotonic function which measures the acidity of the melt. The expression (24) for the active species  $SO_3$  can be introduced into Eq. (21), giving

$$E_c = \frac{2.3 R T}{[\alpha_{17} + (1 - \alpha_{18})] F} \log \frac{A_{18} K_{-,18} K_{22}^{\frac{1}{2}}}{A_{17} K_{+,17} \{M\}} + \frac{2.3 R T}{2 [\alpha_{17} + (1 - \alpha_{18})] F} pO^{2-} \quad (25)$$

Assuming that the ratio  $A_{18}/A_{17}$  as well as  $\alpha_{17}$  and  $\alpha_{18}$  are constant during the overall corrosion reaction (which is not free from error), equation (25) becomes

$$E_c = a + b pO^{2-}$$

$a$  and  $b$  being two constants. Thus, we attain a linear relationship between the corrosion potential and the function  $pO^{2-}$ , which should be valid for all oxyanionic melts.

What has been presented above is a very elementary account of electrochemical corrosion under quite ideal conditions. The details of the complex corrosion phenomena in real systems is out of the scope of this study.

## POTENTIAL- $pO^{2-}$ DIAGRAMS

The major importance of the function  $pO^{2-}$  is made clear from theoretical treatments such as those published by Edeleanu and Littlewood [8] and Littlewood [37,38], for example. The basis of these studies rests on the usefulness of the diagrams resembling those of Pourbaix and his collaborators [39] for corrosion in aqueous solutions, with the modification that the basicity of the system is written in terms of  $pO^{2-}$  instead of pH. The diagrams E- $pO^{2-}$  give information only on the thermodynamic feasibility of electrode reactions. It follows that it is not possible to draw conclusions from the diagrams on whether slow kinetic steps inhibit corrosion, or whether passivity will practically not occur because of a rapid dissolution rate of the surface film. This inconvenience is, however, eliminated by means of the polarization curves: electrode potentials vs. current densities applied to the electrode. Therefore, it is appropriate to consider that the static aspect stresses the potential- $pO^{2-}$  diagrams and that the dynamic aspect stresses the potential-current density curves.

The construction of the equilibrium diagrams E- $pO^{2-}$  is based on the well-known method used by Pourbaix in his E-pH diagrams [40]. The principle of the graphical representation E- $pO^{2-}$  is quite simple, but its application sustains a certain number of difficulties. In fact, if one wants to draw the diagram for a metal-oxyanion melt system, for example, it is necessary to outline the complete inventory of all the likely products of formation and to know the thermodynamic data relevant to these compounds. This basic work being done, it will be necessary to examine all the possible reactions between the compounds considered. In order to make the construction as systematic as possible, any reaction in which a substance A is changed into substance B is written in a form such that the only other species appearing are solvent ions, R (the symbol R is used here to represent the reducible and/or oxidizable species resulting from the acid-base dissociation of the melt), oxide ions,  $O^{2-}$  and anions,  $e^-$ . Such reactions therefore have the following general form, all symbols being collected on one side:



and it was shown in the section on "The Single Potential of an Electrode" that the corresponding conditions of equilibrium can be expressed in the form

$$a\mu_A + b\mu_B + c\mu_R - m\mu_{O^{2-}} - nFE_{0,26} = 0$$

$E_{0,26}$  being defined by the relation (7), which for the present case becomes

$$E_{0,26} = E_{0,26}^0 + \frac{2.3 RT}{nF} [a \log \{A\} + b \log \{B\} + c \log \{R\}] + \frac{2.3 RT}{nF} m pO^{2-} \quad (27)$$

It is therefore possible to consider several classes of reactions:

1. Reactions in which  $e^-$  anions do not take part.  
Equilibrium in these reactions depends or does not depend on  $pO^{2-}$  depending on whether  $m \neq 0$  or  $m = 0$ , respectively. These reactions are, of course, purely chemical reactions.
2. Reactions in which  $e^-$  anions take part.  
These reactions are electronation/de-electronation reactions; therefore, they are electrochemical reactions. Equilibrium in these reactions is given by expression (27). If the coefficient  $m$  is equal to zero, the equilibrium condition (27) is independent of  $pO^{2-}$ ; if  $m \neq 0$  equilibrium depends on both  $pO^{2-}$  and potential.

In these conditions, on the diagram one meets a series of straight lines having several positions. For example, reactions without de-electronation involving  $O^{2-}$  ions are represented by vertical lines; reactions with de-electronation in which  $O^{2-}$  ions do not take part are represented by horizontal lines; in other cases, the lines will have variable slopes depending on the values  $m$  and  $n$ . These groups of lines divide the field of the diagram into several domains, each corresponding to the domain of thermodynamic stability of the particular species.

Let us reproduce as an example the essential steps relative to the construction of a diagram  $E-pO^{2-}$  for Co in  $Na_2SO_4$  at  $900^\circ C$ . Following the above principles, the energetically probable products of the assumed reactions between the melt and the metallic cobalt in contact with it are envisaged. The species and their free energies of formation are given in Table 1. The standard free energies of formation ( $\mu_i^\circ$ ) at  $900^\circ C$  for the species considered were obtained from different sources [41-46]. In a few cases (e.g.  $Co_9S_8$ ,  $Co_3S_4$ ), extrapolation of data to  $900^\circ C$  was necessary.

**Table 1**

Standard free energies of formation for the species present in the Co- $Na_2SO_4$  at  $1173^\circ K$

| Substance  | Standard State  | $-\mu^\circ$ (Kcal/mole) | Reference |
|------------|-----------------|--------------------------|-----------|
| $SO_3$     | gas, 1 atm      | 63.350                   | [41]      |
| $SO_2$     | gas, 1 atm      | 66.050                   | [41]      |
| $Na_2S$    | solid sulphide  | 69.230                   | [41]      |
| $Na_2O$    | liquid oxide    | 59.560                   | [41]      |
| $Na_2SO_4$ | liquid sulphate | 220.080                  | [42]      |
| $CoSO_4$   | solid sulphate  | 113.900                  | [43]      |
| $CoO$      | solid oxide     | 36.076                   | [44]      |
| $Co_3O_4$  | solid oxide     | 110.505                  | [44]      |
| $CoS$      | solid sulphide  | 16.247                   | [45]      |
| $CoS_2$    | solid sulphide  | 14.078                   | [45]*     |
| $Co_4S_3$  | solid sulphide  | 51.871                   | [45]      |
| $Co_3S_4$  | solid sulphide  | 51.206                   | [45]*     |
| $Co_9S_8$  | solid sulphide  | 130.172                  | [46]*     |

\* Extrapolated value

Following the calculation procedure indicated in previous publications [47,48], the same considerations are applied to calculate the potential- $pO^{2-}$  diagram for cobalt. The species that may be formed when molten  $Na_2SO_4$  attacks Co are:  $Co^{2+}$ ,  $CoO$ ,  $Co_3O_4$ ,  $CoS$ ,  $CoS_2$ ,  $Co_4S_3$ ,  $Co_3S_4$  and  $Co_9S_8$ . These species may participate in 36 equilibrium reactions, for which the respective equilibrium conditions have been calculated. It is then possible to try to plot them graphically in a potential- $pO^{2-}$  diagram. However, an overall diagram providing a definite demarcation of the regions of relative predominance of all the species considered could not be obtained: either  $Co_9S_8$  or  $CoS$  has to be omitted or, in other words, it seems that the sulphide "CoS" cannot exist in equilibrium with  $Co_9S_8$  and  $Co_4S_3$  at  $900^\circ C$ . This difficulty is undoubtedly related to the fact that some free energy data used was extrapolated from equations given for temperatures well below  $900^\circ C$  which may introduce a considerable error. By comparing the figures established considering either  $Co_9S_8$  or  $CoS$  as the stable component, we have seen that the area of stability of the  $Co_9S_8$  is narrower than the area of stability of the  $CoS$  body. This fact, as well as the lack of thermodynamic data for the  $Co_9S_8$  at  $900^\circ C$ , led us to eliminate  $Co_9S_8$  with respect to  $CoS$ . Publications devoted to the Co-S-O system [45,49,50] have also contributed for this decision. Therefore, only the following relevant equations were considered here, as listed in Table 2.

Table 2

Electrochemical reactions and their equilibrium conditions for the Co-Na<sub>2</sub>SO<sub>4</sub> system at 1173°K

|                                                                                                    |                                                                        |
|----------------------------------------------------------------------------------------------------|------------------------------------------------------------------------|
| (6) $\text{Co}_3\text{O}_4 + 2 \text{e}^- = 3 \text{Co}^{2+} + 4 \text{O}^{2-}$                    | $E = -7.5354 - 0.3489 \log \{\text{Co}^{2+}\} + 0.4652 \text{pO}^{2-}$ |
| (7) $\text{Co}_3\text{O}_4 + 2 \text{e}^- = 3 \text{CoO} + \text{O}^{2-}$                          | $E = -2.1560 + 0.1163 \text{pO}^{2-}$                                  |
| (8) $\text{CoO} + 2 \text{e}^- = \text{Co} + \text{O}^{2-}$                                        | $E = -2.8892 + 0.1163 \text{pO}^{2-}$                                  |
| (9) $4 \text{CoO} + 3 \text{SO}_3 + 26 \text{e}^- = \text{Co}_4\text{S}_3 + 13 \text{O}^{2-}$      | $E = -3.0644 + 0.1431 \text{pO}^{2-}$                                  |
| (10) $\text{CoO} + \text{SO}_3 + 8 \text{e}^- = \text{CoS} + 4 \text{O}^{2-}$                      | $E = -3.0851 + 0.1454 \text{pO}^{2-}$                                  |
| (11) $4 \text{Co} + 3 \text{SO}_3 + 18 \text{e}^- = \text{Co}_4\text{S}_3 + 9 \text{O}^{2-}$       | $E = -3.1421 + 0.1551 \text{pO}^{2-}$                                  |
| (12) $\text{Co}_4\text{S}_3 + \text{SO}_3 + 6 \text{e}^- = 4 \text{CoS} + 3 \text{O}^{2-}$         | $E = -3.1722 + 0.1551 \text{pO}^{2-}$                                  |
| (13) $3 \text{CoS} + \text{SO}_3 + 6 \text{e}^- = \text{Co}_3\text{S}_4 + 3 \text{O}^{2-}$         | $E = -3.2493 + 0.1551 \text{pO}^{2-}$                                  |
| (14) $\text{Co}_3\text{S}_4 + 2 \text{SO}_3 + 12 \text{e}^- = 3 \text{CoS}_2 + 6 \text{O}^{2-}$    | $E = -3.2995 + 0.1551 \text{pO}^{2-}$                                  |
| (15) $\text{Co}^{2+} + 2 \text{SO}_3 + 14 \text{e}^- = \text{CoS}_2 + 6 \text{O}^{2-}$             | $E = -2.9129 + 0.0166 \log \{\text{Co}^{2+}\} + 0.1329 \text{pO}^{2-}$ |
| (16) $3 \text{Co}^{2+} + 4 \text{SO}_3 + 30 \text{e}^- = \text{Co}_3\text{S}_4 + 12 \text{O}^{2-}$ | $E = -2.7589 + 0.0233 \log \{\text{Co}^{2+}\} + 0.1241 \text{pO}^{2-}$ |
| (17) $\text{Co}^{2+} + \text{SO}_3 + 8 \text{e}^- = \text{CoS} + 3 \text{O}^{2-}$                  | $E = -2.6368 + 0.0291 \log \{\text{Co}^{2+}\} + 0.1163 \text{pO}^{2-}$ |
| (18) $\text{CoO} = \text{Co}^{2+} + \text{O}^{2-}$                                                 | $\log \{\text{Co}^{2+}\} = -15.42 + \text{pO}^{2-}$                    |

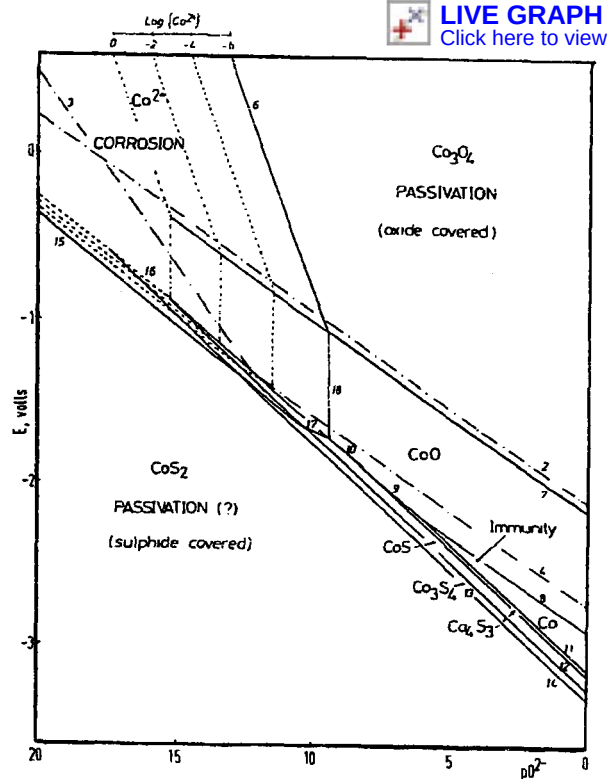


Fig. 4 E-pO<sup>2</sup> diagram for the system Co/Na<sub>2</sub>SO<sub>4</sub> at 1173°K

Fig. 4 shows the E- $pO^{2-}$  diagram for the system Co/ $Na_2SO_4$  at 900°C based on the assumption of sulphide and oxide formation, which occurs in real situations [49,50]. In this diagram, the lines bounding regions of soluble species are defined to represent activities of  $10^{-6}$ .

The diagonal broken lines (2), (3) and (4) in the diagram represent the limits for the thermodynamic stability of molten  $Na_2SO_4$  at 1 atm (101 KNm<sup>-2</sup>) total pressure. The lower lines represent the equilibrium potentials for the production of  $SO_2$  ( $P_{SO_2} = 1$  atm) and  $S^{2-}$  ( $\{S^{2-}\} = 10^{-6}$ ), respectively, as a function of  $pO^{2-}$ . In acid melts ( $pO^{2-} > 12.08$ ) the reduction of  $SO_3$  to  $SO_2$  is likely to occur rather than the reduction to  $S^{2-}$ , whereas in basic melts ( $pO^{2-} < 12.08$ ) the sequence is reversed. The upper limit of  $Na_2SO_4$  stability is that for the equilibrium between sulphate and oxygen ( $P_{O_2} = 1$  atm). This domain of stability provides information concerning the possible existence of mixed potentials and the probable reaction comprised there. Such usefulness is enabling us to correlate kinetic information of the Co electrode in molten  $Na_2SO_4$ , as reported in [51].

Since Fig. 4 takes into account the possibilities of oxide and sulphide formation, the stability of the metal Co can be discussed with any real significance. Such region of stability is limited by the lines defining the Co/CoO and Co/ $Co_4S_3$  equilibria. The most important feature of this region is that it lies outside the region for the stability of  $Na_2SO_4$ , therefore the establishment of conditions of Co immunity in  $Na_2SO_4$  cannot be achieved without the aid of external action. Another region shown in the diagram is the corrosion area, located at higher anodic potentials and low oxide-ion activity ( $9.42 < pO^{2-} < 18.12$ ), and limited by equilibria comprising Co oxides or Co sulphides/Co ion species. The third region shown in the diagram corresponds to the passivation area and it extends over the whole range of  $pO^{2-}$ . This region is limited at high anodic potentials by the reversible  $O_2/O^{2-}$  electrode line, where localised corrosion may occur because of the instability of oxide ion. Fluxing of the oxide scale may also occur in very basic melts, leading to the formation of salt-soluble cobalt anionic species [50] and the resulting accelerated oxidation. In these systems, the term passivation is a vague qualitative concept, but it is believed that it can be applied in principle to sulphide film growth as well as oxide film growth.

If the  $pO^{2-}$  is less than about 6, the potential of electrically insulated Co in contact with molten  $Na_2SO_4$  is near the equilibrium potential of the system Co/CoO illustrated in Fig. 4 by line 8, changing from values -2.2 to -2.9V according to  $pO^{2-}$ . If the  $pO^{2-}$  is increased from about 6 to 9, the potential is virtually that of the equilibria  $Co_4S_3$ -CoO and CoS-CoO, increasing to about -1.7V, as illustrated by lines 9 and 10. Values of  $pO^{2-}$  greater than 9 produce a dissolution of the CoO; then the potential rises to values represented by lines 17, 16 and 15, i.e. -1.7 to -0.5V according to  $pO^{2-}$ . This behaviour is in agreement with observations made by us, in the context of high temperature corrosion studies performed in our Laboratory.

When equilibrium conditions no longer prevail, the picture predicted by the thermodynamic diagram of Co/ $Na_2SO_4$  system may be strongly modified, although it is also possible that during corrosion or passivation in the case of the molten system, equilibrium conditions are closer than in aqueous systems. In any case, on the assumption of both sulphide and oxide formation, only the simultaneous basicity of the melt and cathodic polarization lowering the potential into the region of immunity of the metal may be an effective remedy against cobalt corrosion in the melt. On the other hand, the protection is much more reliable when the applied potential is only slightly more negative than the potential for the Co/CoO equilibrium, as the immunity region is very narrow. It is also obvious that the possibility of controlling cobalt corrosion by alkalis and cathodically polarizing is enhanced if the formation of cobalt sulphides occurs very slowly due to high overpotentials for processes like  $4 Co + 3 SO_3 + 18 e^- \rightarrow Co_4S_3 + 9 O^{2-}$ .

Further details on these diagrams are beyond the scope of this article and, for the practical employment of these methods, the reader is referred to several works published over the last 30 years [9,37,38,47,48,52-65].

It should be noted once more that the domains of thermodynamic stability considered above give only a theoretical possibility of existence, not a certainty. In particular as far as passivation is concerned, it must be pointed out that a proper passivity of molten media has not been obtained up to date, perhaps due to special properties of the film involved, mainly adherence, coherence and deviation from stoichiometry.

## POLARIZATION MEASUREMENTS AND FREE CORROSION RATES

In this section an account is given of several available methods for obtaining the potential-current curves as well as the free corrosion rates.

It is customary to classify the electrochemical methods for obtaining such potential-current curves into potential-sweep, current-sweep, potential-step and current-step methods. The former method, sometimes called potentiodynamic (or potentiokinetic) polarization, is accomplished by continuously changing the applied electrode potential (with feedback control) at a constant rate and simultaneously recording current. In the current-sweep (intensiokinetic) method, the electrolysis current (with feedback control) is varied with time according to a given programme, and the electrode potential is recorded as a function of current. In the potential-step method, electrode potential is rapidly changed over a finite increment, and current measured after a pre-determined time interval, and this process is repeated. In the last (above) method, a current step is applied and the resulting variation of potential with time is recorded. These two step methods are also referred to as potentiostatic and galvanostatic (or intensiostatic) respectively, to indicate that at any instant  $E$  (or  $I$ ) is held constant, by means of feedback control.

All the polarization methods described above are well established in the ambient temperature range [66-70] for electrochemical studies of metals, the best or most accurate of them depending, of course, on its intended use: if the purpose is to study kinetics phenomena, the methods in which the electrode potential is controlled are the best; when the permanent physico-chemical modifications, due to the applied current, are the objective, the methods in which the electrolysis-current is controlled are preferable. Generally speaking, however, potential-step and potential-sweep methods will be more useful for study of corrosion phenomena than current-step and current-sweep methods, because they give more precise indications concerning the quality of the passivation and concerning the conditions of activation. The investigation of corrosion processes in melts by these standard electrochemical techniques was pioneered by a reasonable number of researchers [3,7,71-82] and, in general, it can be said that almost all workers in the field of high-temperature agree that the classic polarization methods appear to be quite suitable in corrosion studies at high temperatures in molten electrolytes.

The polarization curves have several shapes, but near the potential axis their character is similar to that shown by the curves plotted in Figures 1 and 2.

A potentiodynamic polarization curve provides a graphic summary of the corrosion characteristics of tested material so that its plot and evaluation can be used as a very rapid and practically non-destructive corrosion test. However, the corrosion characteristics obtained are accurate only for the medium in which the curve was obtained. The importance of the method, therefore, does not lie in any final evaluation of the rates of corrosion in a particular medium, but rather in the rapid evaluation of fundamental corrosion properties with the possibility of sensitive relative comparison [70]. Another feature of the method is that analysis of such potential-current curves, together with the  $E$ - $pO_2$  diagrams, enables us to pre-determine those reactions theoretically possible and impossible for each electrode potential value.

One of the most important electrochemical values for the determination of the kinetics and mechanisms of primary corrosion processes is the value of the free corrosion current. When the primary corrosion process is slow (absence of concentration polarization) the free corrosion current can be obtained by potentiodynamically polarizing the alloy electrode at a very slow sweep rate, in



the neighbourhood of the free corrosion potential. The alloy-dissolution rate is obtained by plotting potential vs. log current and extrapolating the linear anodic and cathodic branches to the free corrosion potential, the intercept giving the free corrosion current. This method can also be applied when some (relatively small) concentration polarization is present; the latter can be taken into account by using the approximate expression:

$$I = \frac{I_{\text{meas.}} \times I_d}{I_d - I_{\text{meas.}}}$$

where  $I_{\text{meas.}}$  is the measured current in the presence of concentration polarization and  $I_d$  is the diffusion current (of course this correction implies the exact knowledge of the diffusion current). When the primary corrosion processes are sufficiently fast, other methods, namely relaxation methods, must be used. The objective of these methods is the study of the electrode processes before they become diffusion controlled. The experimental techniques associated with these methods are very complex, but they are the most important ways which permit accurate determination of fast charge transfer corrosion rates. Several relaxation methods for these measurements have been considerably revised in 1970 [83], and a useful exposition of the «classical» relaxation methods is that of Damaskin [84]. The selection of the method to measure the free corrosion currents, depending precisely on rate phenomena, is obviously difficult (because the values of these corrosion rates are not known a priori).

In general, the high temperatures of fused salt systems cause most corrosion processes to be rapid (reversible with respect to the non-relaxation methods). Generally speaking, thereby, relaxation methods will be the most appropriate for the determination of corrosion rates in melts.

The measurement of free corrosion rates in molten salts was pioneered by Baudo et al. [3] and by Cutler [6], among others. The first workers determined the corrosion rates using the conventional method, extensively and successfully applied at low temperatures in aqueous systems; they presented the results in the form of Tafel plots but they do not give information on the current-potential measured values from which the plots of  $E$  vs.  $\log i$  were obtained. It is rather surprising in view of the relatively high corrosion rates quoted that it had been possible to obtain pure Tafel zones. It is certain that this method enables the measurement of rough values (more of qualitative than quantitative value) of the free corrosion rates, but it is advisable to put into practice LaQue's opinion that new and more accurate tests should be introduced for a better understanding of the corrosion mechanisms [85]. A cyclic potential sweep method is used by Cutler [6] to determine the free corrosion rates which seems scientifically more appropriate than the conventional one.

The search for accurate methods for the determination of the kinetics and mechanisms of corrosion processes in molten salt systems has led to the study of newer electrochemical methods suitable for corrosion studies in aqueous systems. As a result, d.c. polarization curves, linear polarization resistance methods, a.c. impedance and electrochemical noise/galvanic coupling are continually increasing their application to molten salts, and it can be concluded that apart from being useful additions to investigate high temperature corrosion processes in molten salts, they have a demonstrated feasibility for use in on-line monitoring and for estimating corrosion under realistic operational conditions in boilers, gas turbines and other high-temperature equipment [86-90].

## CONCLUSION

In this paper, a glance at the essential elements concerning the electrochemistry of corrosion phenomena in molten salts was given. The electrochemical equilibrium diagrams, as well as the potential-current curves were shown to be two important tools put at the disposal of the scientist for the solution of corrosion problems. These diagrams, which are of thermodynamic character, can

serve primarily as a guide in carrying out such polarization curves and in the interpretation of the results obtained.

The techniques which can be used to obtain the polarization curves as well as the corrosion rates were briefly described. It was shown that the potentiodynamic measurements are particularly important in the evaluation of a series of experimental alloys. As far as passivation is concerned, analysis of such measurements, together with non-electrochemical examinations of the corresponding surfaces (e.g. by means of visual observation, electron probe micro-analysis) should inform on their true passivation.

The study of the electrode parameters (exchange currents, Tafel slopes and equilibrium potentials of the metal-dissolution and electronation reactions) in melts requires the use of the newer electrochemical techniques; in view of the dependance of the free corrosion rate on these parameters (as it is clearly brought out in Figure 3), its accurate measurement must be made using such techniques.

## SYMBOLS

|                      |                                                                                                                               |
|----------------------|-------------------------------------------------------------------------------------------------------------------------------|
| A                    | Area of electrode                                                                                                             |
| a                    | Constant                                                                                                                      |
| b                    | Tafel coefficient. Tafel slope ( $\partial E / \partial \log I$ )                                                             |
| E                    | Reactional electrode potential or electric potential of an electrode when it carries a current density (i)                    |
| $E_c$                | Free corrosion potential                                                                                                      |
| $E_M$                | Mixed potential                                                                                                               |
| $E_0$                | Single potential of an electrode or electrical equilibrium potential, measured with respect to a standard reference electrode |
| $E_0^0$              | Normal electrode potential, or equilibrium potential $E_0$ when the reactants are all in the standard state                   |
| $e^-$                | Electrons                                                                                                                     |
| F                    | Faraday's constant (96.5 KC/mol or 23.06 Kcal/volt-mole)                                                                      |
| $\Delta G^*$         | Chemical free energy of activation                                                                                            |
| $\Delta \tilde{G}^*$ | Electrochemical free energy of activation                                                                                     |
| I                    | Total current (i x area)                                                                                                      |
| $I_c$                | Free corrosion current                                                                                                        |
| $I_d$                | Diffusion current                                                                                                             |
| i                    | Any reacting species; current density                                                                                         |
| $i_0$                | Exchange current density                                                                                                      |
| K                    | Equilibrium constant                                                                                                          |
| $M_i$                | Chemical symbol of reactant i                                                                                                 |
| $\{M_i\}$            | Activity of constituent i (thermodynamic concentration)                                                                       |
| n                    | Valency of metal, number of electronic charges on solved-cation                                                               |
| P                    | Pressure (in atmospheres)                                                                                                     |
| $pO^{2-}$            | Cologarithm of oxygen-ion activity                                                                                            |
| R                    | Resistance of the electrolyte; gas constant (1.98 cal/°C)                                                                     |
| T                    | Absolute temperature                                                                                                          |
| $\alpha$             | Symmetry factor                                                                                                               |
| $\eta$               | Overpotential                                                                                                                 |
| $\mu_i$              | Chemical potential of constituent i                                                                                           |
| $\tilde{\mu}_i$      | Electrochemical potential of constituent i                                                                                    |
| $\mu_i^0$            | Standard chemical potential of constituent i                                                                                  |

- $\Phi$  Inner potential  
 $v_i$  Stoichiometric coefficient of constituent  $i$   
 Subscripts such as in  $E_{0,n}$  indicate that the symbol refers to reaction  $n$

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# Mechanism of Growth, Composition and Structure of Passive Films Formed on Ni, Fe and their Alloys in Molten Salt Electrolytes

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## Abstract

The growth kinetics, chemical composition and crystallographic structure of oxide films formed on Ni, Fe and their alloys with Cr, Mo, W, Al, Ta in molten salt electrolytes are reviewed. Special attention is paid to the effect of the composition of the molten salt mixture and the gas atmosphere on the stability and protective ability of corrosion layers. First, the thermodynamical background involving solubility calculations for a range of oxides formed on engineering materials in molten salt media is briefly commented. A concise review of the growth kinetics of passive films is also presented. These two introductory chapters serve as a guide for the extensive survey of the nature of oxide and related passive films on Ni, Fe and their alloys (both model and commercial) in molten chlorides, nitrates, sulphates, carbonates, hydroxides and mixtures thereof in gas atmospheres containing  $O_2$ ,  $CO_2$ ,  $SO_2$ ,  $SO_3$  and HCl.

## 1. Introduction

Corrosion problems in molten salts involve a variety of industrial processes, such as waste incineration treatments, corrosion of recovery boilers in the pulp and paper industry, "hot corrosion" of materials in gas turbines, high-temperature descaling and electromachining processes, and corrosion of current collector materials in molten carbonate fuel cells. There is no doubt that those corrosion phenomena are electrochemical in nature, involving the oxidation / dissolution of metal cations from the material, reduction of oxidant species, formation of continuous or porous corrosion films and their fluxing when contacted by the aggressive molten salt mixtures. Far less attention has been paid to the electrochemical study of passivation processes in molten salt electrolytes than in aqueous media or high-temperature dry gas systems. With the continuously increasing demand for alloy materials of a new generation working under extremely aggressive conditions, the study of such processes could provide a new insight in the possible improvement of the application of metallic materials in fused salt technology. A few years ago, we made an attempt to review systematically the corrosion of Fe, Ni, Co and their alloys in molten salt electrolytes [1]. Some general kinetic diagrams of the corrosion mechanism of these materials immersed in bulk melts were proposed and "hot corrosion" mechanisms involving the combined action of a thin molten salt film and an aggressive gas atmosphere were also reviewed. However, the growth mechanism, the nature, composition and structure of the passive films on the materials remained largely unexplored within the frames of that work. In that connection, the main purposes of the present review are as follows:

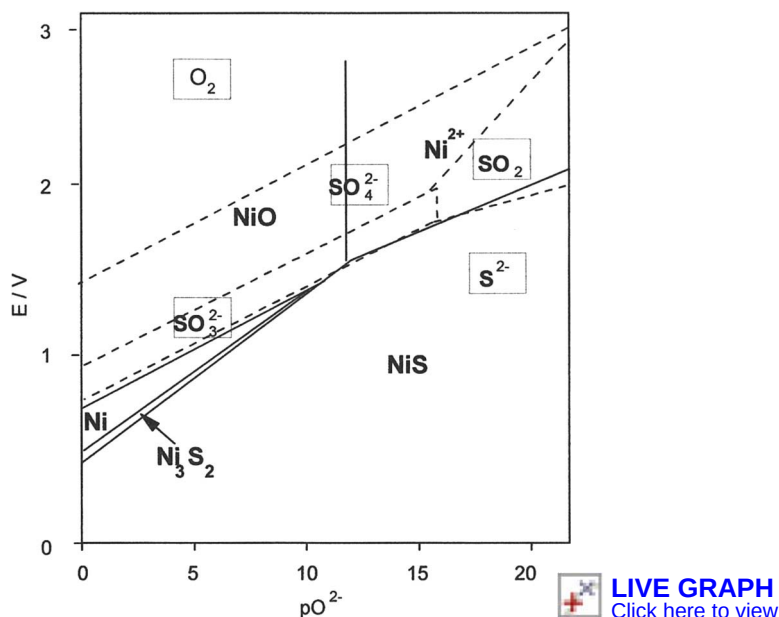
- to review concisely the thermodynamic predictions for solubilities of different oxides in molten salt mixtures and thus define a framework for the description of the nature of passive films formed on engineering materials in such media
- to give a short overview of the existing models for the growth kinetics of passive films
- to summarise the information gained over the recent years on the nature, chemical composition, chemical and crystallographic structure and electrochemical properties of oxide and related passive films formed on Ni, Fe and their alloys (including both model, experimental and commercial

materials) as depending on the melt and gas phase composition, as well as the presence and amount of alloying elements such as Cr, Mo, W, Al, Ta etc. on the protective ability of the corrosion layers.

## 2. Thermodynamical background. Potential- $pO^{2-}$ diagrams

The regions of immunity, corrosion and passivation of a metal in aqueous solutions can be assessed from the so-called Pourbaix diagram (potential-pH diagram). Bearing in mind that the oxygen anion was the most likely to be reduced during the partial cathodic reaction, potential -  $pO^{2-}$  diagrams were devised in analogy to this treatment for a range of metals in molten salt electrolytes to define the zones of corrosion and passivation. Some representative examples are given below.

### 1.1. Nickel [2-10]

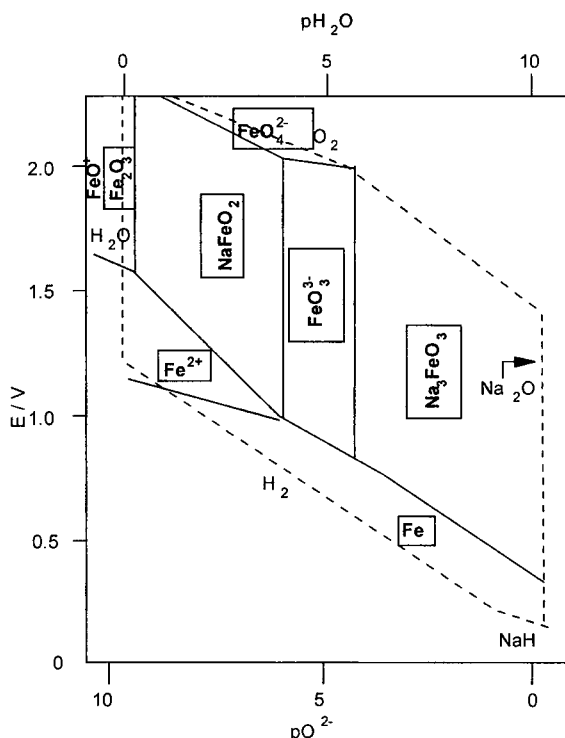


**Fig.1.** Potential -  $pO^{2-}$  diagram for the Ni- sodium sulphate system at 973 K [9].

Potential -  $pO^{2-}$  diagrams for nickel in molten carbonates [2,3], nitrates [4,5], nitrides [6] and sulphates [7-10] were developed. In extending Pourbaix's method to cover molten salts as well. it was necessary to find a function analogous to pH which would express the acidity of the system. It is known that the dissociation of oxygen-containing anions gives rise to a well-defined acid-base behaviour (Lux-Flood equilibria)



In accordance with the Lux-Flood theory, oxygen-containing anions act as a base in the supply of oxide anions and the corresponding gas oxides are their conjugate acids. From the above equilibria it follows that the acidity of the melt may be expressed either by  $pO^{2-}$  or by  $-\log p_{\text{gas}}$ . Accordingly, the  $E/pO^{2-}$  diagram provides a suitable framework for the electrochemical behaviour of different metals. Such a diagram for nickel in fused  $Na_2SO_4$  at 973 K proposed by Gribaudo and Rameau [9] is presented in Fig.1. The diagram at 1173 K given by Sequeira and Hocking [8] is, in principle, analogous to the one presented.



**Fig.2.** Potential -  $pO^{2-}$  diagram for the Fe - fused NaOH system at 523 K [11].

The assumption that the occurrence of corrosion implies an overall activity of ions  $> 10^{-6}$  M allows some predictions. The area of corrosion is distinguished at high potentials and low oxygen ion activity. The passive region comprises the oxide NiO and two sulphides, NiS and Ni<sub>3</sub>S<sub>2</sub>, extending over the whole range of  $pO^{2-}$ . Herein the passivation concept could be misleading because sulphides especially are unlikely to give effective protection. The NiO area extends at potentials above the  $O_2/O^{2-}$  line, i.e. passive film breakdown can occur via oxygen discharge (transpassivity). In basic melts the fluxing of the oxide scale by oxide ions can lead to the formation of soluble species (e.g.  $NiO_2^{2-}$ ) accelerating metal corrosion instead of passivation. It should be noted that this theoretical treatment is not obligatory relevant under the influence of morphology, solubility and kinetic factors.

## 1.2. Iron [9,11-12]



The theoretical background of the Pourbaix-like diagrams of iron in fused NaOH-KOH takes into account Equilibrium 4 and thus variations in acidity correspond to variations in the  $O^{2-}/H_2O$  ratio. The acidity influence the oxidation/reduction of hydroxides: reduction in acidic media leads to  $H_2$  formation, whereas in strongly basic melts,  $H^-$  is formed; oxidation of  $OH^-$  gives superoxides in acidic and peroxides in basic media. The potential -  $pO^{2-}/pH_2O$  diagram of iron [11] in fused NaOH at 350 °C is presented in fig.2.

The major conclusion is that the sole domain of iron solubility in NaOH is the strongly basic one, corresponding to the capacity of Fe(III) reduction. A weak solubility region exists in a strongly acidic medium in the presence of  $H_2O$  under the form of  $FeO^+$  or  $Fe^{2+}$  (in contact with  $Fe_3O_4$  solids). Finally, iron could dissolve as ferrate(VI) in a neutral and extremely oxidizing medium (peroxide+oxygen). The composition of the passive layer on iron is quite complicated and strongly dependent on oxoacidity (Fig.2). It comprises a range of pure and mixed iron oxides ( $Fe_2O_3$ ,  $Fe_3O_4$ ,  $NaFeO_2$ ,  $Na_3FeO_3$ ). The  $E/pO^{2-}$  diagram of iron in sulphate [9] also shows the stability regions of Feo and the iron sulphide, FeS. In the diagram, for iron in  $NaNO_3/NaNO_2$  mixtures [12] at low  $pO^{2-}$  (basic media), a  $Na_4Fe_2O_5$  region is detected. A good correlation was established between the diagram predictions and corrosion tests reported in the literature. Therefore, the thermodynamic studies allow a better understanding of the corrosion and nature of oxide layers in different molten salt mixtures.

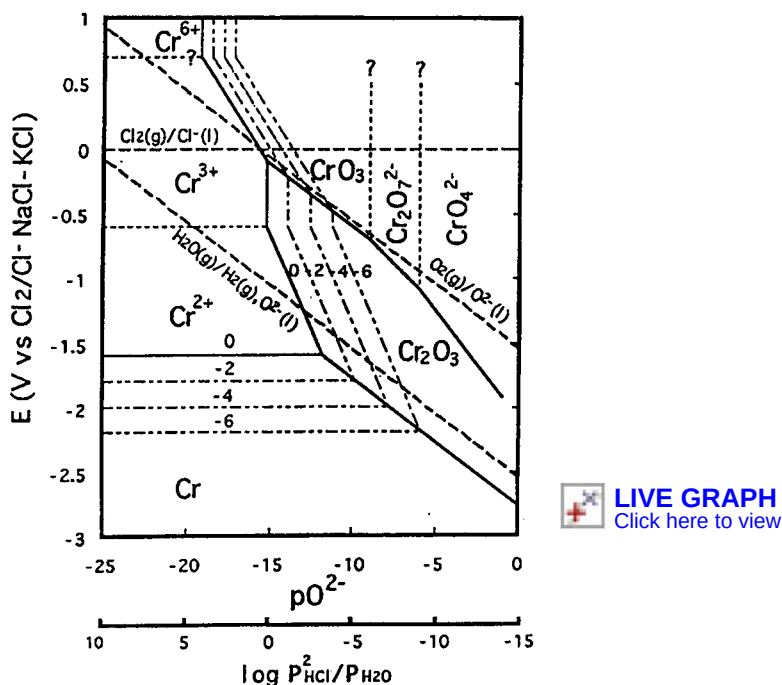


Fig.3. Potential -  $pO^{2-}$  diagram of Cr in molten NaCl-KCl at 1000 K [14].

### 1.3. Chromium [13,14]

Chromium is one of the main alloying elements ensuring better corrosion resistance of both Ni-base alloys of the Inconel or Hastelloy series and stainless steels (ferritic or austenitic). In some environments, however, overalloying with Cr can be considered not to lead to any improvement of the corrosion layer stability towards dissolution in the molten salt. The known experimental fact that

chromia scales dissolve in molten chlorides can be explained on the basis of the potential- $pO^{2-}$  diagram for Cr in NaCl-KCl (Fig.3) as presented by Ishitsuka and Nose [13] following Takahashi [14]. To allow this diagram to be compared with a classical Pourbaix diagram as drawn in aqueous solutions, the abscissa is reversed. According to the diagram, it is predicted that  $Cr_2O_3$  will be oxidised by oxygen in the atmosphere and dissolve as chromate in molten NaCl-KCl when the  $pO^{2-}$  of the salt is small. Indeed, molten salts coloured yellow by chromate are usually observed in synthetic chloride ash on steels containing high-amount of Cr in laboratory corrosion tests. On the contrary,  $Cr_2O_3$  is predicted to be stable in molten sulphates that are formed in gas turbines because  $pO^{2-}$  of the molten sulphates is high enough to minimize the solubility of  $Cr_2O_3$  [15].

### 3. Basic kinetic laws of film growth

Because of the importance of passivity in protecting industrially important metals and alloys from corrosion, extensive work has been carried out over the past hundred years to elucidate the mechanism(s) of the growth of passive films. In spite of the intensive effort that has been invested, relatively little is known of the electronic and physical properties of passive films. However, it is known that many, if not all, films grow according to either a logarithmic-rate law

$$L = A + B \ln t$$

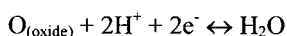
or an inverse logarithmic law

$$1/L = C - D \ln t$$

where  $L$  is the film thickness, and  $A, B, C$ , and  $D$  are constants. Furthermore, many passive films exhibit photoeffects that can be explained only by assigning semiconductor properties to the film. Indeed, a picture is emerging of passive films being highly doped semiconductors existing under the influence of a strong electric field.

One of the earliest models for the growth of passive films is that due to Cabrera and Mott [16]. This model assumed that: (1) The film grows by the transport of cations across the film to the film-solution interface, where they react with electrolyte; (2) the penetration of cations through the film is assisted by the high electric field; (3) the electric field strength is constant throughout the film and is equal to  $\phi_f/L$ , where  $\phi_f$  is the total potential drop across the film. For potentiostatic conditions  $\phi_f$  is constant; and (4) the rate-limiting step for film growth is the emission of metal cations from the metal into the film. The Cabrera-Mott model has been applied extensively for interpreting the growth of oxide films on metal surfaces. However, the model tends to yield unrealistic values for the jump distance  $a$ , and studies since this model was first proposed indicate that passive films tend to grow via the movement of anions through the film to the metal-film interface, where they react with the metal.

Fehlner and Mott [17] modified the original model by assuming that anion diffusion is responsible for the film growth, that the rate-limiting step is the emission of an anion from the environment into the film at the film-solution interface, and that the activation energy for the rate limiting step increases with thickness ( $W = W_0 + \mu L$ ). The principal objection to this model is that experimental evidence indicates that the interfacial reaction



is fast ( i.e., equilibrium is established rapidly) so that emission of an anion from the environment into the film is unlikely to be the rate-limiting step.

On the basis of their experimental work on the growth of passive films on iron in borate buffer solutions, Sato and Cohen [18] proposed the place exchange mechanism to explain the empirical rate law:

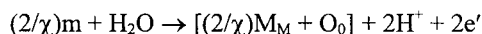
$$i = k' \exp(mV_{app} - Q_t/n)$$

where  $i$  is the current,  $V_{app}$  the applied voltage,  $Q_t$  is the accumulated charge (proportional to  $L$ ) and  $k'$ ,  $m$ , and  $n$  are constants. This equation can be integrated to yield a logarithmic law of the form

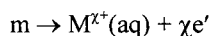
$$L = A + B \ln(t + t^0)$$

in which  $A$  and  $B$  are functions of various fundamental parameters.

More recently, Chao, Lin and Macdonald have developed the point defect model for the growth and breakdown of passive films [19]. The basis for this model is that films are considered to be highly defect structures with the principal defects being cation vacancies ( $V_M^{\chi 1}$ ), anion vacancies ( $V_o$ ), electrons ( $e'$ ) and holes ( $h^o$ ). The various reactions involving these species at the metal-film and film-solution interfaces are assumed to be in quasi-equilibrium, such that during film growth anion vacancies are created and consumed at the metal-film and film-solution interfaces, respectively. Similarly, cation vacancies are created at the film-solution interface but are consumed at the metal-film interface. The net effect of the movement of anion vacancies from the metal-film interface to the film-solution interface (or anions in the reverse direction)



is film (square brackets) growth, whereas movement of cations from the film-solution interface inwards towards the metal leads only to metal dissolution:



Thus, the conclusion is that film growth occurs inwards into the metal phase via the movement of anions through the film. Mathematical development of the point defect model yields the following integral-rate law:

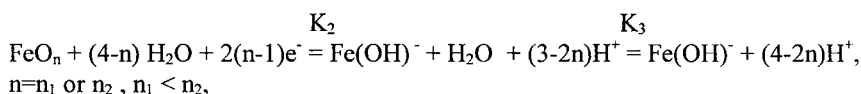
$$\exp(2KL) - 2KL - 1 = 2KA(B - 1)t$$

where  $K = F\varepsilon/RT$ ,  $\varepsilon$  is the electric field strength, and  $A$  and  $B$  are constants that depend upon the fundamental electrochemical and thermodynamic parameters for the system. For sufficiently thick films ( $L > 5\text{\AA}$ ) this equation converts to the logarithmic expression

$$L = [\ln 2KA(B - 1) + \ln t] / 2K$$

This model has been subjected to extensive evaluation for passive films formed on iron and nickel in borate and phosphate solutions, and it has been found to provide a quantitative description of the film growth phenomena.

On the other hand, the growth of a oxide film with variable stoichiometry in which the electrolyte can penetrate through pores or cracks due to e.g. efficient fluxing by the molten salt, can be shown to obey the parabolic rate law. Considering the formation of non-stoichiometric magnetite-like oxide  $\text{FeO}_n$  ( $n=1.0-1.5$ ) on Fe with a stoichiometry  $n_1$  at the metal side and  $n_2$  at the solution side and a saturated solution in the pores of the film [20]:



the diffusion gradient through the oxide of a thickness  $x$  is given by

$$dc/dx = (-1/x) ([\text{H}^+]^{-1} + K_3[\text{H}^+]^{-2}) [p_{\text{H}_2}^{(n_1-1)} \exp\{2(n_1-1)\text{FE}^0(n_1)/RT\} - p_{\text{H}_2}^{(n_2-1)} \exp\{2(n_2-1)\text{FE}^0(n_2)/RT\}]$$

where  $E^0(n_1)$  and  $E^0(n_2)$  are the standard potentials of the oxide electrode having a stoichiometry of  $n_1$  or  $n_2$ .

If the corrosion rate is controlled by this diffusion process then the rate of thickening is given by

$$dx/dt = KJ = -KD (dc/dx)$$

where  $J$  is the flux of dissolved species,  $D$  their diffusion coefficient and  $K$  is a constant involving voidage and tortuosity. Integration with  $x=0$  at  $t=0$  gives

$$x^2 = 2KDt([\text{H}^+]^{-1} + K_3[\text{H}^+]^{-2}) [p_{\text{H}_2}^{(n_1-1)} \exp\{2(n_1-1)\text{FE}^0(n_1)/RT\} - p_{\text{H}_2}^{(n_2-1)} \exp\{2(n_2-1)\text{FE}^0(n_2)/RT\}]$$

which is a parabolic growth law, the rate constant varying with the reciprocal proton concentration or the square of it depending on the relative predominance of  $\text{Fe}(\text{OH})_3^-$  or  $\text{Fe}(\text{OH})_4^{2-}$  as soluble corrosion products. Thus a theory involving a steady state between a dissolved species and a porous oxide of variable stoichiometry explains the continuous formation of the oxide on Fe in high-temperature hydroxide solutions.

#### 4. Mechanism of film growth and composition of passive film on Ni and Ni-based alloys in molten salt electrolytes

##### 4.1. Molten halides

Alkali chloride-based electrolytes are commonly used for electrodeposition of metals and alloys from molten media. Feng and Melendres [21] showed that the anodic dissolution of nickel in the pure LiCl-KCl eutectic at 375-470 °C followed pseudo-Tafel lines for several decades of the current. The addition of oxide ions allowed the exhibition of typical passivation features [21]. Passivation was partially irreversible for nickel. Nishikata and Haruyama [22] found that both the rest potentials and the corrosion rate of nickel and its alloys in molten NaCl-KCl were of the same order of magnitude. Anodic polarization curves for nickel in aerated NaCl-KCl exhibited a pseudo-Tafel behaviour with no traces of passivation at least for current densities lower than  $0.1 \text{ A cm}^{-2}$  [22].

Nishikata and Haruyama [22] demonstrated that chromium in an amount of 5-15 wt% considerably decreased the corrosion current density of nickel and inhibited its anodic dissolution due

probably to the formation of some chromium oxide on the surface [22]. Molybdenum in nickel alloys had a smaller impact on the corrosion rate but a greater one on the anodic dissolution [22].

A Ni-based superalloy (Hastelloy X, 21%Cr, 18%Fe, 9%Mo, balance Ni) was examined on compatibility with molten  $\text{NdCl}_3$ -NaCl-KCl mixture (50:5:45) in relation to its use in a fast breeder reactor for plutonium recycling [23]. In such an environment, the passive oxide film based on NiO or a spinel phase  $\text{Ni}(\text{Cr,Fe})_2\text{O}_4$  dissolves in the melt because of the presence of  $\text{NdCl}_3$ , which tends to get oxygen from the passive film to form a fairly stable oxychloride  $\text{NdOCl}$ . After the removal of the passive film, gaseous chlorides of Ni and especially Fe are expected to form. The chlorides of the minor alloying elements Mo and W, however, will be enriched in the near-surface layers to promote repassivation, especially in the case of a depletion of the water in the system [23].

The anodic behaviour of Ni and alloys 601(Ni-23%Cr-14%Fe) and 625(Ni-22%Cr-8%Mo-4%Fe) was studied in a equimolar NaCl-KCl-ZnCl<sub>2</sub> melt simulating the environment at the water wall tube temperature of 350 °C in a waste incineration plant [23]. Pure Ni as well as the two Inconel alloys present a relatively wide passive region in this environment. The magnitude of the passive region and the value of the passive current were found to depend on the integrity and thickness of the surface NiO layer. The effect of Mo was to suppress the corrosion in the nobler potential range. The thickness of the oxide film was estimated to be only 20 nm and a NiO layer was detected by scanning Auger microscopy. The initial corrosion rate of Inconel alloy 625 in a KCl-ZnCl<sub>2</sub> (1:1) melt at 400 °C was reported to be much slower than that of low-alloyed steels, however, the mass gain was found to increase much faster after several hours of exposure [25]. All over the oxide film Ni was detected in combination with Cr and Mo. Especially at the oxide / melt interface molybdenum was enriched in band-like inclusions. The composition of the scale was rather heterogeneous and also K and Zn were present in the entire scale. Thus the protective character of the oxide formed at 400 °C is quite dubious. To assess the corrosion mechanism of Ni-base alloys in molten chlorides in relation to waste incineration environments dissolution studies of the oxides of Ni, Cr and Fe in molten KCl-NaCl were recently carried out [13].  $\text{Cr}_2\text{O}_3$  was found to be unstable in these chloride melts and to dissolve as  $\text{CrO}_4^{2-}$ . The addition of  $\text{MoO}_3$  to the melt increases its acidity and accordingly decreases the solubility of  $\text{Cr}_2\text{O}_3$ , thus decreasing the overall corrosion rate of austenitic alloys.

The anodic passivation of pure Ni and Monel alloy (63%Ni, 28-34%Cu) was investigated in relation to the use of these materials in the production of fluorine [26,27] and  $\text{NF}_3$  [28-35]. Initial dissolution of Ni was found to be a prerequisite for the onset of nucleation of  $\text{NiF}_2$  in  $\text{KF} \cdot 2\text{HF}$  melt at 85°C [26]. As nucleation acts as a sink for Ni(II) ions the film formation process will lead to an increase in the anodic dissolution currents. Two diffusion regimes were observed in the chronoamperometric curves probably associated initially with diffusion of Ni(II) from the more concentrated region near the surface and then more slowly to the bulk solution. Finally, a constant current in the passive state is reached due to transport of Ni ions through the  $\text{NiF}_2$  layer in the steady state. It has been proposed [26] that the passivation mechanism involves competition between diffusion of Ni(II) ions from the electrode and the nucleation process. The electrochemically grown passive film on Ni was irreducible at potentials less negative than those for hydrogen evolution. A decrease of the currents during passivation with increasing rotation rate of the electrode was observed, in complete contrast to expected regular diffusion-controlled behaviour. This fact shows that the surface species of Ni(II) act as a catalyst to the dissolution of Ni from the substrate - if the concentration of these species in the near surface layer is reduced by rotation, the nucleation process of  $\text{NiF}_2$  will be slowed down causing a reduction in current [27]. The film dissolution time on pure Ni as measured by open circuit decay transients (assumed to be proportional to film thickness) is a function of the passivation time at constant potential and was found obey the direct logarithmic rate law of film growth [27]. In difference to Ni, the film growth on Monel alloy obeyed the inverse

logarithmic growth law which was related to the lower conductivity of the copper fluoride present in the passive film [27].

Concerning the anodic behaviour of pure Ni in  $\text{NH}_4\text{F}$ -HF melts with various additives (alkali metal or organic cation fluorides) in the temperature range from room temperature to 100 °C, it was divided in four regions as follows: active dissolution of Ni (0-1 V vs. SHE), passivation via a Ni(II) film (1-3 V), oxidation of the Ni(II) film to Ni(III) and/or Ni(IV) compounds (3-5 V) and electrochemical fluorination of  $\text{NH}_3$  (at potentials exceeding 5 V)[28]. Further investigations in  $\text{NH}_4\text{F}$ -HF-1%NaF melts with XPS evidenced that the passive film formed by galvanostatic oxidation at 120 °C contained mainly  $\text{NiF}_2$  and  $\text{NiO}$ , with highly oxidised nickel fluorides (either binary or coexisting in a form of Na compounds)[30,31]. The surface layer in  $\text{KF} \cdot 2\text{NH}_4\text{F} \cdot 6\text{HF}$  contained brittle  $\text{KNiF}_3$  without  $\text{NiF}_2$ , which may explain the lower stability of this film towards dissolution. Cyclic changes from a passive film to an electrochemically active film due to the changes in composition and/or thickness of the film with increasing electrolysis time were observed in potentiostatic experiments [32]. Concerning the oxide part of the passive film, it was found to contain more  $\text{NiO}$  in the inner part of the layer and more  $\text{Ni}_2\text{O}_3$  (or Ni(III) substituted in the  $\text{NiO}$ ) in the outer part of the layer. Later results seemed to suggest that there is a smooth transition in the composition between  $\text{NiO}$  in the inner part and  $\text{NiO}_{1+x}$  in the outer part of the passive film [34]. Also the existence of  $\text{Ni}_3\text{O}_4$  was inferred on the basis of open circuit potential decay curves in  $[(\text{CH}_3)_4\text{N}]\text{F} \cdot 4\text{HF}$  molten salt at room temperature [33]. Some evidence of high-valency nickel fluorides was also found in the XPS and open-circuit decay measurements[33]. Results obtained in hydrated  $\text{NH}_4\text{F}$ -HF melts seemed to indicate that the passive film formed on the Ni surface in the water containing melt is also composed of  $\text{NiF}_2$  with a small amount of nickel oxide having plural oxidation state. The content of nickel oxide in the compact film formed in the hydrated melt was found to be high compared to the porous film formed in the anhydrous melt [35].

#### 4.2 Molten nitrates

The study of anodic dissolution of metals in concentrated ionic solutions at high current densities is relevant in electromachining. The phenomenology of the corresponding processes is closely related to the dissolution of passivated metals through an oxide film. A kinetic model of nickel anodization in fused nitrate was proposed [36,37] taking into account the formation of the passive film and the electrodisolution of the metal by transport through the passive film. The rate of the passive film formation via two-dimensional nucleation and growth coupled with a diffusional contribution was expressed at a constant potential. If the metal was prepassivated, the mechanism could be simplified neglecting the metal dissolution through the passive film. The authors concluded that transpassivity is related to the rupture of the passive film resulting in localised corrosion. Solubility studies and thermogravimetric analysis of nickel and iron species in  $\text{NaNO}_2$  -  $(\text{Na,K})\text{NO}_3$  mixtures showed that the most stable sparingly soluble oxides are formed under the influence of the nitrite ion as a source of oxygen dianions [38], thus supporting the likelihood of formation of compact barrier-type oxide films in fused nitrates. Tzvetkoff et al. [39] investigated the different stages of anodic behaviour of Ni in  $\text{KNO}_3$  -  $\text{NaNO}_3$  melts (1:1) at 350 °C by electrochemical methods. Galvanostatic step measurements pointed to the oxidation of the primary passive film (presumably  $\text{NiO}$ ) to  $\text{Ni}_2\text{O}_3$  or a mixed-valency oxide. AC impedance spectra in the passive range were consistent with a cation vacancy transport limited film formation with irreversible injection of defects at the film/ solution interface. The transpassive corrosion was related to local breakdown and enhanced dissolution of high-valent nickel species together with oxidative decomposition of the melt.

#### 4.3. Molten sulphates

The electrochemical behaviour of Ni, Fe and their alloys in molten sulphates has been systematically studied in relation to the accelerated oxidation of aircraft gas turbine components at high temperatures beneath a thin coating of fused  $\text{Na}_2\text{SO}_4$ . The extensive work in identifying the electrochemical nature of the "hot corrosion" phenomenon has been very recently reviewed by Rapp [40]. Some of the general aspects of hot corrosion mechanisms have been reviewed also by us [1].

Sequeira and Hocking [41,42] observed nickel passivation via NiO formation in pure molten  $\text{Na}_2\text{SO}_4$ . The influence of  $\text{SO}_3$  (gas) was also studied [41] and a brief summary is given below: (1) the increased  $\text{SO}_3$  partial pressure led to the initiation of passivation; (2) the effect is more pronounced for preoxidized nickel samples in an  $\text{SO}_3$  atmosphere. Most of the results were confirmed by surface analysis in a subsequent paper [42] - both NiO and a  $\text{Ni}_3\text{S}_2$  sublayer were identified together with a Ni-Ni $_3\text{S}_2$  eutectic structure. Nishikata and Haruyama [22] demonstrated that nickel dissolved through the oxide film in  $(\text{Li,K})_2\text{SO}_4$  melts. Sulphate oxidation occurred at very positive potentials on the passive nickel surface [20]. Abou-Elenien [43] established that the corrosion current densities of nickel increased with the  $\text{SO}_2$  concentration. The role of  $\text{SO}_2$  cannot be separated from that of  $\text{SO}_3$ . Both the metal nobility and the formation of a coherent oxide layer affected the corrosion rate in molten sulphates [43].

An investigation of corrosion of nickel alloys containing carbides of titanium, zirconium, hafnium, vanadium, niobium and tantalum in molten  $\text{Na}_2\text{SO}_4$ -NaCl mixtures was carried out by Dmitrieva et al. [44]. HfC and ZrC additives seemed to ensure better corrosion resistance than pure nickel, whereas the other carbides had a negative impact (most pronounced with TiC) [44]. X-ray microanalysis showed that nickel and oxygen were evenly distributed; titanium was mostly in the carbide inclusions. The basic phases determined in the corrosion layer were NiO,  $\text{Ni}_3\text{S}_2$  in the nickel-containing part, as well as  $\text{NaTaO}_3$ ,  $\text{NaNbO}_3$ ,  $\text{NaVO}_3$ ,  $\text{VO}_x$ ,  $\text{TiS}_x$ , shaping the cathodic areas [44].

The complex plane plot of the electrochemical impedance for the corrosion of  $\text{Ni}_3\text{Al}$  in molten  $(\text{Li,Na,K})_2\text{SO}_4$  was found to be composed of a small semicircle at high frequencies and a line at low frequencies, suggesting a typical charge transfer/ diffusion controlled corrosion reaction[45]. The detection of a Warburg impedance may indicate that the alloy corrodes fast due to the formation of a non-protective oxide and that the corrosion is controlled by the diffusional supply of oxidants. The XRD and EDAX analysis of corrosion products revealed the formation of a non-protective layer composed mainly of uncorroded Ni,  $\text{Ni}_3\text{S}_2$ , NiO and  $\text{Al}_2\text{O}_3$  which are dispersively distributed in the corrosion layer. This was thought to agree to a certain extent with the electrochemical impedance measurements [45].

The resistance of overalloyed Ni alloys and Ni-superalloy coatings of the type NiCoCrAlY has been extensively investigated recently due to the use of these alloys in environments causing catastrophic hot corrosion behaviour (see e.g. Ref. 46). Pure Ni shows an active-to-passive transition in a molten sulphate-molten chloride mixture (equimolar  $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$ -NaCl-KCl at  $560^\circ\text{C}$ ) [47]. In the case of alloy 625, scanning Auger microscopy showed that the passive film consisted mainly of Ni oxide with Cr oxide present in the external part of the film. The concentration of Mo is significant in the inner part of the oxide. The internal sulfidation of alloy 625 was thought to be prevented by the presence of  $\text{MoS}_2$  in the innermost layer of the oxide film. The lower corrosion rate of Inconel 625 in a  $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$ -NaCl-KCl synthetic ash at  $600^\circ\text{C}$  in comparison to superaustenitic stainless steel was also confirmed by impedance spectroscopic measurements [48].

Exposure experiments carried out at  $600^\circ\text{C}$  in a sulphate mixture of 36%  $\text{CaSO}_4$  - 15%  $\text{Na}_2\text{SO}_4$  - 21%  $\text{K}_2\text{SO}_4$  - 21%  $\text{PbSO}_4$  - 7%  $\text{ZnSO}_4$  showed that chromium-free iron oxides and NiO are reprecipitated as external layer on alloys 602 and 625 [49]. The pits growing into the metal and

resulting from insufficient repassivation after fluxing were found to be filled with a layered Cr-rich and Zn-containing oxide with Ni and Fe in a solid solution -  $(\text{Zn,Ni})(\text{Cr,Fe})_2\text{O}_4$ . No Mo was detected in the entire scale for alloy 625. As pyrosulphate is formed in the melt by reaction of sulphates with  $\text{SO}_3$  from the gas phase, acidic conditions are established favouring the formation of Cr-rich phases in the pits (the solubility of  $\text{Cr}_2\text{O}_3$  is low under acidic fluxing). According to the periodic sequence of  $\text{ZnCr}_2\text{O}_4$  and pyrosulphate in the pits, an alternating process of dissolution and spinel formation was suggested. As a first step the melt reaches the metal/oxide interface by fluxing, dissolution of inclusions or penetration through pores, and oxidises the metal with the formation of a porous spinel oxide and pyrosulphate. By the formation of  $\text{ZnCr}_2\text{O}_4$  Cr is consumed which leads to the formation of new soluble products and repetition of the reaction sequence. In tests performed in HCl-containing atmosphere more precipitates of NiO and iron oxides are formed together with enhanced growth of Cr-rich corrosion products. On alloy 602CA, the inner oxide layer consists of thin layers of  $\text{Cr}_2\text{O}_3$  and iron-rich spinels with dissolved Ni. Some Mo was found in the inner layer on alloy 625 in difference to the studies in absence of HCl.

The investigations of several Ni-base superalloys containing Al and Ta was conducted in molten sulphate mixtures resulting from burning of a synthetic sea salt [50, see also Ref. 51]. The initial oxide film on the four new alloys was found to be Al and Ta-rich. The appearance of sulphides in the alloy indicated that S penetrated the outer part of the oxide film. Other scenarios for the fluxing of the oxide film include the effect of W (also an alloying element) in changing the molten salt chemistry to produce acidic fluxing, or a breakdown of the Al-Ta initial layer due to internal stresses leading to an entry of the corrosion reactants in the alloys.

The effect of the addition of vanadium oxides to the sulphate melts which induce fast hot corrosion at relatively low temperatures was also recently studied by several groups [52-56]. The exposure of Ni-20%Cr and Ni-20%Cr-4%Al thermal spray coatings in a  $\text{Na}_2\text{SO}_4$  melt at 900°C after 16 h preoxidation (10  $\mu\text{m}$  oxide, composition: NiO,  $\text{Cr}_2\text{O}_3$  and  $(\text{Ni,Cr})_2\text{O}_4$ ) resulted in fluxing of the oxide by the formed pyrosulphate anion. The XRD analysis revealed some  $\text{NiSO}_4$  presence in the coating, no sulphides or chromates were detected. The slight corrosion of the sample was presumed to be due to synergistic dissolution of NiO and  $\text{Cr}_2\text{O}_3$ . The exposure of a Ni-20%Cr-4%Al coatings to the  $\text{Na}_2\text{SO}_4$  - 30%NaVO<sub>3</sub> melt resulted in the formation of a thick layer of corrosion products containing  $\text{Ni}_3(\text{VO}_4)_2$ , NaVO<sub>3</sub> and traces of  $\text{V}_2\text{O}_4$ . According to impedance spectroscopic studies of sulphate-vanadate melts [57] the dominant oxidising species is a minority species related to  $\text{V}_2\text{O}_5$ . The analysis of the oxide film formed on a Ni-10%Cr-10%Co-10%W-6%Al - 2%Mo-3%Ti superalloy in a 60%  $\text{Na}_2\text{SO}_4$  - 30% Na VO<sub>3</sub> - 10% NaCl at 900-975°C [54,55] revealed a thin outer layer of NiO, thick layer of  $\text{Ni}_3(\text{VO}_4)_2$  with an inner porous duplex layer of oxides of Ni and Cr and CrS. The metavanadate was thought to cause excessive fluxing of the oxide and sulphate thus to reach the metal / film interface and to form Ni-Ni<sub>3</sub>S<sub>2</sub> eutectic layer, which is later transformed to CrS and a series of Ni vanadates. The observed decrease of the corrosion rate was presumably due to the reprecipitation of refractory Ni vanadates such as  $\text{Ni}_3\text{V}_2\text{O}_8$  and  $\text{Ni}(\text{VO}_3)_2$ .

#### 4.4. Molten carbonates

The corrosion and anodic behaviour of a range of metals in molten carbonates were studied in relation to the operation of high-temperature fuel cells. Devereux and co-workers [58-61] contributed greatly to the understanding of corrosion and anodic oxidation of nickel in carbonate melts. A numerical procedure for the analysis of complex polarization curves [6061] was applied in the study of the corrosion nickel electrode in  $\text{Na}_2\text{CO}_3$  melt in a CO/CO<sub>2</sub> atmosphere of various compositions. The procedure was based on the model approaches of Vetter and treated the total



current at any potential as a sum of the partial anodic and cathodic current densities of individual processes assumed to take place under reaction-diffusion control. Passivation was taken into account simply by assuming the independence of current above a certain critical value of the potential [61]. By comparing the environmental dependence of empirical model predictions for the individual reaction with theoretical candidates, a total of four anodic and one cathodic reactions were suggested to run on nickel in carbonate. The existence of NiO and possibly of  $\text{Ni}_2\text{O}_3$  was confirmed by X-ray diffraction studies [61].

Cyclic voltammetric experiments show that the behaviour of binary Ni-Fe alloys in molten  $\text{Li}_2\text{CO}_3$ - $\text{K}_2\text{CO}_3$  exhibits a gradual change from iron-like to nickel-like behaviour [62]. The first oxidation reaction is the oxidation of Fe resulting in a cubic solid solution of FeO and  $\alpha\text{-LiFeO}_2$  formation. At a more anodic potential a solid solution of NiO and  $\alpha\text{-LiFeO}_2$  followed by  $\alpha\text{-LiFe}_5\text{O}_8$  are formed resulting in a dual passive layer on the alloy surface (inner layer of NiO- $\alpha\text{-LiFeO}_2$ , outer layer of  $\alpha\text{-LiFe}_5\text{O}_8$ ). At high anodic potentials, some  $\alpha\text{-Fe}_2\text{O}_3$  was detected, forming slowly on the Fe-rich alloys [62].

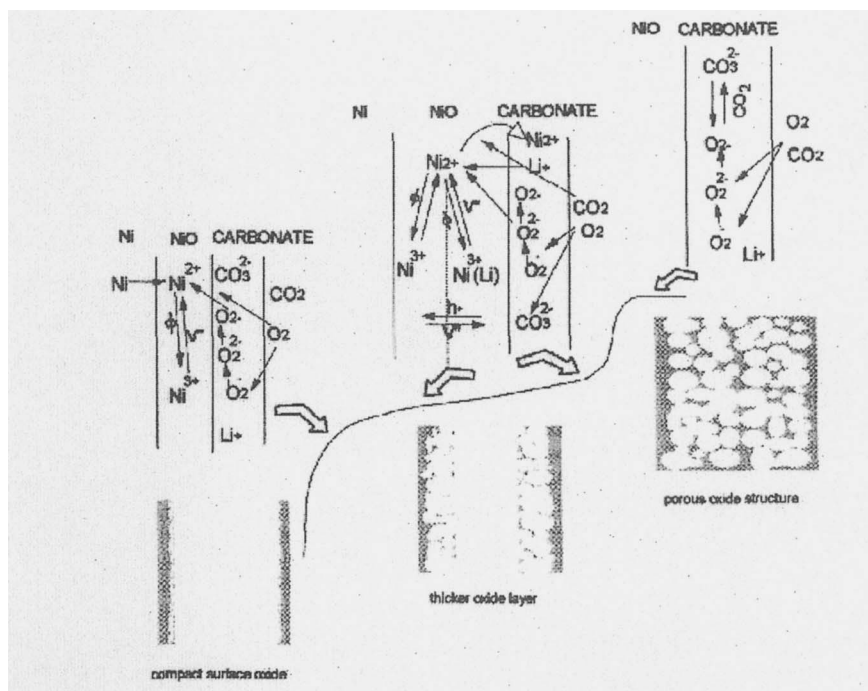


Fig.4. Solid state oxidation of metallic nickel in molten carbonate (after [63]).

The oxidation of Ni was followed in molten  $\text{Li}_2\text{CO}_3$ - $\text{K}_2\text{CO}_3$  (62:38) under standard oxidant gas (15%O<sub>2</sub>-30%CO<sub>2</sub>) at 650 °C by open circuit potential measurements and optical observations [63]. The solid -state reaction scheme for oxidation-lithiation of metallic Ni is shown in Fig. 4. The first stage of the oxidation according to the authors clearly corresponds to the oxidation of Ni to NiO. In the transition stage, further oxidation of the compact NiO layer begins in which Ni(III) ions and nickel cation vacancies are formed. Transport of nickel cation vacancies is assumed to be required to neutralise the charges of the excess oxide ions formed in the further oxidation reaction. During the third stage of oxidation, the oxygen evolution from carbonate is the only reaction taking place on the

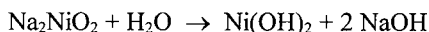
Ni/NiO electrode. This is supposed to lead to a further accumulation of oxygen ions in the oxide lattice presumably as oxygen interstitials [63]. The formation of NiO and its further oxidation to form a Ni(III) containing oxide was inferred from cyclic voltammetric measurements by Petrushina et al. [64].

In more acidic molten carbonates such as  $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$  it was proposed that NiO is formed directly via the reaction of the metal with carbonate anion [65], whereas in  $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$  an intermediate compound (e.g. some metastable form of  $\text{NiCO}_3$ ) was suggested. When such an intermediate compound forms and then decomposes to give NiO the final product has a fine structure resulting in a large active area of the electrode; in contrast, the active area of the electrode apparently increases less during the direct oxidation of Ni in  $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$  [65].

The impedance spectra of Ni in  $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$  (62:38) at 650 °C were shown to exhibit typical characteristics of a charge transfer/diffusion controlled reaction, i.e. a semicircle at the high-frequency part and a line in the low-frequency part [66,67]. Based on the measurement of the diffusion impedance, the diffusion of oxide anion was proposed to be the predominant feature of oxygen reduction. The oxide layer on Ni apparently had sufficient conductivity in order the transport of point defects in it not to be the rate-controlling step in the overall corrosion reaction.

#### 4.5. Molten hydroxides

Nickel corrosion in molten alkali hydroxides was the subject of a series of investigations due to the possible use of the metal as a base material for high-temperature reactors and baths. Budnik and Zarubitskij and Zarubitskij et al. [68,69] showed that during nickel corrosion in hydrated NaOH-KOH melts at 200 °C, the frequency dependence of the electrochemical impedance was consistent with the impedance of a film-covered electrode (most probably by NiO). The potential dependence of both active and reactive impedance components illustrated the possibility of NiO transformation into higher valency nickel oxides. The open circuit evolution of the electrode impedance following anodic polarization was explained by the oxygen exchange at the electrode surface [68]. A further study of the same authors [69] gave evidence of the formation of a corrosion layer of NiO by X-ray diffraction. Thermogravimetric analysis [69] showed that, besides  $\text{Na}_2\text{NiO}_2$ , higher valency nickel compounds are formed. The limiting stage of the process appeared to be either the NiO/ $\text{Na}_2\text{NiO}_2$  transformation or the nickelate dissolution in the melt. Owing to its higher ability to dissolve oxygen, KOH was proven to be more aggressive towards nickel than NaOH [69]. Nickel corrosion in NaOH was further studied in varying atmospheric conditions using X-ray and electron diffraction [70-72]. A primary corrosion layer was found to be mostly NiO (lattice constant 0.421 nm [71]). X-ray and chemical analyses of secondary corrosion products evinced the presence of  $\text{Ni(OH)}_2$  [71] formed via hydrolysis by water steam



The films formed on Ni in dry NaOH melt at 700-850 °C were analysed by X-ray diffraction [73]. NiO was identified as the main detectable product. The reaction products dissolved in the melt were analysed with atomic emission spectroscopy and were found to contain 27%Na and 36%Ni. X-ray diffraction and IR spectroscopy of these products supported the hypothesis of the formation of  $\text{NaNiO}_2$ . It was speculated that an interaction of NiO with  $\text{Na}_2\text{O}_2$  formed in the NaOH melt could produce sodium nickelate.

Studies of Ni alloys in molten hydroxide are scarce. The good corrosion resistance of Inconel 600 in NaOH at 380 °C was attributed by Tran et al. [74] to the formation of a protective passive film of Ni-Cr spinel type oxide which prevents the leaching of Cr as chromite and chromate from the alloy.

## **5. Mechanism of film growth and composition of passive film on Fe and ferrous alloys (stainless steel, iron aluminides etc.) in molten salt electrolytes**

### **5.1. Molten halides**

Pure iron is a rarely used construction material in a molten salt medium, and studies of its behaviour are limited. Iron oxidation in LiCl-KCl eutectic with and without  $\text{Li}_2\text{O}$  addition was studied by Feng and Melendres [21]. Anodic dissolution with a Tafel slope of  $\approx 0.1 \text{ V / decade}$  was measured for iron in the pure eutectic, the departure from linearity suggesting the mixed control of the process [21]. Cathodic and anodic portion of voltammetric waves showed the fine structure of multiple peaks which indicated passivation reactions with the multilayered films obtained. The rate of initial film formation appeared to be a dissolution-precipitation process complicated by a chemical reaction (presumably formation of Fe(II) chloride complexes). Film growth was probably governed by a high-field-assisted migration [21]. Reduction of anodic passive film on iron in LiCl-KCl- $\text{Li}_2\text{O}$  seemed to be a two-step process suggestive of some divalent compound of iron in the film.

The effect of oxyanion addition (sodium carbonate, peroxide, sulphite, sulphate, orthophosphate and diphosphate) on the corrosion and passivation behaviour of ferritic and austenitic stainless steels (corresponding to AISI 405, AISI 429, AISI 301 and AISI 304) in KCl-NaCl- $\text{BaCl}_2$  melt at 600 °C was studied by Abd El-Rahman et al. [75]. The corrosion of the tested alloys led to the formation of loosely adherent scales on the corroding surfaces. The composition of these scales was close to a mixed Fe-Cr oxide (Fe-Cr ratio close to 1:1) for the ferritic steels and Cr-Fe oxide (Fe-Cr ratio less than 1:2) containing some Ni on the austenitic steels. This porous scale did not prevent the selective leaching of Cr from the alloys presumably in the form of chromate. The addition of some oxyanions, especially carbonate and peroxide, was found to partly passivate the surface and to significantly suppress the selective leaching of Cr from the stainless steels into the melt [75].

The corrosion of Fe, Cr, Ni, carbon steel, low alloyed steel and austenitic stainless steel in  $\text{ZnCl}_2$ -KCl melts at 450 °C in pure oxygen was studied to assess the effect of heavy metal chlorides in waste incinerators [76]. The oxide scale formed on Fe was mostly  $\text{Fe}_2\text{O}_3$ , exhibiting distinctive separation from the substrate. The external  $\text{Cr}_2\text{O}_3$  scale on pure Cr spalled readily during the initial corrosion stage, leaving powder like corrosion products - mainly oxide and small amounts of chloride - remaining on the substrate surface. The composition of the scale on carbon steel was very similar to pure Fe, whereas some chromia was detected as an inner layer on the low-alloyed steels [76]. In all cases, chlorine was found to be enriched at the metal / oxide interface. For the two austenitic steels (AISI 310 and a 25%Cr-35%Ni steel marked as HP) a thick scale with a multilayered structure with alternating Cr- and Ni-rich oxides formed during initial stages of oxidation. The scale contained NiO, ZnO and  $\text{ZnCr}_2\text{O}_4$  besides  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . An important result of this study [76] is that the higher Cr content does not lead to an effective passivation and hence protection against the molten chloride. This has been related to selective leaching of Cr due to the dissolution of  $\text{Cr}_2\text{O}_3$  as chromate in the oxidising environment. It is also possible that the dissolution of protective  $\text{Cr}_2\text{O}_3$  scales by acidic fluxing might result in the formation of the highly volatile  $\text{Cr}_2\text{O}_2\text{Cl}_2$  therefore allowing a self-sustaining accelerated corrosion to occur for  $\text{Cr}_2\text{O}_3$ -forming steels [76].

The corrosion resistance of Incoloy 800 and 12CrMoV low alloyed steel in contact of a molten mixture of 52-48%mol.  $\text{PbCl}_2$  - KCl similar to that found in waste incineration plants has been

studied with conventional electrochemical techniques, electrochemical impedance spectroscopy and electron-probe microanalysis to assess the composition of the corrosion layer [77,78]. The influence of the temperature and of the presence of carbon in the salt on the corrosion layer was also assessed. A badly adherent oxide mainly consisting of  $\text{Fe}_2\text{O}_3$  particles is formed on low-alloyed steel in contact with molten  $\text{PbCl}_2$  in 5% $\text{O}_2$  at 500 °C [25]. On the superaustenitic AC 66 alloy (27%Cr-31%Ni) mainly voluminous  $\text{Fe}_2\text{O}_3$  and  $\text{PbCrO}_4$  are detected with a spinel oxide underlayer. No fluxing of the preexisting oxide was assumed to occur since  $\text{PbCrO}_4$  was found to be an insoluble corrosion product. The internal oxide growth is due to the attack of carbide precipitates by chlorine. Under the action of molten  $\text{ZnCl}_2$  at 500 °C an overlayer of  $(\text{Zn,Fe})\text{O}$  covering a spinel  $\text{ZnFe}_2\text{O}_4$  and pure magnetite as an inner layer are formed on low-alloyed steels. The oxide film on the superaustenitic steel AC66 was found to contain mainly  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{ZnO}$  with an additional spinel-type oxide of the type  $(\text{ZnFe})\text{Cr}_2\text{O}_4$  being identifiable by XRD. In this case, insoluble products as  $\text{ZnO}$  and  $\text{ZnCr}_2\text{O}_4$  prevented the fluxing of the preexisting oxide layer. In a  $\text{ZnCl}_2$ -KCl mixture at 400 °C only a  $\text{Fe}_2\text{O}_3$  outer layer and a  $\text{Fe}_3\text{O}_4$  inner layer with significant amounts of dissolved chromia were formed on the low-alloyed steel. Underneath these Fe oxides, a phase containing K, Fe and O is formed (e.g.  $\text{K}_2\text{Fe}_2\text{O}_4$ ), i.e. in this case due to the high viscosity of the potassium melt a full penetration of the fused salt mixture to the metal / oxide interface has been assumed to occur.

The compatibility of structural candidate materials for the force-free helical reactor blanket with Flibe ( $\text{LiF-BeF}_2$  2:1) molten salt mixture was studied extensively recently [79,80]. It was shown that metal oxides such as  $\text{Cr}_2\text{O}_3$ ,  $\text{Cr}_2\text{FeO}_4$  and VO might be stable in Flibe and that corrosion by the HF in Flibe might not occur if these oxides are constituents of the passive films on the surface. For a ferritic AISI430 steel, an Fe-Cr mixed oxide of the spinel type  $\text{Fe}(\text{Cr,Fe})_2\text{O}_4$  is formed in the inner layer and a mixed oxide of the haematite type  $(\text{Cr,Fe})_2\text{O}_3$  as an outer layer. The thickness of the film was of the order of 250 nm, thus the individual phases in it were not detected with X-ray diffraction. Water impurities create certain amount of HF in the system together with BeO. It is supposed that a spinel-type oxide can serve as a protective barrier against HF-induced corrosion in the molten Flibe [80].

## 5.2. Molten nitrates

Baraka et al. [81] revealed the formation of a passivating film of  $\text{Fe}_3\text{O}_4$  mainly during corrosion of mild steel in  $(\text{Na,K})\text{NO}_3$  eutectic at 250-450 °C [80]. Film thickening proceeded according to a parabolic law with an activation energy of 71.3 kJ mol<sup>-1</sup> [81]. Doelling et al. [82] investigated the effect of the NaCl additive on pitting corrosion of St37 in the  $(\text{Na,K})\text{NO}_3$  eutectic. Anodic polarization curves revealed three plateaus separated by Tafel regions probably due to  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  formation, nitrite and nitrate oxidation, respectively [81]. During pitting in NaCl-containing melts, a non-linear dependence of both pitting and repassivation potentials on  $\log c_{\text{Cl}^-}$  was observed. A protective chromium-iron oxide scale was formed on Cr-Ni containing steels; on the austenitic ones, the spinel type scale improved the corrosion resistance of the substrate [82].

The influence of moisture on the oxidation rate of Fe in  $\text{NaNO}_3$  and  $\text{KNO}_3$  melts at 340 °C was investigated by Singh [83]. The lower oxidation rate of Fe in  $\text{NaNO}_3$  melt as compared to  $\text{KNO}_3$  was tentatively explained by the higher stability of sodium oxide vs. potassium oxide formed during the reduction process of nitrate melts. The alkali metal oxides are supposed to react with the native oxide on Fe (e.g.  $\text{Fe}_2\text{O}_3$ ) to form ferrites of the type  $(\text{Na,K})\text{FeO}_2$  which have been detected as an outer layer of Fe in nitrate melts.

The oxidation behaviour of two types of stainless steels (ferritic with 15% Cr and austenitic - 20%Cr, 8%Ni) was further studied by Attia et al. [84] in a molten  $(\text{Na,K})\text{NO}_3$  mixture at 400-600 °C. The variation of potential with time at open circuit was explained in terms of propagation and

thickening of the oxide film at a rate increasing with increasing temperature. It was assumed that the oxide film thickens according to a solid state mechanism under high field strength. The low values of the activation energies (ca. 0.25 eV) suggested an ion hopping transport mechanism in the oxide matrix.

### 5.3. Molten sulphates

Schendler and Schwenk [85] divided the anodic oxidation of Cr-Ni containing steels and Inconel in the ternary (Li,Na,K)<sub>2</sub>SO<sub>4</sub> eutectic melt into three regions: active, passive and transpassive dissolution. Basically, five types of corrosion products were detected: I, inner layer containing oxides and sulphides (Ni-Cr-Ti steels, TiS<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>S<sub>3</sub>); II, no inner layer, porous oxides and sulphides (24%Cr steel, Cr<sub>2</sub>S<sub>3</sub>O layer); III, film of minor elements (Inconel, Ni<sub>60</sub>Cr<sub>23</sub>, active dissolution, Cr<sub>2</sub>S<sub>3</sub>O + Fe and Mn); IV, Inconel, transpassive region, sulphides and oxides of iron, nickel, chromium, vanadium-two layer structure of sulphides and oxides (Ni-Cr-Ti steels, passive region). The authors [85] concluded that inner sulphidation and two-layered films were typical both for the active and the transpassive dissolution (active dissolution being stimulated by reduction of SO<sub>4</sub><sup>2-</sup> to S<sup>2-</sup>, and the transpassive state by oxidation of SO<sub>4</sub><sup>2-</sup> to SO<sub>3</sub> and O<sub>2</sub>) [85].

The hot corrosion kinetic curves of Fe<sub>3</sub>Al-2%Cr in (Li,Na)<sub>2</sub>SO<sub>4</sub> eutectic at 605 and 800 °C were supposed to be divided into a parabolic-like portion for the initial 13 h and a quasilinear portion afterwards [86]. The initial corrosion film at the lower temperature is a mixture of Fe<sub>2</sub>O<sub>3</sub> and the molten salt, developing into a porous ferric oxide film. Gradually two distinct layers, outer of Fe<sub>2</sub>O<sub>3</sub> and inner of Al-sulphide were formed at longer exposure times. In addition, the Cr content was found to be enriched at the metal / film interface at the higher temperature. On Fe<sub>3</sub>Al-5%Cr, a mixture of Al and Cr sulphides was found to constitute the inner layer. Supporting studies of AISI 310 and AISI 321 showed that a much higher Cr content is obviously needed to form a complete chromium oxide inner layer which was supposed to act as a diffusion barrier to Fe ion transport. Electrochemical testing of Fe-40%Al in a 80%V<sub>2</sub>O<sub>5</sub>-20% Na<sub>2</sub>SO<sub>4</sub> molten mixture from 600 to 900 °C showed practically no active-to-passive transition at temperatures below 800 °C and a decrease in the corrosion current density with temperature increase. The oxides formed on the samples were very rich in vanadium and were readily spalling from the electrode surface [87].

Hot corrosion of different grade steels in molten sulphate mixtures with the addition of chloride and/or vanadate has been investigated in a range of recent work [25, 49, 88-90]. The oxide film on low-alloyed steels in 36% CaSO<sub>4</sub> - 15% Na<sub>2</sub>SO<sub>4</sub>-21% K<sub>2</sub>SO<sub>4</sub>-21% PbSO<sub>4</sub>- 7% ZnSO<sub>4</sub> under 5% oxygen at 600 °C was composed of a thick outer layer of Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> separated by a thin layer of FeS with dissolved Cr from the metal substrate [49]. No thick outer layer was formed on the superaustenitic AC66 alloy (27%Cr, 31%Ni). Only pits in the metal were found to be containing chromium rich oxides with various amount of Zn and (Ni,Fe) oxide dissolved in them. The addition of SO<sub>2</sub> to the gas phase resulted in the formation of a mixture of sulphides and oxides of Fe and Cr on the low-alloyed steels accompanied by a chromia-rich layer in pits on the superaustenitic steel. When HCl is added to the gaseous phase, the inner corrosion layer on the superaustenitic steel AC 66 mainly consists of FeCr<sub>2</sub>O<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> with some Zn and higher Fe-oxide content than in the atmosphere without HCl. At the metal/oxide interface, chlorides and sulphides of Cr and Ni were also identified.

### 5.4. Molten carbonates

The possibility of simultaneous or successive formation of  $\text{FeO}$ ,  $\text{Fe}_3\text{O}_4$  and/or  $\text{Fe}_2\text{O}_3$  with lithiation reactions between these steps was suggested for Fe in  $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$  (62:38) at 650 °C [63] (Fig.5). The formation of  $\text{LiFeO}_2$  in the external part of the passive film is assumed by these authors as well [63]. The simultaneous or successive formation of different oxides may cause internal stresses leading to crack formation contributing to a mixed potential between several oxidation and lithiation reactions.

After 25h of exposure of Fe to a  $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$  (62:38) melt and a typical molten carbonate fuel cell cathodic inlet gas (25% $\text{CO}_2$ , 15% $\text{O}_2$ , bal. $\text{N}_2$ ) only  $\text{Li}_5\text{Fe}_5\text{O}_8$  was observed by XRD [91]. This oxide has a cubic structure very similar to wustite  $\text{FeO}$ . In a cyclic voltammogram, the formation of  $\text{FeO}$  and  $\text{Li}_5\text{Fe}_5\text{O}_8$  gave rise to two overlapped anodic peaks. At higher potentials,  $\text{Li}_5\text{Fe}_5\text{O}_8$  is transformed to the spinel oxide  $\text{LiFe}_2\text{O}_4$  which is closely related to magnetite ( $[\text{Fe}^{3+}]_{\text{tet}}[\text{Li}^+_{0.5}\text{Fe}^{3+}_{1.5}]_{\text{oct}}\text{O}_4$ ). With increasing anodic potential the thickness of the passive film increases and additionally  $\text{LiFeO}_2$  overlayer is formed (a cubic oxide with statistical distribution of Li and  $\text{Fe}^{3+}$  ions in the octahedral sites). The protective effect of  $\text{LiFeO}_2$  is related to its low solubility in the eutectic mixture.

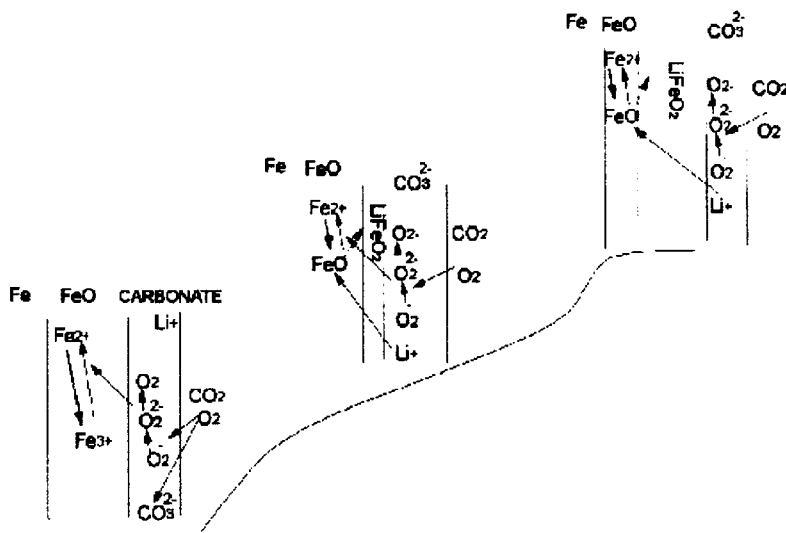


Fig.5. Solid-state reaction scheme for oxidation-lithiation for pure Fe in molten carbonate.

The electrochemical impedance diagram of FeAl in  $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$  (62:38) at 650 °C were found to have the characteristics of a charge transfer/diffusion controlled reaction for short immersion times (ca. 5h)[45,66]. For immersion times higher than 20h, however, the impedance measurements showed two capacitive loops in the complex plane plot, which was ascribed by the authors to the gradual formation of a protective oxide film containing an external  $\text{LiFeO}_2$  layer and an internal  $\text{Al}_2\text{O}_3$  layer. In this stage, the authors suggested that the corrosion is controlled by solid state transport (migration) of the ions in the scale[45,66]. Similarly, a field assisted migration mechanism was suggested to be responsible for corrosion film growth on ferritic (Fe-15%Cr) and austenitic (Fe-18%Cr-7%Ni and Fe-25%Cr-8%Ni) stainless steels under open circuit conditions in a  $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$  (43:31:25 mole %), i.e. a direct logarithmic growth law was inferred from potential vs. time measurements [92]. Both the charge-transfer resistance and the Warburg constant derived from the impedance spectra were found to increase with increasing the Cr content of the alloys,

inferring a blocking effect of Cr in the inner layer on the transport of ions effectively controlling the corrosion process.

The corrosion of AISI310 steel in  $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$  (62:38) at 650 °C resulted in the formation of  $\text{LiFeO}_2$  -  $\text{LiCrO}_2$  passive film [67]. The presence of fissures in  $\text{LiFeO}_2$  was assumed not to provide good protection against corrosion. Up to 80 h of immersion, the oxide gradually transformed into a multilayer structure with an internal spinel layer and an intermediate layer of Cr-rich oxide. Additionally, internal oxidation of the substrate occurred to form  $(\text{Fe,Cr})_2\text{O}_3$  oxide. The dissolution of part of the scale in the melt was assessed by electrochemical impedance measurements from the values of the polarisation resistance [67].

Qualitatively similar conclusions were reached in a study of AISI 304 corrosion in molten carbonate fuel cell environment [93,94]. The outer, porous, iron-containing oxide layer was believed to prevent the inner chromium oxide layer from catastrophic reaction with the molten carbonate in the cathode gas environment. The inner, compact chromium oxide layer containing Ni in turn was believed to provide an effective diffusion barrier against outward transport of metal ions and inward transport of oxygen ions which in overall reduces the growth of the outer iron-containing oxide layer. The oxide film formed at load conditions in the cathode gas indicates reduced corrosion. An outer lithium ferrite layer covers an intermediate layer of iron oxide and an inner layer with some Cr and Ni enrichment and Fe depletion. The corrosion under anode gas at open-circuit results in the formation of a solid solution of FeO and  $\text{LiFeO}_2$  in the outer layer and  $\text{LiCrO}_2$  in the inner layer (Ni is not oxidised). The corrosion under anode gas at load conditions gave as a result an inner lithiated oxide layer which was Cr and Ni enriched and Fe-depleted, and this layer was shown to be covered with the outer  $\text{LiFeO}_2$  layer.

Electrochemical impedance and surface analysis techniques were employed to study the effect of Cr on the corrosion of pure Fe in eutectic  $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$  mixture at 650 °C [95]. The addition of 5-10% Cr has been found to have little effect on the corrosion resistance, whereas additives of 20-25% Cr greatly improved it. The complex plane plot of the impedance for the corrosion of Fe and Fe-Cr alloys in the melt was composed of two capacitive loops which was interpreted as a solid-state migration controlled corrosion process. Thus the growth of a barrier-like layer enriched in Cr was supposed to be taking place on the high-Cr alloys.

The thickness and composition of the corrosion and anodic oxide films on Fe, ferritic (Fe-18%Cr and Fe-25%Cr) and austenitic (AISI 310 and AISI 316) steels were analysed by EDX and glow discharge optical emission spectroscopic (GDOES) techniques to provide a correlation with voltammetric and impedance spectroscopic measurements[96,97]. The single layer corrosion product on pure Fe was found to consist of  $\text{LiFeO}_2$ , magnetite and wustite and not to be a compact barrier-like film. The outer layer on Fe-18%Cr and Fe-25%Cr alloys was found to contain  $\text{Li}_5\text{Fe}_5\text{O}_8$ ,  $\text{Li}_2\text{Fe}_3\text{O}_5$  and  $\text{Fe}_2\text{O}_3$ , whereas the inner layer was enriched in Cr. The compact inner layer on AISI 316 contained mainly Cr and Ni, whereas the outer layer contained Fe,Cr and Ni in almost equal proportion. GDOES results show that Ni contributes to the formation of a thinner oxide film on AISI 316. In general, GDOES results showed that the increase in Cr content gave a thinner and more barrier-like corrosion film on the surface.

Further investigations were carried out on the effect of degree of sensitisation on the anodic behaviour of AISI 316 in the cathode gas environment of the molten carbonate fuel cell [98]. In the passive region, the passive dissolution current tends to increase with the sensitisation treatment time. Additionally, film growth on the sensitised sample proceeds ca. two times faster when compared to

the non-sensitised sample. EPMA analyses of the passive film showed that the chromium distribution in the film on the sensitised sample was less regular in the inner layer and especially the concentration of Ni in the inner layer was significantly decreased. In agreement with the previous study, this points to an important role of Ni in stabilising the inner barrier-like sublayer of the passive film.

Studies on the behaviour of several ferritic steels in standard cathodic gas conditions in a eutectic  $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$  mixture were recently conducted by Zhu and Lindbergh [99]. GDOES studies of a ferritic steel containing 23% Cr and 1.5% Al showed first a formation of an Al-rich layer containing Li, the amount of Cr and Fe decreasing towards the surface. In the latter stage of corrosion, an outer layer mainly composed of Fe, Li and O and an inner part rich in Cr and Al with a lower level of Li was built up. In spite of the fact that the concentration of Al was not sufficient to form a complete  $\text{LiAlO}_2$  layer, a protective Al-rich oxide inner layer was observed. A relatively good correlation was found between the thickness of the layer determined from the GDOES spectra and the polarisation resistance determined from linear sweep voltammetric measurements.

In parallel, the same authors conducted a study on the corrosion behaviour of high-Al containing ferritic steels (20-22%Cr, 4.5-5.8%Al) in the anode gas environment of the molten carbonate fuel cell [100]. GDOES analysis of the samples in three conditions - standard, outlet an inlet anode gas, showed that the thickest oxide was formed in the inlet anode gas situation (ca. one order of magnitude thicker than in the other two conditions). The composition profiles showed that a bilayer structure was formed. In the outer part of the layers grown under outlet and standard anode gas conditions the Al content was increased, while then decreasing towards metal/oxide interface. In the inlet condition the concentration of Al in the outer part of the passive film was small and it increased towards the inner layer. The Li profiles could be interpreted as the formation of lithium aluminium oxide. The Cr content was decreasing from the alloy to the surface of the film for all three conditions.

The effect of temperature and  $\text{CO}_2/\text{O}_2$  partial pressure on the corrosion of stainless steels in  $(\text{Li,Na})_2\text{CO}_3$  was investigated by Lim et al. [101]. From the surface analyses of the corrosion films, a change in the corrosion mechanism around 600 °C was deduced. Namely,  $\text{LiFe}_5\text{O}_8$  with a less crystalline and more porous nature was found to be the major constituent of the passive film at 580 °C vs. a more crystalline and compact  $\text{LiFeO}_2$  at higher temperatures. Further proofs for the unstable and unprotective film formed below 600 °C were found in the absence of active-to-passive transition in the polarisation curves recorded for AISI 316 stainless steel. Also, the leaching of Cr as chromate was observed by cyclic voltammetry and was supposed to be due to the insufficient protectiveness of the  $\text{LiFe}_5\text{O}_8$  oxide film at temperatures below 600 °C. The formation of  $\text{LiFe}_5\text{O}_8$  was also suggested to occur at high  $\text{CO}_2$  pressures due to the increased acidity of the melt at constant temperature.

The corrosion of austenitic FeCrNi and FeCrNiMn steels under cathodic current collector conditions in the molten carbonate fuel cell was extensively studied by Biedenkopf et al. [103-106]. The authors have shown that the corrosion of austenitic stainless steel can be divided in three stages. In the first stage, the stainless steel is oxidised to form an outer  $\text{Fe}_2\text{O}_3$  layer and an inner spinel  $(\text{Fe,Ni})\text{Cr}_2\text{O}_4$  layer. In the second stage, molten carbonate reached the oxidised surface and the formation of lithiated oxides ( $\text{LiFe}_5\text{O}_8$  and  $\text{LiFeO}_2$ ) was thought to begin. In the following third stage, the passive film was supposed to grow by inward diffusion of Li and outward diffusion of Fe(III) ions. Three different cases of coverage with molten carbonate are envisaged: a) if the inner corrosion layer limits the outward diffusion of ferric ions and the coverage with melt is high, the total oxide film is lithiated, thin and well adherent: (b) if the outward diffusion of ferric ions is fast compared to inward Li diffusion, only the outer regions of the film are lithiated, ferric oxides are the main corrosion



products and the outer layer exhibits poor adherence; (c) if the transport rates of ferric and lithium ions are of the same order of magnitude, the inner layer is not affected by carbonate - the passive film is protective only if  $\text{LiFe}_3\text{O}_8$  and  $\text{LiFeO}_2$  are formed in the outer layer. Stainless steels containing addition of Mn formed an additional layer of  $\text{Li}_2\text{MnO}_3$  beneath an Mn-rich  $\text{LiFeO}_2$  outer layer. The formation of an inner layer of a mixed  $(\text{Fe}, \text{Ni}, \text{Mn})_{\text{x}}\text{Cr}_{3-\text{x}}\text{O}_4$  spinel on stainless steels containing both Ni and Mn was supposed to reduce the outward Fe ion migration much better than the usual  $(\text{Fe}, \text{Ni})\text{Cr}_2\text{O}_4$  or  $(\text{Fe}, \text{Mn})\text{Cr}_2\text{O}_4$  spinels formed on FeCrNi and FeCrMn steels under these conditions.

### 5.5. Molten hydroxides

Kozhemjako et al. [107] found that iron passivated in KOH melts at 470 °C. The increase of  $\text{pO}_2$  via the reduction of  $\text{O}_2^{2-}$  and  $\text{O}_2$  resulted in the formation of siluble ferrites and ferrates [107]. Recently, a new concept of the so-called “cathodic corrosion” of Fe in melts based on NaOH was proposed [108]. According to this model, fluxing of the protective magnetite scale formed on Fe is effectuated by an oxidiser,  $\text{Na}_2\text{O}$ , which is formed near the electrode surface during the cathodic and secondary chemical reactions in the melt. According to this concept, the cathodic corrosion of Fe proceeds independently of an oxygen-containing atmosphere. Tzvetkoff [108] compared the corrosion rate of Fe (which was found to follow a quasi-parabolic kinetics) with the dissolution rate of sintered  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  in a NaOH melt at 480 °C and concluded that the corrosion rate of metallic Fe is smaller than the dissolution rate of the oxides. On the basis of X-ray diffraction analysis it was established that the main corrosion product was close to  $\text{Fe}_3\text{O}_4$ .

The corrosion layer formed on AISI304L in fused NaOH at 380 °C contained many cracks and significantly less Cr than the underlying alloy [74]. The oxide film on AISI 310 was found also to be depleted in Cr, however their adherence to the substrate was better. Open-circuit potential measurements suggested that the preferential mode of corrosion for AISI 304L could be crevice or pitting corrosion.

## 6. Summary and conclusions

An overview of the growth kinetics, chemical composition and crystallographic structure of the passive films formed on engineering materials (Ni, Ni-base alloys, Fe and Fe-based alloys) in molten salt electrolytes is presented. The following conclusions regarding the correlation between composition, structure and protective ability of the passive films can be drawn:

- Concerning Ni and Ni-base alloys in molten chloride electrolytes, it can be stated that the most protective oxide layer that forms is based on NiO. Chromium oxides are not stable in molten chlorides because of their dissolution to form chromate and thus overalloying with Cr could be detrimental for the stability of the material. There is some controversy on the effect of Mo on the stability of protective films on nickel alloys in molten chlorides. Ni-containing layers are also expected to enhance the protective ability of passive films on austenitic stainless steels in molten chloride electrolytes. In melts containing heavy metal chlorides, additional protection is offered by the formation of insoluble corrosion products such as  $\text{PbCrO}_4$ ,  $\text{ZnO}$  and  $\text{ZnCr}_2\text{O}_4$ .
- In molten fluorides, Ni passivates via the formation of a compact  $\text{NiF}_2$  layer containing some NiO and possibly high-valency Ni-oxides and fluorides. On ferritic steels, protection against fluoride melts is achieved via the formation of a spinel-type oxides containing significant amounts of Cr.
- Mainly barrier type films are formed both on Ni, Fe and their alloys in fused nitrates. Indeed, the kinetics of film formation and the extent of passivation in nitrate (and nitrite) media bears the closest resemblance to the stable oxide film-based passivity in aqueous media.

- Molten sulphate mixtures are particularly aggressive towards both Ni-superalloys and stainless steels. Partial protection is achieved by the formation of Cr-rich passive films such as spinel-type oxides. At the metal / oxide interface, sulphides are formed which do not offer plausible protection except for a possible positive role of MoS<sub>2</sub> formed on Ni-alloys containing significant amounts of Mo (it has been found to prevent further internal sulphidation of the material).
- NiO with some Ni(III) ions and accordingly nickel cation vacancies is the main constituent of the corrosion films on Ni in molten carbonates, the amount of lithium incorporated in it being significant all over the oxide scale. On steels and Fe-based alloys, dual layers are formed, the inner sublayer containing significant amount of Cr playing the role of diffusion barrier for the transport of Fe towards the molten salt and the outer layer of e.g. LiFeO<sub>2</sub> preventing Cr from direct contact with the molten carbonate mixture which would lead to its leaching as chromate. There are observations concerning the synergism between Ni and Mn in forming very stable quaternary spinel oxides that prevent dissolution of austenitic stainless steels containing both alloying elements by acting as a more effective diffusion barrier against outward Fe transport.
- There are comparatively few data on the kinetics of growth, composition and structure of the passive films formed on Ni,Fe and their alloys in molten hydroxides. The most protective oxide is formed on Ni and is based on NiO with possibly some high-valent Ni cations incorporated in it. There are data on the enhanced dissolution of Cr from stainless steels in molten hydroxides, showing certain analogy of the behaviour to that in some molten chloride mixtures.

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## Hot Corrosion in Gas Turbines

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### Abstract

The phenomenon of high-temperature corrosion in gas turbines is reviewed. Particular attention is given to the chemical and electrochemical aspects of molten salt hot corrosion. Information on the corrosion behaviour of gas turbine alloys and coatings is provided, and methods of overcoming the various problems are suggested.

### 1. Introduction

Alloys for high temperature application usually contain appreciable quantities of nickel: in particular, alloys based on the 80-20 nickel-chromium system have proved extremely successful because they can combine strength with good oxidation resistance at high temperatures. However, in gas turbine applications, where the products of combustion of the fuel used condition the atmospheres, oxidation resistance alone is insufficient, and the resistance of the alloys to carburisation, sulphur attack and corrosion by ash must also be considered.

Three main types of gas turbine may be listed: (i) Aero-engine, (ii) Industrial and (iii) Marine. Aero-engines burn clean fuel, but ingest impurities in the air-intake. This is aggravated in the marine-gas turbines since the air intake includes sea salt. Industrial engines burn inferior fuel containing vanadium and sodium, but the air intake can be filtered. Turbine components are made of Ni- or Co- based alloys. The blades and vanes are subject to cyclic temperature corrosion in alkali sulphate-oxide +/- chloride, +/- vanadic environment. Advanced turbines operate at high inlet temperatures (1350°C) and the industrial turbines at 1150°C. The blades are cooled to 850-900°C. Catastrophic corrosion occurs at lower temperatures 610-750°C for Ni-based alloys and 750-850°C for Co-based alloys. Coatings have been tested extensively in the field of gas turbines and these include multi-component alloy compositions and alloy-ceramic formulae as well as thermal barrier coatings. Superalloys form 50 wt% of gas turbine engines, the rest being about equal parts of Ti-alloys, steels and composites. Development trends in the superalloy systems are inclined towards directional solidification (DS), powder metallurgy (PM) and mechanical alloy processing (MAP).

In gas turbines used for aircraft applications, where highly refined fuels are used, corrosion, although still a problem, is usually secondary to stress considerations, but where turbines are used for marine and chemical plant or for production of cheap electrical power, it is often necessary for economic reasons to run on lower grade fuels, and these can introduce severe corrosion problems.

Thus, in studying corrosion under turbine conditions, the effects may be broadly divided into two categories, the first being the effect of the gaseous products of combustion, the second the effects of deposits. Sulphur present in the fuel and salt in the marine environment would lead to the formation of sodium sulphate. So it is sodium sulphate with or without sodium chloride (or nitrate) that has been most extensively investigated. However, internal sulphidation called «green rot»

which occurs in a carburising environment was reported by Hancock [1] and Strocchi et al. [2] while «black plague» corrosion found on high strength nickel-base turbine alloys was produced when a very dilute salt solution was injected into downstream air in minute quantities. Fuel quality does not cause «black plague» which is primarily metallurgical in origin, and is regarded as an oxidation phenomenon as Belcher et al. report [3].

The object of the present article is to review some fundamental aspects of hot corrosion and the behaviour of gas turbine materials in the presence of sodium sulphate (with or without sodium chloride), oxygen and sulphur-containing gases, which are the contaminants most likely to be commonly encountered in gas turbine combustion environments.

## 2. Engine Description and Materials

The principle of the gas turbine is as follows. Air is drawn into the engine and compressed. Fuel is mixed with the compressed air and burned in a combustion chamber with the object of heating the gas. The hot, compressed gas is then expanded through a turbine that extracts the energy from it; part of this energy is used to drive the compressor and the remainder is available for useful work. The maximum temperature in the cycle is the temperature of the gas entering the turbine, and this temperature is determined by the capability of the turbine to accept it. The hottest part of the turbine is the first stage, which consists of a ring of stationary airfoils, called the inlet nozzle guide vanes; and a ring of rotating blades called the first stage rotor blades or buckets.

The turbine inlet temperature in aircraft gas turbines rose progressively to a maximum of the order of 900°C. Further increases in turbine inlet temperature were achieved as a result of the introduction of cooling of the vanes and blades, using air drawn from the high-pressure compressor.

The earliest alloys used for gas turbines, developed in the 1940s, were based on the Nichrome (Ni-20%Cr) heater alloys, and the Stellite (Co-10%Ni-35%Cr) supercharger alloys. The strength of the nickel-base alloys was increased as a result of the introduction of the  $\text{Ni}_3(\text{Al}, \text{Ti})$  ordered phase, gamma prime. Increasing the volume fraction of gamma prime in the alloy required that the chromium content be reduced. No phase equivalent to gamma prime exists for cobalt-base alloys, and the modern cobalt-base super-alloy has changed relatively little from its origins.

These early alloys owed their oxidation resistance to the formation of a protective layer of chromia,  $\text{Cr}_2\text{O}_3$ , on the metal surface. However, a number of the nickel-base alloys with lower chromium contents also exhibited excellent oxidation resistance due to the formation of protective alumina scales. The components of the first stage of modern gas turbines are now generally coated with an alumina-rich layer designed to develop an  $\text{Al}_2\text{O}_3$  scale.

A major corrosion problem with the lower-chromium nickel-base gas turbine alloys was encountered in the early 1960s, in aircraft that were being used in missions at low altitudes close to the sea. Under these conditions, a rapid corrosion of the blades and vanes was sometimes encountered, leading to severe destruction of the involved materials.

The increasing cost of fuel has resulted in a renewed interest in improving the efficiency of gas turbine systems. In most cases, this involves the modification of the properties of the existing alloys and the production of new materials. A partial listing of companies producing and supplying high-temperature alloys is given below. The alloys referred to in this article and which a particular company produces are given in parentheses. Each company produces a more extensive range of high temperature alloys, and a complete listing can be found at the web addresses provided.

Avesta Sheffield (253MA): [www.avesta-sheffield.com](http://www.avesta-sheffield.com)

Carpenter Technology (309, 310, 600, 625, 718, Waspaloy): [www.cartech.com](http://www.cartech.com)

Haynes International (HR-120, HR-160, 214, 230, 556, 625, 718, Waspaloy, X): [www.haynesintl.com](http://www.haynesintl.com)

Inco Alloys International, Inc. (330, 600, 601, 617, 625, 718, 738, MA754, 800, 800H, 800HT): [www.incoalloys.com](http://www.incoalloys.com)

Krupp VDM Technologies Corp. (330, 600, 601, 602CA, 617, 625, 718, 800H, 800HT, 800L, X): [www.kruppvdm.de](http://www.kruppvdm.de)

Rolled Alloys (253MA, 309, 310, 330, 600, 601): [www.rolledalloy.com](http://www.rolledalloy.com)

Sandvik Steel (309, 310, 330): [www.sandvik.com](http://www.sandvik.com)

### 3. Early Studies

#### 3.1 General

It has been known for many years that at high temperatures in the presence of salt heat-resisting alloys undergo rapid corrosion. This problem was greatly intensified in the 1950's by developments in jet engines and the applications of nuclear energy. The extremely high temperatures (800°C and above) encountered in jet engines and gas turbines necessitated the development of new alloys, which have sufficient resistance to corrosion by the hot combustion gases as well as adequate mechanical properties at the high temperatures encountered. Alloys based on nickel and chromium are well known for their good resistance to oxidation at temperatures in the range 800-1200°C. With the demand for improvement in creep properties at elevated temperatures ( $\approx 900^\circ\text{C}$ ), alloy compositions have been modified, in order to attain these properties. This has been achieved by reducing the chromium content of the alloys, increasing the amounts of some of the elements already present, and introducing new elements. The alloy series – Inconel, Nimonic, Hastelloy and Malco and Disco – are a result of this. Betteridge and Heslop [4], and Sims and Hagel [5] have discussed the Nimonic alloys in detail. Rather unexpectedly, these changes in composition have resulted in a susceptibility to a form of high temperature oxidation in which sulphur acts as a promoter and propagator. This new phenomenon, more severe than the normal sulphur attack and generally referred to as «hot corrosion» [6] has been encountered in gas turbines operating in marine environments. It is acknowledged that this form of attack is associated with the unfavourable operating environment.

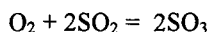
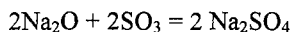
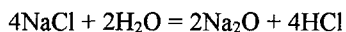
Much research has been done on the chemical nature of the deposits and the mechanism of attack which results, but it is apparent from the diversity of opinions held by various workers in the field that the phenomenon was not adequately understood in the seventies [7, 8].

However, there was general agreement that the corrosion proceeds in three steps:

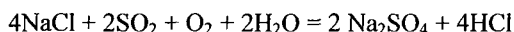
1. Deposition of a molten sulphur-bearing slag on the surface of the superalloy engine components.
2. Breakdown of the protective oxide film.
3. Reaction between the sulphur from the deposit and the base alloy.

The mechanisms that have been postulated differ principally in the explanations for the processes occurring in stages 2 and 3.

The slag that promotes sulphidation corrosion in a marine gas turbine is formed by the reaction of sulphur in the fuel and sodium from the sea salt ingested through the intake air [9]. Under the oxidising or de-electronising operating conditions, sulphur in the presence of a sodium salt such as sodium chloride (NaCl) is then capable of forming  $\text{Na}_2\text{SO}_4$  via  $\text{Na}_2\text{O}$  and  $\text{SO}_2/\text{SO}_3$ . The ability of NaCl to form sodium monoxide ( $\text{Na}_2\text{O}$ ) is well demonstrated by Quest and Drescher [10]. As it is known that sulphur dioxide is more effective in converting sodium chloride to sodium sulphate than sulphur trioxide several workers [11, 12] suggested that the transformation  $\text{NaCl}$  to  $\text{Na}_2\text{SO}_4$  involves the Hargreaves type of reaction which is the basis of an old process for the manufacture of sodium sulphate (salt-cake) [13]. The equations for the formation of  $\text{Na}_2\text{SO}_4$  might then be



or, combining these eqs.





As it has been shown by DeCrescente and Bornstein [9] this reaction, besides being thermodynamically favourable in the temperature range of interest, is quite rapid. Sodium sulphate produced by this means, together with that already present in the sea spray [14] can condense as a slag on the hot engine parts. This concept is supported by the detection of sodium sulphate on parts corroded in service [15].

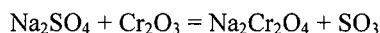
NaCl itself is almost never found in the deposits, due to its high dew point, but this does not rule out the possibility that impacting NaCl particles onto the alloy surface may play a significant part in the corrosion process [16]. Therefore, as discussed by Condé [17] NaCl may be one of the principal agents responsible for Na<sub>2</sub>SO<sub>4</sub> hot corrosion.

### 3.2 Alloy - Na<sub>2</sub>SO<sub>4</sub> reaction

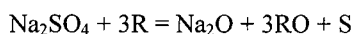
Reaction of a metal surface with its environment can occur only after the protective film is penetrated. In the case of the nickel-base superalloys this film is normally a mixture of Al-Ni-O and Cr-Ni-O phases composed chiefly of chromium and/or aluminium oxides (Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>) and in addition, a pure NiO type of oxide or Ni Cr<sub>2</sub>O<sub>4</sub> spinel oxide may form [18]. Whether Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> or NiCr<sub>2</sub>O<sub>4</sub> is responsible for protection is the subject of much controversy (see above) but it is widely believed that the major contribution comes from Cr<sub>2</sub>O<sub>3</sub> [7, 19, 20].

In the presence of a sodium sulphate slag the oxide film is penetrated, bringing into direct contact the metal surface and the molten salt.

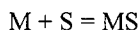
The mechanism of film penetration is uncertain but several possibilities exist [21, 22]. One explanation that has enjoyed wide acceptance suggests that the chromium oxide (Cr<sub>2</sub>O<sub>3</sub>) is dissolved by reactions of the type:



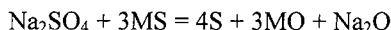
The events that occur after film destruction are not well understood. Earlier studies [15, 23-26] on this aspect have been mainly empirical, and only the experiments of Simons et al. [15] represent a real approach to the problem. They suggest that once the protective oxide film is penetrated, sodium sulphate may be reduced, or electronated, according to the following equations:



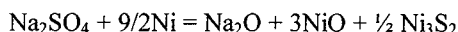
and

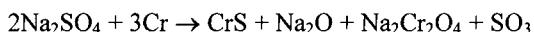


and



where R is an electronising agent, and M, in the case of complex superalloys, is composed of several elements including chromium. Rentz [27] suggests that NaCl acts as the reducing agent. Shirley [26] and Sykes and Shirley [28] also proposed that Na<sub>2</sub>SO<sub>4</sub> had to be chloride-contaminated to promote rapid sulphidation attack. Waddams et al. [29] proposed that Na<sub>2</sub>SO<sub>4</sub> reacts with the base metal at cracks and pores where micro-electronising conditions may exist. Many other workers [6, 10, 18, 30, 31] report that neither the chloride ion nor externally introduced reducing conditions are prerequisites for hot corrosion. Bergman [18], Seybolt [32], and Seybolt and Beltran [6], suggest that depletion of chromium in surface zones through the formation of oxides and sulphides reduces the corrosion resistance of Cr-depleted zones (nickel-rich zones), thereby promoting gross oxidation and/or sulphidation. Quets and Drescher [10] suggest that in order for hot corrosion to occur there must be a simultaneous reaction between the nickel of the alloy and the oxide of one or more of the alloy ingredients, with sodium sulphate. The equations for the corrosion of a nickel-chromium alloy might then be:





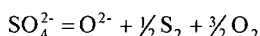
Bornstein and DeCrescente [30, 33, 34] and Bornstein et al. [35] show that the accelerated rates of oxidation associated with sulphidation attack are not related to preferential oxidation by sulphur in the alloy depleted zone and relate the rapid corrosion to the presence of oxide ions in the  $\text{Na}_2\text{SO}_4$  melt.

The most reasonable models available in the seventies for the  $\text{Na}_2\text{SO}_4$  hot corrosion of nickel-base alloys were essentially those due to Goebel and Pettit [31, 36] and Goebel et al. [37, 38]. In order to make progress towards discovery of the mechanism of hot corrosion they constructed thermodynamic diagrams describing the stability and composition of pure  $\text{Na}_2\text{SO}_4$  as well as the phases that may be formed during the exposure of nickel or aluminium to the sulphate environment. It was then necessary to consider reactions between oxides that are formed on the surfaces of alloys and  $\text{Na}_2\text{SO}_4$ , and in addition reactions between the protective oxides and other components that are introduced into the modified  $\text{Na}_2\text{SO}_4$  as a result of the oxide contaminant. Such studies indicated two types of hot corrosion.

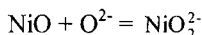
The less severe type, referred to as  $\text{Na}_2\text{SO}_4$ -induced accelerated oxidation, runs along the following lines:

- (i) An oxide layer is formed on the alloy surface, the oxygen required for its formation coming from dissociation of  $\text{Na}_2\text{SO}_4$  (see below).
- (ii) As a consequence of this, the sulphur activity at the oxide scale/  $\text{Na}_2\text{SO}_4$  interface increases to a level at which metal sulphides can be formed in the alloy beneath the oxide scale, providing sulphur can migrate through the oxide.
- (iii) Sulphide formation increases the oxide ion activity of the  $\text{Na}_2\text{SO}_4$ , eventually allowing the dissolution of the oxide as higher ions, for example  $\text{AlO}_2^-$  in the case of aluminium.
- (iv) Accelerated oxidation of the alloy occurs until the oxidation activity of the melt is no longer capable of fluxing the oxide scale.

This model assumes that when the  $\text{Na}_2\text{SO}_4$  comes into contact with nickel, the equilibrium oxygen pressure in  $\text{Na}_2\text{SO}_4$  is sufficient to oxidise Ni to NiO. The oxygen consumed because of NiO formation will displace the following dissociation equilibrium reaction existing in sodium sulphate to the right:



Thus the  $\text{Na}_2\text{O}$  and/or S activities rise at the NiO/  $\text{Na}_2\text{SO}_4$  interface. This sulphur then migrates in through the NiO layer [39] to the Ni-NiO interface where, due to the lower oxygen activities, nickel sulphide phases can be formed. Removal of sulphur from the sulphate increases the  $\text{Na}_2\text{O}$  activity of the  $\text{Na}_2\text{SO}_4$  in the vicinity of the alloy surface. In this  $\text{Na}_2\text{O}$ -rich layer formation of nickelate ( $\text{NiO}_2^{2-}$ ) ions following the reaction



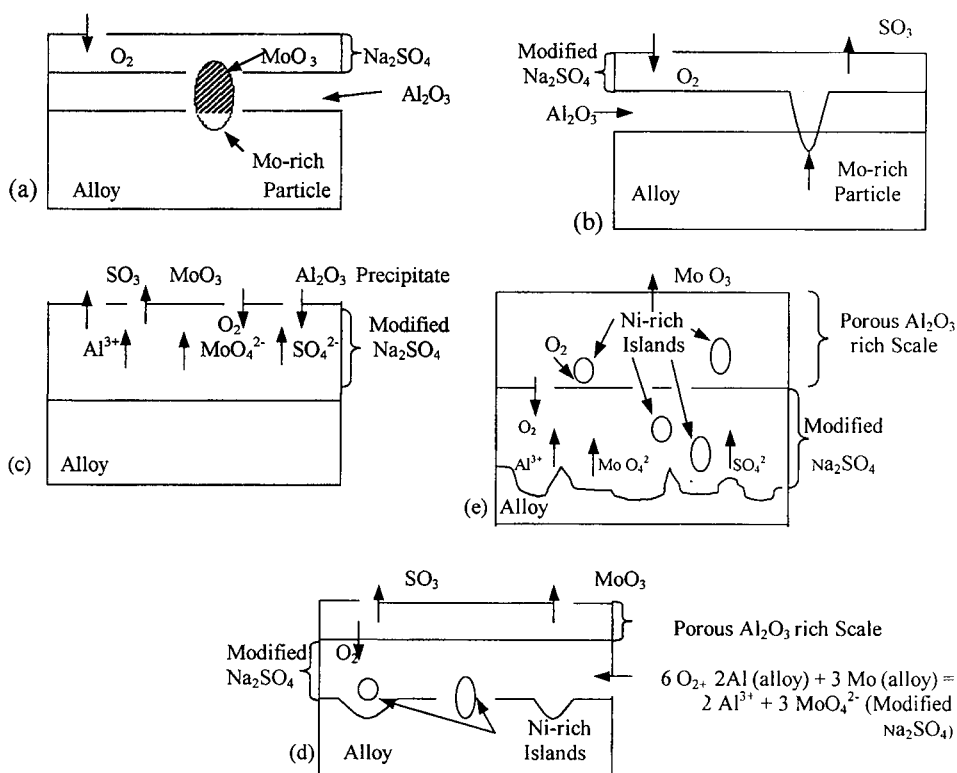
is likely to take place. Since the oxide ion activity of the unmodified  $\text{Na}_2\text{SO}_4$  is not sufficient for nickelate formation,  $\text{NiO}_2^{2-}$  decomposes as soon as it moves out into the  $\text{Na}_2\text{SO}_4$ . Consequently, a porous nonprotective nickel oxide scale is formed, and accelerated oxidation proceeds.

For the other type of hot corrosion, referred to as  $\text{Na}_2\text{SO}_4$ -induced catastrophic oxidation, the following features are believed to be applicable:

- (i) Oxide phases are developed on the alloy surface.
- (ii) Specific oxides (for example  $\text{MoO}_3$ ,  $\text{WO}_3$  or  $\text{V}_2\text{O}_5$ ) of the alloy scale form higher oxides by taking oxide ions from the  $\text{Na}_2\text{SO}_4$ , reducing its oxide ion content to a low enough level so that the protective oxide layer is thermodynamically unstable in the melt.
- (iii) Consequently, decomposition by ionic dissolution into the melt occurs, thereby allowing the salt to come in contact with and react with the metal alloy substrate.

- (iv) Rapid oxidation ensues, being self-sustained because the metal oxides responsible for this type of attack are continually formed in the  $\text{Na}_2\text{SO}_4$  adjacent to the alloy surface.

Goebel et al. [38] have schematically illustrated this model for a Ni-31Al-Mo alloy, as reproduced in Fig. 1, where the basic features above mentioned are well documented.



**Fig. 1** Model for the  $\text{Na}_2\text{SO}_4$ -induced catastrophic oxidation of a Ni-31Al-Mo alloy. (a) Oxygen moves from the gas through the  $\text{Na}_2\text{SO}_4$  to the alloy surface where metal oxides are developed. (b)  $\text{MoO}_3$  reacts with the  $\text{Na}_2\text{SO}_4$  that decreases the oxide ion activity of  $\text{Na}_2\text{SO}_4$ . (c) The modified  $\text{Na}_2\text{SO}_4$  layer reacts with the protective  $\text{Al}_2\text{O}_3$  scale that results in its destruction. However, vaporisation of  $\text{MoO}_3$  causes the  $\text{Al}_2\text{O}_3$  to precipitate as a porous network at the  $\text{Na}_2\text{SO}_4$ /gas interface. (d) Rapid oxidation ensues and aluminium is preferentially removed from the alloy and the alloy/scale interface becomes irregular. (e) The nickel-rich islands developed because of preferential oxidation of aluminium are converted to  $\text{NiO}$ . The rapid oxidation is self-sustaining because  $\text{MoO}_3$  is continually added to the  $\text{Na}_2\text{SO}_4$  by oxidation of molybdenum in the alloy [38].

In summary, the essential point to be emphasized is the crucial role of  $\text{Na}_2\text{O}$  on the  $\text{Na}_2\text{SO}_4$  hot corrosion of nickel-base alloys: if the oxide ion activity of the  $\text{Na}_2\text{SO}_4$  increases to the point where oxide scales can partially dissolve in the melt, induced accelerated oxidation is to be expected; if the  $\text{Na}_2\text{O}$  activity of the melts is so small that they are efficient dissociative fluxes for oxide scales, catastrophic oxidation occurs. In addition, the formation of sulphides beneath the oxide scales in

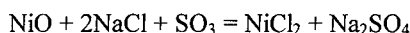
some alloys can cause the specimens to swell [40, 41] which results in increased oxidation [31, 36, 41].

### 3.3 Effect of sodium chloride

The previous discussion has been confined to molten sodium sulphate as a cause for metal destruction in gas turbines. Sodium chloride was shown to be a source of sodium for reaction with fuel-sulphur to form  $\text{Na}_2\text{SO}_4$ . It is also possible that  $\text{NaCl}$  by itself could be responsible for corrosion by flue gas deposits. It is widely reported, as a result of laboratory studies, that mixed sulphate/chloride slags produce a higher corrosion rate than sulphate alone [10, 25, 26, 40, 41-44].

Although a condensate of  $\text{Na}_2\text{SO}_4$  containing  $\text{NaCl}$  is unlikely to be formed above the dew point (the temperature at which salt species will condense on an inert solid surface) for  $\text{NaCl}$  ( $\sim 730^\circ\text{C}$ ) [12] under normal situations, its formation in the case of non-equilibrium conditions may occur [12, 16, 45].

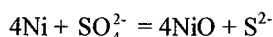
Corrosion by additive  $\text{NaCl}$  may be due in part to the formation of a low-melting-point mixture between these two sodium salts and also to the action of the chloride in causing a breakdown of the film. The  $\text{Na}_2\text{SO}_4/\text{NaCl}$  phase diagram illustrating the influence of  $\text{NaCl}$  on the melting characteristics of the mixture was constructed by Danek [21]. He concludes that since a molten slag is required for sulphidation, the m.p. of the salt mixture and hence the  $\text{NaCl}$  content exerts a serious influence on turbine operating temperature and thus efficiency and fuel economy. Later, Halstead [46] reviewed the general behaviour of oxides in the presence of sodium chloride. This review emphasizes that in gas turbines the nickel oxide/ $\text{NaCl}$  reaction may be better described by a general equation:



Since the  $\text{NiCl}_2$  equilibrium pressure for the preceding reaction is significantly lower than the vapour pressure of  $\text{NiCl}_2$  at temperatures of around  $900^\circ\text{C}$ , such a reaction could lead to a loss of nickel by vaporisation. This loss would lead to an appreciably less protective oxide film than one produced directly by de-electronation. Destruction of the protective chromium oxide film can also occur by the following reaction [47]:



The chloride may also have a catalytic effect on the following reaction:



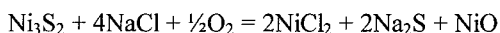
to cause the internal sulphur penetration observed. In an attempt to develop a picture of the role of chloride in the corrosion caused by flue gases and their deposits, Cutler et al. [48] carried out some studies and concluded that the chloride may be especially harmful in those cases in which the deposit environment fluctuates between electronising and de-electronising conditions because in these situations the alloy is never capable of building up a protective layer. Also Goebel et al. [37] have considered that  $\text{NaCl}$  may possibly accelerate the  $\text{Na}_2\text{SO}_4$ -induced hot corrosion but its influence has not been examined.

Sequeira [41] has studied the corrosion behaviour of nickel and Nimonic 105 in molten  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ , and mixtures of these two salts, at  $900^\circ\text{C}$ , in laboratory air and under  $\text{O}_2 + \text{SO}_2/\text{SO}_3$  atmospheres. The following conclusions were drawn from his electrochemical results, which were further supported by topochemical examinations of the corroded samples:

1. Three different regions characterize the electrokinetic behaviour of nickel electrodes in molten sodium sulphate at  $900^\circ\text{C}$ , in air. The first region corresponds to the onset of passivity and consists of the simultaneous nickel dissolution and passivation; the second is related to the dissolution of passive nickel; and the third corresponds to the local

oxidation of passive nickel and sulphate discharge. The passive film on Ni is mainly NiO.

2. The E/I curves for nickel in Na<sub>2</sub>SO<sub>4</sub>-NaCl melts, in air, in the range 0 to 80% NaCl, which are similar to the anodic polarization curve for Ni in pure Na<sub>2</sub>SO<sub>4</sub>, show that halide additions (especially those up to 25%) strongly affect the anodic behaviour of Ni in the active region and have practically no effect on the passive region. These higher dissolution rates are represented by the equation



which also suggested being a critical factor in the Ni passivation. Careful analysis of the transpassive part of the polarization curves also showed that the overpassive dissolution current is smaller in Cl<sup>-</sup> melts than in SO<sub>4</sub><sup>2-</sup> alone. This was further evidenced by particular experiments that have been concerned with determining the inhibiting role of NaCl on Ni in the passive-transpassive area.

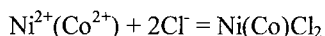
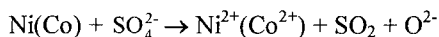
3. Further examination of the E/I curves for Ni in sulphate-chloride melts at 900°C lead to the conclusion that the rate determining step of nickel dissolution in the melts is mainly the diffusion process into the melt.
4. SO<sub>3</sub> atmospheres destroy the passive capability found for Ni in Na<sub>2</sub>SO<sub>4</sub> / NaCl melts, in air. The high rates of corrosion observed at high partial pressures of SO<sub>3</sub> are shown to be mainly due to the effect of SO<sub>3</sub> on the solubility of the corrosion products.
5. Nimonic 105 does not exhibit the active-passive transition characteristic of nickel in sulphate media. In the presence of pure Na<sub>2</sub>SO<sub>4</sub> at 900°C, in air, two different regions characterize the E/I curve. The first region corresponds to the onset of passivity and dissolution of passive Nimonic; it is characterized by a small dissolution rate and is really an «active-passive» zone, as suggested by the physical appearance of the electrode surface polarized within its limits. The second region is a transpassive area and corresponds essentially to the sulphate discharge.
6. Additions of NaCl, up to 15%, to the sulphate melt hardly affected the forward sweep for Nimonic 105 in pure Na<sub>2</sub>SO<sub>4</sub>, but severely affected the reverse one. This non-repair capability of reforming a passive corrosion layer is due to the Al and Cr depletion at the Nimonic surface by NaCl attack, which is observed at high anode potential values and may be explained by reactions of the form



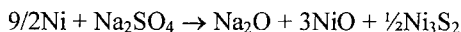
and



NaCl addition greater than 15% increased the c.d. recorded in the portion of the E/I curve representing the passive potential range, mixtures of around 15-35% NaCl being the most aggressive. It seems that the Cl<sup>-</sup> ions crack the Cr<sub>2</sub>O<sub>3</sub> oxide layer, subsequently enabling reactions of the type:



and





to occur. Evidence for these reactions is substantiated by the topochemical studies.

7.  $\text{SO}_3$  pressures below  $5 \times 10^{-3}$  atm do not affect the electrokinetic behaviour of Nimonic 105;  $\text{SO}_3$  pressures above  $5 \times 10^{-3}$  atm produce higher corrosion rates, which may be related to the acid fluxing of the sulphate melt either leading to ionic dissolution of the alloy scale constituents or favouring sulphur diffusion through the oxide scale, and consequently enhancing the sulphidation process.
8. The high dissolution rates and the shape of the polarization curves for Ni and Nimonic 105 in pure NaCl at  $900^\circ\text{C}$ , in air, indicate that these materials are typically active in the NaCl electrolyte. Metal dissolution must occur at the expense of a simultaneous reduction of  $\text{Na}^+$  ions to  $\text{Na}_2^+$  subions, accompanied by the corrosion of the metal interacting with the dissolved oxygen and the chloride ions, as well as with the chlorine and oxide ions formed in the reaction of oxygen with chloride ions.
9. The potential-decay curves for Ni in  $\text{Na}_2\text{SO}_4$ -NaCl melts show that thin passive films are very sensitive to  $\text{Cl}^-$  attack, but once a thick oxide film forms on the specimen, the  $\text{Cl}^-$  addition is accompanied by an increase in the film stability. Hence, there appears to be no simple correlation between the ease of achieving passivity (more likely in pure  $\text{Na}_2\text{SO}_4$ ) and the stability of the passive film (enhanced in  $\text{Cl}^-$  melts).
10. The potential-decay curves for Nimonic 105 in  $\text{Na}_2\text{SO}_4$  and in  $\text{Na}_2\text{SO}_4$ -15% NaCl mixtures followed a similar pattern, showing absence of passivity breakdown.
11. The E/I curves in  $\text{Cl}^-$  melts up to 15% NaCl as well as the film breakdown studies of passive Nimonic 105 suggested the feasibility of anodic protection of this material in the melts at  $900^\circ\text{C}$  over a wide passive range. This is, however, not realisable, as the free corrosion potential measurements indicate. The breakdown of the oxide film that occurs after some hours of immersion in the  $\text{Cl}^-$  melts suggests that a period of incubation is required for the halide ions to accelerate the sulphidation.

Considering the early studies just presented, it could be no doubt that chloride exists in those areas of the turbine where hot corrosion is found. The processes of condensation and/or impaction required further investigation but in general terms it could be assumed that chloride plays a crucial role in the mechanism of hot corrosion. Quite apart from providing a source of sodium for the formation of sodium sulphate it seemed highly probable that the major role of chloride is in destroying the integrity of protective scale layers.

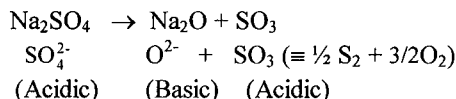
Thermal cycling is a normal phenomenon in the gas turbine and thermal shock combined with chloride effects could be assumed to result in inhibition of the formation of protection layers. Although chloride must have a transient existence if deposited on nozzles or blades its intermittent or continuous replenishment might also provide secondary effects in promoting reduction in the melting point of deposited salts and also in increasing wetting properties. These effects may result in hot corrosion at lower temperatures and over more extensive areas of components. This combined with the volatility of deposits might control the lower and upper temperatures at which the sulphidation/accelerated oxidation effect was found.

#### 4. Mechanisms of Hot Corrosion

The early theories developed to explain the general appearance of the corrosion corresponding to the practical experience [49] are now called Type I Hot Corrosion (HTHC) [50-58]. In laboratory tests, this type appears to be absent below a lower threshold temperature, and above an upper threshold temperature; these temperatures vary with the alloy and with the detailed conditions, but they are usually close to  $800^\circ\text{C}$  and  $950^\circ\text{C}$ , respectively. The primary factor in viewing molten  $\text{Na}_2\text{SO}_4$  with respect to HTHC is that of the availability of the melt and not its mass. An attack will be self-sustaining as long as the melt can participate in the exchange and remain as the intermediate means by which alloy component elements will eventually react to solid corrosion products. In the turbine operating conditions melt can form as and when the component particles are deposited.

Products can remain in solution with the melt, form a eutectic, precipitate out or form a solid complex with the total mass of available melt.

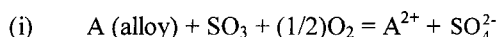
The following reactions will clarify the various points noted above:



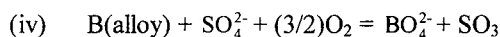
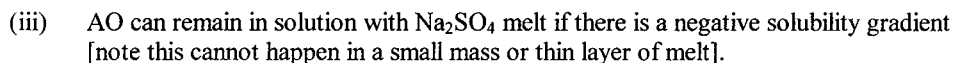
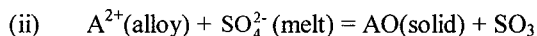
The salt-fluxing processes have received most attention in recent years, and a brief description of the two proposed processes, one in which the salt is displaced in a basic ( $\text{Na}_2\text{O}$ -rich) direction, and the oxide is dissolved as an anionic species, and one in which the salt is displaced in an acidic ( $\text{SO}_3$ -rich) direction, and the oxide or the metal dissolves as a cationic species, is as it follows.

### Acidic Fluxing

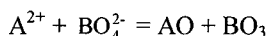
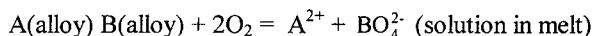
Hot corrosion reactions occur where  $\text{SO}_4^{2-}$  participates with the  $\text{S}_2$ ,  $\text{SO}_2$  and  $\text{SO}_3$  species from the gas or dissociated melt in converting the alloy to corrosion products either by chemical thermodynamic reaction or electrochemically transported as an ion for a subsequent reaction with the gaseous medium. Thus for an alloy AB,



For a continuous solution of  $\text{ASO}_4$  in  $\text{Na}_2\text{SO}_4$ ,  $\text{SO}_3$  and  $\text{O}_2$  must be available, e.g.  $\text{CoSO}_4 + \text{Na}_2\text{SO}_4$ ,



or

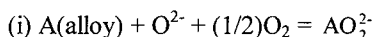


The melt remains as a *via media*; very small amounts of  $\text{Na}_2\text{SO}_4$  can permit a substantial alloy-to-alloy metal oxides conversion.

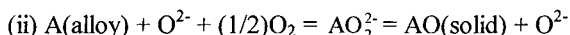
In practical systems virtually all alloys are susceptible to acidic fluxing depending on the level of  $\text{pSO}_3$  or the amount of  $\text{V}_2\text{O}_5$  formed or deposited. The condition is prevalent when chloride is present and induces alloy depletion in gas turbine environment and in carburising conditions when oxygen starvation occurs. Alloys containing Mo, W or V are very vulnerable because they can be auto-generative to acidic oxides, e.g. B-1800, IN 100, Mar M-200, etc. High-chromium alloys present a reasonably, good resistance, as well as silica-formers. IN 738 and some Hastelloys are found to out-perform the above listed alloys. A refractory metal addition has to be restricted to avoid acidic degradation. Hot pressed  $\text{Si}_3\text{N}_4$  performs well in acidic fluxing conditions [59].

### Basic Fluxing

Basic fluxing of the reaction product occurs when the alkali  $\text{Na}_2\text{O}$  or the  $\text{O}^{2-}$  part of the oxy-anionic melt participates in the reaction process.



$\text{Na}_2\text{SO}_4$  is converted to  $\text{Na}_2\text{AO}_2$  and ceases unless fresh melt  $\text{Na}_2\text{SO}_4$  is available.



Melt can act as a transport-precipitation reaction medium as long as it is balanced by an  $\text{SO}_3$  supply; else, it will stifle the reaction when sufficiently basic. This means, that for this reaction to be possible there should be a negative solubility gradient of the oxide in the melt [58].

Viewing melt fluxing in the context of protective oxide scale formation it may be generalized that:  $\text{Cr}_2\text{O}_3$  is more resistant under low  $p\text{SO}_3$  conditions, i.e. basic condition,  $\text{SiO}_2$  has minimal solubility in high  $p\text{SO}_3$ , i.e. it is good to resist acidic fluxing, and  $\text{Al}_2\text{O}_3$  has a lower solubility at low  $p\text{SO}_3$  than  $\text{Cr}_2\text{O}_3$ .

Degradation due to basic fluxing can be resisted effectively by promoting continuous scale growth of  $\text{Al}_2\text{O}_3$  under  $\text{Cr}_2\text{O}_3$ . Since it requires an oxygen gradient for promotion, the best means of counteracting it is by formation of oxide scales that grow at a slow rate and need very low  $p\text{O}_2$ . In Ni-Cr-base superalloys it is better not to have any Al at all than Al in a low level since the chloride effect is particularly marked in low-Al Ni-Cr-Al-alloys. Deposits of carbon are observed to hasten the onset of basic fluxing as it creates local reducing conditions while a 5-micron surface topcoat of Pt inhibits basic fluxing.

Susceptibility to basic fluxing occurs with Ni and Co and their alloy systems, binary e.g. Ni-Al and Co-Al, ternary Ni-Cr-Al, or multi-element systems where Cr and Al levels are lower than is required to form their stable oxides. Alloys with 20Cr or more and 10-12Al with reactive elements such as Y have good resistance in basic fluxing media. If Al has to be lowered for mechanical purposes, then the preference is given to a CoCrAl system rather than a NiCrAl alloy. Alloy depletion caused by chloride reactions and carbon induced oxygen depletion are, once again, the contributory factors [59].

The fluxing mechanisms obviously only operate in the presence of a molten salt layer, and this is quite restrictive: pure sodium sulphate melts at 884°C; pure potassium sulphate at 1069°C. The two forms an extended range of solid solutions, with a minimum melting point of 823°C, and further reductions are possible in the presence of such stable sulphates as those of calcium and magnesium. For example, in the  $\text{Na}_2\text{SO}_4$ - $\text{MgSO}_4$  system there is a eutectic between the solid solution of  $\text{MgSO}_4$  in  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4 \cdot 3\text{MgSO}_4$  at approximately 660°C. There is also a eutectic in the  $\text{Na}_2\text{SO}_4$ - $\text{NaCl}$  system at 630°C. Various other, more complex, phase systems are partially reported which imply that other reductions may be possible. However, the group of compounds of most current interest are those involving the alkali sulphates and the sulphates of the transition metals.

In the late 1970s a new form of hot corrosion was encountered at the resulting lower temperatures. The character of the corrosion was significantly different from that for HTHC. Localized pits developed, with relatively smooth metal-scale interfaces; there was usually little or no sulphidation within the metal, and no depletion of the more reactive alloy elements in the metal ahead of the interface [60]. It proved to be difficult to duplicate the attack in the laboratory until it was realized that it was necessary to control the  $\text{SO}_3$  partial pressure in the gas stream. The upper and lower threshold temperatures for this attack, which is called Type II (originally "low-power") Hot Corrosion (LTHC), are less well-defined than the limits for Type I hot corrosion, because they depend on the  $\text{SO}_3$  partial pressure, and data from service are less well-characterized. However, it appears that the attack is seldom observed above 775°C, or below 700°C. The molten salt in this case is believed to be a mixed alkali sulphate-base-metal sulphate. In general, it appears that cobalt-base alloys are somewhat more sensitive to this form of attack than nickel-base alloys; and increasing the chromium content of the alloy increases its resistance to the corrosion even when the alloy forms an alumina scale. The effect of other elements and of the metallurgical structure is not clear, although it is generally accepted that coarse carbides containing refractory metals are deleterious, and should be avoided by optimising the heat treatment [61, 62].



A third form of high-temperature corrosion is encountered in gas turbines burning low-grade petroleum-based fuels with high vanadium contents. The vanadium is present as an organic species, and during combustion oxidizes to form  $V_2O_4$ , which is present in the combustion gas stream as an aerosol. Later, this oxidizes further to the pentoxide,  $V_2O_5$ , which has a low melting point, close to  $710^\circ\text{C}$ ; other species, particularly sodium sulphate, can lower the melting point still further. This melt is very aggressive, and is capable of dissolving most protective oxides and indeed most metals. Alloys with very high chromium levels, in excess of 35%, have some resistance to vanadium attack, but the problem is usually combated in practice by using fuel additives which are largely based on magnesium oxide: magnesium vanadate has a relatively high melting point [63-65].

Several authors, notably Rahmel [66, 67], Rapp [68] and Sequeira [41], have suggested that the corrosion is essentially electrochemical in nature, with local cells established in the system, and certainly many of the features of the corrosion can be duplicated electrochemically, since the oxide ion concentration of the salt can be controlled in this way. It is difficult to decide to what extent such local cell action may be involved, because as indicated above, such a mechanism is not necessary; concentration gradients induced chemically can also account for the observations.

### 5. Hot Corrosion of Gas Turbine Alloys

Some of the laboratories that have contributed to gas turbine hot corrosion research in the last thirty years are listed here by quoting the group leaders and/or principal workers: -

Alcock, Armijo, Barrett, Bennett, Birks, Booth, Bornstein, Carew, Conde, Coutsouradis, Cutler, Davin, DeCrescente, Douglass, Duret, Elliot, Erdos, Fairbanks, Foster, Fryburg, Gadosmski, Galsworthy, Giggins, Goebel, Goward, Grabke, Hancock, Hart, Hed, Hocking, Jacob, Jones, Kedward, Kofstad, Kohl, Kubaschewski, Lambertin, Luthra, Lloyd, McGill, McCreath, McKee, Meadowcroft, Mevrel, Misra, Mrowec, Natesan, Nicholls, Nicoll, Numata, Pettit, Pichoir, Rahmel, Ramanarayanan, Rapp, Restall, Rhys-Jones, Romeo, Taylor, Saunders, Sequeira, Shinata, Shores, Sidky, Smeggil, Stearns, Stephenson, Stern, Stott, Strafford, Stringer, Swidzinski, Smeltzer, Vasantasree, Wallwork, Wagner, Whittle, Wood, Worrell, Wright.

Many of their publications are listed and can be used for further reference. It should be noted that the list is not exhaustive and several more investigators have published significant works in this area. A number of papers discussing the corrosion behaviour of high-temperature alloys and coatings for gas turbine systems are discussed here.

Clelland et al. [69] studied hot corrosion resistance of various nickel- and cobalt-base alloys in a marine environment, and found that alloy X-40 (Co-25Cr-10Ni-7.5W) was the most resistant among the tested alloys. Zetlmeisl et al. [70] also found that alloy X-40 was significantly better than nickel-base alloys, such as B-1900, U-700, U-500, and IN 738. After 240h, alloy X-40 showed hardly any corrosion attack, while alloy B-1900 (Ni-10Co-8Cr-6Mo-4.3Ta-6Al-1Ti) suffered severe attack. Alloys U-500 (Ni-18Co-19Cr-4Mo-2.9Al-2.9Ti) and IN 738 (Ni-8.5Co-16Cr-1.7Mo-2.6W-1.7Ta-0.9Cb-3.4Al-3.4Ti) were similar, suffering only mild attack. Surprisingly, alloy U-700 (15% Cr) was found to be slightly worse than alloy B-1900 (8% Cr). Stringer [71] considered alloy B-1900 along with IN 100 (10% Cr) and NIMONIC 100 (11% Cr) to be poor in hot corrosion and suggested that they not be considered for use without coatings, even in mildly corrosive environments.

Beltran [72] conducted burner rig tests using residual oil, which contained 3%S and 325 ppm NaCl (equivalent to 5 ppm NaCl in air), at  $870^\circ\text{C}$  for 600h on several cobalt-base alloys with chromium varying from 20 to 30%. All tested cobalt-base alloys suffered little corrosion attack (about 0.04 to 0.12 mm). These values were of the same order of magnitude as those produced under natural gas combustion [72]. Under the same test conditions, alloy U-700 suffered as much as about 0.76 mm of attack [72].

Wagenheim [73] conducted an alloy development program with two goals:

1. Develop and test Co-base alloys (MELCO alloys) for service as a vane material in a typical marine gas turbine having a firing temperature of  $1750^\circ\text{F}$  and a 5000-hour life between overhauls. This could mean that first-stage vane metal temperature may approach  $1900^\circ\text{F}$ .

For this design criterion, a Co-base alloy with the strength of WI-52 at 1900°F and hot-corrosion resistance superior to that of the X-45/X-40 type alloys was needed.

2. Investigate Co-base matrix compositions resistant to hot-corrosion/oxidation atmospheres that could subsequently be utilized as an alloy matrix for dispersion strengthening (DISCO alloys). This alloy would be suitable for vane applications well above the 1900°F service temperature goal ascribed to the MELCO alloys.

The response of the alloys to hot-corrosion attack was apparently dependent upon the salt concentration and test temperature. At the high salt level, sub-surface sulphides were observed beneath the surface oxide or in front of the leading intergranular oxide fingers at both test temperatures. At low salt concentrations, it appeared that the oxidation mechanism played a more prominent role as the test temperature was raised.

The environmental tests indicated that Cr up to 30% and Y were beneficial, while Ta was detrimental above 2000°F. As mentioned above, the response of the alloys to hot corrosion is dependent on the test parameters. MELCO alloys -2, -9, -10, -14, and -16 appeared best in low-salt tests, while MELCO-5 and X-45 were superior in high-salt environments.

The goals stated above have been met successfully by MELCO-14. Although MELCO-14 does not offer the best hot-corrosion resistance or the highest stress-rupture strength capability, it was the only alloy that met both the environmental and strength requirements simultaneously.

Based on short-time/high-salt tests, the DISCO alloys did not show much change from the competitive commercial or MELCO alloys. However, the alloys appear to have promise as a matrix for dispersion strengthening. The corrosion resistance varied somewhat as a function of heat treatment and test temperature. It also appeared that lower Ni contents and addition of Y improved corrosion resistance [73].

Condé et al. [75] performed studies that led to the conclusion that expendable or sacrificial chromium in the form of chromium oxide would inhibit hot corrosion by converting aggressive chloride and sulphate to innocuous products. They describe experiments to assess the efficacy of additions of  $\text{Cr}_2\text{O}_3$  as a disperse phase in alloys and coatings, as well as combustion rig corrosion studies on conventional alloys and coatings in which the inhibitor was added as fuel soluble organic chromium compounds and produced significant reductions in the extent of hot corrosion [74].

The effect of zigzag grain boundaries on the creep rupture properties of a nickel-base superalloy Inconel 751 in hot corrosive environment induced by  $\text{Na}_2\text{SO}_4$ -NaCl (90%:10%) molten salt at 800°C in static air was studied by Miyagawa and Yoshida [75]. It is suggested that the rupture life of alloys subjected to hot corrosion is chiefly determined by the intergranular penetration behaviour of sulphides followed by oxides, which depends strongly upon the grain boundary configuration and the morphology of boundary carbides. Since the straight boundaries provide extremely activated paths for rapid penetrations of sulphides and oxides, a decrease in the rupture life due to hot corrosion is remarkable. On the contrary, the zigzag boundaries and the existence of coarse titanium-rich boundary carbides control the intergranular penetrations to obey a given kinetics, and therefore a decrease in the rupture life is sufficiently restrained [75].

High-temperature corrosion tests in 80%  $\text{Na}_2\text{SO}_4$ -20%NaCl was made by Okanda et al. [76] on five Fe-30% Cr-5% Al alloys containing various amounts of Ce up to 0.68%. After the corrosion tests, samples were examined metallographically and by X-ray diffraction and X-ray microanalysis. It was found that the surface scale formed on each sample decreased in thickness as the Ce content increased. Electron probe microanalyses suggested that this retarding behaviour is related to the early formation of a Ce-induced protective scale of  $\alpha\text{-Al}_2\text{O}_3$ . The role of Ce in promoting the formation of the  $\alpha\text{-Al}_2\text{O}_3$  scale was discussed [76].

Wu et al. [77] studied the resistance of Ni-base superalloys to acidic and basic fluxing in a 90  $\text{Na}_2\text{SO}_4$ -10  $\text{K}_2\text{SO}_4$  melt at 1173K by determining the potential dependence of the corrosion behaviour. The following conclusions could be drawn from their studies:

1. The corrosion behaviour of Ni-base super alloys in sulphate melts depends strongly on the corrosion potential because structure and composition of the scale are influenced by the potential.

2. Alloys with high chromium contents, such as IN-738 LC, IN-939, IN-597, and IN-657, exhibit a potential region of stable protective scale formation. In this region the melt at the specimen surface is neutral or nearly neutral. Such protective scales are not formed on alloys with low chromium and rather high aluminium and molybdenum contents such as IN-100 and IN-713LC.
3. Acidic fluxing occurs above a critical potential leading to severe external and internal corrosion. This critical potential is slightly affected by the alloy composition.
4. Basic fluxing starts below a second critical potential that again leads to severe corrosion. This potential depends on the scale composition. Scales rich in  $\text{Cr}_2\text{O}_3$  have a more negative breakdown potential than scales rich in  $\text{Al}_2\text{O}_3$ .
5. In addition to acidic and basic fluxing scale cracking seems to be another mechanism of hot corrosion initiation that seems to occur preferentially with the alloys IN-100 and IN-713 LC having lower corrosion resistance.
6. Potentiostatically controlled corrosion tests are a means to study acidic and basic fluxing phenomena, and to compare the resistance of different materials to this kind of corrosion.
7. According to these measurements the corrosion resistance increases in the order IN-100, IN-713 LC < IN-738 LC < IN-657 < IN-939, IN-597. This series fairly well agrees with the results of other tests (Dean test, rig test) and with the behaviour in gas turbines [77].

Sodium sulphate-induced hot corrosion of preoxidized B-1900 and NASA-TRW VIA has been studied at 900°C with special emphasis placed on the chemical reactions occurring during and immediately after the induction period [78]. Thermogravimetric tests were run for predetermined periods of time after which one set of samples was washed with water. Chemical analysis of the wash solutions yielded information about water-soluble metal salts and residual sulphate. A second set of samples was run, cross-sectioned dry, and polished in a nonaqueous medium. Element distributions within the oxide layer were obtained from electron microprobe X-ray micrographs. A third set of samples was subjected to surface analysis by ESCA. Evolution of  $\text{SO}_2(\text{g})$  was monitored throughout many of the thermogravimetric tests. Results were interpreted in terms of acid-base fluxing mechanisms.

More specifically it was indicated that hot corrosion is initiated by basic fluxing of the protective  $\text{Al}_2\text{O}_3$  scale. The attack is localized but spreads over the sample until the  $\text{Na}_2\text{SO}_4$  has all reacted. Because the supply of  $\text{Na}_2\text{SO}_4$  is limited, the basic fluxing decreases as the sulphate is consumed leading to a near parabolic rate corrosion.

The sequential, catastrophic corrosion of these alloys results from their molybdenum content. The molybdenum forms a low melting phase ( $\text{Na}_2\text{MoO}_4/\text{MoO}_3$ ) that removes the protective scales by acidic fluxing. The molybdenum phase migrates across the sample beneath the scale, resulting in a linear reaction rate and finally in complete consumption of the sample. The self-sustaining feature is a consequence of the cyclic nature of the acidic fluxing [78].

Hot corrosion studies were conducted at 900°C in a simulated combustion gas atmosphere containing sulphur trioxide at a partial pressure of 750 Pa on a Ni-base superalloy (Nimocast 713) partially immersed in various  $\text{ZnSO}_4$ -10wt.% $\text{NaCl}$ - $\text{Na}_2\text{SO}_4$  molten salt mixtures. Weight changes were measured thermogravimetrically with time and it was found that the overall effect of the zinc sulphate addition was to reduce the degree of hot corrosion. Quantitative scanning electron microscopy investigations revealed no evidence of Zn in the attacked zone. It is postulated that the Zn reduces the chlorine activity in the system by forming a volatile chloride, thereby reducing the corrosive effect of the gas phase/molten salt mixtures [79].

The effect of pre-oxidation on hot corrosion for Ni-20 mass % Cr-5 mass % Al alloy in molten  $\text{Na}_2\text{SO}_4$ -25 mass %  $\text{NaCl}$  at 1173 K has been examined by the measurement of corrosion loss, the electrochemical measurement and the analysis of surface oxide film formed on the alloy by pre-oxidation [80]. Particular attention was given to the influence of pre-oxidation temperature. The pre-oxidation at 1173 and 1273 K led to a stop of the vigorous corrosion for the alloy in the molten salt, whereas the pre-oxidation at 1373 K did not lead to an inhibition of the corrosion. The anodic

polarization curve measured for the alloy after the pre-oxidation, which stopped the vigorous corrosion of the alloy, showed the spontaneous passivation behaviour, while that measured for the alloy without the pre-oxidation showed a large current peak due to the active dissolution reaction. This suggests that the pre-oxidation treatment inhibits the electrochemical corrosion reaction for the alloy. Such an inhibition effect on the corrosion was investigated by the analysis of surface oxide film formed by the pre-oxidation. The formation of oxide films consisting mainly of  $\text{Cr}_2\text{O}_3$  was observed for the alloy after the pre-oxidation at 1173 and 1273 K, while that consisting mainly of  $\text{Al}_2\text{O}_3$  was observed for the alloy after the pre-oxidation at 1373 K. Consequently, it was found that the difference in inhibition effect on the hot corrosion due to the pre-oxidation temperature resulted from a difference in the kind of oxide constituting the oxide film formed by the pre-oxidation [80].

Hara et al. [81] prepared a Ni silicide layer on Ni substrate by electrodepositing Si and alloying it with Ni in molten salt. It was shown that nickel covered by the electrodeposit was more resistant than bare Ni to hot corrosion by molten  $\text{Na}_2\text{SO}_4$  [81].

The proven success of HAYNES HR-120, HR-160, 230, 556, 214, and 242 modern superalloys in several high temperature industrial applications (industrial heating, chemical processing, petroleum refining, and power generation), whose key corrosion properties are resistance to hot corrosion, are reviewed by Paul et al. [82].

Many other references have evaluated the corrosion resistance of different materials in simulated gas turbine environments and actual engine conditions [83-93].

## 6. Methods of Evaluating Hot Corrosion

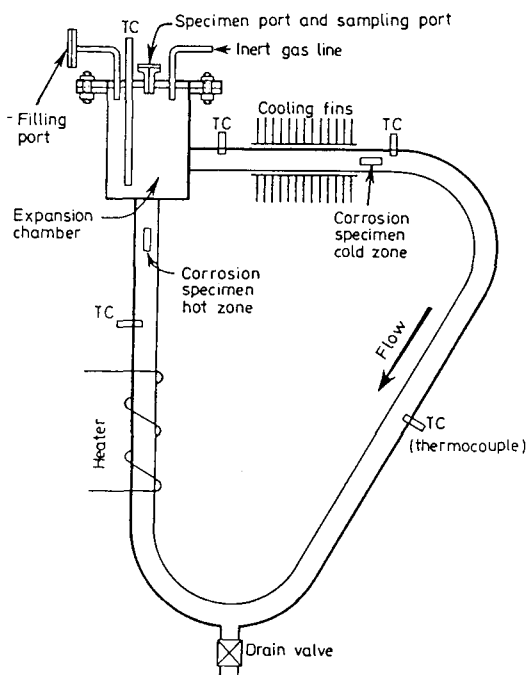
As in all corrosion testing, the procedure that most nearly duplicates the conditions anticipated in service will provide the most satisfactory and useful information for those aspects of corrosion under consideration here. In fact, in view of the extraordinary sensitivity of fused salt corrosion phenomena to minute variations in operating conditions and purity of components, failure to reproduce these conditions with considerable accuracy may well make any test results completely unrealistic and worthless. Then, it should be understood, if not explicitly stated, that all extraneous matter must be carefully excluded from the system and that only materials closely simulating those to be employed in service (including prior history and surface preparation of the metals) should be used. Other factors affecting the corrosion in fused salts include the heat flux of the corroding surface, the volume of liquid to the surface area of the solid, the heat flux of the corroding surface and the liquid flow rate. If, however, screening tests to establish the compatibility of a relatively large number of metals with a given molten salt are to be run, it is often useful to commence with static tests even though the ultimate application involves a dynamic system. This is desirable because static tests are comparatively simple to conduct and interpret, and considerably more economical to operate, and because experience has shown that a metal which fails a static test is not likely to survive the more severe dynamic test.

Static tests have been carried out in crucibles and even electrochemical measurements, with the aim of investigating the fundamentals of hot corrosion using electrochemical cells [94, 95].

Dynamic tests have been carried out by means of spin tests, rotating discs, and loop test installations.

Fig. 2 illustrates the principle of the thermal convective loop widely used in liquid salts. The dynamic burner rig test is the best available test method for assessing hot corrosion characteristics of materials [96]. The rig burns fuel with excess air to produce combustion gases with continuous injection of a synthetic sea salt solution. A special issue of High Temperature Technology published in 1989 contains a number of papers discussing burner rig test procedures [97]. Further description of these tests can be found in a specialty handbook published in 1997 [98].

In recent years, numerous activities have also focused on the interaction between corrosion and mechanical stresses from the viewpoint of cracking and spalling of the protective scales or the acceleration of internal corrosion and final materials failure [99, 100]. In particular for this type of testing, the acoustic emission technique has been shown to be invaluable [87].



**Fig. 2** Loop test for studying the corrosion produced by molten salts.

The large variety of tests shows that in the meantime a good experimental basis exists for the investigation of the complex processes occurring in hot corrosion. However, there are not many standards for hot corrosion testing, which makes it difficult to compare the data measured at different laboratories. At present, efforts are underway to establish guidelines, with the aim to transfer these into standards in the near future. The results of these efforts have largely been published now [101, 102] and workers should adhere to these recommendations when performing hot corrosion tests.

## 7. Prevention of Corrosion

Research over the past 25 years has led to better definition of the relationships among temperature, pressure, salt concentration, and salt vapour-liquid equilibria so that the location and rate of salt deposition in an engine can be predicted. In addition, it has been demonstrated that a high chromium content is required in an alloy for good resistance to HTHC. The trend toward lower chromium levels with increasing alloy strength has therefore rendered most superalloys inherently susceptible to this type of corrosion. The effects of other alloying additions, such as tungsten, molybdenum, and tantalum, have been documented; their effects on rendering an alloy more or less susceptible to hot corrosion are known. The near standardization of such alloys as IN-738 and IN-939 for first-stage blades and buckets, as well as FSX-414 (Co-0.25C-29.5Cr-10.5Ni-7W-2maxFe-1maxMn-1maxSi-0.012B) for first-stage vanes and nozzles, implies that these are the accepted best compromises between high-temperature strength and hot corrosion resistance. It has also been possible to devise coatings with alloying levels adjusted to resist HTHC. The use of such coatings is essential for the protection of most modern superalloys intended for duty as first-stage blades or buckets.

The best way to ensure maximum life of a given turbine must be with stringent control of fuel specifications and good air filtration. The life limitation is then the creep strength or thermal fatigue strength of the first-stage blades or vanes.

Historically, the development of corrosion-resistant coatings was aimed at combating high-temperature hot corrosion. The earliest coatings were the diffusion aluminides. It was found that chromium-modified aluminides offered little additional protection against high-temperature hot corrosion compared to the basic aluminides, but that the platinum-aluminides offered superior protection compared to the basic aluminides. The chromium-modified aluminides have since been found to be particularly beneficial against low-temperature hot corrosion, giving results equivalent to those of the platinum-aluminides; both modified aluminides performed better than the basic aluminides.

Although these diffusion aluminides have been successful in reducing hot corrosion, the chemistry of these coatings is not readily modified for further improvement in corrosion resistance. Thus, increased attention has been given to the development of overlay coatings, which offer significant compositional flexibility.

The actual compositions of these coatings depend on their intended use. Because  $\text{Al}_2\text{O}_3$  is used for protection against high-temperature hot corrosion, coatings that exhibit the greatest high-temperature protection are generally high in aluminium (11%) and low in chromium (<23%). Low-temperature hot corrosion, on the other hand, depends primarily on  $\text{Cr}_2\text{O}_3$  for protection: therefore, coatings exhibiting the greatest low-temperature corrosion protection are high in chromium (>30%) and low in aluminium. Other elements, such as silicon, hafnium, tantalum, and platinum, are added to these coatings in an attempt to improve resistance to corrosion and spalling. High-chromium MCrAlY coatings have been developed to offer superior low-temperature protection without sacrificing high-temperature protection because industrial gas turbines sometimes operate under varying load conditions that could result in exposures to both low- and high-temperature conditions. Overlay coatings have been applied by such techniques as electron beam physical vapour deposition, plasma spray, and sputtering [59].

Apart from overall material wastage due to hot corrosion, an additional concern has been the degradation of mechanical properties, particularly creep and fatigue resistance.

Studies are needed to understand the mechanism of and implications of the environmentally induced mechanical property degradation in the context of the field performance of components.

## 8. Conclusions

A general survey has been made of a number of aspects of high-temperature corrosion in relation to combustion conditions in gas turbines. It is believed that attention has been directed to those features that are most likely to be commonly encountered. It is also obvious that no single material can be recommended as able to meet all the conditions at the gas turbine; any selection must be related as closely as possible to the precise service conditions and, wherever possible, to previous experience of a relevant nature.

All the types of corrosion which have been discussed have in common the ability to disrupt, often locally, the protective oxide films generated by simple oxidation at the surface of practically serviceable heat-resisting alloys. Extrapolation, to longer times, of data obtained before such breakdown is clearly a dangerous procedure, since once breakdown occurs the mechanism of corrosion is changed. The corrosion expert who is called upon to advise for ten or twenty years' operation is, in effect, forced to take a chance that immunity which he has observed during some short period offers sufficient probability of continued freedom from attack to warrant consideration of the material concerned. If, on the other hand, he sees it as his duty to present all the possibilities at their worst, the outlook will often be unduly pessimistic.

Clearly the choice of materials for particular applications or the development of new gas turbine superalloys and coatings with some degree of reliability must await more precise determination of the thermochemical data which are lacking, further elucidation of the part processes leading to sulphidation and accelerated oxidation and more detailed information on the environment and

deposition processes within the gas turbine. In addition to sulphur oxygen, sodium and chloride there are clearly other chemical species present in the environment that may play an important role and require further examination.

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# Fireside Corrosion in Boilers and Waste Incinerators

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**Keywords:** Deposits, Fossil-Fired Boilers, Heavy Metal Compounds, High-Temperature Corrosion, Sulphate and Chloride Melts, Waste Incineration

## Abstract

This chapter covers high-temperature corrosion involving ash/salt deposits in fossil-fired boilers and waste incinerators. The underlying mechanistic aspects are outlined and the corrosion resistance of several metals and alloys is discussed.

## 1. Introduction

Corrosion from the firing of coal or oil is essentially related to specific impurities in the fuels, which can lead to the formation of nonprotective scales or can disrupt normally protective oxide scales. The relevant impurities in coal are sulphur, sodium, potassium, and chlorine. In oil, the important impurities are sodium, and sulphur. During combustion, these impurities can be melted or vaporized and will deposit upon contact with surfaces at temperatures lower than the condensation temperatures of the specific species. This provides a mechanism for the accumulation of deposits of fly ash on cooled surfaces downstream of the burners. Other corrosion mechanisms in coal and oil-fired boilers, as well as in waste incinerators, are particularly damaging when the ash/salt deposits become liquid or semi-liquid. In this article, fireside corrosion by fuel impurities and by municipal and industrial solid waste is briefly described, giving particular emphasis to the molten salt or slag-related attack.

## 2. Coal-Fired Boilers

A large utility boiler consists of a large firebox, within which the combustion takes place. A number of burners are installed in the walls, through which the pulverized coal is blown. The walls of the firebox are fabricated from vertical tubes, typically between 70 and 100 mm in outside diameter, joined by webs of the order of 30 mm width. This is "membrane wall" construction. Preheated water enters the bottom of these walls, which are usually called the water walls, and boils at some location usually a little above the top of the burner array. The effective temperature in the combustion zone is in the range 1200-1800°C. As the combustion gases rise in the furnace, they cool; at the top of the furnace the temperature is of the order of 1000-1200°C, and the gas turns into a horizontal section. In this section, and sometimes in the top of the furnace itself, there are tubular platen heat exchangers hanging down into the combustion gas stream: these are commonly superheaters, and the principal corrosion problems are in the superheaters and the water walls [1-5].

The majority of utility boilers are subcritical recirculating boilers with a main steam pressure of approximately 16 Mpa. The boiling point at this pressure is approximately 350°C, and the outer surface of the water-wall tubes will be about 50°C above this. The superheat temperature is 538°C, and the maximum outer metal temperature in the superheater may be as much as 100°C above this, because of nonuniformities in the temperature distribution across the superheater bank.

The materials for the pressure parts are selected on the basis of their mechanical properties. For the lower temperature parts, the tensile strength is limiting; for the higher temperature parts, the

creep strength is critical. The majority of the tubes, pipes, and drums are fabricated from plain carbon steel or low alloy ferritic steels; the highest ferritic alloy normally used is T (or P) 22, which is essentially Fe-2-1/4Cr-1Mo, although there has been a renewed interest in advanced 9%Cr steels, containing 1 or 2%Mo. The very last sections of the superheater and reheater exchangers may be fabricated from austenitic stainless steel [2-5].

There are two main high-temperature corrosion problems that may be identified in utility boilers. These are:

1. The fireside corrosion of the superheaters and reheaters.
2. The fireside corrosion of the water walls.

Fig. 1 indicates these typical affected regions in a modern fuel fired boiler.

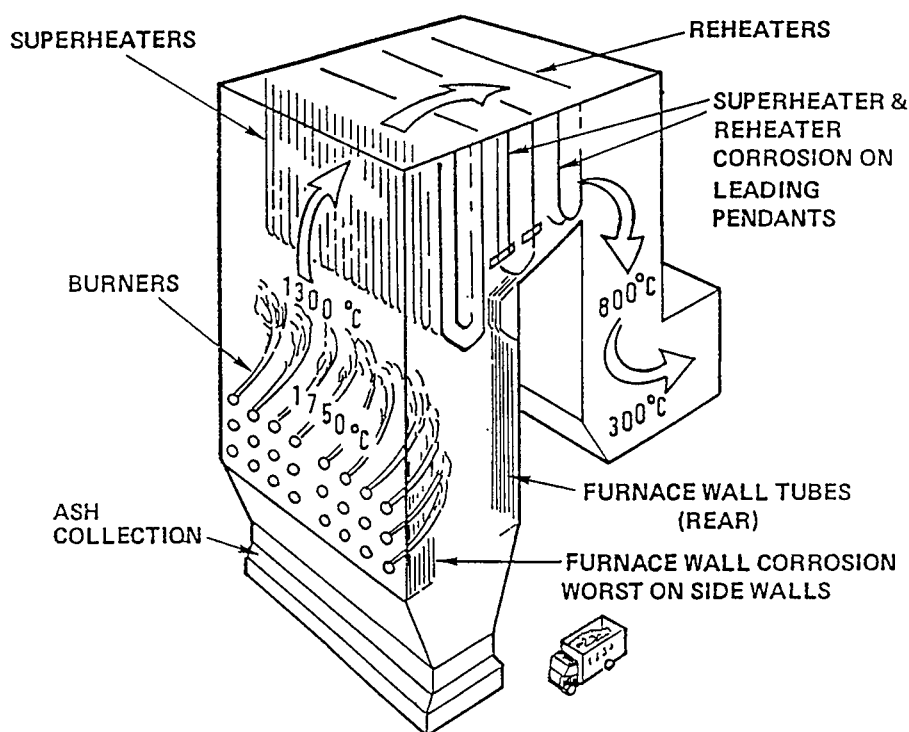


Fig. 1 Schematic of a typical fuel fired boiler showing areas of corrosion.

### 3. Coal-Ash Corrosion

#### 3.1 Water Wall Fireside Corrosion

The water-wall tubes can undergo a very rapid wastage even though the metal temperature cannot have been over 400°C, and sometimes would have been even cooler than this. In the vicinity of the combustion zone much of the ash will still be molten, and some of this is deposited on the water walls as a slag layer. The combustion zone is designed to be located in the center of the furnace enclosure, at a distance from the walls. Poor adjustment of the burners, wear of the burner nozzles, a change in the combustion characteristics of the coal, or several other factors, can result in the combustion zone being displaced, or simply being larger than had been expected. In this case, the

slag deposit in the region where the combustion zone approaches the walls contains unburnt carbon and unoxidized pyrite. It is under these circumstances that rapid wastage can result.

Early investigators thought that this wastage too was associated with alkali sulphate species [6, 7]. In fact, alkali sulphates deposited on the water walls may react with  $\text{SO}_2$  or  $\text{SO}_3$  to form pyrosulphates, such as potassium pyrosulphate ( $\text{K}_2\text{S}_2\text{O}_7$ ) and sodium pyrosulphate ( $\text{Na}_2\text{S}_2\text{O}_7$ ), or possibly complex alkali-iron trisulphate. The latter compounds are formed in thicker deposits after long periods of time at about  $480^\circ\text{C}$ . The  $\text{K}_2\text{SO}_4$ - $\text{K}_2\text{S}_2\text{O}_7$  system forms a molten salt mixture at  $407^\circ\text{C}$  when the  $\text{SO}_3$  concentration is 150 ppm. The corresponding sodium system can become liquid at  $400^\circ\text{C}$  but it requires about 2500 ppm  $\text{SO}_3$  for this to occur; such levels of sulphur oxides are likely only under deposits. Thus, molten salt attack on the tube metal by  $\text{K}_2\text{S}_2\text{O}_7$  is more likely and occurs according to the reaction:



By such a mechanism,  $\text{K}_2\text{S}_2\text{O}_7$  can react aggressively with any protective iron oxide scales on the tubes and lead to accelerate wastage through fluxing of the oxides and attack of the substrate metal. Differential scanning calorimetry of samples of deposits taken from water wall tubes typically indicates melting points in the range of  $335$  to  $410^\circ\text{C}$ .

There is also general agreement that the water wall fireside corrosion is caused by localized reducing conditions [8-11].

Hydrogen chloride gas is considered an important constituent causing furnace wall corrosion for carbon steel [12, 13]. The effect of chlorides on furnace wall corrosion was summarized by Daniel et al. [14] based on CEGB in the UK.

Coal with more than about 0.2%Cl may result in accelerated fireside corrosion for furnace wall tubes under reducing conditions [14].

Carbon steel tubes typically exhibit a maximum corrosion rate of 0.3 mm/y, although corrosion rates of 2 to 6 mm/y have been observed [15].

Meadowcroft [5] reported corrosion rates of 100 to 500 nm/h (0.9 to 4.0 mm/y), or over 1000 nm/h (8.8 mm/y) in extreme cases, for carbon steel tubes.

CEGB in the UK has tested coextruded tubes with Types 304 and 310 stainless steel as an outer layer on a carbon steel tube [12]. The test panel was installed in the furnace sidewalls. After 27,000 h of operation, maximum corrosion rates were found to be 77 nm/h (0.7 mm/y) for Type 304 and 55 nm/h (0.5 mm/y) for Type 310. The carbon steel control sample tubes, however, corroded at 180 to 250 nm/h (1.6 to 2.2 mm/y). Type 310 stainless steel, although significantly more corrosion resistant than carbon steel, still exhibits a relatively high corrosion rate as a cladding material [5].

Solutions to fireside corrosion of furnace water walls are available from changes in operating procedures and changes in tube materials. Where the corrosion results from the presence of reducing conditions near the water walls, operational actions include adjusting the air and fuel distribution to individual burners and among burners in order to promote better mixing and more uniform combustion conditions, as well as resetting to design specification the coal fineness delivered to the burners from the milling plant. Flame impingement can be rectified by changing the characteristics of the offending burners through adjustment of secondary air registers to control air flow and degree of swirl.

Another method of countering reducing conditions near the water walls is to introduce a flow of air along the walls through openings in the membrane between water wall tubes. This is often referred to as air blanketing or curtain air, and it should also be implemented and adjusted in conjunction with local monitoring of the gas composition.

Furnace wall corrosion can also be lessened by reducing the levels of the chemical species in the coal that are responsible for corrosion. Approximately one-half the sulphur and alkali metal content of coal can be removed by standard coal-washing procedures. However, washing generally does not remove the chlorine-containing species from coal; therefore, the net effect is that the chlorine content of washed coal is increased.

Materials solutions to water wall fireside corrosion problems involve either direct replacement with tubes of a more corrosion-resistant alloy or the application of a corrosion-resistant alloy as a cladding on the affected tube. Replacement of the tubes with the same material and the use of regular wall thickness monitoring where wastage rates are only slightly greater than allowable have been recommended to give the desired tube life. For more severe wastage, little difference in performance has been found for alloys containing less than 9% Cr. In this case, the materials choice is probably between thicker-walled carbon steel tubes and tubes with a co extruded outer layer of a high-chromium alloy, such as AISI type 310 stainless steel or 50Cr-50Ni. The technique of cladding a tube fabricated from the alloy typically chosen for the application (based on strength considerations) with an outer layer of a corrosion resistant alloy by co extrusion can provide a cost-effective solution to this problem.

Increased corrosion resistance can also be gained by enriching the surfaces to be protected with such elements as chromium or aluminium. This can be achieved by diffusion treatments or by the spraying of metal overlay coatings. Although pack aluminising can be applied commercially to tubes up to about 6 m there are as yet no reports of utility boiler experience with such materials. Flame or plasma spraying has been used to apply high-chromium, high-aluminium, iron-chromium-aluminium alloy compositions to water wall tubes. Although such alloys have shown good corrosion resistance in laboratory tests, problems have been experienced in practice as a result of a lack of reproducibility of coating application techniques.

### 3.2 Superheater/Reheater Corrosion

Superheater corrosion in boilers has been a problem for many years. During the late 1950s and early 1960s, increasing steam temperatures resulted in some severe instances of corrosion, and a considerable amount of research was conducted. This work is summarised in two important publications: the Proceedings of a conference held at the Marchwood Engineering Laboratories of the CEBG [16], and the book written by Reid [6]. As a result of this work, a number of methods of dealing with the problem were identified, including the moderation in main steam temperatures, improved specification of coals, the use of additives, and the use of protection systems for the surfaces at risk. These approaches reduced the incidence of the problem, and as a result relatively little research was conducted in the following several years. The desire to increase the steam temperatures to achieve higher efficiency and the need to use a wider range of coals has resulted in a renewed interest.

In many cases, deposits form on the leading tubes in the super heaters and reheaters in both coal-fired and oil-fired boilers. In coal-fired boilers the deposit is formed from the fly ash, and builds up what may become a very thick layer pointing in the direction of the gas stream.

Figure 2 is a sketch of the structure of the deposit, taken from Nelson and Cain [7]. The fly ash should be essentially solid at the gas temperatures in the vicinity of the super heater, but it is generally believed that the formation of a deposit does require the presence of a minor amount of a molten phase to act as a "glue". The deposit remote from the tube surface is at the gas temperature, and some sintering can be expected.

A deposit does not necessarily imply that there will be corrosion. However, corrosion does not occur without a deposit. When corrosion does occur, the attack takes the form of pits, which overlap in the later stages of the corrosion, having smooth interfaces with the metal. Sulphur prints reveal the presence of sulphides in the vicinity of the interface, but there is usually little evidence of internal sulphidation of the alloy. Simulation of the corrosion in laboratory tests requires that the partial pressure of  $\text{SO}_3$  in the atmosphere is at least 25 Pa. The corrosion product is largely magnetite,  $\text{Fe}_3\text{O}_4$ , but in addition to the alkali ( $\text{Na} + \text{K}$ ) sulphates, an alkali-iron mixed sulphate has sometimes been detected in the corrosion product. There is an upper and lower threshold temperature: the lower threshold is approximately 550°C, and the upper threshold is approximately 675°C. These temperatures do not vary greatly among the different candidate alloys, although the

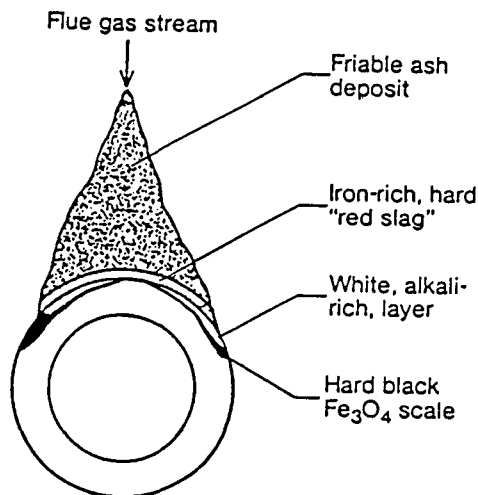


Fig. 2 Deposit layers on a corroding superheater or reheater tube [7].

extent of the attack does vary considerably. While high chromium does usually confer good resistance, the correlation of the corrosion resistance with chromium content is not all that good. The corrosion appears to correlate with the alkali content of the coal, or at least of that part of it that can be released during combustion. It appears that chlorine in the coal acts as a release agent for the alkali metals, and there appears to be a linear relationship between corrosion and chlorine content. However, the alkali chlorides will be dissociated in the combustion zone, and the chlorine will be present in the combustion gas as hydrogen chloride; this does not appear to play any part in the corrosion process.

The mechanism of the reaction appears to be very much like that of Type II corrosion of gas turbines, with the upper and lower threshold temperatures corresponding to the melting point and dissociation point, respectively, of a sulphate mixture in which the iron serves to lower the melting point. As with Type II hot corrosion, a high partial pressure of  $\text{SO}_3$  is required to stabilize the melt; but the partial pressure required is perhaps an order of magnitude higher than that measured in the bulk furnace gas. The oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  is sluggish, and Krause, Levy, and Reid [17] were able to show that in the immediate vicinity of catalytic surfaces the partial pressure of the trioxide was considerably higher than in the bulk. It is also possible that high local partial pressures of  $\text{SO}_3$  are generated by dissociation of sulphates in the outer, hotter, part of the deposit, migrating in towards the colder metal surface, since the corrosion at a fixed metal temperature is known to increase with increasing gas temperature [18].

Empirical procedures are available for predicting the probable corrosivity of a given coal. A known corrosive coal may be blended with another to produce a less corrosive ash, and it may also be possible to use additives, such as limestone. If it is known at the design stage that a corrosive coal must be burned, the super heater can be positioned further back along the gas path where the gas temperature is lower. Such positioning also reduces the amount of corrosive material reaching the super heater, because some corrodent is deposited on upstream tubing.

If control of coal chemistry or design changes is not feasible, corrosion-resistant materials must be used. For a boiler that has exhibited corrosion, it may be sufficient to wrap strips of AISI

type 310 stainless steel around the leading tubes in a platen; this is termed bandaging. If bandaging is insufficient, it may be necessary to replace the finishing super heater tubing with a co extruded material, in which the inner layer is a strong coded alloy and the outer layer is a corrosion-resistant material, such as type 310 stainless steel or Incoloy 671 (Ni-50%Cr). Over the years, there have been many efforts to develop coating systems that could be applied in the field by such techniques as plasma spraying. However, the results have generally been disappointing, although for a particular situation this may still be a cost-effective approach.

Alloys that have been used for super heaters and reheaters are Cr-Mo steels (e.g., 1.25Cr-0.25Mo, 2.25Cr-1Mo, 5Cr-0.5Mo, and 9Cr-1Mo) and austenitic stainless steels (e.g., Types 304H, 316H, 321H, and 347H). The cooler inlet sections are typically tubed with Cr-Mo steels, while the finishing sections may be tubed with 300 series austenitic stainless steel or ESSHETE 1250.

The marked influence of fireside corrosion on tube life is well illustrated by Flatley and Morris [19]. Maximum corrosion rates of 120 nm/h for austenitic stainless steel super heater/reheater tubes have been reported for CEGB boilers. At this corrosion rate, tube life can be significantly reduced. CEGB has tested two types of coextruded tubes: Type 310 stainless steel over ESSHETE 1250 and alloy 671 over alloy 800H [19]. The Type 310/ESSHETE 1250 co extruded tube exhibited a benefit factor of 3, and the alloy 671/alloy 800H co extruded tube exhibited a benefit factor of more than 10. Rudd and Tanzosh [20] also conducted field tests on co-extruded tubes of Type 310 stainless steel over ESSHETE 1250 and alloy 671 over alloy 800H. The tubes were exposed for 7 years with metal temperatures up to 607°C. Type 310 suffered a corrosion rate of 0.15 to 0.18 mm/y, while alloy 671 suffered about 0.08 mm/y. In another field test with a higher metal temperature (704°C) alloy 671 suffered a corrosion rate of about 0.15 to 0.18 mm/y.

Laboratory tests conducted in synthetic flue gas (80N<sub>2</sub>-15CO<sub>2</sub>-4O<sub>2</sub>-1 SO<sub>2</sub>, saturated with H<sub>2</sub>O) with synthetic ash (37.5 mol% Na<sub>2</sub>SO<sub>4</sub>, 37.5mol% K<sub>2</sub>SO<sub>4</sub>, and 25mol% Fe<sub>2</sub>O<sub>3</sub>) covering the samples were conducted by Stringer [21]. Among the tested super heater tubing and cladding samples, alloy 671 was the best performer. A new Japanese alloy, CR35A (45Ni-35Cr-Fe), has been reported to exhibit a performance approaching that of alloy 671 in laboratory testing at 650 and 700°C [22].

#### 4. Oil-Ash Corrosion

Residual fuel oils contain between 50 ppm w/w and 300 ppm of sodium present as the chloride and vanadium as organic compounds in amounts depending on the origin of the crude. Nickel and iron compounds in the oil appear on the tubes; so do clay-mineral components, but these ash-forming materials are in relatively small proportion compared with coal. Typically the deposit on the tubes will be 1-2 mm thick after a year in service. Sodium appears on the tube as sulphate, vanadium as complex vanadates. These two elements are responsible for the corrosiveness of the deposits. The ratio between them (i.e. V/Na wt ratio in the fuel) can be a useful guide to corrosiveness (see [23] for the background chemistry). Other factors mentioned previously apply equally to oil and coal, except that the temperatures at which corrosion occurs are perhaps lower for oil, particularly for austenitic steels [24, 25]; a 'bell-shaped' corrosion/temperature curve has been found to apply for oil as for coal and a sharp increase in the corrosion rate occurs at 600°C with a peak between 700 and 720°C. The rate then falls until at 800-850°C the curve is almost coincident with that obtained in air oxidation without deposit. There is less firm evidence on corrosion resistance of 9% and 12% Cr ferritic steels at metal temperatures above 600°C; the reason for this is that the corrosion of ferritic steel follows a parabolic rate law and very long times are required to observe specific effects. Stainless steels follow a rectilinear corrosion/time curve.

Many comprehensive studies of corrosion in oil-fired plant are available, and the reader is referred to the extensive tests made at Marchwood power station where the gas temperature was 1100°C [25]; corresponding tests have been made at Bankside power station with a flue-gas temperature below 1000°C. On the basis of this work, the CEGB have concluded that the temperature conditions are so critical at a metal temperature above 590°C (metal temperature

c.580°C) and not increased to 565°C, as is common practice in coal-fired plant. At the present high reliability of modern plant is usually worth more than a marginal increase in overall efficiency.

Oil ash corrosion problems are best controlled by proper alloy selection. Severe materials problems due to oil ash corrosion were illustrated by numerous case histories presented in a 1958 NACE Technical Committee Report [26].

McDowell and Mihalisin [27] conducted extensive field rack tests in boilers fired with Bunker "C" oils containing high concentrations of vanadium (150 to 450 ppm). Test racks were exposed in the super heater section. Alloys ranging from low-alloy steels to iron and nickel-base alloys suffered severe corrosion attack. Even the best performer (50Ni-50Cr alloy) suffered a corrosion rate of 3.1 mm/y.

Spafford [28] reported good performance of the 50Ni-50Cr alloy in refinery heaters for coking and catalytic reformer units. The heaters were fired with heavy fuel oil containing 2.5 to 40% S and 50 to 70 ppm V (occasionally up to 150 ppm). The hangers and tube supports made of cast HH alloy (25Cr-12Ni steel) suffered severe corrosion attack. Metal temperatures were in the range of 730 to 890°C. The highest corrosion rates were 6.4 to 9.5 mm/y. Replacements of alloy 657 (a 50Ni-50Cr alloy) were reported to perform very well, with minimal maintenance and repair [28]. In a field rack test in a crude oil heater at 700°C, alloy 657 performed 10 times better than HH and HK alloys [29]. Swales and Ward [29] reported numerous field experiences for alloy 657 as tube supports in refinery heaters. They concluded that the alloy provided satisfactory service at temperatures up to 900°C. At temperatures higher than 900°C, alloy 657 has often suffered severe corrosion attack [29].

Super heaters and reheaters, with much lower temperatures than tube supports, are also susceptible to oil ash corrosion. Bolt [30] evaluated various super heater and reheater materials in an experimental boiler firing with heavy oil containing 2.2% S, 200 ppm V, and 50 ppm Na. The test was conducted on Type 347H tubes and several co extruded tubes, including Type 310 over ESSHETE 1250. Type 446 over alloy 800H, CR35A over alloy 1714 CuMo, and alloy 671 over alloy 800H. Type 347H suffered the worst corrosion attack, followed by Type 310, with maximum corrosion rates occurring at about 670°C. Both alloys showed unacceptably high corrosion rates (>1mm/y) at 630 to 675 °C. Three high-chromium cladding materials, Type 446 (27Cr), Cr35A (a new Japanese cladding material, 35Cr-45Ni-Fe), and alloy 671 (47Cr), performed significantly better than Types 347H and 310.

In a 10,000-h field test in a boiler fired with fuel oil containing 2.65% S, 49 ppm V, and 44 ppm Na, Parker et al. [25] reported that ferritic steels were significantly better than austenitic steels because of sulphidation involved. At 500 to 650°C, 2.25Cr-1Mo, 9Cr, and 12Cr steels performed significantly better than Types 316, 321, 347, 310, and ESSHETE 1250. Among the austenitic stainless steels tested, however, Type 310 was most resistant to the environment.

Another effective method of combating oil ash corrosion problems is to inject additives (high-melting-point compounds) into the fuel to raise the melting point of the oil ash deposit [31].

The additive reacts with vanadium compounds to form reaction products with higher melting points. When magnesium compounds are used, some of the reaction products and their melting points are:

- ◆  $\text{MgO.V}_2\text{O}_5$ : 671°C
- ◆  $2 \text{MgO.V}_2\text{O}_5$ : 835°C
- ◆  $3 \text{MgO.V}_2\text{O}_5$ : 1191°C

When the injection involves magnesium compounds, increasing the Mg/V ratio increases the melting point of the oil ash deposits [32]. Increasing the melting point of oil ash deposits results in lower corrosion rates. Disadvantages of the additive injection approach include additional operating costs and a substantial increase in ash volume, which may require additional furnace downtime for tube cleaning [33].

Reducing the excess air levels for combustion is also effective in mitigating the oil ash corrosion problems. This tends to favour the formation of high-melting-point vanadium oxides,



such as  $V_2O_3$  and  $V_2O_4$ , and to reduce the amount of low-melting-point  $V_2O_5$ . This approach was reported to have received greater success in Europe [33].

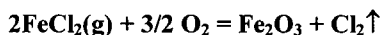
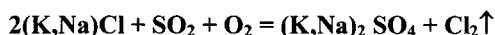
### 5. Corrosion Process in Waste Incinerators

The corrosion problems experienced in boilers fuelled with municipal refuse are different from those encountered with fossil fuels in that chlorine rather than sulphur is primarily responsible for the attack. The average chlorine content of municipal solid waste is 0.5%, of which about one half is present as polyvinylchloride (PVC) plastic. The other half is inorganic, principally NaCl. The chlorine in the plastic is converted to hydrochloric acid (HCl) in the combustion process. The inorganic chlorides are vaporized in the flame and ultimately condense in the boiler deposits or pass through the boiler with the flue gases. Zinc, lead, and tin in the refuse also play a role in the corrosion process by reacting with the HCl to form metal chlorides and/or eutectic mixtures with melting points low enough to cause molten salt attack at wall tube metal temperatures. Investigation of an incinerator wall tube that was corroding at a rate of 2 mm/yr showed that zinc and sodium were both associated with chlorine in the deposit. The presence of NaCl was confirmed by x-ray diffraction. However, the high corrosion rate could not be accounted for in terms of attack by NaCl or HCl. Consequently, laboratory tests were conducted to demonstrate that the corrosion could be caused by the eutectic mixture of 84%  $ZnCl_2$  and 16% NaCl, which has a melting point of 262°C. After a 336-h exposure to this mixture at 315°C, carbon steel had a corrosion rate of 23 mm/yr, indicating that such molten salt attack was the likely mechanism in the incinerator. There is as yet no evidence for participation of  $SnCl_2$  in the incinerator corrosion reactions. However, its low melting point and the possibility of forming a eutectic mixture with NaCl that melts at 199°C make it a likely contributor to molten salt corrosion.

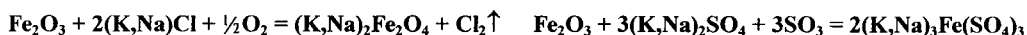
Figure 3 gives a schematic picture of the main reactions in the system gas/fly ash deposit/oxide scale/steel, representing superheater tubes in waste fired power plants [34].



Gas



Deposit



Oxide



Metal

**Fig. 3** Schematics of the main reactions in the system gas / fly ash deposit / oxide scale / steel, representing superheater tubes in waste fired power plants [34].

Most of the methods for preventing incinerator wall tube corrosion exact some penalty in boiler efficiency. The practice of studding the tubes and covering them with silicon carbide refractory has been widely used in European incinerators, but this remedy reduces heat transfer. Increasing overfire air or blanketing the walls with air to prevent reducing conditions in the flue gas has been effective, but either approach will reduce boiler efficiency. Lowering tube metal temperatures by operating at lower steam pressure also has a cost in efficiency.

However, upgrading the boiler tube material to a corrosion-resistant alloy does not involve an efficiency penalty. Although capital costs will be greater, the extended tube life resulting from the use of more resistant alloys can offset the initial expense and can be a cost-effective solution to the problem. Extensive corrosion probe studies in municipal incinerators showed that in the temperature range of 150 to 315°C a number of alloys provided good performance in resisting high-temperature corrosion. In decreasing order, the better alloys were Incoloy 825; AISI types 446, 310, 316L, 304 and 321 stainless steels; and Inconel alloys 600 and 601. However, when subjected to moist deposits, simulating boiler downtime conditions, all of the austenitic stainless steels underwent chloride SCC. The type 446 stainless steel, Inconel 600, and Inconel 601 suffered pitting. Consequently, unless the boilers were to be maintained at a temperature above the HCl dew point during downtime, only Incoloy 825 was recommended.

Many other materials were evaluated in waste incinerators and references [35] to [43] give a good account of the reported results.

## 6. Summary

This chapter covers high-temperature corrosion involving ash/salt deposits in fossil-fired boilers and waste incinerators. Fireside corrosion in coal-fired boilers is reviewed in terms of the corrosion of furnace walls and superheaters/reheaters. Corrosion of furnace wall tubes is believed to be enhanced by the establishment of localized reducing conditions in the vicinity of furnace walls. Corrosion of superheater/reheater tubes may be related to the formation of molten alkali metal-iron trisulphate,  $(\text{Na,K})_3\text{Fe}(\text{SO}_4)_3$ . Fireside corrosion can be a severe problem in oil-fired boilers or furnaces when low-grade fuels with high concentrations of vanadium, sulphur, and sodium are used for firing. Accelerated attack by oil ash corrosion is related to the formation of low-melting-point molten vanadium pentoxide and sodium sulphate eutectics, which flux the protective oxide scale from the metal surface. The corrosion processes generated by incineration of municipal, hospital, industrial, chemical, and low-level radioactive wastes are not very well understood, but sulphidation, chloride attack, and molten salt deposit attack are frequently responsible for the corrosion reaction. Apart from the 43 references already quoted, the attention of the reader is directed to references [44] to [65], for further information on this subject.

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## Corrosion of Alloys and Metals by Molten Nitrates

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**Keywords:** Alkali Nitrate, Carbon Steel, Chemical Equilibrium, Chromium-Molybdenum Steel, Constant Extension Rate Test, Corrosion Fatigue, Cracking, Molten Salt, Nickel, Nickel Alloy, Oxidation, Oxide Solubility, Stainless Steel, Thermal Convection Loop

### ABSTRACT

This review paper examines the corrosion behavior of alloys and metals in molten salts consisting of alkali metal nitrates. The chemistry of this class of molten salt is discussed as it affects the composition of the melt and metal oxide solubility. The corrosion rates and mechanisms of a broad selection of alloys are reviewed, including stainless steel, carbon steel, chromium-molybdenum steel, nickel and nickel alloys. The type of corrosion products that are formed on these materials over a wide range of experimental conditions are discussed. The results of studies of the effect of the molten salt on mechanical properties and cracking behavior of a number of alloys are also summarized.

### INTRODUCTION

Molten nitrate salts are used primarily as heat transfer fluids in the chemical and metallurgical industries [1], although other technological applications are being developed. The prospective applications include solar thermal energy (STE) systems [2] and separation of oxygen from air.[3] Other potential uses have been suggested, including batteries [4], fuel cells [5], and flue gas scrubbers for air pollution control.[6] STE systems have been the most intensive new development. A 10 megawatt solar thermal electric power system that uses focussed sunlight has recently been demonstrated [7] and construction of a commercial-scale power plant is planned.[8] Solar thermal energy systems that use molten alkali nitrate salts as working fluids for heat collection and storage require structural materials that have good corrosion resistance at temperatures up to 600°C. Selecting container materials for such advanced applications raises several questions regarding adequate corrosion resistance for long-term service.

The corrosion behavior of alloys and metals in molten salts consisting of alkali nitrates or nitrate/nitrite mixtures is reviewed in this paper with primary emphasis placed on the suitability of materials for engineering applications. The database regarding corrosion behavior in these molten salts has expanded substantially since the comprehensive review by Rahmel in 1982 [9], particularly with regard to the variety of materials investigated as well as to corrosion at temperatures above 500°C. Such progress was primarily a result of the development of solar thermal energy applications that employ this molten salt to collect and store the energy of focussed sunlight. In this review, the corrosion behavior of classes of alloys suitable for fabricating STE components are summarized and the temperature envelopes for using these materials are estimated. The corrosion rate equations and mechanisms are discussed with regard to the equilibrium chemistry of the molten salts.

### CHEMISTRY OF MOLTEN ALKALI NITRATES

Molten nitrate salts are used industrially almost exclusively as mixtures of  $\text{NaNO}_3$  and  $\text{KNO}_3$ . The liquid-solid boundary in the phase diagram for these two constituents does not indicate a sharp eutectic, but rather, a broad range of low-melting mixtures surrounding the minimum melting point of  $222^\circ\text{C}$  at the equimolar ratio (46 wt.%  $\text{NaNO}_3$ ). [10] The composition 44 mol.%  $\text{NaNO}_3$  - 56 mol.%  $\text{KNO}_3$  (60-40 wt.%), which melts at  $238^\circ\text{C}$ , was chosen for advanced STE applications and was used in several engineering demonstration projects. [7,11] The data suggested that a mixture enriched in  $\text{NaNO}_3$  relative to  $\text{KNO}_3$  would be desirable since the significantly lower cost of the sodium salt would offset the disadvantages of a slightly increased melting point. Low cost is particularly important if the molten salt is to serve as the thermal energy storage media given the large inventories required. [7]

A principal consideration in accepting the "60-40" molten salt composition for long-term use at temperatures near  $600^\circ\text{C}$  was chemical stability because the evolution of decomposition products can affect both its thermophysical properties and corrosion potential. Molten nitrate salts may undergo a variety of reactions depending on the temperature and the composition of the cover gas. [12] The primary reaction with regard to long-term stability is the decomposition of nitrate to nitrite and oxygen; see Eq. 1.



Experimental investigations of the equilibrium of Eq. 1 have determined the equilibrium constant at temperatures up to  $600^\circ\text{C}$ . [13] The nitrite concentration of melts in equilibrium with air is about 3 wt.% at  $565^\circ\text{C}$  and 5.5 wt.% at  $600^\circ\text{C}$ . Decomposition (formation of nitrite) is suppressed by increasing the pressure of oxygen in the cover gas. Fig. 1 compares the concentration of nitrite according to whether the 60-40 nitrate mixture was equilibrated with air or oxygen. Calculated values (lines) and measured values (circles) of the nitrite concentration at various temperatures are shown and agree well. [36]

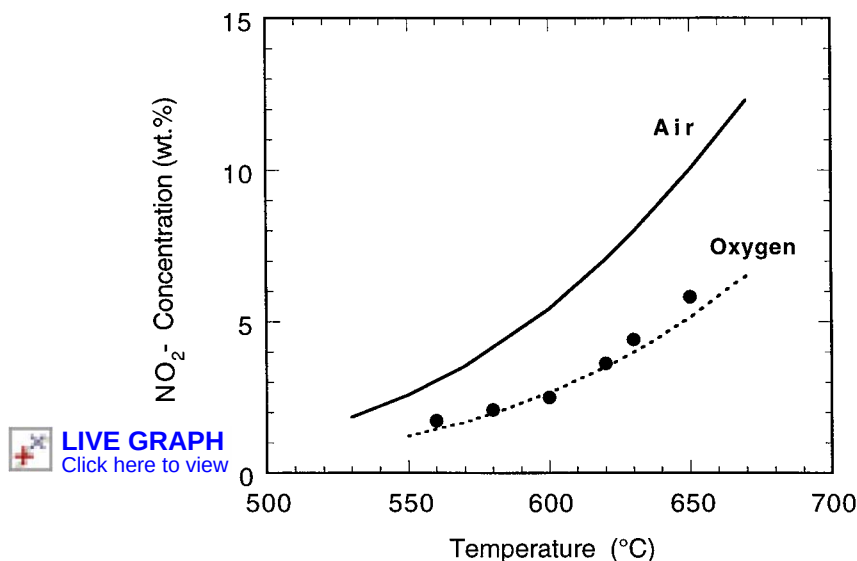


Figure 1. Equilibrium concentration of nitrite in molten nitrate salt vs. temperature. The cover gas is either air or oxygen. The lines represent calculated values and the symbols denote experimental measurements.

Another important chemical property of molten nitrates, with regard to corrosion, is that these melts behave as bases in the Lux-Flood sense, that is, as oxide ion donors. Molten nitrates are quite weak bases, at least at temperatures below 600°C.[14] Thermochemical equilibrium calculations have been used to predict the behavior of nitrate melts over a wide range of conditions. The thermodynamic model included reactions of nitrate and nitrite which yield alkali oxides and gases, such as oxygen, nitrogen and NO<sub>x</sub> and estimated the phase stability diagram of the Na-O-N system at various temperatures.[15] This study determined that the concentration of oxide ions was negligible at STE design temperatures, but increased rapidly above 600°C. This was an important finding because oxide ions are known to exacerbate corrosion. A comparison of the oxide ion concentrations measured in equilibrium melts with predictions of the thermodynamic calculations suggested that oxide ions behave non-ideally in nitrate melts.[16]

Some of the chemical and electrochemical factors relevant to corrosion of metals in molten nitrates have been discussed by Smryl.[17] Of particular interest is that chromium (as well as molybdenum and manganese) can produce soluble anions, e.g., chromate or dichromate. Because of this solubility, chromium can be readily extracted from the surface oxide scales formed on many types of alloys designed for high temperature applications. The chemical behavior of molybdenum in molten nitrate salts is similar to that of chromium and as such, it is likely that molybdenum is also removed from the surface oxide layers. Molybdenum forms oxides (MoO<sub>2</sub>, MoO<sub>3</sub>) that can react with trace amounts of oxide ions in the weakly basic molten salt to form molybdate, MoO<sub>4</sub>.[14] In contrast, nickel and iron do not form soluble species.[17]

Compilations of the physical properties of molten nitrates are available.[18] However, the maximum operating temperature intended for STE systems is 600°C, which is significantly higher than the limits of the published properties. For this reason, a research program was undertaken to measure the physical properties of the equimolar mixture of NaNO<sub>3</sub> and KNO<sub>3</sub> over the complete range of temperatures relevant to advanced STE systems. The results of this experimental program, encompassing viscosity, heat capacity, density, and thermal conductivity, have been summarized elsewhere.[19]

#### CORROSION OF FE-CR-NI ALLOYS

The corrosion behavior of iron-chromium-nickel alloys in molten alkali nitrates is of primary importance for applications that require prolonged containment of the melt at temperatures nearing 600°C, and STE systems in particular. These alloys, which include the austenitic 300-series stainless steels particularly, are essential for fabricating components subjected to both large mechanical stresses and elevated temperature. Corrosion data from a variety of sources prior to 1970 have been compiled by Bohlmann,[20] however, these data concern short-term tests and were not considered adequate for engineering design. Furthermore, little information was available regarding the types of corrosion products formed or the kinetics of the corrosion process. During the preceding 20 years, a good deal of data have been collected from either the immersion of test coupons in isothermal salt baths or the exposure of alloy tubing in thermal convection flow loops or pumped loops. Below, we review key results from a variety of these studies. In subsequent sections, results pertaining to a variety of other alloys and metals are discussed.

Laboratory studies performed at Sandia National Laboratories by Bradshaw, Goods, and others have shown that Fe-Cr-Ni alloys corrode at quite moderate rates at temperatures up to 600°C in a molten salt consisting of 60% (wt.) NaNO<sub>3</sub> and 40% KNO<sub>3</sub>. Isothermal crucible experiments were conducted at 570°C and the extent of corrosion was measured from descaled weight losses. The total metal losses of 316SS and 304SS were about 10 microns after 7,000 hours of exposure.[21,22] Experiments conducted at 560°C produced similar results.[23] Corrosion experiments were also performed using low-velocity fluid flow loops in which coupons were exposed to the molten salt at 600°C. Under these conditions, Alloy 800 (Incoloy® 800, nominally Fe-20Cr-35Ni) experienced about 6 microns of metal loss after 5000 hours [24], while 304SS lost about 8 microns after 4200 hours.[25] Corrosion data obtained from a molten salt pipe loop pumped at a relatively large flow

rate agreed with these results and further demonstrated the adequate corrosion resistance of 316SS and 304SS.[26]

The kinetics of metal loss and scale formation of stainless steels in molten nitrates generally follow a parabolic rate equation at temperatures approaching 600°C.[23] Such an equation describes corrosion that increases proportionally with the square root of time and indicates the formation of a protective, or self-limiting, corrosion product layer on the surface of an alloy. This behavior is indicated in Fig. 2 with regard to the corrosion of 304SS at 570°C in several commercial-purity mixtures of molten nitrates. In Fig. 2, descaled metal losses are plotted vs. the square root of time. Plotted in this way, the good fit of the data to straight lines affirms the applicability of a parabolic rate equation. The parabolic rate constants are approximately  $1 \times 10^{-7}$  cm/sec<sup>1/2</sup>. Thus, the corrosion rate of stainless steel in molten nitrates is less than in a high-pressure steam environment at the same temperature.[27]

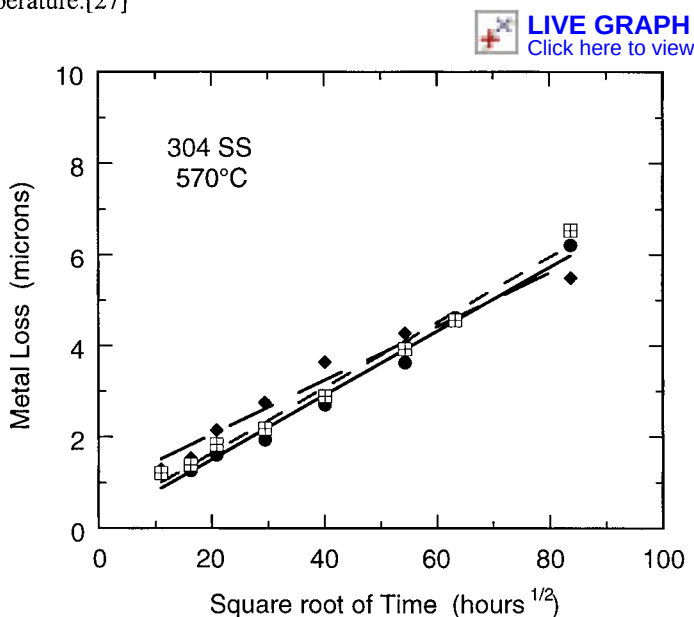


Figure 2. Descaled metal losses of Type 304 SS during corrosion in molten nitrate salt at 570°C. Data for several commercial-purity nitrate mixtures are shown.

Examination of the corrosion scale layers on stainless steel coupons following the tests described above revealed that adherent oxide layers were formed that had a multilayer structure. This morphology was found to be characteristic of oxides formed on all Fe-Cr-Ni alloys at temperatures up to 600°C. This morphology is shown in the SEM micrograph in Fig. 3 in which three distinguishable layers of oxide are indicated. The elemental composition of these layers, and the underlying alloy, is given by the electron microprobe analysis shown in Table 1. The "spot #" in Table 1 corresponds to the locations labeled on Fig. 3. The oxide layers (dark band at top) consists primarily of the iron oxide magnetite, Fe<sub>3</sub>O<sub>4</sub>, as identified by X-ray diffraction.[21,23] The exterior portion of the oxide was partially converted to a sodium-iron oxide, while the innermost layer is a spinel of iron and chromium that provides the protective layer with regard to the corrosion rate. These results have been corroborated by analyses of alloy tubes from experimental solar receivers. Examination of scale layers on the inside surface of Alloy 800 receiver tubes, that had operated for about 1000 hours in a cyclic solar radiation environment, revealed similar oxide layers.[28] These studies established that the primary corrosion products were M<sub>3</sub>O<sub>4</sub> spinels of iron alone and iron mixed with chromium and that chromium was depleted from the alloys and dissolved in the melt.



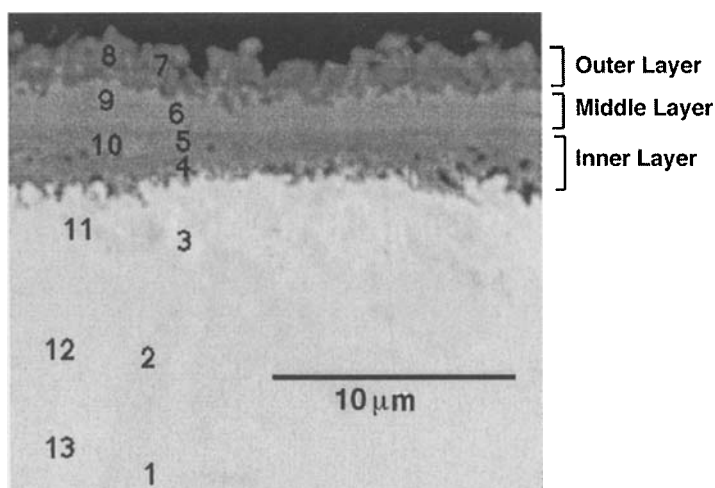


Figure 3. Photomicrograph of the corrosion product layers on 316 SS after 4084 hours of thermal cycling at 560°C (max.) in molten nitrate salt.

TABLE 1. Elemental concentration (wt.%) of selected areas of the corrosion product layers on 316 SS after 4084 hours of thermal cycling at 560°C in molten nitrate salt.

| Region         | Spot # | O    | Fe   | Cr   | Ni   | Mo  | Na   |
|----------------|--------|------|------|------|------|-----|------|
| Outer layer    | 7,8    | 13.3 | 69.4 | 1.4  | 1.9  | 0   | 12.3 |
| Middle layer   | 6,9    | 12.0 | 76.9 | 3.3  | 1.2  | 0.9 | 4.5  |
| Inner layer    | 4      | 18.1 | 13.2 | 63.2 | 1.3  | 3.0 | 0.7  |
| "              | 5      | 16.8 | 21.4 | 54.7 | 4.8  | 1.2 | 0    |
| "              | 10     | 16.1 | 27.0 | 46.2 | 7.5  | 2.4 | 0    |
| Depletion band | 3      | 0    | 71.9 | 6.3  | 18.5 | 2.6 | 0    |
| "              | 11     | 0    | 72.7 | 7.7  | 9.1  | 3.9 | 0    |
| Alloy          | 1,13   | 0    | 68.4 | 18.9 | 9.0  | 3.4 | 0    |
| "              | 2,12   | 0    | 66.4 | 18.9 | 11.9 | 2.8 | 0    |

Corrosion of stainless steels in molten nitrate salts is also influenced by factors such as thermal cycling and the presence of dissolved impurities in the molten salt. Due to the diurnal cycling of solar insolation, the high-temperature components in an STE system are required to tolerate many temperature excursions between the maximum operating temperature and the minimum ambient temperature. Thermal cycling generally aggravates high temperature oxidation, but the degree to which a particular material is affected in any given environment is difficult to predict. The primary effect of thermal cycling on high-temperature oxidation is to damage protective surface oxide layers via mechanical stresses arising from mismatched thermal expansion coefficients between the surface scale and the alloy. Corrosion is also affected by the presence of dissolved chloride impurities in the molten salt. Typically, the least costly grades of nitrate salts tend to have higher impurity concentrations, thus, it was necessary to assess the impact of such constituents on corrosion. A previous corrosion study of both stainless and carbon steels showed a moderate effect

of dissolved chlorides on corrosion.[21] Thermal cycling and impurities in the molten salt act in concert to increase corrosion rates, in that chloride often degrades adhesion of thermally-grown oxides to high temperature alloys.[29] The effect of both of these factors on the metal losses of 316SS thermally-cycled between 565°C and about 100°C is shown in Fig. 4. This plot uses parabolic coordinates, thus the upward deviation of the metal losses for coupons exposed to molten salts containing more than 0.5 wt.% chloride (M-3 and M-4) demonstrates that the protective surface oxide, formed at low chloride concentrations, has been degraded. In this case, a linear rate equation has replaced the parabolic one. Although the linear rate constants pertaining to this test are not remarkably large, metal recession will obviously be much greater during prolonged service than when protective scales form.

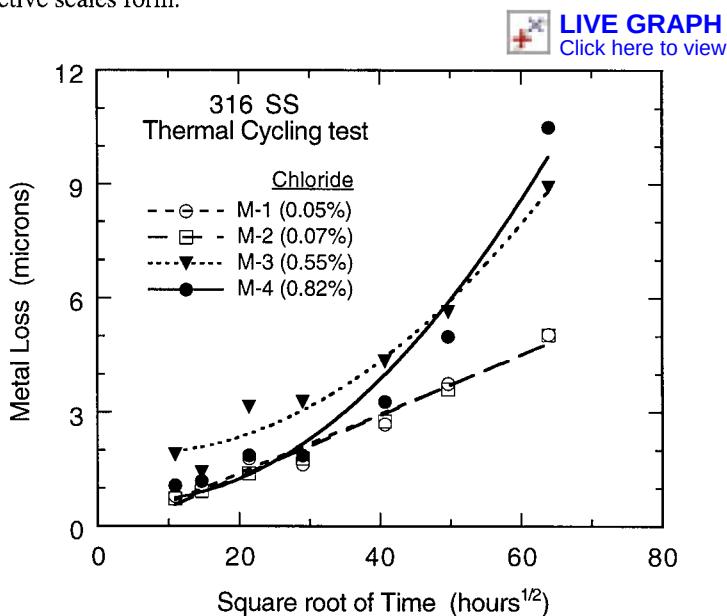


Figure 4. Descaled metal losses of Type 316 SS during thermal cycling corrosion in molten nitrate salt mixtures at 565°C (max.). Data for four different levels of dissolved chloride are shown.

#### Corrosion in Thermal Convection Flow Loops

Corrosion of Fe-Cr-Ni alloys has also been studied using thermal convection flow loops. Thermal convection loops create a circulatory fluid flow due to buoyancy differences resulting from an imposed temperature differential.[30] Such an apparatus can be used to study mass transport of dissolved alloying elements, caused by fluid flow along the thermal gradient, as well as corrosion. The concern with regard to solubility behavior was that dissolved corrosion products might precipitate in the coldest parts of the flow system and foul or plug them, a phenomena called thermal-gradient mass transfer. The alloys 316SS, 304SS, and Alloy 800 were investigated by Bradshaw using loops that operated at temperatures between 300°C and 600°C. The rates of metal losses of these alloys were between 5 and 12 micron/year at 600°C.[24,25] A similar study by Tortorelli and DeVan, using thermal convection loops in which the salt was in contact with an argon cover gas instead of the air atmosphere used in the former experiments, estimated corrosion rates of about 8 microns/year for both 304SS and 316SS at 590°C.[31] These values agree well with expectations based on the data discussed above obtained from isothermal tests at somewhat lower temperatures. Measurements of metal losses by chemical descaling revealed that the majority of metal consumption was due to oxide scale formation rather than depletion of alloying elements as soluble species.[24] However, chemical analyses of the salt in the loops established that

chromium was gradually dissolved, whereas iron and nickel were negligibly soluble. As discussed in a preceding section, the solubility of chromium in molten nitrates is quite large. However, the dissolution of chromium into the melt was kinetically limited by diffusion through the surface oxide scale. Thus, the concentration of chromate in the molten salt is limited to amounts far below solubility limits. Accordingly, no thermal-gradient mass transfer was observed.

#### Corrosion at Temperatures Exceeding 600°C

The corrosion resistance of Fe-Cr-Ni alloys deteriorates significantly at temperatures exceeding 600°C. As noted in the preceding section concerning molten salt chemistry, decomposition of the nitrate melt ultimately forms oxide ions and these species are much more corrosive than nitrate. Slusser, et al, evaluated a large number of alloys in molten nitrates at temperatures up to 670°C and reported metal losses of as much as 120 microns in tests lasting several hundred hours.[32] Other studies found that significant changes in the primary corrosion products occur in this temperature regime. The major change is that the spinel oxides described above are converted to sodium ferrite ( $\text{NaFeO}_2$ ).[33] This compound has been observed at temperatures of 615°C and higher. This change in corrosion mechanism also results in rapid corrosion rates that follow linear kinetics, indicating that  $\text{NaFeO}_2$  is a non-protective scale.[34,35] Corrosion tests have recently been conducted in a molten nitrate salt mixture that was stabilized by using an oxygen cover gas to suppress decomposition of the molten salt. Coupons were exposed to this salt at temperatures up to 650°C and corrosion rates were determined by descaled weight losses. Metal losses were approximately ten times greater at 650°C than at 570°C and the iron-chromium spinel observed at the lower temperature had been completely converted to the sodium-containing oxide by the basicity of the molten salt.[36]

#### **CORROSION OF CR-MO STEELS**

Chromium-molybdenum steels are often used for the evaporator sections of steam generators operating at temperatures up to 500°C rather than stainless steels in order to avoid stress corrosion cracking. In applications involving molten nitrates, these alloys must, of course, also exhibit satisfactory corrosion resistance. Only limited data have been available concerning the corrosion behavior of Cr-Mo steels in molten nitrate salts until recently. Bohlmann compiled corrosion data prior to 1972 based upon a survey of industrial users of molten nitrates and estimated that  $2\frac{1}{4}\text{Cr}-1\text{Mo}$  and  $5\text{Cr}-1\frac{1}{2}\text{Mo}$  would corrode about 200 microns/year at 480°C.[20] Spiteri reported that  $2\frac{1}{4}\text{Cr}-1\text{Mo}$  experienced linear metal loss kinetics equal to about 800 microns/year at 500°C when the alloy was exposed to nitrate salt under a nitrogen cover gas.[37] Corrosion data have also been reported for molten salts containing high proportions of nitrites, such as 40 (wt.%)  $\text{NaNO}_2$ -7  $\text{NaNO}_3$ -53  $\text{KNO}_3$ . Kirst, Nagle and Castner observed corrosion rates as large as 250 microns/year for low chromium steels immersed for several weeks at 538°C.[38] At 500°C, Fe-5Cr steel corroded according to linear kinetics at a rate of nearly 300 microns/year.[39] Kramer, Smyrl and Estill did not report rate data, but identified  $\text{Fe}_2\text{O}_3$  as the primary corrosion product on  $5\text{Cr}-1\frac{1}{2}\text{Mo}$  at 450°C.[40]

Laboratory studies by Bradshaw have provided a better understanding of the oxidation behavior of chromium-molybdenum steels in molten nitrates and have established reliable limits on the use of these materials. Several Cr-Mo steels containing from  $2\frac{1}{4}$  to 9 wt.% chromium were studied in a molten nitrate salt at 460°C.[41] The descaled weight losses observed in these tests are plotted vs. the square root of time in Fig. 5. The  $2\frac{1}{4}\text{Cr}-1\text{Mo}$  steel lost about 50  $\text{mg}/\text{cm}^2$ , equivalent to about 60 microns of metal recession, during the 4000 hour test period. Although parabolic rate equations generally described the corrosion of all three steels, significant differences were apparent. The corrosion resistance increased as the chromium content of the steels increased, but 9Cr-1Mo corroded much slower than the steels containing either  $2\frac{1}{4}\text{Cr}$  or 5Cr. Note that the weight loss of 9Cr-1Mo was multiplied by a factor of ten (10) to provide resolution in Fig. 5. The experimental data presented above show that  $2\frac{1}{4}\text{Cr}-1\text{Mo}$  steel corroded quite rapidly in molten alkali nitrate salt at 460°C. In addition, the chloride impurities typically contained in commercial grades of alkali nitrates significantly aggravated corrosion of this alloy.

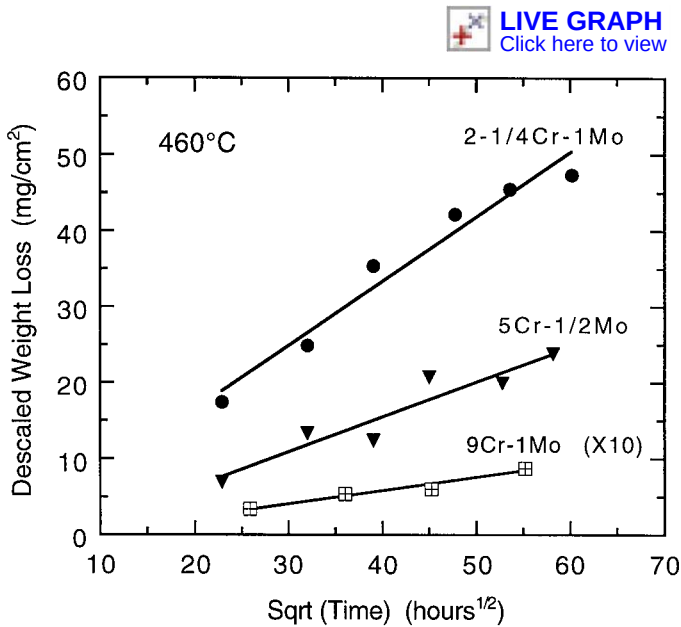


Figure 5. Effect of the chromium content of Cr-Mo steels on metal losses in molten nitrate salt at 460°C.

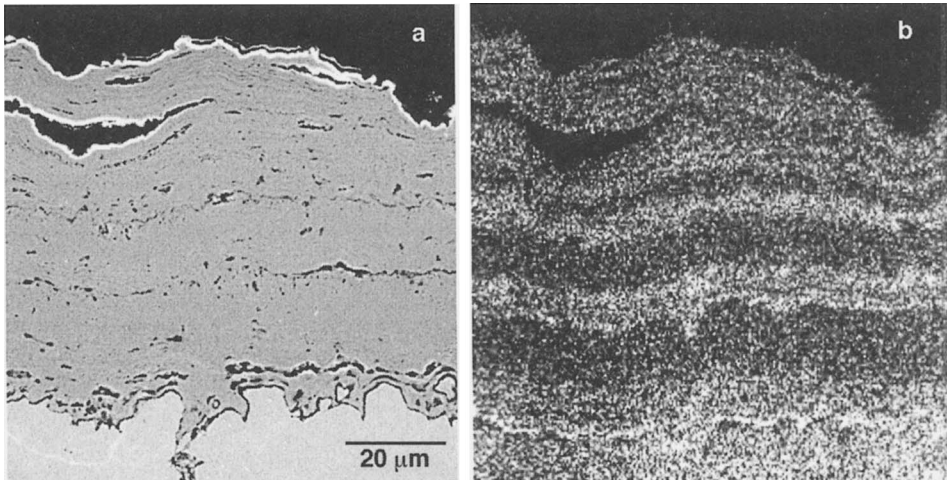


Figure 6. (a) Scanning electron micrograph showing the morphology of the oxide scale formed on 2 1/4Cr-1Mo after 4200 hours of exposure to molten nitrates at 460°C. Discrete lamellae of oxide that are organized on several dimensional scales are apparent. (b) X-ray map of chromium, corresponding to micrograph, reveals that each oxide band is partitioned into alternating layers, approximately 5-10 μm thick, that consist of Cr-rich (bright) and Cr-poor iron oxide.

Metallographic examination of the corrosion products revealed that complex oxide phases were formed during corrosion in the molten salt on the steels containing less than 9% Cr. As an example, Fig. 6(a) shows a scanning electron micrograph of the residual oxidation products formed on a 2<sup>1</sup>/<sub>4</sub> Cr-1Mo steel after 4200 hours of exposure to the molten salt. The oxide layer was composed of many discrete lamellae that were organized on several dimensional scales. Near the salt-exposed surface, these lamellae are only about 1 micron in thickness. Near the alloy interface, the fine lamellae are less evident, but are still visible at very high magnification. On a coarser scale, bands of many of these lamellae, approximately 10-20 microns thick, are delineated by porosity or cracks. Fig. 6(b) is an X-ray map of chromium taken from the same location that reveals that each band appears to be partitioned into alternating layers, approximately 5-10 microns thick, consisting of Cr-rich and Cr-poor iron oxide. In contrast, the 9Cr-1Mo steel formed a single bilayer oxide consisting of Fe<sub>3</sub>O<sub>4</sub> over a layer of (Fe,Cr)<sub>3</sub>O<sub>4</sub>, where both layers were basically the same thickness, about 2 microns.[41]

The use of Cr-Mo steels for molten nitrate salt containment in STE systems is currently restricted to alloys containing 9 wt.% chromium or more, which affords suitable corrosion resistance. A leaner alloy, such as 2<sup>1</sup>/<sub>4</sub>Cr-1Mo, can only be considered if the corrosion resistance can be significantly improved. There is evidence in the literature that relatively small additions of silicon improve the corrosion resistance of Fe-Cr alloys in gaseous oxidants at high temperature. For example, Taylor, et al., observed that 0.6 wt.% silicon significantly decreased the parabolic rate constant of an Fe-9Cr alloy, compared to the pure binary alloy, oxidized in CO<sub>2</sub> at 580°C.[42] Laboratory experiments were conducted by Bradshaw and Goods to evaluate the effect of small additions of silicon to 2<sup>1</sup>/<sub>4</sub>Cr-1Mo on corrosion resistance in molten nitrates.[43] Corrosion measurements based on descaled weight losses showed that steels containing 1 wt.% and 2 wt. % silicon, respectively, experienced two to ten times less corrosion than the standard alloy that contains 0.36 wt.% Si during a 4200 hour testing interval. These data are plotted in Fig. 7. These tests further demonstrated that the silicon-enriched steels had a substantial tolerance to chloride contamination of the molten salt. In addition, the corrosion products formed on the silicon-enriched alloys were considerably more adherent and much less likely to blister than the standard alloy.

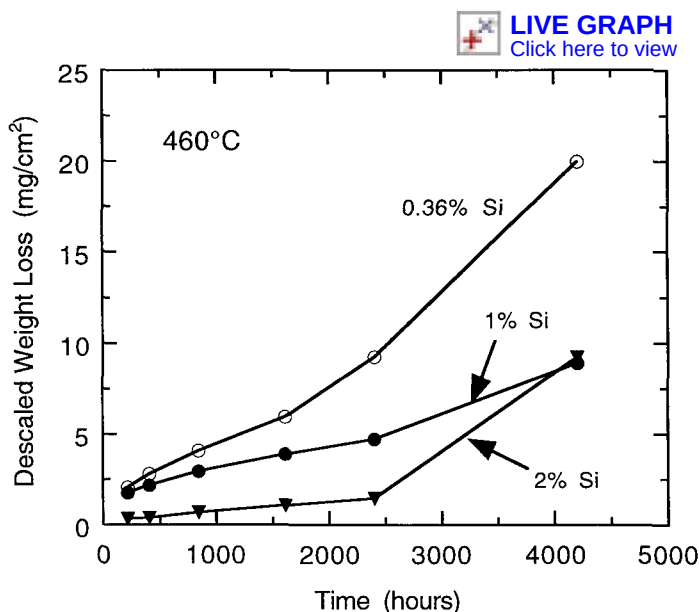


Figure 7. Effect of the silicon content of 2-1/4 Cr-1 Mo steel on metal losses in molten nitrate salt at 460°C.

## CORROSION OF CARBON STEEL

In applications where exposure to nitrate salts can be limited to 400°C or less, the use of carbon steels may be considered. Several papers in the literature describe the results of short-term corrosion tests of carbon steel in molten nitrates. These investigations primarily concerned the effect of dissolved impurities, such as chloride and sulfate, on corrosion as compared to pure nitrate melts. For example, El Hosary, et al, reported that the corrosion rate of mild steel at 400°C increased approximately as the logarithm of the chloride concentration.[44] At 0.6 wt.% NaCl, the corrosion rate increased by a factor of about three compared to a chloride-free melt during an 8-hour test. Other researchers report similar behavior for iron at 400°C-450°C.[45] Corrosion rates increased by about a factor of four during a 25-hour test when the chloride concentration was 0.7 wt.% compared to a chloride-free melt. The effect of dissolved sulfate in nitrate melts on corrosion of mild steel results in corrosion rates increased by 20% when 7.5 wt.% Na<sub>2</sub>SO<sub>4</sub> was added to the pure molten salt.[46]

Long-term experiments have been conducted to verify the corrosion resistance of carbon steel in commercial-purity nitrate salts. Measurements of net weight gains suggested that corrosion rates of carbon steel are suitable for components of STE systems that operate at temperatures below about 320°C.[26] Experiments have also been performed in which corrosion was measured directly, as the descaled weight loss, for pure NaNO<sub>3</sub>-KNO<sub>3</sub> salt, the same salt containing 0.7 wt.% chloride, and a ternary salt mixture containing Ca(NO<sub>3</sub>)<sub>2</sub> as well as the alkali nitrates. Weight loss data for A36 carbon steel specimens at 316°C are shown in Fig. 8.[21] The data fall into two distinct categories depending on the impurities present in the molten salt. The specimens exposed to the high-purity molten salt and the chloride-doped mixtures (upper 3 lines) corroded slowly at this temperature and lost about 1 to 3 mg/cm<sup>2</sup> after 4000 hours. Weight losses increased as the chloride level increased. The specimens exposed to the ternary nitrate salt (lower solid line) corroded very slowly, losing only 0.3 mg/cm<sup>2</sup> after 4000 hours. A binary salt mixture that contained several hundred ppm (wt.) of dissolved magnesium (dotted line) corroded at an intermediate rate.

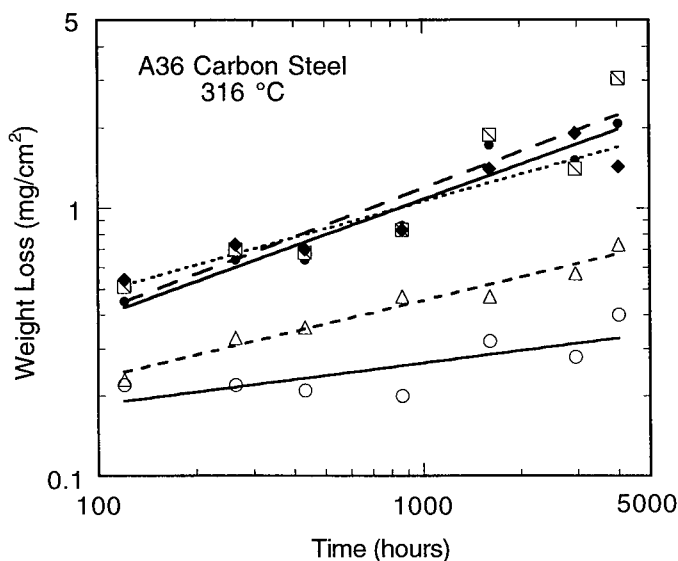


Figure 8. Descaled metal losses of A36 carbon steel during corrosion in molten nitrate salt mixtures at 316°C. Data for several concentrations of dissolved chloride are shown. The open symbols denote experiments in which the molten salt contained several hundred ppm (wt.) of magnesium.

The oxidation products that formed on carbon steel after prolonged exposure to the molten salt have been analyzed by X-ray diffraction and determined to be primarily magnetite.[21] The oxide films formed on A36 carbon steel that displayed unusually small weight losses, in the ternary molten salt described above, have been examined by Auger spectroscopy coupled with sputter depth profiling. This analysis demonstrated that magnesium replaced iron on a majority of the divalent sites in the spinel lattice, and thereby created a significantly more protective oxide film than magnetite.[47]

#### CORROSION OF NICKEL AND NICKEL-BASE ALLOYS

Nickel-base alloys are also candidates for molten nitrate salt applications and generally possess superior mechanical strength compared to the iron-base alloys. The low solubility of nickel oxide, observed during the experiments with stainless steels discussed above, suggests that nickel may form a protective oxide layer in the molten salt. Some information has been published concerning corrosion of nickel and its alloys in molten  $\text{NaNO}_3$ - $\text{KNO}_3$  at temperatures relevant to advanced solar thermal energy systems. Corrosion tests conducted in molten  $\text{NaNO}_3$  at temperatures between 465°C and 529°C for 6944 hours resulted in losses of about 30 microns/year for a group of nickel-base alloys that included IN-600 (Inconel® 600, nominal composition, Ni-15Cr-9Fe), Ni-20Cr and Ni-16Cr-22Fe.[48] In a nitrite-rich molten salt consisting of 52 (wt.%)  $\text{KNO}_3$ -41  $\text{NaNO}_2$ -7  $\text{NaNO}_3$ , a corrosion rate of 450 microns/year was observed at 570°C for Inconel® 600 and corrosion kinetics were linear.[20] Buirola and Bartel reported metallographic analysis of corrosion products on Inconel® 600 following an immersion of 700 hours in  $\text{NaNO}_3$ - $\text{KNO}_3$  at 550°C that revealed internal oxidation of chromium and formation of nickel-rich and iron-rich surface oxide scales.[49] Slusser, et al, observed rapid corrosion of a variety of nickel-base alloys in molten nitrates at temperatures exceeding 650°C.[32]

More recent laboratory studies have provided a somewhat better understanding of the oxidation behavior of nickel and its alloys in molten nitrates.[50] The corrosion of commercial purity nickel, (Nickel 200 grade), a nickel- 4% aluminum alloy (Ni-4Al), and IN-600 was studied at various temperatures in the eutectic nitrate melt. The corrosion products formed on nickel and its alloys were very adherent, thus net weight gain, due to oxide formation, provided a convenient measurement of the extent of corrosion. The net weight gains of these materials are shown in Fig. 9. In general, the trends of weight gain with time indicate that corrosion proceeded according to linear rate equations. Note that the corrosion experiments with the alloys were performed at 600°C and 630°C, compared to 565°C for nickel metal.

Metallographic examination of cross-sections of the test coupons revealed quite different corrosion products between nickel and the two alloys. The optical micrograph in Fig. 10 shows that Ni-200 suffered severe intergranular oxidation at 565°C. After 1500 hours, thick layers of nickel oxide formed along the grain boundaries and these intrusions had penetrated well over 100 microns into the metal. This behavior was apparently due to the relatively large carbon content of Ni-200 (0.08 wt.%). Bricknell has described similar oxidation morphology of Ni-200 in gaseous oxidants and attributed the attack to carbon at grain boundaries.[51]

Metallographic examination of IN-600 after 2800 hours at 630°C revealed a different mechanism of oxidation than for nickel. The micrograph in Fig. 11 shows that the oxidation products consisted of an external layer of NiO (the narrow dark band above the light band) about 4 microns thick. Chromium was absent from the NiO layer that contacts the molten salt. However, internal oxidation of chromium had penetrated to a depth of almost 40 microns. The bright band beneath the oxide layer is metallic nickel and contains no alloying elements. Soluble corrosion products of chromium were also formed.

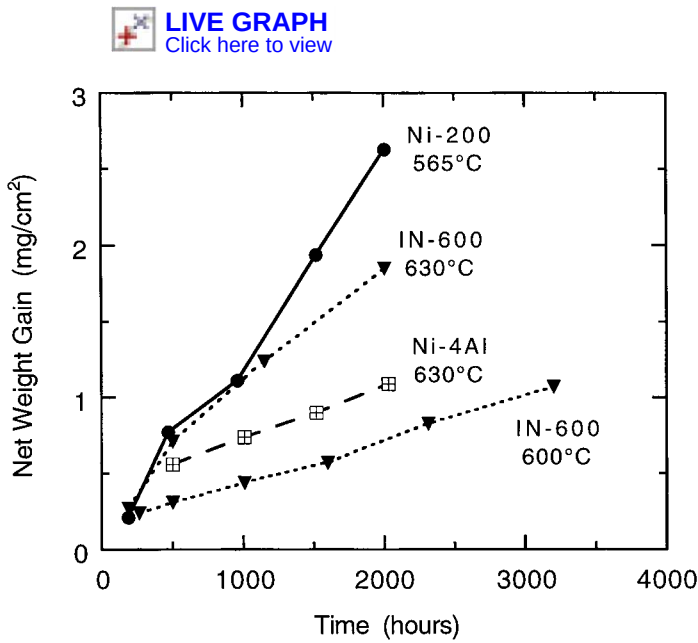


Figure 9. Net weight changes of Nickel 200, IN-600, and Ni-4 Al immersed in molten nitrate salt at various temperatures.

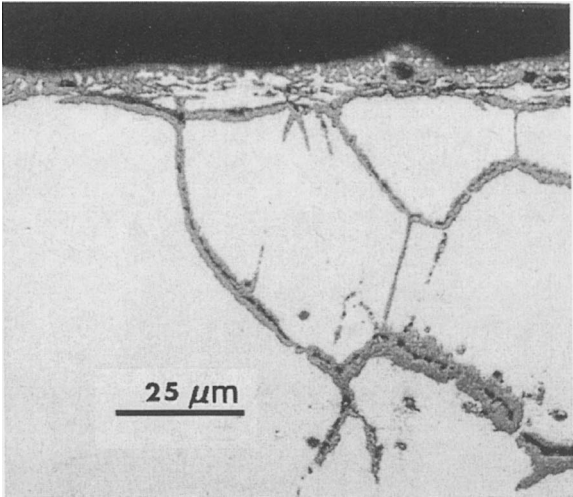


Figure 10. Micrograph showing intergranular oxidation of Nickel 200 after exposure to molten nitrate salt at 565°C for 1500 hours.



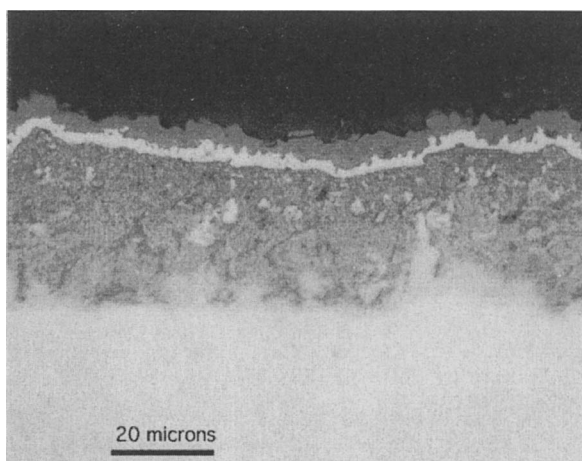


Figure 11. Micrograph showing surface scale and internal oxidation of Inconel 600 after exposure to molten nitrate salt at 630°C for 2800 hours.

#### MOLTEN SALT EFFECTS ON MECHANICAL PROPERTIES

The material performance requirements, other than general corrosion resistance, for molten salt containment alloys have been driven largely by STE applications. In this regard, requirements vary considerably between STE subsystems. For "cold salt" storage tanks, carbon steels have been shown to have adequate corrosion resistance up to 320°C and the mechanical requirements are minimal, resulting only from the thermal cycling-induced stresses and strains along the tank sidewall as the salt level rises and falls. The most challenging salt containment requirements were found in the receiver tubing where the combination of the one-sided heating and the diurnal nature of receiver operation give rise to severe thermomechanical stresses. These operating conditions are manifested as a low-cycle, high-strain amplitude fatigue environment. A key concern that arose because of the unique operating characteristics of the receiver was whether the exposure to the molten salt, in conjunction with the thermomechanical environment, would promote corrosion-induced cracking of the tubing material. Conversely, the question arose as to whether prolonged exposure to nitrate salts would degrade the mechanical properties of various alloys in some fashion that would adversely affect their fatigue properties. The complexity of testing in molten salts limited studies to a few alloys such as Alloy 800, 316 SS and HT-9, a 12Cr-1Mo ferritic steel. The influence of molten salts on mechanical properties of 2<sup>1</sup>/<sub>4</sub>Cr-1Mo steel has been examined as well. Because of the difficulty in reproducing the precise thermomechanical environment experienced by the receiver tubes, most tests have been of a screening nature, usually consisting of monotonic tensile tests performed at very low strain rates.

#### Constant Extension Rate Testing (CERT) of Alloys in Nitrate Salts

The CERT test (also called the slow strain rate test) consists of imposing a constant displacement rate on a tensile specimen of uniform gauge section that is exposed to the environment of interest. Multiple tests are usually performed over a wide range of strain rates to allow for prolonged exposure times. It is not unusual, therefore, for individual tests to run for up to 1000 hours. Because of the somewhat arbitrary test conditions, the results are usually compared to tests performed on specimens exposed to a reference environment under identical conditions of strain rate and temperature. Typically, reduction in area (RA), strain to fracture and ultimate tensile strength (UTS) are measured as parameters that determine the susceptibility of an alloy to environmental degradation. The test is thus a versatile method for the detection of an environmental or stress corrosion cracking phenomenon. It may also be used for the analysis of the critical variables which may contribute to the observed material degradation. The variables which

may be screened include temperature, the nitrate salt composition or impurity content, and the metallurgical condition of the alloy. The CERT test may also be used to examine the influence of deformation on the corrosion characteristics of a material subjected to an oxidizing environment. In particular, for solar thermal applications, it is important to determine if mechanical deformation induces either a change in corrosion mode (from one of uniform surface attack to one that is intergranular in nature) or if it appreciably accelerates the rate of oxidation, resulting in an unacceptable metal loss rate.

Early work examined the CERT response of Alloy 800, 316 SS and HT-9 at 600°C and 2 1/4Cr-1Mo at both 450°C and 525°C in nitrate salts.[52,53] The behavior of sheet tensile specimens in molten salt was compared to the behavior of specimens exposed to air over the same range of strain rate. Fig. 12 shows the influence of a 60 wt.% NaNO<sub>3</sub> – 40 wt.% KNO<sub>3</sub> molten salt mixture on the ductility of these alloys. Ductility loss in the figure is simply computed as the difference in ductility measured in air minus the ductility measured in the salt mixture. For 316 SS, little or no ductility loss due to the salt is apparent over the entire range of strain rates examined. However, both the ferritic steel and Alloy 800 begins to show some small decrease in ductility at the lowest strain rates corresponding to salt exposure times of approximately 1000 hours. In contrast, the lower alloy steel demonstrated marked decrease in ductility even at the substantially lower test temperatures.

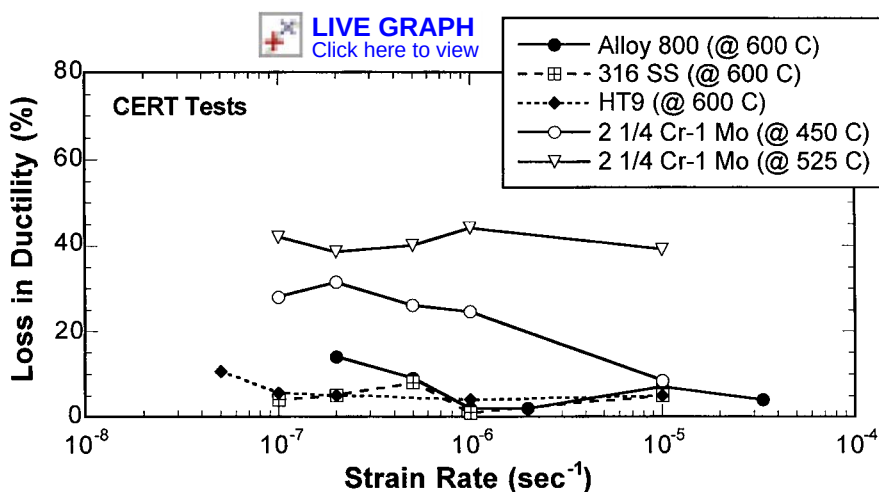


Figure 12. The influence of molten salt exposure on the ductility of high temperature alloys.

Metallographic analysis revealed that the continuously imposed deformation resulted in two principal effects for Alloy 800 and 316 SS. First, there is some intrusion of the oxide film below the nominal oxide-base metal interface. An example of this is shown in Fig. 13(a) for Alloy 800 tested at a strain rate of  $2 \times 10^{-7} \text{ sec}^{-1}$ . This intrusion occurred due to a small amount of near-surface, grain boundary cracking induced by the slow strain rates and elevated temperature. Away from the immediate vicinity of the fracture surface, this cracking extended to a depth of only one or two grain diameters. Further, such cracking was ubiquitous, occurring at these temperatures and strain rates regardless of the environment. Cracking was therefore not an indication of a transition from a relatively benign mode of uniform surface corrosion to an aggressive form of intergranular attack. Continuous straining of these alloys in concert with exposure to the molten salt, however, also resulted in some acceleration of the rate of oxidation. The effect was small, constituting only about a twofold increase in the rate of oxide film formation. In contrast, Fig. 13(b) shows that continuous deformation resulted in a catastrophic acceleration in surface corrosion rates for the 2 1/4Cr-1Mo alloy, leading to the observed loss of ductility.

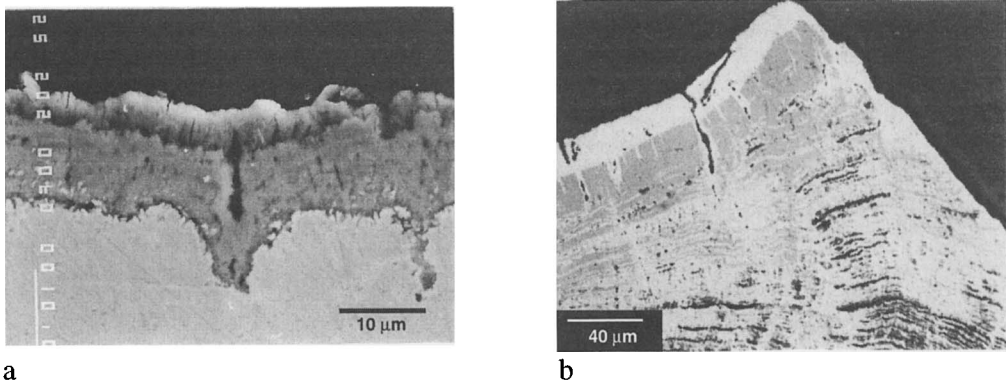


Figure 13. Surface oxide films formed on Alloy 800 (a) and 2<sup>1</sup>/<sub>4</sub>Cr-1Mo (b) specimens subjected to continuous deformation.

#### Corrosion-Fatigue Behavior

A very limited number of studies have examined the behavior of alloys in fatigue environments. In one study, hollow tubes of Alloy 800 (at two carbon levels) were filled with the 60 wt.% NaNO<sub>3</sub> – 40wt.% KNO<sub>3</sub> salt mixture and then tested under low-cycle, high strain amplitude fatigue conditions.[54] The results of these tests are shown in Fig. 14 and reveal that salt exposure had little effect on the fatigue life of the alloy, compared to specimens exposed to air. These tests were performed isothermally at 650°C and thus did not fully replicate the thermomechanical environment of the receiver. More importantly, total exposure times to the molten salt were quite short. At the lowest strain amplitude, the maximum test time was about 40 hours, while at the highest strain amplitudes, test times were only a few hours. These exposure times contrast with a receiver lifetime requirement of nominally 30 years. Given the relatively slow oxidation rates of this alloy reported above, such short tests produced little interaction between the molten salt and the test material.

The fatigue crack growth characteristics of Alloy 800 in molten nitrate salt have also been examined.[55] Pre-cracked specimens were immersed in the same nitrate salt mixture as above and tested at 600°C. While suffering from the same shortcomings as the above work, namely isothermal exposure conditions and limited salt exposure times, the results revealed that the salt-induced formation of oxidation products had little effect on fatigue crack growth rates or crack growth thresholds.

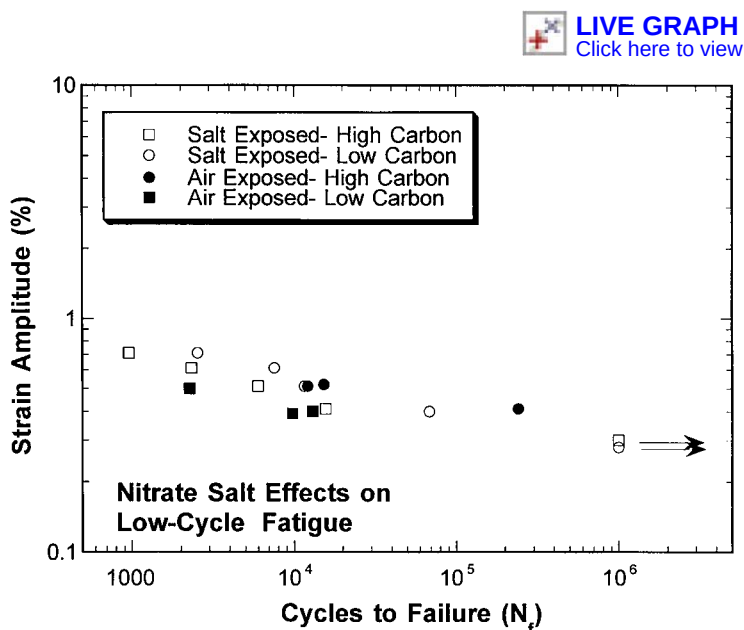


Figure 14. Corrosion-fatigue behavior of Alloy 800 in molten nitrate salt at 650°C.

## SUMMARY

A comprehensive database regarding the corrosion resistance of a variety of alloys and metals in molten nitrate salts has been established that enables materials to be selected with confidence in their long-term performance. Fe-Cr-Ni alloys, e.g., austenitic stainless steels, display acceptable corrosion resistance up to 600°C, regardless of whether thermal cycling is imposed or moderate amounts of chloride impurities are dissolved in the molten salt. Protective surface scales, consisting of spinel oxides of iron and iron-chromium, are formed on these alloys and parabolic corrosion kinetics were observed. Chromium was oxidized and slowly dissolved from Cr-containing alloys by the molten salt, although thermal gradient mass transfer was not observed. Corrosion rates of iron-base alloys increased rapidly at temperatures exceeding 600°C due to fluxing of chromium from the oxide scale and formation of sodium iron oxide. Cr-Mo steels offer corrosion resistance if the chromium content is at least 9% or supplemental silicon is added to 2<sup>1</sup>/<sub>4</sub>Cr-1Mo steel. Carbon steels are corroded very slowly at temperatures up to at least 320°C. Nickel experienced rapid intergranular oxidation at 565°C, although nickel-chromium alloys demonstrated good oxidation resistance. The molten salt did not cause susceptibility to cracking of high-temperature alloys or appear to reduce the corrosion-fatigue lifetime.

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## Corrosion of Structural Materials in Molten Carbonate Fuel Cells: An Overview

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**Keywords:** Bipolar Plate, Corrosion, Galvanic Corrosion, Molten Carbonate Fuel Cell, Scale Fluxing, Stainless Steels, Wet-Seal

### Abstract

The corrosion mechanisms and decay modes of the most critical metallic components of Molten Carbonate Fuel Cells are described with emphasis to galvanic corrosion of wet-seals and hot corrosion of bipolar plate. The effect of corrosion of stainless steel bipolar plate on cell performance is reviewed and the basis for selection of improved corrosion-resistant materials is indicated. Possible directions in the corrosion materials research for next generation MCFC plants are briefly discussed.

### Introduction

The Molten Carbonate Fuel Cell (MCFC) technology is a promising option for powering small-to medium size utilities in the near future. However, demonstration projects currently under way with MCFC systems up to 2MW in Japan and USA have suggested that a number of technical problems such as corrosion and system reliability still have to be adequately solved to make MCFC plants fully competitive with other more conventional power sources. It has been estimated that the capital cost currently involved in a low MW size plant is of the order of 1,500-2,000 \$/kWe with a first target individuated at 1,200-1,500 \$/kWe to promote a more rapid MCFC commercialization [1,2]. A significant cost reduction could come from the alloys used for making the hardware stack components (bipolar plates, current collectors, wet-seals, gas manifolds and stack containers). As the alkaline carbonate melts are particularly aggressive at the MCFC working temperature of ca. 650°C, most metallic materials can be subject to several degradation modes such as oxidation, carburization, galvanic corrosion and hot corrosion type reactions that impose severe restrictions on the choice of the structural materials. As the corrosion of the bipolar plate is particularly harmful for the cell performance, this component is generally made of austenitic stainless steels or nickel alloys and protected by expensive surface protecting treatments such as Ni cladding on the anode side and Al-diffusion coatings on the wet-seal areas. In spite of it, the bipolar plate corrosion behavior in long-term cell operations (> 5,000 hrs) has been often reported to be not fully satisfactory. For instance, from stack tests Plomp et al. observed that the endurance of a Ni clad steel on the anode side depends critically from thickness and quality of the coating with a limit estimated at about 10,000 hrs [3]. As the stack is projected to serve for approximately 40,000 hours, the view that more economical and reliable surface treatments and bulk materials are needed for the bipolar plate is widely shared among the developers.

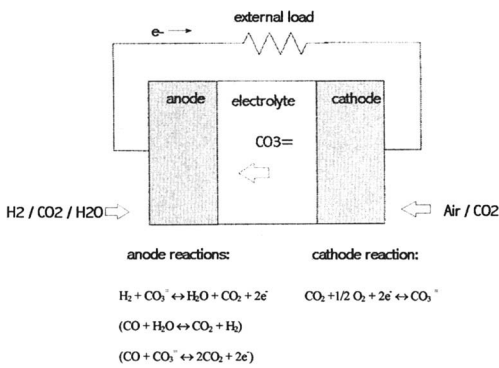
This chapter is not intended to present an exhaustive survey of all the pertinent literature existing on molten carbonate corrosion. Several excellent review articles have recently covered most of the important aspects involved in this field [4-7]. Rather, this paper should be viewed as a concise summary on technological aspects of metallic corrosion in MCFC stacks. So far, the search for corrosion resistant materials has been primarily directed towards modifications of existing materials, whereas little investigation has been concerned with the development of novel materials, specifically designed for MCFC application, though the latter aspect would deserve greater

attention by developers. This chapter will deal first with a description of the bipolar plate and its principal features. It then will briefly describe the principal cell performance decay modes caused by bipolar plate corrosion. A concise assessment of the possible directions of the corrosion materials prevention for the next-generation MCFC stacks will be finally presented.

Engineering aspects of the MCFC structural components will not be covered in this report unless strictly necessary, as these factors, including the design of the stack containers, gas manifolds, bipolar plates, current collectors and other ancillary equipments should be already borne in mind by the reader.

### Description of the cell and principles of operation

Basically, a fuel cell is an electrochemical device that transforms the chemical energy of a fuel and an oxidant into electricity without the intermediate of a thermal energy process. Unlike a battery, the electrolyte/electrode system remains essentially unchanged during fuel cell operation. Several cells must be connected in electrical series in order to obtain the required voltage and power at the



output load. Hydrogen is supplied at the anode compartment and air at the cathode. Hydrogen reacts with carbonate ions giving water and electrons, whereas oxygen is reduced by the electrons to reform carbonate ions. The carbonate ions move through the cell from cathode to anode causing electrons move in the opposite direction. Cathode and anode gas streams contain also carbon dioxide (see Fig. 1 for some details on electrode reactions). Typical gas compositions are given in Table 1 [8].

Fig. 1 – Schematic of the main electrode reactions occurring in a MCFC.

The MCF cell operates at 650°C utilizing an alkaline molten carbonate electrolyte which is highly advantageous in terms of thermal and electrochemical properties. In the present form the cell basically consists of a porous anode of sintered nickel stabilized with Cr or LiAlO<sub>2</sub> for

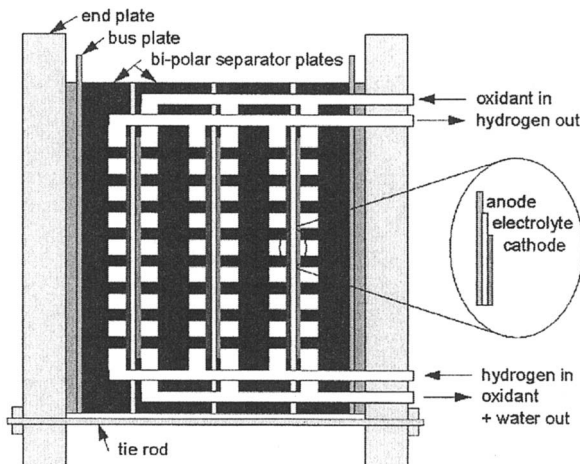


Fig. 2 – Schematic picture showing the basic components of a typical MCFC stack.  
[Source: Clean Energy Research Institute].



creep resistance, a porous cathode of lithium-doped nickel oxide, a tile of lithium aluminate containing the molten electrolyte (the conventional electrolyte is a Li/K mixture with composition  $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$  ratios = 62/38 or 70/30 m/o, though recently there is a renewed interest to alternative Li/Na mixtures). A schematic representation of the cell stack components is given in Fig.2.

Table 1 – Typical composition of MCFC gases. From Ref. [8]

|                | H <sub>2</sub> | CO <sub>2</sub> | H <sub>2</sub> O | CO  | N <sub>2</sub> | O <sub>2</sub> |
|----------------|----------------|-----------------|------------------|-----|----------------|----------------|
| Cathode inlet  | -              | 29.2            | 2.8              | -   | 53.7           | 14.3           |
| Cathode outlet | -              | 18.7            | 3.6              | -   | 68.8           | 9.0            |
| Air            | -              | 0.03            | 2.5              | -   | Bal.           | 20.5           |
| Anode inlet    | 60.9           | 8.4             | 21.6             | 9.1 | -              | -              |
| Anode outlet   | 10.3           | 39.6            | 45.4             | 4.6 | -              | -              |

### Critical cell hardware components: the bipolar plate and the wet-seal

**The bipolar plate :** Needless to say, protection of the bipolar plate from corrosion is essential for the entire stability and performance of the cell. From a design point of view, the bipolar plate is frequently composed of three distinct metallic components: the separator plate, the current collector and the center plate. Schematically, separators are corrugated plates which must fulfill the following main functional requirements: i) separate fuel and oxidant gas streams , ii) create flow channels for the gases to pass to the electrodes; iii) provide electrical contact between adjacent cells ( in combination with the current collectors and the center plates) and iv) provide a tight gas flange by extending the electrolyte tile to the plate edges where it is sandwinched between two plates (wet-seals) (Fig. 3). Purpose of the current collectors and center plates are mostly to reduce the contact and corrosion areas of the separator plate with electrolyte.

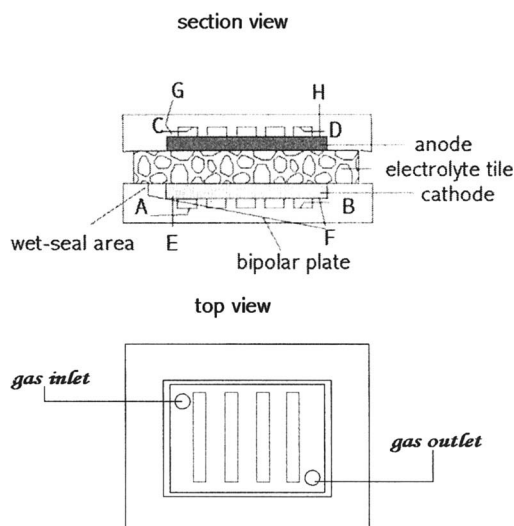


Fig. 3 – Side view and top view sections of a Molten Carbonate single cell showing the different corrosion areas of the bipolar plate: see text for explanation of letters A through H.

Separator plates, current collectors and center plates must simultaneously satisfy various chemical, electrical and mechanical requirements and therefore they are usually made of the same materials. For sake of simplicity, we will refer to them as a whole with the term of bipolar plate.

The most critical requirement is undoubtedly the corrosion resistance as the bipolar plate must tolerate a wide range of aggressive chemical conditions intermediate between the highly oxidizing cathode environment and the highly reducing character of the anode in presence of a liquid salt. Strictly speaking, the bipolar plate experiences different corrosion conditions along its length. In the Fig. 3 the letters A through H identify such corrosion cells as:

- A): regions in contact with thin layers of molten carbonate in a highly oxidizing gas environment
- B): regions in contact with thin layers of molten carbonate in a less oxidizing gas environment
- C): regions in contact with thin layers of molten carbonate in a reducing gas environment
- D): regions in contact with thin layers of molten carbonate in a less reducing gas environment
- E): regions in contact with deep layers of aerated molten carbonate
- F): regions in contact with deep layers of scarcely aerated molten carbonate
- G): regions in contact with deep layers of molten carbonate in a mixed reducing / carburizing gas environment
- H): regions in contact with deep layers of molten carbonate in a poorly reducing gas Environment

In a rather, although widely used, over-simplified approach, these different corrosion areas can be conveniently grouped in a (1) cathode region (points A,B,E,F); (2) anode region (C,D,G,H) and (3) anode (H) and cathode (F) wet-seal regions.

Design modifications have been found useful to mitigate the corrosion problems by reducing the wetting areas with electrolyte. For instance, in Ref. [9] the authors describe a “soft” plate which is flexible enough to adsorb the deformation of the active components by means of flat springs contained inside the wet-seal that ensure the necessary component pressures. In this way, a pressed current collector with a gas flow channel function could be used instead of a corrugated separator to reduce wetting and, in turn, corrosion areas. A similar pressed plate structure directed to reduce the number of the components and the contact areas has been tested with promising results in terms of corrosion and electrolyte loss [10].

Another important requirement is that the bipolar plate material should be a metallic conductor. Additionally, the corrosion products must be also sufficiently conductive ( $\sigma > 10^4$  S/cm) and insoluble in the carbonate melt [11]. Finally, several mechanical requirements are associated with fluid flow, high temperature mechanical resistance, proper contact of the components, weldability and easy formability.

The Table 2 reports a list of about sixty different high temperature alloys which have been so far evaluated by various developers [7].

*Table 2 – candidate alloys evaluated for the MCFC bipolar plate. From Ref. [7].*

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*Fe-based alloys*

304, 304L, 310, 310S, 314, 316, 316L, 330, 347, 405, 430, 446, 17-4PH, 18SR, A118-2, A126-1S, A129-4, A1439, Glass seal 27, Ferralium 255, RA 253mA, Nitronic 50, 20Cb3, Crutemp-25, Sanicro-33, IN800, IN840, A-286.

*Ni, Co-based alloys*

IN600, IN601, IN671, IN706, IN718, IN825, IN925, RA333, Ni200, Ni201, Ni270, Haynes230, Haynes 625, Haynes 188, Haynes 556, Nichrome, Monel400, Hastelloy C-276.

*Al-containing alloys*

MA956, FeCrAl+Hf, Haynes 214, Fecralloy, IJR406, 85H, Kanthal AF, Kanthal A-1, Ni<sub>3</sub>Al, FeAl.

---

The austenitic stainless steels 316L and 310S are the current choices for their appropriate cathode-side corrosion resistance and a relatively low cost. Regarding the role of alloying elements in the corrosion resistance of commercial steels, chromium is the element which confers the best corrosion resistance under both cathode and anode conditions, whereas nickel is less important or has a slight negative effect in oxidizing environments. Aluminum results in high corrosion resistance, but also in corrosion layers with high electrical resistance.

To improve their anode-side corrosion resistance Ni-cladded or Cr-plated stainless steels can be used there (nickel is thermodynamically stable in the reducing anode gas conditions) [4]. Both electroless and electrolytic plating methods have been evaluated [12], but they are rarely used due to their higher costs and to a lesser corrosion resistance. Being the Ni-clad structure very dense, a 50-100  $\mu\text{m}$  thick layer is adequate to provide the best protection to corrosion, thermal cycles, and interdiffusion. High nickel-base alloys show appropriate anode-side corrosion, although they are scarcely used because of their cost and a not sufficiently resistance in the cathode compartment [7].

**The wet-seal:** The concept of the “wet-seal” flange is nowadays largely applied in the MCFC bipolar plate fabrication as a method of minimizing corrosion and sustaining large differential pressures across the stack. Successive improvements have been performed in the seal design from the pioneristic work of Davtyan in the 1940’s [13]. In the “wet-seal technique” the bipolar plate is pressed against the flat surface of the electrolyte tile (i.e. the solid porous support filled with the carbonate mixture). At the MCFC working temperature the molten electrolyte wets the metallic surface and forms the gas wet-seal. Although the width dimension of the wet-seal area is relatively small (usually 5-10 mm, i.e. about only five times the tile thickness) it has long been realized that corrosion of the wet-seal area metal is particularly critical and may lead to a poor sealing with consequent gas leakage and rapid decay of the cell performance. An excessive corrosion may also lead to a critical electrolyte loss from the tile causing catastrophic failure [8]. As it will be shown later, the use of the wet-seal technique results in the onset of galvanic couples whose the corrosion currents are often limited by the mass transfer rates of  $\text{O}_2$  and  $\text{CO}_2$ . Fe and Ni-based alloys have been found to offer limited resistance to this kind of attack since their corrosion products are usually too conductive to block the current paths. Thus, for instance, AISI 316L was so severely corroded as anode wet-seal material during short term tests (2000 hrs) that it cannot be absolutely used without protection [5]. Corrosion in the cathode wet-seal was found to be about two orders of magnitude lower than at the anode side [5], therefore AISI 316L could be used without significant problems in the cathode wet-seals in short term MCFC operation (a few thousands hours).

Methods of minimizing the galvanic corrosion of wet-seals are very limited. A review on this subject has been published by Pigeaud [14]. Based on the consideration that an insulating material is desirable to break the corrosion cells, it was early examined the possibility of using more than one type of material for the bipolar plate. Aluminum-containing alloys such as Kanthal A-1 reduce the corrosion rate in the anode gas environment by at least two orders of magnitude to less than 0.002 cm in 1000 hrs with respect to the AISI 316L [5]. This is ascribed to the formation of an insulating  $\text{LiAlO}_2$  thin surface layer. However, this approach was not pursued for the high costs of fabrication of bimetallic bipolar plates. Aluminum foil gaskets were also investigated but with unsatisfactory results because the Al melting point (ca. 660°C) is so close to the MCFC operating temperature that even small temperature fluctuations in the cells can melt the gasket [15]. Currently, the only followed approach is to protect the stainless steel by deposition of aluminum diffusion coatings in the wet-seal area. Aluminized stainless steels infact are known to provide high temperature corrosion resistance in both oxidizing and reducing environments by forming a dielectric alumina thin film. In the presence of carbonate, alumina converts to  $\text{LiAlO}_2$  which is also effective in inhibiting the corrosion cells with a minimal consumption of electrolyte thus providing the required long-term stability to the wet-seal.

Various aluminizing processes have been so far evaluated for their effectiveness, including painting, thermal spraying, vacuum deposition and pack cementation [7,15]. At present time the ion-vapor deposition (IVD) method followed by a diffusion heat treatment is generally considered to offer the most protective and adherent aluminized coating in the MCFC wet-seal environment. A detailed description of the principles of IVD coating method is given in [16]. Diffusion bonding is obtained at 900-1000°C for 1-3 hrs in a reducing atmosphere. The resultant IVD coating is dense and uniform mainly consisting of an intermetallic  $\text{MAl-M}_3\text{Al}$  structure (M= iron, nickel plus 5-10 wt% Cr). Concentration of Al in the diffusion layer ranges from the 50 wt% of the outer layer to the 30 wt% of the inner layer, values that are much higher than those obtainable by other methods [15]. This confers to the IVD coatings the sufficient long-term stability and durability required for a 40,000 hrs cell operation.

### Corrosion effects on the cell performance

It is easily understood that the formation of a corrosion scale with a poor electrical conductivity could result in a voltage loss so that the ohmic drop at the bipolar plate / electrode interface would tend to increase as the corrosion proceeds. The increase of ohmic drop on the cathode side due to scale growth is estimated to contribute to the cell decay rate for less than 0.8 mV/1000 hrs ( $\approx 1\%$  /1000 hrs), if AISI 316L is used [17]. However, this number may not be acceptable for a 40,000 hrs operation in future MCFC systems, where a cell decay rate of 0.25% /1000 hrs has been recently targeted [18]. The following table evidences that the bipolar plate corrosion is one of the most important items to be solved for reducing the cell decay [18]:

Table 3 – Items to study to realize a 40,000 hrs stack life. From Ref. [18].

|   | Items                         | Countermeasures                                                                                                                                                                                        |
|---|-------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1 | Decay due to polarization     | Optimization of pore structures<br>Control of fill ratio<br>Decrease in electrolyte loss<br>Pressed bipolar plate (smaller contact areas)<br>Li/Na type electrolyte<br>Lower solubility of the cathode |
| 2 | Decay due to ohmic losses     | Soft seal type separator<br>Improved bipolar plate materials<br>Pressed bipolar plate<br>High quality Al coating                                                                                       |
| 3 | Decay due to ionic resistance | Optimization of electrolyte pore structures<br>Restriction of $\text{LiAlO}_2$ phase transformations<br>Decrease in electrolyte loss                                                                   |
| 4 | Decay due to Ni dissolution   | Li / Na type electrolyte<br>Improved cathode ( $\text{NiO} + \text{Mg, Fe}$ )                                                                                                                          |

Based on post-test analysis of failed MCF cells, the influence of corrosion is not limited to ohmic losses, but many results have indicated that corrosion degrades also the functionality of the cell components (both metallic and active ones). A good presentation of this problem has been discussed by Singh [4] to which the reader is invited to refer for a more detailed analysis. Here a brief excerpt of his work is presented. The main corrosion factors contributing to the cell performance decay can be grouped in the following categories: a) dimensional and b) mechanical changes of the plate; c) loss of electrolyte and gas leakage; d) chemical contamination of electrodes and electrolyte.

a) *Dimensional changes*: dimensional stability of the bipolar plate may be undermined if the anodic side of the plate is not being protected by nickel cladding. Uncoated stainless steel in fact experiences excessive scale growth on the anode side resulting in an intolerable increase of plate thickness. These dimensional changes tend to generate compressive stresses in the cell components

causing formation of cracks and breakdown of the most brittle cell components like tile and electrodes. Excessive scaling also results in the scale crack with anomalies in the gas path geometry. The cell decay rate may be enhanced because of fluctuations in the gas composition and localized use of the fuel.

b) *Mechanical changes*: mechanical and load bearing properties of the bipolar plate components have been sometimes observed to be strongly affected by scaling and carburization processes. Excessive scaling on stainless steels reduces in fact the effective thickness of the metallic component, whereas carburization, i.e. precipitation of chromium-rich carbides inside the metal matrix and at grain boundaries, may lead to hardening of the component. Both the effects are deleterious because the reduction of mechanical resistance could cause the breaking of the remaining metallic components.

c) *electrolyte loss and gas leakage*: The electrolyte loss is caused by reactions between the oxide scale grown on the bipolar plate and the molten carbonate resulting in a consumption of the alkali-metal electrolyte components and formation of reaction products like  $\text{LiCrO}_2$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{Li}_2\text{CrO}_4$ ,  $\text{LiFeO}_2$  and others. The increasing and never recovered loss of carbonate melt during cell operation causes an increase of the polarization at electrodes and an increase of the internal resistance at the electrolyte. Likewise, excessive electrochemical corrosion in the wet-seal area may lead to poor sealing with both gas leakage and electrolyte loss effects.

d) *Chemical contamination*: formation of both soluble and insoluble oxide layers normally occurs during the corrosion reactions between the metallic components and the carbonate melt. Thus, at the anode compartment corrosion of stainless steels proceeds with the initial formation of soluble iron oxide which later precipitates at the melt/gas interface (fluxing dissolution). At the cathode side, under very oxidizing conditions, soluble chromates become the more stable corrosion products. The dissolution of these oxide contaminants into the electrolyte changes the melt chemistry in terms of oxide ion activity (acid/basic properties). Also the NiO cathode electrode can be contaminated by incorporation of aliovalent iron(III) or chromium(III) ions. This changes the defective structure of the cathode which could result in changes of its electronic conductivity.

### **Analysis of corrosion mechanisms operating on the MCFC bipolar plate**

The conditions of temperature, gas composition and flow, electrolyte type and electrical potentials existing in the MCFC stacks pose severe and different corrosion conditions to the metallic components. As already seen, the bipolar plate, in particular, experiences three main typical conditions that are those met at the cathode side, anode side and wet-seal.

Hot corrosion of the bipolar plate at both anode and cathode sides has been a major matter of concern in the hystorical development of MCFC. According to current definitions, the phenomenon of hot corrosion is the accelerated oxidation in a high-temperature gaseous environment of a material, whose surface is coated by a fused salt film. Although several studies have demonstrated that accelerated oxidation of iron, nickel and stainless steels occurs in presence of molten carbonates [19-22], the related hot corrosion mechanism has been poorly studied. As a rather simple and general model, one may separate hot corrosion into two main steps: oxidation of metal (anodic dissolution) and dissolution of oxide scales. According to Rapp and Goto [23], an accelerated and non protective corrosion is expected if, after the initial formation of a passive oxide scale (incubation stage), the scale dissolution process is combined with the set-up of a negative solubility gradient resulting in the oxide reprecipitation at the melt/gas interface and in the development of a porous thick scale (oxide fluxing model). Being a detailed description of the fluxing model beyond the purpose of this review, it is sufficient to remind here that scale solubility may be affected by the oxide ion activity of the salt melt, which is, in turn, affected by the gas composition. Because the oxide ions have a similar meaning to what hydrogen ions are for aqueous solutions, acid/base concepts are defined by analogy to pH. Thus, as the basicity of the melts proportional to the activity

of oxide ions, the carbonate basic melts are those with high oxide ion activities (high  $O_2$  gas) and acid carbonate melts are those with low oxide ion activities (high  $CO_2$  gas).

In this section, corrosion phenomenologies and the proposed mechanisms operating on the different regions of the bipolar plate are presented and discussed.

Cathode-side: The work of Spiegel et al. [24] can be taken as a specific example of the application of fluxing theories to molten carbonate corrosion. They have attempted to elucidate the possible fluxing mechanisms of Fe-based alloys in molten carbonates analyzing in detail the electrochemical oxidation and reduction reactions, the chemistry of oxide dissolution and the transport modes of the oxidant species through the melt. As oxygen is known to chemically dissolve in carbonate melts [6], this results in the formation of higher oxides, such as peroxide ( $O_2^{2-}$ ) and superoxide ( $O_2^-$ ) in accordance to:



In the case of metal anodic dissolution ( $M = M^{2+} + 2e^-$ ), the superoxides may be reduced to peroxides and peroxides to oxides by:



Therefore the overall oxidation process can be described as merely due to peroxide ions by:



As this reaction produces oxide ions at scale/melt interface a higher oxide ions concentration is established there than at the melt/gas interface. In these conditions basic dissolution of the oxide can take place by:



and a solubility gradient of the dissolved oxide exists through the melt layer making possible the inverse of Eq. (6) at some distance from the scale/melt interface (fluxing). A schematic representation of the basic fluxing of a MO oxide scale and the reactions sequence is described in Figs. 4 and 5, respectively.

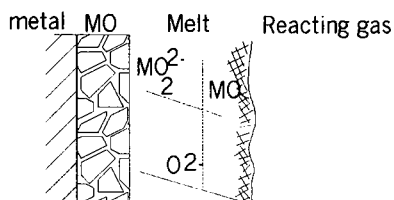


Fig. 4 - Fluxing process in carbonate melts: A negative oxide ion gradient is being established during the reaction (5). The solubility of the dissolved  $MO_2^{2-}$  oxide decreases accordingly and precipitation occurs at melt/gas interface.

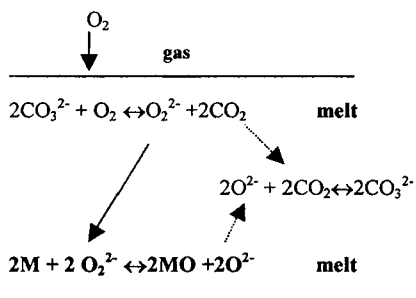


Fig. 5 – Oxidation processes in carbonate melts via peroxide ions. From Ref. [24].

On the other hand, if dissolution occurs by :



The peroxide ions are consumed by Eq. (7) and produced by Eq. (1) so that the peroxide ions concentration is high at the melt/gas interface and low at the scale/melt interface. As a negative oxide solubility gradient can not be established, no fluxing is expected if dissolution occurs directly via peroxide ions. However, if the oxide is soluble in the melt ( as the case of  $\text{CrO}_4^{2-}$  from  $\text{Cr}_2\text{O}_3$ ) it will dissolve until the melt is being saturated with the oxide, but without precipitation phenomena.

Anode side: The unexpectedly fast corrosion rate of uncoated stainless steels in the reducing gas atmospheres has been interpreted as due to fluxing reactions of iron oxide species [4]. Analysis of the salt after short term exposure have revealed infact the presence of iron oxide species at the salt/gas interface interpretable as consequence of a sequence of dissolution and precipitation steps. The mechanisms proposed to explain the formation of a nonprotective and porous scale is visualized in Fig. 6. Initially, Fe and Cr oxide formation takes place at the expense of  $\text{CO}_2$ . As the concentration of  $\text{CO}_2$  goes down, the oxide ion concentration grows leading to partial dissolution of the FeO ( Cr oxides are assumed to be practically insoluble ). A gradient of  $\text{FeO}_2^-$  within the salt layer is thus established. This oxide species precipitates at the salt/gas interface where the oxide ion concentration is lower. The inner  $\text{Cr}_2\text{O}_3$ -rich layer is assumed porous enough to allow continuous diffusion of iron cations to the oxide surface. A weak point of this model concerns the solubility of  $\text{LiFeO}_2$  in the carbonate mixture. As seen, according to the Rapp-Goto criterion for scale fluxing, a gradient in  $\text{LiFeO}_2$  solubility must exist to hypotize a fluxing behavior. Since the solubility of  $\text{LiFeO}_2$  is essentially independent of the  $\text{CO}_2$  and  $\text{O}_2$  partial pressures [25], how the fluxing process of  $\text{LiFeO}_2$  could proceed in these conditions remains a rather obscure point.

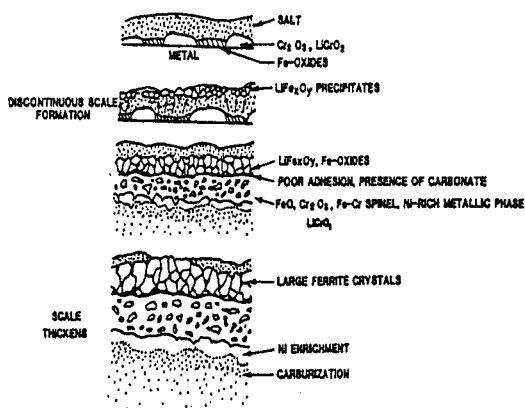


Fig. 6 – Formation of a porous and non-protective scale during scale fluxing in anode environment gas of austenitic stainless steels. From Ref. [7].

**Wet-seal:** Donado et al. [8] have recently made an exhaustive analysis of the galvanic corrosion mechanisms operating in the wet-seal area. They have discussed the various types of corrosion cells active in the wet-seal region and the corresponding corrosion rates at open circuit potential (OCP) and under load conditions. Figures 7 and 8 indicate schematically the corrosion cells present at OCP, where anode and cathode flanges are not electronically connected, and under load, where the corrosion currents are superimposed to the fuel conversion current. In the first situation, the corrosion cells are defined as parasitic or cooperative, depending on whether or not they consume part of the feed gases. Conversely, four types of cells may be distinguished under load: cooperative, parasitic, non-parasitic and parallel (see Fig. 8 for detailed explanations). A semi-quantitative prediction of the corrosion intensities expected in the various cells has been derived from models simulating potential, current, and gas fluxes distributions in the wet-seal and adjacent regions. Thus, for instance, being the edge of the wet-seal more rich of  $O_2$  (air), at OCP the greatest driving force for the corrosion at OCP is estimated to be the cell  $i_1$  (region C-B on the anode flange of Fig. 7). The situation drastically changes under load because anode and cathode are connected electronically through the load and the corrosion cell  $i_5$  across the tile is the most active due to the large driving force and the small tile dimensions (parallel corrosion cell of Fig. 8).

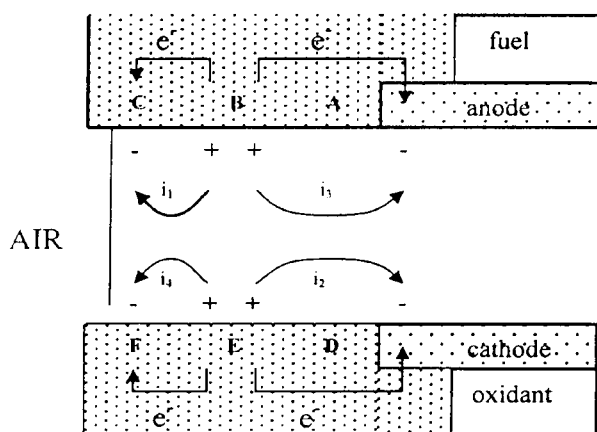


Fig. 7 – Corrosion cells in the wet-seals at OCP:  $i_1$  is the major corrosion cell. From Ref. [8].

### Corrosion modes of MCFC metallic materials

Under the various MCFC gas conditions, corrosion of the hardware metal components which are not in direct contact with the molten carbonate takes place via usual high-temperature oxidation and carburization forms of attack. If the MCFC stack is combined with a coal gasifier, other forms of corrosion may derive by the presence of contaminants in the feed gases, mainly constituted by sulfur and, to a lesser extent, volatilized chlorides [5]. For example, sulfur has been reported to cause cell swelling by sulfur attack of stainless steels [26], but the current use of efficient gas clean-up processes make these problems of minor importance and therefore they will not further mentioned here.

As already seen, the situation of the bipolar plate is markedly different. This component is exposed to the most severe MCFC conditions since it is directly in contact with molten carbonate films in both oxidizing and reducing gas environments and its corrosion products must retain adequate electronic conductivity (except than in the wet-seal areas). The consideration of hot corrosion as an electrochemical phenomenon focuses on the anodic metal dissolution aspect, though this is only one step of a series of other preceding and following mass transport steps (diffusion transport, adsorption of both oxidant and reaction products and so forth).



Thus it should be not surprising that the hot corrosion kinetics is usually not under control of charge transfer processes but rather of oxidant gas diffusion rates, which, in turn, depend on the electrolyte thickness layer. It can be advantageous to distinguish two main cases for the bipolar plate: on the one hand, metal areas covered by deep layers of electrolyte (regions E, F, G and H of the Fig.3) where a protective oxide layer may not form easily but, at the same time, the corrosion rate may remain rather low because of depletion of the oxidant gases in the melt due to the relatively long distance to the gas phase, and on the other hand, areas covered by thin molten carbonate layers (regions A, B, C and D of the Fig. 3) where the high concentration of  $O_2$  (and  $CO_2$ ) dissolved in the melt may promote an initial rapid formation of a protective oxide layer although if the oxide solubility depends on the gas composition, scale fluxing is possible resulting in a accelerated corrosion instead of passivation. In definitive, the following several corrosion processes must be taken in consideration under the various working MCFC conditions: i) oxidation; ii) carburisation; iii) hot corrosion; iv) scale fluxing. As the stainless steels AISI 310S and 316L are currently the most frequently employed materials for the fabrication of MCFC hardware components, the discussion on the various forms of corrosion will concentrate on the austenitic stainless steels.

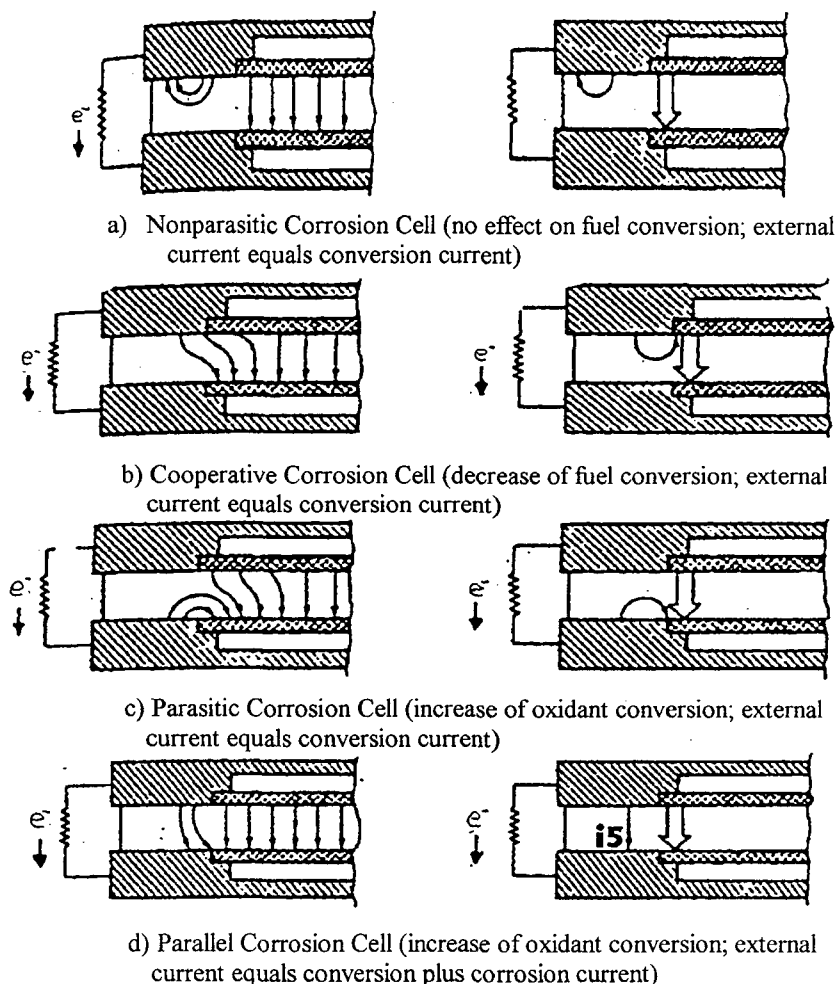


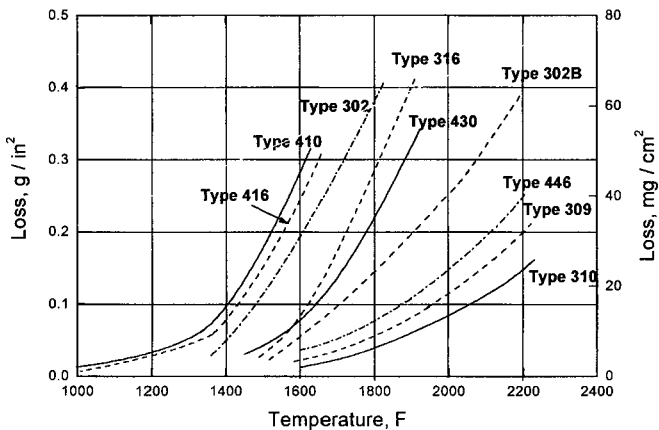
Fig. 8 – Corrosion cells in wet-seals under load:  $i_5$  is the major corrosion cell (crosstle corrosion).  
From Ref. [8].

### Oxidation/carburization

The presence of oxidizing gases ( $O_2$ ,  $CO_2$ ,  $H_2O$ ) in both the cathodic and anodic atmospheres makes the evaluation of oxidation resistance obviously of great importance. At the MCFC working temperatures all the stainless steels are known to be highly oxidation resistant due to the formation of a protective chromic oxide,  $Cr_2O_3$ , layer. However, a minimum of 18 wt% Cr is needed to develop a continuous  $Cr_2O_3$  scale against further oxidation attack. The oxidation resistance in air of several stainless steels as a function of temperature is illustrated in Fig. 9 [27]. It is interesting to note that some ferritic stainless steels such as the AISI 446 and 430 show comparable or even better oxidation performance than the 300 series austenitic stainless steels. However, ferritic steels are more prone to drastically lose their rupture and creep strengths when the service temperature is above 600-650°C (see Figs. 10 and 11) [28]. It has been variously reported that the oxidation rate of stainless steels is significantly increased when water vapour and  $CO_2$  are present in the oxidizing gas. The reasons for it are still not clear, although, for instance, McCarron and Schultz have attributed the detrimental effect of water vapour on the air corrosion behavior of AISI 310 at 1100°C to a decreasing plasticity of the protective scale as consequence of accumulation of hydrogen at the scale/metal interface [29]. Several studies have shown that, although oxidation of stainless steels in  $CO_2$ -containing gas can be defined as protective, a two-layer scale structure is being formed due to adsorption of  $CO_2$  to the scale surface that enhances the iron defect concentration transport through the scale and thereby the oxidation rate [30-a]. Thus, Fujii and Meussner have found that Fe-Cr alloys (1-15 wt% Cr) in 1 atm pure  $CO_2$  at 700-900°C, invariably formed a duplex scale consisting of an outer layer of iron oxides and an inner, porous layer of Fe-Cr spinels [31]. Several authors have also attributed the accelerated oxidation rate to a microporosity developed in the scale as consequence of inward penetration of  $CO_2$  molecules leading to internal carbide formation [30-b]. Thus, Giggins and Pettit have observed that a Fe-35%Cr alloy exposed to  $CO_2$  at 900°C exhibited a protective behavior, although small amounts of carbides were formed beneath the oxide scale justifying their conclusion that  $Cr_2O_3$  scales are pervious to  $CO_2$  transport [32]. Interest in the oxidation behavior of stainless steels in high pressure  $CO_2$  could come by the development of pressurized MCFC stacks. Extensive research has been conducted on this topic due to the use of  $CO_2$  gas cooled nuclear reactors. Unlike mild and 9%Cr steels which show catastrophic oxidation behavior after an initial protective stage at relatively low temperatures (380-500°C), stainless steels form stable protective scales up to nearly 700°C [30-c]. The oxidation of several austenitic stainless steels were compared at  $CO_2$  pressures ranging from 14 to 28 atm. The Fe-20%Cr-25%Ni alloy was found more oxidation resistant than the Fe-18%Cr-8%Ni materials in the range 500-700°C.

In the anode compartment corrosion of metallic materials takes place in a complex gas mixture at very low oxygen partial pressure (ca.  $p_{O_2} \approx 10^{-23}$ - $10^{-24}$  atm) and high carbon activity ( $a_c \approx 0.1$ ). Under such mixed oxidizing/carburizing conditions, nickel and iron-based alloys with high chromium contents are widely employed since they form a stable and compact  $Cr_2O_3$  scale which may protect from further attack and act as a barrier against carbon diffusion and internal carburization. Singh reported the results of a study concerning the oxidation behavior of several stainless steels in  $H_2$ ,  $H_2O$ ,  $CO$ ,  $CO_2$  gas showing that both series 300 austenitic and ferritic series 400 exhibited fairly oxidation resistance even though rather severe internal carburization had occurred [4]. Nickel-based alloys are considered more carburization resistant than stainless steels, thus high nickel steels have been studied in some detail. Holm and Evans examined the behavior of a high Ni steel (20Cr-25Ni) exposed at 650°C to  $CO_2/CO$  environments having oxygen potentials and carbon activities similar to those encountered in the MCFC anode gas [33]. The oxidation exhibited a *quasi* parabolic kinetics over a prolonged exposure period of 2000 h with the development of an uniform and compact oxide scale. Only slight intergranular carbide formation was observed. As nickel is thermodynamically stable in the anode gas conditions, Ni clad stainless

steels have been found the best choice for the anode bipolar plate [34], although the formation of carbide particles along the steel/nickel interface has been described [4].



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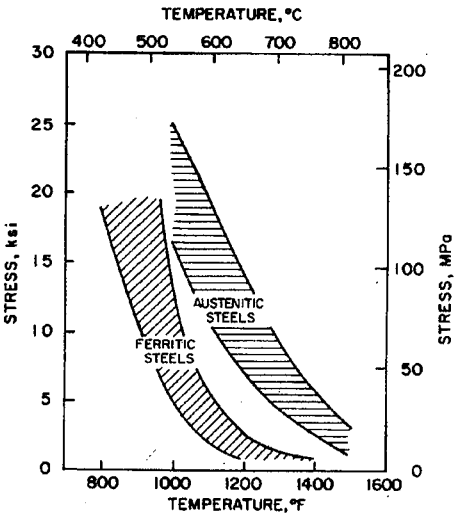
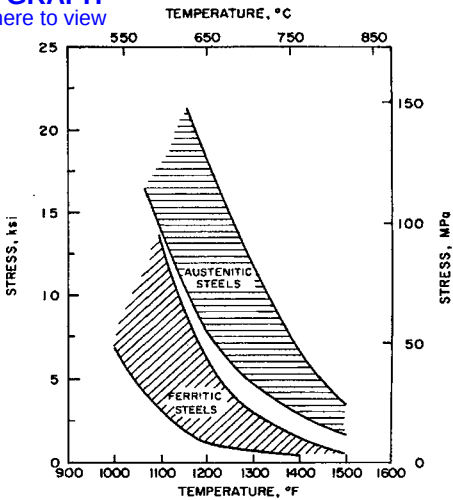
Fig. 9 (above): Oxidation resistance of several stainless steels as a function of temperature. From Ref. [27].

Fig. 10 (below, to the left): Ranges of rupture strength for typical ferritic and austenitic stainless steels. From Ref. [28].

Fig. 11 (below, to the right): ranges of creep strength for typical ferritic and austenitic stainless steels. From Ref. [28].

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### Hot corrosion

It has been already pointed out that molten carbonate corrosion is strongly affected by the chemistry of the environment. Selman reviewed the main factors involved in MCFC corrosion phenomena like cell temperature, gas composition, salt composition and thickness, mass transport conditions and electrochemical potential [35].

An important aspect of the study of molten carbonate corrosion is related to the development of rapid corrosion tests to select the most promising candidate materials and obtain design data. A corrosion test should simulate as much as possible all the above mentioned factors of the cell environment. As a corrosion test capable to simulate simultaneously all these factors is anything else but an expensive operational cell (by definition *in-cell* test), several simpler arrangements (the so-called *out-of-cell* tests) are frequently used. Since standardized methods are not yet established most researchers have been using both short-term and long-term tests. Coupon tests are long-term tests which have been confirmed as an effective tool even if they ignore the effect of electrode potentials. A first kind of coupon test is the fully immersion test in which the corroding sample is deeply covered with a thick electrolyte layer resembling the wet-seal area conditions. A second kind is the partially immersed test in which the corroding sample is immersed in the carbonate film only to some extent. This test is usually carried out to examine the effect of the existence of a meniscus on the corrosion behavior [36]. Similarly, in the salt coating test a thin deposit of film is held on the corroding sample surface with the advantage of simulating better the gas mass transfer conditions. The latter two resemble the situation of the areas of the current collector which are only partially covered by the carbonate film. Short-term polarization tests are sometimes used for preliminary screening purposes. The real significance of electrochemical studies applied to molten carbonate corrosion is still controversial because polarization may induce large shifts of the local melt basicity and of oxidizing potentials resulting in "instantaneous" high corrosion rates [37]. On the other hand, alloys might corrode uncharacteristically slowly if the polarization test is conducted during the initial protective (incubation) stage.

Useful correlations of polarization data with long-term hot corrosion behavior has been sometimes reported ( see, for instance, [38,47]). In Ref. [47] the ranking of corrosion resistance determined with chronoamperometry and salt coating tests roughly agree for several alloys under anode MCFC conditions. Similarly, Shores and Pischke have studied the AISI 310S stainless steel by comparing the results of different tests (*in-cell*, salt coating and electrochemical tests) [39]. As expected, the three tests predict rather different corrosion rates, being the higher corrosion rate measured by the polarization test. Singh evaluated the long-term corrosion resistance of several stainless steels to both anode and cathode gas atmospheres by salt coating test [4]. The steels subject to anode gas experiments were divided into two groups: (a) thick scale formers (AISI 304, 316, 330, 347): the scale was composed of a thick outer layer of iron oxide followed by an inner porous chromium oxide. (b) thin scale formers (AISI 310, 446, Crutemp-25, chromium plated 304 and 310): the scale was composed of a thin outer layer of iron oxide followed by an inner compact chromium oxide layer. In both the groups internal carburization and intergranular attack were observed. Interestingly, some recent investigations seem to suggest that AISI 304L and 316L possess a higher molten carbonate intergranular corrosion resistance than AISI 310S [40]. High-Cr ferritic steels are generally found not sufficiently resistant in both anode and cathode environments [7]. Recent systematic investigations on AISI 310S and 316L corrosion by salt coating tests has lead to the conclusion that AISI 310S is better than AISI 316L in the cathode gas, in spite of the formation of a thicker scale on AISI 316L [2]. The latter scale, though well-conducting, is too porous to be fully protective. Salt coating tests were also used to evaluate the effect of CO<sub>2</sub> partial pressure on the molten carbonate corrosion resistance of AISI 316L [41]. The author found that in pure 1 atm CO<sub>2</sub> gas the corrosion proceeded at a nearly linear rate indicating a non protective behavior in strong acidic (Li,K) melts.

A few investigations have also dealt with the effects of the electrolyte composition on the corrosion of stainless steels. Electrolyte composition is expected in fact to affect the corrosivity of the melt by changing some important melt properties such as basicity, activity of oxidizing species, solubility of the gases, ionic conductivity and so forth. Several fuel cell developers are presently evaluating the viability of changing the electrolyte composition as a possible countermeasure to reduce the dissolution of NiO cathodes. Addition of Ca, Ba and Sr to the (Li,K) electrolyte has been studied by Yanagida et al. [22]. Evaluating the corrosion of AISI 316L by salt coating test the authors have concluded that the corrosion rate is only slightly improved by addition of alkaline earth elements. The effect of (Li,Na) carbonate mixtures has been evaluated in some more detail since the (Li,Na) carbonate is expected to be the preferential candidate for pressurized operations [54]. Degradation of cathode current collectors has been examined by Fujita et al. [55] by *in-situ* tests with the result that the thickness of an AISI 316L corrosion scale was slightly thicker but still comparable to that of the (Li,K) carbonate. Other studies have confirmed that corrosion behavior of stainless steels is nearly the same in (Li,Na) and in (Li,K) melt [48].

Apart the classical early investigations on the corrosion of noble materials such as Au, Ag, Pt, Au-Pd by Janz et al. [42,43], some fuel cell developers have given also attention on copper which, similarly to nickel, is thermodynamically stable in the anode gas conditions [4]. Copper is more cost-effective than nickel but it is not compatible with the state-of-the-art Ni – based anode. *In-cell* tests have in fact demonstrated that copper diffuses into the anode resulting in anode performance decay.

When the cathode and anode sides of the bipolar plate come in contact with the molten electrolyte during MCFC operation, they get polarized from their open circuit potentials (OCP) respectively to the cathode potential (ca.  $-0.1\text{V}$ ) and to the anode potential (ca.  $-0.95\text{V}$ ). Therefore several studies have dealt with the effect of the electrochemical potential on the corrosion behavior of the bipolar plate materials. In general, these studies have been conducted using chronoamperometric [47-49], slow potentiodynamic [15,38,44,48-51] and voltammetric methods [47,48, 50] with flag-type electrodes fully immersed in the electrolyte. For example, Nishina et al. have reported the corrosion currents at OCP for a wide range of metals and alloys under  $\text{CO}_2$ -air gas [44] (Fig. 12). With a threshold value of  $100\text{ uA/cm}^2$  for a 40,000 h endurance, it is observed, for instance, that, among the engineering alloys, Inconel 600 and Hastelloy C-276 corrode much less than both AISI 310 and 304 with the latter steel showing also a strong dependence on the  $\text{CO}_2$  partial pressure. Difference in corrosion rates between OCP and under load conditions are generally marginal since the steels are able to passivate in the molten carbonates [38, 45]. However, in anode gas, corrosion rates of stainless steels at OCP are lower than under load, whereas the opposite is true in cathode gas with corrosion at OCP slightly higher. The anodic polarization curves of austenitic stainless steels in the cathode gas show a passive zone in the range ca.  $-0.5\text{V}$  to  $0.1\text{V}$  above which an abrupt increase of current occurs. Analogous measurements conducted in the reducing anode gas showed an active/passive behavior of the steels but with much higher active and passive currents [38]. The impedance technique has been sometimes used for determination of corrosion rates. Perez et al., for example, determined by impedance a high corrosion rate due to non protective scale formation during the first hours of immersion of AISI 310S steel in the Li/K carbonate [46].

### Scale fluxing

The non protective oxidation behavior of nickel in the molten carbonates under  $\text{O}_2$ - $\text{CO}_2$  atmospheres has been the object of several studies. Lee and Shores attempted to apply the Rapp-Goto theory to the hot corrosion of nickel [19]. On the basis of the reaction steps hypothesized, they were able to demonstrate that flux of dissolved NiO was driven even by a moderate oxide solubility gradient. However, more important is the iron oxide fluxing observed on unprotected stainless steels in the reducing anode atmosphere (see Section V). The combined effects of oxide fluxing

and carburization are usually claimed as the main causes for the high corrosion rates measured on the anode side [7, 52].

Different is the situation under the high oxidizing conditions of the cathode, where scale fluxing of stainless steels is not experimentally observed, though theoretically possible ( see Section V). However, continuous dissolution of Cr oxides into soluble  $\text{CrO}_4^-$  is proposed to explain the still non very low corrosion currents of stainless steels ( ca. 01 mA/cm<sup>2</sup> see [38]) even in the passive state. This leads to the formation of a scale whose the outer layer is mainly composed of the insoluble  $\text{LiFeO}_2$ , whereas the inner compact layer is rich of the protective  $\text{Cr}_2\text{O}_3$  oxide [4]. The instability of Cr in the oxygen-rich gases was also demonstrated in several papers. For instance, Ota et al. have clearly proved the importance of the carbonate coating amount on the Cr corrosion. Thus, Cr behavior is protective in fully immersed tests, whereas accelerated corrosion takes place due to formation of liquid soluble chromate in salt coating tests [53].

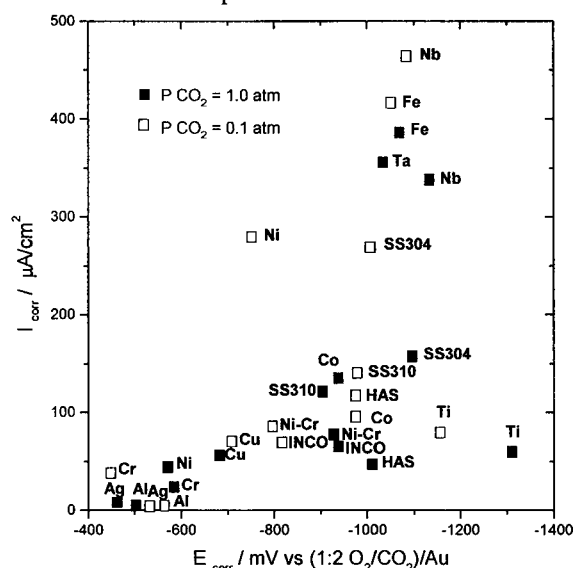


Fig. 12 - Corrosion currents of various metals and alloys in (Li,K) melt at OCP conditions and 650°C.  
HAS= Hastelloy C-276  
INCO= Inconel 600.  
From Ref.[44].

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### Possible directions for corrosion materials control at future MCFC plants

Hot corrosion attack and galvanic corrosion are the major corrosion problems historically afflicting the bipolar plate materials. Although these problems have been solved, at least partially, by appropriate selection of materials and protection techniques, the result is that the capital cost of the current solutions are too high. To reduce the materials costs it is required to improve cell performance (lower cell decay rates) and possibly operate at higher current densities (200-300 mA/cm<sup>2</sup> against the current 150 mA/cm<sup>2</sup>).

Cost of the bipolar plate materials constitutes a relevant part of the total stack cost so that economical Fe-based alloys are desirable. However, Fe-based alloys cheaper than the AISI 316L or 310S stainless steels could be used only if sufficiently cost effective protection techniques can be individuated. Alternatively, the development of highly corrosion-resistant alloys specifically designed for MCFC may result in the final application of uncoated but more expensive materials (for instance, Inconel alloys). In these last years we have assisted to a renewed interest in corrosion studies of metals and model alloys to better understand the effects of alloying elements added to the Fe-based alloys as this appears essential to individuate innovative metallic materials and protective surface treatments [24].

In this context, the work of Nishima et al. [56] is worth mentioning. They have carried out a systematic investigation on binary Fe and Ni-based alloys to evaluate the effect of Al and Ti additions on both electrochemical corrosion behavior and scale conductivity of these alloys. It was

found that the addition of 4 wt% Al to a Fe-21Cr alloy decreases drastically the corrosion current, whereas analogous addition of Al or Ti to a Fe-20Ni alloy does not show any effect. The addition of a 4 wt% Ti to the ternary Fe-21Cr-4Al increases the electrical conductivity of the corrosion protective layer without minimize the corrosion resistance. By a similar approach, a 30Cr-45Ni-1Al-0.03Y-Fe alloy has been developed by Ohe and its group [57]. The alloy shows a much better corrosion resistance than AISI 310S in 300 hrs salt coating test under both anode and cathode gas conditions suggesting that this alloy could be applied without nickel cladding and aluminium-diffusion coatings. The alloys proposed by these two works could represent interesting alternative to the use of stainless steels, provided that their cost-effectiveness would be demonstrated.

A different strategy for material cost savings is finalized to investigate innovative coatings for the wet-seals. In particular, aluminization methods, which does not require the expensive post-deposition diffusion heat treatment would be highly desirable. Recently, some investigators have used thermal spraying of Al-containing powders (FeCrAlY, NiAl, Ni<sub>3</sub>Al, FeAl) with poor results though, due to the porous structure of the coatings produced which are not corrosion protective enough [7]. As the corrosion resistance of the Al-diffusion coating relies on the *in-situ* formation of an intermetallic iron-aluminum structure, the behavior of a bulk intermetallic alloy FeAl has been extensively studied by Frangini et al [41, 58]. It has been found that the corrosion resistance of FeAl aluminide is comparable to that of IVD aluminized 310S steel in both cathode and fuel gas. The use of this alloy for protecting the wet-seal merits further research to individuate a suitable coating technique to deposit FeAl layers with the desired structure and corrosion properties. Other researcher have focused their attention on suitable ceramic coating materials to protect Fe-based alloys under anode gas showing that TiN, TiC and Ce-based ceramics are promising anode-side coatings [11].

### Concluding remarks

Molten carbonate corrosion has always been a major problem in the hystorical development of the MCFC technology. Although the research on MCFC has begun from the late 1950's, some challenging questions associated with the corrosion of metallic materials are still not completely solved and some of these have been pointed out in this chapter.

It is clearly apparent from this overview that the fundamental mechanisms of hot corrosion and scale fluxing of stainless steels, expecially in the anode reducing gas remains to be better defined. The influence of the different corrosion tests on the final results has been mentioned; yet much work remains to find suitable standardized methods for the purpose of materials screening and long-term performance predictions. In addition, the corrosion effects on the various cell performance decay modes merit further attention expecially in long-term stack operation (>20,000 hrs).

However, most of all, it is vital to find advanced solutions for cost reduction of metallic materials and coating technologies than could, in turn, further increase the stack performance and extend the useful life-time. Although MCFC is approaching to a mature technology the search of innovative materials for the second-generation of MCFC plants offers still great opportunities for studies to both scientists and developers.

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# Corrosion Protection in Molten-Carbonate Fuel Cells

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**Keywords:** Ceramics, Coatings, MCFC, Measurement Methods, Titanium Nitride

## Abstract

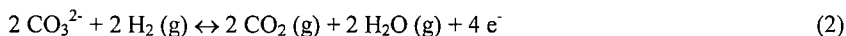
Stainless steel separator plates in molten-carbonate fuel cells need to be protected against corrosion, preferably by a coating of a non-oxide metal/non-metal ceramic material like TiN or TiC as revealed the coating material selection. The corrosion behaviour of several coated samples was studied electrochemically in molten carbonate under MCFC cathode and anode gas, at open-circuit and load conditions. The use of several electrochemical methods to estimate corrosion rates at the four different conditions is discussed. Under cathode gas, the most important corrosion protection is given by keeping the fuel cell constantly at load. Under anode gas, a thick Ni or Au coating on top of a ceramic (TiN) coating might provide the necessary corrosion protection at load conditions.

## 1. Molten-carbonate fuel cells

With fuel cells electrical energy can be obtained electrochemically from the chemical energy of a fuel and an oxidant gas without combustion as an intermediate step. Similar to batteries, fuel cells produce a *dc* current by means of an electrochemical process. Different from batteries, a fuel cell is continuously fed with gaseous reactants while batteries are supplied with solid or liquid reactants in advance. The type of fuel cell is determined by the nature of the electrolyte. The electrolyte in a molten-carbonate fuel cell (MCFC) is a eutectic melt of lithium carbonate with either potassium carbonate or sodium carbonate. Because of its high operating temperature at about 650°C, large size and weight, the most important application of this type of fuel cell is in moderate small-scale electricity production systems such as in power plants. At present the electrical efficiency of a fuel cell approaches 60% against about 40% for conventional power plants. Air is used as oxidant, and H<sub>2</sub> is used as fuel, but also other fuels like methane, methanol, or CO are suitable. At the cathode oxygen is reduced and reacts with carbon dioxide to carbonate ions:



The carbonate ions diffuse to the anode side where they oxidise hydrogen to water:

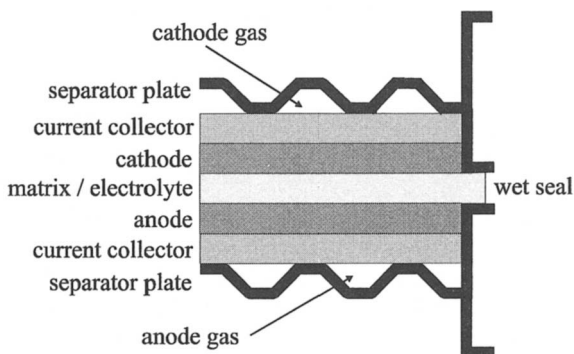


Carbon dioxide is separated from the exhaust gas and fed back to the cathode side giving the overall cell reaction:



The anode reaction produces electrons while at the cathode electrons are consumed. So at open circuit there is a potential difference across the cell. With the MCFC under operation, the electrons are transported through an external load from the anode towards the cathode providing a current. The current flow inside the cell is established through transport of carbonate ions. When current is drawn, the initial cell potential decreases due to polarisation losses inside the cell, such as diffusion

and ohmic losses, and reaction polarisations. Equilibrium potentials can be calculated versus a reference electrode (33% O<sub>2</sub>, 67% CO<sub>2</sub>, 1 atm.). At open circuit conditions, the Nernst equation gives an equilibrium potential of -50 mV for reaction 1 at the cathode (14.3% O<sub>2</sub>, 29.2% CO<sub>2</sub>, 2.8% H<sub>2</sub>O, 53.7% N<sub>2</sub>) and an equilibrium potential of -1121 mV for reaction 2 at the anode (60.9% H<sub>2</sub>, 8.4% CO<sub>2</sub>, 21.6% H<sub>2</sub>O, 9.1% CO) [1]. At load conditions and a current density of 150 mA/cm<sup>2</sup>, the cathode potential is about -100 mV and the anode potential about -950 mV. Hence, the cell voltage of an MCFC under operation is about 850 mV. In order to produce a high power density, the active area of the electrodes needs to be large for a large current, while the individual cells need to be stacked in series for a useful voltage. Figure 1 gives a schematic representation of an MCFC.



**Figure 1** Schematic representation of a single MCFC.

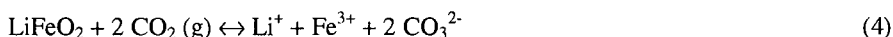
The cells are connected in series by a so-called bipolar plate or separator plate. The separator plates separate individual cells in a fuel cell stack. They are corrugated to create flow channels for the gases on either side. The separator plates have three functions:

- (1) separate the anode from the cathode gas,
- (2) provide electrical contact between cells in combination with the current collectors, and
- (3) provide a 'wet seal'. At the edges of the cell the separator plates are in direct contact with molten carbonate to form a leak-free gas seal called the wet seal [1].

The current collectors connect the separator plates to the electrodes. The current collectors are perforated to let the gases pass to the electrodes. The electrodes are separated by a micro-porous LiAlO<sub>2</sub> matrix, which serves as an electrolyte reservoir and as a barrier for the reactant gases. The state-of-the-art materials in the MCFC are lithiated nickel oxide for the cathode and nickel with 2-10% Cr or Al for the anode. The porous electrodes are partially filled with electrolyte to form a good three-phase contact for the electrode reactions.

## 2 Corrosion of the separator plates

One of the main reasons why the MCFC is not commercially available yet is its limited lifetime. One of the lifetime-limiting factors of the MCFC is corrosion of the stainless-steel separator plates and current collectors. Corrosion of these steel parts limits the MCFC lifetime and its operating efficiency. Lifetime-limiting corrosion processes in molten salts are oxidation to porous structures and dissolution of oxide scales into the melt. Shores and Qu [2] distinguished for metal oxides in molten carbonate acidic and basic dissolution depending on the partial CO<sub>2</sub> pressure. LiFeO<sub>2</sub> e.g., presents acidic dissolution at high partial CO<sub>2</sub> pressures ( $\geq 0.5$  atm CO<sub>2</sub>):



or presents basic dissolution at low partial CO<sub>2</sub> pressures ( $\leq 7.1 \cdot 10^{-3}$  atm CO<sub>2</sub>):



The lowest solubility occurs in the transient range and was determined to be less than 1 mol ppm. Dissolution can eventually lead to holes in the separator plates. Less disastrous but limiting the cell efficiency are the increasing electronic resistance due to growing oxide scales, the decreasing electrolyte conductivity, and short-circuiting due to dissolution of metal oxides (cathode) and subsequent precipitation elsewhere. The corrosion products in molten carbonates are oxides and mixed oxides. As a rule the mixed oxides are thermodynamically more stable than the oxides at 650°C in molten carbonates. Besides the metal, they contain one or more of the alkali metals Li, K, or Na from the melt. These (mixed) oxides usually have a low electronic conductivity compared with the metals. Therefore, dense scales of corrosion products on the separator plates in the working area form a barrier to the electric current, and thereby reduce the fuel-cell operating efficiency.

The lifetime of the MCFC should be increased from the present average 20,000 to at least 40,000 hours (four years). For improved lifetime of the separator plates and current collectors, proven inert materials such as Au and  $\gamma\text{-LiAlO}_2$  would be obvious choices. Gold, however, aside from its high cost, has not enough mechanical strength, whereas  $\gamma\text{-LiAlO}_2$  is an electronic insulator. Nowadays, stainless steel or nickel-based alloys are used, mainly because they offer excellent bulk properties at a reasonable price. However, these steels and alloys corrode too rapidly. Research is aimed at increasing the corrosion resistance of these steels and alloys by choosing the right composition [3-11] or by applying a corrosion-protective coating [12-13]. Alloying [10, 11, 14-16] or coating with aluminium or alumina [17] is often reported to improve the corrosion resistance. In the wet-seal area, where the protective layer should preferably be non-conducting, satisfactory corrosion protection is given by an about 35  $\mu\text{m}$  thick  $\text{LiAlO}_2$ -layer, formed by oxidation of aluminium with lithium carbonate [18].

In the cathodic and anodic area the protective layer should be electronically conducting. Here, the high electrical resistance of an  $\text{Al}_2\text{O}_3$  or  $\text{LiAlO}_2$  scale is not acceptable [8]. On the cathode side, recent choices for the separator plates are the Fe-Ni-Cr austenitic stainless steels 310S, 316, or 316L [11, 19]. These steels contain a sufficient amount of chromium to form a protective oxide layer, which prevents the whole alloy from being oxidised [20]. Disadvantages of these (and other) steels are the induced loss of electrolyte and an increasing ohmic loss due to the formation of corrosion products on the steel. Today's state-of-the-art of preventing corrosion of steel parts on the anode side is electroplating (anode current collector) or cladding (separator plate) with a relatively thick (about 50  $\mu\text{m}$ ) layer of nickel [19]. Nickel cladding is given as solution for the anode separator plate, whereas the parts electroplated with nickel show some corrosion problems. The electroplated nickel layer is not a sufficient diffusion barrier for inward diffusion of oxygen from the surface to the nickel-steel interface. Neither does it sufficiently prevent outward diffusion of steel components (Fe and Cr) [21].

The main goal of this study was to develop a coating in order to protect steel separator plates and current collectors against corrosion in MCFCs. An advantage of using a corrosion protective coating instead of changing the steel composition is that it may permit the use of cheaper steels such as 304 than the currently used stainless steels. The corrosion rate of stainless steel in molten carbonate under anode gas is about two orders of magnitude higher than under cathode gas [1, 22, 23], hence protective layers for the anode side of the fuel cell are of primary interest.

### 3 Selection of coating materials

The selection of suitable corrosion-protective coating materials was earlier described more extensively [12, 22], and was based on satisfying four requirements simultaneously:

- (1) A high corrosion resistance. This is the most critical requirement. The coating should not dissolve or oxidise fast in molten carbonate. It should also have a low ionic conductivity or in general function as diffusion barrier especially for oxygen and metal ions.
- (2) A high electronic conductivity. The coating material should preferably be a metallic conductor ( $\sigma > 10^4$  S/cm). Moreover, the electronic conductivity of its solid corrosion products should be sufficiently high.
- (3) A high high-temperature resistance. The melting point of the coating material and its possible corrosion products should preferably be far above the MCFC operating temperature.
- (4) Low cost. Expensive materials are not likely to be used in commercial MCFC technology.

Coating materials can be divided roughly into three groups:

- (1) Metals and alloys which have a high electronic conductivity, but usually a low corrosion resistance in molten carbonates. The presently used Ni-coating at the anode side increases the corrosion resistance to a large extent, but still the goal of 40,000 hours lifetime cannot be reached.
- (2) Non-metals and ceramics composed of non-metals are known for their good corrosion properties. However, they have a covalent character and are therefore poor electronic conductors. SiC for instance is known to be corrosion resistant even at high temperatures, but only heavily doped it shows some conductivity [24].
- (3) Ceramics composed of a metal and a non-metal combine a high oxidation resistance with a high electronic conductivity as in WC, MoSi<sub>2</sub>, and TiN [24]. This is the group of materials in which a satisfactory corrosion-protective coating material might be found.

First the non-metal component was selected. Within the group of metal/non-metal ceramics, ionic compounds or salts are not suitable for two reasons. They rapidly dissolve in molten carbonate and are electronic insulators. Thus the halides are not preferred even as the poisonous element arsenic.

Some oxide materials are more or less stable in molten carbonate and are used as cathode material e.g. Li doped NiO, LiFeO<sub>2</sub>, and LiCoO<sub>2</sub>. This suggests that oxide materials may be suitable coating materials. However, non-oxide ceramic coatings are preferred, because oxide materials have a comparatively low ionic and high electronic conductivity:

- (1) Mixed oxides and metal oxides generally conduct oxygen ions especially at higher temperatures. This is deleterious for corrosion-protective coatings. Zirconia (ZrO<sub>2</sub>) is a good oxygen-ion conductor [25]. This makes yttrium-stabilised zirconia an excellent electrolyte material in the solid oxide fuel cell, but unfit for corrosion protection in the MCFC. In principle, dense non-oxide ceramic layers provide a better barrier to oxygen ion conduction than oxides.
- (2) The electronic conductivity of metal oxides (or metal chalcogenides in general) is orders of magnitude lower than that of ceramics using B, C, or N as non-metal component. For example, a potential drop of 10 mV at 650°C and a current density of 150 mA/cm<sup>2</sup> (MCFC-load conditions) is obtained using 5 nm TiO<sub>2</sub>, 27 nm Li<sub>2</sub>TiO<sub>3</sub>, or 8 m TiN [12, 22]. Therefore, any TiN-layer of sufficient thickness will show a negligible ohmic loss. Doping might in principle increase the electronic conductivity of the insulating ZrO<sub>2</sub> [25]. However, doped ZrO<sub>2</sub> is thought to be less suitable, because its electronic conductivity depends heavily on the oxygen partial pressure. Also the stability of dopants in molten carbonate is debatable.

Selected non-metal components are B, C, N, Si, and P. The selected non-oxide, non-ionic, and non-covalent ceramics consisting of a metal and a non-metal are refractory materials. They have a high corrosion resistance, a high electronic conductivity, and a high melting point.

Then the metallic component was selected. Alkalines or alkaline-earth metals are, like halides, not preferred because they form ionic components, which rapidly dissolve in molten carbonate, and

which are electronic insulators. Also the expensive lanthanides and actinides are discarded as suitable metal components.

A further selection among the metal group should be made to decrease the number of test materials. However not much is known about the most important requirement, the corrosion resistance, i.e. dissolution and oxidation rate of these ceramics in molten carbonates. It is unlikely that a material exists which stays unaffected in molten carbonate during the desired lifetime, because molten carbonate is a very strong oxidising agent and the exposure time in MCFCs is very long. Passivating materials generally have a higher corrosion resistance, and are therefore of primary interest with the restriction that the passive layer is not electronically insulating.

An initial selection of possibly passivating materials can be made from the requirement that none of the possible corrosion products has a melting point below the maximum MCFC operating temperature. Therefore, first metals were selected of which all possible oxides have melting points above 700°C (see Table 1). In the second selection presented in Table 1, metals were selected of which all possible mixed oxides have (eutectic) melting points above 700°C. All possible mixed oxides with Li, Na, and/or K are considered as possible corrosion products in binary and ternary mixtures of  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{K}_2\text{CO}_3$ . In general, mixing more different alkaline and transition metals increases the number and depth of the eutectics. Many mixed oxides are mentioned [26], but usually without (eutectic) melting point. So possibly metals, which form unstable mixed oxides, have not been discarded here, because of lack of data. In the third selection presented in Table 1, expensive elements were discarded, and the fourth selection is based on oxidation resistance. The metals in the groups 3, 4, and 5 with partially filled d-orbitals generally form stronger bonds with non-metals than metals in the groups 8 to 16. Hence, metals at the left hand side of the periodic Table will probably give ceramics with a higher oxidation resistance than metals at the right hand side, and are therefore preferred.

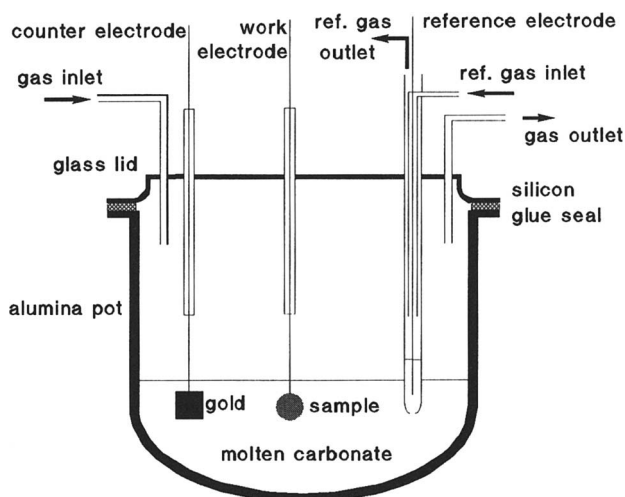
**Table 1** *Metallic component selection with: <sup>1</sup>Elements of which one of the oxides has a melting point below 700°C, <sup>2</sup>Elements of which one of the mixed oxides has a (eutectic) melting point below 700°C, <sup>3</sup>Expensive elements, and <sup>4</sup>Elements with a relative low oxidation resistance.*

|                 |    |    |                 |                |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |
|-----------------|----|----|-----------------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 3               |    |    | 4               | 5              | 6               | 7               | 8               | 9               | 10              | 11              | 12              | 13              | 14              | 15              | 16              |
|                 |    |    |                 |                |                 |                 |                 |                 |                 |                 |                 | Al <sup>4</sup> |                 |                 |                 |
| Sc <sup>3</sup> |    |    | Ti              | V <sup>1</sup> | Cr <sup>2</sup> | Mn <sup>1</sup> | Fe <sup>4</sup> | Co <sup>4</sup> | Ni <sup>4</sup> | Cu <sup>4</sup> | Zn <sup>4</sup> | Ga <sup>1</sup> | Ge <sup>2</sup> |                 |                 |
| Y               |    |    | Zr <sup>2</sup> | Nb             | Mo <sup>2</sup> |                 | Ru <sup>1</sup> | Rh <sup>3</sup> | Pd <sup>3</sup> | Ag <sup>1</sup> | Cd <sup>4</sup> | In <sup>1</sup> | Sn <sup>4</sup> | Sb <sup>1</sup> |                 |
| La              | Ce | Nd | Hf              | Ta             | W <sup>2</sup>  | Re <sup>1</sup> | Os <sup>1</sup> | Ir <sup>3</sup> | Pt <sup>1</sup> | Au <sup>3</sup> | Hg <sup>1</sup> | Tl <sup>1</sup> | Pb <sup>2</sup> | Bi <sup>2</sup> | Po <sup>1</sup> |

Metals selected in Table 1 are Ti, Y, Nb, La, Ce, Nd, Hf, and Ta. These metals combined with the non-metals B, C, N, Si, or P form the first choice of corrosion-protective coating materials to be tested. If not possible to find a suitable coating material within this group, then the list of metals should be extended with metals discarded in the last step (step 4).

#### 4 Experimental coating material selection

The stability of several refractory materials was measured in the eutectic 62/38  $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$  mixture at 650°C in an alumina crucible, also called a pot cell or half cell as shown in Figure 2. Fuel gas, containing 80%  $\text{H}_2$  and 20%  $\text{CO}_2$ , was led over the carbonate in order to create an MCFC-anode gas atmosphere. The fuel gas was not humidified.



**Figure 2** Schematic cross-section of a pot cell.

Although non-oxide coating-materials are preferred, also oxide ceramics were tested in order to determine the stability of these oxides and their thermodynamically favourable mixed-oxides. Despite the fact that ceramics based on Zr were discarded,  $\text{ZrO}_2$  had been tested earlier and showed a fairly good stability. The sample preparation is described extensively in [12, 22]. Most samples were prepared by pressing ceramic powder into pellets (10 mm  $\varnothing$ ) and sintering. The other samples were prepared by nitriding porous titanium (TiN-1) [27], by dynamic compaction of TiN powder (TiN-2),  $\text{TiB}_2$  powder, or a 70/30-vol% mixture of TiN and  $\text{LiAlO}_2$  (TiN- $\text{LiAlO}_2$ ), or by infiltrating dynamically-compacted  $\text{TiB}_2$  with aluminium ( $\text{TiB}_2$ -Al) [28]. The samples were wrapped in a gold wire (0.5 mm  $\varnothing$ ) and immersed in the melt for 24 hours. To compare the stability of different samples, weight loss was used as first criterion for sample stability. Other criteria for stability were volume and colour changes as indicated in Table 2.

**Table 2** Stability experiments indicated with a large weight loss (--), some weight loss (-), a weight and volume increase (+), no apparent weight or volume changes (++), and a colour change (x)

|                         |      |                                  |      |                   |    |                   |    |                  |   |                  |      |
|-------------------------|------|----------------------------------|------|-------------------|----|-------------------|----|------------------|---|------------------|------|
| TiSi <sub>2</sub>       | --   |                                  |      | TaSi <sub>2</sub> | -- | NbSi <sub>2</sub> | -- |                  |   |                  |      |
| TiB <sub>2</sub>        | -    | TiB <sub>2</sub> -Al             | ++ x | TaB <sub>2</sub>  | -  | NbB <sub>2</sub>  | +  | HfB <sub>2</sub> | - |                  |      |
| TiC                     | +    | TiN-LiAlO <sub>2</sub>           | --   | TaC               | -  | NbC               | -- | HfC              | - | ZrC              | -    |
| TiN-1                   | ++ x | TiN-2                            | ++ x | TaN               | -  | NbN               | -- | HfN              | - | ZrN              | --   |
| TiO <sub>2</sub> rutile | + x  | Li <sub>2</sub> TiO <sub>3</sub> | + x  |                   |    |                   |    |                  |   | ZrO <sub>2</sub> | ++   |
|                         |      |                                  |      |                   |    |                   |    |                  |   | CeO <sub>2</sub> | ++ x |

Large parts of most samples were lost in the melt within 24 hours. Refractories have very high melting points and are, therefore, difficult to sinter. Possibly the samples fell apart, because they were not properly sintered (or densified). The samples were very brittle and possibly not resistant against the thermal shock during immersion. It is not clear from these stability experiments whether the ceramics had a low mechanic stability (poorly sintered or densified) or a low chemical stability (melting or dissolution of the ceramics and their corrosion products). However, positively marked samples are definitely interesting, because they showed a high chemical and mechanical stability.

The colour changes (gold TiN and white  $\text{TiO}_2$  to black, white  $\text{CeO}_2$  to greenish, brown  $\text{TiB}_2$ -Al to grey) and volume increases (black TiC and  $\text{NbB}_2$ ) probably indicate the conversion to the thermodynamically more stable mixed oxides (e.g.  $\text{Li}_2\text{TiO}_3$ ,  $\text{LiAlO}_2$ , and  $\text{LiNbO}_3$ ). The colour change of the  $\text{Li}_2\text{TiO}_3$  sample (white to black) and increase of weight and volume were attributed to



the partial reduction of tetravalent to trivalent titanium under influence of the reducing gas atmosphere as written in defect-chemical Kröger-Vink notation:



The blackening of the sample can be the result of free electrons or trapped electrons  $\text{Ti}_{\text{Ti}}^{\cdot}$  in the  $\text{Li}_2\text{TiO}_3$  structure. To retain electroneutrality, the uptake of electrons resulting from the hydrogen oxidation is accompanied with the interstitial insertion of lithium ions from the melt:



The uptake of lithium ions results in a weight increase, and gives together with the titanium reduction tensions in the structure leading to an increased volume and porosity. Carbonate attached to the sample surface contributes to some extent to the weight increase.

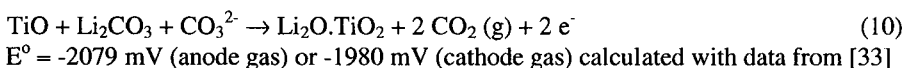
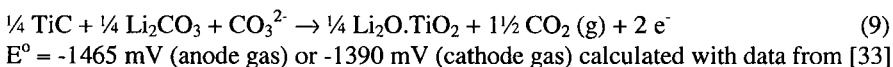
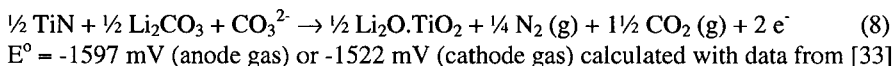
Only the white  $\text{ZrO}_2$  showed no colour, weight, or volume change.  $\text{ZrC}$  and  $\text{ZrN}$  are thermodynamically expected to convert to the electronically insulating  $\text{ZrO}_2$ . The conversion to the probably semi-conducting  $\text{Li}_2\text{ZrO}_3$  is expected only at temperatures above  $750^\circ\text{C}$ . The fact that Ti- and Nb-based ceramics form conducting mixed oxides as corrosion products, makes them more suitable coating materials than Zr-based ceramics.

The stabilisation of the  $\text{TiB}_2$  sample by aluminium infiltration is remarkable, although the Al may form a protective but insulating  $\text{LiAlO}_2$  surface layer. It might be impossible to apply this  $\text{TiB}_2$ -Al as coating on steel substrates. The use of a third element might increase the corrosion resistance of coating materials considerably.  $\text{TiAlN}$  prepared by chemical vapour deposition has been patented as a very promising corrosion-protective coating material in molten carbonate [29].

Most interesting ceramics were  $\text{TiN}$ ,  $\text{TiC}$ , and  $\text{NbB}_2$ . The latter two showed a volume increase, which might be less for test samples with a different morphology or stoichiometry. However, their relatively fast corrosion makes  $\text{TiC}$  and  $\text{NbB}_2$  second choice and  $\text{TiN}$  the first choice as material for corrosion protective coatings.

## 5 Coatings for corrosion protection

In principle, the  $\text{TiN}$ ,  $\text{TiC}$ , and  $\text{TiO}$  coatings are unstable. For Ti-based materials,  $\text{Li}_2\text{TiO}_3$  is the only thermodynamically stable phase in molten carbonates [12, 22, 30-32].



However, especially when the kinetics of the conversion to  $\text{Li}_2\text{TiO}_3$  are slow as presented above,  $\text{TiN}$  and  $\text{TiC}$  are much more favourable coating materials than  $\text{Li}_2\text{TiO}_3$  because of the conductivity demand [12, 22, 30]. Furthermore, after surface oxidation of the  $\text{TiN}$  or  $\text{TiC}$ , the formed  $\text{Li}_2\text{TiO}_3$  layer may behave as passive layer and protect the underlying  $\text{TiN}$  or  $\text{TiC}$  from further corrosion.

The corrosion-protective coating should be non-porous and free from cracks or pinholes, for these allow electrolyte to contact the substrate and cause accelerated substrate corrosion. Dense layers of  $\text{TiN}$  and  $\text{TiC}$  are preferably deposited with chemical vapour deposition (CVD). Several

TiN and TiC coatings differing in composition and morphology were deposited on substrates using thermal and plasma-enhanced CVD. Stainless steel 304 was chosen as substrate material, because it can withstand the high temperatures used during the thermal CVD process (over 900°C for TiN and TiC). Also a titanium monoxide coating was deposited with thermal CVD in order to study the conversion to  $\text{Li}_2\text{TiO}_3$ . Also a coating of chromium carbide was deposited, although chromium carbide had not been selected as promising coating material, because one of its mixed oxides is unstable at the MCFC operating-temperature. However, in air  $\text{Cr}_{23}\text{C}_6$  shows no weight increase due to corrosion up to 1100°C [24], and if the corrosion in molten carbonates is slow, chromium carbide might be a suitable corrosion protective coating as well.

Further, two double-layer combinations were prepared either sputtering nickel or electrodepositing gold on TiN-coated steel samples. The gold and nickel coatings are supposed to provide the corrosion protection. The intermediate TiN layer is supposed to protect the steel substrate against corrosion at cracks, or other defects in the gold or nickel layer, and is also supposed to function as diffusion barrier for small metal ions such as Fe and Cr from the steel substrate. Nickel is only stable under anode gas conditions, not under cathode gas conditions [22, 23]. The gold coating might provide the corrosion protection under cathode gas conditions, because gold is the only metal which is stable under cathode gas conditions. All coatings had a thickness between 1 and 3  $\mu\text{m}$ . The coating deposition and characteristics have been described extensively in [22, 30].

## 6 Corrosion measurement methods

The corrosion behaviour of the bare substrate material and coated steel samples was determined in the pot cell as presented in Figure 2 using MCFC-anode or cathode gas. The cathode gas consisted of 15%  $\text{O}_2$ , 30%  $\text{CO}_2$ , and 55%  $\text{N}_2$ . The anode gas consisted of 20%  $\text{CO}_2$  and 80%  $\text{H}_2$ . The cathode gas was humidified at room temperature and the anode gas was humidified at 60°C by feeding the gas through water of the indicated temperature. The outlet gas was led through a water lock to prevent air inlet. A reference electrode was used which comprises a gold wire immersed in the melt and double alumina tubes with standard reference gas (33.3%  $\text{O}_2$ , 66.7%  $\text{CO}_2$ ). The external tube had a small hole at the bottom to form a salt bridge of molten carbonate. All potentials given are referred to this reference electrode. The (coated) steel samples (surface area about 1  $\text{cm}^2$ ) were spot-welded to a gold wire (0.5 mm  $\varnothing$ , purity 99.9 %) and cleaned with ethanol before the corrosion measurements, in which the samples were fully immersed in the melt.

Four different conditions can be distinguished: MCFC cathode-gas or anode-gas, open circuit or MCFC load conditions. Corrosion under cathode gas is, obviously quite different from corrosion under anode gas. Although anode gas is a reducing gas atmosphere, water vapour and  $\text{CO}_2$  (also present in the carbonate ion) can both act as oxidants under anode gas atmosphere. Under cathode gas, oxygen gas is probably the most important oxidant. Corrosion at load is different from corrosion at open circuit. The open circuit potential (OCP) is a mixed potential, which is a result of the corrosion process and the MCFC-anode gas reaction under anode gas (reaction 2) or the MCFC-cathode gas reaction under cathode gas (reaction 1). At load conditions, the potential of the steel parts is equal to the electrode potentials, being about -950 mV for the anode and about -100 mV for the cathode at a current density of 150  $\text{mA}/\text{cm}^2$  [1].

Under cathode gas at open circuit conditions, the OCP of all samples showed an anodic potential shift from ca. -1.1 V towards the Nernst potential of the cathode gas reaction (-50 mV) during 24 hours of exposure. This presents the decreasing contribution of corrosion reactions to the measured OCP and passivation of the samples. The potential shifts can occur with different time scales. The growth of a corrosion layer is a nucleation and growth process. Hence, small differences in the surface composition can lead to different corrosion products and different kinetics of the

surface passivation and, therefore, the potential change occurs with different time scales. A large potential difference between the OCP and the Nernst potential of the cathode gas reaction appeared to be correlated to a thick corrosion layer. Under anode gas at open circuit conditions, the OCP of most samples was close to the Nernst potential of the anode gas reaction (-1121 mV). Hence, the contribution of the corrosion reaction to the OCP was probably small indicating slow corrosion. Only the OCP of the CrC-coated sample shifted similar as under cathode gas to about -350 mV during 24 hours of exposure, indicating fast corrosion. The Li/Na melt was not significantly more corrosive than the Li/K melt.

Corrosion rates were calculated from measured corrosion currents and determined with cross-section analyses of corrosion layers. Corrosion currents were determined with amperometry and Tafel-extrapolation of quasi-stationary polarisation-curve measurements. Assuming that the measured current is only from the corrosion reaction, and that the steel or coating oxidises to a solid scale which does not dissolve, a corrosion layer thickness or corrosion depth can be estimated from the current density. From the passed charge, which is given by the current density ( $i$ ) integrated over the exposure time ( $t$ ), a corrosion layer thickness or corrosion depth ( $D$ ) can be estimated according to the equation:

$$D = \frac{M}{zF\rho} \int_0^t i dt \quad (11)$$

in which  $F$  is Faradays constant. The corrosion layer thickness on steels can be estimated by assuming  $\alpha$ -LiFeO<sub>2</sub> as main corrosion product, and using oxidation to trivalent metal ions ( $z = 3$ ), an average molar weight ( $M$ ) of 95 g/mole, and a density ( $\rho$ ) of 4.4 kg/dm<sup>3</sup> [34]. For TiN-coated samples, Li<sub>2</sub>TiO<sub>3</sub> is assumed as main corrosion product ( $z = 3$ ),  $M_{\text{Li}_2\text{TiO}_3} = 110$  g/mole [35], and  $\rho_{\text{Li}_2\text{TiO}_3} = 3.5$  kg/dm<sup>3</sup> [36]. The corrosion layer thickness is equal to the estimated corrosion layer thickness divided by factor 2.5 ( $M_{\text{steel}} = 60$  g/mole,  $\rho_{\text{steel}} = 7$  kg/l [10],  $M_{\text{TiN}} = 62$  g/mole, and  $\rho_{\text{TiN}} = 5$  kg/dm<sup>3</sup> [35]).

Although corrosion of steels in molten carbonates has been studied and reported frequently, corrosion rates at the four different conditions (anode or cathode gas, at open circuit or at load) are scarcely reported in literature. This may be due to the limited applicability of electrochemical measurement methods to determine corrosion rates at these four conditions. Care should be taken in drawing conclusions only from measured currents, because it is difficult to separate corrosion currents from contributions of either the MCFC-anode gas reaction under anode gas, or the MCFC-cathode gas reaction under cathode gas.

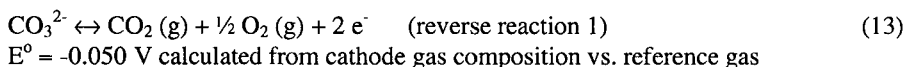
Using amperometry at -950 mV under anode gas, the MCFC anode-gas reaction gives a large positive contribution to the measured current, which leads to higher estimated values for the corrosion layer thickness than the actual values. At -100 mV under cathode gas, the MCFC cathode-gas reaction gives a negative contribution to the measured current, which can even lead to a negative value for the measured current, especially when the corrosion current becomes small due to passivation. Here the so-called gold-flag potential (GFP) is introduced. The OCP of a non-corroding electrode (gold) is equal to the GFP. Hence, by applying the GFP, corrosion currents can be measured without contribution of the MCFC-anode or cathode gas reaction. However, only under anode gas conditions, the OCP of most samples (except CrC-coated steel) was close to the GFP. Therefore, only the measured current at the GFP under anode gas is representative for open circuit conditions, which makes this the only condition where amperometry gives a useful value to estimate the corrosion layer thickness.

Using the Tafel-extrapolation method, quasi-stationary polarisation curves were measured between the OCP minus 0.25 V and the OCP plus 0.25 V after different times of exposure (1, 2, 4, 8, and 24 hours). The sweep rate was 1 mV/s. Usually it is difficult to determine accurate corrosion

rates in molten salts by the Tafel-extrapolation method, because of the very limited Tafel-region observed in molten salts [37]. However, the corrosion potential or OCP differs under cathode gas much from the Nernst potential of the cathode gas reaction. Therefore, the cathodic current of the cathode gas reaction can be regarded relatively potential independent at potentials close to the corrosion potential. Hence, contributions of the cathode gas reaction can be neglected in the determination of the corrosion current with Tafel-extrapolation. However, the corrosion layer thickness estimated with Tafel-extrapolation was under cathode gas much thinner and under anode gas much thicker than the actual value, which indicates that the contributions of the cathode gas reaction and anode gas reaction can not be neglected. Hence, a comparison of corrosion rates of different coated samples should not only be based on determined corrosion currents.

The thickness of the remaining coating, and the thickness, structure, and composition of the corrosion layers need to be examined. Therefore, sample surfaces and cross-sections of the samples were analysed with light microscopy, scanning electron microscopy (SEM) in combination with energy dispersed X-ray analysis (EDX), X-ray diffraction (XRD), and glow discharge optical emission spectrometry (GD-OES). Before the analysis of the corrosion layers, the carbonate adhering to the samples was removed by rinsing in demineralised water.

With cyclic voltammetry, first a fingerprint is given of the corrosion behaviour of the bare steel and of the different coatings. Cyclic voltammetry shows corrosion of steel when the corrosion protection of the coating fails. Cyclic voltammograms were measured between -1600 and +50 mV, the electrochemical window of molten carbonate, which is determined by carbon precipitation and anodic decomposition:



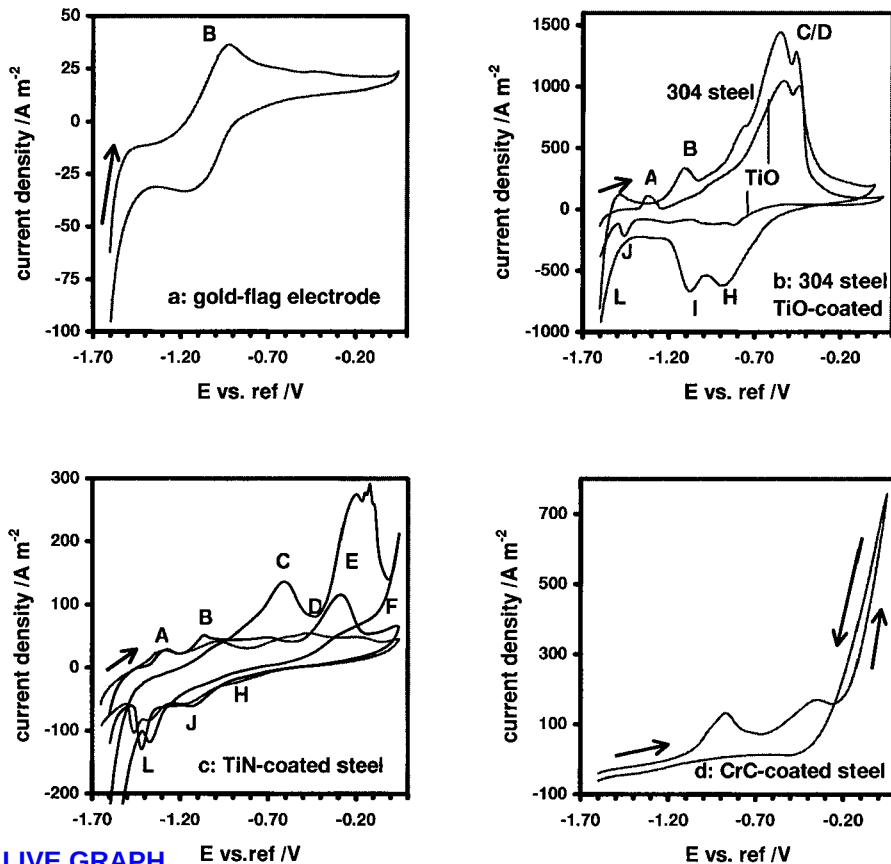
The sweep rate was  $50 \text{ mV s}^{-1}$ , the scan increment was  $10 \text{ mV}$ , and the step time was  $0.2 \text{ s}$ . At load conditions corrosion of 304 steel was most severe under anode gas [22, 23]. Therefore, the corrosion behaviour was studied with cyclic voltammetry under anode gas. Besides the reactions of the coating material, the measured cycles also present reactions of the substrate material and the MCFC anode-gas reaction. The MCFC anode-gas reaction can be measured separately in a cyclic voltammogram using a gold-flag electrode, because gold is considered inert in molten carbonates. The corrosion behaviour of the substrate material, stainless steel 304 was described extensively in earlier publications [22, 23]. Cyclic voltammograms were measured on gold, substrate material, titanium carbonitride, and chromium carbide coatings. Cyclic voltammograms were also measured on an electrode of  $\text{Li}_2\text{TiO}_3$ , which is considered as the main corrosion product of Ti-based coatings. Porous  $\text{Li}_2\text{TiO}_3$  electrodes were prepared by pressing  $\text{Li}_2\text{TiO}_3$  powder into pellets, drilling a hole for a gold lead wire ( $0.5 \text{ mm } \varnothing$ ), and sintering at  $1000^\circ\text{C}$  during 24 hours. The  $\text{Li}_2\text{TiO}_3$  pellets were exposed to the melt for at least 24 hours before measuring cyclic voltammograms.

## 7 Corrosion behaviour of 304 steel and coated steel

### 7.1 Cyclic voltammetry

The corrosion behaviour of steel and steel components was studied extensively with cyclic voltammetry by Vossen *et al.* [10, 39, 40]. The cyclic voltammetry studies of the substrate material, stainless steel 304, the coated steel samples, gold, and the  $\text{Li}_2\text{TiO}_3$  electrode were discussed

extensively elsewhere [22, 23, 30]. Figure 4 presents some characteristic cyclic voltammograms measured on gold, 304 steel, TiO-coated steel, TiN-coated steel, and on CrC-coated steel.



**LIVE GRAPH**  
Click here to view

**Figure 4** Cyclic voltammograms on a gold flag (a), on 304 steel and TiO-coated steel (b), on TiN-coated steel (c), and on CrC-coated steel (d) in molten carbonate under anode gas.

From the current density in the cyclic voltammetry experiments, a rough estimate of the corrosion protection of the different coatings can be given. High anodic peaks in the cyclic voltammograms indicate oxidation sensitive materials. The current density of the TiN and TiC-coated samples is much lower than that of stainless steel, which indicates a much slower corrosion rate than that of steel, and corrosion-protective properties. The titanium monoxide-coated sample shows high current densities, indicating fast corrosion and no protection. The CrC-coated sample shows especially at potentials anodic from about -0.2 V a high current density. Here, the CrC corrodes reactively and probably dissolves as chromate ions.

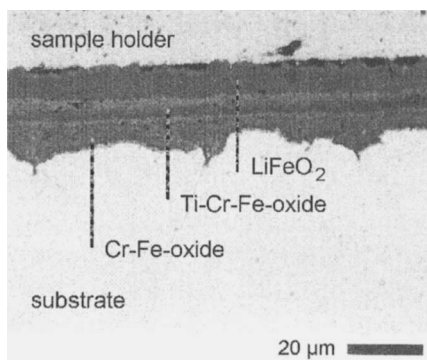
Further, a comparison of the corrosion protective properties of the different coatings has to be made. When the characteristic peaks of the steel substrate become visible in the cyclic voltammogram, the corrosion protective properties of the coating have come to an end. The steel characteristics (peak C, D, H, and I) were visible in the cycle measured just after immersion on titanium monoxide coated steel, which indicates that this coating shows hardly any corrosion protection. Also the presence of pinholes in TiN-coated steel samples was observed using cyclic

voltammetry as a high C-peak. After many cycles, two characteristic peaks of steel components (peak H and I) were also visible in the cycles on the TiN-coated steel samples, indicating degradation during cycling.

Using the cyclic voltammograms measured on gold, substrate material, coated samples, and the  $\text{Li}_2\text{TiO}_3$  electrode, the different peaks were assigned to different oxidation and reduction reactions. The MCFC-anode gas reaction (reaction 2) is weakly represented in peak B. Peak F presents the anodic decomposition of the carbonate. Peak C and D present oxidation reactions of steel components (Fe, Ni, and Cr). Peak H and I present reduction reactions of steel components (Fe, Ni). Peak A and B present oxidation reactions and peak J and L present reduction reactions of titanium in the corrosion layer.

## 7.2 Corrosion layers

Within the potential range measured under cathode gas at open circuit conditions, iron can be oxidised to  $\text{FeO}$ ,  $\text{LiFeO}_2$ , and  $\text{LiFe}_5\text{O}_8$ , nickel to lithiated  $\text{NiO}$ , chromium or  $\text{CrC}$  to  $\text{LiCrO}_2$  and  $\text{Li}_2\text{CrO}_4$ , and TiN, TiC, or TiO to  $\text{Li}_2\text{TiO}_3$ . Steel samples and samples with a Ti-based coating characteristically form a corrosion layer, which comprises three sub-layers as presented in Figure 5.



**Figure 5** Light microscopy cross-section of TiN-coated steel after 30 days of exposure under cathode gas at OCP.

Stainless steel 304 under cathode gas at open circuit is first covered with a stable layer of mostly chromium oxides [19, 20, 41]. Chromium oxidises faster than iron, and chromium oxide dissolves much faster than iron oxide into the carbonate under cathode gas [41]. Hence, when the chromium oxide dissolves, a layer of iron oxide remains on the metal surface. The iron oxide lithiates in lithium carbonate to lithium ferrite ( $\text{LiFeO}_2$ ). The formed lithium ferrite scale does not form a good passive layer, which protects the underlying steel against corrosion. Hence, the underlying iron corrodes to iron oxides, and chromium oxide formed under the lithium ferrite film will dissolve into the melt through cracks in the lithium ferrite film. The chromium dissolution colours the melt deep yellow. This leads to a surface layer of  $\text{LiFeO}_2$ , an intermediate corrosion layer of iron oxide, and an inner corrosion layer with an iron depletion (or chromium and nickel enrichment).

Similarly, the corrosion layer on samples with a Ti-based coating are composed of an outer layer of lithium ferrite, an intermediate layer of Ti-Cr-Fe-oxide, and an inner layer iron depleted (or chromium enriched) Cr-Fe-oxide. Several coatings showed (almost) no Ti remainings after 24 hours of exposure, which is probably due to the dissolution of titanate ions ( $\text{TiO}_3^{2-}$ ) in the melt. Ti was only found in corrosion layers as intermediate oxide or mixed oxide layer with Fe and Cr between an outer  $\text{LiFeO}_2$  layer and an inner Fe-depleted oxide layer. This presents the corrosion mechanism. The oxygen reduction at the sample surface:



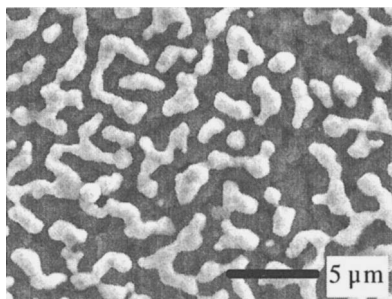
is accompanied with the absorption of lithium ions from the melt and the creation of titanium vacancies and electron holes. Holes are easily transported away from the surface in a p-type conductor as  $\text{Li}_2\text{TiO}_3$ . In order to balance this charge transport, metal ions are transported towards the sample surface and fill the titanium vacancies at the surface. After corrosion of the Ti-based coating, this process continues with iron ions from the substrate creating a  $\text{LiFeO}_2$  layer on top of the  $\text{Li}_2\text{TiO}_3$  layer. The corrosion layer formed underneath the  $\text{Li}_2\text{TiO}_3$  layer can only be due to diffusion of oxygen along the grain boundaries. The diffusion of Fe ions is much faster than that of Cr or Ni, which leads to an Fe depleted (or Cr and Ni-enriched) inner corrosion layer. Here it also becomes clear, that the intermediate Ti-layer does not form a sufficient barrier for the inward diffusion of oxygen and outward diffusion of iron.

At load conditions under cathode gas, corrosion is less fast because the applied  $-100 \text{ mV}$  is in the passive region for the oxidation of iron to  $\text{LiFeO}_2$  and in the passive region for the oxidation of nickel to lithiated  $\text{NiO}$ . Therefore, polarisation of the samples at  $-100 \text{ mV}$  increases passivation of the sample, and suppresses the corrosion process, which is also called anodic protection. The corrosion layers show a layered structure and composition similar as at open circuit conditions.

At load conditions under anode gas, corrosion is fast because the applied  $-950 \text{ mV}$  is in the active region for the oxidation of iron to  $\text{FeO}$  and further to  $\text{LiFeO}_2$ , and of chromium to  $\text{LiCrO}_2$ , whereas nickel is stable. GD-OES analysis showed on a 304 steel sample after 24 hours of exposure an outer  $\text{LiFeO}_2$  layer and an inner lithiated, Fe-depleted oxide layer. Remnants of Ti-based coatings were always present as intermediate layer between the outer  $\text{LiFeO}_2$  layer and the inner Fe-depleted layer.

At open circuit conditions under anode gas, corrosion is less fast than at load conditions. Contrasting with load conditions, no anodic over-potential is applied and the potential remains close to the equilibrium potential of the MCFC anode-gas and corrosion reactions, leading to relatively slow corrosion. Only the CrC-coating was highly sensitive for corrosion at these conditions. It showed similarly as under cathode gas a potential shift from about  $-1.1 \text{ V}$  to about  $-350 \text{ mV}$ .

The double layer coating of Au on TiN-coated steel had formed after 24 hours exposure under cathode gas at load or open circuit many small round gold particles (about  $1\frac{1}{2} \mu\text{m}$  Ø), a corroded TiN-sample surface, and an accumulation of gold on the sample edges. Hence, the gold coating broke up into small particles and the coating showed a low adherence with the underlying TiN-coating. The same results were obtained for the double layer coating of Ni on TiN-coated steel after 24 hours exposure under anode gas at load or open circuit conditions as presented in Figure 6.



**Figure 6** SEM micrograph of the TiN and Ni-coated sample surface after 24 hours of exposure under anode gas at OCP.

### 7.3 Corrosion protection

Coatings differing in composition and morphology were tested in molten carbonate, with emphasis on finding a relation between the coating composition, morphology, and corrosion properties. The TiN coatings showed the best corrosion protection. The TiC coating showed less protection. Similar as in aqueous media, the corrosion resistance decreases with increasing carbon content [42, 43]. The thin titanium monoxide coating showed no corrosion protection at all, and the CrC coating vigorously reacted in molten carbonate at all conditions. Pinholes and a low density are disadvantageous on the corrosion protective properties. A coating which was a multilayer of TiC and TiN/Ti<sub>2</sub>N showed better corrosion protective properties than a stoichiometric TiN coating, although less corrosion protection is expected from substoichiometric coating materials. Literature gives for the substoichiometric Ti<sub>2</sub>N/TiN mixture a superior wear-protection and extreme hardness compared with stoichiometric TiN, but nothing about the corrosion resistance [44].

Under cathode gas, the most important corrosion protection is given by keeping the fuel cell constantly at load. Then passivation retards the corrosion processes. To protect the stainless-steel separator plates and current collectors against corrosion at open circuit conditions (e.g. during start up), the use of a dense 3  $\mu\text{m}$  thick TiN coating is recommended.

Under anode gas at open circuit conditions, lifetime corrosion protection might be provided by a dense 3  $\mu\text{m}$  thick TiN-coating. Under anode gas, corrosion is more severe at load conditions. Here the TiN-coatings showed corrosion protection during one day of exposure, but not enough for lifetime corrosion protection in the MCFC. The double-layer coatings of gold or nickel on a TiN-coating were not successful. The Au and Ni coatings broke up into small particles, which partly coagulated on the sample edges. Wind *et al.* [21] found that cladded Ni coatings were stable, whereas electroplated Ni coatings were not. Possibly, the main reason for the stability of the cladded layer was its large thickness. Then a solution to this problem of unstable Ni and Au coatings on TiN might be to apply thick coatings (about 50  $\mu\text{m}$ ). A thick Ni or Au coating on top of a ceramic (TiN) coating might provide the necessary corrosion protection in molten carbonates under anode gas at load conditions.

### Conclusions

None of the selected non-oxide metal/non-metal ceramic materials is thermodynamically stable in molten carbonates. Still, these coating materials were selected for corrosion protection of steel separator plates because of their relatively high corrosion resistance, high electronic conductivity, high-temperature resistance, and at low cost.

Several electrochemical methods were used to study the corrosion at the four different conditions: under anode and cathode gas, at open-circuit and at load conditions. Potentiometry can indicate corrosion sensitive materials as for the CrC-coating. Cyclic voltammetry can also indicate the corrosion sensitivity of the coating materials and show when the corrosion protection of the applied coating fails. Amperometry and Tafel-extrapolation of quasi-stationary polarisation curves do not give an accurate estimate of corrosion rates at all four conditions, due to contributing currents of either the MCFC anode or cathode gas reaction. Only at the so-called gold-flag potential under anode gas, the corrosion layer thickness estimated from amperometry was comparable with the corrosion layer thickness determined with electron microscopy.

The TiN coatings showed corrosion protection at all conditions, especially the substoichiometric TiN coating, whereas the relatively porous TiC and the corrosion sensitive TiO and CrC coatings did not present an improvement on the corrosion properties. Ti-based coatings corrode (with



different velocities) in molten carbonate to a  $\text{Li}_2\text{TiO}_3$  layer, which does not form a good passive layer because it is not a sufficient barrier for the inward diffusion of oxygen ions or the outward diffusion of iron from the steel substrate. The thin Ni and Au coatings on TiN-coated steel samples appeared to be unstable in molten carbonates. Under cathode gas, the most important corrosion protection is given by keeping the fuel cell constantly at load. Under anode gas, a thick Ni or Au coating on top of a ceramic (TiN) coating might provide the necessary corrosion protection at load conditions.

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## Molten Salt Corrosion of Ceramic Materials

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**Keywords:** Carbides, Ceramics, Molten Salt Corrosion, Nitrides, Oxides, Superconductors, Zirconia-Containing Materials

**Abstract.** High temperature corrosion of ceramic materials in molten salts occurs by a complex chemical mechanism. The concept of acidity-basicity, thermodynamic considerations, the principles of penetration dissolution and spalling all are presented to assist in predicting the corrosion phenomenon. A review of corrosion resistance by broad classes of materials is included, with particular mention to silica-formers. The last part of this chapter addresses the problem of the appropriate material selection required to minimize molten salt corrosion of industrial ceramics.

### 1. Introduction

The successful use of ceramics in high-temperature systems involving severe corrosive conditions covers a wide range of applications. This chapter is focused on the molten salt corrosion of ceramics that substitute for high temperature metallic alloys in, for example, gas turbine components in the automotive and aerospace industries and in heat exchangers in various segments of the chemical and power generation industries.

Corrosion of ceramics in molten salts involves dissolution and invasive penetration, where diffusion, grain boundary and stress corrosion may all be present, and oxidation-reduction reactions where absorption, desorption, and mass transport phenomena all come into play. The interplay between dissolution, penetration, redox reactions, microstructure and surface characteristics of the ceramic, make the study of corrosion of ceramics in molten salts very complex. Carniglia and Barna [1], McCauley [2] and Lay [3] provide useful information on these complexities.

Much work was performed in the 1950's and 60's on what has been called the galvanic corrosion of ceramics by glasses. Galvanic corrosion must occur between two materials in contact with one another and both must be in contact with the same electrolyte. Much of what has been reported should more correctly be called electrochemical corrosion. One of the first reports of the existence of an electrochemical potential between ceramic and glass was that of Le Clerc and Peyches [4] in 1953.

Godrin [5] has published a review of the literature on electrochemical corrosion of ceramics by glasses. It has been shown that a potential difference does exist in such systems; however, no quantitative relationship between corrosion and potential has been reported. Since a potential difference exists in corroding systems, it has been tempting to assume that the potential is at least partly responsible for the corrosion, however, the application of a bias potential has been unsuccessful in eliminating corrosion. Even though not totally reliable, Godrin concluded that ceramics that have an electrical potential with respect to glass that is positive 0.4 to 0.7V are fairly resistant to corrosion, that ceramics with a potential greater than 1.0V have rather poor resistance, and that ceramics that have a negative potential with respect to glass should not be used.

Pons and Parent [6] have concluded that the oxygen ion activity is a very important parameter in corrosion and that its role is determined by the difference in oxygen potential between the molten glass and the ceramic oxide. An additional interesting case is that of two different oxide materials (i.e., a multiphase polycrystalline material) in contact with the same glass, that have oxygen potentials on either side of that of the glass. In such a case, it is assumed that oxygen migrates from the oxide of higher potential towards that of lower potential. If the conduction mechanism of the

two oxides is different (ionic versus electronic) the situation becomes more complex. When the oxygen potentials of the oxides are greater than the glass, oxygen ions are assumed to be transported from the ionic conductive oxide to the electronic conductive one, which may ultimately result in pitting caused by the release of oxygen. If the oxygen potential of the oxides is lower than the glass, alkali ions of the glass are transported to the electronic conductive oxide with oxygen release at the interface between the two oxides.

Although in theory the application of a bias potential to minimize or eliminate corrosion, which implies that the corrosion process is one that involves charge transfer, should produce noticeable results, a major practical problem has been that of making the electrical connection to the ceramic. The other problems relating to the success of a bias potential in eliminating corrosion are the other factors in corrosion – chemical reaction, diffusion, viscosity, solubility, etc. In other words, although in certain specific situations we can consider that the corrosion of ceramics in glasses proceeds by electrochemical dissolution, it is absolutely certain that corrosion of ceramics in high temperature molten salts is essentially a complex chemical phenomenon. Accordingly, to predict the corrosion of ceramics in molten environments it is necessary to consider the concept of acidity-basicity and to estimate the driving force for corrosion using thermodynamic laws. Then, to select the best ceramic for a specific application, kinetic data are required, penetration, dissolution and spalling being important factors requiring consideration.

Silica ( $\text{SiO}_2$ ) is the best example of a solid acidic oxide that should be used in applications where the destructive materials (liquids) are chemically acidic, for example, coal gasifier ash or ironmaking slags. Magnesia and dolomite are basic in nature and should be used in applications where slags are generally basic, for example, steelmaking slags and liquid clinker melt in the rotary cement kiln. These generalizations are first approximations that are insufficient in many cases because, in many industrial processes, the corrosive environment changes from acidic to basic during the operation. Nevertheless, the first rule is to make the acid-basic character of the ceramic constituents similar to that of the corrosive liquids to increase the corrosion resistance.

The second approach to predict the corrosion resistance of industrial ceramics is to make the appropriate thermodynamic calculations, to evaluate the thermal stability of each constituent prior to melting, to consider the melting and dissolution behaviour, using phase diagrams, and finally to assess redox potentials.

It is useful to distinguish between physical penetration and chemical invasion. Physical penetration, without dissolution at all, occurs when a strictly nonwetting liquid is forced into the pores of a solid by gravity or external forces. Chemical invasion occurs when dissolution and penetration are tied together. Both physical and chemical penetration are favoured by effective liquid-solid wetting and by low-viscosity liquid. Silicates, particularly silicate glasses, are usually viscous; simple oxidic compounds and basic slags are less viscous; and halides and elemental molten metals are, in general, the most fluid liquids.

Penetration is the result of an interplay between capillary forces (surface tension), hydrostatic pressure, viscosity, and gravity. Mercury penetration in a capillary glass tube is the best example of physical penetration.

When the pore size distribution is narrow (i.e., pores of the same size), penetration and filling of the porosity by capillarity produce a relatively uniform front moving gradually from the hot face and remaining parallel to it. When pore size distribution is wide (i.e., very large and very small pores) or when open joints, cracks or gaps between bricks in a refractory wall are accessible at the hot face, rapid, and irregular liquid intrusion do occur. There are many penetration paths in a refractory, and the texture of the material is of primary importance; it is important to distinguish between interconnected versus isolated porosity, between open and total porosity, pore sizes and unbounded boundaries between grains (aggregates and/ or matrix) due to thermal mismatches during heating.

For a given temperature gradient, the pertinent eutectic temperature of the penetrating liquid determines its maximum liquid penetration depth.

The simplest case of pure dissolution is to consider the following reaction:  $S_1 + L_1 \rightarrow L_2$ , where  $S_1$  is the solid ceramic,  $L_1$  is the molten liquid,  $L_2$  is a solution  $L_1 + S_1$ . The dissolution rate,  $j$ , may be visualized as the ratio of a potential difference ( $C_{\text{sat}} - C_{\infty}$ ) divided by a resistance term  $K^{-1}(1+K\delta/D)$ . Here  $K$  is the surface reaction rate constant,  $\delta$  is the thickness of the boundary layer in the liquid phase,  $C_{\text{sat}}$  is the concentration of the dissolving solid, in the liquid, at the interface;  $C_{\infty}$  is the concentration of the dissolving phase in the bulk of the liquid; and  $D$  is the effective diffusion coefficient in the solution for the exchange of solute and solvent.

Three different cases will be briefly treated.

1. When  $K \gg D/\delta$ ; that is, when the chemical reaction takes place so rapidly at the solid solvent interface that the solution is quickly saturated and remains so during the dissolution process; in this case, the dissolution rate,  $j$ , is controlled by mass transport:

$$j = \frac{D}{\delta}(C_{\text{sat}} - C_{\infty}) \quad (1)$$

This process is often called direct dissolution.

2. When  $K \ll D/\delta$ ; that is, when the dissolution rate is phase-boundary controlled as opposed to mass-transport controlled, equation (1) turns to:

$$j = K(C_{\text{sat}} - C_{\infty}) \quad (2)$$

The phase-boundary reaction rate is then fixed by the movement of ions across the interface, and hence, is governed by molecular diffusion.

This process is often called indirect dissolution.

3. When  $K \approx D/\delta$ , both phase boundary and mass-transport are controlling; in this case of mixed control, the potential difference ( $C_{\text{sat}} - C_{\infty}$ ) can be seen as divided into two parts. ( $C_{\text{sat}} - C^*$ ) is the part that drives the phase boundary condition, and ( $C^* - C_0$ ) the part that drives the transport process, so as to keep the dissolution rates for each process equal.

Of course, in the case of very pure ceramics, where porosity is very low, dissolution is more important than penetration.

While spalling is a general term for the cracking or fracture caused by stresses produced inside a refractory, chemical or structural spalling is a direct consequence of corrosion penetration. It should not be confused with pure thermal or pure mechanical spalling. Structural spalling is a net result of a change in the texture of the refractory, leading to cracking at a plane of mismatch, at the interface of an altered structure and the unaffected material.

When slag penetration does not cause direct loss of material, the slag does partially or completely incase a volume of refractory, reducing its apparent porosity (by sometimes more than one half), causing differential expansion with the associated development of stresses. As a result, there is a degradation in material strength and stiffness, the appearance of microcracks and, eventually, totally disruptive cracks parallel to the hot face of the lining; this is structural spalling [7].

A model developed by Cook et al. [8] in their study of hot corrosion of ceramic (alumina) barrier coatings by sodium, sulphur, and vanadium molten salts gives the rate of solution of a ceramic when a steady state condition prevails for the rate of salt removal equal to the rate of salt deposition. This provides a salt layer of constant thickness. The ceramic solution rate is then dependent upon the rate of salt deposition:

$$d(M_c/A)/dt = [C/(1-C)]d(M_s/A)/dt \quad (3)$$

where  $M_c$  is the mass of ceramic dissolved,  $A$  is the surface area,  $M_s$  is the mass of salt deposited, and  $C$  is the concentration of ceramic in the layer.

At low deposition rates when salts become saturated the solubility in the salt becomes important. Use of this model requires the calculation of the gas phase and condensed solution equilibria using a computer program such as that developed by the NASA-Lewis Research Center [9]. In addition to the steady state assumption for salt deposition and removal, other assumptions included the parabolic rate law, known equilibrium solubilities, and congruent dissolution.

Corrosion by molten salts has several beneficial applications. One very important application where dissolution of a ceramic is desired is in the removal of the ceramic cores from metal castings manufactured by the investment casting technique. The solvent used for core removal must be highly reactive to the ceramic at rather low temperatures while not damaging the metal. The ceramic must be stable towards molten metal attack at high temperatures and highly reactive towards solvent attack at low temperatures. In a study of the leaching rates of  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{ThO}_2$ , and  $\text{MgO}$  by molten  $\text{Li}_3\text{AlF}_6$ , Borom et al. [10] found that the corrosion appeared to involve a solid reaction layer and a boundary layer in the liquid. Vigorous solvent circulation was required to overcome the diffusion-controlled process. Thus it appears that congruent dissolution is required for optimum core removal, since incongruent dissolution may form reaction layers that require forced convection for removal.

Numerous methods have been tried to measure the corrosion resistance of ceramics under deposit conditions, but very few methods have reached the status of standard operating practices and none have yet been accepted for universal use.

The main reason is that corrosion resistance data obtained in a laboratory environment very rarely simulate the conditions that prevail in service: sample size and geometry, state of stresses in the lining, thermal gradient and thermal cycling, as well as time, which are very difficult to be scaled down to fit with acceptable laboratory test conditions. It must always be remembered that accelerated tests, specially those done using very severe conditions, can lead to erroneous predictions.

Compared with laboratory testing, field-trial testing is, of course, much more costly, and, in some instances, unsafe. It may then be worthwhile to test small panels rather than to carry out full-size testing; the larger the installation the more confidence one will have in the selection of the proper material to use.

Postmortem examination of in-service trials also provides very useful insights to understand and determine the controlling mechanisms in the degradation of ceramics. Detailed investigations include the use of a wide variety of characterization methods, including chemical analysis, X-ray diffraction, mineralogical analysis, and scanning electron microscopy (SEM)/ energy dispersive spectroscopy. Selecting sample and carrying out sample preparation are often very challenging. Observations of the uncorroded part often yield clues as to what may have happened in the corroded part.

Crescent and Rigaud [11] reviewed and classified some 106 different experimental setups, all falling into one of 12 categories. Among the non-standard tests, the most commonly used are the crucible test, the rotary disk and the finger test. Further information on corrosion testing of ceramics can be found in reference [12].

Having postulated that corrosion of ceramics in molten salts is essentially the result of a chemical reaction, where the rate-determining step does not involve electronic charge transfer at the reaction interface, this section continued with a few considerations on the basic principles of corrosion. Then, it concluded with a short reference to corrosion testing. In the next section a review of corrosion resistance by broad classes of materials is considered.

## 2. Corrosion of Specific Classes of Ceramics

### 2.1 Oxides

The importance of molten salt reactions is well known in alumina reduction cells for the production of aluminium metal (Hall-Heroult Process). In this process, the electrolyte consists of a solution of alumina (<10 wt %) dissolved in molten cryolite ( $\text{Na}_3\text{AlF}_6$ ) [13]. Pure molten cryolite contains  $\text{AlF}_6^{3-}$ ,  $\text{AlF}_4^-$ ,  $\text{F}^-$ , and  $\text{Na}^+$  ions. When alumina is added the complex ion  $\text{AlOF}_x^{(1-x)}$  ( $x = 3-5$ ) forms in addition to the others. In a study of the cryolite-mullite and cryolite/ sodium fluoride-mullite systems, Siljan and Seltveit [14] reported that materials with high Si/ Al ratios experience high weight losses in contact with NaF-cryolite eutectic melts due to the formation of gaseous  $\text{SiF}_4$ . They reported that mullite dissolved readily in cryolite and cryolite-NaF melts and that NaF reacted with alumina to form beta-alumina.

The corrosion of fused silica by molten sodium sulphate in atmospheres containing either 1%  $\text{SO}_2/\text{O}_2$  or pure oxygen at 700 and 1000°C has been described by Lawson et al. [15] to take place according to the ease of sodium diffusion in the various phases that form. Sodium diffuses into the fused silica, leading to the nucleation of cristobalite. Once a continuous layer of cristobalite formed, sodium diffusion was minimized. The sodium at the cristobalite/ fused silica interface then diffused further into the fused silica. The basicity of the reaction determines whether or not a cristobalite layer forms, with less cristobalite forming as the reaction becomes more acidic. Cristobalite globules, however, were reported to precipitate from the salt solution. Low partial pressures of  $\text{SO}_3$  were reported to promote the fluxing action of the molten sulphate by increasing the activity of  $\text{Na}_2\text{O}$ .

In the evaluation of cathode materials for molten carbonate fuel cells, Baumgartner [16] reported solubility data for NiO, CuO, ZnO,  $\text{LiFeO}_2$ , and  $\text{LaNiO}_3$  in a molten binary carbonate of Li/ K (62/ 38 molar ratio) between 823 and 1223°K. Both NiO and CuO exhibited dissolution (CuO being more soluble than NiO) into the molten carbonate and diffusion towards the anode until the local pressure of oxygen was sufficiently low for metal precipitation. At temperatures exceeding 1223°K  $\text{LaNiO}_3$  decomposed to  $\text{La}_2\text{NiO}_4$  and NiO, which dissolved and reduced to metallic Ni. A similar situation was found for  $\text{LaCoO}_3$ , which decomposed to  $\text{La}_2\text{CoO}_4$  and CoO at temperatures exceeding 1073°K. Dissolution of  $\text{LiFeO}_2$  into the molten carbonate resulted in reduction at the anode to  $\text{LiFe}_5\text{O}_8$ , while ZnO at the anode became nonstoichiometric. The solubilities of these oxides were in the order  $\text{LaNiO}_3 < \text{NiO} < \text{LiFeO}_2 < \text{CuO} < \text{ZnO}$  below 1023°K. Above this temperature the relative solubilities of CuO and ZnO reverse.

An example of when corrosion is beneficial is the removal of ceramic cores in the investment casting process. The new process of directional solidification and the new alloys involved (NiTaC) require contact between the molten metal and the core material for times up to 20 hours at temperatures as high as 1800°C [17]. The requirement that the core material must withstand these conditions and then be chemically removed is a contradiction in stability. Core removal requires high dissolution rates at low temperatures. Potential core materials are  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ,  $\text{LaAlO}_3$ , and  $\text{Mg Al}_2\text{O}_4$ , which all possess satisfactory resistance to the casting conditions as reported by Huseby and Klug [17]. These materials, except for  $\text{Y}_2\text{O}_3$ , are insoluble in aqueous acids or bases. The solvents used must be aggressive towards the core material but not towards the alloy. Borom et al. [10] reported the weakly basic amphoteric oxides of  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$  can be dissolved by molten  $\text{M}_3\text{AlF}_6$ ,  $\text{M}_3\text{AlF}_6 + \text{MF}$ ,  $\text{M}_3\text{AlF}_6 + \text{M}'\text{F}_2$ , or  $\text{M}_3\text{AlF}_6 + \text{MCl}$ , where  $\text{M} = \text{Li, Na, or K}$  and  $\text{M}' = \text{Mg, Ca, Ba or Sr}$ . The more acidic core materials such as  $\text{ZrO}_2$  or  $\text{ThO}_2$  required alkali or alkaline earth oxide additions to make the molten salt more basic.

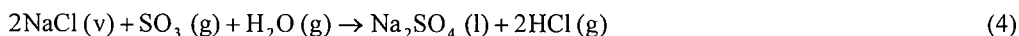
Another field of study where the solution in molten is beneficial is that of crystal growth. The solubility of  $\text{Be}_2\text{SiO}_4$  and  $\text{ZrSiO}_4$  in various solvents was studied by Ballman and Laudise [18]. Solvents studied included alkali vanadates and molybdates. Due to solvent volatility problems (more important for molybdates than vanadates) most of their data contain substantial error at higher temperatures. The reported ion solubilities were greater for  $\text{Be}_2\text{SiO}_4$  ranging from 3 to 5 ½

mol % in the 900-1000°C range than for  $\text{ZrSiO}_4$ , which ranged around 1 mol % in the 900-1400°C region. Except for the solution by  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$ , which was as much as 6 mol % at 1400°C, the vanadates were more corrosive than the corresponding molybdates of those studied. The greater solubility of  $\text{Be}_2\text{SiO}_4$  over that  $\text{ZrSiO}_4$  can also be predicted from acid/ base theory, since  $\text{BeO}$  is a stronger base than  $\text{ZrO}_2$ .

## 2.2 Non-oxides

Non-oxides ceramics are promising materials for a range of high temperature applications (turbine engine components, combustor liners, blades and vanes, at 900-1400°C; industrial furnaces, heat exchangers, at 900-1400°C; coal combustion, particle filters, at 700-1000°C). In all such applications, the ceramics are exposed to high temperature gases and molten salts (Na, Mg, Ca sulphates; sodium vanadates, various molten deposits, slag deposits) [19-22]. Therefore it is critical to understand the response of these non-oxide materials to their environment.

In combustion environments sodium impurities are very common. These can lead to highly corrosive salt deposits. An example is ingested  $\text{NaCl}$  in combustion air, which reacts with sulphur impurities in the fuel to form highly stable  $\text{Na}_2\text{SO}_4$  [23]:



The sodium may come from a marine environment in a gas turbine, process chemicals in an industrial furnace, or even fuel impurities. Under the appropriate conditions,  $\text{Na}_2\text{SO}_4$  forms as a condensed phase, depositing on parts. Deposition of corrosive salts is a continuous process. It is difficult to simulate this in a laboratory furnace. For this reason many salt corrosion studies are done by seeding a flame in a burner rig. Jacobson et al. [24] studied the behaviour of  $\text{SiC}$  treated in a burner without salt and with a flame seeded with  $\text{NaCl}$ . Extensive corrosion took place in the later case.

McKee and Chatterji [25] described several different modes of behaviour of  $\text{SiC}$  in contact with gas-salt mixed environments relating to the formation of various interfacial reaction layers. Salt mixtures containing  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{S}$ , or graphite were tested. McKee and Chatterji found that a  $\text{SiO}_2$  protective layer corroded in a basic salt solution but not in an acidic salt solution. With low oxygen pressures, active corrosion took place by formation of  $\text{SiO}$  gas.

The activity of  $\text{Na}_2\text{O}$  has been shown to be an important parameter in the action of molten sodium salts by Jacobson and coworkers [24, 26-30]. The higher this activity the greater the potential reaction with silica. The relationship of soda activity and  $\text{SO}_3$  partial pressure can be obtained from the following equation:



The partial pressure of  $\text{SO}_3$  (g) effectively sets the activity of  $\text{Na}_2\text{O}$  (s). A high activity of  $\text{Na}_2\text{O}$  is a basic molten salt; a low activity of  $\text{Na}_2\text{O}$  is an acidic molten salt [31, 32]. Since  $\text{SiO}_2$  is an acidic oxide, it is readily attacked by a basic oxide:



The solid protective  $\text{SiO}_2$  layer has been replaced by a liquid, non-protective sodium silicate layer. This leads to rapid corrosion as described by Jacobson et al. [24].

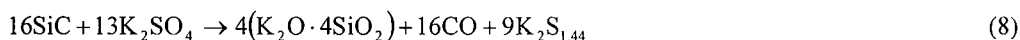
The reaction of  $\text{Na}_2\text{O}$  (or some sodium sulphur containing compound) with silica according to (6) or:





is the one of importance in the dissolution of silica in the manufacture of soda-lime-silica glass and is most likely the one of major importance in the corrosion of the silica layer formed on SiC or Si<sub>3</sub>N<sub>4</sub>. Continued reduction of Na<sub>2</sub>SO<sub>3</sub> to Na<sub>2</sub>S, although still reactive with silica is not necessary for excessive dissolution of carbides and nitrides. The more reduced forms of the sodium-sulphur compounds are the basis of the amber colour formed in the manufacture of brown bottles.

Jacobson and Smialek [26] found that the partial decomposition of Na<sub>2</sub>SO<sub>4</sub> enhanced the oxidation of SiC, forming a layer of tridymite, a sodium silicate glass, and some Na<sub>2</sub>SO<sub>4</sub>. Any free carbon in the SiC enhances the corrosion, since it aids in the reduction of the sulphate. This enhanced corrosion is due to the ease of diffusion of oxygen through the predominantly sodium silicate amorphous layer compared to that of a crystalline silica layer. A somewhat different mechanism has been proposed for the corrosion of SiC by potassium sulphate, although details of the behaviour have not yet been reported [33]. In the case of the potassium salt, no silica layer is formed on the carbide, since it immediately is dissolved by the sulphate according to:



presumably due to dissolution being faster than oxidation.

The corrosion of hot pressed silicon nitride (HPSN), reaction bonded silicon nitride (RBSN) and silicon carbide by molten sodium sulphate, sodium chloride and the eutectic composition between these two salts at temperatures from 670 to 1000°C for up to 120 hours was reported by Tressler et al. [34]. Molten sodium sulphate was the most corrosive, the eutectic composition was intermediate, and sodium chloride was the least effective in dissolving the silica surface layer present on these materials. HPSN was the most resistant, whereas silicon carbide completely dissolved in sodium sulphate at 1000°C within 20 minutes. The lower reactivity of Si<sub>3</sub>N<sub>4</sub> compared to SiC with molten Na<sub>2</sub>SO<sub>4</sub> was reported by Fox and Jacobson [29] to be due to the formation of an inner protective layer of silica that stops the continued reaction of Si<sub>3</sub>N<sub>4</sub>. The formation of this inner protective layer was highly dependent upon whether oxidation or dissolution was the faster mechanism. Sato et al. [33] reported that this inner protective layer of silica formed on pressureless sintered Si<sub>3</sub>N<sub>4</sub> containing 5 wt% Y<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> in contact with molten potassium sulphate at 1200°C when the tests were conducted in air but not when conducted in nitrogen. This same situation was not true for attack by molten potassium carbonate at 1013°C. In this case, attack occurred in both nitrogen and air, with air causing a greater degree of reaction. Compared to studies performed in molten sodium and lithium sulphate and carbonates, Sato et al. found that the corrosion rate, in a nitrogen atmosphere, was independent of the alkali present, with the sulphates yielding an activation energy of 430 kJ/ mol compared to that of the carbonates of 106 kJ/ mol.

The preceding examples illustrate essentially the chemistry for Na<sub>2</sub>O reactions with silica and silica-forming ceramics. They also indicate why carbon in a ceramic promotes corrosion [23, 28, 35, 36].

In addition to Na<sub>2</sub>O, other oxides can potentially attack the protective SiO<sub>2</sub> film. Sea salt leads to MgSO<sub>4</sub> and CaSO<sub>4</sub> deposits as well as Na<sub>2</sub>SO<sub>4</sub> deposits. This mixed sulphate can be described by molten salt solution models [37, 38] and leads to magnesium, calcium, and sodium silicates [39]. Many fuels contain vanadium impurities. V<sub>2</sub>O<sub>5</sub> is an acidic oxide and thus does not react directly with SiO<sub>2</sub>. However, it accelerates Si<sub>3</sub>N<sub>4</sub> oxidation, possibly due to the solubility of SiO<sub>2</sub> in V<sub>2</sub>O<sub>5</sub> [40]. Similar principles apply to molten slags, which are complex mixtures of oxides. Here it is more difficult to define basicity, however a useful index has been the weight percent ratio of basic oxides. These are the basic and acidic oxides commonly encountered [41]:

- Basic oxides: Na<sub>2</sub>O, K<sub>2</sub>O, MgO, CaO, Fe<sub>2</sub>O<sub>3</sub>
- Acidic oxides: SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>

The basic slags clearly degrade silica-forming materials more readily than the acidic slags. In a locally low partial pressure of oxygen, metal silicides may form [42].

It has been shown that molten salt-induced corrosion can lead to substantial attack of SiC and Si<sub>3</sub>N<sub>4</sub>. It is important to discuss the influence of this corrosion on microstructure and mechanical properties.

The strength loss of  $\alpha$ -SiC and siliconized-SiC tubes exposed to a combustion flame into which a sodium silicate/ water solution was injected was evaluated by Butt and Mecholsky [43]. The corrosive exposure was for times up to 373 hours, at temperatures from 900 to 1050°C, with an oxygen partial pressure of about 4 kPa. Strength losses exceeded 50% for the  $\alpha$ -SiC and were 25 to 45% for the siliconized-SiC. Strength tests were conducted on C-ring samples after most of the reaction products were removed. Those samples for which the reaction products were not removed prior to strength testing exhibited no significant loss of strength, although an increase in scatter of the data was reported. Surface or corrosion pits were identified as the fracture origin for both types of SiC. In addition the  $\alpha$ -SiC exhibited grain boundary attack, whereas the siliconized-SiC exhibited oxidation of the silicon matrix and attack of the large SiC grains.

In a study of the effects of molten salt upon the mechanical properties of silicon nitride, Bourne and Tressler [44] reported that hot-pressed silicon nitride exhibited a more severe degradation in flexural fracture strength than did reaction sintered silicon nitride, even though the weight loss of the hot-pressed material was less than that of the sintered one as reported by Tressler et al. [34] in a previous study.

In the application of ceramics to turbine engines, the static fatigue life is of prime importance. Compared to the other types of mechanical testing in corrosive environments, little work has been reported on the long time exposure effects to static fatigue life. Swab and Leatherman [45] reported that at stresses between 300 and 500 MPa, there was a significant decrease in the time-to-failure for Si<sub>3</sub>N<sub>4</sub> containing magnesia exposed to Na<sub>2</sub>SO<sub>4</sub> at 1000°C. At stresses above 500 MPa and below 300 MPa, little change in the time-to-failure was noted. Since the molten salt was not replenished during the test, corrosion pits were unable to grow to a size sufficient to decrease the time-to-failure at stresses levels between 300 and 500 MPa. Although the decrease in room temperature strength for a yttria-containing silicon nitride after exposure to sodium sulphate was about 35%, it retained a greater strength than the magnesia-containing material (549 MPa for the Y-containing material vs. 300 MPa for the Mg-containing material) [46]. Fox and Smialek [47] tested sintered silicon nitride in a simulated gas turbine rig where the corrosive environment was continued throughout the 1000°C/ 40 hr of the test. Room temperature MOR fracture origins were located at pits in 17 of 22 samples. Pit formation was attributed to gas evolution during the oxidation of the silicon nitride and subsequent reaction of the silica with sodium sulphate-forming a low viscosity sodium silicate liquid. Fracture stresses were on the order of 300 MPa after exposure.

Boron- and carbon-doped injected molded sintered  $\alpha$ -SiC sprayed with thin films of Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> were exposed to several gas mixtures at 1000°C for 48 hours by Smialek and Jacobson [27]. The gas mixtures used were 0.1%SO<sub>2</sub> in oxygen and 0.1%CO<sub>2</sub> in oxygen in combination with the sulphate or carbonate thin films, respectively. The sulphate covered sample was also exposed to pure air. The strength degradation was the most severe in the sulphate/ SO<sub>2</sub> exposure (49% loss in strength), intermediate in the sulphate/ air exposure (38% loss in strength), and the least in the carbonate/ CO<sub>2</sub> exposure. The latter exposure caused a statistically insignificant decrease in strength when analysed by Student's *t*-test. The primary mode of degradation was the formation of pits that varied in size and frequency depending upon the corrosion conditions. The size of the pits correlated quite well with the strength degradation (i.e., larger pits caused greater strength loss). Jacobson and Smialek [48] attributed this pit formation to the disruption of the silica scale by the evolution of gases and bubble formation. A proposed mechanism for this is illustrated in Fig. 1.

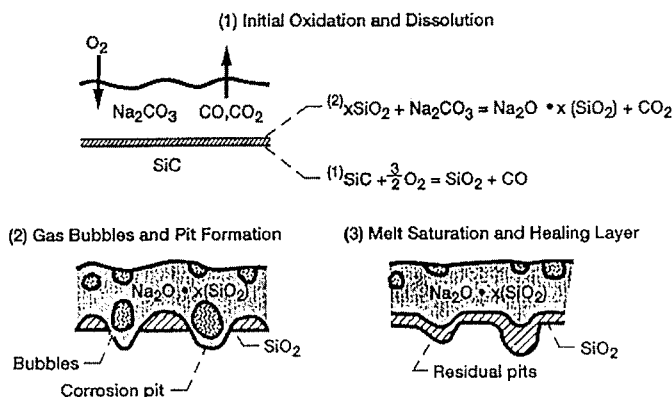


Figure 1 – Proposed pitting mechanism for SiC hot corrosion [48].

### 2.3 Superconductors

In an investigation of the molten-salt synthesis of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (123), Raeder and Knorr [49] reported the stability of 123 against decomposition towards several molten salts at 1173°K. They concluded that 123 was not stable in molten LiCl or the dichlorides of Cu, Ca, Mg, or Ba or their mixtures. However, minimum decomposition was found in the NaCl-KCl system. The mechanism of decomposition was postulated as being one of selective dissolution of the barium in 123 forming  $\text{BaCl}_2$  and causing the 123 to decompose into several oxide phases that were consistent with the phase diagram reported by Lee and Lee [50]. These oxide phases were generally CuO and  $\text{Y}_2\text{Cu}_2\text{O}_5$  or CuO and  $\text{Y}_2\text{BaCuO}_5$  depending upon the amount of barium in the initial mixture.

### 2.4 Zirconia-Containing Materials

Although a considerable amount of scatter existed in the data of Swab and Leatherman [45], they concluded that Ce-TZP survived 500 hours at 1000°C in contact with  $\text{Na}_2\text{SO}_4$  at stress levels below 200 MPa. At stress levels greater than 250 MPa, failure occurred upon loading the samples. Swab and Leatherman also reported a 30% decrease in the room temperature strength of Y-TZP after 500 hours at 1000°C in the presence of  $\text{Na}_2\text{SO}_4$ . This lowered strength for Y-TZP was probably due to leaching of the yttria from the surface, which caused transformation of the tetragonal phase to the monoclinic phase.

## 3. Preventing Corrosion

Minimizing corrosion of ceramics under molten salt conditions at high temperature is a very important task that requires an appropriate selection of materials, considering both intrinsic and extrinsic characteristics. It is therefore necessary to make the acid-basic character of the ceramic constituents similar to that of the corrosive liquids, and then to control the penetration-dissolution mechanisms to improve the corrosion resistance. Such improvement has been obtained through porosity and texture control resulting from the evolution in manufacturing processes toward much larger size distribution, better mixing, better pressing, and purer raw materials. Regarding porosity of high strength ceramics, various sintering and densification techniques have been developed, such as reaction-bonded sintering and hot pressing, using very pure, fully densified powder of very small grain size. For example, to achieve full density,  $\text{Si}_3\text{N}_4$  an Si C can be impregnated, either with an organo-silicon compound that is subsequently decomposed to produce a pore-filling oxide, or with a material that is subsequently exposed to a nitriding or a carburizing treatment.

Once porosity has been adjusted to its optimal value, penetration can be reduced by composition adjustment of the penetrant liquid, changing the wetting characteristics, adjusting the thermal gradient, and use of glazing or coating. Careful selection of the matrix additives can change the melting temperature or viscosity of the liquid penetrant, minimizing the depth of penetration [51]. By using highly conductive material, and by increasing the thermal conductivity of the lining by conductive back up material, it is possible to oblige the penetrant liquid to solidify as closely as possible to the hot face, so that the rate of penetration is minimized [52-54]. Simple heat pretreatments to establish a silica scale of sufficient thickness before exposure to hot corrosion can be used to give protection to silica formers [55]. Glazing or coating the working face, or in some specific cases the back or cold face when oxidation of non-oxide constituents is important, is another factor governing penetration.

There are a number of important considerations in the application of a coating. The first is a good match between coefficients of thermal expansion (CTEs) and the substrate. Table 1 lists CTEs for SiC, Si<sub>3</sub>N<sub>4</sub>, and several refractory oxides. Note the remarkably close match of SiC and mullite. Mullite coatings on SiC were first developed by researchers at Solar Turbines [56] and further refined at the NASA Research Center [52, 53]. Critical issues are substrate surface roughening for adherence and application of fully crystalline mullite.

Table 1 – Coefficients of thermal expansion for silica-forming ceramics and several refractory oxides [52].

| Material                                                                                | CTE (10 <sup>6</sup> K <sup>-1</sup> ) |
|-----------------------------------------------------------------------------------------|----------------------------------------|
| SiC                                                                                     | 5.2                                    |
| Si <sub>3</sub> N <sub>4</sub>                                                          | 3.2                                    |
| Mullite (3Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> )                           | 5.4                                    |
| Alumina (Al <sub>2</sub> O <sub>3</sub> )                                               | 9                                      |
| Partially stabilized zirconia<br>(0.09Y <sub>2</sub> O <sub>3</sub> ·ZrO <sub>2</sub> ) | 10                                     |

Mullite-coated SiC exhibits substantially improved behaviour in Na<sub>2</sub>SO<sub>4</sub>-induced corrosion as compared with uncoated SiC [57]. This is due to the formation of higher melting sodium-alumino-silicates. However, in time, sodium penetrates the mullite coating and forms sodium silicate at the mullite/ SiC interface. In the case of water vapour containing environments, mullite coatings offer limited benefits as the silica activity is only 0.4. Hence silica is readily volatilised from mullite by water vapour [52, 53].

Dissolution of ceramics is controlled by both the chemical reactivity and the specific area of the constituents: the smaller the grains, the faster they dissolve; but in ceramics, the smallest grains, by design, bond with the coarser grains (the aggregate), and since this bonding occurs by liquid-solid sintering, the matrix materials (the bonding phases) have the lowest melting temperatures and the highest reactivity. In general, the dissolution of the bonding phases (or the matrix) leads to debonding between the coarser grains, the dissolution of which is inherently slower and usually apparent only at the refractory hot face.

To minimize dissolution of the matrix, the composition can be altered to raise its melting temperature by increasing the chemical purity of the matrix, so as to decrease the importance of segregated impurities. Alternatively, to raise the melting temperature of the matrix, finely powdered matrix additives can be included in the refractory mix. Because the matrix is a flux in sintering, these additions require higher sintering temperatures, to optimise the bonding and the mechanical properties of the resulting products. The logic of reducing or eliminating additives of low melting temperature for improved corrosion resistance is compelling, but the consequence is that the sintering temperature must be raised [58-60].

#### 4. Summary

As high-strength ceramics find more applications in high temperature systems, molten salt corrosion at high temperatures becomes an important field of study. In this chapter, some key issues in this domain have been surveyed. Oxide and non-oxide ceramics, apart from other technical ceramics, have been considered. Most of the literature covers silica formers since there are a number of near-term applications for them. Salt-induced corrosion mechanisms were discussed for silica-forming ceramics. Further information is also given on the routes to test and minimize the reported corrosive degradation.

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## Corrosion of Ceramic and Cermet Inert Anodes for Use in Aluminium Electrolysis

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**Keywords:** Aluminium Electrolysis, Corrosion of Inert Anodes, Inert Anodes

### Abstract

The present work gives a short literature review concerning the corrosion of oxygen-evolving so-called inert anodes for use in the electrolysis of cryolite-alumina melts. Two systems were chosen as examples, i.e. tin oxide and a nickel ferrite cermet. These materials corrode by dissolution of the constituent oxides into the electrolyte or by reacting with the dissolved metal in the electrolyte, with subsequent deposition at the cathode, contaminating the aluminium produced. It is important to reduce the metal contamination and to prolong the life of the anodes. Selected results are given for corrosion rates as a function of the concentration of alumina, aluminum fluoride as well as the effect of the anode potential. At potentials below the decomposition potential of alumina, the anode is attacked by aluminium dissolved in the electrolyte. During normal electrolysis, the regular dissolution process predominates, while at very high potentials so-called “catastrophic corrosion” takes over, due to decomposition of the constituent oxides of the anode. Furthermore, structural changes of the anode can occur. To protect inert anodes against corrosion, cerium compounds can be added to the electrolyte, whereby a protective layer of cerium oxyfluoride is deposited on the anode, resulting in substantially lower corrosion rates. Ways of improving the performance of inert anodes are discussed.

### 1. Introduction

The Hall-Heroult process for aluminium production uses consumable carbon anodes. For several reasons this is not the ideal solution. One reason is the high price of carbon anodes, which corresponds to about 15% of the production cost of aluminium. Also the production of carbon anodes from petroleum coke and pitch is a process that consumes energy (about 1 kWh/kg Al), emitting CO<sub>2</sub> and tar fumes.

Moreover, the electrolysis of cryolite-alumina melts using carbon anodes produces a large quantity of greenhouse gases in the form of CO<sub>2</sub> and perfluorocarbons (particularly CF<sub>4</sub>). At present the entire aluminium industry in the world emits into the atmosphere a quantity of 40 million metric tons of greenhouse gases (CO<sub>2</sub> equivalents).

The primary cell reaction in the electrolysis with carbon anodes is [1],



Some CO may also form. The following secondary reaction takes place,





In addition, the carbon anodes represent an important source of impurities, which to a large extent pass into the aluminium metal, lowering the quality of the metal.

Reaction (1) and the reoxidation reaction of aluminium dissolved in the melt,



lead to an increase in the consumption of carbon anodes and of electrical energy.

Due to these disadvantages efforts are being made to find new materials, that can serve as oxygen-evolving, inert anodes, replacing the carbon anodes. The primary cell reaction when using inert anodes is,



for which  $\Delta G^\circ = 1264 \text{ kJ at } 1300 \text{ K}$ .

The reversible potential for this reaction at  $980^\circ\text{C}$  is approximately 2.2 V, compared to 1.2 V for the case of carbon anodes (Eq. 1). This potential difference of 1 V can partly be compensated due to the fact that the anodic overvoltage on inert anodes is about 0.1 V [2], as against 0.5 - 0.6 V on carbon anodes [1]. Moreover, inert anodes can be operated at a substantially shorter interpolar distance than carbon anodes, and in this way the electrical energy consumption can be lowered by 23% [3]. This requires a cell that is very well insulated with respect to heat losses.

If the use of inert anodes is combined with that of inert cathodes, a 32% [3] reduction in electrical energy consumption can be achieved. Inert cathodes are prepared from titanium diboride ( $\text{TiB}_2$ ) or  $\text{TiB}_2$  - carbon composites, which are wetted by liquid aluminium. Inert anodes and cathodes can be used together in a so-called "drained cell", where the aluminium deposited at the cathode forms a thin film from which it is drained into a storage pool. This cathode is a solid covered by a thin liquid film, in contrast to the deep pool of aluminium serving as cathode in Hall-Heroult cells.

Ideally, desirable properties of inert anodes are the following [1,4,5,6,7]:

- low solubility in molten cryolite-alumina mixtures at about  $980^\circ\text{C}$ ,
- resistance towards the oxygen produced at the anode,
- thermal stability up to  $1000^\circ\text{C}$  with adequate thermal shock resistance,
- high electronic conductivity,
- negligible ionic conductivity,
- resistance toward fluorination (the oxides must not react with fluorides in the electrolyte),
- good mechanical strength,
- easy to make electrical connections,
- readily fabricated into the right shapes and sizes,
- non-polluting in manufacture, use and disposal,
- acceptable contamination of the aluminium produced,
- economically attractive.

Over the years many materials have been proposed as inert anodes, and the most promising have proved to be metallic oxides and cermets. Generally pure metallic oxides have a high electrical resistivity, and in addition they sinter with difficulty. Additions of other oxides as dopants have been tested to overcome these disadvantages. In this way the sintering temperature could be lowered, and ceramic masses with high mechanical resistance, high electrical conductivity and also acceptable corrosion resistance were obtained [4]. Cermets are materials prepared by mixing powders of oxides with metallic powders (alloys), to be sintered in inert atmosphere.

Although many studies of the use of inert anodes for aluminium electrolysis have been made in universities, research institutes and companies, these materials have not yet been used in commercial cells. This is due to the fact that materials with acceptable corrosion resistance and ways to operate cells with inert anodes have not yet been found.

## 2. Corrosion of inert anodes

The corrosion mechanism of inert anodes during electrolysis in cryolite-alumina melts is very complex and it depends to some extent on the ceramic material used. There are several processes that finally can lead to the corrosion and destruction of inert anodes.

First of all the constituent oxides of inert anodes should have a low solubility in cryolite-alumina melts in order to achieve a high corrosion resistance. The solubility of some oxides in cryolite-alumina melts is given in Table 1 [8].

Table 1. Solubility of various oxides in molten cryolite and in cryolite-alumina mixtures at around 1010°C [8].

| Oxide                          | Solubility in cryolite (wt%) | Solubility in cryolite + 5wt% Al <sub>2</sub> O <sub>3</sub> | Solubility in cryolite + Al <sub>2</sub> O <sub>3</sub> (sat) | References |
|--------------------------------|------------------------------|--------------------------------------------------------------|---------------------------------------------------------------|------------|
| Cu <sub>2</sub> O              | 0.38                         | 0.23                                                         | 0.34                                                          | /9/        |
|                                | 0.28                         |                                                              |                                                               | /10/       |
| ZnO                            | 2.9                          | 0.17                                                         | 0.025                                                         |            |
| FeO                            | 5.6                          | 3.0                                                          | 0.30                                                          | /11/       |
|                                | 5.5                          |                                                              |                                                               | /12/       |
|                                | 5.4                          |                                                              |                                                               | /13/       |
| NiO                            |                              | 0.08                                                         | 0.0076                                                        | /14/       |
|                                | 1.0                          | 0.09                                                         |                                                               | /9/        |
| CuO                            | 0.41                         | 0.44                                                         | 0.56                                                          | /15/       |
| Co <sub>3</sub> O <sub>4</sub> | 1.1                          |                                                              |                                                               | /10/       |
| Cr <sub>2</sub> O <sub>3</sub> | 7.3                          |                                                              |                                                               | /12/       |
| Fe <sub>2</sub> O <sub>3</sub> | 0.70                         | 0.23                                                         | 0.22                                                          | /9/        |
|                                | 0.8                          | 0.4                                                          |                                                               | /16,17/    |
| TiO <sub>2</sub>               | 5.6                          |                                                              | 4.45                                                          | /9/        |
|                                | 5.2                          |                                                              |                                                               | /18/       |
| ZrO <sub>2</sub>               | 3.2                          |                                                              |                                                               | /9/        |
| SnO <sub>2</sub>               | 0.05                         | 0.015                                                        | 0.01                                                          | /19/       |
| CeO <sub>2</sub>               | 3.4                          | 1.0                                                          | 0.6                                                           | /20/       |

It is seen from Table 1 that practically all oxides have a finite solubility in cryolite-alumina melts, and this must be taken into account when selecting ceramic materials for inert anodes.

The dissolution of oxides in the electrolyte can be described as an exchange reaction with cryolite or aluminium fluoride in the electrolyte, as for example,



The dissolved species are metal cations, or metal fluoride or oxyfluoride anions. For reaction (5) it is seen that a decrease in the Al<sub>2</sub>O<sub>3</sub> activity increases the solubility. The activity of

the dissolved compound ( $\text{NiF}_2$ ) would in this case be inversely proportional to the activity of alumina to the one-third power [14].

Other dissolution reaction of the oxides used for inert anodes is:



$$\Delta G_{980^\circ\text{C}}^0 = 115 \text{ kJ/mol}$$

The oxides in the anode may in certain cases react with dissolved aluminium in the electrolyte according to the reaction,



Reaction (7) shows the formation of the metal Me which is dissolved in aluminium pool. If alumina is more stable than the anode oxide, then the equilibrium of reaction (7) will be shifted to the right.

It is interesting to see what happens with a metal oxide once it has dissolved in cryolite. The metal can be electrodeposited at the cathode, passing into the aluminium product. The total reaction is,



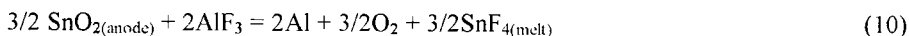
For all the compounds listed in Table 1, reaction (8) will go to the right as long as reaction (4) is occurring.

The metal ions can also be reduced in contact with the molten aluminium through the following type of reaction,

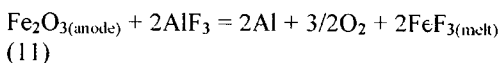


Thermodynamic data for reactions (5) – (9) have been given by McLeod et al. [21].

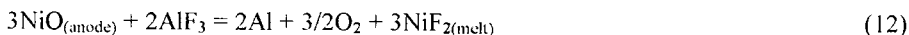
A special type of corrosion was observed by Wang and Thonstad [22] and by Xiao et al. [23], which was called “catastrophic corrosion”. This takes place at low alumina concentrations or at high current densities. In that case reactions of the following type take place,



$$E_{1020^\circ\text{C}}^0 = -2.50 \text{ V}$$



$$E_{1027^\circ\text{C}}^0 = -2.21 \text{ V}$$



$$E_{1027^\circ\text{C}}^0 = -2.32 \text{ V}$$

Details about this type of corrosion, which also has been named fluorination [22], will be given later.

Evans and Keller [24] suggested that the corrosion rate ( $r$ ) is mass transfer controlled.

$$r = k_A (c_{sat} - c_b) A_A = k_C c_b A_C \quad (13)$$

where  $k$  and  $A$  are mass transfer coefficients and surface areas of anode (subscript A) and cathode (subscript C) respectively, and  $c_{sat}$  and  $c_b$  are the saturation and bulk concentrations of the corrosion product. The rate of the dissolution depends on the mass transfer coefficient at the electrode and on the saturation concentration. Because the mass transfer coefficient at a gas-evolving electrode will be much higher than at the relatively stagnant cathode surface, the concentration in the bath ( $c_b$ ) should be fairly close to the saturation concentration. Table 1 shows that the saturation concentration ( $c_{sat}$ ) of oxides is low in electrolytes with high alumina contents. It will be also beneficial for the anode life to make the cathode area as small as possible. The implications of this model have been discussed by Keller et al. [25]. The model has been tested on a laboratory scale, but the results are somewhat inconclusive [26].

A remarkable method to reduce the corrosion of inert anodes is the application of cerium oxide, which forms a protective layer on the anode surface. The way of forming such a protective layer, and the way it acts will be treated later.

In the open literature most works on the corrosion of inert anodes have been centred on two materials; one is tin oxide ceramics and the other is a nickel ferrite- copper cermet. In the following, corrosion studies made on these types of anodes are presented.

### 3. Corrosion of $\text{SnO}_2$ – based anodes

$\text{SnO}_2$  – based inert anodes can have the following composition:  $\text{SnO}_2 + 1\text{-}2\% \text{ Sb}_2\text{O}_3 + 1\text{-}2\% \text{ CuO}$ . Corrosion studies made on these anodes have shown that the corrosion rate depends on the alumina concentration in the electrolyte, the cryolitic ratio CR (molar ratio  $\text{NaF}/\text{AlF}_3$ ), the anode potential and the current density.

In a series of patents, Alder [27] claimed that the corrosion can be substantially reduced if the current density is higher than  $0.025 \text{ A}\cdot\text{cm}^{-2}$  all over the anode surface. In this way, the oxygen formed by electrolysis protects the anode against the attack of aluminium dissolved in the electrolyte. Xiao et al. [28,29] found that the corrosion rate of tin oxide anodes decreased with increasing alumina concentration in the electrolyte, as shown in Fig. 1, [28,29]. At alumina concentrations lower than 1.5 wt%, so called “catastrophic corrosion” took place, while at alumina concentrations higher than 5 - 6 wt%, the corrosion decreased to acceptable levels.

Xiao et al. [28,29] also studied the corrosion rate as a function of the cryolite ratio (CR), and the results are presented in Fig. 2. A minimum in the corrosion rate at  $\text{CR} \approx 3$  is noticed, and this could be explained by the fact that at this electrolyte composition, the alumina solubility is at its maximum [1].

Furthermore, Xiao et al. [28,29] investigated the dependence of the corrosion rate on the anode potential. As shown in Fig. 3, a minimum in the corrosion rate was observed at a potential of about 2.1 - 2.3 V versus aluminium, indicating that the corrosion mechanism may be different at different potentials. One of these mechanisms is chemical dissolution according to reaction (6).

 **LIVE GRAPH**  
Click here to view

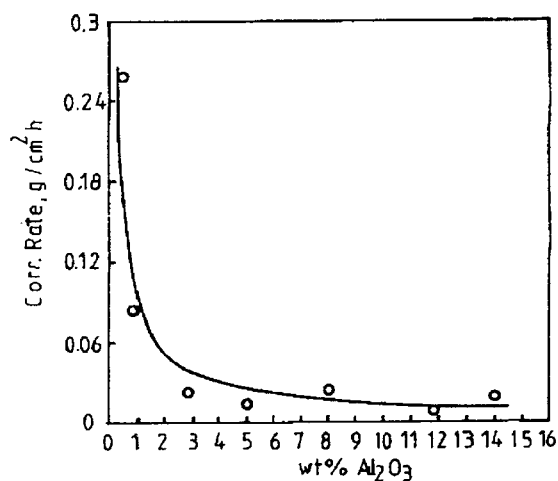


Fig.1 Corrosion rate of SnO<sub>2</sub>- based anodes at different alumina concentrations in Na<sub>3</sub>AlF<sub>6</sub>-Al<sub>2</sub>O<sub>3</sub> melts at 1030°C;  $\approx 0.8 \text{ A.cm}^{-2}$  [28,29].

 **LIVE GRAPH**  
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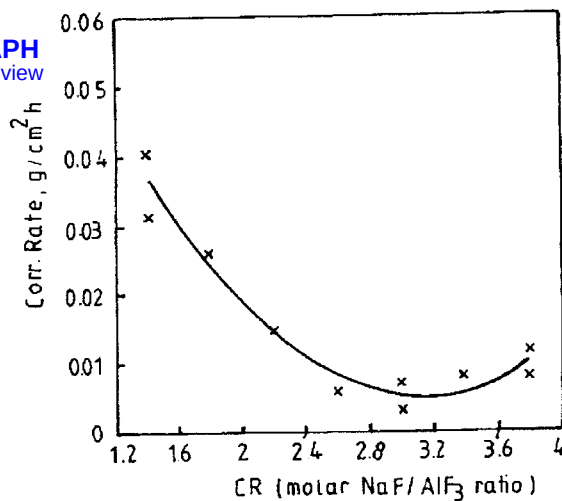


Fig.2. Corrosion rate of SnO<sub>2</sub>-based anodes versus the cryolite ratio in melts containing 4 wt% each of LiF, MgF<sub>2</sub>, CaF<sub>2</sub> and saturated with Al<sub>2</sub>O<sub>3</sub>;  $\approx 1 \text{ A.cm}^{-2}$  [28,29].

Another corrosion mechanism is the reduction by dissolved metal according to the reactions,



$$\Delta G_{980^\circ\text{C}}^0 = -533 \text{ kJ}$$



$$\Delta G_{980^\circ\text{C}}^0 = -265\text{kJ}$$

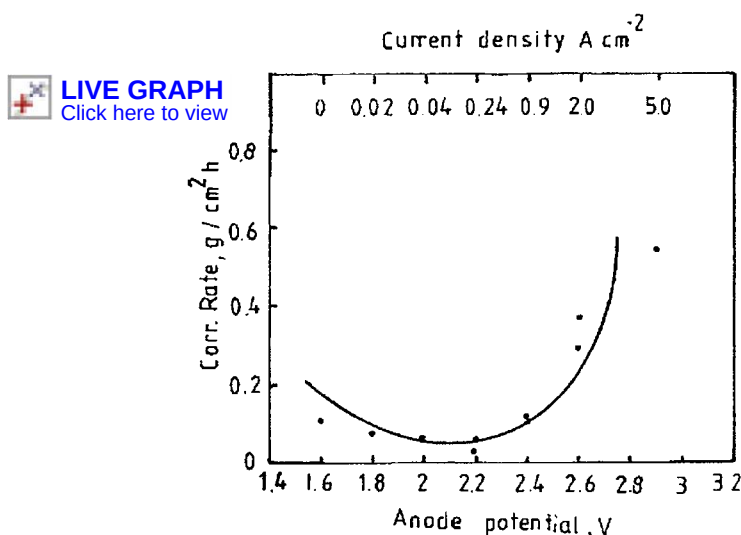


Fig.3. Corrosion rate of  $\text{SnO}_2$ -based anodes as a function of the anodic potential in the electrolyte:  $\text{Na}_3\text{AlF}_6 + 1\% \text{Al}_2\text{O}_3$  at  $1020^\circ\text{C}$  [28,29].

The reduction of  $\text{SnO}_2$  with aluminium dissolved in the electrolyte can take place in case the current density approaches zero, as mentioned above. In this case the dissolved aluminium can get into contact with the anode surface, and the anode oxides are reduced. The increase in the anode corrosion rate at anodic potentials below 2.2 V, shown in Fig. 3, can be explained in this way. During normal electrolysis, (at an anode potential of 2.2 – 2.4V) oxygen is present on the anode surface, and it will oxidise the dissolved aluminium in the electrolyte, thus lowering the corrosion rate.

In Fig. 3 a pronounced increase in the corrosion is noticed at anode potentials of 2.5 – 2.6 V. This effect, named “catastrophic corrosion” by the authors [22,28,29], is due to the fact that at this potential,  $\text{SnO}_2$  provides the oxygen for the anode reaction. Catastrophic corrosion occurs at low concentrations of alumina and at high current densities, and in this case reaction (10) takes place.

In pure molten cryolite, at current densities higher than  $0.3 \text{ A}\cdot\text{cm}^{-2}$ , reaction (10) will dominate, while in cryolite-alumina melts reaction (4) of alumina decomposition takes place. Hence, in melts with low contents of alumina a part of the current may be used for the decomposition of the anode.

It was also suggested [28,29] an intergranular corrosion, due to the dissolution of  $\text{CuO}$  in the electrolyte,  $\text{CuO}$  having a high solubility in the electrolyte (see Table 1). When  $\text{CuO}$  dissolves, pores or holes appear in the anode body, into which the electrolyte can penetrate.

Xiao [28,29] observed an anode corrosion rate of  $0.0025 \text{ g/cm}^2\cdot\text{h}$ , corresponding to an anode wear rate of about 3 cm/year (corrosion depth per year = corrosion rate  $\times 24 \times 365$  / anode density), in an electrolyte with the composition:  $\text{CR} = 2.5 + 5\% \text{CaF}_2 + \text{Al}_2\text{O}_{3(\text{sat})}$ , at a current density of  $0.64 \text{ A}\cdot\text{cm}^{-2}$  and at the temperature of  $980^\circ\text{C}$ . It has been recommended that inert anodes should corrode at a rate of less than 1 cm/year [30,31]. This rate of corrosion is acceptable from the point of view

of anode life, but it could still be unacceptable from the point of view of contamination of the aluminium.

The migration of copper to the exterior of the anode and its dissolution into the electrolyte, resulting in anode disintegration, was considered by Galasiu et al. [32,33] to be the main reason for corrosion of  $\text{SnO}_2$ -based anodes. The migration of copper was demonstrated by means of SEM studies. The dissolution of copper into the electrolyte leads to the destruction of the anode, because the copper contributes to the sintering of this ceramic material. By sintering  $\text{CuO}$  and  $\text{SnO}_2$  form a eutectic [34]. In this way a ceramic mass is obtained. If  $\text{CuO}$  is dissolved in the electrolyte, the ceramic mass will disintegrate.

#### 4. Corrosion of nickel ferrite cermet anodes

As mentioned above many types of inert anodes have been tested. One type was metallic anodes, but some of them were strongly corroded [35]. Other types were semiconducting ceramic anodes (like  $\text{SnO}_2$ -based anodes), which are more resistant to corrosion, but having a higher electrical resistance.

Materials that combine the properties of ceramics with those of metals are cermets. Those are prepared by adding metallic powders (alloys) to oxide mixtures before mixing and sintering. These materials have a high electrical conductivity due to the excess metal and a high corrosion resistance due to the ceramic material. At the beginning of electrolysis, the metal phase present at the surface is oxidised, protecting the metal in the interior from oxidation.

The method of preparing cermets consists in mixing powders of oxides, metals or alloys, pressing into the desired shape and sintering in an inert atmosphere to avoid metal oxidation. In particular, the following oxides have been used:  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{NiO}$  and the metals:  $\text{Ni}$ ,  $\text{Fe}$ ,  $\text{Cu}$  or their alloys. These oxides were chosen due to their low solubility in cryolite-alumina melts. It is important to obtain anodes of high density and low porosity, to increase their corrosion and erosion resistance during electrolysis. These materials, named cermets, have a more complicated structure than the  $\text{SnO}_2$ -based ceramics. For this reason the interpretation of corrosion data is more difficult.

Alcoa [36] proposed the use of a nickel ferrite anode with a copper addition, forming a cermet, and this material was studied extensively [37-41]. The material consisted of  $\text{NiF}_2\text{O}_4$  with an excess of 18%  $\text{NiO}$  and 17% metallic copper. For these anodes, as for  $\text{SnO}_2$ -based anodes, a decrease in the corrosion rate was observed with increasing alumina concentration in the electrolyte, as seen in Fig. 4 [28,29]. This variation in the corrosion rate could be explained by the fact the solubility of nickel ferrite decreases with the  $\text{Al}_2\text{O}_3$  concentration [14].

Tarcy [39] studied systematically the corrosion and passivation of several types of cermet anodes as a function of the composition of the metal phase. During electrolysis of anodes with a copper metal phase, the copper was covered with a passivating film, as noticed by Tarcy [39]. By X-ray diffraction this film was found to be composed of 60-70%  $\text{CuAlO}_2$  and 30-40%  $\text{Cu}_2\text{O}$ , which protected the metal from further oxidation.

Tarcy [39] found three important parameters that influenced the passivation of these anodes. First of all, the best structure was that of a cermet, not a metal. If metallic anodes are used, after a time of electrolysis, the passivating oxide that forms, has a tendency to spall off the surface. The ceramics in the cermet act as a mechanical barrier to spalling of the passivating layer.

Secondly, the metallic phase should be a  $\text{Cu-Ni}$  alloy, rich in copper. In this alloy nickel cathodically protects the copper. In this way, only a part of the alloy ( $\text{Ni}$ ) is oxidised and the major part ( $\text{Cu}$ ) is left unaltered. The oxidation potential of nickel is 1.5 V with respect to aluminum, while that of copper is 1.8 V vs  $\text{Al}$  [39]. Upon oxidation, nickel forms  $\text{NiO}$ , which remains in the bulk of the anode, plugging its pores, and due to the small quantity of electrolyte getting into the pores,  $\text{NiO}$  is not attacked by the electrolyte. This was confirmed by SEM studies.

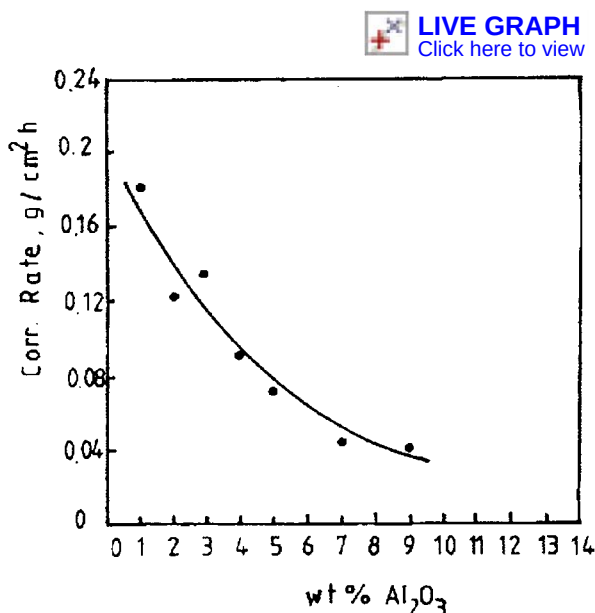


Fig. 4. Corrosion rate of cermet anodes as a function of the alumina concentration in a melt with CR = 2.3 + 5% CaF<sub>2</sub>; t = 980 °C; i = 1.0 A.cm<sup>-2</sup> [28,29].

Tarcy [39] noted that the third requirement for passivation is a high concentration of Al<sub>2</sub>O<sub>3</sub> in the electrolyte. The explanation was found by means of X-ray diffraction studies, showing that it develops a protective layer consisting of 60 - 70% CuAlO<sub>2</sub> and 30 - 40% Cu<sub>2</sub>O. Tarcy [39] found that the corrosion current was lower than the detection limit for a cermet anode with the alloy composition 80wt%Cu + 20wt%Ni. The corrosion current was the current passing through anode at potentials below the potential of oxygen evolution. This type of anode was claimed to be very resistant to corrosion.

Windish et al. [40] studied copper anodes and cermet anodes containing copper. By means of cyclic voltammograms these authors found that a Cu<sub>2</sub>O layer was formed on the copper surface by oxidation, and subsequently the Cu<sub>2</sub>O reacted with alumina in the electrolyte, forming CuAlO<sub>2</sub> in the exterior part of the oxide layer, but not at the metal surface. From these observations the authors concluded that CuAlO<sub>2</sub> did not play any role in anode passivation, being only a reaction product between Cu<sub>2</sub>O and alumina.

Peterson et al. [42] and Strachan et al. [43] carried out pilot cell studies of inert anodes prepared from a cermet NiFe<sub>2</sub>O<sub>4</sub> + NiO + 17%Cu. After electrolysis it was observed that on the part of the anode surface that had been immersed in the electrolyte, the copper was oxidised to Cu<sub>2</sub>O, while CuO was formed above the electrolyte. Likewise, on the anode surface below the bath the formation of two compounds, CuAlO<sub>2</sub> and CuAl<sub>2</sub>O<sub>4</sub>, was observed by reaction of the copper oxides with the electrolyte. Inside the metal phase of the cermet an increase of the copper concentration and a decrease of the nickel concentration were observed. It was not clear whether the oxidising agent was oxygen or a species from the electrolyte and whether diffusion of the oxidising agent or diffusion of nickel from the alloy was rate limiting.

Olsen et al. [44-47] studied the performance of anodes made of nickel ferrite/nickel oxide-copper cermets during electrolysis in cryolite-alumina melts. The compositions used were NiFe<sub>2</sub>O<sub>4</sub> with additions of various proportions of NiO (0 - 23 wt%). The metallic phase was made from 17%



Cu+3% Ni. Nickel was added because it is well wetted by the oxide phases, and in this way smaller metal grains were obtained after sintering.

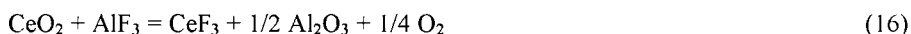
After electrolysis, SEM studies showed that the material seemed to have worked very well as there were no visible structural changes when going from the undisturbed interior of the electrode to the surface [45]. On all anodes a dense all-oxide layer was formed on the surface, being about 50  $\mu\text{m}$  thick. The Ni content in the metallic phase decreased gradually from the interior of the anode to the interface. The data suggest that Ni is transferred preferentially to the electrolyte through the structure, since the compositions of both oxide phases did not exhibit any significant changes [45].

It was noted [46] that at the beginning of electrolysis, metal grains directly exposed to the electrolyte were dissolved. A meta-stable all-oxide outer layer was formed which seemed to dissolve slowly, inhibiting selective dissolution of the underlying metallic grains. The total concentration of impurities in aluminium due to anode corrosion was 0.116 wt%. The anodes studied by Olsen et al. [44-47] had a low corrosion rate, corresponding to 1.2 – 2.0 cm/year.

Blinov et al. [48,49] prepared cermet anodes of the type Ni-Fe-Cu-O with various compositions and tested the corrosion resistance at different electrolysis conditions. For the purpose of reducing the corrosion rate, the authors worked with an electrolyte containing  $\text{BaF}_2\text{-NaF-AlF}_3\text{-Al}_2\text{O}_{3(\text{sat})}$  at 800  $^\circ\text{C}$ . Under these conditions, the corrosion rate was 1.4 – 2 cm/year, while the corrosion rate at 950  $^\circ\text{C}$ , was 11 cm/year.

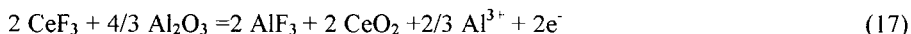
### 5. Reduced corrosion by means of a Cerrox coating

The Moltech Company [50, 51] has shown that a layer of bluish colour, consisting of a tetravalent cerium oxyfluoride,  $\text{CeO}_x\text{F}_y$ , is formed on a ceramic inert anode, if trivalent cerium or  $\text{CeO}_2$  is added to cryolite-alumina melts. This coating that was named “Cerrox”, reduced substantially the corrosion rate of inert anodes during electrolysis [7,52,53]. If  $\text{CeO}_2$  is added to the electrolyte, it reacts according to [7,52,53],



$\text{CeF}_3$  is soluble in cryolite-alumina melts, while  $\text{CeO}_2$  is not [7,52,53,54]. In the electrolyte  $\text{CeF}_3$  is complexed to  $\text{Na}_2\text{CeF}_5$  [54,55].

The anodic deposition of a layer of Cerrox, written as  $\text{CeO}_2$  for the sake of simplicity, probably takes place according to the following reaction,



The deposition of  $\text{CeO}_2$  could also take place by a chemical way in the presence of oxygen,



The standard Gibbs energy for reaction (18) at 1300 K is 590 kJ, and the emf for this reaction is –3.06 V [52]. The anodic deposition of  $\text{CeO}_2$  takes place simultaneously with the decomposition of alumina (reaction (4)). This data seems to indicate that reaction (18) should not take place. However, the  $\Delta G$  of reaction (18) depends on the activity of  $\text{AlF}_3$  in the electrolyte. Thus, at an  $\text{AlF}_3$  activity lower than  $10^{-2}$ , at normal potential of the oxygen deposition,  $\text{CeO}_2$  deposition on the anode becomes thermodynamically feasible [52]. In very acid melts, with high  $\text{AlF}_3$  activity, deposition of  $\text{CeO}_2$  probably does not take place [52].

The thickness of the anodic Cerox layer increases with increasing current density and increasing cerium concentration in the electrolyte [52,53]. Protection against anode corrosion should be effective if the entire anode surface is covered with a Cerox layer.

In the case of a  $\text{SnO}_2$ -based anode Walker et al. [52] established that the aluminium produced was contaminated with 0.52% Sn when  $\text{CeO}_2$  was not introduced into the electrolyte. When 1.5%  $\text{CeO}_2$  was introduced into the electrolyte, the aluminium contamination with Sn was reduced to 0.03%. That means that the concentration decreased by approximately twenty times in the best case.

The disadvantage of adding cerium compounds to the electrolyte is that cerium contaminates the aluminium in proportions of up to 2% Ce. Therefore, the aluminium must be purified and the cerium recycled to the electrolyte [56]. Another disadvantage is the fact that the Cerox layer has a high electrical resistivity [57,58,59], and thus the anode resistivity and the consumption of electrical energy may increase. Furthermore, the Cerox coating is not absolutely dense, so some corrosion of the underlying substrate will occur. One more problem is to control the thickness of the Cerox deposit.

Systematic studies of the behaviour and corrosion resistance of cermet inert anodes coated with Cerox were made by Gregg et al. [58]. A cermet,  $\text{NiFe}_2\text{O}_4$  -  $\text{NiO}$  -  $\text{Cu}$ , was tested by electrolysis in the laboratory, with and without a Cerox coating. It was established that the best coatings were formed and the least corrosion occurred at a cryolite ratio of 3.2 and at a current density of  $1.3 \text{ A.cm}^{-2}$ . Corrosion data for cryolite ratios from 2.8 to 3.4 at a current density of  $1.3 \text{ A.cm}^{-2}$  are given in Fig. 5, showing minimum corrosion at CR 3.0 to 3.2. An anode not coated with Cerox, electrolysed under the same conditions, showed a total contamination of 1.87 wt% Fe, 1.95 wt% Ni, 1.3 wt% Cu (total concentration of 5.11 wt% in the aluminium). An anode with a protective layer of Cerox gave a contamination of 0.25 wt% Fe, 0.20 wt% Ni, 0.28 wt% Cu (total concentration of 0.73 wt% in the aluminium). These results imply that the Cerox coating reduces the total corrosion by seven times. Gregg et al. [58] also observed that the lowest corrosion rate was obtained in an electrolyte saturated with alumina, and the corrosion rate increased with decreasing alumina concentration.

SEM studies [58] showed that after electrolysis there was a layer with a thickness of 200-1100  $\mu\text{m}$  under the Cerox layer. In this layer Cu was depleted. In the interior of the anode there was another layer, 0.5 to 20 mm thick, in which Cu was oxidised, probably to  $\text{Cu}_2\text{O}$ . Farther inward metallic Cu was present. The layer in which copper was oxidised, showed a high porosity. This layer was thicker the higher the current density; the cell potential also increased with the thickness of this layer.

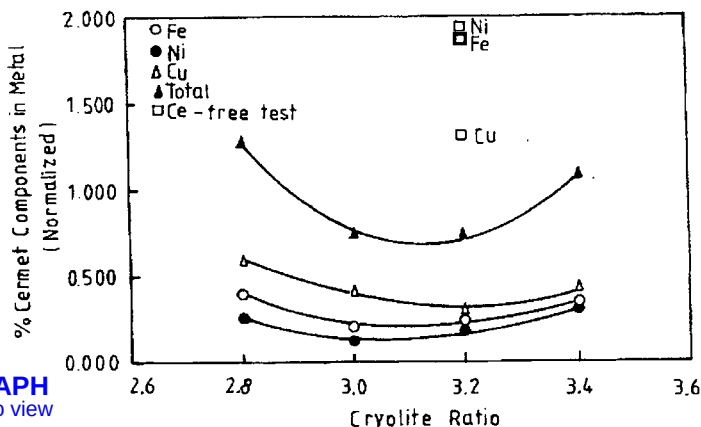


Fig. 5. Corrosion of Cermet as a function of CR at  $1.3 \text{ A.cm}^{-2}$  [58].

By means of SEM studies it was observed that the Cerox layer obtained at a cryolitic ratio of 2.8, had an uneven thickness, and it was discontinuous. A certain corrosion of the cermet was also observed. In contrast, the Cerox layer obtained in an electrolyte with a CR of 3.2, was dense with a uniform thickness. Corrosion of the cermet underneath the Cerox layer was very low. Anodes not coated with Cerox corroded much more strongly than those coated.

Gregg et al. [59] also made pilot cell tests of cermet anodes coated with a Cerox layer. Firstly, due to the large dimensions, the anodes cracked due to thermal shock. Secondly, the Cerox layer was not uniformly deposited on the entire anode surface, and hence the protection against corrosion was not satisfactory. The conclusion was that the corrosion was much more severe in the pilot cell than in the laboratory cell.

## 6. Conclusion

This chapter gives a short review of research on inert anodes for the electrolysis of cryolite-alumina melts concerning corrosion problems and ways to reduce the corrosion. The final purpose of such research is to obtain a material that can resist the conditions in aluminium electrolysis cells for long times. In this way a new technology for making aluminium could be developed, showing less pollution, higher efficiency and a low energy consumption. So far this objective has not been achieved, in spite of all research efforts. However, there are still prospects that it will be possible to develop an acceptable inert anode material.

Firstly, it should be possible to find new materials, with other compositions, that could be used for inert anodes. Also, the quality and the way of preparing ceramics should be improved. Up to the present, one has used the fabrication technology used for common ceramic materials to prepare inert anodes, and it is seen from the treatment above that this approach did not give very good results. Improved ways of preparing inert anodes could probably give materials of higher quality. Furthermore, the geometry of the electrolysis cell may play an important role in reducing the corrosion of inert anodes. This is demonstrated by the fact that, generally, the corrosion rate has been much higher in pilot cells than in laboratory cells.

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## Corrosion of Refractory Materials by Molten Glass

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**Keywords:** Ceramics, Corrosion, Metals, Molten Glass

**Abstract.** The purpose of this work is to look into the chemical and electrochemical degradation phenomena of metal and refractory ceramic materials used in the industrial procedures to produce glass when in contact with molten glass.

### Introduction

The use of glass is as remote as ancient times and it has always raised an enormous technological interest. The use of glass varies from the most common objects of every daywear to its use in new composite materials that put together good mechanical, optic and non-corrosive properties.

The recent growth of the glass industry created the need to produce glass in a cheaper way and with better quality. So, those needs lead, obviously, to scientific investments in two areas: the use of better raw materials especially concerning the chemical content of impurities and the use of materials resistant to the corrosion phenomena at high temperatures, that by nature involve molten substances and gases which are aggressive.

Large ranges of refractory materials with a traditional use in high temperature procedures such as ceramic materials have been well used in glass industry. However, knowledge of the corrosion mechanisms of the materials in use – metals and ceramic - appears with great importance, so that a correct selection and use of these materials can be made.

This work does not intend to make an exhaustive bibliographical presentation. It brings up the subject within a non-corrosive prospective that may lead us to understand the environment – material – corrosion triangle. So, after a brief chemical analysis of the main substances involved in the glass producing procedures and its operating conditions (environment), in the following sections we will look into the different materials used in the glass industry (material) and its degradation (corrosion).

### Glass Production

**Types of Glass.** Glass is an inorganic material produced at high temperatures that in the solidification process does not crystallize. Then the material presents an amorphous structure without a regular and repeated order. It has such a high viscosity that it can be considered as rigid. It is common to call “glass” to the material resulting from fusion and solidification of silica ( $\text{SiO}_2$ ). However, different materials can exist in vitreous state especially boron ( $\text{B}_2\text{O}_3$ ), germanium ( $\text{GeO}_2$ ) and phosphate ( $\text{P}_2\text{O}_5$ ) oxides.

Inorganic glasses are made of silicon oxide and are formed by  $\text{SiO}_4^{4-}$  units where a silicon ion  $\text{Si}^{4+}$  occupies the inside of a tetrahedron formed by four  $\text{O}^{2-}$  ions, which are connected with each other by its vertexes. In the crystalline silica the tetrahedrons are connected forming a regular structure. In a glass such regularity is not possible in a material extent. This difference is shown in figure 1.

Nevertheless, an enormous quantity of glasses can be obtained by introducing other substances (mainly oxides), which modify the basic structure of glass giving it new properties. As an example, the introduction of oxides from the first and second groups ( $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$ ) promotes the reduction of the molten glass viscosity facilitating the shaping procedure. That is due to the breaking of the connections between the tetrahedrons leaving the cations to compensate the electrical charge of the thread's interstices.

The introduction of intermediate oxides such as aluminium ( $\text{Al}_2\text{O}_3$ ) and lead ( $\text{PbO}$ ) oxides, promotes the stabilization of glass enabling it to resist to higher temperatures. The composition of most glasses is not fix and it has been changing trough the years and it depends on the used raw materials. Also, the quality of the raw materials is of influence in glass quality as if when good optic qualities are required.

The soda-lime glass is the type of glass most produced. In industry it is known by class A glass and its non-rigid composition is around 70-73%  $\text{SiO}_2$ , 12-14%  $\text{Na}_2\text{O}$ , 10-12%  $\text{CaO}$ , 1-4%  $\text{MgO}$  and 1%  $\text{Al}_2\text{O}_3$ . This type of glass is mainly used in laminate and compressed objects and blown recipients, such as bottles, jars, glasses, etc, where chemical and heat resistance is not required.

Borosilicate glasses (class E glass) have great resistance to thermic shock and chemical acid aggressions. Pyrex is an example of such glass, commonly used in laboratory equipments, pipes, etc. A typical composition has about 80%  $\text{SiO}_2$ , 12%  $\text{B}_2\text{O}_3$ , 4%  $\text{Na}_2\text{O}$ , 2%  $\text{Al}_2\text{O}_3$  and smaller percentages of  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{K}_2\text{O}$ . The presence of boron oxide in the glass structure leads to its weakness, producing a glass with less thermic expansion.

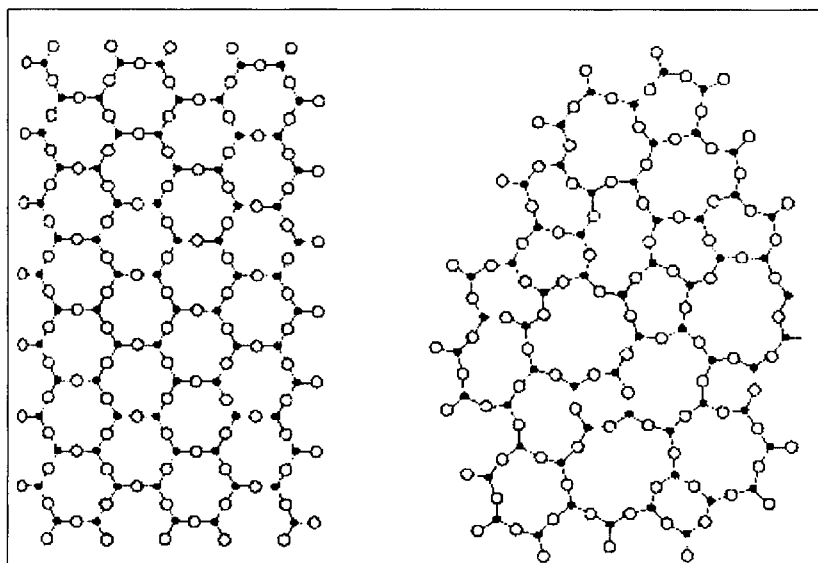


Figure 1 - Two dimensions schematic drawing of a crystalline silica crystal and of a silica glass [1].

Finally, flint glass, which has a PbO content, that may rise up to 60%. The obtained molten glass easily melts and it has good producing characteristics. Because of its high content of lead this kind of glass shows high refractory levels being used in optic instruments, X-ray filters and decorative "Crystal glass".

**Chemical Reactions.** Apart from the constitutive oxides there is also a big set of substances that generate a system of great chemical complexity. Those substances are mainly impurities belonging to raw material, such as iron oxide, manganese oxide, phosphorous oxide and water, etc. And, there are also substances that are introduced to facilitate the dissolution of raw materials, such as fluorides and sulphates. We must refer also to the introduction of carbonates such as  $\text{CaCO}_3$  (limestone) and  $\text{CaCO}_3 \bullet \text{MgCO}_3$  (dolomite) and of carbonaceous materials in order to reduce, for instance, the sulphates.

Some of the reactions verified in the molten glass, at a temperature between 1000-1500°C, form sodium, calcium and potassium silicates according to the following reactions, in the case of calcium and with different proportions between them:



Other relevant reactions provoke the formation of gases, namely carbon dioxide and sulphur oxide because of the decomposition of carbonates, sulphates and sulphites:



To release the existing gas ( $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{H}_2\text{O}$ ) the molten glass must remain for a while at high temperatures. This action relies on the viscosity of the molten glass.

As an example, we must say that in most technical glasses it is usual to get percentages of 0,4% of sulphur trioxide, leading to strong impacts if we consider the degradation of metal materials, as we will refer to later on this work.

**Materials.** The producing chain of a glass has three stages: mixture of the glass materials: conversion in the furnaces to obtain homogeneous molten glass and finally shaping. Shaping of glass may occur by different procedures like lamination, blowing, draining or pressing.

Concerning the materials used in the different parts of the equipment: in the melting phase (furnaces) the used materials are mainly ceramic refractory materials and as the temperatures go down in the procedure the metal materials have a preference. Nevertheless, there are a group of metal materials that are used in contact with molten glass, such as electrodes, parts of the mixture system, thermocouples, discharge pipes, molds, etc. And, these materials are also subjected to the corrosive action of the molten glass.

Cast materials are the materials with a larger application in the glass industry. Among these, cast irons, such as grey cast iron and alloys of iron and nickel, chromium and molybdenum are extremely used as structure materials and mould materials. There is also an enormous use of a set of steels, chromium and nickel alloys, as well as bronze and platinum in certain applications, and titanium, etc.

Kirsch has made a very complete study of the materials used in the glass industry [2].

One of the biggest difficulties of glass industry is the selection of materials to build the furnaces resistant to molten glass. Actually, most refractory ceramic materials that could be used in face of the temperatures reached in glass industry are strongly attacked by molten glass because they possess many of the materials that form glasses.



Most glass furnaces use neutral refractory materials, such as “clay” (fire clay, flux clay, duty clay); aluminium silicates hydrated with the general formula  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ; high alumina refractory materials with the general formula  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (mullite); it is also common to use chrome ( $\text{Cr}_2\text{O}_3$ ) refractory materials and alumina –silica – zirconia ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{ZrO}_2$ ), to be in direct contact with molten glass.

### Corrosion of the Refractory Ceramic Materials

The corrosion of refractory materials used in glass production is essentially a dissolution process along with a penetration process. Nevertheless, the corrosion of ceramic refractory materials is a complex procedure that involves chemical aspects such as: the dissolution phenomenon, electrochemical aspects, solid-gas reactions of oxide-reduction, physical and mechanical aspects, where the molten glass is transported, the absorption of chemicals and penetration are relevant [3-4].

On the other hand, next to the uniform corrosion of ceramic material there are frequently conditions to other localized phenomena like under stress corrosion, selective corrosion, corrosion in the glass line and intragranular corrosion, which lead to more complicated failures that will be further analysed.

To make a rigorous analysis of the corrosion process – as an interface process – it is required a characterization of the material structure, particularly its surface structure concerning porosity, the sides, impurity contents, degree of crystal, the size of the grains and its morphology. All these aspects are important to understand a certain failure provoked by corrosion and it always lead to a particular analysis of the problem. So, small variations in porosity in a certain refractory material lead to different corrosive performances when the material is at service. Like in every study on corrosion there is always the need to consider thermodynamic and kinetic aspects to have a correct evaluation of the process.

**Thermodynamics.** Concerning thermodynamics, one of the first aspects to consider is the chemical nature of the refractory materials shown in its acid or basic character. In fact, molten glass is formed by molten silica, which is a material with acid properties and so should be the contact materials in order to increase the resistance to corrosion. The relative acidity of some of the most relevant oxides in these systems is:



where the last ones show a basic character. Nevertheless, the solubility of refractory materials in molten glass and its stability may be obtained from phase's diagrams, which allow the knowledge of the saturation composition at a certain temperature [5-8].

Such diagrams also allow us to obtain information on the stability of the refractory material facing the working temperatures. Many of the working conditions of the refractory materials involve temperatures and pressures that might lead to the existence of a balance between the refractory in the solid state and in the liquid state. In such conditions, depending on the ratio liquid/solid, the material shows different non-corrosive properties, but it is clear that the formation of large quantities of liquid must be avoided inside the refractory.

An important aspect in the analysis of the corrosive process, in which the phase diagrams are a good help, is the formation of scales of reaction product that might present barrier properties and so, give some protection to the material.

This type of dissolution that forms surface layers is called heterogeneous dissolution or incongruent dissolution.

Finally, we must consider the chemical and structural changes that may occur with temperature variations like vitreous transition, decomposition of mixed oxides such as:



in the case of a silica – zirconium refractory.

Polymorph transformations (changes in the crystalline structure) may also occur with implications in the internal structure of the materials, changes of volume and densities and porosity variations.

**Kinetics.** Knowing that the degradation of refractory materials in molten glass involves essentially a process of dissolution of the material in the molten glass and the penetration of the liquid in the structure of the refractory material, the kinetics of the corrosive process is firstly controlled by the phenomena of mass transport.

It is frequent to the corrosive mechanism to involve both dissolution and penetration and that is called chemical invasion. In reality that corresponds to a selective corrosive process where one of the phases of the refractory material dissolves in a higher speed creating the conditions for the penetration of the melted liquid. Whenever there are penetration phenomena purely physical or related with selective corrosion, the viscosity and moistness characteristics of the liquid, the porosity of the refractory material are relevant to the kinetics of the corrosion. So, slightly viscous liquids like the silicate glasses inhibit penetration.

The dissolution process may be described by a kinetic equation like the one proposed by Berthoud [9], where a mixed control is admitted between the mass transport that is being dissolved in the melting phase and the kinetic process of dissolution:

$$j = \frac{K}{1 + \frac{K\delta}{D}} (C_{\text{sat}} - C_{\infty}) \quad (6)$$

K is the constant of the superficial speed of the dissolution reaction;  $\delta$  is the thickness of the boundary layer in the melting phase; D is the effective diffusion coefficient of the type that is dissolving in the melting phase and  $C_{\text{sat}}$  and  $C_{\infty}$  are the concentrations of the type on the surface undergoing corrosion and in the middle of the melting phase. If the chemical reaction is too rapid, that is, if K is much larger than  $D/\delta$  the process will be controlled by bulk/mass transport. When the chemical reaction is slower (if K is smaller than  $D/\delta$ ), the process will be controlled by the dissolution process.

In both cases, several authors have verified dependence between the speed of corrosion and the temperature, based on the Arrhenius equation [10-11]:

$$j = Ae^{\frac{E}{RT}} \quad (7)$$

Almost all refractory materials used in glass industry are composite materials because they are formed by different components. So, the dissolution process is never completely uniform because different components present different resistances to dissolution. The most important example of this type of corrosion is the alumina–zirconia-silica system, which is a refractory commonly used in the class A glass production furnaces – soda-lime glass and potassium-lime glass. This type of refractory is produced by fusion of oxides and presents a microstructure where we can find the several crystalline phases of zirconium, alumina and alumina with zirconium, and a vitreous phase (with about 15% in volume) that surrounds the crystalline phases. The corrosive mechanism involves in a first phase the diffusion of the sodium and potassium ions of the melting phase into

the vitreous phase of the refractory. This addition leads to the lower viscosity of the refractory vitreous phase creating the conditions to start with the dissolution of the crystalline phases. Especially, with alumina because the zirconium is not very soluble in this kind of glasses. The corrosive action of the sodium glasses is two or three times more intense than the potassium glasses [3].

Some authors presented the layer formation mechanism that in certain conditions may bring some protection. It is the case of the formation of nepheline crystalline layers ( $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ ) in soda-lime and leucite ( $\text{K}_2\text{Al}_2\text{Si}_4\text{O}_{12}$ ) glasses, and also in potassium-lime glasses. Nevertheless, in convection conditions these layers are easily eliminated which facilitates the corrosive process.

Next to the total corrosion of the refractory surface exposed to molten glass, or a selective attack, it is frequent to have better localized attacks. One of these cases occurs in the separation line between the molten glass and the surrounding atmosphere and it is known as the corrosion phenomenon of the glass line, where dissolution is stronger. In spite of being a well-known phenomenon there is not yet a definitive explanation for the mechanism. But, it has been suggested that this localized attack is related with the differences of oxygen partial pressure, the atmosphere and the inside of the molten glass. It is possible that the natural convection phenomena of molten glass, provoked by changes in the superficial tension as long as the refractory dissolution occurs also has an influence in the process [10].

This kind of attack is very strong to the alumina–zirconia–silica refractories and to the alumina refractories, but almost inexistent in the chrome refractories.

### Corrosion of Metal Materials

The corrosion of metal materials in contact with molten glass involves a metal oxidation process as molten glass only allows the inclusion of ion types in its structure. The understanding of a corrosive phenomenon involves the knowledge of the oxidisers in the reaction.

The most frequent oxidisers in molten glasses are oxygen, water, sulphur trioxide and fluoride, in the glasses where it appears. There are also a number of other chemicals, with special reference to metal ions from noble metals associated to oxygen and with thermodynamic conditions for reduction, like Fe (III), Co (II), Na, Mn (II), Cr (III), etc.. The oxidation power of molten glass is a function of the quantity and variety of the present oxidisers [2, 12-16].

**Oxygen.** Molecular oxygen is the main oxide agent and it is almost always present in the system metal–molten glass. The oxygen that is dissolved directly in the molten glass or that goes into the surrounding atmosphere reacts with the metals that form the alloys based on the following reaction:



But, opposite to what happens to an oxidation in a gas atmosphere at high temperatures, the oxidation does not lead to the formation of an oxide layer on the metal surface. The oxides that are formed dissolve in the molten glass. Sometimes, in limited situations that depend on the hydrodynamic conditions in which a melted layer is formed and it is saturated with corrosion products, but it never presents protecting properties. What is said about the formed oxides is also applicable to all the other oxidation reactions that follow.

**Water.** Oxidation with water that is present in all molten glasses in quantities that go up to 0,05% occurs according to the following reaction, in the case of iron:



Hydrogen gas bubbles are formed during the corrosive process. The hydrogen that is formed can also produce decarburisation phenomena in the carbon steels and hydrogen attacks with the obvious consequences in mechanical resistance and frailty. Fissuration of the material may also occur.

**Sulphur Trioxide.** As said before most technical molten glasses have enormous quantities of sulphur, especially  $\text{SO}_2$  and  $\text{SO}_3$ .  $\text{SO}_3$  can exist in molten glasses up to 4%. The existence of these oxides at high temperatures leads to strong attacks to the metallic materials. Different corrosion reactions have been proposed depending on the type of metals that form the alloys. In the case of iron, the corrosive reaction may occur only with the formation of iron oxide (II). In the case of the existence of large quantities of  $\text{SO}_3$  and small quantities of iron in the alloy, corrosion can occur according to the following reaction:



or with the formation of iron sulphide in alloys with high percentages of iron and, according to the following reaction:



If we consider kinetics, some works point out a linear speed of corrosion of pure iron in molten glass with contents of  $\text{SO}_3$  close to 0.4% at  $1300^\circ\text{C}$ . The rate of corrosion is around  $1\text{mg}/\text{cm}^2 \text{ h}$ . A similar behaviour is observed with pure chromium but with a rate that is three times higher.

Nickel oxidises in reactions similar to the iron reactions. Nevertheless, a while after the exposure to the molten glass, the rate of corrosion becomes very low. That is explained by the formation of a nickel sulphide layer that avoids the progression of the corrosive process. On the other hand, as far as the  $\text{SO}_3$  content rises in the molten glass there is an acceleration of corrosion [13-14].

In the cases of the Fe-Ni-Cr-C alloys the rate of corrosion is several times larger than that verified in the pure metals and with significant intragranular attack. That increases with the level of nickel of the alloys and this metal accelerates corrosion in iron and chromium. So, it has been suggested a mixed corrosion mechanism as shown by the following reactions for iron and chromium:



Actually, gas generation is smaller in nickel alloys comparing with Fe-Cr alloys where the degradation mechanism follows reaction (10).

**Halogenous.** Molten glasses that contain halogen, especially fluoride may provoke the oxidation of the metals in the alloys according to the following reaction:



**Metals.** In the situations where the dissolved oxygen content is reduced and the system is working under inert atmospheres the corrosion of metals may proceed by metallic ions that are in the molten glass, such as Fe(III) or Mn(II). The oxidation occurs according to the following example:



Equation (16) is usually applied for the aluminium alloys.

**Alkaline oxides.** In the case of soda-lime glasses with the addition of oxides from alkaline metals like  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  it has been verified that especially in low oxidation molten glasses and in order to get low concentrations of oxidising agents the following corrosion reactions may occur as shown for the iron alloys:



Increases of the quantities of alkaline oxides lead to increases in the corrosion rate. On the other hand, with large amount of alkaline oxides and as a consequence in basic molten glass, the tendency to dissolve gases and water vapour will be higher and leading to an increase in the rate of corrosion of the metallic materials [2].

Figure 2 shows the variation of free enthalpy in some oxidation reactions of pure metals with temperature [12] and it summarizes quite well the processes already discussed. Actually, such diagram allows us to predict the thermodynamic tendency of a certain corrosion reaction to occur. But the oxidising power of the environment is always a direct function of the quantity of oxidisers present in the medium.

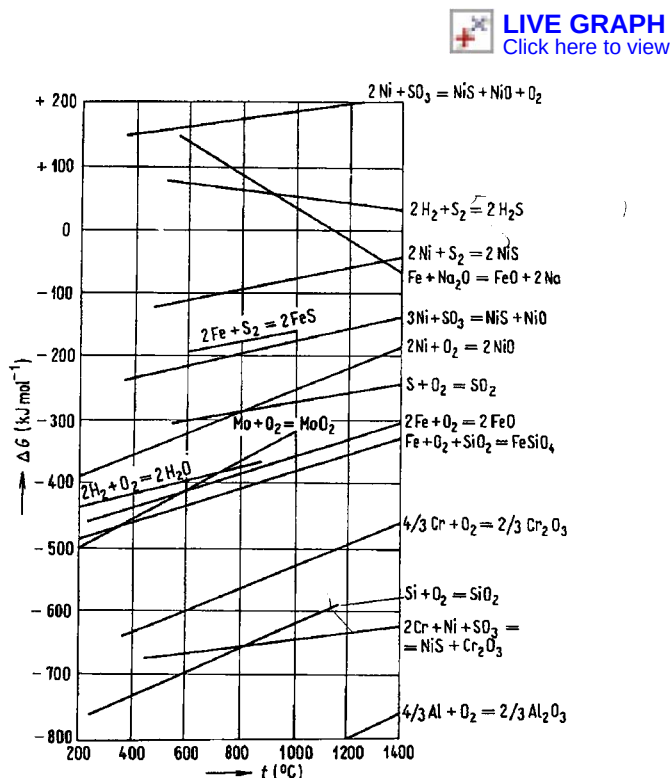


Figure 2 - Temperature dependency of the free energy change for some relevant oxidation reactions [12].

The oxidation procedures that we have been discussing are normally very strong and because of that the metal materials in direct contact with molten glass (with temperatures between 1000° and 1200°C) have a relatively small lifetime, not more than a few months.

Allied to the uniform and selective corrosion phenomena, with uniform loss of the material thickness are localized attack phenomena, especially in areas suffering tensions, leading to corrosion under tension with fissuration that damages equipment parts very early.

## Summary

This work is intended to present a broad picture of chemical and electrochemical procedures involved in the corrosion of refractory materials in contact with molten glass. The analysis of the failures as well as the selection of materials involve a strong knowledge of the environment, as to the chemical types present and the operating conditions, without forgetting the knowledge of the reactions that may occur. The “ensemble” of all these situations determines the appropriate selection of materials that would promote a better quality and efficiency of production.

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## Molten Salt Corrosion of Intermetallic Materials

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**Abstract.** Intermetallics are high-performance materials with a wide variety of interesting and useful properties. Here we discuss the molten salt-related hot corrosion aspects of intermetallic phases, namely some aluminides and silicides, which are of particular interest for high-temperature applications.

### 1. Introduction

An intermetallic can loosely be defined as a compound formed by the combination of two or more metal (metalloid) elements, generally, but not always, falling at or near a fixed stoichiometric ratio and ordered on at least two or more sublattices [1-4]. There are many intermetallics with a wide variety of interesting and useful properties for applications as diverse as resistors, magnets, superconductors, heating elements, structural alloys, and corrosion-resistant coatings. Of interest here is the development and application of intermetallic alloys that can be used at high temperatures in the aerospace and power-generation industries. Ni-base superalloys are largely used in these industries, but they generally melt in the 1300-1400°C range, and since many intermetallics have melting points in excess of 1500°C [2, 4, 5], they can potentially realize further increases in operating temperatures, and thus efficiency.

High temperature oxidation and corrosion studies of intermetallics performed during the last 30 years have shown that they are not particularly corrosion resistant in most molten salts, but recently developed and refined multi-component intermetallic coatings are very promising for future applications in first-stage gas-turbine blades, disks, vanes, and other highly demanding applications subjected to hot corrosion and other molten salt corrosive environments [6-9].

The key fundamental issues related to the high temperature oxidation and corrosion resistance of intermetallics are well described in the open literature by means of excellent reviews [2, 10-12] and reference books [13-19]. Intermetallics of interest here are those with potential applications from 600°C to 1500°C, and for these temperatures the main oxide scales that can be protective are Cr<sub>2</sub>O<sub>3</sub>, BeO, Al<sub>2</sub>O<sub>3</sub> ( $\alpha$ ) and SiO<sub>2</sub> [2, 11, 12, 20]. Of course, those intermetallic phases, which are particularly prone to the formation of one or more of these oxide scales, during corrosion, are the materials that deserve primary consideration. Here, we summarize some key points relating to the molten salt corrosion behaviour of notable intermetallics and update their characteristics with some recent results.

### 2. Nickel Aluminides

An important characteristic of NiAl is its ability to form a protective Al<sub>2</sub>O<sub>3</sub> scale. The ease of formation of protective Al<sub>2</sub>O<sub>3</sub> is primarily because of a combination of low oxygen permeability, relatively high Al diffusivity, a clean thermodynamic advantage of Al<sub>2</sub>O<sub>3</sub> over NiO [2, 21], and the relatively slow growth rate of NiO [2, 11]. Accordingly, NiAl intermetallics are the most widely used oxidation-resistant coatings in gas turbines [6, 22], where hot corrosion conditions are common. Hot corrosion is the degradation of materials by the presence of a liquid deposit or ash.

Type-I corrosion occurs primarily at metal temperatures ranging from 850°C to 950°C. This attack involves molten ash and deposits containing sodium sulphate and/ or potassium sulphate salts. Very small amounts of sulphur and sodium or potassium can produce sufficient  $\text{Na}_2\text{SO}_4$ . Other impurities such as vanadium, phosphorus, lead, chlorides, or unburned carbon can be involved in lowering salt melting temperatures. Under this Type-I hot corrosion, it would be expected that any  $\text{Al}_2\text{O}_3$  scale would be rapidly dissolved in the molten salt. Given no shift in the basicity of the salt (lower solubility levels) after dissolution of the scale, the rate of dissolution of further  $\text{Al}_2\text{O}_3$  formed on the alloy would not be expected to slow significantly, assuming that the  $\text{SO}_2$  and/ or  $\text{SO}_3$  liberated from the salt were removed from the reaction zone (as gas, or by the formation of internal sulphides). As a result, Type-I hot corrosion of NiAl would be expected to result in intense localized consumption of Al.

In burner rig tests at 913 and 982°C with JP-5 fuel (plus 200 ppm NaCl), Kaufman [23] found that Ni-50.9Al at.% suffered hot corrosion attack with the formation of a porous scale of NiO and  $\text{Al}_2\text{O}_3$ . Whereas NiAl was apparently considered relatively resistant, Al was removed from the alloy surface faster than it could be replaced by diffusion from the interior of the specimens, with the result that a layer of  $\text{Ni}_3\text{Al}$  was formed at the reaction front.  $\text{Ni}_3\text{Al}$  seemed to be even more susceptible to attack, and accelerated hot corrosion ensued. The volume increase that accompanied the NiAl to  $\text{Ni}_3\text{Al}$  phase-change led to void formation within the alloy, and cracking of any protective scale with ingress of the molten salt. Addition of ca. 8-9 at.% Cr or Ti improved the resistance to hot corrosion, as did additions of ca. 1.5 at.% Cr and 2-4 at.% of, for instance, Ti or Mo.

Romeo and McKee [24] found that the resistance of NiAl to hot corrosion was excellent, whereas  $\text{Ni}_3\text{Al}$  was highly susceptible to attack. McCarron et al. [25] found that NiAl was more resistant to hot corrosion than  $\text{Ni}_3\text{Al}$  in burner rig tests using 1% S fuel (plus 125 ppm Na, as sea salt) with a specimen temperature of 871°C. NiAl containing ca. 8-9 at.% Cr (that stabilizes the NiAl) was the most resistant alloy – minimal corrosion penetration was apparent after 800h.

Ellis [26] described a three-phase mode of attack observed on Ni-50 at.% Al in sodium sulphate-coated oxidation tests at 900°C in oxygen. The initial phase consisted of the formation of protective  $\text{Al}_2\text{O}_3$ , and was only slightly influenced by preoxidation of the intermetallic alloy. Phase II involved Al depletion and  $\text{Ni}_3\text{Al}$  formation. Phase III involved rapid internal oxidation in the  $\text{Ni}_3\text{Al}$  phase, with no reformation of a protective scale because of the presence of continuing basic fluxing conditions. On Ni-45 at.% Al, Phase I was not observed. When, however, 2 at.% Cr was added to Ni-46Al (or 5 at.% Cr to Ni-45 Al) only Phase I behaviour was observed throughout exposures up to 560h. The effects of addition of Hf, Ti, and Ga on the hot corrosion behaviour of single-crystal NiAl were investigated by Nesbitt [27] at 900°C. Synthetic sea salt was added to the fuel at a level that resulted in a concentration of 2 ppm w/w in the combustor exhaust. Increasing the Ti level from 1 to 5 at.% increased the susceptibility to hot corrosion, whereas alloys with 1-2 at.% Cr and 4-5 at.% Ti were less susceptible than even the lower-Ti alloys. The attack was localized initiating as pits and evolving to a rampant attack consisting of the rapid, inward growth of  $\text{Al}_2\text{O}_3$ .

### 3. Titanium Aluminides

Ti-Al based intermetallics are promising for engineering use [28] due to their low density and good stiffness and strength [29]. But their environmental resistance is limited at higher temperatures, so the target application temperatures range for them is approximately 600 – 800°C. Ti-based alloys have long been known to be susceptible to stress corrosion cracking in molten salts media [30]. Recent work by Nichols et al. [31] indicates that TiAl-based alloys suffer from accelerated Type – II hot corrosion attack in the temperature range 650 to 750°C. In the case of Type-II hot corrosion of gas turbines, it has been suggested that low-melting point mixtures involving the sulphates of cobalt and possibly also of nickel are important. These are also unstable, and thus the corrosion depends on the partial pressure of  $\text{SO}_3$  in the atmosphere. The mechanism of these processes has been reviewed



by Luthra and LeBlanc [32]. The analysis of these models requires a better understanding of the thermodynamics of the salt mixtures. Misra, Whittle, and Worrell [33] conducted a theoretical and experimental analysis of the  $\text{Na}_2\text{SO}_4$ - $\text{NiSO}_4$  system, and a less-detailed treatment of the  $\text{Na}_2\text{SO}_4$ - $\text{CoSO}_4$  system. At  $727^\circ\text{C}$ , the partial pressure of  $\text{SO}_3$  required to stabilize a molten sulphate phase in the  $\text{NiSO}_4$  system is approximately  $5 \times 10^{-4}$  atm (50 Pa). In the  $\text{CoSO}_4$  system, the corresponding partial pressure is 10 Pa. The earlier studies tended to predict lower values for the equilibrium partial pressures. The mechanism of hot corrosion suffered by the TiAl alloys coated with sea salt and oxidized in air for up to 100h [31] involved interactions among the deposited salt, the predominantly  $\text{TiO}_2$  scale and the alloy substrate to form volatile metallic halides, which were subsequently oxidized (pyrohydrolyzed) to form non-protective oxides on the outer surface of the scale. In addition, the salt deposit became enriched in chlorides so that its melting temperature was lowered, allowing it spread laterally over the surface and increase the area susceptible to attack. Consequently, it was indicated an increase in metal consumption rate by a factor of up to 20 compared with air oxidation.

In chloride-free ( $\text{Na}$ ,  $\text{K}$ ) $_2\text{SO}_4$  melts at  $850^\circ\text{C}$ , Ti-50Al (at.%), Ti-48Al-2Cr-Nb and Ti-50Al-10Cr had excellent resistance to corrosion in 100h crucible tests [34]. The addition of NaCl to the melt, however, resulted in severe corrosion.

#### 4. Vanadium Aluminides

The oxidation behaviour of vanadium is very poor and one of the major avenues investigated for improving its corrosion resistance was the addition of Al in the hope of forming a continuous, protective  $\text{Al}_2\text{O}_3$  scale. Addition of up to ca. 45 at.% Al and ternary addition of Cr and Ti did not overcome the significant problem that  $\text{V}_2\text{O}_5$  melts at  $\approx 690^\circ\text{C}$  [35]. This melting results in catastrophic oxidation/ corrosion at temperatures higher than about  $700^\circ\text{C}$ .

#### 5. Silicides

Silicides have long been considered for high-temperature service because of their potentially high strength, certain attractive physical properties and, when protective  $\text{SiO}_2$  can form, oxidation resistance [3]. The major limitation of silicides is their generally poor ductility, which has hampered their development for use as high-temperature structural components [28]. Consequently the use of silicides is essentially limited to heating elements ( $\text{MoSi}_2$ ) and corrosion-resistant high temperature coatings [3, 6, 36-39].

Several authors [36, 40, 41] have indicated that the resistance of  $\text{MoSi}_2$  to hot corrosion is good in certain media. After exposure of dense  $\text{MoSi}_2$  to a synthetic slag at 700 and  $850^\circ\text{C}$  for 1000h a thin oxide scale formed with no evidence of sulphidation [41]. In burner rig tests,  $\text{MoSi}_2$  seems to be more resistant to corrosion by NaCl,  $\text{V}_2\text{O}_5$ , and  $\text{H}_2\text{S}$  than the best superalloys, but it is attacked in the presence of  $\text{Na}_2\text{SO}_4$  and the  $\text{Na}_2\text{CO}_3$  deposits [40] as are other Si-based ceramics [42].

Among the other refractory metal silicides  $\text{WSi}_2$  is generally considered to be the most oxidation-resistant disilicide after  $\text{MoSi}_2$  [43, 44].

#### 6. Iron Aluminides

Properties such as good resistance to oxidation and corrosion (in particular sulphidation), low density, inexpensive raw materials, and low content of strategic elements have driven the development of iron aluminides. However, their maximum resistance to corrosion is at temperatures higher than  $900^\circ\text{C}$  and their higher strength is at temperatures of the order of  $600^\circ\text{C}$ . Therefore, oxide dispersion strengthened alloys have been used to increase their mechanical strength at temperatures  $> 900^\circ\text{C}$ . The tendency of the iron aluminides to form continuous  $\text{Al}_2\text{O}_3$  scales with virtually no external layer of transient oxides (of Fe or other alloying elements) in all except severely reducing conditions suggests that the susceptibility to attack by species other than oxygen

will depend largely on the capacity of the environment to chemically react with or breach the  $\text{Al}_2\text{O}_3$  layer.

Because  $\text{Al}_2\text{O}_3$  is readily dissolved by molten salts such as sodium sulphate [45] it is clear that FeAl alloys will not be particularly resistant to molten salt-related hot corrosion. In fact, several authors [6, 46-48] have observed the deleterious effect of molten salts on the corrosion of FeAl in  $\text{SO}_2$ -containing mixed gases. Hot corrosion mechanisms suggest that addition of Cr to Fe-Al alloys should reduce corrosion rates in sulphate melts, and there is some limited evidence of this for iron aluminides [46]. The solid-phase sulphidation of FeAl in contact with solid  $\text{CaSO}_4$  surface deposits in fluidised-bed coal combustors is much less severe than that by molten alkali sulphates, and the resistance of an  $\text{Fe}_3\text{Al}$  alloy was good under such conditions [49].

Laboratory studies on ash deposit and flue-gas compositions typical of coal-fired boilers showed that after 800h at 650 and 700°C,  $\text{Fe}_3\text{Al}$ -2 at.%Cr was more strongly attacked than stainless steels whereas for  $\text{Fe}_3\text{Al}$ -5 at.%Cr the weight change and thickness loss were of the same order as for type 347 stainless steel [50]. In field exposures for 16000h in the superheater area of a 250-MW coal-fired boiler (620-730°C), however, an  $\text{Fe}_3\text{Al}$ -5 at.%Cr aluminide performed surprisingly better than other candidate alloys under conditions promoting corrosion by molten alkali-iron trisulphates [51]. Preliminary metallurgical examination showed that total wastage of iron aluminide was between a tenth and a half that of type 347 stainless steel and comparable with or better than that of the most resistant alloys (HR3C and Ta-modified type 310 stainless steel). In molten  $\text{Na}_2\text{SO}_4 + \text{NaCl}$  at 600°C, protective parabolic corrosion kinetics were observed for an Fe-40 at.% Al-Zr, B, C alloy during 100h exposure, whereas in an  $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$  salt mixture, the kinetics seemed to be linear [52].

Corrosion of FeAl by molten  $\text{NaNO}_3$ - $\text{KNO}_3$ - $\text{Na}_2\text{O}_2$  at 650°C, used in chemical air separation processes, has been shown to proceed by oxidation and slow release of an Al-rich product layer into the melt. Alloys richer in Al were much more resistant [53]. Particularly for Al concentrations higher than 30 at.%,  $\text{Fe}_3\text{Al}$  alloys have good resistance in such nitrate melts at  $T < 600^\circ\text{C}$ , or in  $\text{Na}_2\text{O}_2$ -free nitrate melts [54]. FeAl exposed to molten  $\text{NaCl}$ - $\text{Na}_2\text{CO}_3$  (used as an oxidiser for waste disposal) at 900°C showed corrosion resistance to be significantly better than that of Inconel 600 [55].

## 7. Summary

The resistance of intermetallic alloys to molten salt-related hot corrosion in gas turbines, fired boilers, incinerators and other high-temperatures systems is reviewed. Some aluminides and silicides seem to be very promising for these applications, particularly if used as coatings or if their protective corrosion behaviour is improved by addition of reactive elements. Other compositions and other approaches are currently being tried to increase their potential application in industries subjected to molten-salt corrosion.

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## Molten Salt Corrosion of Intermetallic Materials by Electrochemical Impedance Spectroscopy

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**Abstract.** Molten salt corrosion of metallic materials commonly occurs in high temperature industrial environments involving ash/salt deposits in gas turbines, fossil-fired boilers and waste incinerators, and some systems utilizing molten salt as a medium for heat transfer, energy storage and reaction. The main types of corrosion modes in different molten salts as well as the electrochemical and physical analysis techniques which have been employed to elucidate this kind of corrosion are briefly reviewed. Electrochemical Impedance Spectroscopy (EIS) has proved an effective technique providing useful information about mechanisms and kinetics of corrosion processes in the presence of molten salts. The electrochemical impedance spectra of both inactive and active metals with formation of different scaling features in  $(\text{Li}, \text{K})_2\text{CO}_3$  and/or  $(\text{Li}, \text{Na}, \text{K})_2\text{SO}_4$  melts of protective and non-protective behaviour in the corrosion of aluminide-based alloys and of pure metals are examined. The electrochemical impedance models are also proposed accordingly.

### 1. General Aspects

Molten Salt Corrosion or Hot Corrosion is an accelerated form of attack suffered by metallic materials exposed at high temperatures in the presence of molten salt deposits. The industrial applications involving the presence of molten salts may be divided into two main categories. One of them includes the operation of boilers, mainly used for the production of electricity by combustion of fossil fuels, but also that of gas turbines used for aircraft and ship turbine engines or for the generation of electricity by means of land-based plants. In this case the most important salt components are metal sulfates, and especially sodium sulfate, which forms by reaction of sodium chloride with sulfur compounds and oxygen. In this classical form of hot corrosion due to alkali sulfates, two main kinds of attack have been identified, which are commonly denoted as Low Temperature and High Temperature Hot Corrosion, or also as Hot Corrosion of Type I and of Type II [1-6]. The low temperature hot corrosion is typical of temperatures ranging from a lower limit close to 600°C up to the melting temperature of the salt deposits, which depends on the nature of the mixture involved and may range from the melting point of the salt in the case of pure compound involved (884°C for sodium sulfate) to much lower temperatures for salt mixtures forming low-melting eutectics. In these conditions, the salt deposit is solid if pure, because the temperature of the system is below its melting point. The formation of a liquid salt layer, which is considered the prerequisite for the initiation of the hot corrosion attack, requires the formation of eutectic mixtures between the alkali sulfates and the sulfate of at least one alloy component [1-11]. In turn, this requires  $\text{SO}_3$  pressures in the gas larger than a critical value corresponding to the formation of the eutectic required for starting the hot corrosion process [1-11]. On the contrary, for the high temperature hot corrosion the system temperature is already above the melting point of the salt deposit, so that this form of attack does not require a critical content of  $\text{SO}_3$  in the gas. Thus, the type II hot corrosion starts from the upper limit of the low temperature form of hot corrosion and extends up to a maximum temperature of about 950°C, when the vapour pressures of the salts are generally sufficient to prevent their condensation on the metal surface. However, the two forms of hot corrosion due to sulfate deposits differ also for the morphology of the attack. In fact, the low

temperature hot corrosion is generally rather irregular and associated with formation of pits over the metal surface, while there is little or no internal sulfidation as well as a little depletion of the most reactive components in the alloy [1-11]. On the contrary, the high temperature hot corrosion due to sulfate deposits is more regular in thickness and does not involve the formation of pits, while it is commonly associated with the formation of internal sulfides and with a depletion of the corresponding alloy components in a subsurface layer of the metal substrate [1-6]. In extreme cases, the high temperature form of hot corrosion may also form an inner scale region where the alloy grains are mixed with the compounds produced by the oxidation of the most reactive alloy components.

A second kind of industrial process involving molten salt corrosion is waste incineration, where the accelerated attack is connected with the presence of chlorine compounds and especially with chlorides of heavy metals, which have rather low melting points and can be detrimental even at quite low temperatures [12-16]. This reaction has been studied initially in connection with the formation of chloride deposits on metal substrates, but has later become important in connection with the reaction of metals in environments containing HCl and/or Cl<sub>2</sub>, such as those produced in the combustion of wastes in incinerating systems used for waste disposal. The general effects observed in the presence of chlorine compounds in the gas are an acceleration of the corrosion rate associated with a mechanical failure of the scales due to blistering, cracking and possibly spalling as well as with a general loss of adherence between the metal and the scale [12-16]. Furthermore, chlorine is generally present in the scales, even in small amounts, and tends to concentrate at the alloy/scale interface. The scales grown in these environments are not protective and allow an easy penetration of gaseous species such as HCl and/or Cl<sub>2</sub> down the scale, which at sites of sufficiently low oxygen activity can react to form metal chlorides [12]. At the reaction temperature these chlorides have often quite high vapour pressures, so that, if the scales are porous, they can diffuse outwards by transport through the gas phase. At places of high oxygen activity they can react with oxygen and form metal oxides plus Cl<sub>2</sub>, which then can migrate inwards and repeat the same process [12-16]. In this way, even relatively small amounts of chlorine can produce long-lasting negative effects over the corrosion resistance of metallic materials. In the special case of waste incineration, the situation is further exacerbated by the presence of heavy metal chlorides, which have quite low melting points and form deposits over the metal surface. These deposits act as sources of chlorine for the reaction with the metal but can also dissolve the metal oxides to a significant extent, thus decreasing the protective effect of the external scale. For this reason, corrosion in waste incineration environments can be very aggressive even at temperatures at which most metallic materials have a good resistance to simple oxidation in the absence of chloride deposits and chlorine compounds.

An important mechanism for the accelerated corrosion due to the presence of salt deposits is associated with the partial dissolution into the molten salt layer of the oxide scales which would grow on the alloys in the absence of salts in the same gas mixtures [1-11]. A first negative effect of the scale dissolution is related to the decrease of the thickness of the oxide layer in comparison with the corrosion in the same environment in the absence of salts, which makes the scale less protective. A second negative effect is related to the reprecipitation of the oxides initially dissolved in the salt within the external region of the molten salt layer, producing an external porous scale zone which is not protective. When the molten salt layer contains sulfates it becomes possible also to form sulfides inside the alloy. The reaction with sulfur consumes the more reactive alloy components, such as chromium, so that the remaining alloy becomes less resistant to oxidation [1-11]. The formation of sulfides is favored by the presence of very low oxygen activities at the alloy/scale interface, which allow relatively large sulfur activities to be established at the same site. Thus, sulfur can dissolve in the alloy and produce internal sulfidation of the most reactive components. This process, once initiated, may become self-sustaining even in the absence of further sulfur supply from the salt. In fact, sulfides can be transformed into oxides by reaction with oxygen, and the free sulfur can migrate further inwards within the alloy and produce a new internal sulfidation at larger depth into

the alloy [1-11]. The formation of internal sulfides is particularly dangerous if they are molten at the reaction temperature, because their rapid penetration along the alloy grain boundaries leads to a fast deterioration of the material involved, especially as a result of a severe degradation of its mechanical properties [3, 10].

A detailed analysis of the mechanism of dissolution of metal oxides into molten sulfates, either pure or composed of mixtures of sulfates of different cations, such as sodium plus potassium, has shown that the dissolution can be either acidic, leading to the production of metal sulfates, or basic, which involves a reaction of the metal oxide with  $O^{2-}$  ions leading to the formation of anionic species [1-6]. In any case, the soluble ionic species containing the metal alloy components diffuse outwards through the salt layer and then reprecipitate from the melt in regions where their solubility products are exceeded, forming again oxide, but in the form of isolated particles which do not provide any important protection against further oxidation. The solubility of a given oxide in the melt is in most cases a function of the local acidity or basicity and generally shows a minimum for a particular value of the melt acidity. This change of the oxide solubility with the local acidity of the melt is considered to be an important factor in affecting the conditions for the precipitation of oxide particles in the molten salt layer [1,2,5,6].

Concerning the alloy composition, the most important element for achieving good resistance to hot corrosion is chromium. A minimum Cr content of 15 wt% is necessary for Ni-base alloys against type I hot corrosion, and about 25% Cr for Co-based alloy [1-6]. Moreover, Co-based alloys are more sensitive than Ni-based alloys to type II hot corrosion [1-6]. On the contrary, the effects of aluminium are irregular [6-7], since in some cases Al is beneficial and in other is not. However, in general alumina-former alloys are not particularly resistant to this form of attack [1-6]. In particular, a good resistance of MCrAlY coatings to type II hot corrosion requires high-Cr and low-Al contents, while a better oxidation resistance requires less chromium and more aluminium [3].

The aggressiveness of salt deposits composed of mixtures of sulfates of sodium and other metals can be significantly increased by the simultaneous presence of vanadium compounds such as vanadic oxide and/or sodium vanadates [1-6]. Vanadium, sulfur and sodium are normally present in crude oils. Sulfur is present as mercaptans and disulfides plus large ring-type molecule, vanadium as metal-organic complexes and sodium as sodium chloride [1-6,17]. During refining, these impurities become concentrated in the heavy distillates and residues, where they can reach concentrations as high as 4% for S and 500 ppm for vanadium. These fractions are used as fuels in utility boilers, large diesel engines and also in the operation of land-based or marine gas turbines. The concentration of sodium, mainly as NaCl, in oils is normally low (below 100 ppm). Sodium chloride is more commonly ingested in the engines with air, especially during marine operation or in gas turbines installed close to the sea coast. During combustion the main products containing these impurities are NaOH,  $SO_2/SO_3$  and vanadium oxides, which in the combustion zone are mostly present as gaseous species [1,13]. Deposition of condensed phases occurs on cooler parts of the engines when temperature drops below the dew point of the various compounds [17-18]. When sulfur is the main contaminant of the fuel, deposits consist mainly of sodium sulfate. In the presence of vanadium compounds, sodium sulfate is present up to a  $V_2O_5$  content of 50-60%, above which sodium sulfate is absent [17].

One of the effects of the presence of vanadium is to depress the melting point of the salt deposits [1,17]. In fact, the melting point of V-rich Na-V-O mixtures can be around 700°C, but it may decrease down to about 535°C for an  $Na_2O$  content of about 35 wt% in  $V_2O_5$ - $Na_2O$  mixtures. The effect is considerably larger in the presence of metal oxides dissolved in sodium vanadates, in which case the eutectic temperatures can decrease even down to 400°C [1,17]. The solubility of metal oxides in sodium vanadates can be of the order of 30 to 50 wt% [1,6,17]. The presence of molten vanadates deposits on metallic components produces an accelerated corrosion due to the dissolution of the scales in the salt and to an increased rate of transport of oxygen through the melt as compared to the rate of matter transport through the scales in the absence of deposits. The mechanism of the reaction is quite complex and not completely understood, also on account of the complex chemistry



of the Na-V-O system. The aggressiveness of the hot corrosion attack by vanadates can increase significantly if sulfates are simultaneously present, possibly as a result of the reaction of the Na-V-O deposits with  $\text{SO}_3$  present in the gas [1,6,17,18]. The corrosion attack in the presence of  $\text{SO}_3$  in the gas becomes much faster than in the presence of pure  $\text{O}_2$  under the same temperature, while the scale composition also changes, since it involves the formation of sulfides together with oxides and often also an internal sulfidation of the most reactive alloy components. A reduction of the corrosive attack by sodium-vanadium oxides even in the presence of sulfates can be obtained in different ways. Firstly, the partial pressure of  $\text{SO}_3$  in the gas should be kept small to avoid the formation of sulfate-vanadate mixtures [1]. Secondly, the oxygen pressure in the gas should also be kept small, because this favors the formation of lower vanadium oxides such as  $\text{VO}_2$  and/or  $\text{V}_2\text{O}_3$ , which are solid at the reaction temperature. Finally, it is possible to add  $\text{MgO}$ , which reacts with these mixtures by forming Mg vanadates with high melting points [1].

## 2. Electrochemical Studies

High temperature hot corrosion in molten salts at both high and low temperatures involves important electrochemical reactions, with some similarity in nature to aqueous corrosion. The reactions at the melt/metal interface is also electrochemically similar to those at aqueous solution/metal. Thus, many of the principles that apply to aqueous corrosion, such as anodic reactions leading to metal dissolution and cathodic reduction of an oxidant, may also apply to molten salt corrosion. However, in spite of their similar corrosion mechanism, there are major differences between molten-salt corrosion and aqueous corrosion, which result mainly from the fact that molten salts are partly electronic and ionic conductors. Molten-salt systems operate at higher temperatures than aqueous systems, which may lead to much faster corrosion (producing a thick scale) and to different forms of corrosion attack, such as uniform corrosion, localized corrosion and internal corrosion. Moreover, the rate-controlling step in most molten-metal systems is ionic diffusion such as transport of species in the scale and diffusion of oxidants in the melt rather than the charge transfer reactions that are typical of aqueous systems.

In the past decades, a great progress has been made to establish different electrochemical techniques to investigate molten salt corrosion, such as Free Corrosion Potential, Scanning Polarization, Cyclic Voltammetry, Potentiostatic Polarization, Weak Polarization Curve Fitting, Linear Polarization resistance and so on [19-21]. These methods have proved to be effective in simulating basic-acidic fluxing processes, understanding corrosion mechanisms and evaluating corrosion resistance, even though the information obtained by these techniques is limited in some cases.

Electrochemical impedance spectroscopy (EIS) is a technique which has proved effective in understanding reaction mechanisms and kinetics, and by which more information on corrosion processes may be obtained. Thus, from eighties of last century EIS has been applied in some investigations of hot corrosion [22-32]. Farrell et al. [22] employed impedance technique to study the corrosion behaviour of Nimonic 75 in bulk  $\text{Na}_2\text{SO}_4$  and in  $\text{Na}_2\text{SO}_4$ -1%NaCl at 750 and 900°C. They observed that the shape of the impedance spectra has the characteristics of a diffusion-controlled reaction, which results from the separation of the specimen from the gaseous environment by a deep melt. By examining the impedance at a fixed low frequency (50mHz), the authors concluded that the corrosion rate was higher at 900°C and with the addition of sodium chloride. Gao et al. [23] also observed impedance spectra characteristic of a diffusion-controlled reaction by monitoring the hot corrosion of Ni-1%Co and alloy 800 in molten  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ -10%NaCl. Wang et al. [24] studied the electrochemical reduction reactions of  $\text{SO}_3$  gas by EIS. As the amount of  $\text{SO}_2$  in  $\text{O}_2$  increased, and therefore  $\text{SO}_3$  increased accordingly, the rate of charge transfer also increased. However, the models for fitting the impedance data were not discussed in the above studies [22-24]. Using the electrochemical impedance technique, Wu et al. [25] studied the hot corrosion of preoxidized Ni by a thin-fused  $\text{Na}_2\text{SO}_4$  film at 1200K in a catalysed 0.1% $\text{SO}_2$ -

O<sub>2</sub> gas mixture. By varying the specimen purity and preoxidation conditions for Ni, three distinct features of hot corrosion (passive, pseudo-passive, and active) were observed. Wu [26] further measured the double-layer capacitance at the preoxidized Ni/molten Na<sub>2</sub>SO<sub>4</sub> interface. The study of reduction reactions in molten-salt corrosion by EIS has also been reported [27-29]. Zheng et al. [27] used EIS to study the cathodic reaction on the Pt electrode in molten Na<sub>2</sub>SO<sub>4</sub> in SO<sub>2</sub>-O<sub>2</sub> environments. The shape of the impedance diagrams indicated a diffusion-controlled reaction, mainly due to the diffusion of S<sub>2</sub>O<sub>7</sub><sup>2-</sup>. Nishina et al. [28] made precise measurements of the Warburg coefficient of the impedance of a gold electrode fully immersed in molten (Li,K)<sub>2</sub>CO<sub>3</sub>, (Li,Na)<sub>2</sub>CO<sub>3</sub> and (Li,K,Na)<sub>2</sub>CO<sub>3</sub> (at rest potential) at 615 to 800°C under an atmosphere of O<sub>2</sub> with CO<sub>2</sub>. By using the Randles-Ershler equivalent circuit and Warburg coefficients to analyse the graphical reaction order, it has been concluded that the simultaneous diffusion of O<sub>2</sub><sup>-</sup> and CO<sub>2</sub> is the dominant feature of the oxygen reduction path in molten carbonates. Makkus et al. [29] investigated the reduction reaction of oxygen on the porous NiO, LiFeO<sub>2</sub> and LiCoO<sub>2</sub> in molten carbonate fuel cells. The Nyquist plots for all electrode materials are composed of two arcs, which indicated a finite diffusion-controlled reaction, and are different from the impedance diagrams of a diffusion-controlled reaction reported by the others [27-28]. The authors concluded that molecular oxygen and carbon dioxide are predominant diffusing species. Rouquette et al. [32] studied the corrosion and passivation processes of magnesium in molten 2HF-KF mixtures by EIS. The authors proposed that the reaction pathway involved oxidation, desorption, diffusion and precipitation steps, and accordingly established the impedance models.

In the previous studies, the diffusion of oxidants in the melt was widely proposed as the controlling step of molten-salt corrosion. However, besides the diffusion of oxidants, it is necessary to consider also the transport of species in the scale, which may be the controlling process of molten-salt corrosion when a protective scale forms on the alloy surface. Furthermore, there are limited investigations concerning the establishment of models for fitting the impedance spectra. Successful application of the EIS technique requires suitable models for fitting the impedance spectra after the impedance measurements. As compared with, The molten-salt corrosion processes are more complicated than aqueous corrosion. Thus, it is helpful to correlate the EIS with the analysis of the corrosion products so as to establish suitable models for molten-salt corrosion. The following section presents some recent results by the authors on the EIS measurements and on the establishment of theoretical impedance models for molten-salt corrosion, taking into account the scaling features of materials.

### 3. Experimental

The experimental apparatus used in the present study is shown in Fig. 1. A closed end and grounded stainless tube was used for reaction chamber to eliminate the possible effect of electric and magnetic fields caused by the furnace on the impedance measurements. A three-electrode system was used for the electrochemical measurements. The working electrodes (WE) used in the present study are of pure platinum, copper and intermetallic alloys based on FeAl and Ni<sub>3</sub>Al. The chemical composition of FeAl is Fe-40Al-0.5B, and that of Ni<sub>3</sub>Al is Ni-21.2Al-0.1B-0.3Zr (atom percent). The working electrode of Pt is prepared by spot welding a Pt foil with an area of 2 cm<sup>2</sup> to a Pt wire sealed in an alumina tube. The specimens for the working electrodes of Ni<sub>3</sub>Al and FeAl were welded to a Fe-Cr wire for electric connection. The welding spot was sealed in an alumina tube. The working electrode surface was polished again on 600<sup>#</sup> SiC paper, degreased and dried prior to the test. The reference electrode (RE) is a silver wire dipped into a 0.1AgCl-0.9 working salt (mole fraction) contained in an alumina tube. The counter electrode (CE) is a platinum foil. The impedance measurements of Pt, Cu and FeAl were conducted at 650°C in (0.62Li, 0.38K)<sub>2</sub>CO<sub>3</sub> (mole fraction) mixture under air, and Ni<sub>3</sub>Al at 700°C in (0.36Li, 0.64(Na,K))<sub>2</sub>SO<sub>4</sub> (mole fraction) in air. All the impedance measurements were conducted at the rest potential. The working salts (100 g) were placed in an alumina crucible. After the mixed salts were dried at 300°C for 24 hours, the furnace was heated to

the experimental temperatures. The impedance measurements were carried out between  $0.01\sim 9.9\times 10^4$  Hz by an M398 impedance system composed of Princeton Applied Research (PAR) 5210 lock-in amplifier, a PAR 263 potentiostat interfaced through an IEEE 488 bus to a compatible computer. The amplitude of input sine-wave voltage is 10mV. A Fourier transform technique was employed for frequencies from 0.01~1.13Hz to increase measurement speed and to reduce the degree of perturbation to the cell. A software developed by Zhang [33] was used to fit the impedance spectra.

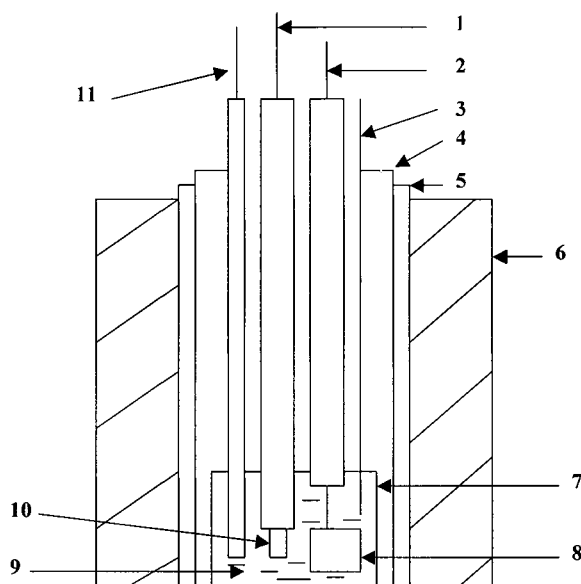


Fig. 1 - Schematic diagram for the experimental setup: (1) working electrode; (2) counter electrode; (3) thermocouple; (4) stainless steel pot; (5) alumina tube; (6) furnace; (7) alumina crucible; (8) Pt foil; (9) melts; (10) specimen; (11) reference electrode

## 4. Results and Discussions

### 4.1 EIS for inactive metal/ molten salt systems

Inactive metals have a large chemical stability and cannot be corroded by the melt, because the charge transfer through the double-layer capacitance at the metal/melt interface is inhibited owing to the large charge transfer resistance. Thus, the electrochemical charge transfer could be the rate-limiting process for inert metal/molten-salt systems. Systems of this kind can be described by a simple parallel circuit, as shown in Fig. 2, where  $R_s$  represents the molten-salt resistance,  $C_{dl}$  the double-layer capacitance at the metal/melt interface and  $R_t$  the electrochemical transfer resistance. The typical impedance diagram for this equivalent circuit is a capacitance loop with large radius. Fig. 3 gives the impedance spectrum of platinum in eutectic  $(\text{Li,K})_2\text{CO}_3$  mixture at  $650^\circ\text{C}$  in air. The impedance spectrum is clearly composed of a large capacitance loop that can be attributed to the impedance of the charge transfer reaction at the Pt/melt interface. Before giving the impedance expression of the equivalent circuit shown in Fig. 2, it is necessary to introduce the concept of the dispersion phenomenon. The center of semi-circle lies on the real axis, provided that the double layer is a perfect capacitor. However, in many cases, the center of semi-circle does not lie on the real axis, and can be considered as a semi-circle rotated clockwise around the origin by an angle  $\alpha$ . An inclined semi-circle on the complex plane is associated with dispersion. The dispersion phenomenon may be attributed to the non-uniform electric field at the electrode/solution interface owing to the roughness of electrode surface [34-35]. Dispersion is a significant feature for molten-salt corrosion as shown below. During molten-salt corrosion, the non-uniform electric field may be

related to the roughness of the scale grown on the metal surface and even to the molten-salt system. This dispersion effect may be represented by the term  $C \cdot \omega \cdot \text{ctg}(\beta \cdot \frac{\pi}{2})$ , where  $\beta = 1 - \alpha \frac{2}{\pi}$  ( $0 < \beta \leq 1$ ) presents the dispersion coefficient [36]. Thus, the electrochemical impedance  $Z$  corresponding to the equivalent circuit of Fig. 2, taking into account the resistance produced by the dispersion effect, can be expressed by the equation

$$Z = R_s + \frac{1}{j \cdot \omega \cdot C_{dl} + \omega \cdot C_{dl} \cdot \text{ctg}(\beta \cdot \frac{\pi}{2}) + \frac{1}{R_t}} \quad (1)$$

where  $\beta$  represents the dispersion coefficient of the capacitance loop, and  $\omega \cdot C_{dl} \cdot \text{ctg}(\beta \cdot \frac{\pi}{2})$  the resistance caused by the dispersion effect.

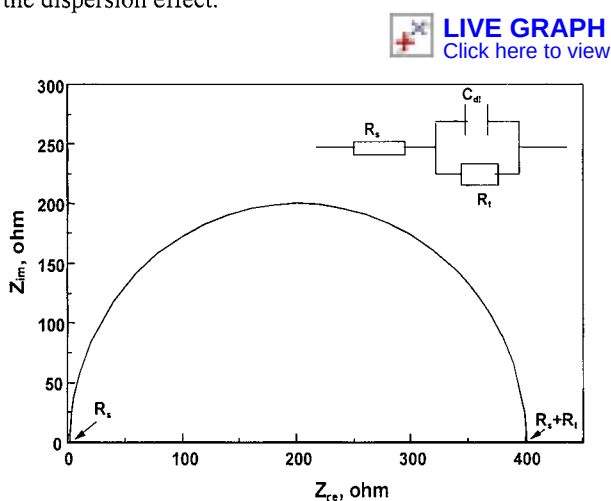


Fig. 2 - Equivalent circuit representing reactive-metal electrodes in molten salts and its schematic impedance spectrum

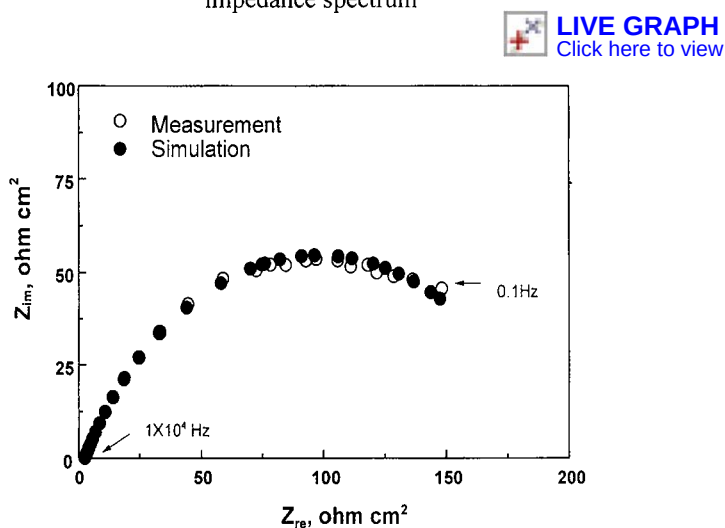


Fig. 3 - Nyquist plot for a platinum electrode in eutectic  $(\text{Li,K})_2\text{CO}_3$  at  $650^\circ\text{C}$

#### 4.2 EIS for active metals forming a porous scale

Differing from aqueous corrosion, in most cases the charge transfer reaction of active metals during molten-salt corrosion can occur easily and may not be rate limiting. Instead, the transport of ions in the scale and the diffusion of oxidants in the melts may become the rate-limiting process, which will further depend on the protectiveness of the scale formed on the metal surface. When a porous scale forms on the metal surface, the corrosion may occur at relatively high rate. The diffusion of oxidants to the scale/melt interface is not fast enough to meet their consumption rate in the reaction. In this case, the processes of anodic and cathodic charge transfers are fast and are not rate-limiting. The cathodic process, including mainly the cathodic charge transfer and the diffusion of oxidants, is controlled by the diffusion of oxidants in the melt, which will control the overall corrosion. This kind of diffusion-controlled reaction corresponds to typical features of impedance spectrum, involving a semi-circle at high frequency and a line at low frequency, and can be represented by the equivalent circuit of Fig. 4, where  $R_a$  represents the anodic charge transfer resistance,  $R_c$  the cathodic charge transfer resistance, and  $Z_w$  the Warburg resistance. Fig. 5 shows the Nyquist plot for the corrosion of the intermetallic compound  $Ni_3Al$  in molten  $(Li,Na,K)_2SO_4$  at  $700^\circ C$ , which is composed of a small semi-circle at high frequency and a line at low frequency, as expected for a diffusion-controlled reaction. The presence of Warburg resistance at the low-frequency section indicates that the alloy undergoes a fast corrosion due to the formation of a porous scale composed of a mixture of  $NiO$ ,  $Al_2O_3$ ,  $Ni_3S_2$  and metallic  $Ni$  particles. The nature of this non-protective corrosion layer is in agreement with the features of impedance diagram to some extent. The small semicircle at the high frequency may indicate that the charge transfer reaction at the scale/melt interface can occur easily, and therefore is not the rate-limiting process. The impedance spectrum of a  $Ni_3Al$  electrode can be described by the equivalent circuit of Fig. 4. Considering the dispersion effect, the electrochemical impedance  $Z$  can be expressed by the equation

$$Z = R_s + \frac{1}{j \cdot \omega \cdot C_{dl} + \omega \cdot C_{dl} \cdot ctg(\beta \cdot \frac{\pi}{2}) + \frac{1}{R_a} + \frac{1}{R_c + Z_w}} \quad (2)$$

while the Warburg resistance  $Z_w$  may be expressed by the equation [37]

$$Z_w = A_w \cdot (j \cdot \omega)^{N_w} \quad (3)$$

where  $A_w$  is the modulus of the Warburg resistance associated with the solubility and diffusion coefficient of oxidants in the melt, and  $N_w$  is the Warburg coefficient ( $-0.5 \leq N_w < 0$ ). The parameter  $N_w$  is related to the diffusion direction of oxidants. When  $N_w$  is equal to  $-0.5$ , the diffusion direction of the oxidants is parallel to the respective concentration gradients. When  $N_w$  is larger than  $-0.5$ , the diffusion direction of oxidants deviates from that of their concentration gradients, i.e. "tangential diffusion". The typical feature of the tangential diffusion is that the slope of the line at low frequency is smaller than 1. A porous scale formed on the metal surface may be considered to be permeable to the molten salts, and thus may influence the diffusion direction of oxidants. At present, a quantitative correlation of  $N_w$  with the porosity of the scale is not available. The values of the dispersion coefficient  $\beta$  and the Warburg coefficient  $N_w$  may reflect some common properties of the scale to some extent.

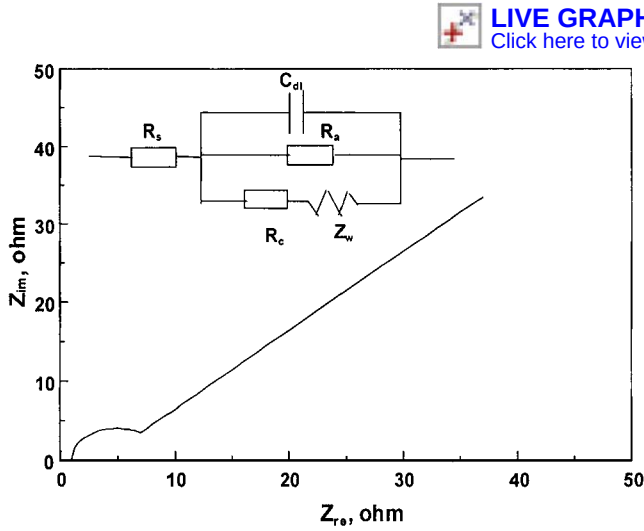


Fig. 4 - Equivalent circuit representing the corrosion of metals forming a porous scale in molten salts and its schematic impedance spectrum

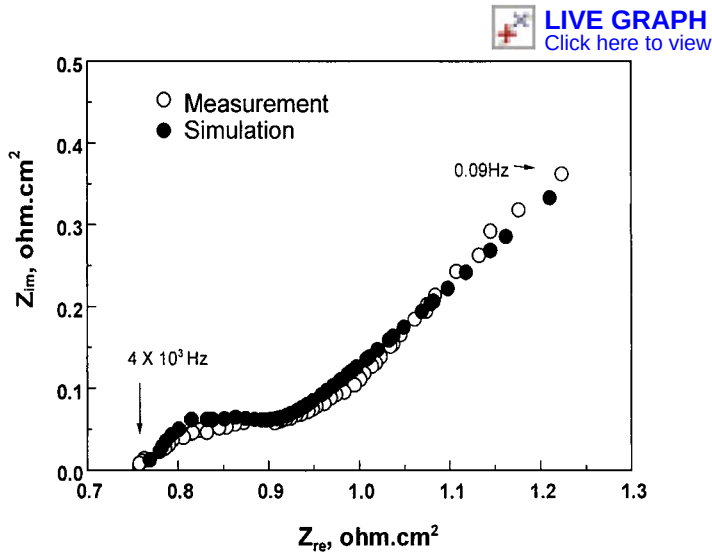


Fig. 5 - Nyquist plot for the corrosion of  $Ni_3Al$  after two-hour immersion in molten  $(Li, Na, K)_2SO_4$  at  $700^\circ C$

According to equations (2) and (3),  $R_c$  is much greater than  $Z_w$  at high frequency. Thus equation 2 can be simplified to

$$Z = R_s + \frac{1}{j \cdot \omega \cdot C_{dl} + \omega \cdot C_{dl} \cdot ctg(\beta \cdot \frac{\pi}{2}) + \frac{1}{R_l}} \quad (4)$$

where  $R_l \equiv \frac{R_a \cdot R_c}{R_a + R_c}$  represents the charge transfer resistance.

As mentioned above, the modulus of the Warburg resistance,  $A_w$ , is related to the solubility and diffusion coefficient of the oxidants in the melt, and can be given by the equation under conditions of semi-infinite diffusion [38]

$$A_w = \sum \frac{RT}{n_i^2 F^2 \sqrt{2}} \left( \frac{1}{C_i \sqrt{D_i}} \right) \quad (5)$$

where  $i$  denotes the diffusing species,  $n_i$  the electron number per molecule of species  $i$ ,  $F$  the Faraday constant, while  $C_i$  and  $D_i$  are the solubility and the diffusion coefficient of the species  $i$  in the melts. Based on equation (5), varying the composition of the gas phase the measurements of  $A_w$  could contribute to a better understanding of the diffusion and reduction mechanism of the oxidants in the melts.

### 4.3 EIS for active metals forming a protective scale

When a material can form a protective scale, the transport of oxidants to the scale/melt interface may be fast enough to support the growth of the scale. In this case, the rate of corrosion of the material will be decided by the transport of ions in the scale, not by the diffusion of oxidants in the melt. The scale can be considered as a capacitor and in series with the double-layer capacitance at the scale/melts interface. Thus, the EIS for this electrode system can be presented by the serial equivalent circuit of Fig. 6, where  $C_{ox}$  represents the oxide capacitance and  $R_{ox}$  the transfer resistance of ions in the scale. Correspondingly, the Nyquist plot is composed of double capacitance loops as shown in Fig. 6.

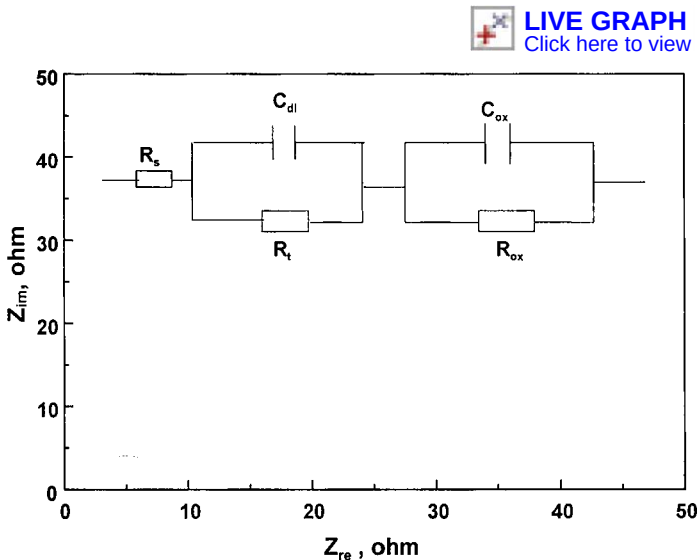


Fig. 6 - Equivalent circuit representing the corrosion of metals forming a protective scale in molten salts and its schematic impedance spectrum

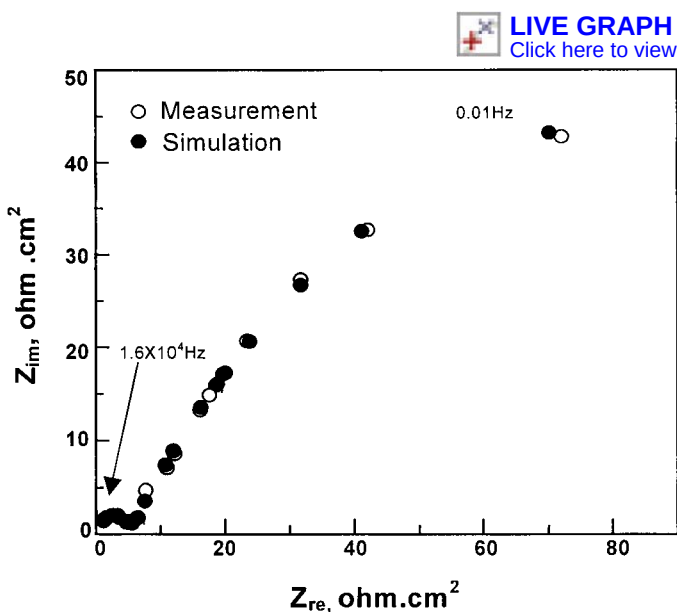


Fig. 7 - Nyquist plot for the corrosion of FeAl in eutectic (Li, K)<sub>2</sub>CO<sub>3</sub> melt at 650°C for 48 h

Fig. 7 shows a typical impedance diagram for the corrosion of the intermetallic compound FeAl in the eutectic (Li, K)<sub>2</sub>CO<sub>3</sub> melt at 650°C in a later stage, already reported earlier [39]. The Nyquist plot is composed of two capacitance loops, i.e. a small semi-circle at high frequency and a large semi-circle at low frequency. The analysis of the corrosion products indicated that the alloy formed a protective scale containing an external LiFeO<sub>2</sub> layer and an inner Al<sub>2</sub>O<sub>3</sub> layer at this stage. Therefore, it is reasonable to conclude that at a later stage the corrosion of FeAl is controlled by the transport of ions in the scale, not by the diffusion of oxidants in the melts, a situation which can be well represented by the equivalent circuit of Fig. 6.

The electrochemical impedance for this equivalent circuit may be expressed by the equation

$$Z = R_s + \frac{1}{j \cdot \omega \cdot C_{dl} + C_{dl} \cdot \omega \cdot \operatorname{ctg}(\beta_{dl} \cdot \frac{\pi}{2}) + \frac{1}{R_i}} + \frac{1}{j \cdot \omega \cdot C_{ox} + C_{ox} \cdot \omega \cdot \operatorname{ctg}(\beta_{ox} \cdot \frac{\pi}{2}) + \frac{1}{R_{ox}}} \quad (6)$$

where  $\beta_{dl}$  and  $\beta_{ox}$  represent the dispersion coefficient of the first and second capacitance loop respectively. Accordingly,  $C_{dl} \cdot \omega \cdot \operatorname{ctg}(\beta_{dl} \cdot \frac{\pi}{2})$  and  $C_{ox} \cdot \omega \cdot \operatorname{ctg}(\beta_{ox} \cdot \frac{\pi}{2})$  are the impedance elements caused by the dispersion effect. Because the corrosion is controlled by the transport of species in the scale, the radius of the second capacitance loop should be much larger than that of the first loop. Moreover, in this case the corrosion resistance of the metals in the molten salts may be represented by the parameter  $R_{ox}$ .

#### 4.4 EIS for active metals suffering from localized corrosion

Besides uniform attack, molten-salt corrosion often exhibits localized fast attack, used here to indicate the local fast growth of scale, not internal oxidation and/or sulfidation. For example, when a protective scale suffers from partial failure, the alloy may go through localized fast corrosion, provided the scale cannot heal. The localized corrosion zone may be covered with a non-protective scale or directly exposed to the molten salts, while the rest (slow corrosion zone) is covered with a more protective scale. The reaction along the slow corrosion site and that along the



fast corrosion site occur simultaneously, so that they are physically parallel. At the slow corrosion zone, the charge transfer resistance at the scale/melt interface may be neglected as compared with the transport resistance of ions in the scale. Thus, this kind of localized corrosion can be represented by a parallel equivalent circuit as shown in Fig. 8, where  $C_{dl}$  and  $R_t$  represent the double-layer capacitance and the charge transfer resistance along the localized corrosion zone, respectively, and  $C_{ox}$  and  $R_{ox}$  are the oxide capacitance and the transfer resistance of ions in the scale along the slow corrosion zone. The Nyquist plot corresponding to the equivalent circuit of Fig. 8 also consists of two capacitance loops.

 **LIVE GRAPH**  
Click here to view

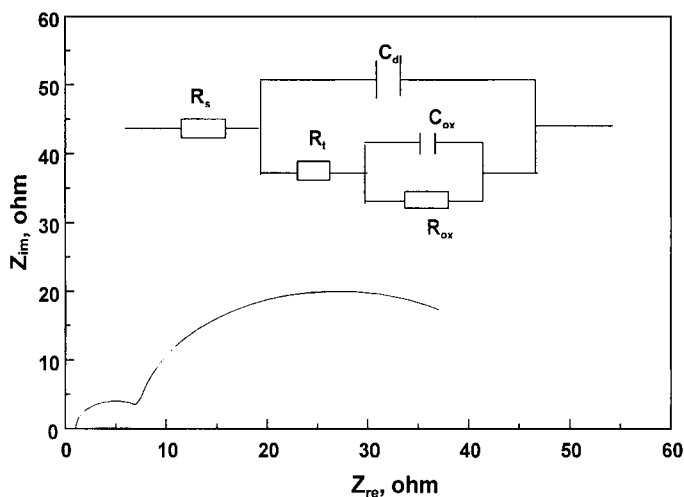


Fig. 8 - Equivalent circuit representing metals suffering from localized corrosion in molten salts and its schematic impedance spectrum

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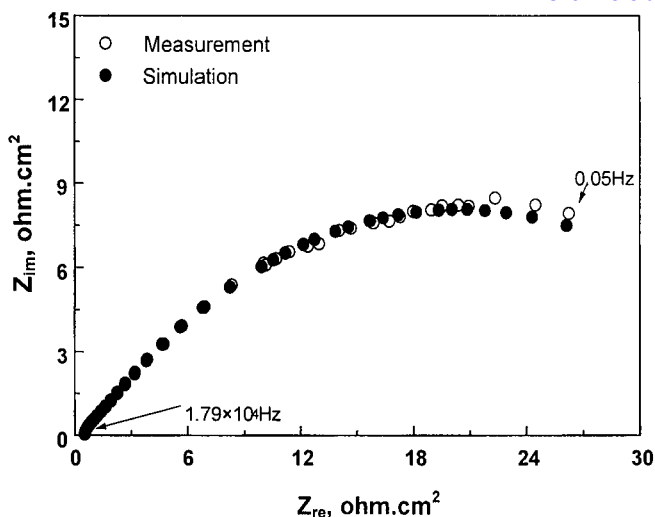


Fig. 9 - Nyquist plot for the corrosion of pure Cu in eutectic  $(\text{Li, K})_2\text{CO}_3$  melt at  $650^\circ\text{C}$  for 65h

Fig. 9 shows the Nyquist plot of pure Cu after corrosion in eutectic (Li, K)<sub>2</sub>CO<sub>3</sub> mixture at 650°C for 56 h. The plot is composed of a small semi-circle at high-frequency and a large semi-circle at low frequency. Examination of the corrosion products showed the existence of a discontinuous scale on the copper surface owing to the scale dissolution in the melt. Thus the features of double capacitance for the corrosion of copper in the melt may result from a non-uniform corrosion process. The equivalent circuit of Fig. 8 can be used to represent the impedance characteristics of copper. In this case, the electrochemical impedance  $Z$  can be expressed by the equation

$$Z = R_s + \frac{1}{j \cdot C_{dl} \cdot \omega + C_{dl} \cdot \omega \cdot \operatorname{ctg}\left(\beta_{dl} \cdot \frac{\pi}{2}\right) + \frac{1}{R_i} + \frac{1}{j C_{ox} \cdot \omega + C_{ox} \cdot \omega \cdot \operatorname{ctg}\left(\beta_{ox} \cdot \frac{\pi}{2}\right) + \frac{1}{R_{ox}}} \quad (7)$$

According to the above discussion, the electrochemical impedance diagrams for metals undergoing either uniform corrosion with formation of a protective scale or localized corrosion present always the characteristics of double capacitance loops. Thus, an analysis of the corrosion products is required to establish the correct impedance model.

The impedance spectra presented above can be fitted well based on the equivalent circuits proposed, and the fitting results are shown respectively in Figs. 3, 5, 7 and 9. Due to the space limitation, the fitting results of some electrochemical parameters presented in the above impedance equations are not reported here.

## 5. Concluding Remarks

Four theoretical impedance models were proposed for the molten salt corrosion of metals and FeAl and Ni<sub>3</sub>Al-based alloys by taking into account the chemical stability of metals and their scaling features. The charge transfer resistance for inactive metals is relatively large, so that the charge transfer reaction is rate-limiting and the corresponding impedance diagram is composed of a large semi-circle. Compared with the inactive metals, the charge transfer reaction for active metals can easily occur, and may not be rate-limiting process. In this case, the rate-limiting process and the corresponding impedance diagrams are related to the properties of the scales formed on the metal surfaces. When a porous scale forms on the metal surface, the corrosion is controlled by the diffusion of oxidants in the melt, and the Nyquist plot consists of a small semi-circle at high frequency and a line at low frequency. On the contrary, when the material forms a protective scale, the transfer of ions in the scale may be rate-limiting process and the Nyquist plot is composed of double capacitance loops. An equivalent circuit of double layer capacitance in series with oxide capacitance can be used to describe this kind of impedance diagram. When a metal suffers from localized corrosion, the impedance diagram is also composed of double capacitance loops. An equivalent circuit of double layer capacitance at the localized corrosion zone parallel to oxide capacitance can be set up to describe this impedance response behaviour.

Although practical impedance measurements of Ni<sub>3</sub>Al, FeAl, Pt and Cu in molten salt systems proved partly the proposed impedance models, much work is still needed to verify the correctness and the general applicability of the impedance models proposed.

## Acknowledgments

Financial supports by the NSFC (China) are gratefully acknowledged.

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## **SECOND PART**

### **LATEST RESEARCH INFORMATION**

# Hot Corrosion in Fossil Fuel Fired Power Plants

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**Keywords:** Austenitic 304 Stainless Steel, Austenitic 310 Stainless Steel, Chromium, Chromium Carbide, Inductively Coupled Plasma Atomic Emission Spectroscopy, Iron, Machined Crucibles, Molten Sulfate, Nickel, Passive Cr<sub>2</sub>O<sub>3</sub> Layer, Pre-Carburised, Pre-Oxidised, Reheater, Spallation, Superheater, Synthetic Flue Gas, Thin Film Hot Corrosion

## Abstract

A specially designed and machined crucible has been used to investigate hot corrosion studies while replicating thin films of molten sulfate. Coupons of type 304 and 310 austenitic stainless steel have been totally surrounded by a 1 mm molten salt layer. Pre-oxidised and pre-carburised coupons were kept at 650°C in the melt under a synthetic flue gas for up to 2000 h and analysed at 200 h intervals for the concentrations of Fe, Cr and Ni entering the melt. After initial attack the concentration of these elements remained essentially constant for around 800 h, after which spallation of the protective Cr<sub>2</sub>O<sub>3</sub> layer and rapid attack occurred over the next 400 h, by which time the protective layer had reformed and concentration levels remained constant for around 700 h when the process was repeated. The pre-carburised coupons produced a several-fold increase in iron, chromium and nickel concentrations in the melt over pre-oxidised coupons. This is, to our knowledge, the first time the stop-start corrosion mechanism has been identified experimentally, and confirms that increased corrosion can take place if superheater and reheater tubes made of 304 or 310 type steels are subjected to reducing conditions during a failed start-up procedure or subsequently.

## 1. Introduction

Hot corrosion can be expected when the hot gases from the combustion of fossil fuels impinge on metal surfaces. The two major users of fossil fuels today are electricity generating utilities and gas turbine engines. The current largely media engendered fear of the public and politicians, and fostered by large “green” environmental groups, have deflected interest away from the building of nuclear power stations and so fossil fuel fired power plants will be with us for a long time yet. Alternatives to turbines for aircraft engines are not even on the horizon. We therefore will have to continue with the use of fossil fuel plant well into the next millennium, and attempt to understand and reduce the effects of hot corrosion so that maintenance intervals can be extended, and the originally expected lifetimes of plant can be safely and economically prolonged.

At the present time researchers in this area are somewhat limited in what they can do that will be implemented by plant managers. When industry has solved to their (economic) satisfaction a problem, or implemented a new process or plant that was expensive to build, they are not keen to suggest or sponsor research that extends their knowledge of the problem or might produce an improved alternative process. If the alloy on which the hot flue gases impinge, for example, lasts up to and beyond the planned lifetime of the plant then they see little need for any related research: research managers fortunately will sometimes take the longer view, budgets permitting. Support from national research councils is also sometimes more enlightened, but they also reflect the perceived needs of industry. This chapter reports supported studies into the hot corrosion process by a novel technique that provides more intimate details than was possible with previous techniques.

Hot corrosion is the consequence of the chemical reaction between a metal or alloy in contact with a layer of molten sulfate. The novel feature here is that attention is focused on what is happening in the melt, rather than to the metal.

There are essentially three distinct high temperature corrosion problems in fossil fuel steam boilers:

- (1) Fireside corrosion of the steam-containing superheater and reheater tubes due to the deposition of fuel impurities from the flue gas at its highest temperature.
- (2) Fireside corrosion of the tubes containing water located in the furnace enclosure, and
- (3) Steam-side oxidation and exfoliation in the superheater and reheater steam currents.

The first was recognised as a significant problem in the late 1950's, and considerable research has since been carried out concerning this corrosion process. Much of this work has involved exposing metals and alloys to molten salt baths: in practise only a thin film, around 1 - 2 mm thick, of sulfate builds up, and the work described here explains our success in developing laboratory techniques that replicated and enabled detailed information to be obtained for the first time from thin films of molten sulfate. The other two corrosion problems are nowadays considered less serious as lower temperatures are involved and, being somewhat different to molten salt corrosion, we have not investigated them and thus make no further mention of them here.

### 1.1. Nature of the molten salt layer

Early investigations[1] showed that accelerated wastage of superheater and reheater tubes occurred under an ash deposit. The appearance of a typical deposit is shown in Fig. 1.

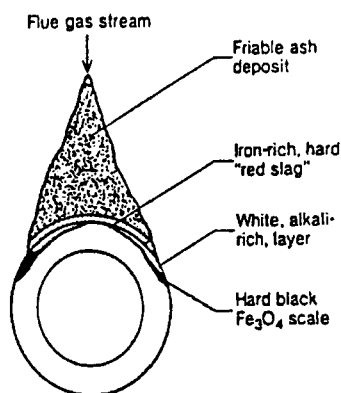


Fig. 1. Section showing deposit layers on a leading superheater or reheater tube.

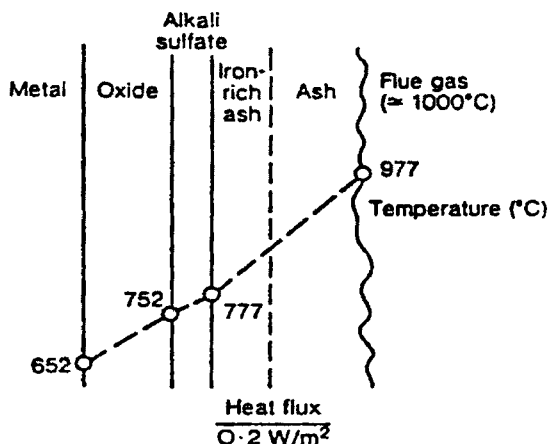


Fig. 2. Schematic of a typical thermal gradient through a deposit from flue gas to superheater metal.

The black inner layer is iron oxide, essentially  $\text{Fe}_3\text{O}_4$ , and is typically  $2.20\text{ }\mu\text{m}$  thick. The white layer contains majorly sulfates of Na, K and Al, with some Fe. This is the molten sulfate layer and is usually around 1 mm thick. The "red slag" layer is high in Fe, low in alkali, and with a sulfate content intermediate between that of the white deposit and the ash. The adhering fly ash is rich in  $\text{Fe}_2\text{O}_3$  and remains porous, even if sintered. Dissolution of both white and red layers in water produce acidic solutions.

Fig. 2 shows the temperature distribution through the system for a typical set of circumstances. This

diagram is however oversimplified. The overall heat flux to a superheater tube is in the order of  $0.2 \text{ MW/m}^2$ . It is however evident from Fig. 1 that the thickness of the insulating ash layer is greater at the front, leading, position of the tube than the rear, trailing, area. This results in a variation in the heat flux around the tube. Wastage takes place at the “2 o'clock” and “10 o'clock” positions relative to the flow of the flue gases, the “12 o'clock” position. The heavy build-up of ash on the front surface reduces the temperature flux within the deposit below that required for the salt layer to be molten. The thinner ash levels at the side of the tube allow for a higher heat flux, and a molten layer beneath, at the deposit - metal interface.

The origin and role of the molten salt layer, and its associated fly ash, may be summarised as follows. The cations arise largely from the clay component of the coal, and the sulfate ions from the oxidation of the sulfur in the fuel to  $\text{SO}_2$ . The air entering the combustion chamber contains around 10% more oxygen than necessary for stoichiometric combustion and  $\text{Fe}_2\text{O}_3$  in the fly ash acts as a catalyst to convert the  $\text{SO}_2$  to  $\text{SO}_3$ . Fuels containing vanadium, such as fuel oil, often used in the start-up process in boilers, provide an even more effective catalyst for  $\text{SO}_3$  formation. The  $\text{SO}_3$  readily dissolves in the molten sulfate, forming essentially pyrosulfate ions,  $[\text{S}_2\text{O}_7]^{2-}$ :  $\text{SO}_3$  and  $\text{O}_2$  are the main oxidants and  $\text{SO}_2$  is insoluble in sulfate melts.

## 1.2. Mechanistic aspects of the hot corrosion process

Corrosion is normally understood to mean the oxidation of metals, whereby the metal is leached away or transformed into a coherent layer of oxide. The  $\text{SO}_3$  present in the flue gas has the major effect on the corrosion of metal tubes, since this determines the oxidising potential of the sulfate deposit, in terms of the redox equilibria:



The corrosion process is thus two separate reactions. First, as anodic oxidation, by



to form metal ions in the corrodant: (n may be 2 or 3, but for our purposes will here be assumed as 2.). Thus



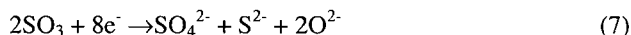
Second, the cathodic reaction is transfer of electrons to the oxidising agent



More specifically, for the reduction of  $\text{SO}_4^{2-}$  and/or  $\text{SO}_3$  we can write



These equations are over-simplified and the reaction mechanism is better understood by considering a steady state in which  $\text{SO}_2$  and  $\text{O}_2$  from the flue gas enter the porous fly ash. The catalytic action of  $\text{Fe}_2\text{O}_3$  then produces equilibrium concentrations of  $\text{SO}_3$ . The  $\text{SO}_3$  dissolves in the melt, migrates to the oxide - melt interface, and through the porous oxide to the oxide - metal interface. The  $\text{SO}_3$  on reaching the metal is reduced



This is regarded as the overall result of the electrode reactions (6) and (7). Solid metal oxides and sulfides result from the subsequent oxidation of the metal, together with metal ions in the sulfate melt. Dissolution of the metal oxides at the oxide - melt interface takes place, viz.,



with some of the metal sulfide being converted to the oxide, introducing imperfections in the oxide scale as it forms.

The solubility, and stability, of the dissolved metal ions in the melt is dependent upon both  $\text{SO}_3$  partial pressure and on temperature, increasing with increase in  $\text{SO}_3$  content, but decreasing with



increasing temperature. A mutual opposition is thus seen for the effects of  $\text{SO}_3$  partial pressure and temperature on traversing from the oxide - melt to the melt - fly ash interface such that a temperature is reached where the dissolved metal ion is precipitated as the oxide. A resulting concentration gradient of dissolved metal ions across the melt was thus envisioned and has been shown[2].

The corrosion process is therefore considered as the continuous dissolution of metal and metal oxide, reprocessing to form a non-protective oxide layer at the melt - fly ash interface. Considering all the factors involved, the rate determining step for the dissolution of the protective layer that the steel tubes generate, the overall rate of the corrosion process, is that of the diffusion of metal ions away from the metal - metal oxide interface.

The transition metal ions from the steel tubes in the sulfate melt do not behave like the alkali metal ions  $\text{Na}^+$  and  $\text{K}^+$ : they form complexes with the sulfate ions:



The evidence for this comes from the electronic absorption spectra of such melt systems. The spectra obtained all correspond to the presence in solution of the metal ions surrounded octahedrally by six oxygen atoms. It is therefore concluded that each of the metal ions has three bidentate sulfate ions co-ordinating to it.

## 2. Replicating hot corrosion in the laboratory

Research into the corrosion mechanisms for metals immersed in molten salts has been largely carried out using electrochemical techniques. Hart *et al.*[3] determined the potential of a platinum electrode in a  $(\text{Li},\text{Na},\text{K})\text{SO}_4$  eutectic melt as a function of  $\text{SO}_2$  and  $\text{O}_2$  partial pressures in the gas phase in equilibrium with the melt. They were also the first to report systematic electrochemical corrosion experiments on steels in molten sulfates, and made qualitative assessments of the reductive corrosion resistance of various steels, based on the effect of the oxide film growth on the electrode potential, and also on the corrosion currents, measured using the potential sweep method. This method was next used by Cutler *et al.*[4] to measure the electrode potentials of a number of iron-chromium binary alloys in a sulfate melt. They later examined the partial pressure effects of  $\text{O}_2$  and  $\text{SO}_3$  on the corrosion of Fe-18Cr-8Ni steels in the  $(\text{Li},\text{Na},\text{K})\text{SO}_4$  eutectic. They found that the partial pressures of  $\text{O}_2$  had only an indirect influence on the corrosion process, through its participation in the  $\text{SO}_2/\text{SO}_3$  equilibrium.

Many studies using electrochemical techniques have reported corrosion rates for steels that relied on applying a potential to the system and measuring the response. Techniques such as these, where the corrosion is driven, allow for rapid determination of corrosion rates. However, electrochemical laboratory studies have the disadvantage that it is very difficult to replicate plant conditions, *i.e.*, thin molten salt films, and still study corrosion with accuracy. Electrochemical studies have, however, provided much valuable information, information that assisted in the design of and materials for the construction of power stations. In addition, subsequent studies have helped reveal various observations and deficiencies in the operation of such stations, and enabled suitable choices of remedial action. Techniques that focus not so much or exclusively on the materials used but instead on understanding the chemistry of the transition metal corrosion products formed in the molten sulfate deposit, and employing thin film conditions, will enhance considerably the present understanding, and have been the object of our attention.

In order to replicate thin film environments and measure the hot corrosion rates for austenitic steels, both pre-oxidised and pre-carburised, we have developed a series of novel techniques. These have allowed the monitoring of corrosion over a time period of 2000 h, without driving or disturbing the

system. Analytical techniques employed include electron micro probe analysis (EMPA) and inductively coupled plasma atomic emission spectroscopy, ICP-AES. A preliminary account has been published[5] which we now summarise, expand and report further findings.

### 2.1. Maintaining thin film conditions

This was achieved by placing vertically steel samples, of dimensions 8 x 8 x 3 mm, in a crucible shaped from a machinable glass ceramic that was impervious to molten sulfate attack. The centre had been drilled so that the metal coupon would be in contact with molten salt to a depth of ca. 1 mm and the bottom corners were notched to keep the specimen in place and uniformly distant from the crucible walls (except around the notches). The upper specimen surface was some 15 mm from the entrance slot of the crucible, so that initially all the sulfate powder needed to surround the sample when molten could be placed into the crucible. The crucible was not covered, so that gases formed could escape, and the molten sulfate could be exposed to and react with a synthetic flue-gas atmosphere. Subsequent sectioning of removed, cooled crucibles showed that the coupons had been intimately surrounded by molten sulfate and the sulfate attack appeared uniform.

### 2.2. 2000 hour experimental run

An experiment was designed to monitor thin film sulfate attack over 2000 h, and compare the effect of using both pre-oxidised and pre-carburised samples. Type 304 and 310 austenitic stainless steel samples were used, common steels for superheater and reheater tubes in power plants. The choice of pre-oxidised and pre-carburised surface treatments derived from two possible start-up scenarios. Normally, before the sulfate layer builds up on these tubes they experience some oxidation from the excess oxygen in the hot flue gases. Initially oil, often low grade, is injected into and burned in the combustion zone, to heat up the furnace so that when the fuel is switched over to pulverised coal in an air stream it will burn: sometimes, during the change-over, the fire is extinguished; the interior of the furnace gets covered in oil and powdered coal; and after a successful restart the coated tube surfaces become carburised before any deposits are laid down. It was suspected that such surfaces were more susceptible to hot corrosion attack and that this could explain some incidents of accelerated corrosion and unplanned shut-downs.

Forty machined crucibles were prepared, one half containing pre-oxidised coupons and the other half pre-carburised ones. At 200 h intervals two crucibles were removed for examination, so that the extent and nature of corrosion on the two different pre-treatments could be compared.

To conform as closely as possible with on-site conditions the crucibles were continuously maintained at 650°C under a synthetic flue gas, consisting of (by volume) 4% O<sub>2</sub>, 16% CO<sub>2</sub>, 2000 ppm SO<sub>2</sub> and N<sub>2</sub> balance. This flue gas was initially passed over a platinised kaowool catalyst, at 425°C, to effect the correct partial oxidation of the SO<sub>2</sub> to SO<sub>3</sub>, after first ensuring complete mixing of the component gases and filtering to remove particulate matter.

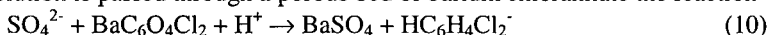
### 2.3. Analysis of sulfur oxide

As indicated above, molten sulfates do not react with or dissolve SO<sub>2</sub>, and thus any formed therein escapes, albeit slowly, into the surrounding atmosphere. Molten sulfates readily dissolve and react with SO<sub>3</sub>, effectively forming reactive pyrosulfate ions, S<sub>2</sub>O<sub>7</sub><sup>2-</sup>. The presence in fly-ash of Fe<sub>2</sub>O<sub>3</sub>, a suitable, though not particularly efficient catalyst, ensures the conversion of some of the SO<sub>2</sub> to SO<sub>3</sub>.

It was therefore necessary to establish, measure and control the extent of conversion of SO<sub>2</sub> to SO<sub>3</sub>. A mass flow controller was modified for use with SO<sub>2</sub>, and adjusted so that, after mixing, there was 2000 ppm SO<sub>2</sub> in the synthetic flue gas. The concentration of SO<sub>3</sub> had to be determined before and

after the synthetic flue gas passed over the crucibles containing the molten sulfate. Previous hot corrosion studies had not, as far as we have been able to establish, monitored both  $\text{SO}_2$  and  $\text{SO}_3$  for concentration levels and  $\text{SO}_3$  uptake.

We initially attempted to absorb  $\text{SO}_3$  quantitatively in sodium hydroxide solutions, and with condensation traps, but were unsuccessful. However, a flow-photometer, borrowed from a power station analytical laboratory, worked well. It operated on the principle that the gas was bubbled through an aqueous solution of isopropanol (4:1, water alcohol), in which  $\text{SO}_3$  reacted to form  $\text{SO}_4^{2-}$  but  $\text{SO}_2$  is not oxidised. Continuous direct determination of low levels of sulfate ion concentration is not possible, but if the solution is passed through a porous bed of barium chloranilate the reaction



goes effectively to completion. The absorbance of this coloured anion at 535 nm was continuously measured, and displayed on a chart recorder as ppm levels.

The optimum flow rate into the furnace was determined as  $50 \text{ ml min}^{-1}$ , and remained constant when the hot zone of the furnace was changed from 200 to  $700^\circ\text{C}$ . The amount of  $\text{SO}_3$  in the exiting flue gas would yield the up-take of  $\text{SO}_3$  by molten sulfate. Static experiments showed a take-up rate per sample of ca.  $90 \pm 5 \text{ ppm h}^{-1}$ . Under flowing conditions, and with twenty test crucibles containing sulfate and steel samples, the amount of  $\text{SO}_3$  absorbed per sample decreased, but only slightly.

#### 2.4. Preparation and analysis of metal coupons

The austenitic steel samples, types 304 and 310, of dimensions indicated above, (8 x 8 x 3 mm), were polished to within  $\pm 0.08 \text{ mm}$ , degreased, dried and thereafter handled with tweezers. The samples had been cut from 20 mm diameter bars, and care was taken to ensure that the rolling plane for the bar was in the same direction for all samples: conflicting results had at times earlier been obtained if there was a change in rolling plane orientation between samples. Some of these clean coupons were surface oxidised by heating in air at  $900^\circ\text{C}$  for 24 h. Several randomly selected coupons were sectioned and polished to  $0.25 \text{ }\mu\text{m}$  and upon microscopic examination showed a surface-oxide layer of thickness between 10 and  $20 \text{ }\mu\text{m}$ .

Other clean coupons were carburised. In an iron box they were covered with a carburising powder (carbon granules and a fluxing agent, barium carbonate) and heated at  $1000^\circ\text{C}$  for an hour followed by cold water quenching. Coupons, also chosen at random, were sectioned, polished to 1000 grit and finally polished with diamond pastes from 9 to  $1 \text{ }\mu\text{m}$ . Microhardness analysis revealed carburisation profiles. Type 304 and 310 austenitic steels have an average nominal hardness of 160 Hv: hardness measurements made every  $10 \text{ }\mu\text{m}$  from the edge to the centre of the carburisation zone showed that the average had increased to 430 Hv. The coupons had therefore been uniformly carburised throughout this layer. This was confirmed by electron microprobe analysis (EMPA), which showed carbides predominated at grain boundaries throughout this region.

### 3. Analysing corroded samples

#### 3.1. Cooling

Every 200 h two crucibles were removed from the synthetic flue gas atmosphere of the furnace and immediately placed in an air furnace at  $500^\circ\text{C}$ , which was then slowly cooled over several hours to room temperature. This obviated the cracking of the crucible, due to differential contraction of the sample, a problem that had to be solved.

### 3.2. Sectioning

The crucible and sample were then sectioned vertically with a diamond-edged wafering saw, 0.4 mm thick, under oil to prevent the sample being exposed to the moisture in the air. After cleaning ultrasonically in acetone to remove the oil the two halves were stored in a dry-box maintained at 2 ppm moisture.

### 3.3. EMPA studies

For EMPA studies samples must be polished down to 0.25  $\mu\text{m}$ . However, standard polishing techniques would remove some of the soft salt surrounding the metal and create focusing problems for the electron microscope. Methods are available for geological specimens containing both soft and hard materials, which we modified for our purposes. The most efficient technique was first to polish (Struers planapol) from 300 to 1000 grit, using Streaan DP type matt (paper composite base) with diamond paste of the corresponding grit size. Final polishing to 0.25  $\mu\text{m}$  employed a lead plate and a diamond suspension. Minimum pressure on the sample ensured a polish with essentially no relief, and good EMPA results.

### 3.4. Transition metals in the thin salt layer

Techniques were also developed to determine the concentrations of iron, chromium and nickel in the 1 mm molten salt layer around the pre-treated coupons. Salt was carefully removed from the other half of the divided crucible for analysis.

## 4. Results and Discussion

When the concentrations for iron, chromium and nickel were plotted over the 2000 h time period of the experimental run certain general features and trends emerged. After a rapid initial attack during the first 200 h a period of passivity occurred for up to 900 h, after which the protective chromium oxide layer that had formed spalled off into the melt and a period of rapid attack again took place until more chromium diffused to the steel surface to form another protective layer. This corrosive attack may be termed catastrophic corrosion and now lasted for around 400 h before a second session of passivity was established. With less chromium now available this second layer now lasts for not more than 600 h before catastrophic corrosion is renewed. Fig. 3 is a stylised outline. Such

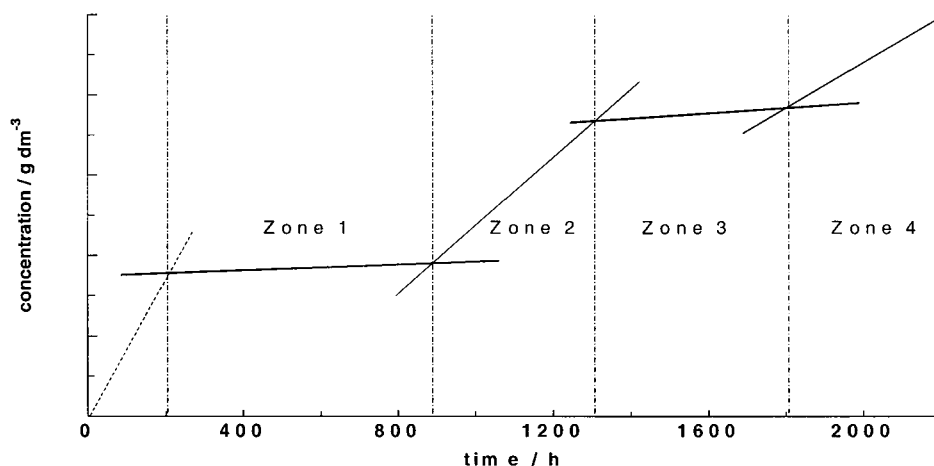


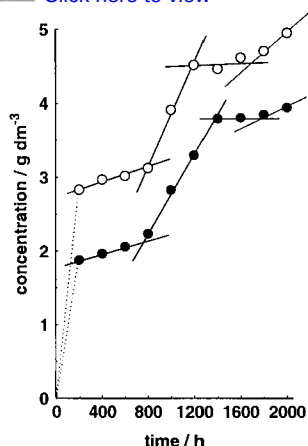
Fig. 3. Idealised plot of concentration corrosion products *versus* time profile.

a stop-start behaviour and mechanism has for some time been suspected for superheater and reheater hot corrosion but this is the first time direct supporting chemical evidence has been obtained. The evidence includes the appearance of spallation in the appropriate sectioned crucibles.

## Iron

The concentration of dissolved iron, determined from ICP-AES data, as a function of time for the thin film corrosion by molten (Na,K,Al)sulfate on samples of pre-oxidised and pre-carburised types 304 and 310 austenitic steels are shown in Figs. 4 and 5, respectively. The iron levels detected arise from oxidation and sulfidation at the oxide-melt interface. Micrographic examination revealed largely alternating layers of oxide and sulfide. This implies oxygen penetration of the initial thin oxide layer in the pre-oxidised coupons. Continued oxide formation at the metal oxide interface results in high local sulfur activity. The newly formed oxide layer is then penetrated by the sulfur present, and a sulfide layer is formed between the metal and oxide. This increases the oxygen partial pressure, and hence a new oxide layer is formed beneath the sulfide layer. Repetition of this process increases the scale thickness. In due course this layer will spall off. The total concentration of iron in the melt can therefore be related to the ability of the steel to resist oxidation and sulfidation, and the extent to which this occurs is generally associated with the concentrations of Ni and Cr alloyed in austenitic steels.

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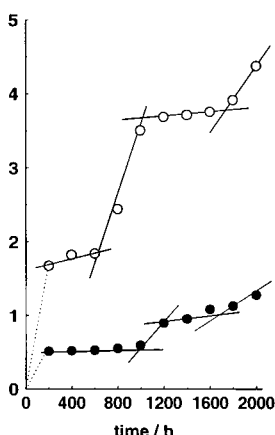


Fig. 4 (left). Concentration of iron determined by ICP analysis in a thin film of molten sulfate in contact with type 304 austenitic stainless steel, and sampled every 200 h. Open circles, pre-oxidised; filled circles, pre-carburised.

Fig. 5 (right). As above, but for type 310 austenitic stainless steel.

Truman and Pirt[6] have reported that nickel has a beneficial effect on the oxidation and corrosion resistance when alloyed with 20% chromium. They compared a number of chromium : nickel ratios, and found 25%Cr - 20%Ni superior in oxidation resistance. The marked effect of alloying iron and chromium on the oxidation resistance of austenitic steels has long been known[7]. Halstead[8] has presented data showing how the major steel components iron, chromium and nickel were likely to behave chemically when exposed to 85 mole%  $\text{Na}_2\text{SO}_4$  and 15 mole%  $\text{K}_2\text{SO}_4$  in an atmosphere containing  $\text{SO}_2$  and  $\text{SO}_3$ . This data showed clearly that increasing Cr and Ni levels reduces oxidation rates. Wood and Stott[9] have stated that iron oxidises at a greater rate than nickel at high temperature. This is because  $\text{FeO}$ , (the predominant oxide in the layer structure of  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ), contains more cation vacancies than  $\text{NiO}$ , the sole oxide for nickel. On this basis, increases in the concentration of nickel alloyed with iron would tend to suppress the oxidation rate for iron within the steel.

A major initiator of failure of high temperature steel alloys is the cracking and spallation of the oxide scale, which contains about 75%  $\text{Cr}_2\text{O}_3$ . These alloys rely for corrosion resistance on the establishment of a healing or passive  $\text{Cr}_2\text{O}_3$  layer. This oxide is thermodynamically very stable with respect to the metal, with slow transporting processes through the scale. The factors determining the formation of a porous  $\text{Cr}_2\text{O}_3$  layer are well documented[10,11].

The alloying element concentrations of chromium and nickel for types 304 and 310 steels are Fe-18%Cr-9%Ni and Fe-25%Cr-20%Ni, respectively. The latter steel thus has more of both of the alloying elements. Stott *et al.*[12] have examined the development of the porous layer of  $\text{Cr}_2\text{O}_3$  on Cr-Ni alloys containing 10 - 20 wt% Cr. This is analogous to the levels for type 304 and thus the results obtained here for pre-oxidised type 304 can be explained in terms of the  $\text{Cr}_2\text{O}_3$ -forming ability at the metal surface. Specifically, since  $\text{Cr}_2\text{O}_3$  is more stable than NiO, precipitates of the former are able to nucleate at or near the scale interface. Eventually the  $\text{Cr}_2\text{O}_3$  particles are of sufficiently high population to coalesce and form a continuous porous layer. However, for these 10 - 20wt% steels, there is insufficient chromium for the passive  $\text{Cr}_2\text{O}_3$  layer to form immediately, and it is only established following diffusion of chromium from the bulk alloy matrix to the surface, to replenish that already oxidised. Experiments have shown[12] that the passive layer initially forms at the intersection of the alloy grain boundaries. This transport of chromium denudes the steel matrix of chromium, resulting in areas between the grain boundaries not forming a protective porous  $\text{Cr}_2\text{O}_3$  layer. This allows for the preferential oxidation and sulfidation of iron (and nickel) at these sites. This oxidation and sulfidation are shown (Fig. 5) in terms of a value for the overall iron concentration, and is approximately four times greater than that found for type 310.

Our results for the type 310 steel, Fe-Cr25%-Ni20%, may be compared with those steels studied by Stott *et al.*[12] having chromium levels above 20 wt%. For these steels they concluded that, due to the greater concentration of chromium in the bulk alloy, sufficient was supplied across the width of the oxide front without denudation of chromium in the matrix. This allows the rapid development of a protective porous layer of  $\text{Cr}_2\text{O}_3$ , thereby greatly reducing or preventing the oxidative and sulfidation process leading to corrosion. This is shown in Fig 4 as a very low overall concentration profile for iron.

#### **4.1.1. Effect of carburisation on the overall iron concentration**

The total concentrations of iron entering the thin sulfate film from the pre-carburised samples of type 304 and 310 steels are significantly different from those of the pre-oxidised samples. An increase of 80% for the iron concentration for type 310, compared with a rise of only 20% for that of type 304, may be seen (Figs. 4 and 5). This is consistent with the results of Cain and Nelson[1] who revealed that, as a result of carburisation, grains were prematurely separated from the metal surface, and they associated this with the non-formation of a protective oxide layer. Further, Ramanarayanan and Petrovic-Luton[13], investigating the mechanical properties of a 30Cr-30Ni austenitic steel carburised under various thermodynamic conditions, identified a non-protective layer of  $\text{MnCr}_2\text{O}_4$  at the surface with an internal carbide of formula  $\text{M}_{23}\text{C}_6$ . Later Stewart[14], using Mossbauer spectroscopy, showed grain boundary depletion of chromium in 302 steel.

Potentiodynamic studies on the effect of chromium content on the resistance to corrosion of austenitic steels have shown that increasing the chromium content depresses the corrosion potential. This has the effect of extending the range of stable passivity; however it also increases the critical current so that higher corrosion rates are obtained in the absence of passivity. Chromium is a strong carbide former (twice as readily as iron), and would be anticipated, as any prior contamination of the metal surface with carbon will, upon heating ( $>600^\circ\text{C}$ ), initiate carburisation. This adversely affects

the oxidation resistance by the preferential precipitation of chromium carbide at grain boundaries, resulting in the depletion in the alloy matrix of chromium. This encourages the formation of the iron oxides,  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and iron-rich spinel oxides, with also the formation of  $\text{Fe}_2\text{S}$ , instead of the formation of chromium-rich sesqui-oxides ( $\text{Cr}_{2-x}\text{Fe}_x\text{O}_3$ , where  $x < 0.1$ ) and  $\text{Cr}_2\text{O}_3$ . The latter two are the more protective because of their high resistance to cationic diffusion, and to sulfidation by the molten salt.

It is therefore reasonable that high chromium bearing steels, (20 wt% and above), i.e., type 310, would be affected adversely to a greater extent than the lower chromium bearing steels, (10 - 20 wt%), i.e., type 304, on the grounds that type 310, containing 25%Cr, would produce a greater concentration of carbide than type 304 (18 wt% Cr). The greater concentrations of carbide thus have a deleterious effect on oxide scale formation and, as observed upon sectioning the Macor crucibles, increase scale spallation at carbide-oxide boundaries.

Precise calculations of the amount of chromium tied up by carbon are difficult to perform because of the probability that some carbon will be associated with other minor constituents contained within the steel. However, assuming that most of the carbide is present as  $\text{Cr}_{23}\text{C}_6$ , with an average content of 60% iron, then an austenitic matrix containing diffused quantities of carbon would reduce the chromium content from, in the case of type 310, from 25 wt% to < 20%, and for type 304 steel from 18 wt% to ca. 10 wt%. With regard to these new chromium concentrations we note that, for type 310, the chromium level now corresponds to a composition typical of type 304. Thus upon comparing the overall iron concentration of the carburised type 310 (Fig. 5) to that of oxidised type 304 (Fig. 4), the iron level is seen to rise, for type 310 carburised to an overall concentration approximately equal to that for the oxidised type 304. Because type 304 has a much lower resistance to oxidation compared to that of type 310 a transfer is made from high oxidative resistance to one of lower resistance. This result manifests itself as a four-fold increase in the concentration of iron, bringing about levels equivalent to those for oxidised type 304. For this steel type the reduction in chromium due to carburisation does not significantly change the characteristics of the steel, i.e., the concentration of chromium is still such that the steel remains categorised in the lower chromium-bearing steel group, and hence its resistance to oxidation is still only marginally affected.

#### 4.1.2. Type 304 oxidised – a detailed analysis

For this lower chromium content steel the development of a continuous protective  $\text{Cr}_2\text{O}_3$  layer is relatively slow, after the rapid attack during the first 200 h. An initial quantity of iron will thus be oxidised and sulfidised. These oxides and sulfides are subsequently dissolved by the molten sulfates to form sulfato iron complexes in solution. These complexes correspond to an initial concentration of around  $0.187 \text{ g dm}^{-3}$ . The very small increases in iron concentration ( $0.01 \text{ g dm}^{-3}$ ) are, we propose, due to cracks in the oxide layer that develop on the edges and corners of the sample due to stress. These cracks, observed in photomicrographs, allow the molten salt to penetrate to the metal surface, giving rise to metal dissolution and the formation of microgram quantities of the sulfato complexes.

The formation and growth of the passive oxide layer at the metal-metal oxide interface are a result of the continuous oxidation. This may be achieved by either transport or diffusion of oxidants through the scale. Analysis has shown[15] that oxidant transport may not be possible if it involves anion and cation vacancy motion. However, molecular diffusion of the oxidants in scales may result from chemical potential gradients. This diffusion mechanism is believed to be operating here, and the oxidants,  $\text{O}_2$  and  $\text{SO}_3$ , diffuse through the  $\text{Cr}_2\text{O}_3$  scale, forming iron (and nickel) oxides and

sulfides. This proposed mechanism is supported by EDAX analysis of the scales in which iron and nickel oxides and sulfides were found beneath a layer of  $\text{Cr}_2\text{O}_3$ , and confirmed by elemental distribution maps. The growth of the mixed oxide layer continues until scale fracture and failure, which is then followed by sulfidation.

Oxide scale failure, spallation, occurs as a result of the fracture of the oxide away from the metal surface. This was observed in the appropriate samples and confirmed by the sudden rise in the iron concentration after 600h. The two major factors influencing this occurrence are the extent of the scale alloy bond strength, and the properties of the oxide scale.

For many chromium bearing alloys, fracture at elevated temperature may result in the formation of stratified scales[16]. Such scales are established because the relative alloy interdiffusion coefficients and the diffusion rates of Cr(III) ions in  $\text{Cr}_2\text{O}_3$  mean that selective oxidation leads to depletion of chromium in the matrix at the alloy-scale interface. The scale fracture, leading to spallation, results in the exposure of the chromium depleted metal surface to the corrosive molten sulfate. The  $\text{Cr}_2\text{O}_3$  layer is unable to re-establish rapidly, allowing the oxidation and sulfidation of iron (and nickel), increasing their concentration. As the scale-alloy interface encroaches into the less chromium-depleted regions, the protective covering of  $\text{Cr}_2\text{O}_3$  is able to re-establish.

Proposals have been made that the segregation of sulfur impurities at the metal-oxide interface results in the weakening of the interfacial bond strength of scales on nickel-base alloys[17]. Detection of sulfur impurities adjacent to the metal has been here achieved by EDAX analysis, thus suggesting that this mechanism is operating 304 (and 310) type steels.

We conclude that all the above mechanisms for oxide and scale spallation contribute to the iron concentration increase for the oxidised type 304 steel, and such continue by the reaction of the molten sulfate and its oxidants, largely dissolved  $\text{SO}_3$ , at the metal surface in the absence of the passive oxide scale. This reaction is subsequently halted by the re-formation of a passive oxide layer that begins to take effect after 1200 h exposure.

After this time period the concentration of iron entering the melt now remains essentially constant for around the next 500 h, and the system is now behaving again as it did initially, but not for quite as long. Spallation is once again observed towards the end of the experiment, as an increase in the corrosion product concentration for iron. However, the gradient of the slope, and hence the rate of increase of iron into the melt, is now less than that for the initial spallation time period. We propose that a diffusion-controlled dissolution process is the controlling mechanism here. Such dissolution will proceed until the melt becomes saturated with dissolved metal ions.

It is pertinent here to consider this saturation in terms of the phase diagram for the (Na,K,Al,M) sulfate, where M is Ni, Cr and Fe. The increase in the transition metal cation fraction would eventually move the composition to another region of the phase diagram. A number of possibilities may result from this transition. The new phase may require the precipitation of one of the components of the system, not necessarily containing the transition metal. Alternatively, the new phase may no longer be liquid, and a solid solution would be formed. A combination of these processes would therefore slow down the rate at which the spalled scale reacts with the melt.

#### **4.1.3. Type 304 carburised – a detailed analysis**

For all four of the time zones, the increase in the concentration of iron follows the same profile as that for the oxidised metal, albeit the iron concentrations are higher. This greater concentration is a



result of chromium depletion. The initial concentration for iron was found to approximate to  $0.3 \text{ g dm}^{-3}$ , 50% greater than for the pre-oxidised steel. This percentage increase is also essentially constant through the four time zones and thus we conclude that the carburisation of a type 304 austenitic steel does not significantly change its chemistry, but that it behaves similarly to the pre-oxidised steel. The mechanistic corrosion processes discussed above for type 304 oxidised also apply to type 304 carburised steels.

#### **4.1.4. Type 310 oxidised – a detailed analysis**

The major difference here arises from the higher chromium content of type 310 steels, 25 wt%. There is now sufficient chromium in the steel to replace readily that lost in the formation of  $\text{Cr}_2\text{O}_3$  rather than relying on replenishment by diffusion from the matrix, as above. This rapid formation of the passive  $\text{Cr}_2\text{O}_3$  layer was observed as a very low initial concentration, approximately  $0.05 \text{ g dm}^{-3}$  (75% lower than that for type 304). Here the very small increase in concentration due to the cracking of the oxide is not seen. Thus we must conclude that, when the oxidising molten salt contacts the metal, as a result of oxide cracking, the formation of the passive  $\text{Cr}_2\text{O}_3$  layer at the metal-salt interface is sufficiently fast that no metal dissolution takes place.

The later process of spallation, seen as the increase in the concentration of the corrosion products for iron, is only recognisable by a small concentration increase. Concentrations for iron in solution associated with passivation are also still present in this second time zone. When the oxide spalls from the metal then formation of the passivating  $\text{Cr}_2\text{O}_3$  layer is very rapid, enabling only the dissolution of small quantities of metal ( $0.03 \text{ g dm}^{-3}$ ) before a complete covering of this oxide prevents further reaction.

In the third and fourth time zones the processes of passivation and spallation are repeated. We note that the gradient in the last time zone for the increase in iron concentration is approximately that of the second time zone, indicating that the saturation point of the salt by corrosion products has probably been reached.

#### **4.1.5. Type 310 carburised – a detailed analysis**

The first concentration measurement, after 200 h, of approximately  $0.17 \text{ g dm}^{-3}$  is a result of carburisation leading to chromium depletion, and thus oxide formation rates for  $\text{Cr}_2\text{O}_3$  are reduced. This allows for an extended period of metal dissolution, before sufficient chromium has diffused from the bulk of the alloy to the metal surface to form a passive  $\text{Cr}_2\text{O}_3$  layer. The very slight increases in iron concentration are due to cracks in the oxide layer but, unlike the oxidised samples, these cracks are not rapidly healed and hence dissolution of the metal takes place, with minimal increase in the corrosion product concentration in the melt.

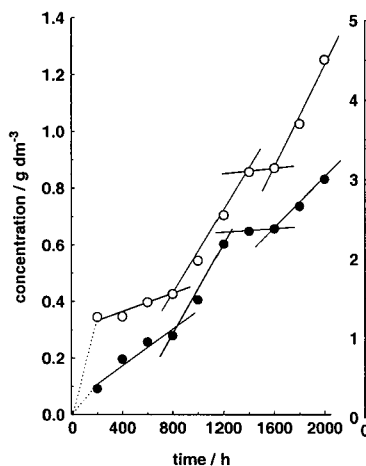
When the relative rates are compared, for the increase in iron concentration resulting from spallation for type 310 and 304 carburised, a far greater relative increase for the former is seen. This may be explained by recognising that the areas adjacent to the precipitated deposits of chromium carbide at grain boundaries are depleted in chromium to a greater extent than in the bulk alloy. Hence only a thin passive layer of  $\text{Cr}_2\text{O}_3$  is formed. Consequently,  $\text{O}_2$  and  $\text{SO}_3$  are able to diffuse to the metal, to form a layer of iron (and nickel) oxides and sulfides beneath the  $\text{Cr}_2\text{O}_3$  layer. This mixed oxide scale will continue to grow until spallation. Due to the steel at the grain boundaries being so depleted in chromium a passive layer is not formed, with the consequence of preferential dissolution of the metal adjacent to the carbide precipitates. This process continues unchecked, creating pits, or, as the corrosion process repeats itself, crevices down the grain boundaries. This is intergranular corrosion, and in the most severe cases may lead to the dropping of grains from the metal surface.

## 4.2. Nickel

The ICP-AES results for nickel are shown in Figs. 6 and 7) for the austenitic steels type 304 and 310, respectively. The characteristics and trends of these results are analogous to those for iron. The explanation for the concentrations of nickel is now discussed in terms of the relative ability of nickel to resist oxidation and sulfidation when alloyed in steel, together with the effect of the chromium content and its influence on the reactivity of nickel. Nickel is an important alloying element in stainless steel because it confers additional corrosion resistance and improved mechanical and engineering properties but its greatest advantage is where high temperature environments are encountered. Its most relevant advantage here is a good resistance to attack by molten sulfates.

The story for nickel commences with essentially the same explanations for the mechanistic features of corrosion that give rise to the initial concentrations of iron, and is thus not repeated. The overall profile for the concentration of nickel for type 304 is approximately double that of type 310. This is one result not expected since type 310 contains about double the amount of nickel as type 304, 20 and 9 wt%, respectively. Truman and Pirt[6] and Halstead[8] have separately concluded that the alloying, and increase in nickel concentration, produced steels with superior oxidation and corrosion resistance: the ratio 25%Cr - 20%Ni was reported as the most effective combination in reducing corrosion rates. Therefore, even though type 310 has double the nickel content of type 304 it does not necessarily follow that the concentrations recorded here should be of the same order, because the type 310 alloys have exceptional corrosion resistance.

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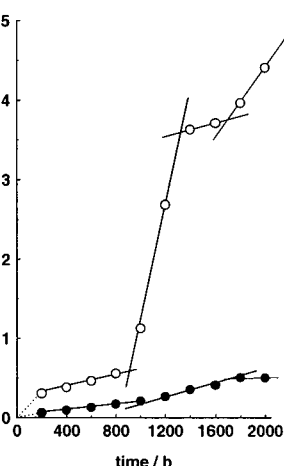


Fig. 6 (left). Concentration of nickel determined by ICP analysis in a thin film of molten sulfate in contact with type 304 austenitic stainless steel, and sampled every 200 h. Open circles, pre-oxidised; filled circles, pre-carburised.

Fig. 7 (right). As above, but for type 310 austenitic stainless steel.

For type 304 the ratio of nickel to iron is 1 : 7, and thus a difference in the first recorded concentrations, after 200 h, for these two elements would be expected. However this was not seen, the concentrations giving a ratio of 1 : 9. In accounting for this anomaly and other of our observations the free energies of formation of the oxides for iron, chromium and nickel are relevant since  $\text{Cr} (-261 \text{ kJ mol}^{-1}) \gg \text{Fe} (-176 \text{ kJ mol}^{-1}) > \text{Ni} (-126 \text{ kJ mol}^{-1})$ . These values are for the individual pure metals, and not determined from alloys, but were measured in molten salt and thus indicate the observed trends. Wood and Stott[9], in a study on the relative passivity of iron and nickel, have shown that iron oxide has a greater porosity and diffusion rate of oxidant through the oxide, consequently allowing the relatively slow build-up of the passive layer  $\text{Cr}_2\text{O}_3$ , for type 304.

nickel, have shown that iron oxide has a greater porosity and diffusion rate of oxidant through the oxide, consequently allowing the relatively slow build-up of the passive layer  $\text{Cr}_2\text{O}_3$ , for type 304.

A corrosion mechanism for oxidised nickel in type 304 steel is now proposed. On initial attack by the molten sulfate on the steel a protective  $\text{Cr}_2\text{O}_3$  layer forms. Due to the relatively low level of chromium in the steel matrix, build-up of the thin layer is slow. During build-up, oxidants reach the metal surface. Since iron is readily oxidised, any oxidant at the metal surface will preferentially react with iron. Only a little nickel within the steel will thus be oxidised, producing a lower than expected value for nickel entering the melt. This explanation also applies for the low levels of nickel found for type 310.

#### **4.2.1. Carburisation**

The nickel concentration increases measured for carburised type 304 specimens over oxidised 304 ones follow the same pattern observed for iron in the melt. In all four time zones, the increase in nickel concentration in the melt is constant. Thus again, as with iron concentrations, since carburisation leads to chromium depletion the passive  $\text{Cr}_2\text{O}_3$  layer forms at a slower rate.

However, with carburised type 310, significant differences were observed. Initially the small increase is as in the previous cases due to cracking of the oxide scale at the specimen edges and corners. In the second time zone a dramatic increase in nickel concentration was observed, several orders of magnitude greater than the corresponding increase for type 304. This feature is intimately linked with the reduced chromium concentration within the steel, resulting from the formation of chromium carbide.

The key factor here is the reaction mechanisms within the scale in the absence of chromium oxide. These mechanisms result in the formation of a network of nickel sulfide within the scale. This sulfide network serves as a rapid diffusion path for the outward diffusion of nickel to form nickel sulfide and pyrosulfates at the oxide-metal interface. Thus a steel, in this case type 310, containing the greater quantity of nickel will provide a greater network of nickel sulfide, subsequently observed as the dramatic increase in nickel concentration within the melt.

### **4.3. Chromium**

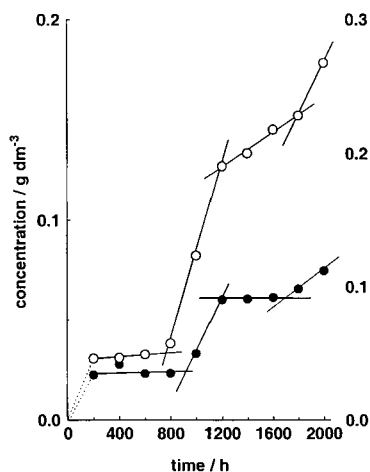
The above results and discussion show that the concentrations of iron and nickel entering the thin molten salt film were dependent upon the rate of build-up of the  $\text{Cr}_2\text{O}_3$  layer. Here it will be shown that levels of chromium found in solution are related also to the formation of this layer. However, this only applies to the oxidised steels. The increases in chromium concentration for the carburised steels are due almost exclusively to carbide formation and its subsequent dissolution. Chromium concentrations in solution are much less than those for iron and nickel, for both pre-oxidised and pre-carburised steels, by approximately two orders of magnitude, Figs. 8 and 9. Garrett and Penfold[18] studied the relative stability of the oxides of iron, nickel and chromium to resist sulfidation by molten sulfates and obtained the order  $\text{NiO} > \text{Fe}_2\text{O}_3 > \text{Cr}_2\text{O}_3$ .

#### **4.3.1. Overall comparisons**

The greater initial concentration detected for pre-oxidised chromium for type 310 (Fig. 4) compared to that for type 304 (Fig. 7) is not a result that would be expected, because type 310 forms the passive  $\text{Cr}_2\text{O}_3$  layer at a greater rate than that for type 304, effectively halting the dissolution processes sooner. Hence a lower initial chromium concentration for type 310 would seem more likely. No explanation involving mechanistic or corrosion processes is able to reconcile this anomaly. We therefore assume that after sectioning the Macor crucible containing the sample, when

were dissolved in  $0.5 \text{ mol dm}^{-1}$  HCl for analysis. The analysis concentrations of chromium in the melt, for type 310 only, will be enhanced by the presence of particles of the passive layer. In future studies it will therefore be important to filter or centrifuge an aqueous solution of the solidified salt before acidification, to test this suggestion and enable the proper concentrations of only the sulfato complexes of chromium to be determined.

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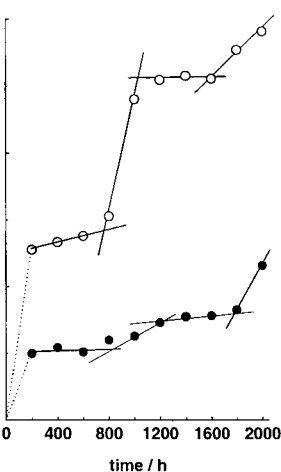


Fig. 8 (left). Concentration of chromium determined by ICP analysis in a thin film of molten sulfate in contact with type 304 austenitic stainless steel, and sampled every 200 h. Open circles, pre-oxidised; filled circles, pre-carburised.

Fig. 9 (right). As above, but for type 310 austenitic stainless steel.

However, as would be expected, a greater increase in the overall concentration for chromium was obtained for type 310 when the data for the pre-carburised coupons were compared but, unlike iron and nickel, where concentrations were dependent upon  $\text{Cr}_2\text{O}_3$  formation rates, increases in chromium concentration are here due to quantities of chromium carbide dissolving. This becomes apparent upon examining the mechanisms and processes obtaining in the individual time zones.

#### 4.3.2. Pre-oxidised type 304

The initial concentration (200 h) for chromium in the first time zone is due to the simultaneous formation and dissolution of oxide and sulfide at the metal surface, for which equations analogous to Eq. 2, Eq. 8 and Eq. 10 may be written. These reactions are only able to proceed while the oxide layer is forming, and even then the rates of reaction are very slow. Once the  $\text{Cr}_2\text{O}_3$  layer is complete then reaction with  $\text{SO}_3$  and  $\text{O}_2$  at the metal- $\text{Cr}_2\text{O}_3$  interface is only possible by diffusion. The low porosity of  $\text{Cr}_2\text{O}_3$  effectively prevents this, and hence no further increase in chromium levels in the melt is detected.

Explanations of the processes in the second time zone leading to spallation have been given above, due to the build-up of oxide scale. Thus increases in chromium levels seen here are due to spallation. In the last two time zones re-passivation followed by spallation now takes place, with the mechanisms previously described for chromium diffusion, and oxide scale build-up, so no further explanation is needed here.

#### 4.3.3. Pre-carburised type 304

The marginal increase in the first time zone in chromium concentration is due to the partial dissolution of chromium carbide at the surface of the steel coupled with the simultaneous formation and dissolution of quantities of  $\text{Cr}_2\text{O}_3$ . In the second zone the increase in the dissolution arises because the protective layer is destroyed by spallation and the underlying metal is attacked, now

and dissolution of quantities of  $\text{Cr}_2\text{O}_3$ . In the second zone the increase in the dissolution arises because the protective layer is destroyed by spallation and the underlying metal is attacked, now being denied the beneficial effect of chromium due to the precipitation of chromium carbide. Dissolution of exposed carbides concentrated at grain boundaries will also occur.

We now propose that the overall mechanism operating here is as follows. Initially a mixed oxide scale is formed; transport of oxidants through the scale leads to its growth, and eventual spallation; there is now insufficient chromium in the denuded areas to re-form rapidly a passive  $\text{Cr}_2\text{O}_3$  layer and so dissolution of the metal adjacent to the grain boundary now occurs; this results in the formation of pits, exposing the carbide to the molten sulfate; this process continues until the carbide particles are eventually released (dislocated) from the metal due to intergranular corrosion around them; these carbide particles are then transported into the body of the melt and are then partially dissolved, increasing the concentration of the sulfato chromium complexes in the melt; and the process is finally terminated when sufficient chromium has diffused from the body of the steel to the metal-melt interface to re-form the protective oxide scale of  $\text{Cr}_2\text{O}_3$ .

In the last two zones the re-passivation of the surface of the steel is once again observed as a cessation of the increase in chromium concentration, and then followed a concentration rise as the process is repeated and spallation again occurs. This time the duration of passivity is somewhat shorter than the first time as the chromium available in the steel has become somewhat depleted and hence the protective layer will be slightly less effective.

#### **4.3.4. Pre-oxidised type 310**

The unexpected initial high concentration of chromium has been explained above. In the next zone the spallation process for the separation of oxide from the metal appears here as a small increase in chromium concentration, the gradient for this increase is less than that for type 304. This indicates that type 310 forms the passive  $\text{Cr}_2\text{O}_3$  layer at a greater rate, limiting the dissolution of the metal. As before, the last two time zones show the repetition of passivation followed by spallation.

#### **4.3.5. Pre-carburised type 310**

Upon comparing the initial levels of chromium concentrations for types 304 and 310, a marked increase is seen for the latter, 0.013 compared with  $0.005 \text{ g dm}^{-3}$  for type 304. This nearly three-fold increase does not reflect the relative chromium content, 25 : 18. Additional quantities of oxide entering the melt for type 310 have been noted above but this is not sufficient to produce the three-fold increase. Thus, the most feasible explanation is the more extensive removal of chromium from carburised high chrome steels than from similarly carburised low chrome steels.

The mechanism by which this takes place has also been described above but there are certain differences between the two steel types. Although they both have the same time period for their first passive layer, 800 h, the high chrome steel now has a shorter period before the second passivation period commences, at 1200 h for type 304 but 1000 h for type 310. Thus although more chromium is entering the melt in the latter case this datum confirms that higher chrome steels regenerate their protective  $\text{Cr}_2\text{O}_3$  layer faster than type 304.

### **5. Conclusions**

Hot corrosion studies using thin films of molten sulfate are reported here in detail for the first time. This was achieved by the use of a specially designed and machined crucible to hold coupons of type 304 and 310 steels in the melt essentially totally surrounded by molten salt to a uniform depth of 1 mm. Pre-oxidised and pre-carburised coupons were held at  $650^\circ\text{C}$  in the melt under a synthetic flue

gas atmosphere for up to 2000 h and analysed at 200 h intervals for the concentrations of iron, chromium and nickel entering the melt. A clear pattern emerged. After initial attack the concentration of these elements remained essentially constant for around 800 h, after which spallation of the protective  $\text{Cr}_2\text{O}_3$  layer and rapid attack occurred over the next 400 h, by which time the protective layer had reformed and concentration levels remained constant for around 700 h when the process was repeated.

The pre-carburised coupons produced a several-fold increase in iron, chromium and nickel concentrations in the melt over pre-oxidised coupons. Surprisingly the high chrome steel, type 310, released three times as much chromium into the melt as the low chrome type 304 steel. This may be due to some of the passivating  $\text{Cr}_2\text{O}_3$  layer not adhering to the coupon when it was removed from the quenched melt in certain sectioned crucibles. Instead, some of this layer appeared in the quenched melt removed for analysis and thus artificially slightly increased the chromium levels.

This is, to our knowledge, the first time the stop-start corrosion mechanism has been identified experimentally in this film hot corrosion, and confirms and quantifies the increased corrosion that takes place if superheater and reheater tubes made of type 304 or 310 steels are subjected to reducing conditions during a failed start-up procedure or subsequently.

## 6. Acknowledgements

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# The Role of Molten Salts in the Corrosion of Metals in Waste Incineration Plants

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**Keywords:** Chloride and Sulfate Melts, Deposits, Heavy Metal Compounds, High Temperature Corrosion, Waste Incineration

## Abstract

Analysis of deposits taken from heavily corroded boiler tubes of waste fired plants have indicated the presence of molten phases i.e. eutectic mixtures of chlorides and sulfates containing heavy metal compounds like  $\text{PbCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{PbSO}_4$  and  $\text{ZnSO}_4$ . The aim of this work is to study the corrosion behaviour of steels and nickel-based alloys in contact with synthetic Zn and Pb containing chloride and sulfate mixtures. Thermogravimetric experiments were conducted on 2.25Cr-1Mo beneath molten  $\text{PbCl}_2$ ,  $\text{ZnCl}_2$  at 500 and 600 °C in He-5 vol.%  $\text{O}_2$  as well as beneath a eutectic 50 wt.% KCl-50 wt.%  $\text{ZnCl}_2$  mixture in the temperature range from 250-400 °C in an He-5 vol.%  $\text{O}_2$  atmosphere. Additionally, exposure tests of low- and high alloy steels were carried out beneath a molten  $\text{CaSO}_4$ - $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$ - $\text{PbSO}_4$ - $\text{ZnSO}_4$  mixture at 600 °C in an  $\text{N}_2$ -5 vol.%  $\text{O}_2$  atmosphere with and without additions of 1000 vppm  $\text{SO}_2$  or 1000 vppm HCl.

## 1. Introduction

The process of burning waste produces very corrosive combustion products, due to the complex and heterogenous composition of the fuel. Especially the increasing amount of chlorine containing compounds such as PVC have caused severe corrosion problems in waste fired boilers. As shown in Table 1, deposits on boiler tubes from waste fired plants not only contain chlorine as corrosive species, but also Pb and Zn. The deposits were taken from three different plants in Germany and analysed by the author.

**Table 1:** Heavy-metal contents (Pb and Zn) and concentrations of chloride (wt. %) in deposits from three different waste fire fired boilers in Germany.

|           | $\text{Pb}^{2+}$ | $\text{Zn}^{2+}$ | $\text{Cl}^-$ |
|-----------|------------------|------------------|---------------|
| deposit 1 | 7.4              | 2.3              | 0.5           |
| deposit 2 | 1.6              | 2.9              | 0.1           |
| deposit 3 | 7.5              | 9.7              | 1.2           |

The tables shows quite clearly that heavy-metals are present in deposits in significant amounts, in addition to chlorine. Especially heavy-metal chlorides, but also sulfates are forming low melting eutectics within the deposits so that the occurrence of molten phases is expected. Table 2 gives an overview of some of those low melting salt mixtures (partially extracted from [1]).

**Table 2:** Melting points of salt mixtures containing heavy-metal compounds. Especially the chlorides have low melting points down to 250 °C.

| Composition [wt. %]                                                                  | melting point [°C] |
|--------------------------------------------------------------------------------------|--------------------|
| ZnCl <sub>2</sub>                                                                    | 318                |
| PbCl <sub>2</sub>                                                                    | 498                |
| 48ZnCl <sub>2</sub> - 52 KCl                                                         | 250                |
| 82ZnCl <sub>2</sub> - 18 KCl                                                         | 262                |
| 84ZnCl <sub>2</sub> - 16 KCl                                                         | 262                |
| 73ZnCl <sub>2</sub> - 27PbCl <sub>2</sub>                                            | 300                |
| 31NaCl - 69PbCl <sub>2</sub>                                                         | 410                |
| 21KCl - 79PbCl <sub>2</sub>                                                          | 411                |
| 17NaCl - 83PbCl <sub>2</sub>                                                         | 415                |
| 39ZnCl <sub>2</sub> - 50KCl - 11PbCl <sub>2</sub>                                    | 275                |
| 35ZnCl <sub>2</sub> - 48NaCl - 17PbCl <sub>2</sub>                                   | 350                |
| 16NaCl - 40KCl - 44PbCl <sub>2</sub>                                                 | 400                |
| K <sub>2</sub> SO <sub>4</sub> - Na <sub>2</sub> SO <sub>4</sub> - ZnSO <sub>4</sub> | 384                |
| KCl - ZnCl <sub>2</sub> - K <sub>2</sub> SO <sub>4</sub> - ZnSO <sub>4</sub>         | 292                |
| K <sub>2</sub> SO <sub>4</sub> - Na <sub>2</sub> SO <sub>4</sub> - CaSO <sub>4</sub> | 776                |

Analysis of corrosion phenomena and also laboratory corrosion studies under waste incineration conditions were carried out since many years. A lot of work was done by Krause and coworkers from the Battelle Institute in the United States. Systematic studies on the effect of chlorine content in the waste on the corrosion of carbon steel were conducted in the temperature range from 204 to 538 °C. It was found that addition of PVC to the waste increases the chlorine content in the deposits and, therefore, the corrosion rate of the steel is enhanced by a factor from 40-150 % [2]. From these experiments, the more corrosive effect of chlorides in the deposits with respect to the sulfates was seen. Several reactions were put forward by Vaughan et al. [3], involving chlorine and sulfur species, partially releasing HCl or Cl<sub>2</sub> or forming solid NaCl as reaction products.

Reese and Grabke [4, 5] have shown the corrosive effect of *solid chlorides* like KCl, NaCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> on low- and high alloy steels in He-O<sub>2</sub> and He-O<sub>2</sub>-SO<sub>2</sub>-atmospheres at 500 and 700 °C by thermogravimetric experiments. The salt reacts with the oxide scale of the preoxidized sample forming ferrate or chromate and releasing chlorine. The chlorine diffuses through cracks and pores of the oxide scale to the metal/scale interface, reacting to FeCl<sub>2</sub>(s). As the vapour pressure of the chloride is 10<sup>-4</sup> bar at 500 °C, it evaporates and the volatile chloride diffuses outward through the oxide scale. At the interface oxide/gas atmosphere the reaction to Fe<sub>2</sub>O<sub>3</sub> takes place, releasing chlorine again. The growth of the Fe<sub>2</sub>O<sub>3</sub> in cracks and pores of the oxide destroys the scale and corrosive gas can react with the unprotected metal. Hence, a scale is produced on the metal substrate which is not passivating and for this reason, the mechanism was nominated 'active oxidation' by Lee and McNallan [6]. The chlorine plays a catalytic role in this corrosion process, because it is not consumed. In depth thermogravimetric studies on the mechanism of 'active oxidation' were carried out by Reese and Grabke [4], showing that evaporation of FeCl<sub>2</sub>(g) from the metal/scale interface is the rate determining step in NaCl induced corrosion.

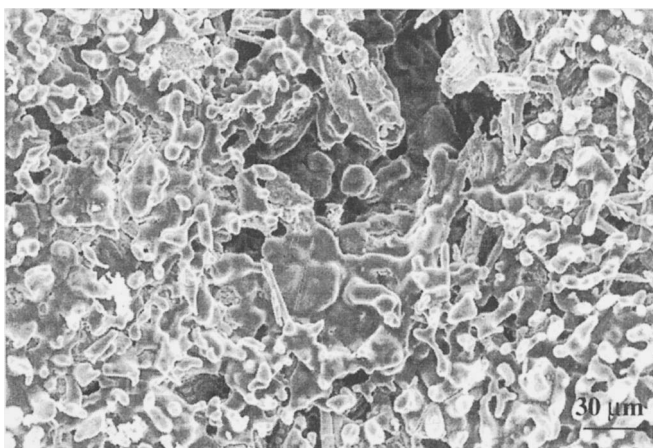
Further work with *fly ash deposits* from waste incinerator plants was carried out by Spiegel and Grabke [7-9], using thermogravimetric experiments and exposure tests. Deposition of fly ash deposits on the 2.25Cr-1Mo steel leads to enhanced corrosion at 500 °C in He-O<sub>2</sub> atmospheres due to chlorides, present in the deposits [7, 8]. The corrosion was severe in He-O<sub>2</sub>-HCl atmospheres due to the formation of alkali- and heavy-metal chlorides in the deposits by reaction of sulfates with HCl gas. Addition of SO<sub>2</sub> to the He-O<sub>2</sub>-HCl mixture leads to decreased corrosion due to the



stabilization of the sulfates in the deposits. In exposure tests on high alloy steels at 600 °C in N<sub>2</sub>-O<sub>2</sub>, a molten sulfate/chloride phase was observed in the deposits [9] and heavy-metal rich corrosion products like PbCrO<sub>4</sub> and ZnCr<sub>2</sub>O<sub>4</sub> were observed on top of the oxide scale beneath the deposits. The corrosion process was recognized as basic fluxing by a heavy-metal rich salt melt. In N<sub>2</sub>-O<sub>2</sub>-SO<sub>2</sub>, acidic fluxing takes place and the corrosive attack is less severe. These experiments show quite clearly the inhibiting effect of SO<sub>2</sub> on chlorine induced corrosion beneath fly ash deposits.

Studies on the effect of *molten phases* in deposits on the corrosion of steels were carried out especially in the United States and also in Japan. Otsuka et al. [10] studied the effect of a KCl - NaCl-FeCl<sub>2</sub> mixture with additions up to 30 mol. % PbCl<sub>2</sub> on the corrosion of steels and nickel-based alloys in the atmosphere N<sub>2</sub>-20 vol.% H<sub>2</sub>O-7.5 vol.% O<sub>2</sub>-7.5 vol. % CO with 1500 vppm HCl -300 vppm SO<sub>2</sub>. They observed enhanced corrosion already at 400 °C, and the extent of attack decreases with increasing nickel content of the alloy. Compared with a deposit containing chloride, application of a Na<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub> mixture below its melting point not significantly affects on the corrosion of the tested alloys in the same gas atmosphere. Further investigations on this topic were carried out by Kawahara et al. [11]. They studied the effect of additions of PbCl<sub>2</sub>, ZnCl<sub>2</sub> and ZnSO<sub>4</sub> to a waste incinerator ash on the corrosion of steels and coating materials like 80Ni20Cr. The experiments were carried out at 350 and 230 °C in an N<sub>2</sub>-20 vol.% O<sub>2</sub>-10 vol.% CO<sub>2</sub>-10 vol.% O<sub>2</sub>-atmosphere with additions of 1000 vppm HCl and 100 vppm SO<sub>2</sub>. After addition of PbCl<sub>2</sub> and ZnCl<sub>2</sub>, enhanced corrosion of the materials was observed, whereas after addition of ZnSO<sub>4</sub> the corrosion decreases compared to the unmodified ash.

Failure case analysis from german waste fired boilers were carried out by Spiegel [12]. It was found that in every case, severe corrosion of low alloy steels and also of nickel-based alloys was observed only in the presence of deposits. In most of the deposits molten phases were detected, as shown in Figure 1.



**Figure 1:** SEM micrograph of deposits from a heavily corroded boiler tube. The molten phase is a KCl-ZnCl<sub>2</sub> eutectic.

These salt melts were identified either as sulfates in contact with the flue gas or as chlorides at the deposit/scale phase boundary. The chemical composition of the sulfate melts is generally within the

CaSO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>SO<sub>4</sub> system, including heavy-metal compounds like ZnSO<sub>4</sub> and PbSO<sub>4</sub>. The chloride melt is mainly composed of KCl-ZnCl<sub>2</sub> with some additions of NaCl and PbCl<sub>2</sub>.

## 2. Experimental

The laboratory studies beneath molten chlorides were carried out using thermogravimetric experiments, in the case of the tests beneath molten sulfate exposure test were conducted. The thermogravimetric experiments were performed in a horizontal microbalance, connected to a gas mixing equipment. Experiments were carried out in an He-5 vol.% O<sub>2</sub> atmosphere with a water content less than 10<sup>-4</sup> bar at temperatures ranging from 250-600 °C. The salts used, were PbCl<sub>2</sub>, ZnCl<sub>2</sub> and a 50 wt.% ZnCl<sub>2</sub>-50 wt.% KCl mixture. The testing gas was established by mixing the commercial bottled gases helium and oxygen which were dried by passing through columns filled with P<sub>2</sub>O<sub>5</sub>. The salt was deposited after 24 hours of preoxidation on top of the oxide scale, the amount of salt was 15 mg/cm<sup>2</sup>. The materials used were 10 CrMo 9 10, its compositions is given in Table 3:

**Table 3:** Composition (wt. %) of the alloys used in the thermogravimetric experiments and exposure tests.

|                           | Fe    | Cr      | Ni    | Si   | others             |
|---------------------------|-------|---------|-------|------|--------------------|
| <b>10 CrMo 9 10</b>       | bal.  | 2.21    | -     | -    | Mo: 0.91           |
| <b>X 20 CrMoV 12 1</b>    | bal.  | 10/12.5 | -     | -    | V: 0.25/0.35       |
| <b>X 5 CrNiCeNb 32 27</b> | bal.  | 27.35   | 31.45 | 0.21 | Nb: 0.83; Ce: 0.09 |
| <b>Alloy 602 CA</b>       | 9.65  | 25.3    | bal.  | -    | Al: 2.13           |
| <b>Inconel 625</b>        | 4.65  | 22.2    | bal.  | 0.09 | Mo: 9.2; Nb: 3.5   |
| <b>Alloy 45 TM</b>        | 22.65 | 27.40   | bal.  | 2.66 | Mn: 0.36           |

Before starting the experiments, the samples were ground with 1000 grid SiC- paper, measured and cleaned in acetone in an ultrasonic bath.

The furnace for the exposures was connected in the same way, however, the N<sub>2</sub>-5 vol.% O<sub>2</sub> mixture was supplied as a premixed commercial gas. The gas was also dried by passing through columns filled with P<sub>2</sub>O<sub>5</sub> before entering the furnace. According to the large temperature constant zone, it was possible to test 24 samples at the same time. The exposure experiments were carried out at 600 °C, using the sulfate mixture shown in Table 4 and also different metallic materials, listed in Table 7.

**Table 4:** Salt mixture (wt. %) used in the exposure tests.

| CaSO <sub>4</sub> | K <sub>2</sub> SO <sub>4</sub> | Na <sub>2</sub> SO <sub>4</sub> | PbSO <sub>4</sub> | ZnSO <sub>4</sub> |
|-------------------|--------------------------------|---------------------------------|-------------------|-------------------|
| 36                | 21                             | 15                              | 21                | 7                 |

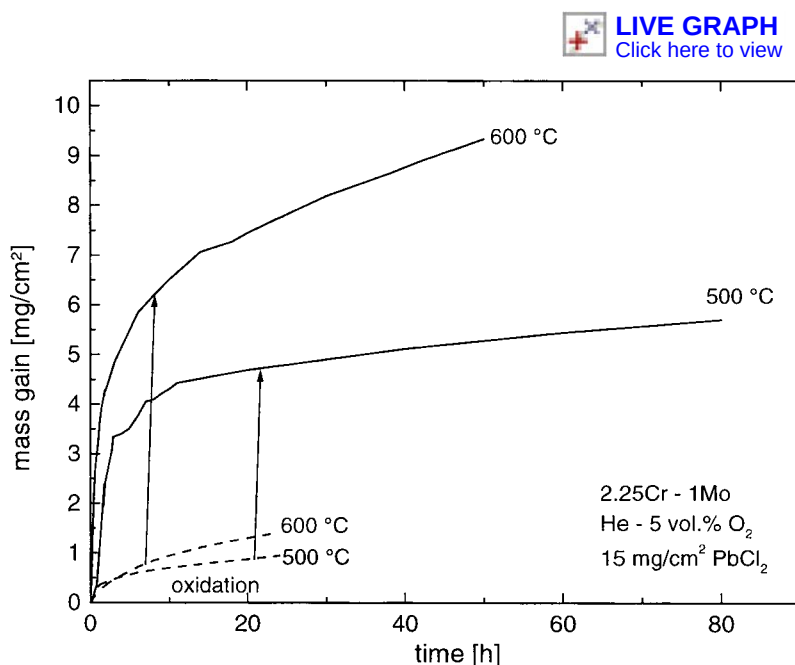
The samples were preoxidized at 600 °C in N<sub>2</sub>-5 vol. % O<sub>2</sub> for 5 hours and embedded in approx. 1.5 g of the salt mixture afterwards. The extent of corrosion was determined by measuring the mass loss after 360 h of reaction after removal of the corrosion products by chemical etching in a KMnO<sub>4</sub>-

NaOH-solution at 80 °C. The samples were prepared by grinding with 600 grid SiC-paper, measuring and weighing before the experiments.

### 3. Thermogravimetric experiments beneath molten chlorides

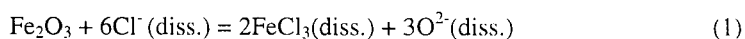
#### 3.1 Corrosion beneath $\text{PbCl}_2$

The influence of  $\text{PbCl}_2$  on the oxidation of 2.25Cr-1Mo was investigated in He-5 vol.%  $\text{O}_2$  at 500 and 600 °C. In Figure 2, the mass gain of 2.25Cr-1Mo, covered with 15  $\text{mg/cm}^2$   $\text{PbCl}_2$ , is shown.

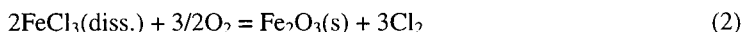


**Figure 2:** Enhanced corrosion of 2.25Cr-1Mo in He-5 vol.%  $\text{O}_2$  at 500 and 600 °C covered with 15  $\text{mg/cm}^2$   $\text{PbCl}_2$ .

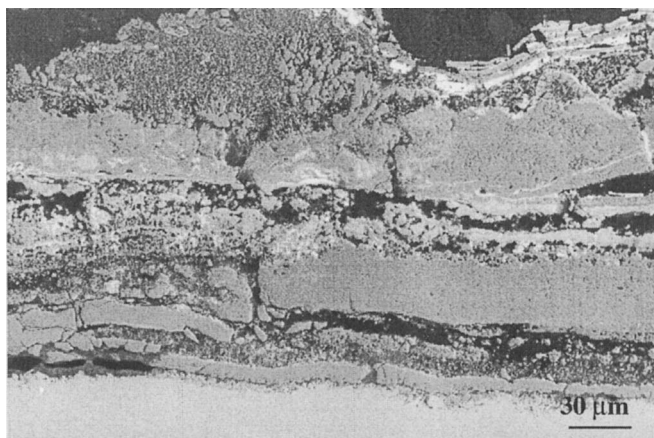
Compared to the oxidation without the salt, the mass increases significantly after deposition of the chloride. The corrosion is much severe at 600 °C and still significant at 500 °C. Investigations of the samples after the experiments show at 500 and 600 °C the formation of a thick and voluminous scale of  $\text{Fe}_2\text{O}_3$  with small amounts of  $\text{FeCl}_2$  at the metal/oxide interface. At 500 °C, no Pb-rich phase was detected by XRD, although lead was identified all over the scale by EDX-analysis. In Figure 3, a metallographic cross section is shown. Especially on top of the scale at the former melt/gas interface  $\text{Fe}_2\text{O}_3$  precipitates are visible. The formation of the precipitates occurs by a fluxing mechanisms i.e. dissolution of the  $\text{Fe}_2\text{O}_3$  scale in the chloride melt at the melt/scale interface by reaction (Eq. 1):



As the concentration of dissolved  $\text{FeCl}_3$  is much higher in contact with the oxide scale than at the melt/gas interface,  $\text{FeCl}_3$  diffuses towards the melt film to the melt/gas phase boundary. In contact with the gas phase,  $p(\text{O}_2)$  is much higher than at the melt/scale interface and, therefore,  $\text{Fe}_2\text{O}_3$  is formed by the following reaction (Eq. 2):



As the oxide scale, formed by this dissolution/precipitation process is not protective, the corrosion of the metal is markedly enhanced by deposition of  $\text{PbCl}_2$ .

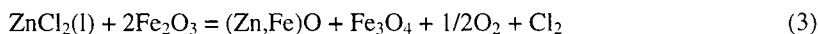


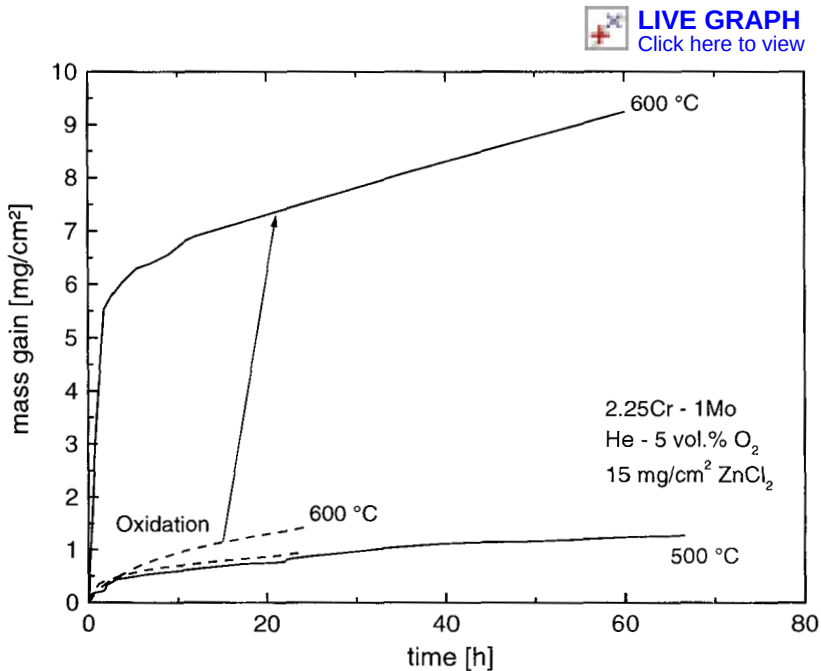
**Figure 3:** Metallographic cross section of 2.25Cr-1Mo, formed by reaction beneath  $\text{PbCl}_2$ -deposits in He-5 vol.%  $\text{O}_2$  at 500 °C. The scale is porous and broken. Especially at the former melt/gas interface fine-grained  $\text{Fe}_2\text{O}_3$  particles are formed.

### 3.2 Corrosion beneath $\text{ZnCl}_2$

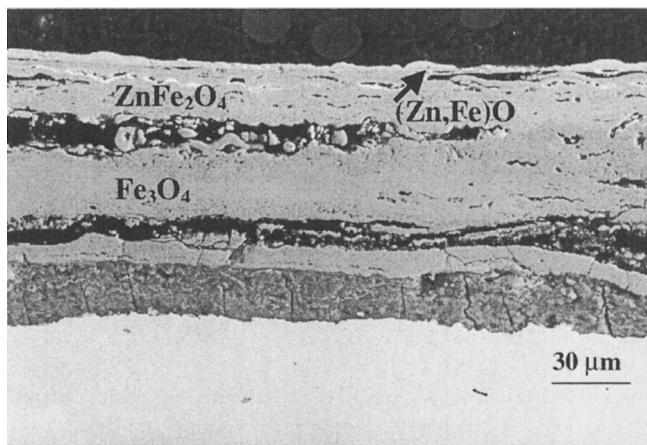
In Figure 4 the influence of  $\text{ZnCl}_2$  on the corrosion of 2.25Cr-1Mo is shown. The oxidation is enhanced at 600 °C, at 500 °C it is comparable to the normal oxidation rate.

Microprobe analysis (EPMA) has shown that the oxide scale, formed at 500 °C, consists of a thick  $\text{Fe}_3\text{O}_4$  scale, covered with an intermediate layer of  $\text{ZnFe}_2\text{O}_4$  and a thin  $(\text{Fe},\text{Zn})\text{O}$  scale on top in contact with the gas atmosphere (Figure 5). At the metal scale interface, an enrichment of molybdenum and chromium was observed. According to the low mass gain and the morphology of the corrosion products, no dissolution and reprecipitation of the scale takes place. Obviously,  $\text{ZnFe}_2\text{O}_4$  is an insoluble corrosion product. As the scale mainly consists of  $\text{Fe}_3\text{O}_4$ , the  $\text{Fe}_2\text{O}_3$  formed during preoxidation was reduced due to the low  $p(\text{O}_2)$  in contact with the molten salt (Eq. 3):





**Figure 4:** Mass gain of 2.25Cr-1Mo in He-5 vol.%  $\text{O}_2$  at 500 and 600 °C covered with  $15 \text{ mg}/\text{cm}^2$   $\text{ZnCl}_2$ .



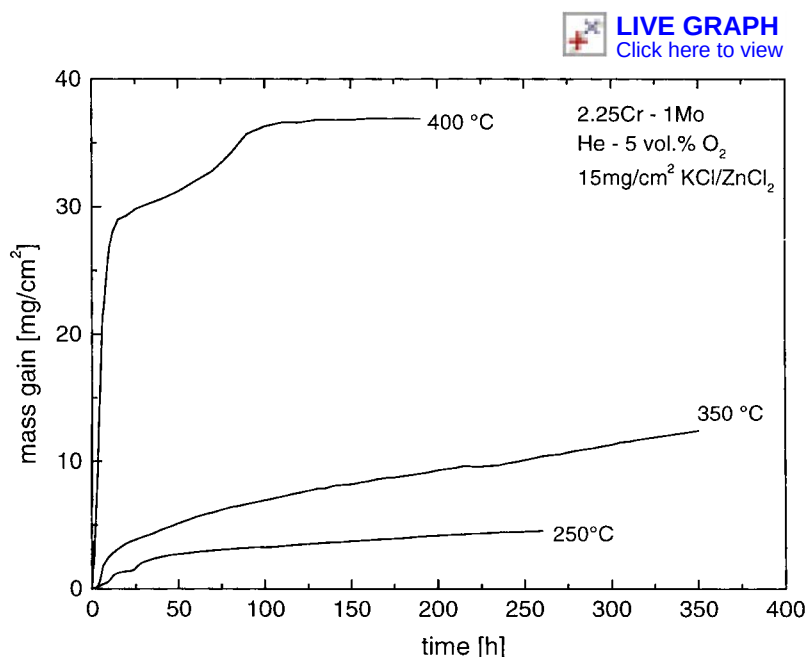
**Figure 5:** Metallographic cross section of 2.25Cr-1Mo, formed by reaction beneath  $\text{ZnCl}_2$ -deposits in He-5 vol.%  $\text{O}_2$  at 500 °C. The dense layer consists of  $(\text{Zn,Fe})\text{O}$  (arrow) on top,  $\text{ZnFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  underneath. The dark phase underneath the  $\text{Fe}_3\text{O}_4$  is enriched in Mo and Cr.

At 600 °C, a rapid mass gain was observed and the scale consists of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  in contact with the metal. Neither  $\text{ZnFe}_2\text{O}_4$  nor  $(\text{Zn,Fe})\text{O}$  was observed in the entire scale. The accelerated

scale growth is due to accelerated diffusion of iron through the  $\text{Fe}_3\text{O}_4$  scale. It is well known from other spinels like  $\text{CoFe}_2\text{O}_4$  that incorporation of divalent cations ( $\text{CoO}$  and  $\text{MgO}$ ) into the spinel structure increases the tracer diffusion coefficient of cations in these compounds [13]. On the other hand, also chlorine induced 'active oxidation' will play a role, since small amounts of  $\text{FeCl}_2$  were detected at metal/scale phase boundary.

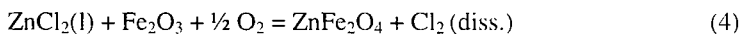
### 3.3 Corrosion beneath a $\text{KCl-ZnCl}_2$ mixture

Figure 6 shows the mass gain of 2.25Cr-1Mo-steel beneath the  $\text{KCl-ZnCl}_2$  mixture in He-5 vol.%  $\text{O}_2$  in the temperature range from 250-400 °C. At 400 °C the corrosion is markedly enhanced in the first 100 hours of the experiment and then retards to a much slower rate. At 350 °C the mass gain is much less but still enhanced, whereas at 250 °C the mass gain is a little bit smaller than at 350 °C.

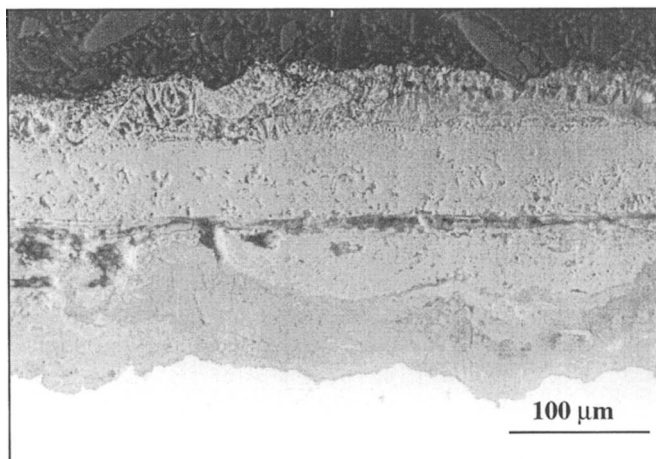


**Figure 6:** Mass gain of 2.25Cr-1Mo-steel beneath  $\text{KCl-ZnCl}_2$ -deposits in He-5 vol.%  $\text{O}_2$  at 250 – 400 °C.

Figure 7 shows a metallographic cross section of the corrosion scale, formed at 400 °C. Three different scale morphologies have formed during the corrosion process. An outer, porous scale, consisting of  $\text{ZnFe}_2\text{O}_4$ , formed by reaction (Eq. 4):

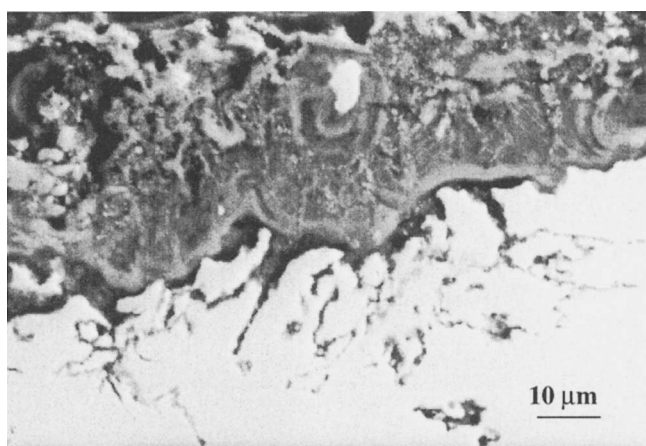


Underneath this corrosion layer, a thick scale of  $\text{Fe}_2\text{O}_3$  is formed, exhibiting an inner and an outer part, where the inner part also contains dissolved chromium. In contact with the metal, a heterogenous scale exists, containing iron, potassium and chromium in combination with oxygen and chlorine.



**Figure 7:** Metallographic cross section of 2.25Cr-1Mo-steel after reaction beneath KCl-ZnCl<sub>2</sub>-deposits in He-5 vol.% O<sub>2</sub> at 400 °C. The inner layer consists of dark and bright shaded areas.

This inner layer is subdivided into a dark and a much brighter areas. The dark phase is an iron-rich oxide, containing mainly potassium and small amounts of chromium and chlorine. The bright areas at the metal/scale interface are iron-chlorides, with significant amounts of dissolved chromium, whereas the light area underneath the former metal/scale interface consists of iron-oxide. Obviously, metal-chlorides are formed during the corrosion process and are converted to oxides with time. In order to prove these assumption, short term experiments were conducted. Figure 8 shows the metal/scale interface of a sample, reacted for 24 h.

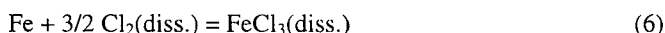


**Figure 8:** Metal/scale interface of 2.25Cr-1Mo-steel, formed after 24 h of reaction beneath KCl-ZnCl<sub>2</sub>-deposits in He-5 vol.% O<sub>2</sub> at 400 °C.

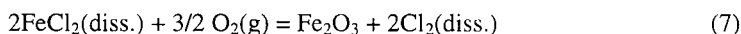
The corrosion front proceeds into the metal and some grains are completely detached from the metal structure. The light phase is iron-chloride, with some dissolved chromium.

Hence, the metal grain is converted to metal-chloride. The dark phase is also oxide, containing iron and potassium, however, the chlorine content of the dark phase is much higher than observed after longer reaction times. The morphology of the inner scale and also the very high corrosion rate strongly implies the formation of a molten phase at the metal/oxide interface. Since a lot of potassium is present in this part of the scale and iron-chloride is formed during the experiment, the molten phase is a KCl-FeCl<sub>2</sub> eutectic with a melting point of  $T_m$  ( $47\text{KCl}-53\text{FeCl}_2$ ) = 355 °C.

The corrosion process starts with the formation of ZnFe<sub>2</sub>O<sub>4</sub> on the surface of the scale and the melt is enriched in KCl due to consumption of ZnCl<sub>2</sub>. As a lot of potassium and only small amounts of zinc were detected at the metal/oxide interface, the potassium-rich melt penetrates the scale and reaches the metal substrate, dissolving iron and chromium from the alloy as chloride. As the oxidizing agent, chlorine gas stemming from reaction equation (4) is dissolved in the melt and transported to the metal surface where FeCl<sub>2</sub> and/or FeCl<sub>3</sub> is formed (Eqs. 5, 6):



The dissolved iron-chloride diffuses from higher concentrations (metal surface) to lower concentration (metal/gas interface) and oxidation takes place in regions with higher  $p(\text{O}_2)$  (Eq. 7):



Hence, the crystallization of the Fe<sub>2</sub>O<sub>3</sub> forms the inner oxide scale. With time, oxygen transport through cracks and pores of the oxide scale to the melt/scale interface takes place and the molten chloride is transferred to solid oxide and the corrosion rate retards.

The morphology of the scale, formed at 350 °C is quite similar. Precipitates of ZnFe<sub>2</sub>O<sub>4</sub> are detected on top of an Fe<sub>2</sub>O<sub>3</sub> scale, with a chlorine and potassium containing corrosion product underneath. The main difference to the sample reacted at 400 °C is the much thinner Fe<sub>2</sub>O<sub>3</sub> scale. Furthermore, the amount of zinc in the inner chloride containing scale is slightly higher. Hence, also at 350 °C a molten phase has formed, containing metal-chlorides. The small amount of zinc in the inner scale slightly decreases the melting point of the KCl-FeCl<sub>2</sub> eutectic. The lower corrosion rate can be explained by the retardation of diffusion processes through the melt and, therefore, a much thinner oxide scale has formed.

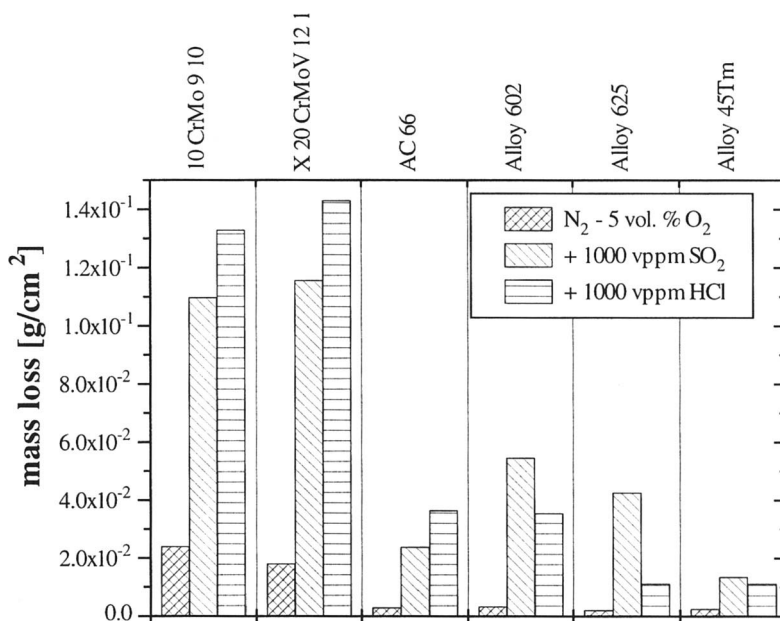
At 250 °C, the scale morphology is very different. A thick layer of solid FeCl<sub>2</sub> has formed on the metal surface without any potassium and zinc. On top of the scale, alternating layers of Fe<sub>2</sub>O<sub>3</sub> and potassium-rich oxides with FeCl<sub>2</sub> are detected. On top of the scale also ZnFe<sub>2</sub>O<sub>4</sub> was found.



## 4. Exposure tests beneath molten sulfates

### 4.1 Tests in $N_2-O_2$

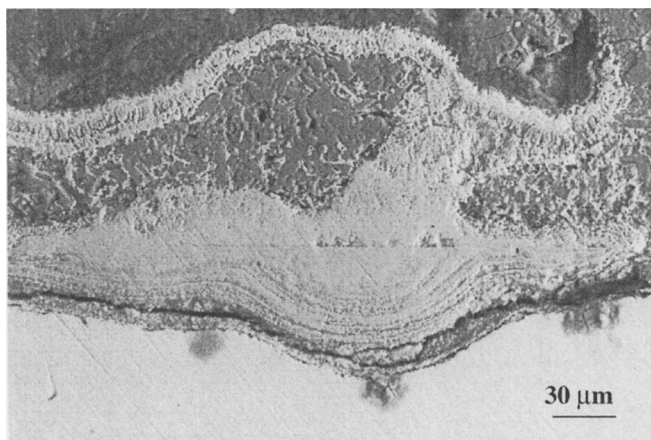
The effect of a  $PbSO_4$  and  $ZnSO_4$  containing molten sulfate mixture on the mass loss of low- and high-alloy steels and also on nickel-based alloys is shown in Figure 9.



**Figure 9:** Mass loss of steels and nickel-based alloys beneath  $PbSO_4$  and  $ZnSO_4$  containing sulfate in  $N_2$ -5 vol. %  $O_2$ ,  $N_2$ -5 vol. %  $O_2$ -1000 vppm  $SO_2$  and  $N_2$ -5 vol. %  $O_2$ -1000 vppm HCl at 600 °C.

The low alloy steels 10 CrMo 9 10 and X 20 CrMoV 12 1 exhibit the highest mass loss, whereas the high chromium- and also the nickel-based alloys are much better resistant. The corrosion product on 10 CrMo 9 10 is a thick and porous scale of  $Fe_2O_3$ , including solidified  $K_2SO_4$  and FeS underneath at the metal/scale interface. If the chromium content increases, the morphology of the products changes and pits are formed, as shown in Figure 10 for the X 20 CrMoV 12 1 steel. These pits are filled with layers of solidified  $K_2SO_4$ , alternating with chromium- and zinc-rich corrosion products ( $ZnCr_2O_4$ ), containing only small amounts of iron. In addition, voluminous  $Fe_2O_3$  is formed on top of the pits in the case of the X 20 CrMoV 12 1 alloy.

Along with those pits, chromium-free precipitates of iron- and nickel-oxides are found in the melt, containing various amounts of zinc, whereas the amount of the precipitating oxide decreases with increasing chromium content of the alloy.



**Figure 10:** Metallographic cross section of X 20 CrMoV 12 1, reacted beneath the molten  $\text{CaSO}_4\text{-Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-PbSO}_4\text{-ZnSO}_4$  salt mixture in  $\text{N}_2\text{-5 vol.\% O}_2$  at 600 °C.

With respect to the solubilities of the oxides in a pure  $\text{Na}_2\text{SO}_4$  melt [14], the basic solubility of  $\text{Fe}_2\text{O}_3$  and  $\text{NiO}$  seems to be higher than for  $\text{Cr}_2\text{O}_3$  under these certain conditions. The preformed  $\text{Fe}_2\text{O}_3$  and  $\text{NiO}$  are dissolved by basic fluxing (Eqns. 8,9):



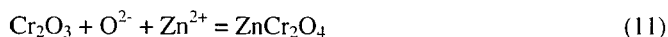
The  $\text{O}^{2-}$  - ions, involved in this process are produced by the dissociation of the sulfate ion according to reaction (Eq. 10):



At the melt/scale phase boundary the concentration of  $\text{O}^{2-}$  is high, because  $p(\text{O}_2)$  is quite low, due to the low solubility of  $\text{O}_2$  in the sulfate melt. Hence, basic fluxing of oxides takes place.

As the concentration of dissolved species is high at the oxide melt interface and low at the melt/gas phase boundary, the species diffuse towards the gas phase and precipitation takes place in regions of a lower concentration of  $\text{O}^{2-}$  according to the revers of reaction (Eqns. 8,9)

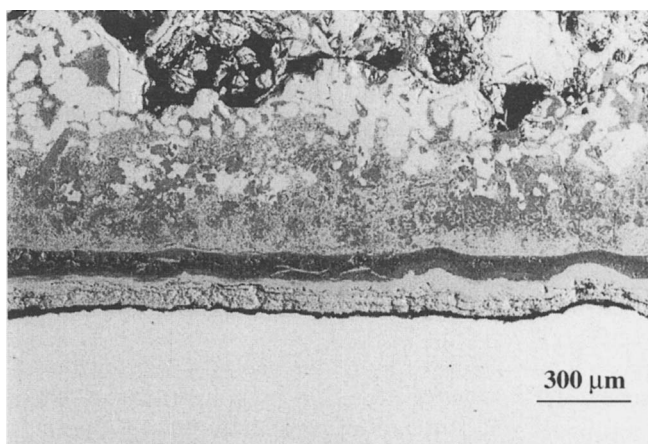
Chromia reacts to insoluble zinc-spinel (Eq. 11):



#### 4.2 Tests in $\text{N}_2\text{-O}_2\text{-SO}_2$

Figure 10 also shows the effect of 1000 vppm  $\text{SO}_2$  addition to the  $\text{N}_2\text{-5 vol.\% O}_2$ -atmosphere on the mass loss of the materials beneath the  $\text{PbSO}_4$  and  $\text{ZnSO}_4$  containing salt. In comparison with the atmosphere without  $\text{SO}_2$  a significant increase in mass loss occurs.

Considering the  $\text{SO}_2$ -containing gas, a separation of the melt takes place and the corrosion products are different from those, identified in the atmosphere without  $\text{SO}_2$ . The low alloy steels 10 CrMo 9 10 exhibit  $\text{Fe}_2\text{O}_3$  precipitates in the outer Ca-rich parts of the salt melt with much smaller amounts of zinc than in the precipitates formed in  $\text{N}_2$ -5 vol.%  $\text{O}_2$  without  $\text{SO}_2$ . The precipitates are separated by a K-rich melt containing dissolved iron from a Cr-containing oxide in contact with the metal and Fe- and Cr-sulfides underneath (Figure 11).



**Figure 11:** Metallographic cross section of 10CrMo 9 10, reacted beneath the molten  $\text{CaSO}_4$ - $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$ - $\text{PbSO}_4$ - $\text{ZnSO}_4$  salt mixture in  $\text{N}_2$ -5 vol.%  $\text{O}_2$ -1000 vppm  $\text{SO}_2$  at 600 °C. The melt is separated in a K-rich part (dark) and Ca-rich part with oxide precipitates.

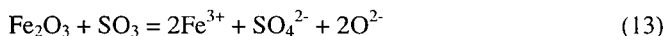
The AC 66 exhibits a layered corrosion product, consisting of  $\text{Cr}_2\text{O}_3$  and solidified salt, sometimes with small amounts of zinc. The product is also separated by a K-rich melt with dissolved iron and nickel from a Cr-sulfide layer in contact with the metal.

The corrosion products on the nickel-based alloys are slightly different from each other. Alloy 602 CA exhibits high amounts of  $\text{NiSO}_4$ , formed in pit-like structures with  $\text{Cr}_2\text{O}_3$  and some  $\text{Al}_2\text{O}_3$  underneath. The scale on Alloy 625 consists also of layers of  $\text{NiSO}_4$ , alternating with Ca-, K-sulfate containing dissolved nickel, at the metal scale interface also  $\text{Cr}_2\text{O}_3$  and Cr-sulfide is formed. The iron-rich alloy 45 TM exhibits internal layers of  $\text{Cr}_2\text{O}_3$ , mixed with some fine grained  $\text{SiO}_2$  within a matrix of solidified K-, Ca-sulfate, containing dissolved iron and nickel with Cr-sulfide underneath.  $\text{NiSO}_4$  was not detected. Chemical analysis of the salt on the nickel-based alloys shows significant amounts of dissolved nickel, the lowest concentration was measured for Alloy 45 TM and the highest for Alloy 602 CA.

In contrast to the corrosion products, formed in the atmosphere without  $\text{SO}_2$ , no heavy-metal-rich corrosion product was formed. The  $\text{SO}_2/\text{SO}_3$  from the gas phase is dissolved in the molten sulfate and a separation of the melt takes place, resulting in a Ca-rich part containing sodium sulfate and the heavy metals and a part rich in K, most probably  $\text{K}_2\text{S}_2\text{O}_7$  spreading along the metal surface. At 600 °C the formation of  $\text{K}_2\text{S}_2\text{O}_7$  is favoured compared to  $\text{Na}_2\text{S}_2\text{O}_7$  according to (Eq. 12):



At the low alloy steels the pyrosulfate melt dissolves  $\text{Fe}_2\text{O}_3$  by acidic fluxing (Eq. 13) :

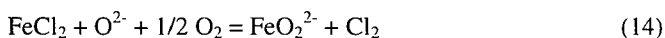


The dissolved  $\text{Fe}^{3+}$  diffuses through the  $\text{K}_2\text{S}_2\text{O}_7$  melt to the Ca-rich sulfate and precipitation of  $\text{Fe}_2\text{O}_3$  takes place due to the lower acidity of the melt. Also in this case  $\text{Cr}_2\text{O}_3$  is nearly insoluble, as already known for acidic environments. The solubility of NiO under acidic conditions is much higher than that of  $\text{Fe}_2\text{O}_3$ , therefore,  $\text{NiSO}_4$  is formed on the nickel-based alloys. Hence, no NiO precipitates are observed in the solidified melt.

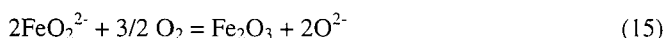
### 4.3 Tests in $\text{N}_2\text{-O}_2\text{-HCl}$

Compared to the  $\text{N}_2\text{-O}_2\text{-SO}_2$ -atmosphere, the mass loss is less in the HCl-containing gas for the nickel-based alloys, but enhanced for the iron-based materials. The morphology of the corrosive attack is comparable to that observed in  $\text{N}_2\text{-5 vol.}\% \text{ O}_2$  i.e. pit formation and precipitates in the solidified salt. The low alloy steels exhibit precipitates of  $\text{Fe}_2\text{O}_3$  in the salt melt and a voluminous scale of  $\text{Fe}_2\text{O}_3$  on top of the metal. In the case of X 20 CrMoV 12 1, pits are formed containing Cr-rich oxides, mainly  $\text{FeCr}_2\text{O}_4$ . At the metal/scale interface, some Cr-chloride was identified. The iron content of the corrosion product in the pits, formed on AC 66 is reasonable higher than in pits formed in the  $\text{N}_2\text{-5 vol.}\% \text{ O}_2$ -atmosphere. In addition small amounts of Cr-chlorides and Ni-sulfides are formed at the metal/scale interface. The behaviour of the nickel-based alloys is quite similar, the precipitates are iron- and nickel-oxides (Alloy 45 TM) or nickel-oxides respectively. Pits are formed, filled with layered  $\text{Cr}_2\text{O}_3$  with small amounts of dissolved ZnO. At the bottom of the pits, sulfides and chlorides of chromium and nickel are identified. No  $\text{NiSO}_4$  has formed as in the case of the  $\text{SO}_2$ -containing gas and only small amounts of dissolved nickel are analysed in the remaining salt. In conclusion, the amount of precipitates in the melt is much higher than in the case of the  $\text{N}_2\text{-5 vol.}\% \text{ O}_2$  atmosphere and the layered, Cr-rich corrosion product in the pits contains less amounts of zinc. For example, Figure 12 shows a metallographic cross section of X 12CrMoV 12 1 after reaction in the HCl-containing gas. In comparison with Figure 10, much more precipitates are formed.

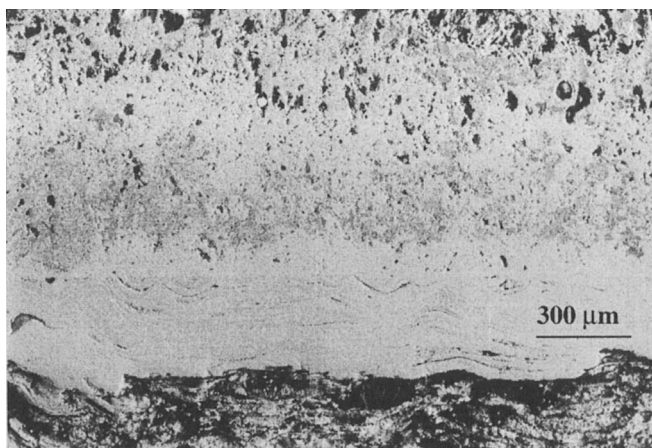
According to the higher amounts of precipitates in the solidified melt, the solubility of iron- and nickel oxide is enhanced under the influence of the HCl-containing gas. As additional experiments have shown, the heavy metals are gradually removed from the sulfate mixture by the formation of the volatile chlorides  $\text{ZnCl}_2$  and  $\text{PbCl}_2$ . The amount of dissolved chlorine from HCl in the sulfate melt is negligible and, therefore, no molten chloride phase forms. A possible mechanism is the formation of iron-, chromium- and nickel-chlorides by reaction with HCl-gas and subsequent dissolution in the sulfate melt (Eq. 14):



The precipitation takes place in regions with lower concentration of  $\text{O}^{2-}$  and a higher concentration of  $\text{O}_2$  (Eq. 15):



Chromium chloride is nearly insoluble, according to the low amount of Cr in the precipitates.



**Figure 12:** Metallographic cross section of X20 CrMoV 12 1, reacted beneath the molten  $\text{CaSO}_4$ - $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$ - $\text{PbSO}_4$ - $\text{ZnSO}_4$  salt mixture in  $\text{N}_2$ -5 vol.%  $\text{O}_2$ -1000 vppm HCl at 600 °C. The amount of precipitates is much higher than in the atmosphere without HCl.

## 5. Conclusions

Analysis of failure cases from boiler tubes in waste fired boilers have shown that severe corrosion occurs only in the presence of deposits. In these deposits, molten phases are formed, especially chlorides  $\text{KCl}$ - $\text{ZnCl}_2$  with additions of  $\text{PbCl}_2$  and  $\text{ZnCl}_2$  and sulfate mixtures containing  $\text{CaSO}_4$ - $\text{K}_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4$ - $\text{PbSO}_4$  and  $\text{ZnSO}_4$ . These mixtures have low melting points and severe corrosion is observed in the presence of these melts.

Laboratory experiments were carried out in order to investigate the effect of molten  $\text{PbCl}_2$ ,  $\text{ZnCl}_2$  and of a  $\text{KCl}$ - $\text{ZnCl}_2$  mixture in the temperature range between 250-600 °C. Accelerated corrosion was observed for 10 CrMo 9 10 in the presence of  $\text{PbCl}_2$  at 500 and 600 °C. A fluxing mechanism is proposed according to the occurrence of  $\text{Fe}_2\text{O}_3$  precipitates at the melt/gas interface.

In contact with  $\text{ZnCl}_2$  accelerated corrosion was observed for 10 CrMo 9 10 at 600 °C, whereas at 500 °C inward diffusion of zinc into the oxide scale takes place and no accelerated corrosion was observed. In contact with the  $\text{KCl}$ - $\text{ZnCl}_2$  melt, severe corrosion of the low alloy 2.25Cr-1Mo- steel was observed at 250-400 °C. A complex multilayered scale is formed at 350 and 400 °C, consisting of precipitates of  $\text{ZnFe}_2\text{O}_4$  at the melt/scale phase boundary, a compact scale of  $\text{Fe}_2\text{O}_3$  underneath and a molten  $\text{KCl}$ - $\text{FeCl}_3$  eutectic at the metal/scale interface.

In addition, the corrosion of steels and nickel-based alloys was studied beneath a  $\text{CaSO}_4$ - $\text{K}_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4$ - $\text{PbSO}_4$ - $\text{ZnSO}_4$ -mixture at 600 °C. In contact with the sulfate melt, also accelerated corrosion was observed, whereas the nickel-based alloy behave rather resistant. The experiments clearly show the corrosive effect of a molten  $\text{CaSO}_4$ - $\text{K}_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4$ - $\text{PbSO}_4$ - $\text{ZnSO}_4$ -salt mixture in the corrosion of steels and nickel based alloy at 600 °C. The corrosion products formed are oxide precipitates in the salt melt, containing zinc, iron and nickel, depending on the alloy. In the case of 10 CrMo 9 10 and X 20 CrMoV 12 1 an outer scale of zinc-free  $\text{Fe}_2\text{O}_3$  is formed. Except for the 10

CrMo 9 10 alloy, pits are formed on the other alloys containing layers of  $K_2SO_4$  and chromium-rich corrosion products with reasonable amounts of zinc.

The addition of 1000 vppm  $SO_2$  leads to an increase in corrosion of each alloy and a separation of the melt in a  $K_2S_2O_7$ - and a Ca-rich part takes place. The nickel-based alloys are much more sensitive in this atmosphere compared to the iron-based alloys because high amounts of  $NiSO_4$  are formed.

In the atmosphere containing 1000 vppm HCl also accelerated corrosion was observed on each alloy, even compared to the  $SO_2$  containing gas. More  $Fe_2O_3$  precipitates are formed than in the atmosphere without HCl. In this case, the iron-based alloys are much more sensitive than the nickel-based materials.

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# Electrochemical Polarization Study of Hot Corrosion of Iron and Iron-Based Alloys in Alkali Sulfate Containing Iron-Sulfate

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**Keywords:** Alkali-Sulfate, Corrosion Product, Electrochemical Study, Iron-Based Alloys, Polarization Resistance Method

## Abstract

Corrosion behavior of Fe, Ni, Cr, stainless steels and Cr-Mo alloy in  $(\text{Na,K})_2\text{SO}_4\text{-Fe}_2(\text{SO}_4)_3$  has been studied with the electrochemical polarization technique at 923 and 973K. With an increase in chromium content, the rate of corrosion decreases shifting the corrosion potential to noble direction. The anodic polarization curves exhibit a active-passive transition, where the currents at the peak and the passive state decrease with an increase in chromium content. The rate of corrosion estimated from polarization resistance was well consistent with that obtained by Salt-coating test.

On the other hand, mechanism of hot corrosion of Fe in  $(\text{Na,K,Li})_2\text{SO}_4$  melt containing different amount of ferric ion at 973K under an  $\text{SO}_2\text{-O}_2\text{-N}_2$  atmosphere has been studied by electrochemical polarization measurement. The polarization curves showed that corrosion reaction was described by the anodic dissolution of Fe and the diffusion-limited cathodic reduction of ferric ion. With increasing the concentration of ferric ion the corrosion rate increased, which shows that the corrosion reaction is controlled by cathodic reduction of ferric ion. The cathodic reaction is promoted by introducing the corrosion products which is oxidized under an  $\text{SO}_2\text{-O}_2$  atmosphere and served as oxidant for corrosion reaction of Fe. Thus, the accelerated corrosion of Fe in molten sulfate was explained by an autocatalytic corrosion mechanism of the corrosion products.

## 1. Introduction

Hot corrosion of heat-resistant alloys in combustion engines, boilers or heat exchangers is usually caused by the existence of combustion products such as vanadium pentoxide and sodium sulfate in a liquid phase. A different type of hot corrosion[1] has been reported on a coal-fired boiler, where the surface of super-heater tubes is exposed to an  $\text{O}_2$ -rich  $\text{SO}_3$  atmosphere at intermediate temperatures (873~1023K)[2]. It has been established that  $(\text{Na,K})_2\text{SO}_4\text{-Fe}_2(\text{SO}_4)_3$  deposits, the so-called white layer, are highly corrosive to conventional construction materials at 923K[3]. A similar enhanced corrosion was reported for Ni and Cr in molten alkali-sulfate containing  $\text{CoSO}_4$ [4].

There is no doubt that the most important objective for solving high temperature corrosion problems is understanding the reaction mechanisms. Luthra et al.[5-6] have shown accelerated corrosion of cobalt-based and nickel-based chromium alloys with  $\text{Na}_2\text{SO}_4$  deposits in the atmosphere where the formation of a low temperature liquid phase: base metal sulfate- $\text{Na}_2\text{SO}_4$  melt was substantiated under the given  $\text{SO}_3$  partial pressures and temperatures. Analysis of the stationary corrosion products formed in  $\text{Na}_2\text{SO}_4\text{-CoSO}_4$  elucidated that the formation of porous iron sulfide

facilitates inward penetration of  $\text{SO}_3$ , the acidic dissolution (or sulfation) of Co and CoO at the scale/salt interface and the resulting precipitation as  $\text{Co}_3\text{O}_4$  and/or  $\text{CoSO}_4$  at the salt/gas interface. There was also suggested countertransport of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  in the salt film. More fundamental study of hot corrosion established thermodynamic phase stability regimes of the key constituents of corrosion scales, e.g., iron oxides, NiO,  $\text{Cr}_2\text{O}_3$  etc. in  $\text{Na}_2\text{SO}_4$  at 1200K[7]. From the  $\text{pO}_2$ -basicity diagram, there was predicted the solubilities of the oxides as a function of basicity in  $\text{Na}_2\text{SO}_4$ , which were well agreed with those measured by chemical and electrochemical methods. Furthermore, Rapp and Goto[8] suggested the existence of a negative concentration gradient for the acid or the base in the melt to sustained hot corrosion. Shi[9] has examined the corrosion behavior of iron with  $\text{Na}_2\text{SO}_4$  deposits in pure  $\text{O}_2$  at 1023K. Although there is no  $\text{SO}_3$  in the atmosphere, new low temperature hot corrosion has occurred, indicating that an eutectic  $\text{Na}_2\text{SO}_4$ - $\text{Na}_2\text{O}$  melt might prevent the formation of a protective oxide scale at the metal/melt interface under basic conditions.

Electrochemical techniques are the promising tool especially for *in-situ* measurements of corrosion potential and instantaneous corrosion current, as well as for usual polarization and potentiometric measurements where laboratory experiment well simulates the corrosion process under suitable experimental conditions, e.g., synthetic flue gas, deposits and operating temperatures. For example, the electrochemical polarization technique has a wide potential application to material screening test and elucidating the reaction mechanisms.

There is of great interest in an accelerated corrosion in alkali-sulfate, which is influenced by the  $\text{SO}_3$  partial pressure in the existence of  $\text{O}_2$ , operating temperatures and the corrosion products such as  $\alpha$ - $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and iron-sulfate (liquid phase). Because of limited experimental applications of this technique, however, the mechanism of this type of hot corrosion remains unsolved. In this paper, the corrosion of iron and iron-based alloys in alkali-sulfate containing  $\text{Fe}_2(\text{SO}_4)_3$  in an  $\text{SO}_2$ - $\text{O}_2$ - $\text{N}_2$  atmosphere has been studied using an electrochemical polarization technique. The rate of corrosion was evaluated by the electrochemical polarization resistance method. Interest was focussed on the role of the corrosion products;  $\alpha$ - $\text{Fe}_2\text{O}_3$ , the ferrous ion and  $\text{Fe}_2(\text{SO}_4)_3$  in alkali-sulfate corrosion.

## 2. Experimental

### 2.1 Experimental procedure and apparatus

The experimental apparatus is illustrated in Fig.1 (a). The experimental cell was placed in an alumina tube  $5.3 \times 10^{-3}$  m in diameter and  $6.0 \times 10^{-1}$  m in length. The top of the tube was plugged by a rubber stopper which supported the three electrodes.

Electrolyte Equimolar binary and ternary mixtures of  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ , and  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{Li}_2\text{SO}_4$  containing ferric ion were used as the electrolytes. Two types of electrolyte were prepared in the following manner:

(1) An equimolar mixture of reagent grade  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  was dried in an oven at 453K for more than 20h. Reagent  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  readily loses water at 403K. Approximately  $3 \times 10^{-2}$  kg of the  $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$ - $\text{Li}_2\text{SO}_4$  mixture was placed in an alumina crucible cell (99.5 % purity)  $4.1 \times 10^{-2}$  m in inner diameter, which was set on a refractory plate in the hot zone of a furnace (Fig.1 (a)). An alumel-chromel thermocouple sheathed in a thin alumina tube was attached to the bottom of the plate to control the temperature of the furnace. After heating the cell to 973K under a stream of  $\text{O}_2$ ,  $\text{SO}_2$  and  $\text{N}_2$  gas mixture ( $\text{SO}_2$ : $\text{O}_2$ : $\text{N}_2$  = 1:5:94%) which was dried through  $\text{CaCl}_2$  and  $\text{P}_2\text{O}_5$  columns, dried  $\text{Fe}_2(\text{SO}_4)_3$  powder was passed through a silica tube. Since pure  $\text{Fe}_2(\text{SO}_4)_3$  is expected to decompose at 973K and



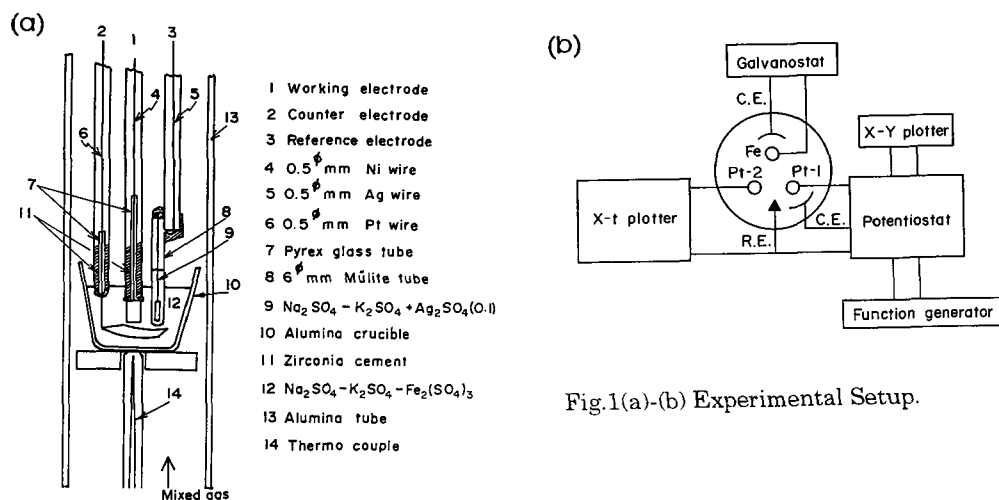


Fig.1(a)-(b) Experimental Setup.

evolve  $\text{SO}_3$  gas under this experimental condition, the reagent was transferred rapidly into the crucible, followed by stirring the melt. A Pt electrode reached a stable potential within a couple of hours after the addition of  $\text{Fe}_2(\text{SO}_4)_3$ . This confirmed that a dissociation equilibrium of the dissolved  $\text{Fe}_2(\text{SO}_4)_3$  was established in the melt.

(2) Dried reagent grade  $\text{K}_2\text{S}_2\text{O}_7$  and  $\text{Na}_2\text{S}_2\text{O}_7$  were thoroughly ground and mixed with reagent grade  $\alpha\text{-Fe}_2\text{O}_3$  in an alumina mortar. It is well known that alkali-pyrosulfate decomposes at about 573K and yields a nascent  $\text{SO}_3$ . Hence, heating of the mixture with  $\alpha\text{-Fe}_2\text{O}_3$  results in the formation of alkali-ferrie sulfate:



Since the pyrolysis of alkali-pyrosulfate proceeds gradually under 1%  $\text{SO}_2$ -5%  $\text{O}_2$ - $\text{N}_2$  gas, the temperature of the solution was raised slowly and kept at 973K for 12h to complete the reaction. Those two different methods for preparing the electrolyte made no difference to the results of the polarization measurements.

**Electrodes** The working electrode was a platinum plate  $1.0 \times 10^{-4} \text{ m}^2$  in area. It was spot-welded to a platinum wire which was sealed into a Pyrex tube. The Pyrex tube was inserted into an alumina tube and the gap between the Pyrex tube and the alumina tube was filled with a commercial zirconia cement to protect Pyrex glass from attack by the melts. A square plate with a handle (Fe, Ni and Cr) and a square rod (alloys) were used for the metal electrodes (Fig.2). The handle was spot-welded to a nickel lead wire ( $1.0 \times 10^{-3} \text{ m}$  in a diameter), which was sealed into the Pyrex tube. The electrodes were polished with emery paper #1500 and washed with methanol.

The counter electrode was a platinum plate  $1 \times 10^{-4} \text{ m}^2$  in area. It was spot-welded to a platinum wire which was sealed into a Pyrex tube in a similar manner to that of the working electrode. The reference electrode was composed of Ag wire and the salt containing 10 mol %  $\text{Ag}_2\text{SO}_4$  which were contained in a mullite ( $\text{Na}^+$  conducting) closed-end tube of  $4 \times 10^{-3}$

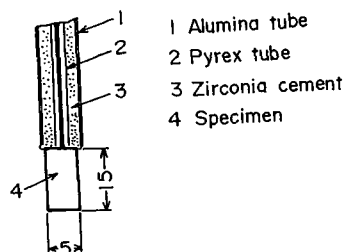


Fig.2 Structure of working electrode.

m in a diameter. The electrode potential was referred to the Ag/Ag<sup>+</sup>(10 mol %) electrode. Another cell set up shown in Fig.1 (b) was utilized to examine the effect of the dissolved ferrous ions. A square plate of platinum with a handle was used as the working electrode (Pt-1 in Fig.1 (b)) and the indicator electrode (Pt-2), the former for potentiostatic measurement and the latter for measuring the oxidation-reduction potential of the melt. It also has an extra iron electrode, from which ferrous ions were introduced into the melt by galvanostatic oxidation.

**Electrochemical measurement** The details of electronic equipments and procedures for polarization measurements are described elsewhere[10]. Current-potential curves were obtained using a potentiostat with a potential sweep rate of  $1 \times 10^{-3} \text{ V s}^{-1}$ . The potential of the working electrode was measured against the Ag/Ag<sup>+</sup>(10 mol %) reference electrode by means of a high input impedance voltmeter. The polarization resistance was obtained from the value of current at potentials 10mV positive or negative of the corrosion potential. The corrosion current was estimated from the polarization resistance ( $R_p$ ) using Stern-Geary relation[11] (Eq.3),

$$R_p = [E/i]_{E_{\text{corr}}} = K / i_{\text{corr}} \quad (3)$$

where  $i_{\text{corr}}$  and  $E_{\text{corr}}$  indicate the corrosion current and potential, respectively.  $K$  is a constant involving the Tafel slopes for the anodic and cathodic polarization curves,

$$K = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \quad (4)$$

where  $\beta_a$  and  $\beta_c$  are Tafel slopes of anodic and cathodic polarization curves, respectively.

The rate of corrosion, i.e., the rate of mass loss (mass gain in the case of an adherent corrosion product formed) is known as the material wastage as a result of an electrochemical reaction between a metal and an environment, thus,  $i_{\text{corr}}$  and the amount of metal loss are related by Faraday's law,

$$i_{\text{corr}} = \frac{nFm}{tM} \quad (5)$$

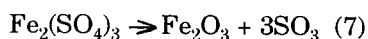
where  $i_{\text{corr}}$  is in amps,  $t$  is the time (in seconds),  $nF$  is the number of coulombs required to corrode 1mol of metal, where  $n$  is the number of electrons involved in the metal dissolution reaction, and  $F$  is the Faraday constant (96480C/mol), and  $M$  is the molecular weight, and  $m$  is the mass of corroded metal (in grams).

### 3. Results and discussion

#### 3.1 Stability of iron and iron compounds in (Na,K,Li)<sub>2</sub>SO<sub>4</sub>

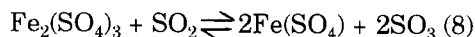
Kerridge et al.[12] have studied the stability of transition-metal species in molten alkali sulfate using thermogravimetry and X-ray diffraction method. The thermogravimetric results show that the transition-metal compounds, e.g., Fe<sup>2+</sup> and Fe<sup>3+</sup> sulfates are decomposed/oxidized slowly by the air atmosphere at the temperatures where weight loss became apparent according to the reaction,



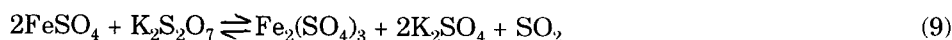


It was found that these cations are considerably stabilized when dissolved in sulfate melt at 550°C and the order of stability is

$\text{Fe}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$ . Ferric ions:  $\text{Fe}^{3+}$  in an eutectic sulfate melt is reduced by  $\text{SO}_2$  with an evolution of  $\text{SO}_3$ ,

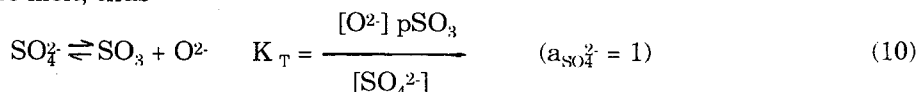


while with an addition of potassium pyrosulfate the extent of the above reduction is rendered by a nascent  $\text{SO}_3$  evolved by the pyrosulfate decomposition as,



In an eutectic sulfate melt the stability and oxd./red. reaction of the iron compounds as functions of the  $\text{SO}_3$  partial pressure and temperatures has been established[13].

A knowledge of the stable chemical entities in the melt as functions of the electrode potential and the basicity ( $\text{pO}^{2-} = -\log a\text{O}^{2-}$ ) should be helpful for understanding the products of the corrosion. Thermodynamic phase stability diagram of the Na-Fe-S-O system at 1000K is shown in Fig.3 [14]. The thermodynamic data needed to establish the diagram are shown in ref.15. In this diagram, the relative basicity is expressed as the logarithm of  $\text{pSO}_3$ , assuming an acid-base equilibrium in alkali-sulfate melt, thus



$$\text{pO}^{2-} = -\log a\text{O}^{2-} = -\log (K_T / \text{pSO}_3) = -\log K_T + \log \text{pSO}_3 \quad (11)$$

Point A in Fig.3 at -0.287V and  $\text{pSO}_3 \cdot 5.77 \times 10^2 \text{ Pa}$  represents the regime of stable  $\alpha\text{-Fe}_2\text{O}_3$  assuming gaseous equilibrium between  $\text{SO}_3$ ,  $\text{O}_2$  and  $\text{SO}_2$ [16]. Although the point lies in the  $\alpha\text{-Fe}_2\text{O}_3$  stable region as seen in Fig. 3, the experimental results indicate that the dissolved  $\text{Fe}_2(\text{SO}_4)_3$  exists stable in alkali-sulfate melt at 923K under an  $\text{SO}_2\text{-O}_2$  atmosphere. According to the result reported by Zhang and Rapp[17], point A corresponding to this experimental condition is in the region of  $\text{Fe}^{3+}:\text{Fe}_2(\text{SO}_4)_3$ , right side (acidic) of equal concentration of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}^{3+}$ . The diagram shows the existence of free  $\text{Fe}^{3+}$  ion under this experimental condition. The unknown solubility of iron oxide or  $\text{Fe}_2(\text{SO}_4)_3$ , however, limits the further consideration of the corrosion product.

### 3.2 Corrosion potential and corrosion current density of iron-based alloys in $(\text{Na,K})_2\text{SO}_4$ containing $\text{Fe}_2(\text{SO}_4)_3$ [27]

#### 3.2.1 Corrosion potential and anodic polarization curves

The corrosion potentials of each alloy shifted towards the positive direction by about 0.1–0.15V and showed stable values after immersion in the electrolyte. The electrolyte:  $\text{Fe}_2\text{O}_3:\text{K}_2\text{SO}_4:\text{Na}_2\text{SO}_4$  (= 2:3:3 molar ratio) was used to simulate the main constituent of the combustion ash of pulverized-coal-fired boilers. The alloys tested

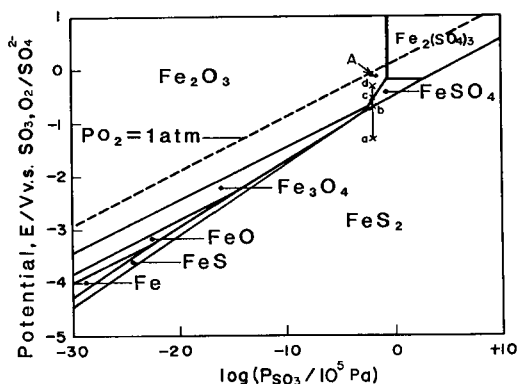


Fig.3 E/pSO<sub>3</sub> diagram of Fe in alkali-sulfate.

(composition in Table 1) were accepted as the candidates for the superheater tube material. Figure 4 shows the dependence of the corrosion potential on the chromium content of the alloys at 923K and 973K. In this figure the error bars show the scatter of the corrosion potentials under the same test conditions. The corrosion potential of SUS304H was relatively unstable in comparison with the other alloys. The corrosion potentials of each alloy showed a higher value at 973K than at 923K, even after taking into account the temperature dependence of the reference electrode. All of the alloys except STBA24 showed higher corrosion potentials with increasing chromium content. STBA24 showed a higher corrosion potential value than the Fe-Cr alloy that had the same chromium content. This phenomenon is thought to be due to the effect of the Mo component in the alloy[18]. Figures 5(a)-(d) show the anodic polarization curves of iron-based alloys in  $(\text{Na,K})_2\text{SO}_4$  containing  $\text{Fe}_2(\text{SO}_4)_3$  at 923K and 973K. The polarization measurements were conducted at up to 6V at both anodic and cathodic sides. All of the electrodes examined show a peak current ( $i_p$ ) and passive current ( $i_{pp}$ ) derived from the anodic polarization curves. Both STBA24 and SUS304H show an anodic dissolution current that rises at around 0.22V and falls around 0.8V.

Table 1 Composition of alloys (mass%).

| Alloy   | Fe   | Cr    | Ni    | Si   | Mn   | C    | S     | P     | Other element      |
|---------|------|-------|-------|------|------|------|-------|-------|--------------------|
| STBA 24 | Bal. | 2.20  | —     | 0.40 | 0.47 | 0.09 | 0.006 | 0.013 | Mo 1.10            |
| SUS304H | Bal. | 18.22 | 8.75  | 0.63 | 1.61 | 0.06 | 0.005 | 0.024 |                    |
| SUS310S | Bal. | 24.40 | 20.85 | 0.68 | 1.67 | 0.06 | 0.002 | 0.016 |                    |
| CR 35A  | Bal. | 36.59 | 44.95 | 0.04 | tr.  | 0.05 | 0.001 | 0.003 | Nb 0.49<br>Al 0.12 |

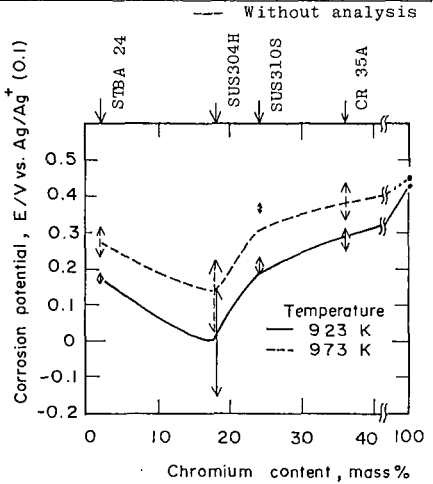


Fig.4 Effect of Cr content on corrosion potential at 923 and 273K.

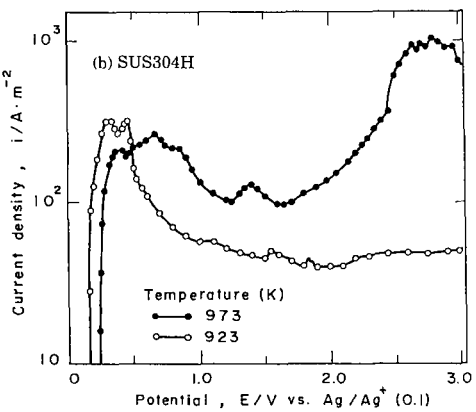
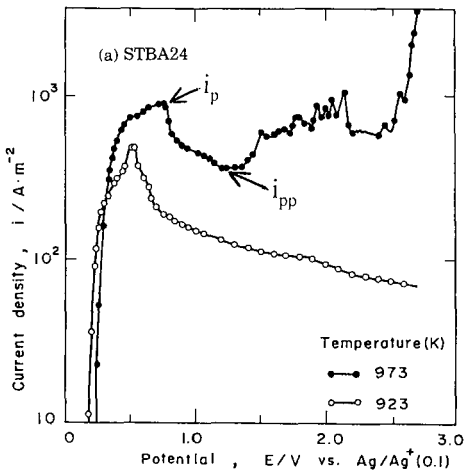


Fig.5(a)-(b) Anodic polarization curves of STBA24 and SUS304H.

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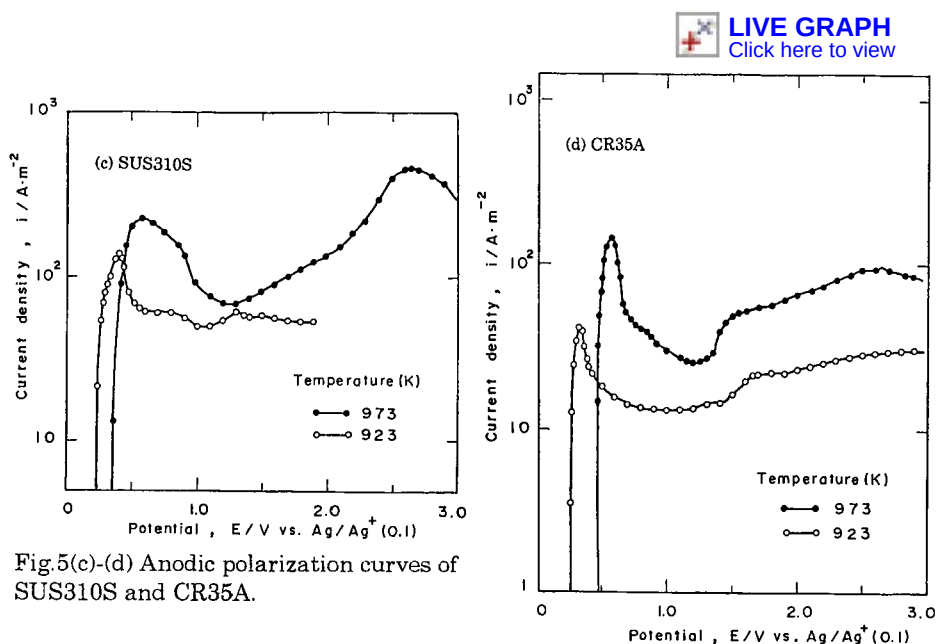
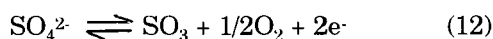


Fig.5(c)-(d) Anodic polarization curves of SUS310S and CR35A.

On the other hand, SUS310S and CR35A show a current that increases at around 0.4V and decreases again at around 0.4V, with a sharp peak. All of the alloys tested show a lower anodic dissolution current at 923K than at 973K, and all of them have almost the same pattern as each other. Figure 6 shows  $i_p$  and  $i_{pp}$  at 923K and 973K respectively, and also the dependence on chromium content of the corrosion current  $i_{\text{corr}}$  obtained by the above mentioned polarization resistance method. The figures at 923K and 973K both show a decrease in anodic dissolution current and passive current  $i_{pp}$  with increasing chromium content. The same tendencies are evident for the corrosion currents. At 973K, all of the electrodes of the alloys show an increase in anodic current at electrode potentials higher than about 2.5V, and they show a maximum peak of more than  $0.3 \times 10^4 \text{ A} \cdot \text{m}^{-2}$  at 2.7V. SUS310S shows a maximum peak value of  $0.045 \times 10^4 \text{ A} \cdot \text{m}^{-2}$  at 2.65V. This phenomenon is considered to be due to the reaction described in Eq.12, because the reversible potential of the anodic oxidation reaction of the sulfuric ion is 2.487V.



This anodic current value decreases with increasing chromium content of the alloys corresponding to the properties of the surface film on the materials (SUS304H;  $950 \text{ A} \cdot \text{m}^{-2}$ , SUS310S;  $450 \text{ A} \cdot \text{m}^{-2}$ , CR35A;  $95 \text{ A} \cdot \text{m}^{-2}$ ).

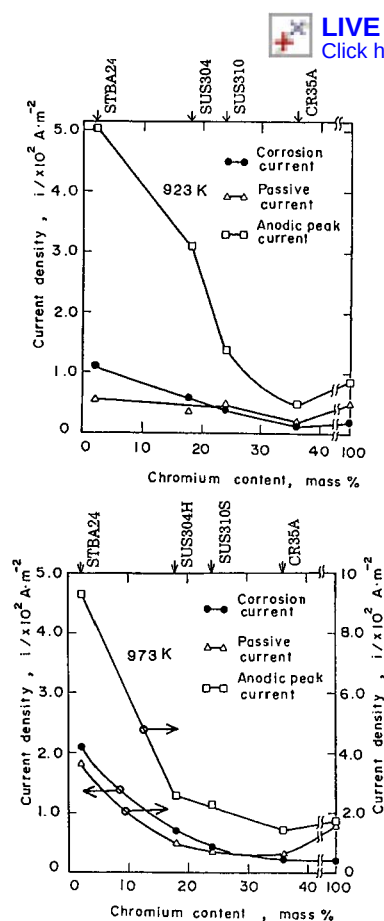


Fig.6 Effect of Cr content on  $i_{\text{corr}}$ ,  $i_p$ , and  $i_{pp}$  at 923 and 973K.

The electrochemical characteristics of the alloys can be explained by classification of the alloys into A-alloys, such as STBA24 and SUS304H, which have a higher iron content, and B-alloys, such as SUS310S and CR35A that have a higher nickel and chromium content. A-alloys show rapid anodic dissolution with only a small slope of the Tafel lines at 923K and 973K, and they show a rapid increase in cathodic current when the potential moves towards the less noble direction, and they also show a large difference in dissolution current depending on the temperature. Thus, A-alloys are considered to form the surface films that lead to a poor inhibition for anodic dissolution, similar to the situation for Fe. B-alloys, on the other hand, start the anodic dissolution slowly, and their cathodic current is the limiting current. They also exhibit a small difference in dissolution current with respect to temperature. B-alloys are therefore considered to form surface films that have a strong inhibition for anodic dissolution.

### 3.2.2 Electrochemical explanation of the corrosion potential and the corrosion current

So far, measurements of molten salts corrosion at high temperatures have been performed mainly by mass loss measurement in the corrosion salt coating test. Here, we will explain the corrosion potential and the corrosion rate obtained by the electrochemical measurement as a superposition of the partial anodic and the partial cathodic currents.

The corrosion reaction in molten salt can be explained as a superposition of the partial anodic current (metal dissolution;  $M \rightarrow M^{n+} + ne^-$ ,  $i_a$ ) and partial cathodic current (oxidant reduction reaction;  $Ox + ne^- \rightarrow Re$ ,  $i_c$ ), similar to the corrosion reaction in aqueous solution[19].

The current with an equivalent absolute value to both currents  $i_a$  and  $i_c$  at corrosion potential ( $E_{corr}$ ) is known as the corrosion current,  $i_{corr}$ , and which can be defined as (see Fig.7(a)),

$$i_{corr} = i_a = |i_c| \quad \text{at } E = E_{corr} \quad (13)$$

The actual polarization curve (total polarization curve:  $i_T$ ) is the sum of each partial polarization curve ( $i_a$ ,  $i_c$ ), and each polarization curve can be estimated by the Tafel extrapolation method, as schematically shown in Figs.7(a)-(c). Because the exchange current density of metals in molten salt is large[20],  $i_a$  will increase exponentially if immersed in an alkali chloride or other oxidant-free salt. On the other hand,  $i_c$  is generally controlled by diffusion due to low concentration of oxidant, as shown in Fig.7(b). In this case, the corrosion current  $i_{corr}$

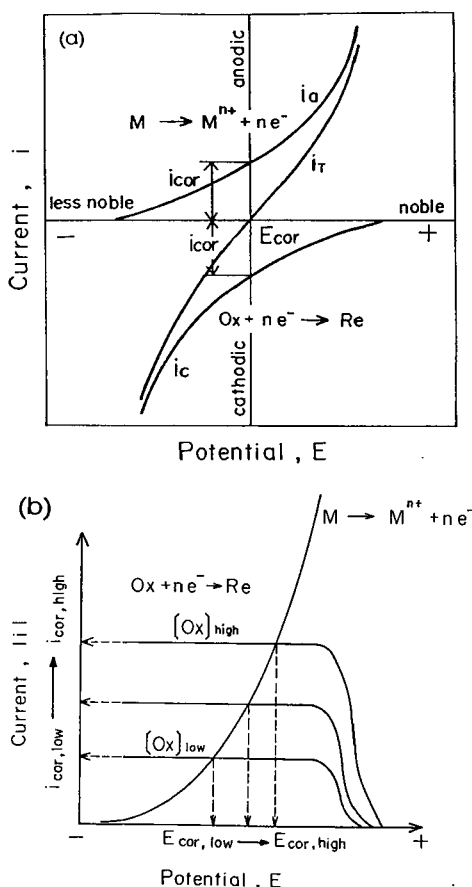


Fig.7(a)-(c) Schematic of  $i_{corr}$  obtained by a superposition of  $i_a$  and  $i_c$ . (a) Typical corrosion system, (b) Diffusion-limited cathodic control

becomes equal to the diffusion-limiting current  $i_{\text{diff}} (= nFD_{\text{ox}}[\text{Ox}]/\delta, \delta$ : the thickness of a diffusion layer) and is proportional to the concentration of oxidant in the salt (diffusion-limited cathodic control, refer the section 3.3.2). Actually oxidants in the salt are  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , dissociative reaction products and impurities. Therefore, to decrease the corrosion rate oxidants must be removed from the salt (for example, in a chloride or fluoride melt).

On the other hand, metals in alkali nitrate are passivated, and corrosion reactions are controlled by anodic reaction (anodic control, refer the section 3.2.2), as shown in Fig.7(c). In this case for sufficiently high cathodic current the metal corrodes actively, and then for passivation to occur (active to passive) the corrosion current is equal to the dissolution current of a passive film ( $i_{\text{pp}}$ ). To decrease the corrosion rate, it is necessary to study what kind of alloy could form a stable passive film (low  $i_{\text{pp}}$ ). Thus, data on oxidants that affects the corrosion rate and rate-determining steps can be obtained by measuring the polarization curves of metals in molten salt under various conditions. In what follows, examples of the corroding systems termed as diffusion-limited cathodic control type and anodic control type will be described from an electrochemical kinetic viewpoint.

Using the results of the polarization curves obtained in this experiment (Fig.5), Fig.8 shows a schematic diagram illustrating the dependence of  $i_a$  on the chromium content of the various alloys, under conditions of constant- $i_c$ . Here, the assumption is the constant- $i_c$ , which is the same as for the cases that the corrosion reaction is rate-controlled by partial anodic reactions such as that for alkali sulfate or molten  $\text{V}_2\text{O}_5$ [21]. As shown in ref.21 in alkali sulfate or molten  $\text{V}_2\text{O}_5$ ,  $i_a$  corresponds to the metal dissolution reaction that occurs through oxides or sulfates formed on the surface of alloys at the initial stages of immersion. On the other hand,  $i_c$  near to  $E_{\text{corr}}$  corresponds to the reduction reaction of ferric ions, and is constant with respect to the individual alloys. This assumption is valid as far as the salt contains more than 12 mol%  $\text{Fe}_2(\text{SO}_4)_3$  (or  $\alpha\text{-Fe}_2\text{O}_3$ ), as is explained in the section 3.3.3.

In Fig.8,  $E_{\text{corr}}$  and  $i_{\text{corr}}$  are obtained by superposition of the partial polarization curves indicated by allow-marks. Here,  $E_{\text{corr}}$  increases but  $i_{\text{corr}}$  decreases along with

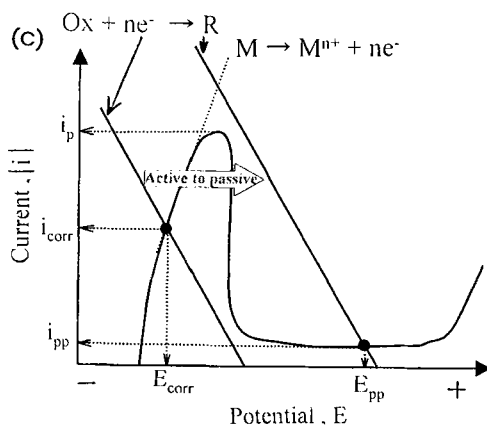


Fig.7(c) Schematic of corrosion system of anodic control.

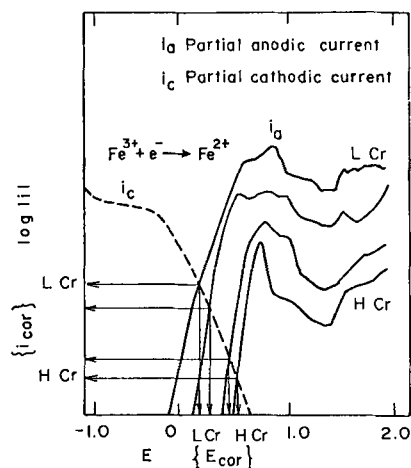


Fig.8 Schematic illustration of effect of Cr content on  $i_{\text{corr}}$ .

$i_T$ : Total current,  $i_a$ : partial anodic current,  $i_c$ : partial cathodic current, L Cr: low chromium content alloy, H Cr: high chromium content alloy

increasing chromium content of the alloys. This phenomenon is consistent with the dependence of the chromium content of the alloys on the actual measured corrosion potentials and corrosion rates (Figs. 4 and 6). Therefore, high chromium content alloys give improvement in corrosion resistance due to their inhibition of the anodic dissolution reaction. As seen in Fig. 6, the results of this decrease in corrosion rate with an increase of chromium content in alkali iron sulfate is consistent with the report made by Kihara et al.[22]. However, prior to our current investigation, there had been no previous report using an electrochemical measurement technique that describes the inhibition of the maximum current of anodic dissolution for high-chromium content alloys, nor any observation of the low passive current or the presence of a passive surface film with good corrosion resistance.

### 3.2.3 Comparison of anodic polarization behavior between alloys and Fe, Ni and Cr[27]

As described above, the characteristics of the anodic polarization curves of alloys are very important aspects of the corrosion behavior of alloys. On the other hand, with regard to the corrosion resistance of alloys, the performance of the added alloying elements (e.g. chromium) is a key issue. Therefore, we compared the polarization curves of alloys, Fe, Ni and Cr on the same potential axis in order to confirm the performance of the alloying elements and their characteristics with respect to anodic polarization curves.

In Fig.9, the upper portion shows the polarization curves of each alloying element.  $E_{\text{corr}}$  for Fe, Ni and Cr are 0.230V, 0.055~0.227V and 0.460V, respectively. Cr shows the highest potential among the alloying elements. Fe shows anodic dissolution behavior that has a high maximum current density ( $i_p$ ;  $9.0 \times 10^2 \text{ A} \cdot \text{m}^{-2}$ , at 0.76V), and which subsequently gives a high passive current density ( $3.0 \times 10^2 \text{ A} \cdot \text{m}^{-2}$ ). Ni shifts the corrosion potential in the positive direction after immersion, and gives a stable potential of 0.055~0.227V. The anodic current increases with oscillation and gives a limiting current density of  $2.0 \times 10^3 \text{ A} \cdot \text{m}^{-2}$  at about 0.65V. This shows that the initial nickel oxides were dissolved easily, and subsequent dissolution of the bare nickel metal has occurred. Cr shows an increase in anodic current at 0.450V, and almost constant current behavior at 0.9V. Furthermore, it is considered that formation of high valence chromium oxides or that trans-passive dissolution behavior occurred at over 1.2V.

In the case of A-alloys, the surface seems to be covered with a film consisting mainly of iron oxides, because A-alloys show a similar corrosion potential and anodic dissolution curve to iron, and that

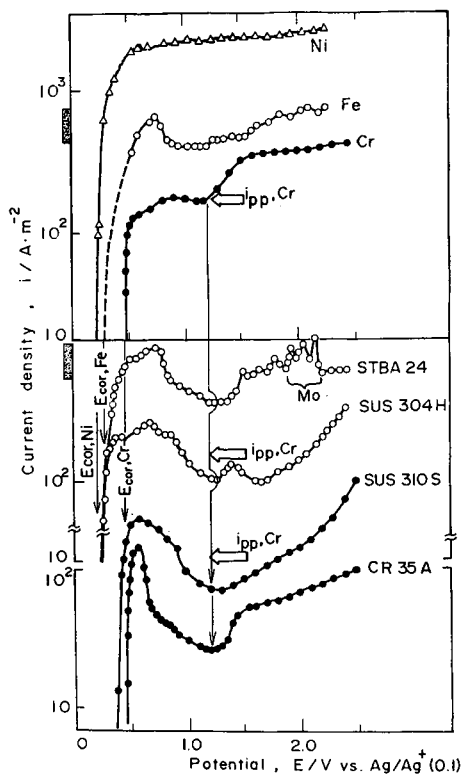


Fig.9 Characterization of  $E_{\text{corr}}$ ,  $i_p$ , and  $i_{pp}$  with regard to alloying elements at 973K.



nickel gives high dissolution reaction. As seen in Fig.9,  $i_p$  of Fe, shown with a dot, is equivalent to that of STBA24, and SUS304H shows lower anodic dissolution current than iron due to the addition of chromium. Also, SUS304H shows an equivalent  $i_{pp}$  value to that of chromium, and shows a small peak current at near 1.2V, which is almost consistent with the trans-passive dissolution potential of chromium. As indicated in this figure, the anodic dissolution of Mo is considered to occur at a relatively higher potential than chromium. Therefore, A-alloys are recognized as being an improvement in the corrosion resistance due to the addition of chromium.

The corrosion potential of B-alloys is equivalent to that of chromium. Therefore, it is considered that the chromium oxide surface film is formed at the beginning of immersion. Then by the addition of chromium, the high maximum current near to the corrosion potential does not appear, and  $i_{pp}$  values for SUS310S and CR35A are  $7.0 \times 10^{-4} \text{ A} \cdot \text{m}^{-2}$  and  $2.5 \times 10^{-4} \text{ A} \cdot \text{m}^{-2}$  (1.2~1.3V) respectively, and are lower than that of chromium (as shown in the figure with the allow mark), and an increase of current is seen similar to that of chromium at over 1.2V. The protective chromium oxide at the initial stages is in accordance with the report made by Strafford et al.[23]. That report described how the low corrosion rate of Ni-25Cr steel at 973K in an  $\text{SO}_2\text{-O}_2$  atmosphere in the initial stages is caused by the protective  $\text{Cr}_2\text{O}_3$  scale. However, the  $i_{pp}$  with a lower value than that of chromium cannot be explained only by the effects of chromium. Yamanouchi et al.[24] reported that the Fe-20%Cr alloy gave an obvious minimum corrosion rate at about 40% nickel content, according to the measured results of corrosion rate with changing nickel content of Fe-18%Cr and the 20% Cr alloy groups in the same corrosion atmosphere. Therefore, in the case of B-alloys (containing more than 24% of chromium), the reason why CR35A shows the lowest  $i_{pp}$  (or  $i_{corr}$ ) must be due to the effects of nickel. However, this corrosion resistance can't be estimated by the superposition of the anodic polarization behaviors of nickel and chromium. There is no obvious explanation for this corrosion resistance behavior except for the co-operative performance of chromium and nickel.

As described above, the anodic dissolution behavior is explained successfully by the characteristics of Fe, Ni and Cr respectively. It is shown that since the cathodic reaction don't change depending on the type of alloys used, the corrosion reactions of the alloys in alkali-sulfate containing  $\text{Fe}_2(\text{SO}_4)_3$  can be described by evaluating the anodic dissolution characteristics of the alloys with in a potential range close to the  $E_{corr}$ .

### 3.2.4 Morphology observation of typical corroded specimens in alkali-sulfate containing $\text{Fe}_2(\text{SO}_4)_3$ [25]

The cross sectional areas of the alloys after corrosion salt coating test have been observed by optical microscope and characteristic X-ray image. Figures 10 (a)-(c) show cross sectional microstructures of scale formed on SUS304H corroded for 100h at 973K, showing the three layer corrosion scale. The thickness of the corrosion scale for SUS304H at 973K is evaluated almost  $2 \times 10^{-4} \text{ m}$  where the original alloy surface is recognized as a brighter horizontal line dividing between  $\Delta_{oxide}$  (external scale) and  $\Delta_{Cr_2O_3}$  (internal scale) layers. The same morphology was observed with the STBA24 and SUS310S salt coating tests, having various scale thicknesses. These scales consist of an outer most layer with net work microstructure (abbreviated as  $\Delta_{oxide}$ ), coherent lamellar layers ( $\Delta_{Cr_2O_3}$ ), and a mixed layer of  $\text{Ni}_3\text{S}_2$  and Cr sulfide ( $\Delta_{(Cr,Ni)Sx}$ ) as an inner most layer.

The  $\Delta_{oxide}$  mainly consists of NiO and iron oxides, as indicated by X-ray diffraction, while the  $\Delta_{Cr_2O_3}$  contains less amount of  $\Delta_{oxide}$  and largely  $\text{Cr}_2\text{O}_3$ , and hence the coherent lamellar layers exhibit as a whole rich in chromium content. Here, the morphology of the lamellar layers is a result of the initial selective dissolution of the

base elements, i.e., nickel and iron. From Fig.9 it is seen that for STBA24A and SUS304H the anodic dissolution currents evolved at the potential regions equal to those of Ni and Fe. (On the contrary, for SUS310S and CR35A the potentials corresponding to the anodic current appeared approached to that of Cr, indicating that the surface of these alloys was covered by the chromium rich oxide scale.) Subsequently, there have been remained the nickel and iron depleted, that is, chromium rich layer adjacent to the inner scale side. It is seen that these two layers of chromium rich brighter layers and chromium depleted layers were stacked periodically. Thus, the lamellar structure was formed as the internal scale growth, as shown in Fig.10. This is not the case where the selective dissolution followed by a less noble compound formation on the surface, leaving voids, since a sufficient flux of oxygen to the lamellar layers/alloy interface renders the void formation during the internal scale growth.

The microstructure features of  $\Delta_{\text{oxide}}$ , i.e., the network structure and chromium rich crust at the outer most layer indicate that the nickel and iron once dissolved

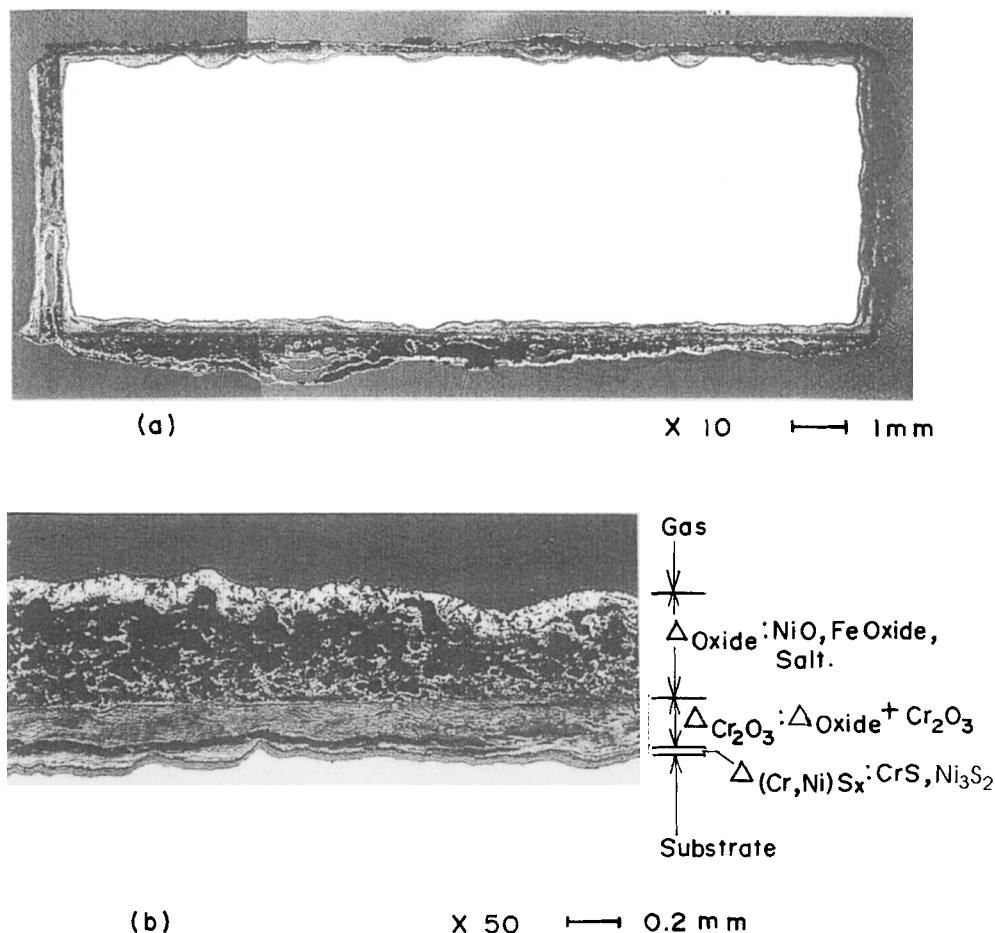


Fig.10(a)-(c) Cross-sectional micrographs of scale formed on SUS304H exposed under  $\text{SO}_2\text{-O}_2\text{-N}_2$  atmosphere for 100h at 973K.

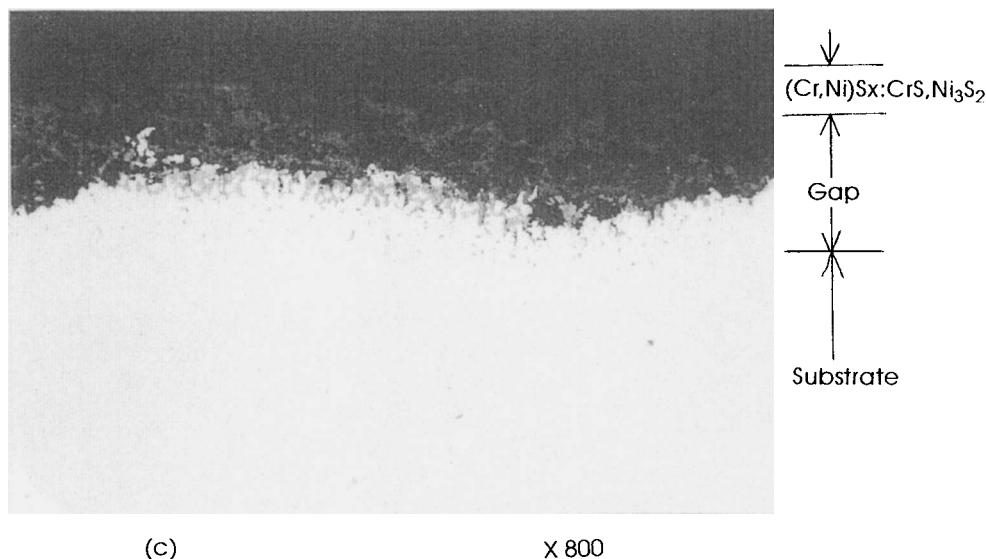


Fig.10(a)-(c) Cross-sectional micrographs of scale formed on SUS304H exposed under  $\text{SO}_2\text{-O}_2\text{-N}_2$  atmosphere for 100h at 973K.

into the outer part of the scale precipitated to form the external oxide scale somewhat including the salt. Some of large pores therein are as a result of the removal of aqueous soluble salts during specimen preparation.

Occasional external and internal scale formations were also observed, indicating the scale formation penetrated into the alloy matrix, as shown in Fig.10(a) at a low magnification. Uneven attacks observed for, e.g., SUS304H were rarely seen for CR35A where a chromium rich protective and more adherent scale developed. Figure 10(c) shows the enlarged one of  $\Delta_{(\text{Cr,Ni})\text{S}_x}$  and the surface, apparently appearing the gap in the scale. The gap is probably caused by the thermal stress, where the overlayer is not strongly adhered to the surface.

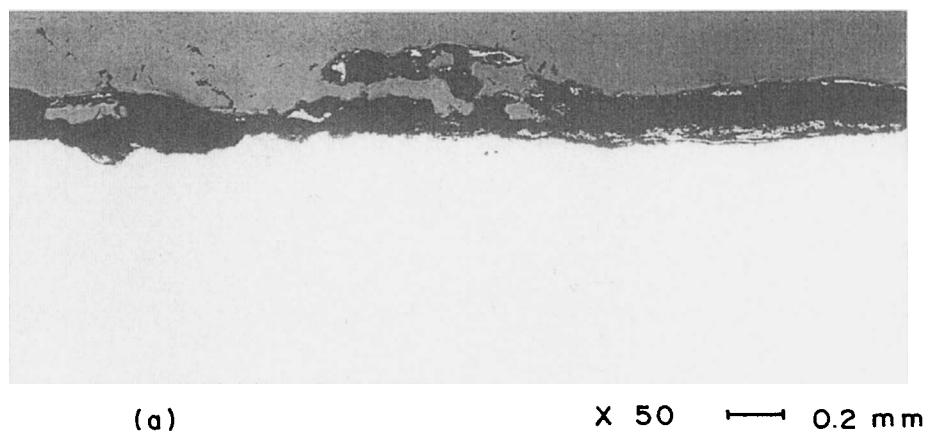


Fig11(a)-(c) Cross-sectional micrographs of scale formed on CR35A exposed under  $\text{SO}_2\text{-O}_2\text{-N}_2$  atmosphere for 100h at 973K.

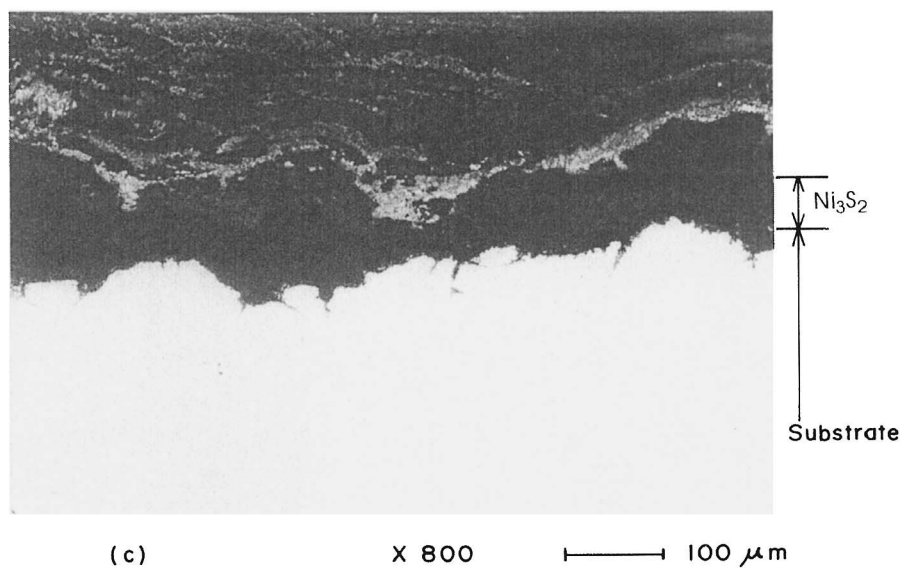
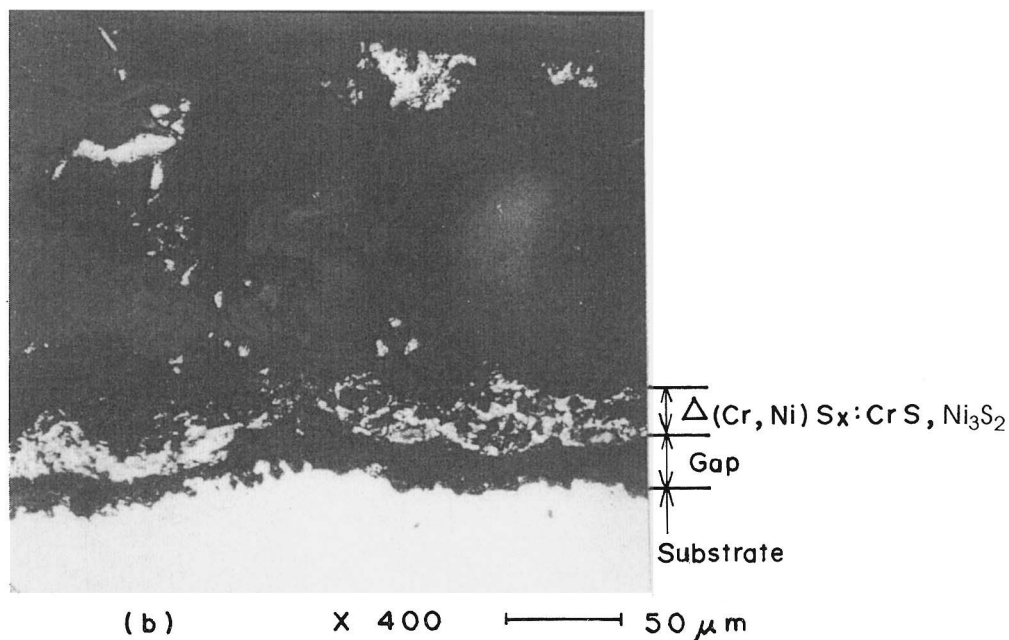
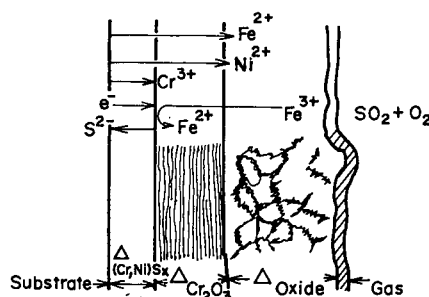


Fig11(a)-(c) Cross-sectional micrographs of scale formed on CR35A exposed under  $\text{SO}_2\text{-O}_2\text{-N}_2$  atmosphere for 100h at 973K.

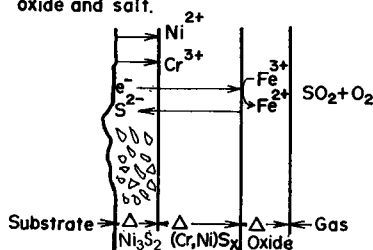
In the case of CR35A, the corrosion rate decreased by a factor of eight at 973K, compared to that of SUS304H, while the surface was covered by the thinner corrosion scale (Figs.11(a)-(c)). Typically, the better corrosion resistance means the exist

ence of a coherent, thinner corrosion resistant scale where the rate-determining step in corrosion processes is ion or electron diffusion in the scale because the charge transfer step is unlikely to play a major role[20]. Figures 11(a)-(c) show SEM micrographs of scale formed on CR35A for 100h at 973K. There appears the three corrosion scale, which is composed of an outer most layer with chromium rich oxides containing aqueous soluble salt ( $\Delta_{\text{oxide}}$ ), Ni and Cr sulfides, mainly Cr sulfide ( $\Delta_{(\text{Cr,Ni})\text{S}_x}$ ) and Ni sulfide:  $\text{Ni}_3\text{S}_2$  (grown into the alloy matrix) as an inner most layer. There locally  $\Delta_{(\text{Cr,Ni})\text{S}_x}$  is seen delineated on the alloy surface as a chromium rich band with less than  $1\mu\text{m}$  thickness, as indicated by characteristic X-ray images. Observation of the whole surface showed the absence of gap and convolution, which proved to be strongly adhered corrosion scale to the surface. Figure 12



(a) SUS 304 H and SUS 310 S

$\Delta_{(\text{Cr,Ni})\text{S}_x}$ :  $(\text{Cr,Ni})\text{S}_x$  Sulfide,  $\Delta_{\text{Cr}_2\text{O}_3}$ : lamellar structure consisting iron oxide, nickel oxide, chromium oxide and salt,  $\Delta_{\text{Oxide}}$ : net work structure consisting iron oxide, nickel oxide and salt.



(b) CR 35 A (973 K)

$\Delta_{\text{Ni}_3\text{S}_2}$ :  $\text{Ni}_3\text{S}_2$ ,  $\Delta_{\text{Oxide}}$ : chromium oxide containing salt.

Fig.12 Schematic of corrosion reaction and corrosion scales (a) SUS304H and SUS310S and (b) CR35A (973K).

shows the schematic illustration of structure of scales formed on SUS304H and CR35A in  $(\text{Na,K})_2\text{SO}_4\text{-Fe}_2(\text{SO}_4)_3$  at 973K under an  $\text{SO}_2\text{-O}_2$  atmosphere, indicating ions and electron transport through individual corrosion scale.

### 3.2.5 Correlation of microstructure features and characteristics of polarization curves

The effect of alloying elements on the corrosion behavior has been studied using an electrochemical polarization technique[26-27]. Here, the correlation between microstructure features and the electrochemical polarization measurement is briefly mentioned.

Aforementioned, since the higher the chromium content, the lower  $i_{\text{corr}}$ ,  $i_p$  and  $i_{pp}$  were obtained (Fig.6), the protective scale (at least rich in chromium) formation which gives low  $i_{\text{corr}}$ , necessitates a small amount of the base metal dissolution given by low value of  $i_p$ . According to the dissolution/precipitation model with respect to passivation, the amounts of the base metals dissolved determines the properties of a precipitated scale; for SUS304H a large amounts of nickel and iron dissolution (refer  $i_p$  in Fig.6) results in the dense less-protective  $\Delta_{\text{oxide}}$  and protective  $\Delta_{\text{Cr}_2\text{O}_3}$  and a small amounts of dissolution for SUS310S and CR35A (refer  $i_p$  in Fig.6) leads to the coherent chromium rich scale.

From the polarization study  $i_{pp}$  and  $i_{\text{corr}}$  decrease with an increase in chromium content and the corrosion reaction is controlled by the anodic dissolution of the

alloys and then exhibits a passivation for longer time. Firstly, higher chromium content of the alloys is superior to the formation of a chromium rich oxide scale exhibiting lower corrosion rate. It is quite common that ion or electron transport in a chromium rich coherent layer is the rate determining step of the corrosion reaction. Such layers are the lamellar layers for, e.g., SUS304H and nickel and chromium sulfides layer for CR35A, whose ionic (nickel and iron) or electron conductivity gives the  $i_{\text{corr}}$ . Secondary, in many molten salt corrosion systems the transition of active to passive state often occurs. Thus, in the initial stages the corrosion reaction is rate controlled by the anodic dissolution, whatever the metal surface is bare or covered by the initially formed scale, and then the alloy becomes passivated accompanied with the protective scale growth. For the 100h salt coating test the alloys might have been passivated and it is shown that the  $i_{\text{corr}}$  becomes equal to  $i_{\text{pp}}$ , which is dependent on the oxide scale properties (chromium content and characteristics of scale morphology).

On the other hand, the anodic dissolution current,  $i_p$  for CR35A showed the lowest value; lower than that of pure Cr (Figs.6 and 10) and the co-operative performance of nickel with chromium has been anticipated. From the microstructure features the corrosion resistance of these alloys might be achieved by the thinner mixed sulfides scale containing mainly chromium sulfide. The addition of nickel with chromium content more than 25% showed a significant reduction in the corrosion rate corresponding to the case of SUS310S and CR35A[24]. On this occasion, the addition of nickel in the co-existence of chromium suppresses the passive current,  $i_{\text{pp}}$ , and hence the nickel as an alloying element plays a role of co-operative performance with chromium on inhibiting anodic dissolution of the passive film. Additionally, the solubility product of  $\text{Ni}_3\text{S}_2$  was  $10^{-5}$ - $10^{-4}$  times lower than that of  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  sulfides in a sulfur-free  $\text{LiCl-KCl}$ [28].

Presently, it is equivocal whether this corrosion resistance for CR35A is attributable to Cr rich  $\Delta_{(\text{Cr},\text{Ni})\text{Sx}}$  or Cr depleted  $\text{Ni}_3\text{S}_2$  layer, though Ni sulfide:  $\text{Ni}_3\text{S}_2$  is easily formed as an inner most scale. Further experimental analysis of the corrosion behavior of CR35A might be needed.

### 3.2.6 Application of polarization resistance method to iron-based alloy corrosion in $(\text{Na},\text{K},\text{Li})_2\text{SO}_4$ containing $\text{Fe}_2(\text{SO}_4)_3$ [27]

May et al.[29] first evaluated the polarization resistance method to obtain instantaneous corrosion current of high Ni alloys in molten salts- $\text{V}_2\text{O}_5$  systems at 1023-1173K. Comparing the data obtained from mass loss measurement and the polarization resistance method according to the Stern-Geary relationship (Eq.3), the correlation was fell in the 95% confidence limit, which exhibits that this technique adequately applicable to corrosion screening test of heat-resistant alloys in molten salts. Cutler and Grant[30] and Wu and Rahmel[31] critically reviewed this technique in terms of the validity of K in Eq.4, which frequently varies from system to system, which makes lessen the correlation derived from both methods.

We estimated the corrosion rate by two methods, the polarization resistance technique and the corrosion salt coating test. In the corrosion salt coating test,  $2.3 \times 10^{-1}$  g of the mixed salts:  $\text{Fe}_2\text{O}_3\text{:K}_2\text{SO}_4\text{:Na}_2\text{SO}_4 = 2\text{:}3\text{:}3$  molar ratio, were coated onto a  $1.15 \times 10^{-3}\text{m}^2$  surface of the alloys, and after testing for 100h, the scale was removed and the mass loss was measured[24]. The measurement of the polarization resistance was conducted within several hours after immersion, and so the estimated corrosion rate is an instant value for that timing. On the other hand, the average corrosion rate for 100h is measured in the coating test. Therefore, we have to think about the possibility that the results of the long-term corrosion test for 100h can be replaced with results of the short time polarization resistance technique.

Figure 13 shows the relationship between polarization conductance and corrosion current density estimated by the mass loss method. As can be seen, even though the K-value is different depending on temperature, all of the points are on the line with 45° slope and satisfy the Stern-Geary relation (Eq.3). Therefore, if we estimate the K-value using the method as shown in Fig.13 beforehand, we can obtain the material selection data in a short time.

The corrosion rate of CR35A at 923K obtained with the polarization resistance technique is almost the same or smaller than that measured at 973K. On the other hand, the mass loss value at 923K is 1.8 times larger than that at 973K[24]. The reason for this phenomenon is thought to be that the anodic corrosion reaction has been changed during the 100h test time at 923K. Figure 14 shows the polarization curves of CR35A at 923K and 973K. In the case of 973K, both the cathodic polarization curve and the anodic polarization curve rise rapidly near the corrosion potential, the current peak is high and the corrosion potential is stable for a long time. On the other hand, in the case of 923K, the anodic dissolution current density shows only a small peak. This is considered to be because the corrosion rate increases due to the effect of the cathodic polarization curve, (shown as a dotted line in the figure), which shifts towards the noble potential direction as the corrosion proceeds, and the corrosion potential enters the trans-passive region of the partial anodic polarization curve. CR35A must give good corrosion resistance at 923K due to the co-operative performance of chromium and nickel. Thus, the trans-passive dissolution of chromium occurs in the melt that contains ferric ions, because the ferric ion acts as a strong oxidizing agent, and the corrosion potential shifts towards the noble direction for longer corrosion test.

### 3.3 Auto Catalytic Corrosion Mechanism

#### 3.3.1 Effect of iron sulfate added on corrosion potential of iron in

(Na,Li,K)<sub>2</sub>SO<sub>4</sub> containing Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> [15]

Rest potential The potentials of the Pt and Fe electrodes was studied in (Na,Li,K)<sub>2</sub>SO<sub>4</sub> containing different concentrations of ferric sulfate. Plots of the potentials against ferric ions are shown in Fig.15. The potential of the Pt electrode exhibits a more noble

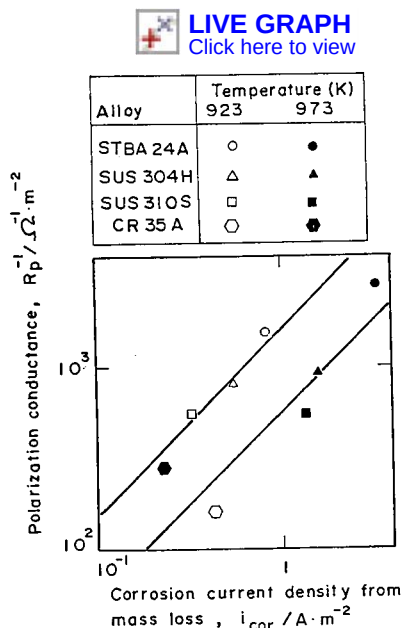


Fig.13 Bi-logarithmic plots of polarization conductance and  $i_{cor}$  estimated from coating test.

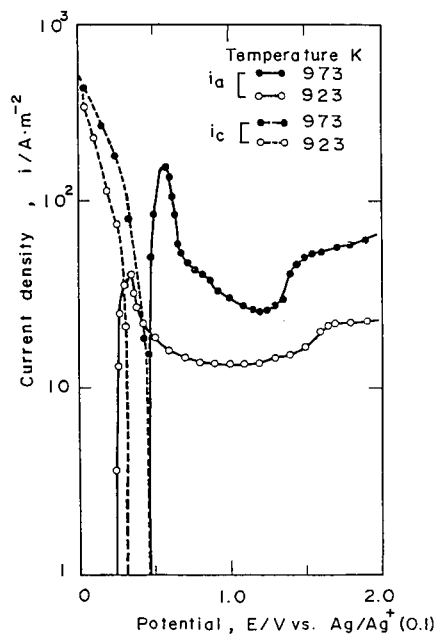
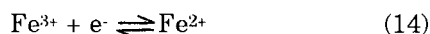


Fig.14 Polarization curves of CR35A at 923 and 973K.



value and approximately obeys the Nernst equation for the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  equilibrium



$$E = E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} + \frac{RT}{F} \ln \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \quad (15)$$

where  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ ,  $[\text{Fe}^{3+}]$  and  $[\text{Fe}^{2+}]$  indicates the standard electrode potential, and the activities of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ion. The value of  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$  is estimated to be 0.428V in  $(\text{Li}, \text{K})_2\text{SO}_4$  at 900K[32] and those of the activity coefficient of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  are reported to be,  $3.6 \times 10^{-3}$  and 0.83 at 1200K, respectively[17].

Increasing the concentration of the ferric ions resulted in a shift of the potentials of the Fe electrode to more noble potentials with a much steeper slope compared with that of Pt. This indicates that the potential of the Fe electrode is a corrosion potential which is determined by the combination of the cathodic reduction of the ferric ions and the anodic dissolution of the metal. Just after immersion, the potential of the Fe electrode shifts from its initial value to a stationary 0.5V noble value. This potential shift towards noble values is attributable to the dissolution of the electrode and the formation of an oxide film on the surface. Sequeira and Hocking[33] reported that a Ni electrode in  $\text{Na}_2\text{SO}_4$  at 1173K exhibited a potential in the active region initially and a subsequent shift of the potential to a noble value was attributed to



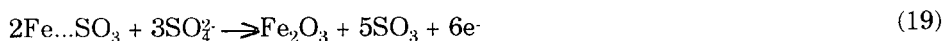
and



The dissolution and the formation of oxide film on the Fe electrode can be expressed in a similar way as



and



where  $\text{Fe} \dots \text{SO}_3$  indicates that the dissolution of Fe is catalyzed by the adsorption of  $\text{SO}_3$ .

### 3.3.2 Effect of iron sulfate and artificially introduced corrosion products on corrosion behaviors

The rate of corrosion of iron estimated from mass loss measurement are plotted vs the ferric ion concentration in Fig.16. Below 12 mol%, the corrosion rate of Fe increases almost proportional to the concentration. Above 12 mol%, however, this

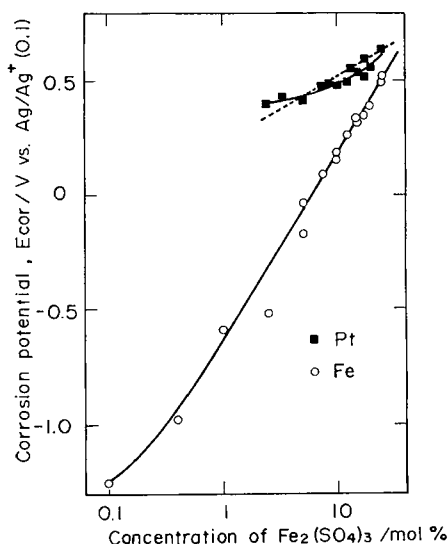


Fig.15 Potential of Pt and Fe electrodes in alkali sulfate containing  $\text{Fe}_2(\text{SO}_4)_3$  at 973K.

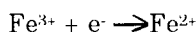




current decreases with increasing ferric ion concentration; the reason for this will be discussed in the section 3.3.3.

**Polarization Curves** The anodic polarization curves of Fe were measured in sulfate melts containing various concentrations of ferric sulfate. At low concentrations of ferric ion, the polarization curves exhibit the Tafel lines with the slope of 0.48V/decade, exhibiting an asymptotic behavior at noble potentials. The potential range of the linear portion decreases with increasing ferric ion concentration until 15 mol%. Furthermore, these curves approach the same limiting current value at higher potentials while that of 25 mol% exhibits a decrease in current. It is probable that, above 15 mol %, the amount of ferric ion exceeded a saturation and a sluggish precipitate such as  $\alpha\text{-Fe}_2\text{O}_3$  or  $\text{Fe}_2(\text{SO}_4)_3$  was formed in the melt. Thus, the sluggish precipitate inhibited anodic dissolution as well as cathodic reduction. The cathodic polarization curves for Pt in the melt containing different amounts of  $\text{Fe}_2(\text{SO}_4)_3$  are shown in Fig.17. It is seen that  $\text{SO}_3$  and  $\text{O}_2$  are not cathodically reduced at these potentials, because only a small residual current is observed in the absence of  $\text{Fe}_2(\text{SO}_4)_3$ . Therefore,  $\text{SO}_3$  and  $\text{O}_2$  do not act directly as an oxidant for corrosion here.

Below 10 mol %  $\text{Fe}_2(\text{SO}_4)_3$ , the cathodic polarization curves exhibit a limiting current in the potential region from -0.2 to -0.5V. As shown in Fig.18, a plot of the limiting current density vs.  $\text{Fe}_2(\text{SO}_4)_3$  content yields a line, although some scatter is evident above 17.5 mol %. Therefore, it is likely that the cathodic reaction in this potential region is a diffusion-limited reduction of ferric ion, as



(20)

The increase in cathodic current at potentials less noble than -0.5V is probably attributable to the reduction of decomposition products of sulfate, such as  $\text{SO}_3$  and  $\text{SO}_2$ . Shores and Fang[34] claimed that the cathodic limiting current on Pt is mostly attributable to the diffusion of pyrosulfate ion through the thin film of  $\text{Na}_2\text{SO}_4$  melt under  $\text{O}_2$ -rich  $\text{SO}_3$  atmosphere. Since the cathodic current in this region increases with an increase of ferric ion concentration, however, it is also possible that the cathodic current at less noble potentials involves the cathodic reduction of ferrous ion to metallic iron.

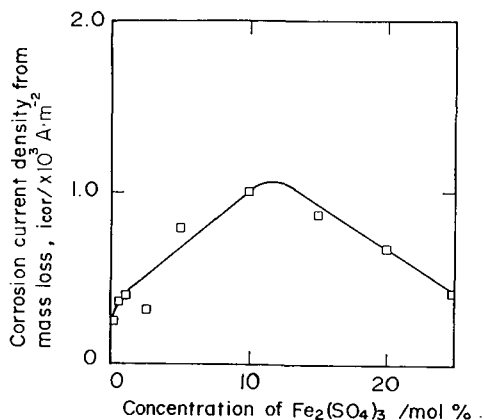


Fig.16 Effect of  $\text{Fe}_2(\text{SO}_4)_3$  on corrosion current from mass loss in  $(\text{Na,K,Li})_2\text{SO}_4$  at 973K.

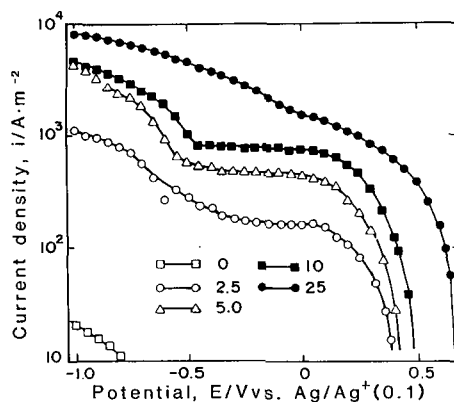


Fig.17 Cathodic polarization curves of Pt in  $(\text{Na,K,Li})_2\text{SO}_4$  containing  $\text{Fe}_2(\text{SO}_4)_3$  at 973K.



Similar polarization measurements were carried out on an Fe electrode after the same immersion time since the cathodic current increases with immersion time. The cathodic polarization curves for the Fe electrode also exhibit a limiting current, similar to that on Pt (Fig.17). A plot of the cathodic limiting current for Fe against the concentration of ferric ion yields a straight line as shown in Fig.18, but the slope of the line is higher than that on Pt. The magnitude of this slope increases with immersion time before the polarization measurement. The extraordinarily large limiting current on Fe is probably caused by a participation of corrosion products in the cathodic reaction of ferric ion.

Thus, the polarization study showed that the rate of corrosion of Fe is also controlled by diffusion-limited cathodic reduction of ferric ions, as schematically shown in Fig.7(b) in terms of partial polarization curves. It is shown that the corrosion current of Fe increases with increasing concentration of  $\text{Fe}_2(\text{SO}_4)_3$ , resulting in the shift of the corrosion potential in the anodic direction, termed as under diffusion-limited cathodic control.

#### Effect of dissolved ferrous ion

In order to examine the effect of the ferrous ions produced by corrosion, an experiment was made in the cell shown in Fig.1 (b) under a mixed  $\text{SO}_2$  and  $\text{O}_2$  atmosphere where the ferrous ions were introduced by galvanostatic dissolution of the auxiliary Fe electrode at 0.1A for 6h. The amount of dissolved ferrous ion

corresponded to 10 mol %. After producing ferrous ions, cathodic polarization curve for the Pt-1 electrode and the electrode potential of Pt-2 were measured at appropriate time intervals. The time dependence of the cathodic polarization curves on the Pt-1 electrode is shown in Fig.19. All the curves exhibit a diffusion-limited current at potentials between -0.5 and 0.3V, similar to that for Pt and Fe in the melts containing ferric ions (Fig.17). The increase in the limiting current with time indicates that ferrous ions initially generated are slowly oxidized to ferric ion under  $\text{SO}_2$ - $\text{O}_2$  atmosphere. Figure 20 shows changes in the potential (Pt-2) and the limiting current (Pt-1, at -0.1V) with time after cessation of anodic dissolution of the Fe. The potential of the Pt-2 electrode shifts slowly to more noble potentials, which is attributable to the oxidation of dissolved ferrous ions to ferric ions by  $\text{SO}_3$  gas:

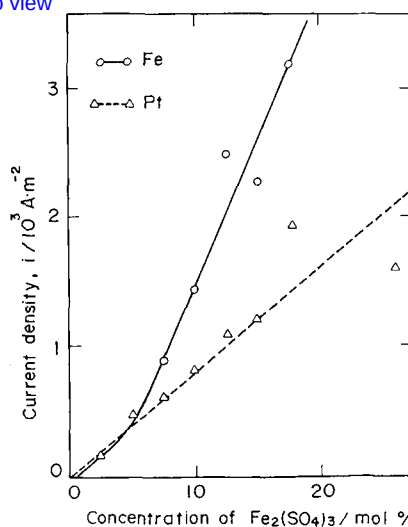
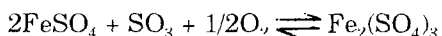


Fig.18 Effect of concentration of  $\text{Fe}_2(\text{SO}_4)_3$  on cathodic limiting current at 973K.

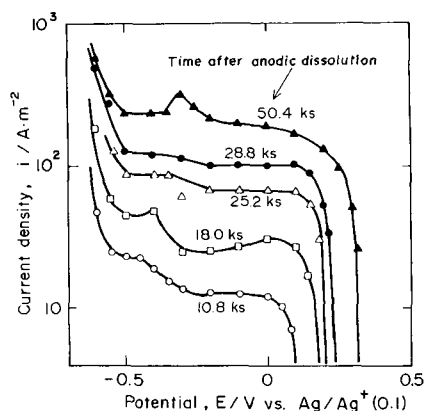


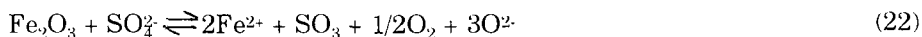
Fig.19 Change in cathodic polarization curves (Pt-1) with time after anodic dissolution of Fe in  $(\text{Na,K,Li})_2\text{SO}_4$  at 973K.



When the potential reached -0.1V after 3h, a cathodic current corresponding to reduction of ferric ion to ferrous ion occurs on the Pt-1 electrode and increases with time. This indicates that the ferrous ion formed as corrosion product of steel is oxidized to ferric ion in  $\text{SO}_3\text{-O}_2$  atmosphere and then serves as an oxidant for corrosion.

**Effect of  $\alpha\text{-Fe}_2\text{O}_3$**   $\alpha\text{-Fe}_2\text{O}_3$  is the thermodynamically stable corrosion product under the experimental conditions (see Fig.3). In order to examine the effect of  $\alpha\text{-Fe}_2\text{O}_3$  on corrosion, an electrochemical measurement was made in the melt containing  $\alpha\text{-Fe}_2\text{O}_3$  using the cell shown in Fig.1(b).

$\alpha\text{-Fe}_2\text{O}_3$  was introduced into the melt followed by  $\text{N}_2$  bubbling to stimulate the dissolution of  $\alpha\text{-Fe}_2\text{O}_3$ . As shown in Fig.21, the potential shifts to less noble values during the initial period. Over this time, the dissolved ferric ions should be reduced to ferrous ions because of the deaerated atmosphere as follows;



After the introduction of  $\text{SO}_2$  and  $\text{O}_2$  gas into the atmosphere, the potential of the Pt-2 electrode rose gradually to 0.12V. When the potential of the Pt-2 electrode reached -0.1V, a cathodic current was observed on the Pt-1 electrode and a slight positive shift of its potential. Thus, the changes in potential (Pt-2) and the cathodic current (Pt-1) after changing the atmosphere are similar to that shown in Fig.20. Summarizing the results, the potential of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  electrode in bulk electrolyte is basically controlled by the oxygen potential of the atmosphere that is determined by the partial pressures of oxygen and  $\text{SO}_3$  according to Eq.21 but it takes appreciable time to reach the reversible potential after a perturbation.

The cathodic limiting currents on Pt are indicative of the corrosion rates, which are approximately proportional to the concentration of ferric ion. Since  $\text{SO}_3$  and  $\text{O}_2$  are not cathodically reduced with high negative potentials, they should not serve directly as an oxidant for corrosion. However, they oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  which is an aggressive oxidant for corrosion. Then, ferrous ion formed a corrosion product of iron functions as a catalyst for accelerating corrosion.

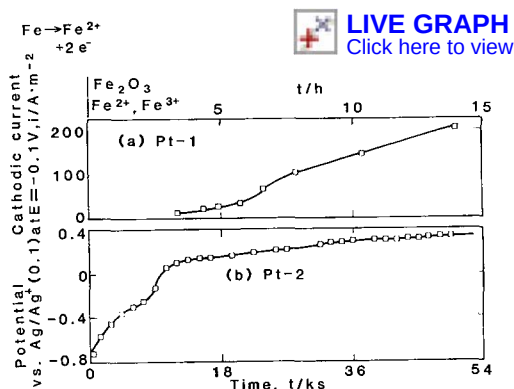


Fig.20 Change in potential (Pt-2) and cathodic limiting current (Pt-1) with time after anodic dissolution of Fe in  $(\text{Na,K,Li})_2\text{SO}_4$  at 973K.

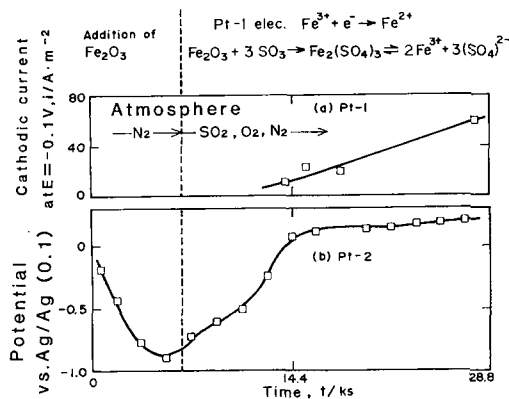


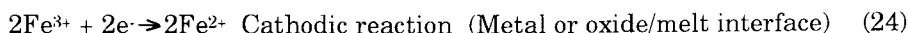
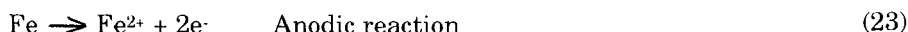
Fig.21 Change in potential (Pt-2) and cathodic limiting current (Pt-1) with time after introducing  $\text{Fe}_2\text{O}_3$  into  $(\text{Na,K,Li})_2\text{SO}_4$  at 973K.

### 3.3.3 Autocatalyzed corrosion in molten sulfate

Heat-resistant alloys at high temperatures in a  $\text{SO}_3$ -rich atmosphere are oxidized rapidly in the presence of a deposited molten sulfate layer on the surface, which contains high concentration of corrosion products. However, there have been few studies to examine the effect of corrosion products on the corrosion processes.

Shores and Fang[34] reported that the partial cathodic reaction for corrosion in a  $\text{Na}_2\text{SO}_4$  melt is the reduction of  $\text{SO}_3$  (or  $\text{S}_2\text{O}_7^{2-}$ ) in an acidic melt and the reduction of oxygen becomes an important process at low  $\text{SO}_3$  partial pressures. Nishikata and Haruyama[35] claimed that the cathodic reduction of  $\text{SO}_3$  and  $\text{O}_2$  occurred only in the presence of water in a reasonable potential region. Rapp and Goto[8] suggested that a rapid counter diffusion process of  $\text{M}^{2+}$  and  $\text{M}^{3+}$  ( $\text{M}^{n+}$ : transition metal ion) or electronic conduction might occur through a contaminated salt film. The charge transfer reaction of  $\text{M}/\text{M}^{n+}$  systems is usually very rapid[20] and it is likely that the net rate of corrosion is controlled by the diffusion of oxidants in the melt. Since the rate of corrosion is proportional to the concentration of ferric ion as shown in Fig.16, the cathodic reduction of  $\text{SO}_3$  (or  $\text{S}_2\text{O}_7^{2-}$ ) is less important in the corrosion in molten sulfate containing ferric ions.

Considering counter diffusion process of ferric and ferrous ions, the rate determining step for the corrosion becomes the diffusion-limited cathodic reduction of ferric ion and the overall corrosion reaction is



The concentration of ferric ion corresponds to the amount of added  $\text{Fe}_2(\text{SO}_4)_3$ . Since the oxide film formed initially has no significant role for protection, somewhat more ferric ion dissolves to increase the concentration. As a stable corrosion rate has been attained, the diffusion layer of ferric and ferrous ions is developed in the melt (Fig.22). Since the transportation of these metal ions is rapid, as suggested by Rapp and Goto[8], the oxidant (ferric ion) and the corrosion products (ferrous ion) counterdiffuse and these metal ions react with  $\text{SO}_2$  and  $\text{O}_2$  at the melt/gas interface. If the permeation of oxidant,  $\text{SO}_3$  (or  $\text{S}_2\text{O}_7^{2-}$ ) is sufficiently high, the reaction zone shifts somewhat into the melt. Thus, the corrosion product (ferrous ion) is oxidized by the oxidizing gas, which serves as an oxidant; di- and tri-valent ions move between the metal or oxide/melt and melt/gas interfaces. Thus, an accelerated corrosion of iron in molten sulfate can be explained by an autocatalysis involving the corrosion products. Rapp and Goto[8] suggested high diffusivities and concentrations of  $\text{M}^{2+}$  and

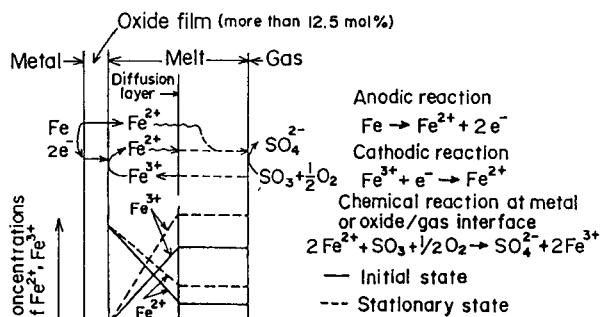


Fig.22 Schematic of corrosion reaction, anodic dissolution of metal and cathodic reduction of ferric ion whose concentration is illustrated.



$M^{3+}$  or electronic conduction in the corrosion mechanism of the salt film. Their model results in a basicity gradient in the molten salt film where the most basic site is located at the salt/gas interface. These results could not substantiate the existence of the basicity gradient because the partial pressure of oxygen was fixed at a low value. However, it is seen that the cathodic reduction of  $SO_2$  and  $O_2$  is less important.

Above 12 mol %, the rate of corrosion decreases with increasing ferric ion concentration. Numata et al.[36] reported that the corrosion potential of nickel in LiCl-KCl

containing nitrate ion was fully explained by the superposition of the anodic dissolution of nickel and the diffusion-limited reduction of nitrate ion, based on the mixed potential theory. The corrosion potential can be determined from superposition of the partial anodic dissolution current and the diffusion-limited reduction current of ferric ion in this case.

In the absence of ferric ions, the anodic polarization curve is consistent with the partial anodic polarization curve as long as the potentials are reasonably apart from the corrosion potential. Figure 23 shows the partial anodic polarization curves (dotted line) and the cathodic diffusion limiting currents, where the corrosion potentials are estimated by the above procedure. The results indicate that the corrosion reaction above 12 mol % is controlled not by the cathodic reduction of ferric ion. It is likely that a sluggish precipitate (illustrated in Fig.22) was probably formed on the surface above 12 mol %. It decelerates the anodic dissolution considerably and results in the shift of the corrosion potential to a less noble value. It is noted that this is the case of the corrosion of iron-based alloys in alkali sulfate containing 25 mol%  $Fe_2(SO_4)_3$ , as shown in the section 3.2.2.

Understanding the results comprehensively, the corrosion behavior of the iron alloys in alkali sulfate is qualitatively illustrated in acceleration and deceleration factors in terms of anodic and cathodic behaviors (Fig.24).

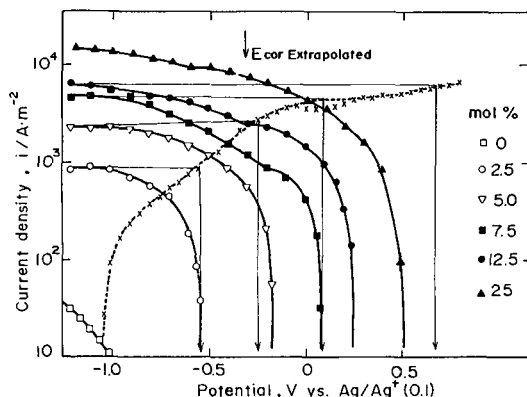


Fig.23 Polarization curves of anodic dissolution of Fe and cathodic reduction of ferric ion and extrapolated corrosion potentials.

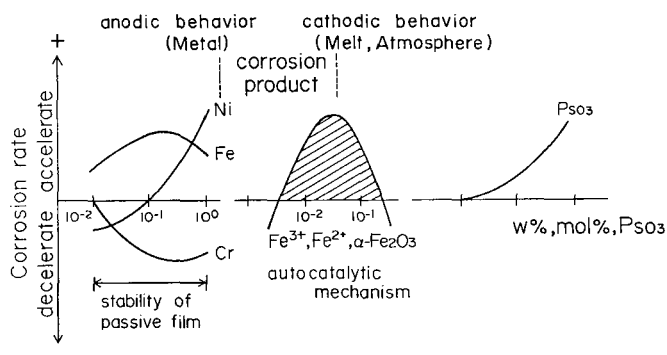


Fig.24 Schematic of accelerating and decelerating factors of sulfate-corrosion which is evaluated by electrochemical anodic and cathodic behaviors.

#### 4. Conclusion

The following conclusions are obtained from the electrochemical measurement of hot corrosion of various materials in alkali sulfate containing  $\text{Fe}_2(\text{SO}_4)_3$  that was synthesized from the mixed salts of alkali pyrosulfate and  $\alpha\text{-Fe}_2\text{O}_3$ .

(1) The corrosion potentials shifted to higher values and the corrosion rate decreased along with increasing chromium content. The dependence of chromium content on the corrosion potential and the corrosion current were explained successfully by superposition of  $i_c$  as the cathodic reduction reaction of ferric ions, and of  $i_a$  as the anodic dissolution reaction that was variable with temperature and the chromium content of the alloys.

(2) The mass loss measured in the corrosion salt coating test for 100h showed a good relationship with polarization conductance and satisfied the Stern-Geary Equation. Therefore, it became obvious that the corrosion rate can be estimated from the polarization resistance measurement.

(3) The anodic polarization curves of alloys showed clearly the maximum current and the passive current corresponding to the anodic dissolution. These currents decreased with increasing chromium content, and in the case of high chromium content steels, a low anodic dissolution current and passive current were observed and the existence of a passive film that has high corrosion resistance was confirmed.

(4) The corrosion of Fe in  $(\text{Na}, \text{K}, \text{Li})_2\text{SO}_4$  melt containing  $\text{Fe}_2(\text{SO}_4)_3$  is accelerated with increasing the concentration of ferric ion below 12 mol %. It was found that the rate of corrosion was controlled by the diffusion-limited cathodic reduction of ferric ions.

(5) It was found that the cathodic reaction was also promoted by the corrosion product such as ferrous ion which was chemically oxidized and functioned as an oxidant. Thus, the accelerated corrosion of iron in molten sulfate was explained by an autocatalytic corrosion mechanism of the corrosion product.

#### Acknowledgements

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# Electrochemical Corrosion Studies of Uncoated and Coated Ni-Base Superalloys in Molten Sulphate

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**Keywords:** Coatings, Corrosion Resistance, Electrochemistry, Molten Sulphate, Ni-Base Superalloys, Sulphidation

**Abstract** An electrochemical method was used to investigate the sodium sulphate induced corrosion of coated and uncoated Ni-base superalloys at 900 °C under heat engine conditions. The polycrystalline Waspaloy and IN100 as well as the single crystal alloy CMSX-2, and two overlay coatings, air-plasma-sprayed LCO22 (Co-31Ni-21Cr-8Al-0.5Y) and electron-beam physical-vapour-deposited PWA270 (Ni-20Co-19Cr-12.5Al-0.35Y), served as reference materials. Current density vs. potential curves were utilized for studying corrosive processes. The corrosion potential and the corrosion current density obtained from these curves can be used as a measure for the corrosion resistance. The electrochemical data indicate that the high chromium alloy Waspaloy is more corrosion resistant than the alloys IN100 and CMSX-2 containing less chromium. Both coatings greatly protected the substrate alloys against corrosion and sulphidation attack. The electrochemical results show a good correlation with results of a hot corrosion study achieved by burner rig tests.

## 1 Introduction

During the combustion stage in heat engines, particularly in gas turbines, sodium and sulphur impurities, which may be present either in fuel or in combustion air, react to form sodium sulphate. If the concentration of the sulphate exceeds the saturation vapour pressure at the operating metal temperature for turbine blades and vanes (700 - 1100 °C), then deposition of the sodium sulphate will occur on the surface of these components. At higher temperatures  $\text{Na}_2\text{SO}_4$  is deposited as a thin liquid film (melting point: 884 °C) and can cause accelerated attack of the Ni- and Co-base superalloys. This type of corrosion attack is commonly called hot corrosion. Since the molten sulphate inducing the corrosion is an electrolyte, hot corrosion should really be considered as an electrochemical phenomenon. To investigate this a device was developed to perform electrochemical experiments in molten salts. Another motivation was to have a rapid corrosion test for preliminary screening supplementary to the high-cost burner rig test which has normally been used for simulating hot corrosion in gas turbines. However, since molten sulfate is present as bulk electrolyte at the electrochemical method, the hot corrosion attack of turbine components really induced by thin films of fused sulphate can be simulated only approximately.

## 2 Experimental procedure

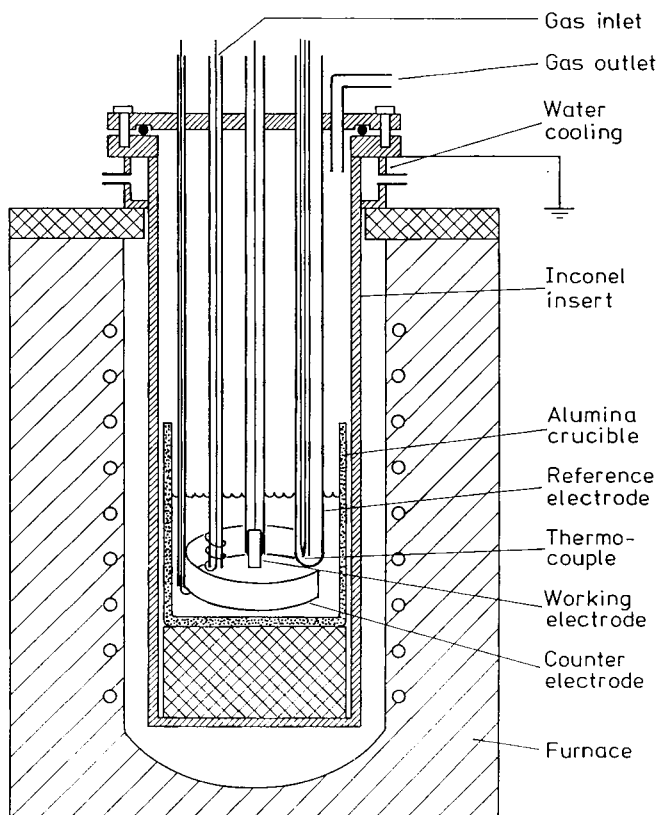
### 2.1 Electrochemical technique

Electrochemical methods, analogous to those widely used in aqueous corrosion studies, have been used in molten sulphates to investigate the corrosion mechanisms and to measure corrosion



rates [1-15]. Novel experimental arrangements were introduced for electrochemical studies of the hot corrosion of metals and coatings beneath thin fused salt films [13-15].

In a previous paper [16] the development of our experimental technique as well as preliminary measurements were described in detail. The design of the electrochemical cell used for experiments in molten sulphates is shown in Fig. 1. The three-electrode arrangement includes the working electrode, the reference electrode, and the inert counter electrode made of platinum. The  $\text{Pt}(\text{O}_2)/\text{ZrO}_2(\text{Y}_2\text{O}_3)$  electrode was applied as reference electrode and all potentials quoted in this report are referred to this electrode.



**Figure 1.** Schematic diagram of the three-electrode cell.

The investigations were carried out in molten 90 mole-%  $\text{Na}_2\text{SO}_4$  - 10 mole-%  $\text{K}_2\text{SO}_4$  at 900 °C. The atmosphere was either laboratory air or synthetic air with a content of 250 vpm  $\text{SO}_2$  to simulate combustion gas of gas turbines and heat engines [17, 18]. The gas was passed over a coil of Pt wire at the experimental temperature to ensure the equilibrium among  $\text{SO}_2$ ,  $\text{SO}_3$ , and  $\text{O}_2$ . The equilibrium between the gas phase and the melt was established by bubbling the gas into the melt at a rate of  $5 \cdot 10^{-3} \text{ m}^3 \text{ h}^{-1}$ .

For measuring current versus potential, a Solartron potentiostat (Electrochemical Interface 1286) controlled by a personal computer was employed. This instrument automatically maintains the desired potential between the working and reference electrode by passing the appropriate current between the

working and the counter electrode. The polarization of the working electrode was accomplished potentiodynamically, that means the potential was continuously changed. This changing occurred at sweep rates of 20 mV/h or 40 mV/h.

Before polarization diagrams were established by experiments the corrosion potential of the working electrode was determined against the  $\text{Pt}(\text{O}_2)/\text{ZrO}_2(\text{Y}_2\text{O}_3)$  electrode under open-circuit conditions, i.e. the applied current was zero. An approximate constant value of the open-circuit potential was usually achieved after 18 to 25 hours. Then, the working electrode was anodically polarized starting at a potential 100 mV more negative than the open-circuit potential.

## 2.2 Materials

The wrought nickel-base alloy Waspaloy (Ni-13.5Co-19.5Cr-1.4Al-3.0Ti-4.0Mo-0.08C-0.08Zr-0.007B) was involved in this test program because of its high resistance against hot corrosion. The polycrystalline IN100 (Ni-15.0Co-10.0Cr-5.5Al-4.7Ti-3.0Mo-0.18C-0.06Zr-0.9V-0.014B) and the single crystal CMSX-2 (Ni-4.6Co-8.0Cr-5.6Al-1.0Ti-0.6Mo-8.0W-6.0Ta) were selected as typical candidates from a group of advanced nickel-base superalloys applied for blade materials in gas turbines. Both overlay coatings, the PWA270 (Ni-20Co-19Cr-12.5Al-0.35Y) deposited by an electron-beam physical-vapour-deposition (EB-PVD) process on Waspaloy and IN100, as well as the air-plasma-sprayed LCO22 (Co-31Ni-21Cr-8Al-0.5Y) on CMSX-2, have been developed to protect blades and vanes against oxidation and corrosion in gas turbines.

## 3 Electrochemical corrosion measurements

Grant and Cutler [3, 19, 20] have attributed the anodic and cathodic processes at inert metal electrodes, such as platinum and gold, in molten sulphates to the redox reaction

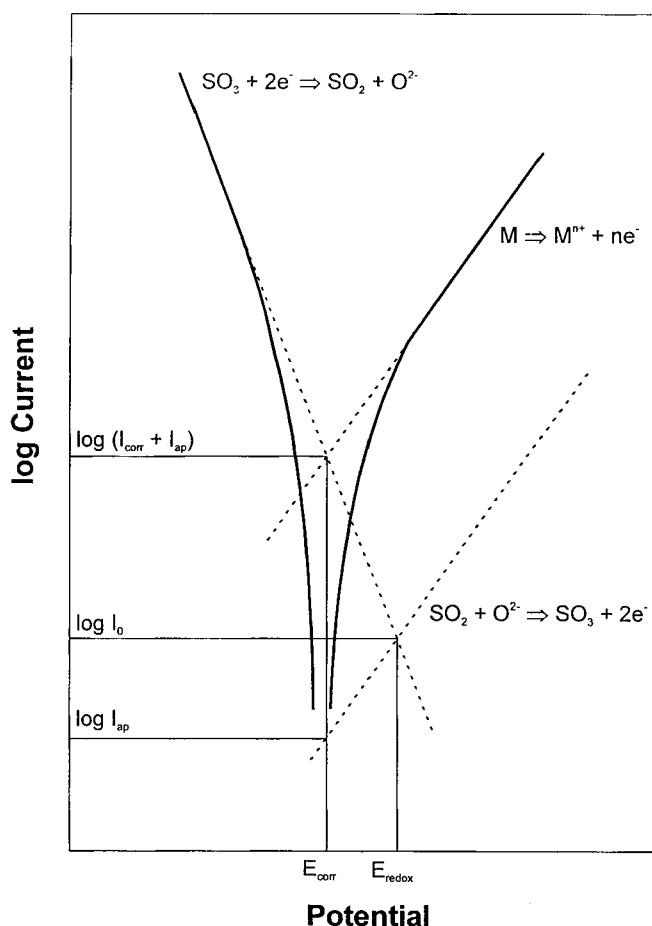


The open-circuit potential  $E_{\text{redox}}$  of an inert electrode is determined by the equilibrium of this reaction (Fig. 2). An irreversible electrode reaction occurs if the metal corrodes in molten sulphates. This process consists of the dissolution of metal according to the anodic reaction



The rates for the anodic oxidation of the metal of Eq. 2 and the cathodic part of the redox reaction given in Eq. 1 can be described electrochemically in terms of the current as a function of the potential. If metal dissolution is the only oxidation process, the rate of corrosion is equivalent to the corrosion current  $I_{\text{corr}}$  which is determined by the balance between the anodic and cathodic charge transfer processes which is established at the corrosion potential  $E_{\text{corr}}$ . When the test specimen is polarized at some potential relative to the corrosion potential, the corrosion behaviour will be influenced by the imposed potential and may differ from the normal corrosion behaviour corresponding to the balance between the anodic and cathodic charge transfer reactions at the unpolarized metal surface. The current vs. potential relationship for the separate anodic and cathodic electrode processes can be described by the general equation

$$I = I_0 \exp b(E - E_0) \quad \text{Eq. 3}$$



**Figure 2.** Schematic log current vs potential curves for reactions relating to corrosion of metal in molten sulphate (after Grant [20]).

where  $I_0$  is the exchange current corresponding to the rate of the charge transfer reaction at the reference potential  $E_0$ , and  $b$  is a parameter which has an opposite sign for the anodic and cathodic charge transfer reactions, respectively.  $I_0$  and  $b$  are constants for a given metal and environment and are both dependent on temperature.

Using the general Eq. 3 for the metal corrosion in molten sulphate, the current  $I$  at the polarized electrode is described as a function of the potential  $E$  by the equation

$$I = I_{\text{corr}} [\exp b_a(E - E_{\text{corr}}) - \exp b_c(E - E_{\text{corr}})] \quad \text{Eq. 4}$$

where  $b_a$  and  $b_c$  are constants for the anodic and cathodic charge transfer reactions that are involved in the corrosion process. The current  $I$  corresponds to the difference between the rates for the anodic and cathodic parts of the corrosion reaction when the potential of the metal electrode is varied. It is useful to construct polarization diagrams of corroding metals according to Eq. 4, sometimes called Evans diagrams, as log current versus potential graphs (Fig. 2).

Eq. 4 is valid if  $E_{\text{redox}} - E_{\text{corr}} \gg RT/F$  ( $R$  is the gas constant,  $T$  is the temperature in K, and  $F$  is the Faraday's constant) since the rate for the anodic direction of the redox process of Eq. 1 is then negligible. If the electrode is linearly polarized in anodic direction the first term in Eq. 4 will become dominant and a linear log current vs potential region will be reached when  $E - E_{\text{corr}} \gg 1/b_a$ . Similarly, if the potential variation is negative, the second term will dominate and a linear log current vs potential region will be observed when  $E - E_{\text{corr}} \ll 1/b_c$ . If the linear log  $I$  vs  $E$  relationships established for the anodic and cathodic processes are extrapolated to the corrosion potential  $E_{\text{corr}}$  as shown in Fig. 2 they will intersect at the corrosion current  $I_{\text{corr}}$  which can thus be obtained from the electrochemical measurements. The additional dashed line constructed in Fig. 2 considers the anodic reaction of Eq. 1 which is attributed to the oxidation of  $\text{SO}_2$ .  $I_{\text{ap}}$ , the contribution of this redox process to the anodic current at the corrosion potential can be neglected in the present work because the condition  $E_{\text{redox}} - E_{\text{corr}} \gg RT/F$  is valid for Ni- and Co-base alloys corroding in molten sulphate.

## 4 Results

### 4.1 Current density vs. potential curves

The procedure described above is appropriate to measure corrosion rates for the alloys and coatings selected for the present programme. However, for comparing polarization curves of different sample surfaces it is useful to consider the current density instead of the current. All polarization diagrams of this work are represented as current density vs. potential curves whereby the values of the current density are plotted on a logarithmic scale.

Fig. 3 shows the current density vs. potential curves for the uncoated Ni-base alloys IN100, CMSX-2, and Waspaloy measured in molten sulphate under ambient air. Waspaloy and IN100 were also investigated in molten sulphate under an atmosphere of synthetic air + 250 vpm  $\text{SO}_2$  (Fig. 4).

The current density vs. potential curves for the NiCoCrAlY coating on Waspaloy and IN100, as well as for the LCO22 coating on CMSX-2, in molten sulphate being in equilibrium with ambient air are separately plotted in Fig. 5. As the two NiCoCrAlY coatings came from different batches, the difference between their  $i$  vs  $E$  curves can be attributed to variations in composition of the coating alloy. This result proves the high sensitivity of the electrochemical method to variations of components in alloys. The polarization curves measured for the NiCoCrAlY on Waspaloy and the LCO22 on CMSX-2 in the melt under synthetic air + 250 vpm  $\text{SO}_2$  are shown in Fig. 6. The NiCoCrAlY coating on IN100 was not investigated at these conditions.

The  $i$  vs  $E$  curve of Waspaloy shown in Fig. 3 illustrates how  $E_{\text{corr}}$  and  $i_{\text{corr}}$  can graphically be determined. Applying this procedure the values of  $E_{\text{corr}}$  and  $i_{\text{corr}}$  of all Ni-base alloys and coatings were determined and are summarized in the Table 1. If alloys and coatings were tested in both environments, in the melt under  $\text{SO}_2$ -containing air  $E_{\text{corr}}$  is more negative and  $i_{\text{corr}}$  is higher than the corresponding values measured in the melt under laboratory air. This result confirms that the sulphate melt is more corrosive if the gas atmosphere consists in synthetic air + 250 vpm  $\text{SO}_2$ .

All alloys and coatings show a certain range of passivation if anodic polarization takes place. In this potential range, anodic dissolution of the alloys occurs through the oxide scale. The passivity leakage current density flowing in this passive potential range was used by Baudo [21] as criterion for the corrosive resistance of ferritic steels in alkali metal sulphate eutectic melt at 600 °C. It could be shown that the leakage current density decreased when the chromium content of the steel raised. Steel, high in

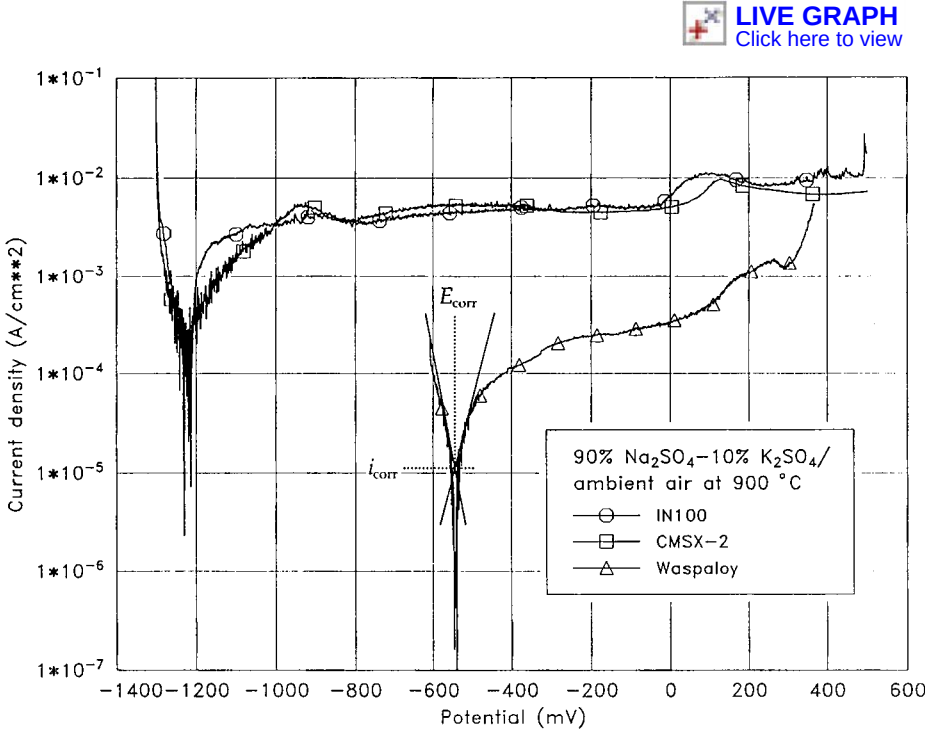


Figure 3. Polarization curves of uncoated Ni-base alloys in molten sulphate under ambient air.

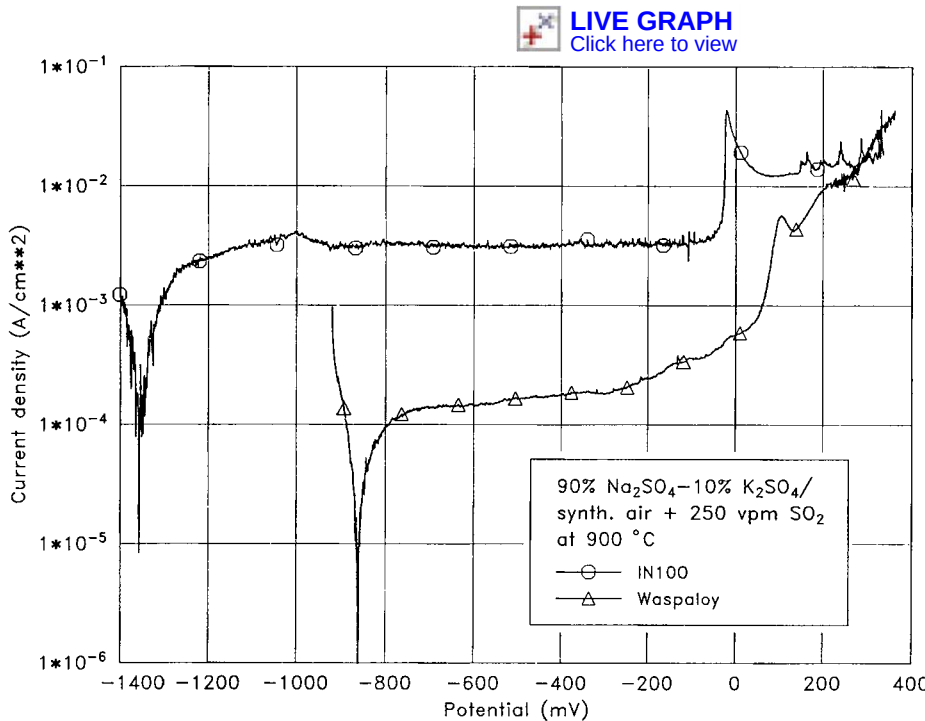
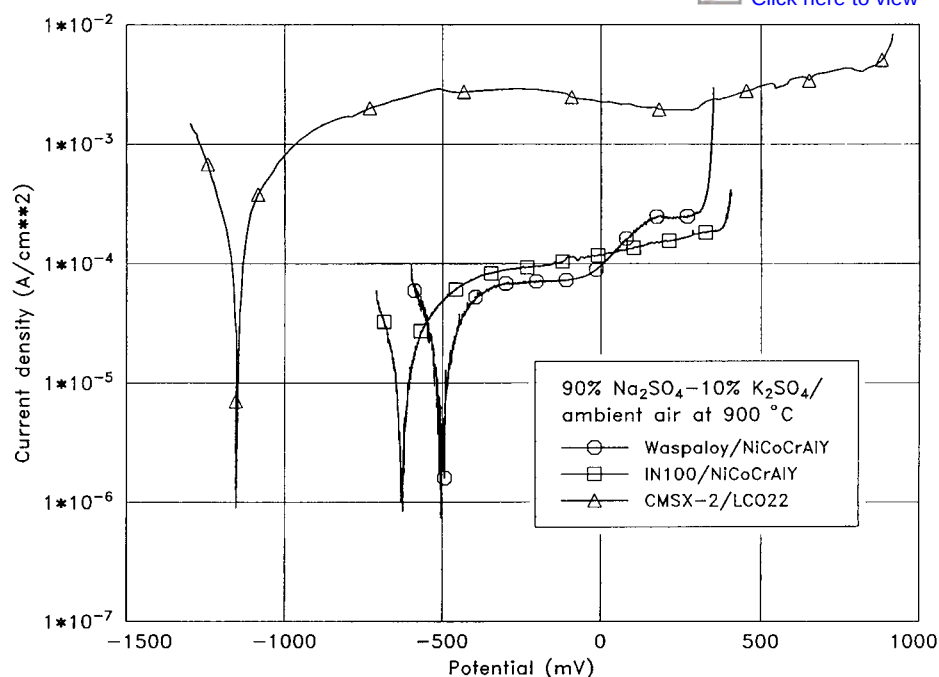


Figure 4. Polarization curves of uncoated Ni-base alloys in molten sulphate under synthetic air + 250 vpm  $SO_2$ .

chromium, obviously forms a more protective oxide film at the surface. This correlation is also satisfied for the uncoated Ni-base alloys studied in this work (Fig. 3 and Fig. 4). The leakage current density of CMSX-2 and IN100 which contain 8 and 10 wt.% chromium, respectively, was considerably higher than the corresponding value for Waspaloy (19.5 wt.% Cr). However, in case of the coatings the dependence of the dissolution current on the chromium content was not observed in the passive range (Fig. 5 and Fig. 6). The high cobalt content of about 40 wt.% containing in the LCO22 coating obviously affected the anodic oxide film formation detrimentally. Since the chromium content (21 wt.%) of this alloy is even a little higher than the chromium content (19 wt.%) of NiCoCrAlY, the LCO22 coating should be more corrosion resistant.



**LIVE GRAPH**  
Click here to view



**Figure 5.** Polarization curves of coatings in molten sulphate under ambient air.

After the end of passivation on the anodic side the transpassive region begins. In this potential range the current again increases rapidly which is explained by Nishikata and Haruyama [10] with the anodic oxidation of sulphate ions according to the following reaction:



A current peak is observed in the anodic polarization curves of the uncoated samples at potentials above -50 mV. The peak potentials are listed in Table 1. The peak is higher and sharper for those curves measured under synthetic air + 250 vpm SO<sub>2</sub> (Fig. 4). Among the polarization curves of coatings only the curve of NiCoCrAlY on Waspaloy under SO<sub>2</sub>-containing air shows a small current density peak at 18.4 mV. Generally, the potential position of the peak obviously depends on the alloy composition and the SO<sub>2</sub> content of the atmosphere. For the same material the peak potential was shifted toward negative potentials when polarization occurred in molten sulphate under synthetic air + 250 vpm SO<sub>2</sub>. Nishikata et al. [10, 12] refer the current peaks measured for Ni and the Ni-base alloy Inconel600 to oxidation of the oxide film to higher valence states.

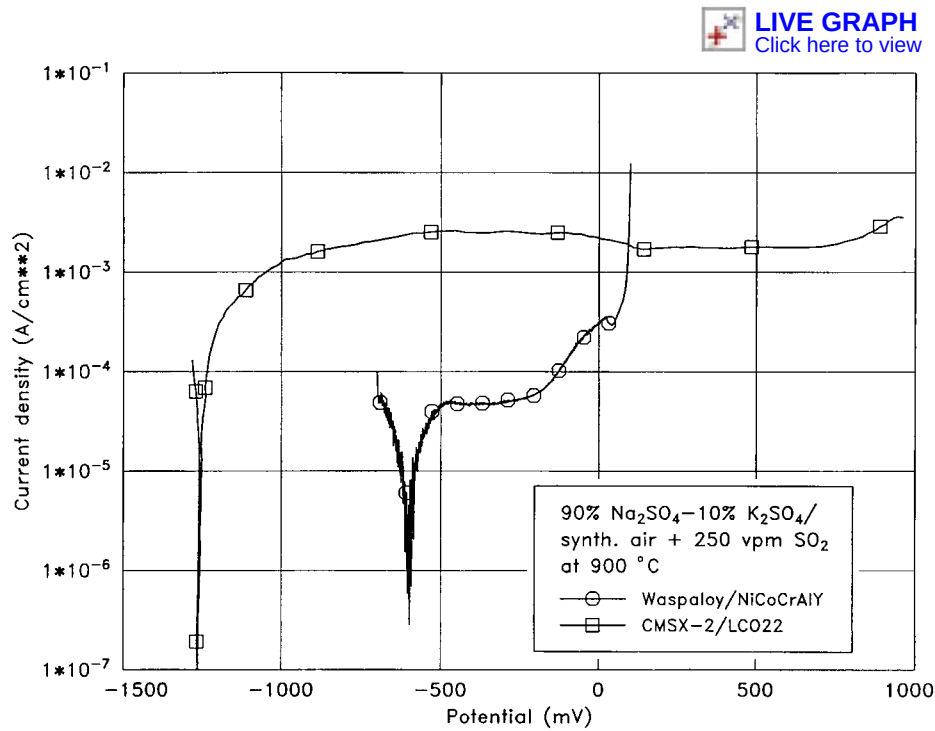


Figure 6. Polarization curves of coatings in molten sulphate under synthetic air + 250 vpm SO<sub>2</sub>.

| Alloy/<br>Coating      | Atmosphere                   | Open-circuit<br>potential, E <sub>oc</sub><br>in mV | Corrosion po-<br>tential, E <sub>corr</sub><br>in mV | Corrosion cur-<br>rent density, i <sub>corr</sub><br>in µA/cm <sup>2</sup> | Anodic peak<br>potential, E <sub>ap</sub><br>in mV |
|------------------------|------------------------------|-----------------------------------------------------|------------------------------------------------------|----------------------------------------------------------------------------|----------------------------------------------------|
| Waspaloy               | ambient air                  | -540                                                | -543                                                 | 13.1                                                                       | 265                                                |
| Waspaloy               | synth. air + SO <sub>2</sub> | -816                                                | -861                                                 | 16.9                                                                       | 106                                                |
| IN100                  | ambient air                  | -1124                                               | -1253                                                | 304.3                                                                      | 100                                                |
| IN100                  | synth. air + SO <sub>2</sub> | -1316                                               | -1351                                                | 359.4                                                                      | -22.5                                              |
| CMSX-2                 | ambient air                  | -1100                                               | -1228                                                | 370.3                                                                      | 125                                                |
| Waspaloy/<br>NiCoCrAlY | ambient air                  | -500                                                | -500                                                 | 4.4                                                                        | 85                                                 |
| IN100/<br>NiCoCrAlY    | ambient air                  | -610                                                | -630                                                 | 2.1                                                                        |                                                    |
| Waspaloy/<br>NiCoCrAlY | synth. air + SO <sub>2</sub> | -635                                                | -605                                                 | 3.0                                                                        | 18.4                                               |
| CMSX-2/<br>LCO22       | ambient air                  | -1100                                               | -1147                                                | 20.5                                                                       |                                                    |
| CMSX-2/<br>LCO22       | synth. air + SO <sub>2</sub> | -1269                                               | -1257                                                | 30.2                                                                       |                                                    |

Table 1. Comparison of open-circuit potentials, corrosion potentials, corrosion current densities, and anodic peak potentials determined for Ni-base alloys and coatings in molten sulphate at 900 °C under ambient air and synthetic air + 250 vpm SO<sub>2</sub>.

## 4.2 Open-circuit potentials

The open-circuit potentials  $E_{oc}$  of the uncoated Ni-base alloys and the coatings which were measured before polarization was started are summarized in the Table 1. The potential  $E_{oc}$  should correspond with the corrosion potential  $E_{corr}$  obtained from the current density vs. potential curves. With the exception of the measurements for IN100, CMSX-2, and LCO22 on CMSX-2, under ambient air the values of  $E_{oc}$  and  $E_{corr}$  are close together with differences in potential usually smaller than 50 mV, and for Waspaloy and NiCoCrAlY on Waspaloy under ambient air, both potentials are even nearly identical.

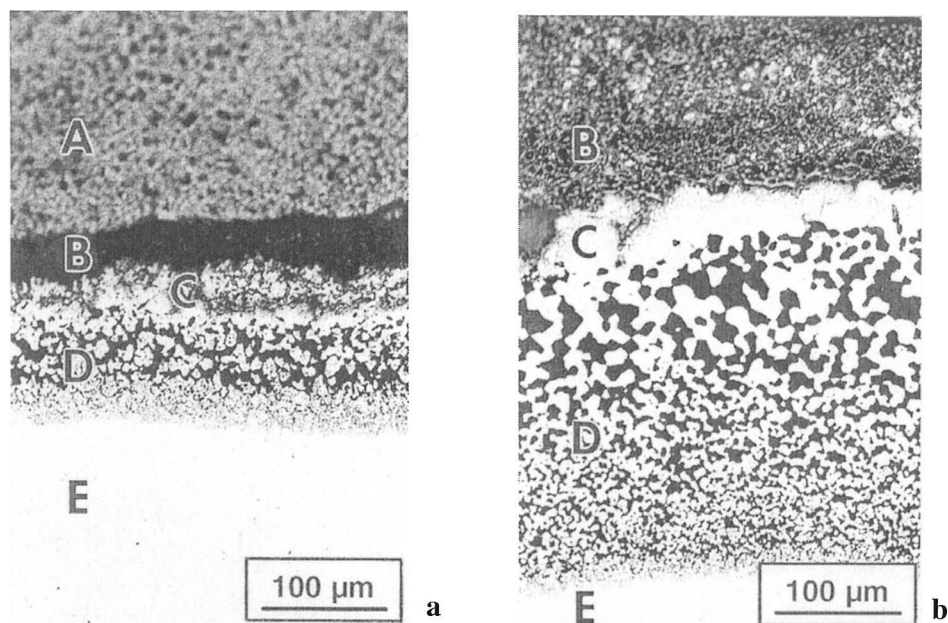
## 4.3 Microstructural investigations

Scales formed during the polarization tests on the samples were metallographically examined. The microscopic photographs in Fig. 7 show the cross sections of the surface zone for uncoated Waspaloy at the two environmental conditions. The scale consists of an external porous oxide layer and an internal penetration zone containing oxide particles. Precipitates were developed within the alloy ahead of the advancing oxide. These precipitates were identified via energy dispersive X-ray spectroscopy (EDX) analysis as chromium rich sulphides (Fig. 8). The most advanced zone of the internal sulphide layer contains a fine dispersion of chromium sulphide particles. The main zone of this layer consists of a network of chromium sulphide. A standardless EDX spot analysis of this phase gave the composition: 41 wt.% (51 at.%) S, 40 wt.% (31 at.%) Cr, 11 wt.% Ni, 2.9 wt.% Co, 2.2 wt.% Ti, and 0.5 wt.% Al. The atomic ratio of chromium and sulphur derived from this analysis is 0.61 indicating  $Cr_2S_3$  as sulphide phase. The matrix beside the sulphide phase contains 82 wt.% of the base-metal Ni, 12.7 wt.% Co, 1.5 wt.% Al, but it is chromium depleted (1 wt.% Cr) and contains none sulphur. It is evident, that the porous oxide scale as well as the zone of sulphide precipitates are more expanded in case of the synthetic air atmosphere with 250 vpm  $SO_2$ .

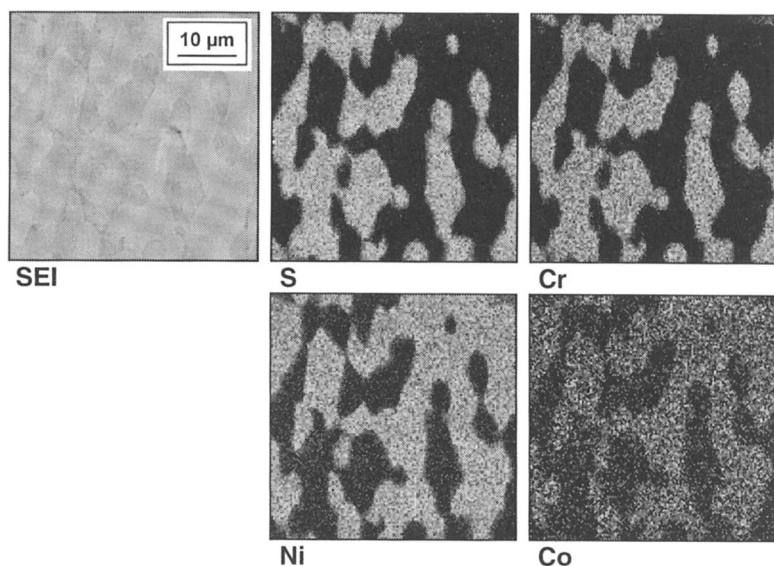
A continuous zone of oxides and sulphides was also developed in CMSX-2 (Fig. 9). The cross-section pattern of the internal oxides and sulphide precipitates is similar to those formed in Waspaloy (Fig. 7). The sulphide was clearly identified as chromium sulphide (Fig. 10). The composition of this phase analysed as 41 wt.% (50 at.%) S, 40 wt.% (30 at.%) Cr, 12 wt.% Ni, 1.5 wt.% Co, and 0.7 wt.% Al by the EDX spot analysis was identical with the corresponding sulphide phase in Waspaloy determined as  $Cr_2S_3$ . The secondary electron image (SEI) shows beside these chromium sulphide precipitates some areas of brighter phases containing sulphur and nickel, but the chromium content is small. The EDX spot analysis identified 68 wt.% (51 at.%) Ni, 24 wt.% (33 at.%) S, and, beside 0.5 wt.% Co and 1 wt.% Al, only 0.9 wt.% S. The ratio of nickel and sulphur atoms is 1.54 which is in accordance with the stoichiometry of  $Ni_3S_2$ .

The corrosive attack of IN100 is quite different from that of Waspaloy and CMSX-2. Fig. 11 shows the cross section of the surface zone of IN100 after polarization under synthetic air + 250 vpm  $SO_2$ . An oxide scale which partially protected the other both alloys was obviously not formed. Thus corrosion of IN100 was rather severe and resulted in a rugged surface. Only small areas with sulphide precipitates exist but they are not so expanded as in case of Waspaloy and CMSX-2. Rahmel [22] also found at electrochemical studies under similar conditions that the alumina forming alloy IN100 did not form a protective scale in any potential regime. In contrast to these results Erdös et al. [7] observed a thick porous scale on IN100 formed during anodic polarization in molten sulphate at 900 °C.

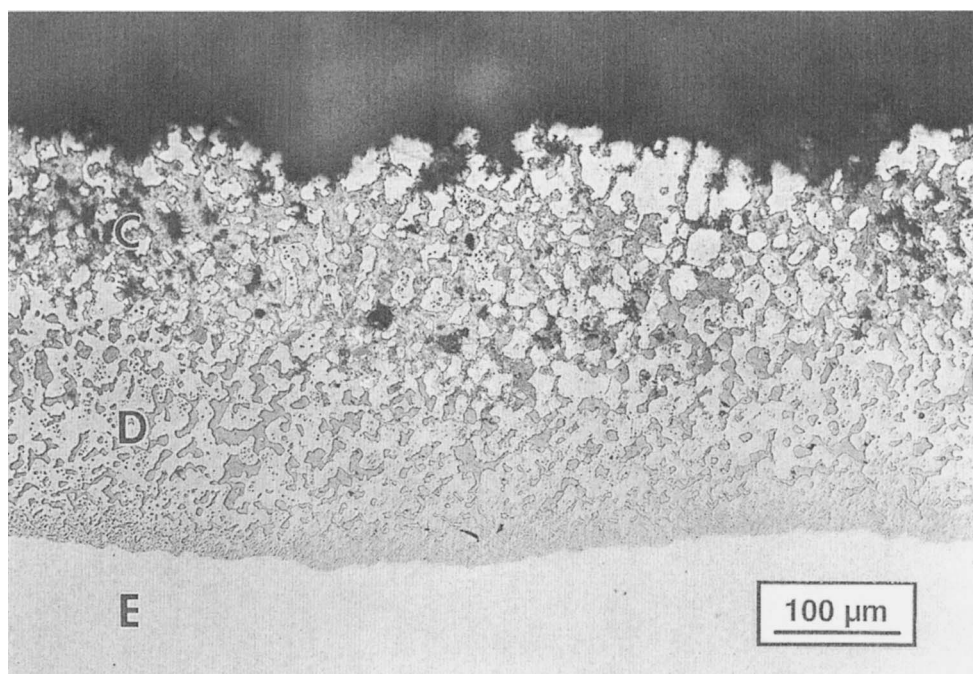




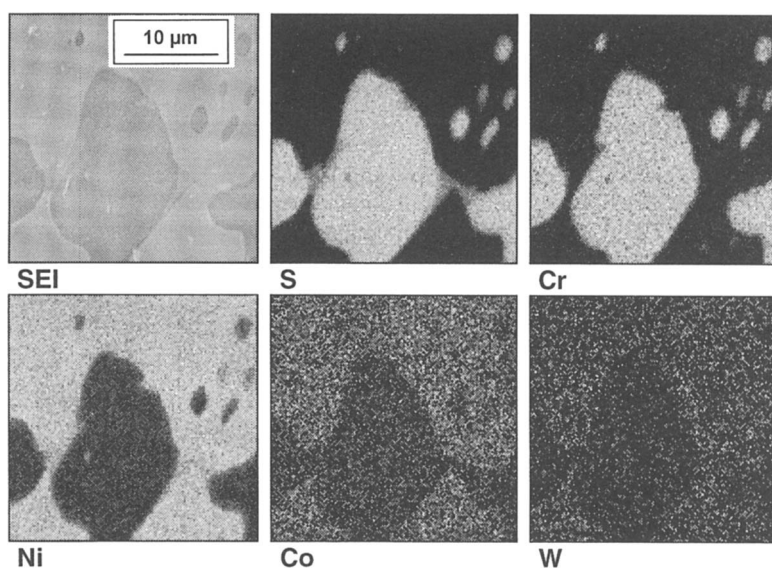
**Figure 7.** Scale morphology of Waspaloy formed during anodic polarization in molten sulphate under ambient air (a) and synthetic air + 250 vpm  $\text{SO}_2$  (b) at 900 °C. (A) mounting media, (B) porous oxide scale, (C) internal oxide, (D) internal sulphide, and (E) unaffected alloy.



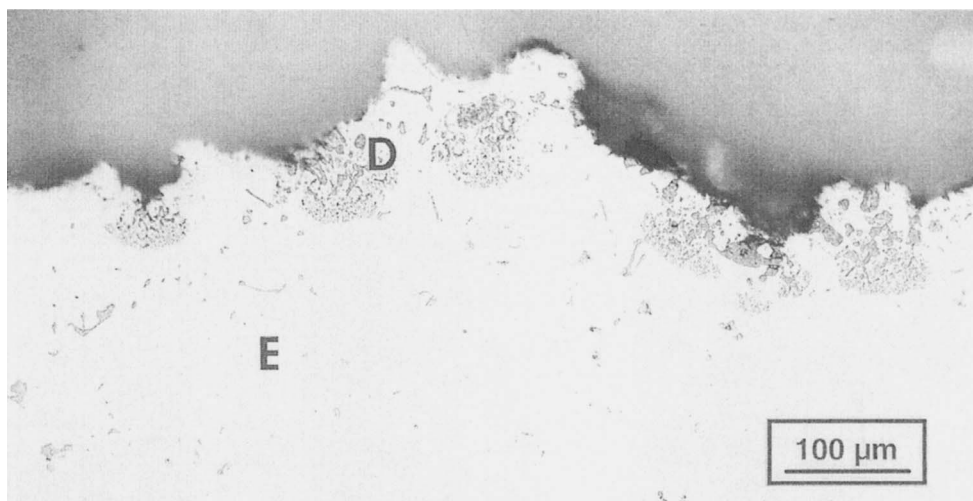
**Figure 8.** Secondary electron image (SEI) of the cross section of Waspaloy anodically polarized in molten sulphate under synthetic air + 250 vpm  $\text{SO}_2$  at 900 °C and the corresponding X-ray maps for sulphur, chromium, nickel, and cobalt.



**Figure 9.** Scale morphology of CMSX-2 formed during anodic polarization in molten sulphate under ambient air at 900 °C. (C) internal oxide, (D) internal sulphide, and (E) unaffected alloy.



**Figure 10.** Secondary electron image (SEI) of the cross section of CMSX-2 anodically polarized in molten sulphate under ambient air at 900 °C and the corresponding X-ray maps of sulphur, chromium, nickel, cobalt, and tungsten.



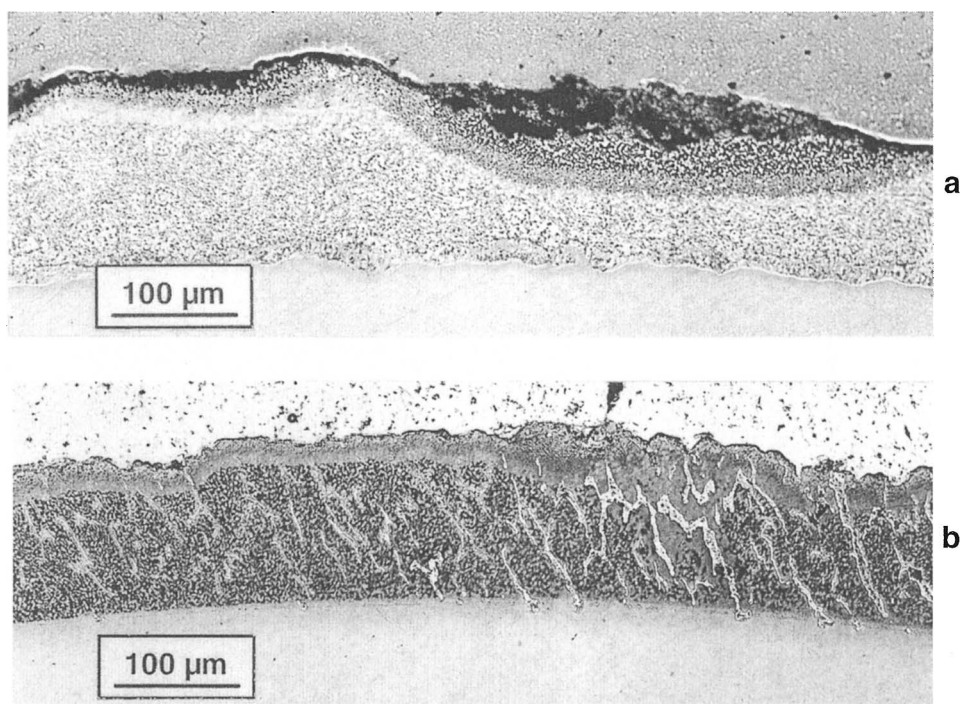
**Figure 11.** Scale morphology of IN100 formed during anodic polarization in molten sulphate under synthetic air + 250 vpm  $\text{SO}_2$  at 900 °C. (D) internal sulphide, (E) unaffected alloy.

Fig. 12 shows the microstructure of the LCO22 coating and the NiCoCrAlY coating after anodic polarization in molten sulphate. The metallographic examination revealed that the corrosive attack of both coatings is small in comparison with the uncoated alloys. The LCO22 coating was attacked by internal oxidation and sulphidation in some regions (photograph (a) in Fig. 12). EDX analysis identified chromium sulphide for the internal sulphide phase precipitated in this coating (Fig. 13). The EDX spot analysis yielded 42 wt.% (50 at.%) S, 32 wt.% (23 at.%) Cr, 12 wt.% (7.6 at.%) Ni, 5 wt.% Co, and 5.6 wt.% Al as composition for the sulphide particles. It shows that nickel is associated with the chromium sulphide. The atomic ratio of chromium + nickel to sulphur is 0.61 indicating that the sulphide phase consists of  $(\text{Ni,Cr})_2\text{S}_3$ . The adjacent chromium-depleted phase contains about 59 wt.% Ni, 31 wt.% Co, 4 wt.% Cr, and 1.6 wt.% Al which is rather different from the nominal composition of the LCO22 coating. The benefit of the NiCoCrAlY coating is the even corrosive degradation around the specimen. However, this coating is damaged in some areas by cracks and fissures which extend as network through the coating. In contrast to the Co-base coating alloy LCO22, the NiCoCrAlY coating was resistant to sulphidation. The EDX analysis identified about 56 wt.% Ni, 20 wt.% Co, 14 wt.% Cr, and 10 wt.% Al (Y was not detectable) for the NiCoCrAlY coating which approximately corresponds with the nominal coating composition.

## 5 Discussion

As the corrosion current density is equivalent to the corrosion rate it can be taken as a measure of hot corrosion resistance. Considering the values in Table 1, the ratio between  $i_{\text{corr}}$  of IN100 and  $i_{\text{corr}}$  of Waspaloy is approximately 23 for the melt under ambient air and 21 for the atmosphere containing 250 vpm  $\text{SO}_2$ . CMSX-2 was investigated only in the environment with ambient air and  $i_{\text{corr}}$  is approximately 28 times higher than  $i_{\text{corr}}$  of Waspaloy. From this comparison, Waspaloy is the most corrosion resistant among the Ni-base alloys electrochemically tested. The corrosion resistance of IN100 as well as CMSX-2 is rather poor whereby CMSX-2 is least resistant. The corrosion current density determining the ranking of corrosion resistance depends very sensitively on the chromium content in the alloys in such a way that a higher concentration yields a higher resistance. Waspaloy, the most corrosion-resistant alloy in this test, contains 19.5 wt.% chromium whereas the chromium

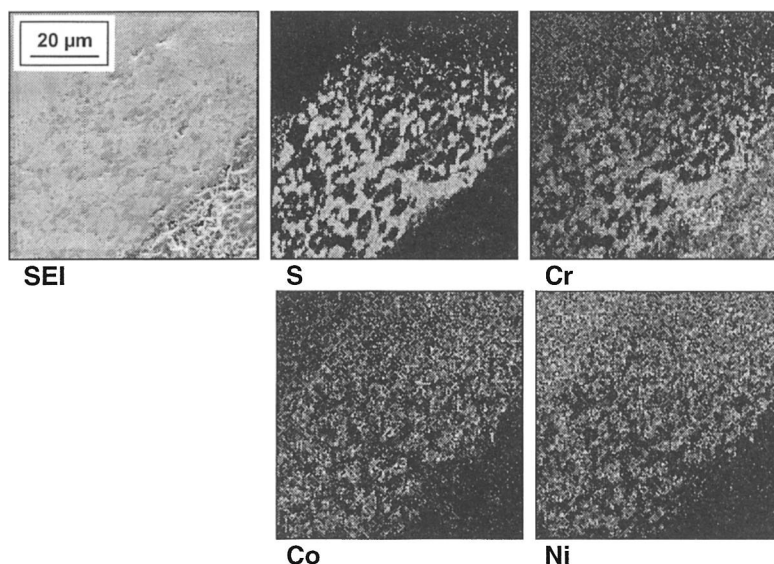
concentration of IN100 and CMSX-2 is 10.0 wt.% and 8.0 wt.%, respectively, in reverse order to their corrosion rate.



**Figure 12.** Microstructure of the LCO22 coating on CMSX-2 (a) and of the NiCoCrAlY coating on Waspaloy (b) formed during anodic polarization in molten sulphate under ambient air and synthetic air + 250 vpm SO<sub>2</sub>, respectively.

A useful correlation can be established between the electrochemical testing procedure and a high-velocity burner rig test at 900 °C under marine conditions [23] which included all Ni-base alloys and coatings investigated in the present work. The weight change and corrosive degradation data obtained from the burner rig test confirm the good hot corrosion resistance of Waspaloy, whereas IN100 and CMSX-2 behave worse. However, in contrast to the electrochemically determined ranking of hot corrosion resistance which suggests that IN100 is better than CMSX-2, the burner rig test shows a reverse behaviour of these two alloys, i.e. IN100 is less resistant than CMSX-2. This can be explained with the detrimental effect of molybdenum contained to 0.6 wt.% in CMSX-2 and 3.0 wt.% in IN100, which only appears after longer testing in the burner rig. The correlation between the two test procedures can be additionally established by metallographic examinations which show that basically the same kinds of corrosion reactions occur in both tests [23, 24]. The two predominant appearances of the cross-sectional morphology of hot corrosion attack are large quantities of unprotective oxide scale and the presence of oxides and sulphides in the underlying metal. The sulphides are always found to penetrate deeper into the alloys than the internal oxides.

EDX analysis identified the typical internal sulphides as Cr<sub>2</sub>S<sub>3</sub>. This corresponds with thermodynamic data for sulphides [25] which show that the formation of Cr<sub>2</sub>S<sub>3</sub> should preferably occur. In contrast to that, Cr<sub>3</sub>S<sub>4</sub> was found as composition of sulphide precipitates at sulphidation studies of an 85Ni-15Cr alloy in the presence of Na<sub>2</sub>SO<sub>4</sub>-ash deposits [26, 27]. However, actual thermodynamic data for Cr<sub>3</sub>S<sub>4</sub> which could confirm the formation of this type of sulphide have been not available.



**Figure 13.** Secondary electron image (SEI) of the cross section of a LCO22 coating on CMSX-2 anodically polarized in molten sulphate under ambient air at 900 °C and the corresponding X-ray maps of sulphur, chromium, cobalt, and nickel.

Small areas of  $\text{Ni}_3\text{S}_2$  precipitates were identified adjacent to the  $\text{Cr}_2\text{S}_3$  main phase in the internal sulphide zone of CMSX-2 (Fig. 10). Viswanathan and Spengler [27] developed a mechanism for explaining the formation of  $\text{Ni}_3\text{S}_2$  although the formation of chromium sulphide is favoured thermodynamically. According to that, sulphide can be formed as  $\text{Ni}_3\text{S}_2$  in chromium-depleted areas close to the chromium sulphide phases if the activity of sulphur is sufficiently high.

Regarding the coatings, the values of  $i_{\text{corr}}$  determined for NiCoCrAlY coatings on Waspaloy vary between 4.4 and 3.0  $\mu\text{A cm}^{-2}$  at the two different atmospheres. Thus, they are lower than the corrosion current densities for uncoated Waspaloy with values of 13.1 and 16.9  $\mu\text{A cm}^{-2}$ , respectively.  $i_{\text{corr}}$  for IN100 with a value of 304.3  $\mu\text{A cm}^{-2}$  is 145 times higher than the corresponding value of 2.1  $\mu\text{A cm}^{-2}$  for the NiCoCrAlY coating deposited on IN100.  $i_{\text{corr}}$  of the LCO22 coating on CMSX-2 is 20.5 and 30.2  $\mu\text{A cm}^{-2}$ , respectively and thus about ten times higher than  $i_{\text{corr}}$  of the the NiCoCrAlY coatings. However, these values are much lower than 370.3  $\mu\text{A cm}^{-2}$  measured as corrosion current density for the substrate material CMSX-2 in the sulphate melt under ambient air. In general, all coatings selected for this study reduced the corrosion rate considerably.

This behaviour of both coatings obtained from the electrochemical test again correlates with the burner rig test which showed that the NiCoCrAlY and LCO22 coating protect the substrates effectively and provide improved hot corrosion resistance [23, 24]. Moreover, metallographical examination and EDX analysis revealed that coatings were not attacked by sulphidation during this realistic test procedure.

## 6 Conclusions

The corrosion resistance of Ni-base alloys measured electrochemically depends essentially on the alloying element chromium. So, the high chromium-containing alloy Waspaloy (19.5 wt.% Cr) is more

corrosion resistant than the alloys IN100 and CMSX-2 containing 10.0 and 8.0 wt.% Cr, respectively. Both coatings, PWA270 (NiCoCrAlY) and LCO22 (CoNiCrAlY), improve the corrosion resistance of the substrate alloys mainly, because sulphidation attack does usually not occur.

A correlation can be established between values of the corrosion current density from the electrochemical procedure and the surface attack measured as weight loss and corrosive penetration from a high-velocity burner rig test. In general, the electrochemical test has the advantage that it is much faster and requires lower costs than the burner rig test. Hence, this procedure could become an appropriate preliminary screening test to select the most promising candidate alloys, which can subsequently be tested in the burner rig under service conditions.

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## The Use of Electrochemical Techniques to Study Steel Corrosion in Halide Molten Salt

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**Keywords:** Corrosion Rate, DC Polarization Techniques, Diffusion Process, Electrochemical Impedance, Electrochemical Potential Noise, Weight Loss

### ABSTRACT

The deterioration of metals and alloys in the atmosphere by the presence of molten salts is a specific type of corrosion known as *hot corrosion*. High temperature corrosion has been widely studied using weight loss coupons, and less attention has been paid to electrochemical techniques. Therefore, the interest to extend the use of these techniques to study and monitor molten salts metallic corrosion. As the aggressive media a NaCl and ZnCl<sub>2</sub> molten salt was chosen, since these salts melt below 300 °C, which is advantageous because this facilitates the design and setup of the corrosion system as well as the reference electrode construction. DC techniques including polarization curves and polarization resistance were applied to obtain corrosion rates and compared with weight loss measurements. Also, electrochemical impedance and potential noise were performed to obtain mechanistic information of carbon and stainless steel immersed in the molten salt. Electrochemical results obtained demonstrate the feasibility to apply electrochemical techniques to study and monitor steel corrosion in molten salts, and eventually extend it to on-line hot corrosion monitoring.

### INTRODUCTION

The deterioration of metals and alloys in the atmosphere by the presence of molten salts is a specific type of corrosion known as *hot corrosion*. High temperature corrosion has been widely studied using weight loss coupons, and less attention has been paid to electrochemical techniques. These techniques applied under aqueous conditions, provide valuable mechanistic information regarding metallic corrosion processes. Therefore, the interest to extend the use of electrochemical techniques to study and monitor molten salts metallic corrosion.

While tests for corrosion of metals and alloys in deep melts acting as the electrolyte, involve primarily immersion tests, electrochemical techniques have been used by a number of researchers to determine the corrosion resistance of metals and alloys [1-7], and also to investigate the properties of salt mixtures [8-11].

Paul and Daniel [12], applied electrochemical techniques such as polarization resistance and Tafel extrapolation to determine hot corrosion rates of steel in a mixture of zinc and sodium chloride salts under different temperatures. Results obtained indicate a direct relation between corrosion

potential, oxidation kinetics and temperature increase. These results compared favorably with weight loss measurements. Rahmel [13] applied polarization resistance and open circuit potential measurements, to study and demonstrate the film rupture, repassivation process of pure chrome immersed in a molten mixture of sulfate and potassium salts at 634 °C.

Farell et. al. [14], applied electrochemical noise and impedance spectroscopy to monitor the corrosion behavior of Nimonic 75 alloy in sodium sulfate and in a mixture of sodium sulfate and sodium chloride at 750 and 900 °C. They reported a diffusion controlled process and suggested an increase in corrosion rate when the temperature was raised and in the presence of sodium chloride. A correlation was found between the charge transfer resistance and the electrochemical noise signal.

Gao et. al. [10], using the same techniques studied hot corrosion of Ni-1%Co and an 800 series alloy immersed in a similar molten salt combination. Besides the depth of the molten salt in the crucible, a thin film over the metal surface was also considered. They suggested a decrease in the charge transfer resistance due to the film rupture in the protective oxides present. They also attributed the corrosion behavior and film oxide growth, to a charge transfer-diffusion process. Recent developments in plant corrosion monitoring processes using electrochemical techniques, enabled the assessment of the corrosion condition of metals in high temperature environments [15]. Rapp [16] provides a good account on the subject of chemistry and electrochemistry of the hot corrosion of metals, providing a list of electrochemical works and results on the subject.

The aim of the present work is to demonstrate the feasibility of using electrochemical techniques to study steel corrosion in molten halide salts at lower temperature (around 300 °C). This approach can have clear advantages over the traditional weight loss methods, providing information on the instantaneous rate and mechanism of corrosion attack.

## EXPERIMENTAL PROCEDURE

In order to apply electrochemical techniques to study molten salt corrosion, the following experimental elements and procedure was considered.

### High Temperature Equipment.

Experiments were carried out in a 21100 Thermolyne oven with an internal cylinder geometry of 6 cm diameter and 30 cm long. Two K thermocouple inserts, one at the top and the other at the center of the oven were located to measure the temperature of the molten salt and the inside temperature of the cylinder. An Eliwell 910/T controller was included to control the temperature within one degree in the range 0 to 999 °C. This controller acting upon a current relay to allow the electric current to pass through the electrical resistance of the tube oven. Preliminary trials were performed in order to establish the temperature setup parameters and operational conditions to maintain oscillations within the required temperature (around 5 °C).

### Molten Salts

Two types of salts were prepared, one for the reference electrode, and the other as the working corrosion electrolyte. The chemicals were  $\text{ZnCl}_2$  (98%),  $\text{AgCl}$ ,  $\text{NaCl}$  and  $\text{NaOH}$ . Care was taken



during mixture preparation and storage, since the hygroscopic nature of zinc chloride allows absorption of water. This was critical for the reference electrode when it was used continuously, since their properties are modified when the temperature decreases and the electrode absorbs water. As the working electrolyte, an 84 %  $\text{ZnCl}_2$  and 16 %  $\text{NaCl}$  mixture was prepared. Mixtures were melted in 15 ml ceramic lacquered crucibles.

### **Electrodes.**

To prepare the reference electrode, 100 mg  $\text{AgCl}$ , 277 mg  $\text{NaCl}$  and 623 mg  $\text{ZnCl}_2$  were mixed and melted at 300 °C for 15 minutes, in a crucible. After solidification, the reference salt mixture was crushed and ready for the reference electrode recipient containing a silver wire (99.99 %).

A Pyrex glass tube, 0.6 cm diameter and 7 cm long was used as the reference electrode container, reducing one side to a 0.2 cm orifice. This container was preferred over to the mulite tube recommended in the literature [5]. During preliminary trials at 300 °C temperature working conditions, no potential difference between two metal electrodes was recorded indicating that mulite did not present electrical conductivity at this working temperature condition.

The orifice was covered with two type of membranes: ceramic or glass fiber, dried up at room temperature and then heated at different temperatures (500, 600 and 700 °C) for 30 minutes. During this period, potential differences between two reference electrodes were recorded. The best overall conditions were established, considering a compromise between the electrical response stability and the physical conditions of the electrodes after the test. The ceramic reference electrode heated at 700 °C was preferred.

### **Electrochemical cell**

Carbon steel and 316 stainless steel coupons 4 by 4 mm were cut, to hold the coupons. Copper rods were threaded at one end and screwed to the specimens to provide electrical contact. Insulation was achieved by means of a small ceramic tube and a glass tube inserted on top of it. To avoid a galvanic couple between the copper rod and the metal sample, a ceramic cement was used to cover up the electrical contact between the two metals on the top of the sample. The 0.4 mm exposed area was grounded with silicon carbide paper (up to 1200 grit). The specimens were washed with distilled water, degreased with ethanol and dried under an air stream, before testing.

An electrochemical cell holder was designed for easy access and removal from the oven. The holder is a cylindrical stainless steel lid with 4 drilled holes for electrodes and thermocouple insertion and 2 other opposing holes with a steel wire insert to sustain the arrangement. A channeled section maintains the lacquered ceramic crucible cell in a fixed position providing thermal insulation.

### **Electrical Resistance**

To determine the electrical resistance of the molten salt mixtures, two platinum wires were immersed in the electrolyte within the oven. Every five minutes the temperature was raised 10 °C and the electrical resistance was registered before increasing the temperature again. The measurements were obtained with a 7060 Schlumberger digital voltmeter in the ohmmeter mode.

## Weight Loss

Weight loss measurements were obtained only for carbon steel coupons immersed in the working molten salt electrolyte. The oven was set at 300 °C and the crucible containing the salt mixture and the weighed coupons were placed in the oven. Afterwards the crucible was removed and cooled down at room temperature. The coupon was separated, cleaned with distilled water and the corrosion products were easily eliminated. The specimen was weighed again using a Sauter D-7470 digital balance. The procedure was repeated for different periods of immersion.

## Electrochemical Measurements

Electrochemical measurements, namely polarization curves, linear polarization resistance, electrochemical impedance and potential noise were performed in carbon and/or 316 stainless steels immersed in the working molten salt mixture at 300 °C. The three electrode setup included the working, the reference electrode and a platinum wire encapsulated in a glass tube acting as auxiliary electrode. For DC polarization techniques a 173 Princeton Applied Research PARC potentiostat and a 175 PARC Universal Programmer and a RE0074 PARC X-Y Plotter were used.

Polarization curves were obtained for both the carbon and 316 stainless steel samples. A 0.1 mV/s sweep rate was performed from –500 up to –200 mV. This was performed after the oven reached the working temperature under steady state conditions. Then the samples were introduced in the oven and left there for three hours. Linear polarization resistance was applied only to the carbon steel samples at different periods of immersion. A 10 mV anodic pulse was applied and the current response was registered, allowing the transient behavior to disappear. Once the current values reached an asymptotic steady state level, the current value was recorded and the polarization resistance calculated. For each test the working electrolyte was renewed.

Electrochemical impedance and potential noise were performed using a 1286 Schlumberger electrochemical interphase and a 1253 gain-phase analyser coupled to a PC computer acting as data logger-analyser. Impedance measurements at corrosion potential, were carried out imposing a 40 mV (rms) amplitude sinusoidal waveform in the frequency range 20 kHz to 0.01 Hz. The frequency range was logarithmically swept at about 7 frequency values per decade. For increased accuracy each frequency was measured for 10 cycles (integration time). Impedance simulation was performed using the Boukamp impedance analysis software.

Potential noise was obtained measuring the potential fluctuations between a reference and working electrodes, at a sampling rate of one reading per 0.7 seconds. After gathering the data as potential-time record of sufficient length (1024 samples), the DC trend was removed, fitting a straight line to the original data. The deviations of individual points to that line produce a new set of data that comprises negative and positive values around the base line. The spectral density vs. Frequency plots were obtained using an algorithm based on the Fast Fourier Transform (FFT). The resolved frequency bandwidth of interest lies between 1 to 700 mHz. The spectral density will be represented using the traditional unit, the decibel (dB), in the frequency domain stated. Since the voltage fluctuations are of interest, these were represented as noise amplitude rather than noise power, where noise amplitude is the square root of noise power and is given by:

$$\text{dB}=20 \log (\text{voltage ratio})$$

(Eq. 1)

an amplitude of 1 V was defined as 0 dB.

## RESULTS

### Electrical Resistance

Corrosion of metals in molten salts occurs at higher temperatures than fusion salt temperatures. Therefore, the need to evaluate the fusion point of the salt mixtures, that is the working salt ( $\text{ZnCl}_2 + \text{NaCl}$ ) and the reference salt ( $\text{ZnCl}_2 + \text{NaCl} + \text{AgCl}$ ) with reported fusion points: 275 °C and 260 °C, respectively [12]. Figure 1 presents the electrolyte's electrical resistance obtained for different temperatures. The electrical resistance of both electrolytes (salt mixtures) decreases as the temperature increases. For the working salt the resistance reaches the lowest and almost constant value above 240 °C, as reported in the literature [12]. For the reference salt it is indispensable to know at which temperature it behaves as an electrolyte to be used in the reference electrode. Similar behavior was observed as before, but this time the lowest and constant value was reached at about 270 °C. The observed electrical resistance behavior indicates that salt conductivity increases when temperature raises reaching a constant value related to the fused state.

 **LIVE GRAPH**  
Click here to view

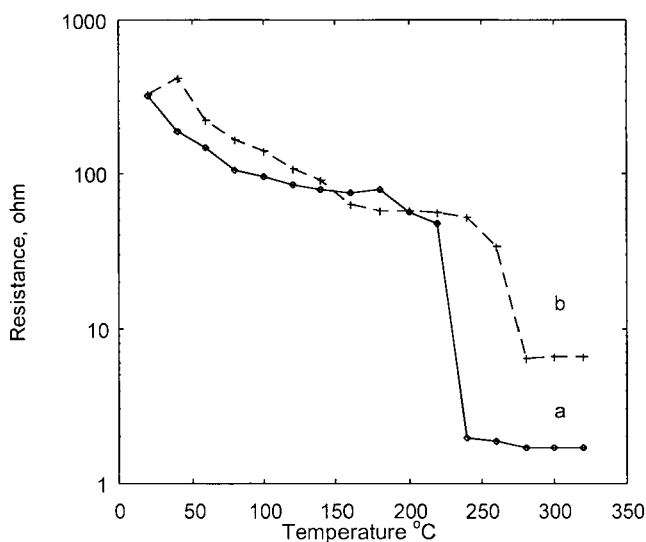


Fig.1. Electrical resistance vs. temperature for (a) working and (b) reference salt.

### Polarization Curves

Potentiodynamic polarization curve for carbon steel between -600 to 800 mV was obtained and presented in Figure 2. The corrosion potential is around -380 mV, the cathodic branch presents a

linear region while the anodic did not present a clearly defined linear region. A passive region is observed, starting around 150 mV, decreasing the current almost a decade. This result suggests the formation of protective species film over the metal surface. The possible corrosion reaction of steel immersed in the molten salt could be:

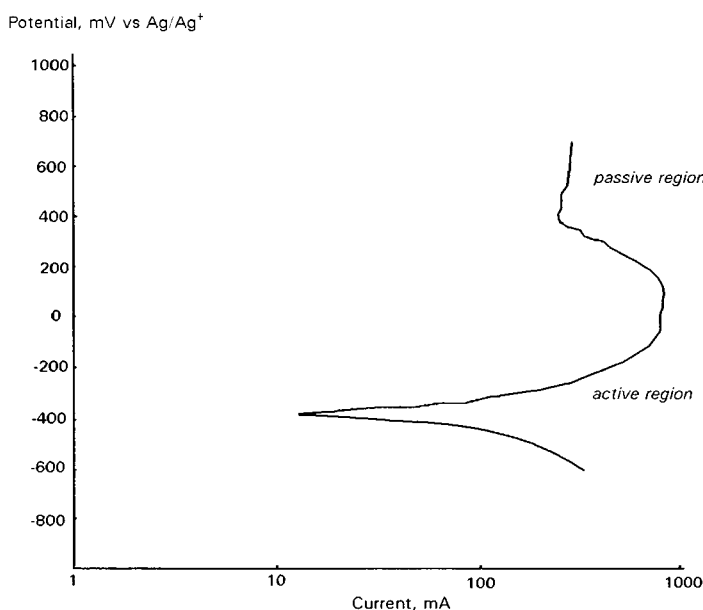
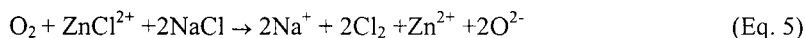


Fig. 2. Polarization curve for carbon steel in molten salt.

Under the experimental conditions, the possible corrosion mechanism could be associated to chloride ions present in the molten salt as follows [8, 13]:



If oxygen is taken into consideration during electrolyte heating up, its composition could be expressed according to the equation:



or



Furthermore,  $\text{Fe}^{2+}$  ionic species could form protective oxides according to:



explaining the passive region observed in the polarization curve, similar to the oxides or corrosion products produced in aqueous media [1, 12].

A comparison was made between the corrosion behavior as a function of time, for carbon steel and stainless steel immersed in the molten salt. As an example, Figure 3 presents polarization curves for both materials at 300 °C and the electrochemical parameters obtained for different temperatures are presented in Table 1. Tafel extrapolation was obtained from the cathodic branch since the anodic did not present a clearly defined linear region, maybe due to diffusion effects [7].

Table 1. Electrochemical parameters obtained for different temperatures

| Temperature °C | Carbon Steel           |                                         | Stainless Steel        |                                         |
|----------------|------------------------|-----------------------------------------|------------------------|-----------------------------------------|
|                | E <sub>corr</sub> (mV) | I <sub>corr</sub> (mA/cm <sup>2</sup> ) | E <sub>corr</sub> (mV) | I <sub>corr</sub> (mA/cm <sup>2</sup> ) |
| 280            | -365                   | 1.49                                    | -345                   | 0.125                                   |
| 300            | -356                   | 2.06                                    | -338                   | 0.283                                   |
| 320            | -340                   | 2.56                                    | -323                   | 0.683                                   |

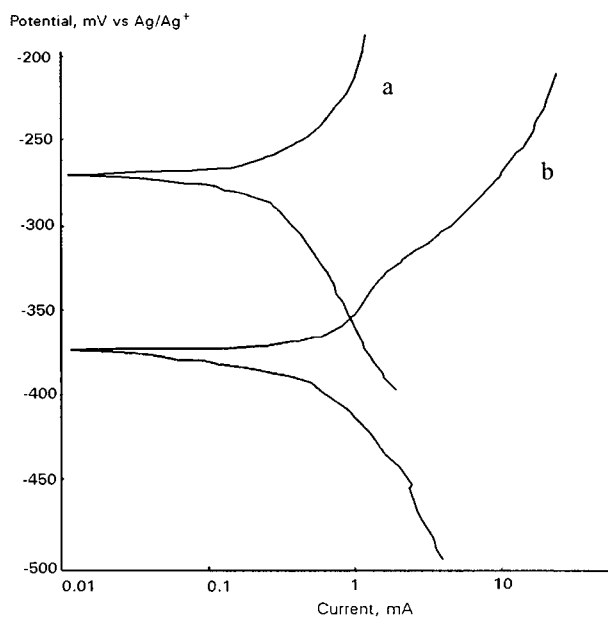


Fig. 3. Polarization curves for (a) stainless steel and (b) mild steel at 300 °C.

From the results presented it can be seen that as temperature is raised, the corrosion potential becomes more positive and the current density increases. For stainless steel, the corrosion potential is more positive and the current density is lower than carbon steel. This was expected since the corrosion potential is directly related to temperature, as well as molten salt conductivity, as presented before. These results compare favorably to previous results reported [12, 14].

### Weight Loss vs. Polarization Resistance

Table 2 presents the average corrosion rate obtained from weight loss coupons, and the corrosion current density obtained from polarization resistance measurements for carbon steel under different periods of immersion. The corrosion rate presents an increase from 10.81 after a few hours of immersion, up to almost 18 mm/year after eleven hours. Afterwards, a slight decrease was registered down to 15.35 at the end of the experiment. Current densities showed an increase from 1.61 up to 7.32 mA/cm<sup>2</sup> after seven hours of immersion, decreasing constantly down to 3.76 mA/cm<sup>2</sup> at the end of the experiment.

A similar trend was observed for current densities obtained from polarization resistance and weight loss values obtained, confirming the relationship between both parameters. These results showed that carbon steel corrosion in the molten salt is not constant, and that the electrolyte presents more aggressive conditions during the first few hours, decreasing for longer periods of immersion, probably due to the low volume of the electrochemical cell containing the molten salt. This increases the diffusion effects on the anodic polarization and a greater electrolyte IR drop could be introduced when dissolved ionic species concentration is lowered [7, 12].

Table 2. Comparison between corrosion rate and current density for carbon steel.

| Time of immersion<br>Hours | Corrosion rate<br>mm/year | Current density<br>mA/cm <sup>2</sup> |
|----------------------------|---------------------------|---------------------------------------|
| 2                          | -                         | 1.61                                  |
| 4                          | 10.81                     | 6.95                                  |
| 7                          | -                         | 7.32                                  |
| 11                         | 17.97                     | -                                     |
| 24                         | 16.40                     | 5.53                                  |
| 48                         | 15.35                     | 3.76                                  |

### Electrochemical Impedance

In order to study corrosion mechanisms and to obtain electrochemical parameters impedance measurements for both carbon and stainless steel at corrosion potential immersed in molten salts at 300 °C were performed. Figure 4 presents the Nyquist plots as well as simulated data obtained using an RC equivalent circuit with a Warburg impedance element. The electrochemical parameters obtained from the electrochemical circuit simulations are presented in table 3. A finite diffusion limit layer was considered for stainless steel.

For carbon steel, a small semicircle at higher frequencies was obtained, while at lower frequencies a 45° straight line was registered. For stainless steel, similar behavior was observed, although at lower frequencies the straight line starts to fold down towards the real axis, associated to the time constant dispersion [15]. Also the impedance values obtained for stainless steel are an order of magnitude higher, indicating the greater corrosion resistance when compared to carbon steel.

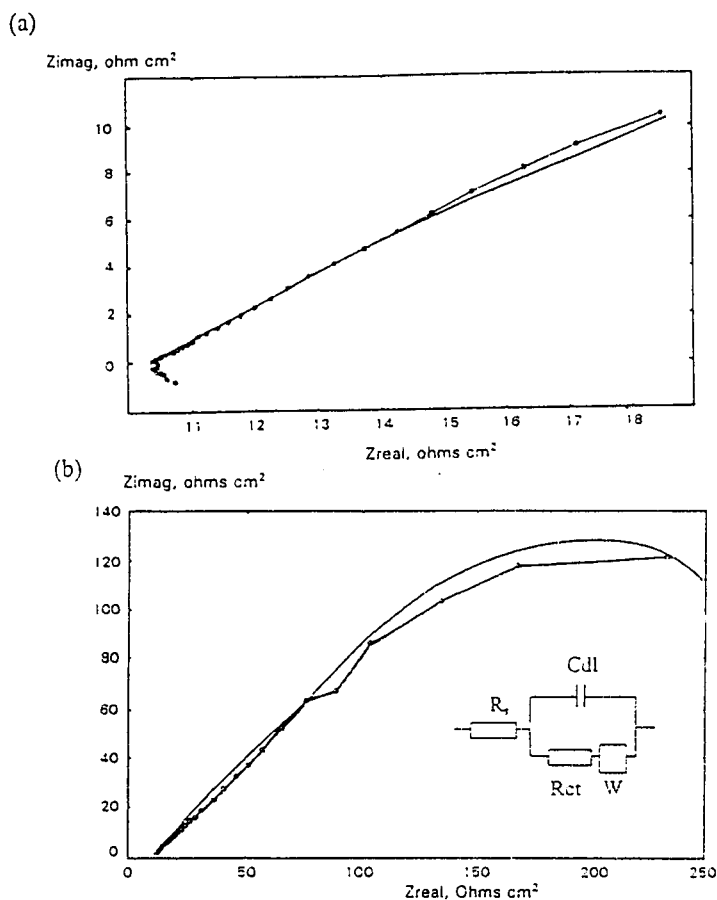


Fig. 4. Nyquist plots obtained for a) Carbon steel and, b) Stainless steel.

The impedance diagrams and the difference between charge transfer resistance and Warburg impedance parameters obtained suggest a diffusion process either within the electrolyte or within the film, controlling the corrosion kinetics in both cases. Restriction with the supply of oxygen to the metal surface is expected under deep immersion in the bulk salt electrolyte.

Table 3. Electrochemical parameters obtained from the electrochemical circuit simulations.

| Electrochemical Parameters        | Carbon steel | Stainless steel |
|-----------------------------------|--------------|-----------------|
| $R_s$ (ohms $\text{cm}^{-2}$ )    | 10.7         | 12              |
| $R_{ct}$ ohms $\text{cm}^{-2}$    | 1            | 9               |
| $C_{dl}$ Farads/ $\text{cm}^{-2}$ | 0.001        | 0.00015         |
| $W$ (ohms $\text{cm}^{-2}$ )      | 45           | 135             |
| $K$ ( $\text{s}^{1/2}$ )          | -            | 2.3             |

As with DC measurements, greater resistance values were registered for stainless steel, supporting again the better corrosion resistance behavior observed compared to carbon steel under the experimental conditions considered. Also the lack of linearity in the anodic branch of the polarization curves observed and reported before, could be explained in terms of the contribution of diffusion species involved in the corrosion process. Similar results were obtained and reported elsewhere [14, 15].

### Electrochemical Potential Noise

Electrochemical potential noise was performed between a working and reference electrodes for both carbon and stainless steel immersed in molten salts at 300 °C. Before metal measurements, a two reference electrodes potential noise measurements were carried out to establish the background noise level, that should be below the system noise [16, 17]. Thermal noise associated with electrode processes is known to occur but is thought not to interfere with corrosion monitoring because the amplitude of the signal is well below that obtained from the corrosion reactions [14].

The reference electrode potential noise-time record and spectra is presented in Figure 5. Low frequency oscillations accompanied by high frequency low amplitude are present with a  $3.29\text{E-}5$  V. standard deviation. This is reflected in the spectra where a  $-20$  dB/decade slope is observed, starting at  $-70$  dB/Hz<sup>1/2</sup> down to  $-120$  dB/Hz<sup>1/2</sup> at higher frequencies.

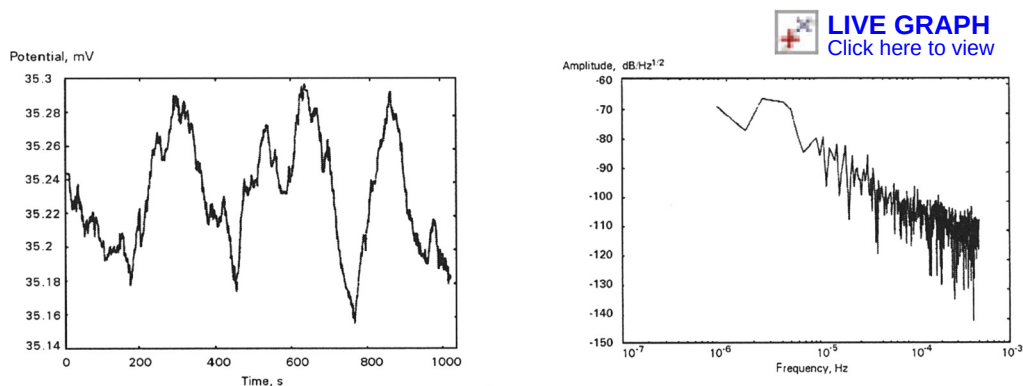


Fig. 5. Reference electrode potential noise-time record and spectra

A typical example of potential noise-time records and corresponding spectra for the systems studied, are presented in Figure 6. For carbon steel the potential noise-time record presents a basic low frequency oscillation with superimposed higher frequency and low amplitude oscillations. The standard deviation was  $8.29\text{E-}5$  V, just above the reference electrodes noise level. The spectra obtained presents a slope of  $-20$  dB/decade, starting at  $-50$  dB/Hz<sup>1/2</sup> at  $0.001$  Hz, down to about  $-100$  dB/Hz<sup>1/2</sup> at  $0.5$  Hz.

For stainless steel the potential noise-time record presents quasi-periodic low frequency oscillations with very little high frequency components, and a  $2.65\text{E-}4$  V standard deviation, reflected in the spectra. The  $1/f$  behavior starts at about  $-40$  dB/Hz<sup>1/2</sup> rolling down to  $-110$  dB/Hz<sup>1/2</sup> presenting a



steep slope of more than -25 dB/decade. This behavior is similar to the one observed for carbon steel and associated to the presence of passive or oxide protective conditions, characteristic of diffusion controlled systems under general corrosion conditions [18,19]. No significant transients associated to breakdown repair of the oxide were observed. Therefore, it was concluded that the process is not under a constant crack healing process, as observed for other metals under similar conditions [6, 13]. These results correlate with impedance measurements obtained and discussed above.

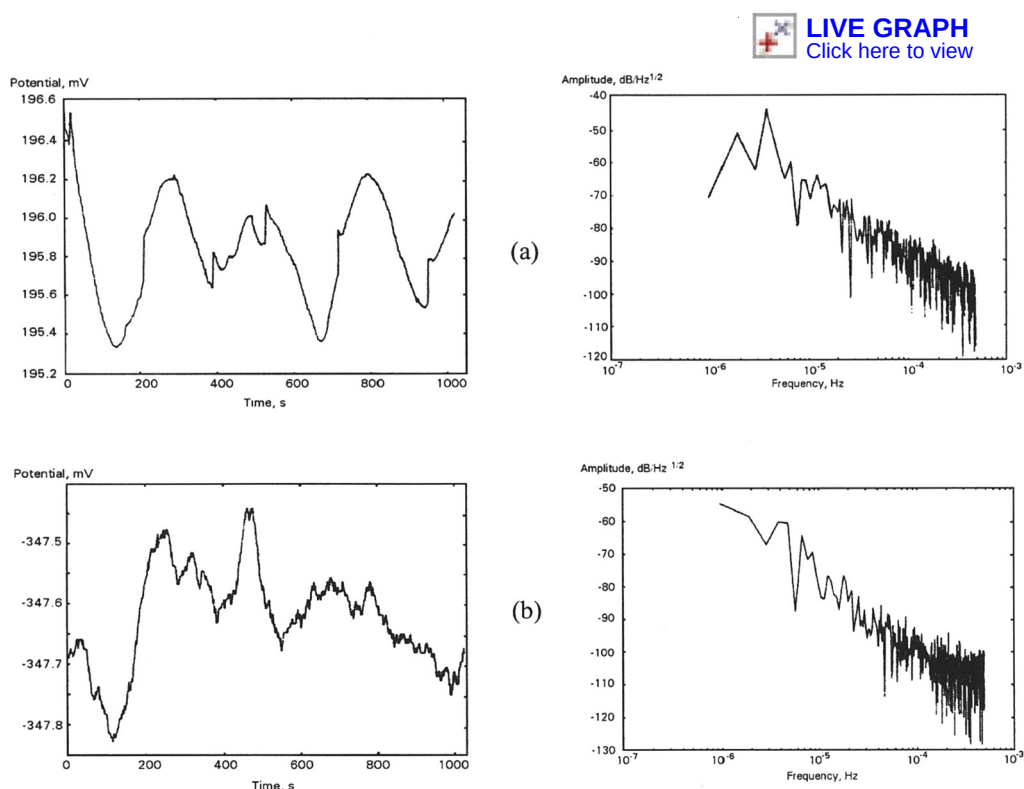


Fig. 6. Potential noise-time records and spectra for (a) stainless steel and (b) carbon steel.

For potential noise measurements, it was suggested that high standard deviations are indicative of passive or more protective oxide conditions and lower standard deviations of less protective or more active conditions [19-21]. Table 4 presents the potential noise standard deviations obtained for carbon and stainless steel in molten salt for different periods of immersion. More than an order of magnitude decrease was observed for carbon steel, increasing slightly at the end of immersion. For stainless steel, the standard deviation oscillated between 2.27 E-4 and 8.27 E-4 Volts. Nevertheless, the stainless steel standard deviations remained higher than the carbon steel, suggesting a more protective film as expected, and confirmed by the electrochemical results obtained and presented.

Table 4. Standard deviation for different times of immersion

| Time of immersion<br>Hours | Carbon steel<br>Standard deviation, V | Stainless steel<br>Standard deviation, V |
|----------------------------|---------------------------------------|------------------------------------------|
| 2                          | 2.39E-3                               | 2.27E-4                                  |
| 3                          | 8.29E-5                               | 2.65E-4                                  |
| 4                          | 7.42E-5                               | 8.47E-4                                  |
| 6                          | 1.49E-4                               | 8.06E-4                                  |
| 8                          | -                                     | 3.19E-4                                  |

## CONCLUSIONS

Electrochemical methods can be used to study molten salts steel corrosion processes. Mechanistic information as well as corrosion rates can thus be obtained. From the results presented, the following conclusions can be drawn:

- a) Corrosion of steel in molten salts is an electrochemical process
- b) The corrosion rate is a direct function of molten salt temperature
- c) Stainless steel is more corrosion resistant than carbon steel.
- d) Diffusion process controls the kinetics of corrosion of steel in molten salts.

It is understood that bulk salt measurements are not representative of plant conditions where thin films of deposits are present. Nevertheless, these results have shown the feasibility to apply electrochemical techniques to study and monitor steel corrosion in molten salts, and eventually extend it to on-line hot corrosion monitoring.

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## Copper Catalytic Self-Dissolution in NaCl-KCl Melt Containing Rare Refractory Metal Complexes

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**Keywords:** Coatings of Refractory Metals, Heterogeneous Catalytic Reaction, Intermetallic Compound, Rate of Corrosion, Stationary Potential

### Abstract

Copper interaction with NaCl-KCl melt has been studied. The catalytic mechanism of copper self-dissolution in NaCl-KCl melt containing refractory metal complexes has been established. The process of copper dissolution is referred to the type of heterogeneous catalytic reactions where by the catalyst, i.e. Cu(II) is in the liquid phase and the substance dissolved, i.e. copper substrate is in the solid phase. The mechanism of the autocatalytic process of copper self-dissolution was shown to reside in facilitation of copper depolarization with Cu (II) ions accepting electrons from the metal surface and passing them to the oxidizer, i.e. refractory metal complexes.

The catalytic mechanism of copper self-dissolution is not observed in fluoride and chloride-fluoride melts (with a great excess of fluorine anions as regards copper), since in these melts copper self-dissolution occurs in one stage  $\text{Cu} - 2e \rightarrow \text{Cu(II)}$ , which results in the absence of the reaction of intervalent interaction.

### Introduction

The study of copper interaction with molten salts is important, since copper is frequently used as substrate for plating with refractory metals [1,2].

At the same time, there are few works dedicated to corrosion behavior of copper in molten salts [3-7], and still fewer for the equimolar mixture of NaCl-KCl [7], whereas for the melts containing rare refractory metals they are altogether absent.

### Experimental

First copper interaction with NaCl-KCl melt was studied on samples from electrolytic special-purity copper preliminarily polished and degreased. For weighing the samples, thin platinum wire was used, the sample area was 2-5 cm<sup>2</sup> and the time of corrosion tests was 4 hours. Stationary copper potentials in the equimolar mixture of NaCl-KCl were determined relatively a silver reference electrode Ag/NaCl-KCl-AgCl (2 w/o) and calculated for the chlorine one. The electrochemical cell, method of recording the voltammetric curves and salt preparation are thoroughly described in works [8,9]. The rate of copper corrosion was determined by gravimetric method, by analysis of the salt fusion cake and from the values of stationary potentials.

### Results and discussion

Recording of the voltammetric curves showed that copper passes to the melt incorporated in the Cu(I) complexes [9], which agrees with the data of work [10]. If corrosion has an electrochemical

nature and is controlled by diffusion of its product from the copper surface to the deeper layers of the molten salt, then between the rate of the process expressed in the form of the corrosion current ( $i_{\text{corr.}}$ ) and the values of stationary potentials ( $E_{\text{st.}}$ ) the ratio is fulfilled (Eq. 1) [11]:

$$\lg i_{\text{corr.}} = \frac{5040}{T} n \left( E_{\text{st.}} - E_{\text{Cu(I)/Cu}}^* \right) + \lg \frac{nFD_{\text{Cu(I)}}d}{\delta M} \quad (1)$$

where  $E_{\text{Cu(I)/Cu}}^*$  is formal standard copper potential;  $D_{\text{Cu(I)}}$  is diffusion coefficient Cu (I);  $\delta$  is diffusion layer thickness ;  $d$  and  $M$  are density and molecular mass of the solvent salt ;  $T$  is temperature;  $n$  is valence of metal ions in the melt.

According to our findings, the temperature dependence  $E_{\text{st.}}$  in NaCl-KCl melt relatively the chlorine reference electrode is described by the following equation (Eq. 2):

$$E_{\text{st.}} = -1.867 + 1.33 \cdot 10^{-4} T \pm 0.001 \quad (2)$$

In work [7] the  $E_{\text{st.}}$  value is given, which at 1123K equals -1.7383V.

The Cu(I) diffusion coefficients were earlier [9] determined by the method of linear sweep voltammetry (LSV) and can be calculated in the temperature interval 973-1123K by the dependence (Eq. 3):

$$\lg D = -2.79 - \frac{1407}{T} \pm 0.03 \quad (3)$$

The  $E_{\text{Cu(I)/Cu}}^*$  values were also determined by the LSV data and described by equation (Eq. 4) [9]:

$$E_{\text{Cu(I)/Cu}}^* = -1.368 + 2.4 \cdot 10^{-4} T \pm 0.003 \quad (4)$$

The  $E_{\text{Cu(I)/Cu}}^*$  values found by us, and the data of other researchers obtained by the potentiometry method are given in Table 1.

Table 1

Formal standard potentials  $E_{\text{Cu(I)/Cu}}^*$  in equimolar mixture NaCl-KCl

| Work         | T, K   |         |        |        |
|--------------|--------|---------|--------|--------|
|              | 973    | 1023    | 1073   | 1123   |
| [12]         | -1.103 | -1.091  | -1.079 | -1.066 |
| [13]         | -      | -1.130* | -      | -      |
| [10]         | -0.002 | -0.991  | -0.990 | -0.989 |
| our data [9] | -1.134 | -1.122  | -1.110 | -1.098 |
| [14]         | -1.133 | -1.114  | -1.096 | -1.078 |

\* T = 1000 K

From Table 1 it can be seen that our values are in good agreement with the results of works [13] and [14] and are noticeably different from works [10, 12].

The diffusion layer thickness was calculated from the limiting current of stationary voltammetric curves using the equation (Eq. 5):

$$\frac{D}{\delta} = \frac{i_{\text{lim.}}}{nFC} \quad (5)$$

The copper corrosion losses determined by the sample weight loss, analysis of the fusion salt cake and the stationary potential values are given in Table 2.

Table 2

The rate of copper corrosion in NaCl-KCl melt

| T, K | Corrosion rate $\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}\cdot 10^4$ |                           |                     |             |                     |
|------|--------------------------------------------------------------------------|---------------------------|---------------------|-------------|---------------------|
|      | our data                                                                 |                           |                     | [7]         |                     |
|      | by the mass loss                                                         | by the salt cake analysis | from $E_{st}$ value | by the mass | from $E_{st}$ value |
| 973  | 0.6                                                                      | 0.4                       | 28.0                | -           | -                   |
| 1023 | 0.6                                                                      | 0.8                       | 40.9                | -           | -                   |
| 1073 | 1.1                                                                      | 1.0                       | 58.8                | -           | -                   |
| 1123 | 1.5                                                                      | 1.4                       | 80.2                | 1.83        | 1.35                |
| 1173 | -                                                                        | -                         | -                   | 2.31        | 1.9                 |

Note the good agreement between our data obtained from the weight loss, salt cake analysis and those cited in the literature [7] at the temperature of 1123K. At the same time, the results obtained by measuring the stationary potentials differ considerably from all the other data. However, analysis of the results of work [7] showed that there is a good agreement between our data and [7] taking into account the fact that there is monovalent copper present in the melt. In work [7], when calculating the corrosion current, the value of  $n=2$  was erroneously used.

Hence are the significant discrepancies between the data obtained from measuring the stationary potential and the results on the copper mass loss and the cake analysis. This is possible when the oxidizer is not the salt medium cations but the impurities. The rate of corrosion is controlled by their diffusion and the stationary potential is determined by the ratio (Eq. 6) [11]:

$$E_{st.} = E_{ox/red}^* + \frac{RT}{mF} \ln \left( \frac{nFD_{red}}{\delta i_{cor}} \cdot \frac{M}{d} [ox] - \frac{D_{red}}{D_{ox}} \right) \quad (6)$$

$[ox]$  is oxidizer concentration in the melt in molar fractions;

$E_{ox/red}^*$  is formal redox potential of the medium, V;

$D_{ox}$  and  $D_{red}$  are diffusion coefficients of the oxidized and its reduced form.

Thus, notwithstanding the careful preparation of the melt, it is the impurities that are in the first turn the copper oxidizers, but not the solvent salt cations. The impurity content in NaCl-KCl melt is quite insignificant, which is proved by the low rate of copper corrosion (Table 2) that in the temperature interval 973-1123K was  $0.6\text{--}1.5\cdot 10^{-4}\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ .

In the subsequent experiments, copper interaction with NaCl-KCl- $\text{K}_2\text{TaF}_7$  (5 w/o), NaCl-KCl- $\text{K}_2\text{HfF}_6$  (5 w/o) and NaCl-KCl- $\text{K}_2\text{NbF}_7$  (5 w/o) melts that are in equilibrium with the niobium metal was studied. On immersing the metal in the NaCl-KCl- $\text{K}_2\text{NbF}_7$  melt the metal-salt reaction occurs spontaneously with the formation of a reduced form of niobium (Eq.7) [15]:



The reaction equilibrium is practically shifted to the right [15]. As the reaction occurs against the background of NaCl-KCl melt, the  $\text{NbF}_5\text{Cl}^{2-}$  complex formation is preferential. It is not inconceivable that  $\text{NbF}_6^{2-}$  and  $\text{NbF}_6\text{Cl}^{3-}$  complexes may be formed.

The results of corrosion studies are presented in Table 3.

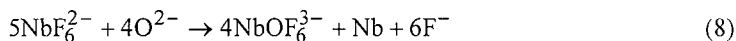
Table 3

The rate of copper corrosion in equimolar mixture of NaCl-KCl containing complex refractory metal fluorides ( $\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}\cdot 10^4$ )

| Melt                                         | T, K |      |      |
|----------------------------------------------|------|------|------|
|                                              | 973  | 1023 | 1073 |
| NaCl-KCl-K <sub>2</sub> TaF <sub>7</sub>     | 12.3 | 36.3 | 60.3 |
| NaCl-KCl-K <sub>2</sub> NbF <sub>7</sub> -Nb | 34.6 | 58.2 | 69.6 |
| NaCl-KCl-K <sub>2</sub> HfF <sub>6</sub>     | 6.6  | 11.4 | 15.2 |

The data in Table 3 on the sample mass loss do not reflect the copper corrosion losses in full measure as on the copper surface, in the case of melts containing K<sub>2</sub>TaF<sub>7</sub> and K<sub>2</sub>NbF<sub>7</sub>, tantalum or niobium films are formed (the data of XRD analysis). It should be noted that at 973K the tantalum and niobium films are weakly connected with the copper substrate and peel off when washed with water. XRD analysis of a copper sample after exposure in K<sub>2</sub>HfF<sub>6</sub> melt is hindered since on it only individual crystals of the new phase are observed. Outward appearance of the copper substrate prior and after exposure in NaCl-KCl-K<sub>2</sub>NbF<sub>7</sub>-Nb and KCl-NaCl-K<sub>2</sub>HfF<sub>6</sub> melts is presented in Fig. 1 and Fig. 2.

Let us discuss the possible mechanisms of refractory metal formation on the copper substrate. In the case of niobium, one of the ways of a metal coating formation may become the presence of oxide films on copper. During the oxide film dissolution in the molten salt, oxygen anions capable of initiating the occurrence of reaction of disproportionation (DPP) appear on the substrate surface (Eq.8) [16]:



However, the exposure of copper samples without the oxide film also results in the formation of

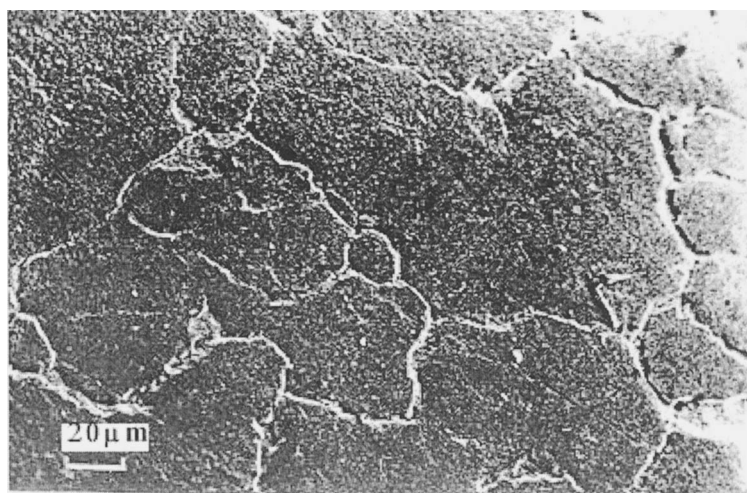


Figure. 1. Niobium coating on a copper substrate after exposure in NaCl-KCl-K<sub>2</sub>NbF<sub>7</sub> melt in equilibrium with niobium metal. T=1073K,  $\tau$ =4h.

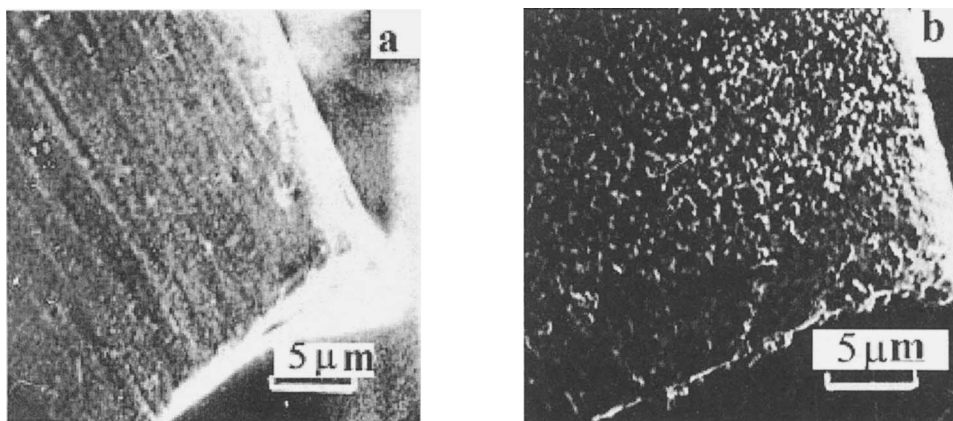
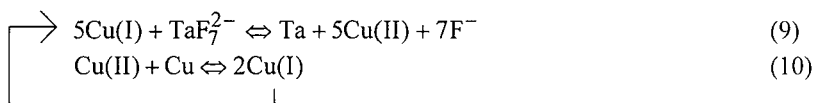


Figure. 2. Outer appearance of the copper substrate prior (a) and after (b) exposure in NaCl-KCl-K<sub>2</sub>HfF<sub>6</sub> melt. T=1073K,  $\tau = 4$ h.

niobium coatings on them. To remove the oxide film, electrolysis of the NaCl-KCl melt was first used with discharge of alkali metals at the copper cathode and only then a niobium compound was introduced into the melt.

Another cause of the niobium coating formation may be currentless transfer. The Nb(IV) complexes diffuse to the copper substrate and disproportionate on its surface with the formation of the metal. The driving force of the DPP reaction is the energy of alloy formation. But in the case of niobium with copper it is small, as well as for the tantalum-copper couple, since in these systems solid solutions with limited solubility in copper are formed. This mechanism does not suggest significant copper losses on corrosion, and if the mechanism of refractory metal transfer were like this, then no tantalum or hafnium would be formed on the substrate, since tantalum and hafnium within  $\text{TaF}_7^{2-}$  and  $\text{HfF}_6^{2-}$  complexes are in the highest oxidation states. Thus, for the tantalum and hafnium transfer onto the copper substrate excess electrons of the molten salt should participate in this process.

By recording of the voltammetric curves it was found that on the copper contact with melts containing  $\text{TaF}_7^{2-}$ ,  $\text{NbF}_6^{2-}$  and  $\text{HfF}_6^{2-}$  complexes they contained mostly monovalent copper. The Cu(I) particles in ionic melts represent nothing but Cu(II) ions with localized electrons [17]. These lower valence particles are donors of electrons. At the same time there are oxidizers in the melt, i.e. the refractory metal complexes, which, when meeting with monovalent copper at the copper substrate surface and accepting localized electrons, are reduced to the metal by oxidizing copper to the bivalent state, for instance by the reaction (Eq. 9,10):



The bivalent copper formed interacts with the copper substrate by forming monovalent copper which again passes its localized electrons to the oxidizer-depolarizer. The equilibrium constant of reaction (10) in the NaCl-KCl melt is described by equation (Eq. 11) [9]:

$$\log K^* = 0.562 + \frac{3927}{T} \pm 0.01 \quad (11)$$



Since the refractory metal complex concentration in the melt is unmeasureably higher than that of copper, the process will continue until the Cu(I) complexes arrive at the melt, i.e. until a coherent layer is formed. It should be noted that if there were thermodynamically stable complexes of lower oxidation states than  $\text{TaF}_7^{2-}$ ,  $\text{NbF}_6^{2-}$  and  $\text{HfF}_6^{2-}$  in the melt, the process of reduction would occur not to the metal but to the lower valence forms. It is the absence of intermediary valence complexes that leads to the metal formation on the copper substrate.

The scanning electron photography of the niobium coating on a copper substrate is shown in Fig. 3. It can be seen that the niobium coating has pores, which clearly define the grain boundaries of the copper substrate. The presence of pores is due to accumulation of impurities, interstitial impurities in the first place, in the vicinity of the grain boundaries that reduce the copper activity. Since in these sections of the copper substrate there is no copper ion supply, they remain uncoated.

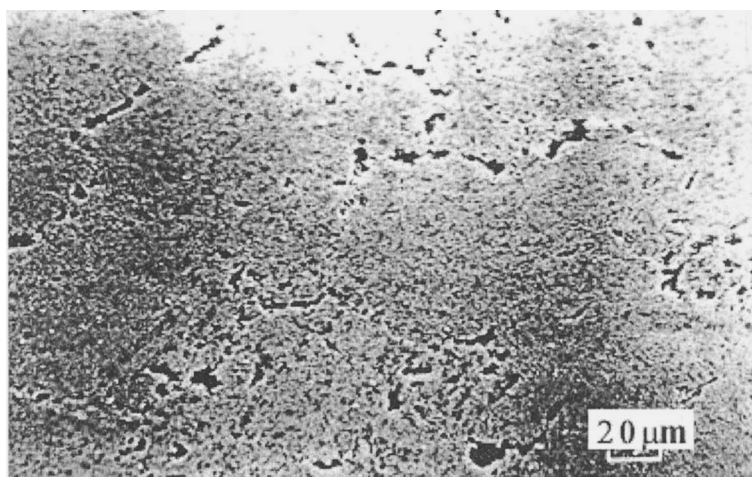


Figure. 3 Niobium coating on a copper substrate with pores along the grain boundaries. NaCl-KCl- $\text{K}_2\text{NbF}_7$ -Nb melt.  $T=1073$ ,  $\tau=4\text{h}$ .

As was noted above, the coatings are formed on the copper substrate when niobium and tantalum are used, whereas in the case of hafnium only individual crystals of the new phase are formed. Apparently, this is related to greater overlapping of the wave functions of copper complexes with niobium and tantalum in comparison with hafnium, which ensures the electron transfer from one particle to another. The probability of an electron passing from one ion to another may be connected in its turn with the difference of formal standard potentials  $E_{\text{Cu(I)}/\text{Cu}}^*$  and  $E_{\text{Nb(IV)}/\text{Nb}}^*$ ;  $E_{\text{Ta(V)}/\text{Ta}}^*$ ;  $E_{\text{Hf(IV)}/\text{Hf}}^*$ .

The difference between the formal standard potentials at 1023K of copper and niobium is, according to our data, 0.09V, and in the case of tantalum and hafnium it is 0.21V and 0.7V, respectively. The great difference between the  $E_{\text{Cu(I)}/\text{Cu}}^*$  and  $E_{\text{Hf(IV)}/\text{Hf}}^*$  values may seem to render impossible the hafnium transfer to the copper substrate. However, at these temperatures it is accompanied by the formation of intermetallic compounds [2]. It should be noted that in the case of formation of an intermetallide of the  $\text{HfCu}_4$  composition the depolarization is 0.63V.

The process of refractory metal transfer onto a copper substrate is characterized by a change in equilibrium potentials as well. When copper is immersed into the melt containing niobium and tantalum, the potentials are observed to shift to the region of negative values, and in 20 minutes the

electrode assumes values close to niobium and tantalum stationary potentials. The copper equilibrium potential after contact with a melt containing hafnium becomes a little more positive and attains the stationary value after approximately 3 hours. The shift in the equilibrium potentials to the positive side according to the Nernst equation (Eq. 12):

$$E_{st.} = E^0 + \frac{RT}{F} \ln \frac{[Cu(I)]}{[Cu]} \quad (12)$$

is possible either in the case of increasing the Cu(I) concentration or is due to the change in the copper substrate activity. Anodic polarization of a copper sample leading to an increase in the Cu(I) ions concentration in the melt should have resulted in the  $E_{st.}$  shift to the more positive side, however the copper currentless potential acquires a more negative value. As a consequence it may be suggested that the potential shift in time is caused by the change in the substrate activity.

The anodic chronopotentiogram of the copper electrode after attaining the stationary potential shows the presence on the discharge curve plateau of a potential delay at the value of 0.63V relatively the hafnium electrode. This points to the formation of the intermetallic compound  $HfCu_4$  and  $Cu_\alpha$  -solid solution of hafnium in copper [2].

The electrochemical reaction in the process of hafnium transfer can be written in the following form (Eq.13):



The electrochemical nature of the process of hafnium incorporation into copper during currentless transfer requires that alongside with reaction (13) a coupled reaction of copper ionization occur (Eq. 14):



Reaction (13), as well as the reaction of copper ionization from the intermetallic compound  $HfCu_4$  cannot be potential-determining, since otherwise, as the  $HfCu_4$  is accumulated, the potential, in keeping with the Nernst equation, must have shifted to the negative side. Therefore it should be inferred that the potential-determining reaction is reaction (14). Apparently, this can be accounted for by a greater value of the exchange current of reaction (14) in comparison with (13) and the reaction of ionization from the intermetallic compound. The shift of the copper potential to the positive side on hafnium introduction is caused by decrease in the copper activity due to the  $Cu_\alpha$  -solid solution formation [2].

It should be noted that at the very first moment of the copper substrate contact with the melts, when there are no copper ions in them yet, the copper self-dissolution will proceed by the usual electrochemical mechanism due to the coupled electrochemical reactions (14) and reduction of oxidizers, for instance, of the oxygen dissolved in the melt. And in the first turn, the impurities having a more positive electroreduction potential than the potential of copper deposition will act as oxidizers, however insignificant their concentrations are in the melt. When Cu(I) ions appear in the melt, the reactions (9) and (10) become possible and the electrochemical mechanism of self-dissolution is displaced by the catalytic mechanism. The process of copper dissolution is referred to the type of heterogeneous catalytic reactions whereby the catalyst, i.e. Cu(II), is in the liquid phase and the substance dissolved, i.e. the copper substrate, is in the solid phase. The mechanism of the copper autocatalytic self-dissolution resides in facilitation of the copper depolarization with copper ions Cu(II) accepting electrons from the metal surface and passing them to the oxidizer, i.e. refractory metal complexes. While the copper ions are accumulated in the melt, the contribution of the catalytic mechanism will be increasing until it becomes practically the only one.

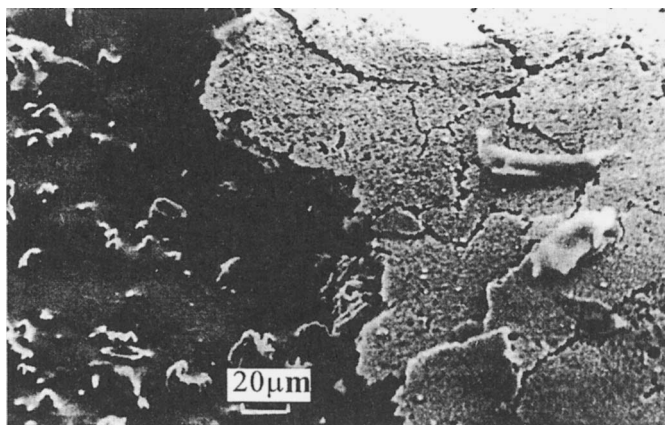


Figure. 4. Outer appearance of «filament» structures under niobium coatings.  $T=1073\text{K}$ ,  $\tau = 4\text{h}$ .

The  $\text{Cu(I)}$  ions interact with the oxidizer not only on the substrate surface but they leave the electrode surface, diffuse to the melt bulk and reduce the refractory element complexes to the metal.

The metal crystals, by coupling with each other, form filament-shaped structures stretching from the substrate to the melt bulk (Fig. 4). The  $\text{Cu(I)}$  ions diffusion from the substrate between the crystal filaments to the melt bulk and their meeting with the oxidizer leads to overlapping between the filament structures. The «roof» thus formed rests on the substrate and is connected with it only through the filament crystals whereas under the roof there is a great amount of cavities (Fig. 4).

The processes considered concerned the currentless transfer of refractory metals onto the copper substrate, however, all of them precede the process of electroplating, since the article to remove the temperature gradients is for some time exposed to the molten salt. The refractory metal formation on some parts of the substrate results in that during the electrolysis the crystallization will mostly occur on these «islands» and the tangential growth causes their joining into a coherent layer. Hence are the cavities remaining under electrolytic layer.

On the other hand, the formation of  $\text{Cu(I)}$  ions leads to the appearance of a near-electrode layer with electronic conductivity, which results in shifting of the electrode's electrochemically active surface into the melt bulk; and the electroreduction may occur in the melt bulk, but not on the substrate surface. This causes deterioration of the electrolytic layer adhesion to the substrate.

From the above part of the work it can be concluded that during the refractory metal electrodeposition onto the copper substrate from  $\text{NaCl-KCl}$  melts containing refractory metal complexes one should avoid currentless exposure of the copper substrate in the melt, and its immersion into the melt should be carried out under cathodic polarization.

In chloride-fluoride melts, at least at the molar ratio  $\text{F/Cu} \geq 6$ , only  $\text{Cu(II)}$  complexes are present [9]. Therefore in melts like these not a two-stage process of copper dissolution:  $\text{Cu-e} \rightarrow \text{Cu(I)-e} \rightarrow \text{Cu(II)}$ , but a one stage process:  $\text{Cu-2e} \rightarrow \text{Cu(II)}$  is observed. The absence of two stages during the dissolution causes the absence of reaction (10) of intervalent interaction (IVI). As the catalytic process of copper dissolution is due to the occurrence of reaction (10), it can be suggested that in fluoride and chloride-fluoride melts the rate of corrosion, due to the absence of IVI reaction, will be lower in comparison with  $\text{NaCl-KCl}$  melt.

The copper corrosion data in  $\text{NaF-KF}$  eutectic containing refractory metal fluoride complexes are given in Table 4.

Table 4

The rate of copper corrosion in a eutectic mixture of NaF-KF containing complex refractory metal fluorides ( $\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}\cdot 10^4$ ). Time of exposure in the melt is 4 hours

| Melt                                       | T, K  |       |       |
|--------------------------------------------|-------|-------|-------|
|                                            | 1023  | 1073  | 1123  |
| NaF-KF                                     | 0.00  | -0.52 | -0.55 |
| NaF-KF- $\text{K}_2\text{TaF}_7$ (5w/o)    | 0.00  | 0.00  | -0.06 |
| NaF-KF- $\text{K}_2\text{NbF}_7$ (5w/o)-Nb | +0.02 | +0.02 | +0.02 |
| NaF-KF- $\text{K}_2\text{HfF}_6$ (5w/o)    | 0.00  | 0.00  | -0.06 |

As can be seen from Table 4, copper corrosion is practically unobservable in fluoride melts, whereas in the case of a molten salt containing niobium an insignificant additional weight is observed due to the currentless transfer of niobium onto the copper substrate.

It can be inferred from the results obtained that in fluoride and chloride-fluoride melts (at a great excess of fluoride anions relative to copper) the catalytic mechanism of copper dissolution is not observed due to the absence of IVI reaction. It was experimentally established that using purely fluoride and chloride-fluoride melts during the niobium electrodeposition onto a copper substrate permits to substantially improve the quality of coatings.

## Conclusion

The catalytic mechanism of copper self-dissolution in an equimolar mixture of sodium and potassium chlorides containing refractory metal compounds has been established. It consists in facilitating the copper depolarization with Cu(II) ions accepting electrons from the metal surface and passing them to the oxidizer, i.e. refractory metal complexes. The effect of the phenomenon of the copper catalytic dissolution on the quality of the electrolytic coatings from refractory metals is discussed. It is shown that the copper catalytic dissolution is not observed in chloride-fluoride ( $\text{F}/\text{Cu} \geq 6$ ) and fluoride melts.

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## Solubility of Silica and Alumina in Sodium Sulphate-Sodium Vanadate-Vanadium Pentoxide Melts

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### Abstract

The solubilities of silica and alumina in  $\text{Na}_2\text{SO}_4/\text{NaVO}_3/\text{V}_2\text{O}_5$  melts at temperatures between 700° and 1100°C, are determined. The solubility of silica in  $\text{V}_2\text{O}_5$  ranges from 1.8% at 700°C to 2.9% at 1100°C and the addition of  $\text{Na}_2\text{SO}_4$  to this melt causes solubility to decrease until 20 mole %  $\text{Na}_2\text{SO}_4$ , from there it increases to a maximum at 60 mole %  $\text{Na}_2\text{SO}_4$  and decreases to almost zero in the pure salt. The solubility of alumina in  $\text{V}_2\text{O}_5$  ranges from 1.4% at 700°C to 3.3% at 1100°C. The addition of  $\text{Na}_2\text{SO}_4$  to this melt causes the solubility to rise to a slight maximum at 15 mole %  $\text{Na}_2\text{SO}_4$  and from there decreases steadily to zero in the pure salt.

### INTRODUCTION

Due mainly to logistics and economics the large naval vessels burn residual fuel oil in their steam raising installations. This heavy fuel is a non-distillate oil which remains after the higher fractions have been removed from crude oil. Residual oil contains metals as organic derivatives of high boiling point i.e. low vapour pressure. When the oil is burned, these derivatives breakdown. Sulphur containing compounds such as mercaptans and sulphides form  $\text{SO}_2$ . Some of this  $\text{SO}_2$  then combines with the metal breakdown products to form sulphates, which collect on all fireside boiler surfaces. Vanadium is a major metallic impurity in the fuel oil and this forms with the sulphates, mainly sodium, low melting point mixtures which flow down boiler brickwork when at operating temperatures causing considerable corrosion. In order to identify the elements of fuel oil ash which are particularly damaging to marine boiler refractories and thereby clarify the mechanism of corrosion, it was decided to treat this dissolution process as an example of mass transfer under streamline conditions. The apparatus permitted a melt, in transit through a refractory tube, to dissolve the tube walls. This method necessarily involved the measurement of concentration gradients near the refractory wall which provides the driving force for the dissolution process. Towards this end, the kinetics of the reaction between sodium sulphate and vanadium pentoxide to produce vanadates, which aggravate corrosion, has been studied [1], and alumina and silica have been tested for corrosion rates in sodium sulphate/vanadium pentoxide melts [2]. The main conclusions of these works are: -

1. At temperatures above about 480°C, vanadium pentoxide will decompose sodium sulphate to release sulphur trioxide and form sodium vanadates. The reaction to form sodium vanadyl vanadate I is faster than the reaction to form sodium vanadyl vanadate II which is in turn faster than that to form sodium metavanadate. All reactions are considered to be complete after 300 hours at 1100°C. Apparent activation energies for the formation of these three compounds are 21.0, 27.5 and 31.1 kcal/mole, respectively, with probable errors of about  $\pm 12\%$  [1].
2. The corrosion rates of silica and alumina in  $\text{Na}_2\text{SO}_4/\text{V}_2\text{O}_5$  melts are approximately equal for a given melt at a given temperature between 700°C and 1100°C. The corrosivity of pure  $\text{V}_2\text{O}_5$  is increased by the addition of  $\text{Na}_2\text{SO}_4$ . Similarly,  $\text{V}_2\text{O}_5$  increases the corrosivity of

$\text{Na}_2\text{SO}_4$ . Melts containing between 30 and 70 mole %  $\text{Na}_2\text{SO}_4$  have roughly equivalent corrosion rates for both refractories. It seems that alumina will resist corrosion by such melts above  $1100^\circ\text{C}$  better than silica [2].

It is well known [3, 4] that one of the main reasons why refractories are attacked by slags is that they are soluble in them and by dissolution the system tends towards a lower energy. Although it is not always the case, increase in temperature usually results in an increase in the saturation solubility of a refractory in a melt. This increases the driving force for the reaction. Being aware of the importance of the "solubility" parameter in systems where a slag is in contact with a refractory, our work progressed attempting to determine the solubilities of silica and alumina in  $\text{Na}_2\text{SO}_4/\text{NaVO}_3/\text{V}_2\text{O}_5$  melts, at temperatures between  $700^\circ\text{C}$  and  $1100^\circ\text{C}$ . This study is reported in this paper.

### EXPERIMENTAL TECHNIQUE

The technique involved is essentially that of heating a sample of refractory in a melt to constant loss of weight. To simplify the process and to facilitate evaluation of results, non-porous, pure refractory oxides were used, i.e. sapphire and silica glass. The melts were contained in platinum crucibles heated in small electrical resistance furnaces. Rods of alumina and silica were held in the chucks of stirring motors (Fig. 1) which were mounted on a carriage capable of vertical movement on a threaded rod.

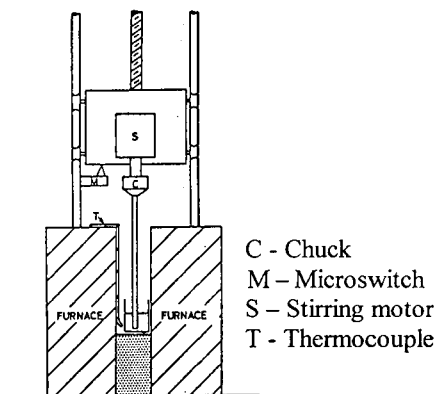
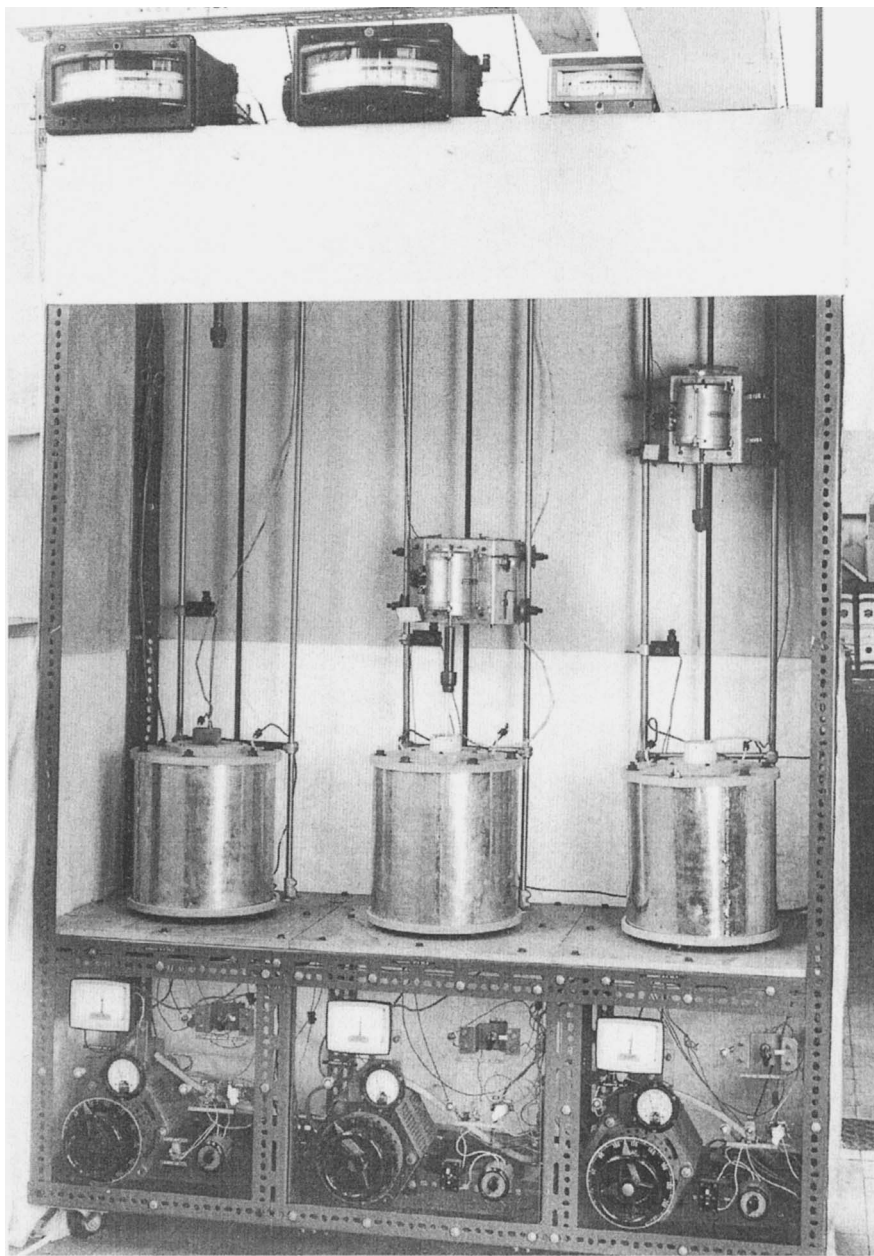


Fig. 1 Apparatus for the determination of the solubility of refractories.

Operation of an electric motor (the "lifting" motor) at the upper end of the threaded rod caused the rod to ascend out of or descend into the melt. Microswitches determined the position at which the motor stopped, which effect ensured that rods were immersed to approximately the same depth in the melt each time. A time switch was capable of starting the lifting motor (and switching off the starting motor) after any period up to four hours. This also enable a rod to be put into the melt at the end of the working day thereby increasing the number of observations per day and shortening the duration of the experiment. The lifting motor was capable of three speeds, the slowest of which enable alumina rods to enter the furnace without fear of thermal shock. The stirring motors only rotated at one speed – 960 r.p.m. These were not always used as some melts dissolved the rods rapidly under static conditions. Three such units were built into one compact assembly shown in plate 1 which included an extractor hood for vapours such as  $\text{SO}_3$  and  $\text{V}_2\text{O}_5$ .

### EXPERIMENTAL PROCEDURE

A platinum crucible was weighed empty and then plus mixture. This was then placed in the furnace and brought to the required temperature. The length of time before the rod first entered this melt depended upon the composition of the mixture and the conditions required. If mixtures of sodium metavanadate and sodium sulphate were used, the experiment could start immediately. Vanadium pentoxide and sodium sulphate mixtures were allowed 4 days at  $1100^\circ\text{C}$  which ensured



**Plate 1      The solubility testing apparatus**



that at least 90% of the available  $\text{SO}_3$  was expelled. Some  $\text{V}_2\text{O}_5/\text{Na}_2\text{SO}_4$  mixtures were not allowed this time to react and the experiment was commenced immediately the components became molten. This was to enable a comparison to be drawn between a reacted and a "non-reacted" melt.

Throughout the solubility experiments B.D.H. 98.5%  $\text{V}_2\text{O}_5$  and "Analar"  $\text{Na}_2\text{SO}_4$  were used. The initial period that the first rod spent in a melt depended on temperature and corrosivity of the melt. For silica the time varied between 1.5 min. and 2 hr. and for alumina 1 day and 4 days. The actual procedure for alumina and silica varied and so they will be described separately.

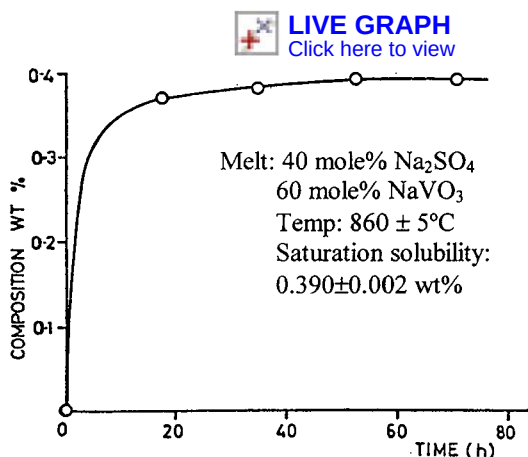


Fig. 2 Typical results for the dissolution of alumina.

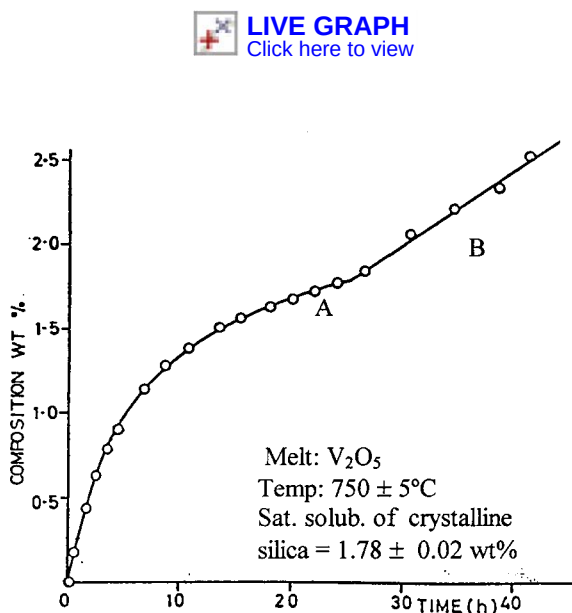


Fig. 3 Typical results for the dissolution of silica.

### Alumina

As it is well known [3-6], alumina will reach a constant weight loss in a  $\text{V}_2\text{O}_5/\text{Na}_2\text{SO}_4$  melt. Therefore, the sapphire rod was lowered into the melt and left stirring for about one day. It was then lifted out, weighed, cleaned and reweighed. The amount of slag lost during the cleaning process was deducted from the amount known to be in the crucible. The rod was then replaced in the melt and this procedure continued until a constant weight loss was achieved. A typical result is shown in Fig. 2. For the system shown the melt was saturated with alumina after about 60 hr. The temperature was then increased by approximately  $100^\circ\text{C}$  and a new constant weight loss measured. To reclean the rods for weighing, cold or warm running water was found to be satisfactory.

### Silica

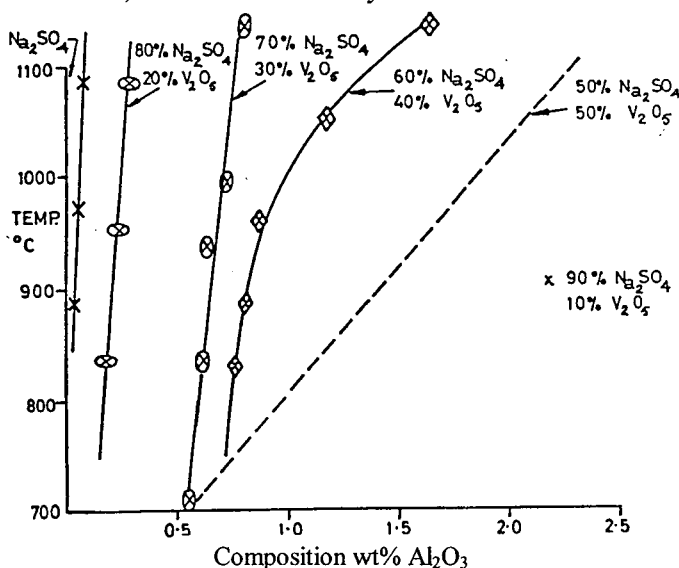
It is also well known [3-7] that at  $721^\circ\text{C}$ ,  $\text{V}_2\text{O}_5$  dissolved 48 wt.% silica after about four months. This experiment was repeated and the weight loss of the rod plotted against time as the experiment progressed. Two aspects of this graph were noticed. Firstly that although the points followed an approximate straight line, the locus of this line did not pass through the origin. Secondly, the early readings for this system deviated from the straight line more than the later points. Therefore the experiment was repeated taking smaller and smaller intervals of time until the form of the graph shown in Fig. 3 evolved. The section of the graph marked OA represents the simple dissolution of silica glass in the melt. Such a mechanism should follow an equation of the type:-

$$\frac{dc}{dt} \propto (C_{eq} - C_t) \quad (1)$$

Plots of  $dc/dt$  versus  $C_t$  produced approximate straight lines indicating that the assumed equation was being obeyed and enabling  $C_{eq}$  to be evaluated. However, silica glass is not the stable phase at the temperatures investigated and the line AB represents the steady transfer of silica glass in the rod to cristobalite, which was usually deposited on the crucible walls at the slag line. Thus the silica glass in the rod was using the melt as a method of reaching a lower energy form. Therefore at A the melt was saturated with cristobalite and the values of  $C_{eq}$  calculated by equation (1) refer to the apparent saturation solubilities of silica glass. Upon removal of a rod from a melt after reaching point A, small crystals of cristobalite could be seen in the slag on the rod surface. These were presumably picked up from the surface of the melt where they would have been floating.

## RESULTS FOR ALUMINA

The results are seen in Figs. 4 to 6. They show that as the percentage of sodium sulphate increases beyond 50 mole %, the saturation solubility of alumina decreases.

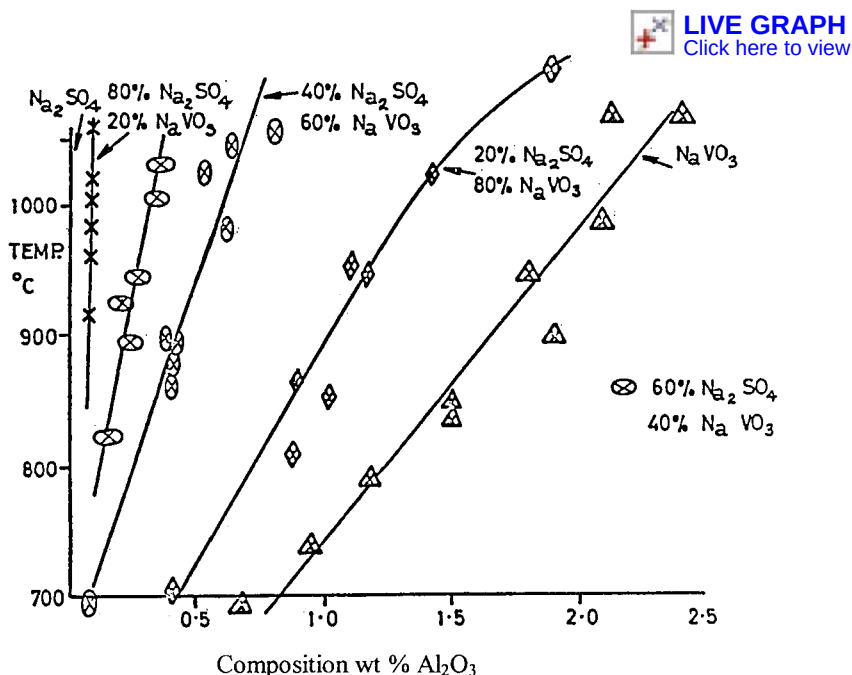
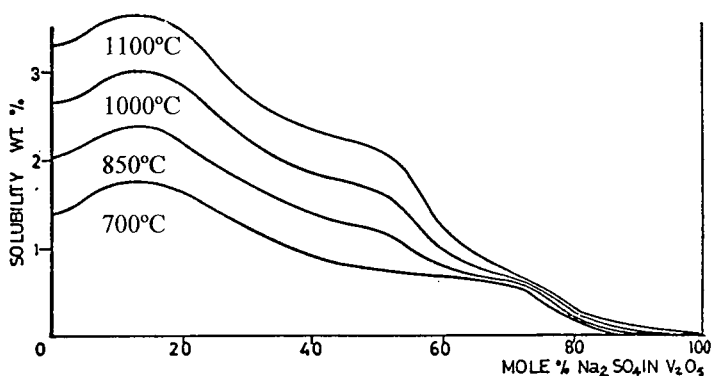


**LIVE GRAPH**  
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Fig. 4 Solubility of Al<sub>2</sub>O<sub>3</sub> in Na<sub>2</sub>SO<sub>4</sub>/V<sub>2</sub>O<sub>5</sub> melts.

### Solubility of Al<sub>2</sub>O<sub>3</sub> in Na<sub>2</sub>SO<sub>4</sub>/V<sub>2</sub>O<sub>5</sub> melts

In these melts containing more than 50 mole% Na<sub>2</sub>SO<sub>4</sub>, the solubility of alumina is quite low, being below 2.5 wt% at 1100°C (Fig. 4). All these mixtures were allowed four days at 1100°C to expel at least 90% of the available SO<sub>3</sub> before adding any alumina. The 50 mole % Na<sub>2</sub>SO<sub>4</sub> mixture is very dependent upon temperature. The 60 mole % mixture is quite dependent upon temperature above 1000°C, but mixtures containing 70 or more mole % Na<sub>2</sub>SO<sub>4</sub> are relatively independent of this parameter, e.g. raising the temperature of the 70 mole % Na<sub>2</sub>SO<sub>4</sub> mixture from 700 to 1100°C only causes the solubility to increase from 0.55 to 0.76 wt %. The addition of sodium sulphate caused the solubility to drop rapidly and the solubility of alumina in Na<sub>2</sub>SO<sub>4</sub> is too small to be shown on the graph. Values obtained were: less than 0.0022 wt % at ≈920°C and less than

Fig. 5 Solubility of  $\text{Al}_2\text{O}_3$  in  $\text{Na}_2\text{SO}_4/\text{NaVO}_3$  melts
 [Click here to view](#)
Fig. 6 Effect of temperature on the solubility of  $\text{Al}_2\text{O}_3$  in  $\text{Na}_2\text{SO}_4/\text{V}_2\text{O}_5$  melts.

0.0027 wt % at  $\approx 980^\circ\text{C}$ . The reason for quoting these values in the “less than” form is that after 30 hr. the rods began to gain weight due to ionic penetration by sodium sulphate in some form. This fact was proved by subsequent analysis. The values quoted are the maximum thought possible to have been dissolved in 60 hr. ignoring weight gains. Now the single crystal sapphire rods showed no evidence of macrostructure before use. However, in all melts tested, with the exception of pure sodium sulphate, on removal from a melt the rod end that had been immersed had developed flat sides. These were symmetrical about a diameter of the rod and the shape of the faces were reproducible using different rods in other melts. These were therefore sapphire crystal faces, which had been exposed by the dissolution process. This effect indicates that the dissolution mechanism is probably reaction controlled. This may also be the case with the pure sodium sulphate, but the amount dissolved was so small that such observations were impossible.

### Solubility of $Al_2O_3$ in $Na_2SO_4/NaVO_3$ melts

The melts tested besides pure  $NaVO_3$  and  $Na_2SO_4$  had the compositions 20, 40, 60, 80 mole %  $NaVO_3$ . These melts are equivalent to 10, 20, 30, 40 mole %  $V_2O_5/Na_2SO_4$  melts respectively at equilibrium. In Figs. 4 and 5 comparison is possible between these various melts. It was not expected that the results would be vastly different but it was not known what effect small percentages of available sulphur trioxide would have. It is seen that over some temperature ranges for certain mixtures, the "fully equilibrated" melts accept more alumina. It can be argued that this is solely due to the fact that in fig. 4, percentages are based on the original weight of the  $Na_2SO_4/V_2O_5$  mixture before reaction.  $Na_2SO_4/NaVO_3$  melts lose no weight due to chemical reaction. Table 1 compares the saturation solubilities of the two kinds of melts based on the weights that they would have had as unreacted mixtures of  $Na_2SO_4$  and  $V_2O_5$ .

**Table 1** Solubility of  $Al_2O_3$  in  $Na_2SO_4/V_2O_5$  and  $Na_2SO_4/NaVO_3$  melts.

| Melt (mole %)                 | Solubility (wt %) |       |        |        |
|-------------------------------|-------------------|-------|--------|--------|
|                               | 700°C             | 850°C | 1000°C | 1100°C |
| $Na_2SO_4$                    |                   |       | 0.0025 | 0.0032 |
| 90% $Na_2SO_4$ 10% $V_2O_5$ A |                   | 0.030 | 0.052  | 0.073  |
| 80% $Na_2SO_4$ 20% $NaVO_3$ B |                   | 0.072 | 0.076  | 0.079  |
| 80% $Na_2SO_4$ 20% $V_2O_5$ A | 0.15              | 0.19  | 0.23   | 0.27   |
| 60% $Na_2SO_4$ 40% $NaVO_3$ B | 0.09              | 0.13  | 0.23   | 0.40   |
| 70% $Na_2SO_4$ 30% $V_2O_5$ A | 0.57              | 0.61  | 0.67   | 0.75   |
| 40% $Na_2SO_4$ 60% $NaVO_3$ B | 0.14              | 0.28  | 0.42   | 0.63   |
| 60% $Na_2SO_4$ 40% $V_2O_5$ A | 0.66              | 0.76  | 0.92   | 1.24   |
| 20% $Na_2SO_4$ 80% $NaVO_3$ B | 0.44              | 0.68  | 0.92   | 1.24   |
| 50% $Na_2SO_4$ 50% $V_2O_5$ A | 0.76              | 1.19  | 1.64   | 2.11   |
| $NaVO_3$ B                    | 0.76              | 1.09  | 1.43   | 1.74   |

- A. Results for  $Na_2SO_4/V_2O_5$  melts based on original weight of the unreacted mixtures.  
 B. Results for  $Na_2SO_4/NaVO_3$  melts based on the weight that these would have had as unreacted  $Na_2SO_4/V_2O_5$  mixtures.

So it is seen that under these conditions the mixtures containing small percentages of available sulphur trioxide, or sodium vanadyl vanadate II dissolve slightly more alumina than completely equilibrated melts. The exception to the statement is the 90%  $Na_2SO_4/10\% V_2O_5$  melt. This is presumably due to the fact that sodium vanadyl vanadate II dissolves more alumina than sodium metavanadate (Fig. 6).

### The solubility of $Al_2O_3$ versus melt composition

As the sodium/vanadium ratio found in marine boiler slags varies, it is of interest to know how the possible solubility of alumina will vary with this ratio. Conditions will be very different, of course, with many other components in the melt, which may either increase or decrease its corrosivity. Fig. 6 shows the saturation solubility of sapphire in pure  $Na_2SO_4/V_2O_5$  melts at 700, 850, 1000 and 1100°C.

Starting with pure  $V_2O_5$ , the solubility ranges from 1.4 wt % at 700°C to 3.3 wt % at 1100°C. The addition of soda increases the solubility until a maximum is reached somewhere between 12 and 18 mole %  $Na_2SO_4$ . Further addition of sodium sulphate after this maximum serves only to reduce the solubility. After 50 mole %, i.e. at the first appearance of free sodium sulphate in the melt, the solubility drops rapidly to very nearly zero in pure sodium sulphate. Up to 50 mole %  $Na_2SO_4$  the solubilities are all of the same order, i.e. approximately between 1 and 3.5 wt %. Therefore, it would appear that free sodium sulphate in a melt acts as a modifier. A few years ago it was reported that the sodium/vanadium ratio on a superheated tube of a fighting ship was approx. 0.9. Therefore, if these results are capable of application to boiler surfaces, this ratio would need to increase to about 4 to have effect. This is unlikely to happen, as vanadium contents appear to be increasing while attempts are being made to reduce sodium contamination.

## RESULTS FOR SILICA

The results for silica are given in Figs. 7 to 10. Generally, silica is more soluble in a melt than alumina. Except for high sodium sulphate contents, melts, which dissolved much alumina dissolve relatively small amounts of silica and vice versa.

### Solubility of $SiO_2$ in $Na_2SO_4/V_2O_5$ melts

The result of adding 10 and 20 mole %  $Na_2SO_4$  to  $V_2O_5$  is to decrease the solubility of silica (Fig. 7). It is possible that changes in the slopes of these curves also occur corresponding to the quartz-cristobalite transformation, but too few results were taken to discover whether this is so. At 30 mole %  $Na_2SO_4$ , the melt dissolves approximately the same amounts, as did pure  $V_2O_5$ . However 40 and 50 mole %  $Na_2SO_4/V_2O_5$  melts dissolved more silica, than those with lower  $Na_2SO_4$  concentrations, at all temperatures investigated. Also the temperature dependence of the saturation solubility increased as  $Na_2SO_4$  concentration increased. The size of the points in Fig. 7 indicates the approximate estimated error.

The scatter of results in Fig. 8 is considerably more than that with melts containing 0-50 mole %  $Na_2SO_4$ . This is due to the fact that in high sodium sulphate melts and particularly at high temperatures the silica glass rods devitrified faster than they dissolved. While the rods were in the melt, the devitrified layer was usually coherent and whole. On removal from the melt, even with slow cooling, hair-line cracks appeared. If the devitrification product was  $\beta$ -cristobalite (or "high cristobalite"), this would have had a different coefficient of thermal expansion to that of silica glass. The cracks probably appeared when  $\beta$ -cristobalite transformed to  $\alpha$ -cristobalite at a temperature between 270 and 180°C. This transformation is accompanied by a 3.7% volume shrinkage. Upon placing such rods into water or HCl solution for cleaning, the devitrified layer and slag often audibly flaked off. This problem of devitrification increased with increasing temperature and increasing sodium sulphate content, although the devitrified layer was more coherent from melts of pure sodium sulphate. If a melt contained enough sodium sulphate and was at a high enough temperature for the rate of devitrification to exceed the rate of dissolution, then the point of inflexion ("A" in Fig. 3) did not occur, as silica glass was no longer being presented to the melt. Instead a smooth curve was obtained much as that in Fig. 2 but generally equilibrium was achieved in a much shorter time. The occurrence of devitrification is summarised in Table 2.

At first, when devitrification became a nuisance, the method used to combat this effect was the use of shorter and shorter immersion times for the rods. When using 70 and 80 mole %  $Na_2SO_4$  melts this entailed using dozens of rods. Then one rod was accidentally left in the melt for about 2 hr. and this devitrified layer was found to be more coherent.

Therefore, when devitrification was experienced in a system, times of 2 hr. were used at first increasing to 8 hr as equilibrium was approached. These devitrified layers produced from long immersion times were not always coherent, but in most cases an estimate of the silica dissolved was possible by deducting an average slag loss value from the weight of the rod plus slag.

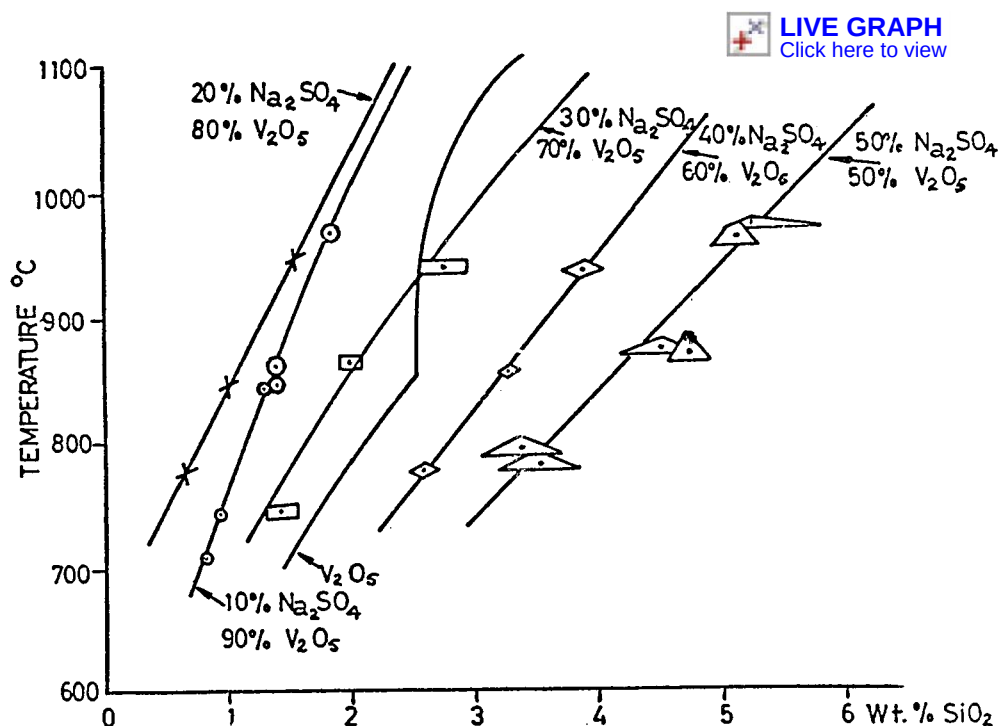
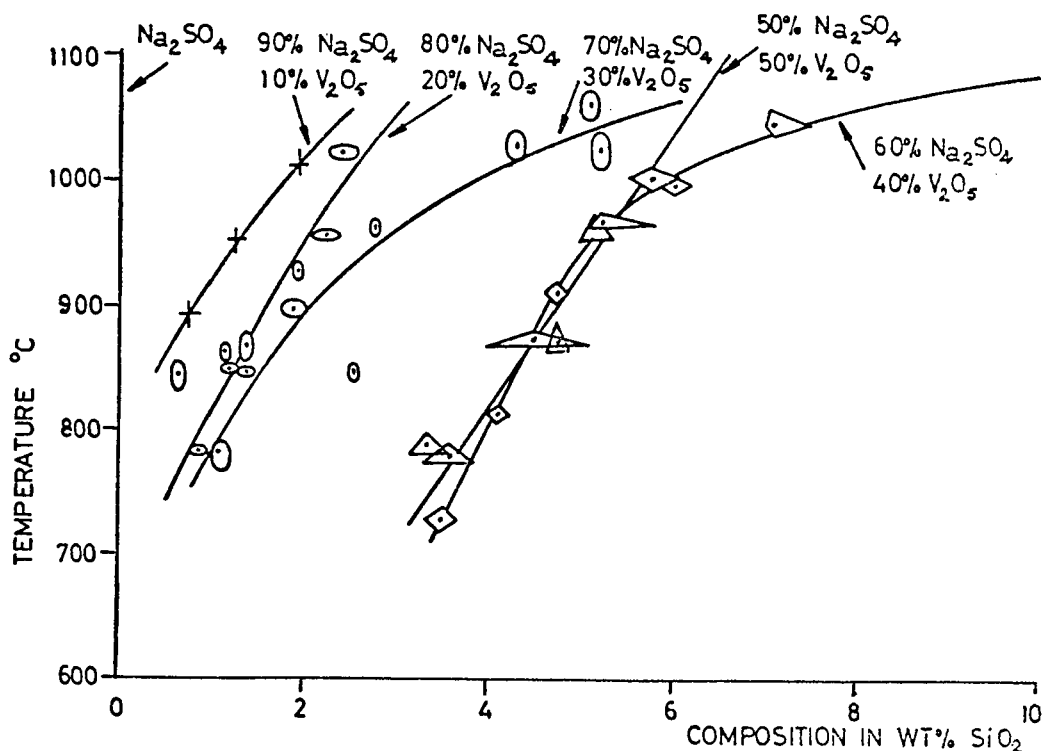


Fig. 7 The solubility of  $\text{SiO}_2$  in  $\text{V}_2\text{O}_5$ /0-50 mole %  $\text{Na}_2\text{SO}_4$



**LIVE GRAPH** Fig. 8 Solubility of  $\text{SiO}_2$  in  $\text{Na}_2\text{SO}_4$  /  $\text{V}_2\text{O}_5$  melts

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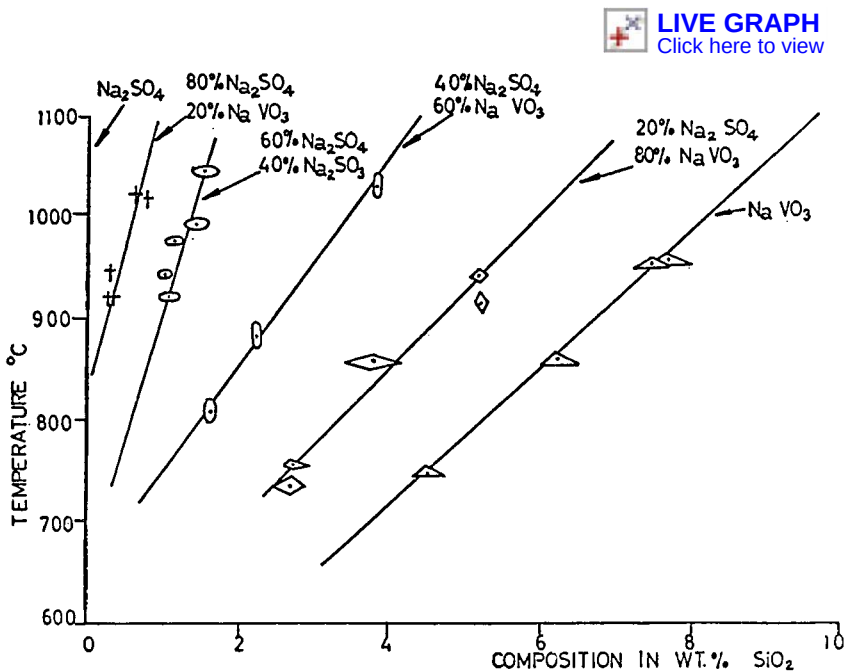


Fig. 9 Solubility of SiO<sub>2</sub> in Na<sub>2</sub>SO<sub>4</sub>/NaVO<sub>3</sub> melts

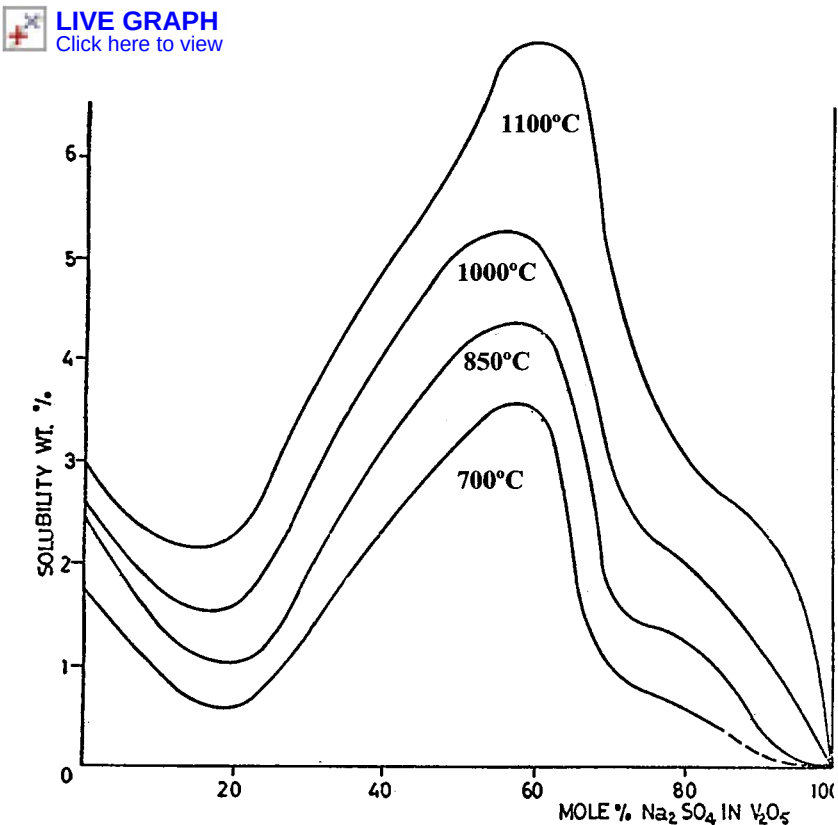


Fig. 10 Effect of temperature on the solubility of SiO<sub>2</sub> in Na<sub>2</sub>SO<sub>4</sub>/ V<sub>2</sub>O<sub>5</sub> melts

**Table 2** Occurrence of devitrification of vitreous silica in  $\text{Na}_2\text{SO}_4/\text{V}_2\text{O}_5$  melts

| Melt Composition Mole %  |                        | Temp. °C          | Devitrification                                                                                      |
|--------------------------|------------------------|-------------------|------------------------------------------------------------------------------------------------------|
| $\text{Na}_2\text{SO}_4$ | $\text{V}_2\text{O}_5$ |                   |                                                                                                      |
|                          | 100                    | 1175              | No devitrification                                                                                   |
| 10                       | 90                     | 970               | No devitrification                                                                                   |
| 20                       | 80                     | 950               | No devitrification                                                                                   |
| 30                       | 70                     | 938               | No devitrification                                                                                   |
| 40                       | 60                     | 936               | No devitrification                                                                                   |
| 50                       | 50                     | 974<br>875<br>784 | Devitrification with some loss of devitrified product<br>Devitrification of surface layer only       |
| 60                       | 40                     | 758               | Devitrification with some loss of devitrified product                                                |
| 70                       | 30                     |                   | Severe devitrification and loss of devitrified product                                               |
| 80                       | 20                     |                   | Product at all temperatures investigated                                                             |
| 90                       | 10                     | 1012              | Devitrification but no loss (i.e. surface only)                                                      |
| 100                      |                        | 903<br>1031       | Devitrification with loss of product after 53hr.<br>Devitrification with loss of product after 17hr. |

**Solubility of  $\text{SiO}_2$  in  $\text{Na}_2\text{SO}_4/\text{NaVO}_3$  melts**

As with alumina, melts containing 20, 40, 60, 80 and 100 mole %  $\text{NaVO}_3$  were tested (Fig. 9). These are equivalent to fully reacted sodium sulphate mixtures containing 10, 20, 30, 40 and 50 mole %  $\text{V}_2\text{O}_5$ . Melts containing 100, 80 and 60 mole %  $\text{NaVO}_3$  are seen to be capable of dissolving more silica than their  $\text{Na}_2\text{SO}_4/\text{V}_2\text{O}_5$  equivalents. Those containing 40 and 20 mole %  $\text{NaVO}_3$  dissolved less. This is comparable with the results for alumina where all melts dissolved more. The results in Table 3 compare solubilities in  $\text{Na}_2\text{SO}_4/\text{V}_2\text{O}_5$  melts with  $\text{Na}_2\text{SO}_4/\text{NaVO}_3$  melts where the latter are considered as being derived from a  $\text{Na}_2\text{SO}_4/\text{V}_2\text{O}_5$  mixture.

So it is seen that for all compositions in table 3 except the equimolecular mixture, the “fully equilibrated” melts dissolve less silica than the “near equilibrated” melts. This is similar to the results for alumina in table 1.

**The solubility of  $\text{SiO}_2$  versus melt composition**

In Fig. 10 it is seen that the composition of the melt greatly affects the solubility of silica. Addition of soda to vanadium pentoxide serves initially to decrease the amount of silica the melt can dissolve (cf.  $\text{Al}_2\text{O}_3$  which increases). The 12-18 mole %  $\text{Na}_2\text{SO}_4$  which produced a maximum in the solubility of alumina (Fig. 6) may be compared with the 14-20 mole %  $\text{Na}_2\text{SO}_4$  which produced a minimum in the solubility of silica. The equimolecular mix dissolved more silica than pure  $\text{V}_2\text{O}_5$  whereas it dissolved less alumina.



**Table 3** Solubility of SiO<sub>2</sub> in Na<sub>2</sub>SO<sub>4</sub>/ V<sub>2</sub>O<sub>5</sub> and Na<sub>2</sub>SO<sub>4</sub>/ NaVO<sub>3</sub> melts.

| Melt (mole %)                                                           | 700°C | 850°C | 1000°C | 1100°C |
|-------------------------------------------------------------------------|-------|-------|--------|--------|
| Na <sub>2</sub> SO <sub>4</sub>                                         |       |       | 0.017  | 0.058  |
| 90% Na <sub>2</sub> SO <sub>4</sub> 10% V <sub>2</sub> O <sub>5</sub> A |       | 0.4   | 1.3    | 2.4    |
| 80% Na <sub>2</sub> SO <sub>4</sub> 20% NaVO <sub>3</sub> B             |       | 0.09  | 0.38   | 0.75   |
| 80% Na <sub>2</sub> SO <sub>4</sub> 20% V <sub>2</sub> O <sub>5</sub> A | 0.6   | 1.25  | 2.0    | 3.0    |
| 60% Na <sub>2</sub> SO <sub>4</sub> 40% NaVO <sub>3</sub> B             | 0.36  | 0.6   | 1.0    | 1.4    |
| 70% Na <sub>2</sub> SO <sub>4</sub> 30% V <sub>2</sub> O <sub>5</sub> A | 1.0   | 1.7   | 2.9    | 5.0    |
| 40% Na <sub>2</sub> SO <sub>4</sub> 60% NaVO <sub>3</sub> B             | 0.8   | 1.7   | 2.5    | 3.4    |
| 60% Na <sub>2</sub> SO <sub>4</sub> 40% V <sub>2</sub> O <sub>5</sub> A | 3.6   | 4.3   | 5.1    | 7.3    |
| 20% Na <sub>2</sub> SO <sub>4</sub> 80% NaVO <sub>3</sub> B             | 2.2   | 3.2   | 4.3    | 5.0    |
| 50% Na <sub>2</sub> SO <sub>4</sub> 50% V <sub>2</sub> O <sub>5</sub> A | 3.1   | 4.1   | 5.1    | 6.1    |
| NaVO <sub>3</sub> B                                                     | 3.4   | 4.6   | 5.7    | 6.9    |

For A and B – see table 1

Also the presence of free sodium sulphate, definitely a modifier for alumina, gives a maximum on the curve for silica. The solubility of silica in pure sodium sulphate is very small being approximately 0.017 wt % at 1000°C and 0.058 wt % at 1100°C.

#### ***The dissolution of SiO<sub>2</sub> in 60% Na<sub>2</sub>SO<sub>4</sub>–40% V<sub>2</sub>O<sub>5</sub> under different conditions***

To investigate further, the effect of melt condition on the solubility of silica, it was decided to perform three experiments.

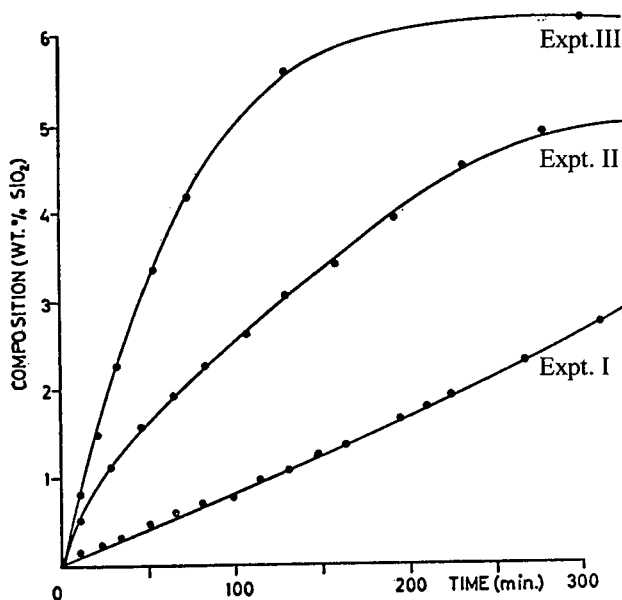
- I. Dissolution of silica glass in 60% Na<sub>2</sub>SO<sub>4</sub>/40% V<sub>2</sub>O<sub>5</sub> the dissolution process to start immediately the mixture was molten. Thus the mixture would contain free V<sub>2</sub>O<sub>5</sub> at first, then some sodium vanadyl vanadate I and perhaps some sodium vanadyl vanadate II and sodium metavanadate.
- II. Dissolution of silica glass in 60% Na<sub>2</sub>SO<sub>4</sub>/40% V<sub>2</sub>O<sub>5</sub> previously stabilized for 10,000 min. at 950°C. Thus this melt would contain both sodium metavanadate and sodium vanadyl vanadate II and perhaps others.
- III. The dissolution of silica glass in 20% Na<sub>2</sub>SO<sub>4</sub>/ 80%NaVO<sub>3</sub> that is equivalent to a fully equilibrated 60% Na<sub>2</sub>SO<sub>4</sub>/40% V<sub>2</sub>O<sub>5</sub> mole mixture.

The results are shown in Fig. 11. The variation between the melts is surprising. The rate of dissolution in Expt. III is approximately twice that of Expt. II and six times that of Expt. I in the first 100 mins. The slope of the Expt. I curve increases with time, due to the formation of sodium metavanadate, which is known from previous experimentation to dissolve silica more rapidly than V<sub>2</sub>O<sub>5</sub>.

Whether the three experiments would have reached the same saturation solubility after a long time was impossible to discover due to the fact that even after about 100 min. devitrification of the glass rods was a problem. In these three experiments, the rods were unstirred as the dissolution is rapid. It is possible that SO<sub>3</sub> bubbles formed on the surface of the rods used in experiment I greatly reducing the area exposed to the melt.

## **CONCLUSIONS**

The conclusions of the work just described explain why there is a problem of refractory corrosion in marine boilers. High vanadium pentoxide melts will dissolve considerable quantities of alumina. Melts containing roughly equal proportions of sodium sulphate and vanadium pentoxide will dissolve considerable quantities of silica. Also, if the glassy phase in the brick contains high proportions of silica, the high sodium sulphate melts will cause this to devitrify.



**Fig. 11** Dissolution of silica glass in 60% Na<sub>2</sub>SO<sub>4</sub>/40% V<sub>2</sub>O<sub>5</sub>  
 (Expt. I – 60% Na<sub>2</sub>SO<sub>4</sub>/40% V<sub>2</sub>O<sub>5</sub> dissolution of silica started immediately the mixture was molten. Temp. 937°C  
 Expt. II - 60% Na<sub>2</sub>SO<sub>4</sub>/40% V<sub>2</sub>O<sub>5</sub> mixture allowed 10,000 min. at 950°C to approach equilibrium before dissolving silica. Weight loss of mixture about 19.5%. Temp. 914°C  
 Expt. III - 20% Na<sub>2</sub>SO<sub>4</sub>/80% NaVO<sub>3</sub> (≡60% Na<sub>2</sub>SO<sub>4</sub>/40% V<sub>2</sub>O<sub>5</sub> at equilibrium). Weight loss 20.3% at equilibrium. Temp. 916°C)

When alumina dissolves in Na<sub>2</sub>SO<sub>4</sub>/NaVO<sub>3</sub>/V<sub>2</sub>O<sub>5</sub> melts the alumina reaches saturation solubility in tens of hours, depending on the temperature. When silica dissolves in melts containing up to 50% Na<sub>2</sub>SO<sub>4</sub>, the composition follows equation (1) until a point is reached where the melt is saturated with cristobalite. After this point, the silica glass uses the melt as a medium for reaching the lower energy form – cristobalite. The addition of up to 14-20 mole % Na<sub>2</sub>SO<sub>4</sub> to V<sub>2</sub>O<sub>5</sub> causes the solubility of silica to decrease and the solubility of alumina to increase. Further additions of sodium sulphate up to 60 mole % cause the solubility of silica to increase approximately linearly and the solubility of alumina to decrease. From 60-100 mole % Na<sub>2</sub>SO<sub>4</sub> the solubility of both silica and alumina decreases to a very low level at pure sodium sulphate. V<sub>2</sub>O<sub>5</sub> and Na<sub>2</sub>SO<sub>4</sub> react together to release SO<sub>3</sub>. A melt containing 60 mole % Na<sub>2</sub>SO<sub>4</sub> which had reached complete equilibrium dissolved silica approximately six times faster than a melt far from equilibrium. Melts containing 50 mole % and above Na<sub>2</sub>SO<sub>4</sub> were found to devitrify silica glass faster than they dissolved it. This problem of devitrification, accompanied by loss of devitrified product, increased with increasing temperature. In most systems, the maximum temperature investigated was about 1000°C. Several systems whose higher temperature region was complicated by devitrification were investigated up to 1150°C. This latter temperature is the temperature to which most of the lines produced are

extrapolated. It is thought that above this temperature the effect of small increases in temperature will become more and more critical, e.g. 60% Na<sub>2</sub>SO<sub>4</sub>/40% V<sub>2</sub>O<sub>5</sub> (Figs. 4 and 8).

## SUMMARY

The saturation solubilities of alumina and silica in Na<sub>2</sub>SO<sub>4</sub>/NaVO<sub>3</sub>/V<sub>2</sub>O<sub>5</sub> melts have been determined. The solubilities of silica and alumina in V<sub>2</sub>O<sub>5</sub> are approximately equal: 1.8 wt% at 700°C and 2.9 wt% at 1100°C for silica; and 1.4 wt% at 700°C and 3.3 wt% at 1100°C for alumina. In pure Na<sub>2</sub>SO<sub>4</sub>, both oxides are almost insoluble. However, solubilities of these two oxides in mixtures of Na<sub>2</sub>SO<sub>4</sub> and V<sub>2</sub>O<sub>5</sub> show quite different behaviour. The solubility of alumina has a maximum at approximately 15 mole % sodium sulphate (the composition of a compound commonly found in marine boiler slags – sodium vanadyl vanadate I). Silica has a minimum at about 20 mole % and a maximum at 60 mole % sodium sulphate. Thus melts containing up to about 90 mole % sodium sulphate are capable of dissolving considerable quantities of silica and alumina. Melts containing much sodium sulphate can be expected to cause devitrification of the glassy phase which binds brick particles.

The present results agree with data published in the open literature by other research workers.

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