

Introduction to

# HIGH TEMPERATURE OXIDATION and CORROSION

A.S. Khanna



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*Dedicated to  
my wife*

# Foreword

The attainment of high temperatures has been important in the development of civilization for many centuries. Fired ceramics, extraction of metals from their ores, and the development of casting, forging, and the optimization of metal properties by heat treatment are all high temperature processes of considerable antiquity. However, the high temperatures were contained by refractories, and in use most metals saw only modest temperatures. This began to change with the industrial revolution. The first heat engines introduced at the end of the 18th century were large steam pumps to remove water from deep mines, and these operated at fairly low temperatures. However, the desire for improved efficiency pushed boiler temperatures progressively higher, first to develop engines for power production in factories, and then for locomotives. Today, the main steam temperatures in advanced utility boilers are approaching 650°C, with the outer surface of the heat exchangers in contact with the combustion gases perhaps 50°C higher. In Europe, Japan and the USA, plans are now afoot to raise the main steam temperature to perhaps as high as 750°C.

The introduction of the internal combustion engine in the late 19th century introduced the need for materials capable of operating for long times exposed to high temperature combustion gases without noticeable surface damage, in particular the exhaust valves, which are difficult to protect by cooling. Again, as part of the drive for higher efficiencies and higher specific power outputs, the idea of supercharging was introduced, and the most common method was the turbocharger. The conditions to which the small turbocharger rotor was exposed resulted in the development of a class of castable high temperature alloys, of which Co-10%Ni-35%Cr-7, 5%W-0.5%C is an example. The introduction of electricity as a major energy source at the beginning of the 20th century led to the development of electric heating for industrial systems, and the problem of producing a wire capable of forming a radiant heater with a surface temperature of the order of 850°C became a major challenge which was solved by the development of Ni20%Cr alloys, which can be drawn into wires, but which have adequate creep strength and good oxidation resistance at the desired use temperature.

The next major challenge was the introduction of the aviation gas turbine in 1940 in Germany and the UK, and this continues to be the pacing technology for the development of high temperature alloys to this day. For this application, it becomes difficult to reconcile alloy design demands for adequate high temperature mechanical properties and those for adequate corrosion resistance, and this has led to a separation of these functions. An alloy

with good mechanical properties and perhaps marginal corrosion resistance is protected by the application of a coating that has excellent corrosion resistance but marginal mechanical properties. A further complication is that the turbine inlet temperatures have now risen to over 1350°C; while the intrinsic strength capability of the best alloys currently available does not exceed 1000°C. This is handled by cooling the hot components, but the formation of the cooling passages places further demands on the castability of the high temperature alloys.

All of these high temperature applications of metals and alloys demand materials which have a variety of properties such as strength, toughness, fatigue resistance, creep resistance, formability; and not least resistance to degradation by reaction with the environment. Essentially all potential metallic materials are unstable in these high temperature environments, and the various oxidation processes are highly exothermic. The only reason it is possible to have materials that can be used at all is that the reaction product — the oxide — forms a 'protective layer' on the component surface, and it is the ways in which this is possible which form the basis of the science of high temperature oxidation and corrosion resistance.

The first paper which expressly addresses high temperature oxidation was that by G. Tamman, in 1920. However, the first paper which lays out the basics of the problem as we know it was that by Pilling and Bedworth in 1923. They defined 'high temperature' as that at which the transport of the reactive components through the protective layer was the principal determinant of the reaction rate (as opposed to the situation in aqueous corrosion processes at close to ambient temperatures). They showed that under these circumstances it could be expected that the rate of reaction would diminish as the protective scale thickened, leading to a 'parabolic rate law'. They also high-lighted the problems associated with forming an adherent crack-free protective oxide layer on the oxidizing surface because of the volume changes associated with the oxidation process. The discussion to this seminal paper shows that others were thinking along similar lines at the time. A few years later, the discovery that oxides contained lattice defects, and that the transport processes within them are determined by the motion of these defects allowed a more quantitative approach. This was recognized by Carl Wagner, who produced an important body of work over the course of the next twenty years largely defining how we now look at the basic theory of the bulk transport processes in oxides. In recent years, however, the recognition that in many cases the transport processes involve short-circuit paths, such as grain boundaries, has introduced further complications into this elegant picture.

The problem of the integrity of the protective oxide was not part of Wagner's contribution, and its practical solution for the high temperature alloys which were developed for the applications mentioned above was discovered essentially by accident in the early 1940's. It was found that very small amounts of what are now called 'reactive elements' added to the alloys introduced a remarkable improvement in the apparent integrity of the protective oxide, particularly in its resistance to thermal cycling. The reasons for this effect are still a matter of considerable debate.

The earliest theoretical treatments of oxidation problems considered simple systems, with a single oxidant (usually oxygen) and a pure metal, although in practice high temperature-resistant materials were always alloys. More recently, approaches such as in multi-component

diffusion theory have been applied, and the growth of oxides on polyphase materials have been analyzed. These approaches have been greatly assisted by the development of modern characterization techniques.

In recent years, the problem of high temperature corrosion in relatively complex environments, such as mixed gases with low oxygen activities but significant carbon or sulfur activities, or environments in which molten alkali salts may be deposited on the alloy surface, has become of much greater importance. Theoretical models for some aspects of these situations have been developed, but they are still not fully understood. Many challenges still exist!

In view of the practical importance of this area, and the intellectual problems it presents, it is surprising how few teaching texts have been produced. The well-known books by Kubaschewski and Hopkins, Kofstad, and Benard are now rather old, and the subject has developed quite a lot since they were written. It is clearly timely for a textbook such as this, and the range of topics covered are clearly relevant to the current state of knowledge. Professor Khanna is an international authority in this field, and his book will be welcomed by both the research community and those concerned with teaching this interesting and exciting subject.

**John Stringer**  
Palo Alto, California, 2000

# Preface

Material degradation at high temperatures is a serious problem in several high tech industries. Gas turbines in aircraft, fossil fueled power plants, refineries and petrochemical industries, and heating elements for high temperature furnaces are some examples where corrosion either limits their use or reduces their life, considerably affecting the efficiency. Why high temperature corrosion should be treated as a separate subject from general corrosion is mainly due to its difference in the mechanism of occurrence, high rate and very specific environments. Unfortunately there are not many universities or institutions where a systematic study on high temperature corrosion is given. After working for more than fifteen years in the field of high temperature oxidation and corrosion when I finally joined Indian Institute of Technology at Bombay, to teach high temperature corrosion, I found there was hardly any book which is complete for a basic course on this subject, suitable for a beginner in the industry. Although, there are a few good books, viz. by Kofstad; Birks and Meier; and that by Lai. However, while the Kofstad book is excellent for a practicing engineers/scientists, it is not very simple for a beginner. Birks and Meier book is brief and incomplete while Lai's book is mainly for a plant designer. It is at that time, I thought of writing this course book. At IIT Bombay, we have a core course on High Temperature Corrosion and this book is basically to suit such a 40 lecture course.

This book is written in a manner suitable for a beginner to understand the fundamentals of high temperature corrosion and related topics. It starts with a basic chapter on the fundamentals of high temperature corrosion, especially the thermodynamics and kinetics of oxidation with experimental details to measure kinetics. The next two chapters are the basic knowledge that is required to understand the mechanism of high temperature corrosion, viz., defect structure of oxides and diffusion in oxides. From then onwards the chapters start with thin layer oxidation to thick layer oxidation. Oxidation of pure metals and alloys is considered next. More complications in high temperature oxidation come when the environment becomes more complex, i.e. more than a single environment. Basic concepts of mixed gas environment have been dealt in this chapter with a few practical examples of corrosion in mixed environments. Hot corrosion is a special form of mixed gas corrosion in the presence of salt deposits. Why scales spall, and why suddenly a highly protective system corrodes catastrophically is dealt with in next two chapters with the remedial measures of the addition of active elements.

It is not possible in many cases to choose an alloy which either does not corrode at high

temperatures or its corrosion rate is within the desired limit. In such cases, the metals and alloys are protected by coatings. This chapter gives the principles of various high temperature coatings to combat corrosion. One item which is missing in many important books is the analytical tools available to characterize oxide scales in order to understand the mechanism of oxidation. Most of optical and electron-optical techniques are described which are used for an oxide scale characterization. The last chapter deals with practical examples of high temperature corrosion.

I hope this book will be of great asset for graduate and post graduate students, a good introduction for persons working in industries, especially in chemical, petrochemical, power plants etc. The basic knowledge given in the book can be further substantiated with some of the advanced books given in the bibliography and review articles in the appendix 1. This is in my opinion a first step in imparting basic knowledge in a difficult and complicated subject called high temperature corrosion.

I must acknowledge a lot of people who either helped me or provided suitable environment to write this book. The book was written during my several visits to Germany under my bilateral Indo-German programme. I must also acknowledge the help I got in the form of useful discussions with Joe Quadakkers of Forschungszentrum Juelich, Roland Streiff of University de Provence, Marseille, France, my students Arun Pattnaik, K.M.N. Prasanna, S.K. Jha, Sujata Mahapatra and Madhu Jeevan Reddy who helped me in editing the book. The special thanks and sincere gratitude goes to Dr. Ken Natesan of Argonne National laboratory, USA, who critically edited the book and made several important suggestions and almost rewrote the chapter on mixed gas environment.

Finally I dedicate this book to my wife who stayed alone during my visits to Germany where I wrote this book.

**A.S. Khanna**



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stability at high temperatures. Once these requirements are fulfilled, additional requirements for high temperature corrosion resistance are as follows:

1. Choose a metal which either has very low rate of oxidation at the temperature of interest or forms a scale which is thin, slow growing and impervious to the atmosphere.
2. Since only a few metals have properties mentioned in (i), the alternative way is to choose an alloy which contains at least one such element that forms a protective, thin and slow growing oxide layer.
3. The last alternative is to apply a coating of another element or compound which has all those properties mentioned in 1 and 2 above.

In this book, an attempt has been made to achieve the objectives set in preceding paragraphs. The first chapter deals with the basics of oxidation: thermodynamic principles, measuring techniques and kinetics of oxidation. Defect structure and diffusion in solids, which is essential to understand oxide growth phenomena, are discussed in next two chapters. Oxidation under thin and thick scale regime is discussed in chapters 4 and 5. This is followed by oxidation of pure metals and alloys in next two chapters. Oxidation in mixed environments and hot corrosion is discussed next. Important phenomena such as stresses during oxide growth and active element effect would be discussed in next two chapters. Different methods of coatings required to protect metals and alloys from oxidation at high temperatures are covered in "High Temperature Coatings". Use of optical and electron optical techniques, required to characterize oxide scale and the mechanism of oxidation, is the subject of next chapter. A few examples of high temperature oxidation, hot corrosion and other material degradation have been discussed in the last chapter.

The reader is expected to have a basic knowledge of physical metallurgy principles and must make himself up to date by referring other text books. This book is for beginners and is perhaps the first course in high temperature corrosion. For more details and additional literature on certain specific topics, reader is requested to refer books and guides suggested in Appendix I.

# 1

## High Temperature Oxidation–Basics

Oxidation is the most important high temperature reaction. Oxidation of metals or alloys takes place when they are heated in a highly oxidizing atmosphere such as air or oxygen. Oxidation can also take place in other environments, such as sulphur dioxide and carbon dioxide, which have relatively low oxidation potentials. In the simplest form, an oxidation reaction is represented by the interaction of metal with oxygen to form an oxide. However, there are a variety of factors on which the oxidation behaviour of a metal depends and the reaction mechanism involved may often be quite complex. An oxidation reaction begins with adsorption of oxygen molecules from the atmosphere, nucleation of oxides, formation of a thin oxide layer, followed by its growth to a thicker scale. Processes like nodule formation and scale spallation may also take place during the growth process and what path the transporting species chooses for scale growth would decide the nature of the oxide formed. All these factors will be considered one by one in the subsequent chapters, but the most important aspect for oxide formation is their thermodynamic stability which will be considered first.

### THERMODYNAMIC CONSIDERATIONS

An oxidation reaction between a metal (M) and the oxygen gas ( $O_2$ ) can be written as:



Thermodynamically, an oxide will form on the surface of a metal when the oxygen potential in the environment is greater than the oxygen partial pressure in equilibrium with the oxide. This equilibrium oxygen pressure, also called the dissociation pressure of the oxide in equilibrium with the metal is determined from the standard free energy of formation of the oxide. The standard free energy of the oxidation reaction (Eq. 1.1) can be written as

$$\Delta G^\circ = -RT \ln (a_{MO_2} / a_M p_{(O_2)}) \quad (1.2)$$

where  $a_{MO_2}$  and  $a_M$  are the activities of the oxide and the metal respectively and  $p_{(O_2)}$  is the partial pressure of the oxygen gas. In general, element activity in alloy is given by  $a_M = \gamma_M X_M$ , where  $\gamma_M$  and  $X_M$  are the activity coefficient and mole fraction respectively of M in the alloy. If a value coefficient  $\gamma_M$  is not available, ideal behaviour is assumed and  $\gamma_M$  is assigned

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the value of unity. Assuming unit activity of the solid constituents, i.e. the metal and oxide, the Eq.1.2 becomes

$$\Delta G^\circ = RT \ln p_{(O_2)} \quad (1.3)$$

or 
$$p_{(O_2)} = \exp (\Delta G^\circ / RT) \quad (1.4)$$

Equation 1.4 permits the determination of the partial pressure of oxygen in equilibrium with the oxide from the standard free energy of formation. A plot of the standard free energies for the formation of oxides as a function of temperature is known as *Ellingham/Richardson diagrams*, which are used to get information about the partial pressure of oxygen required for any metal to form oxide at any temperature.

### ELLINGHAM/RICHARDSON DIAGRAMS

Ellingham diagrams (modified later by Richardson and Jeffes) were plotted from experimentally determined  $\Delta G^\circ$  vs  $T$  for the oxidation and sulphidation of a series of metals. The most general expression for the variation of free energy with  $\Delta G^\circ$  as a function of absolute temperature  $T$ , in the form:

$$\Delta G^\circ = A + BT + C/T + DT^2 \quad (1.5)$$

is approximated to straight lines over temperature ranges in which no change in physical state has occurred. The relation could thus be expressed by neglecting terms involving  $T^2$ ,  $1/T$  etc.:

$$\Delta G^\circ = A + BT \quad (1.6)$$

This equation if compared with the standard free energy change of a reaction in terms of its enthalpy and entropy

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (1.7)$$

implies that the constant  $A$  is the temperature-independent standard enthalpy change of the reaction,  $\Delta H^\circ$ , and the constant  $B$  represents the negative of the entropy change of the reaction,  $-\Delta S^\circ$ .

The slope of the free energy vs temperature plot would thus be  $(-\Delta S)^\circ$ , the entropy change of the reaction and the intercept the enthalpy value. Such a plot for the oxidation of various metals is illustrated in Fig. 1.1.

### Salient Features of Ellingham Diagrams

1. The free energy of most of the metals shows linear relationship with temperature with a positive slope. This implies that most of the oxidation reactions take place with decrease in entropy. This is obvious, as in most cases the reaction involves the formation of a solid oxide from a solid metal and a gas, i.e., the product has a higher order than the reactants. For example in the case of oxidation of silver, one mole of oxygen reacts to give two moles of

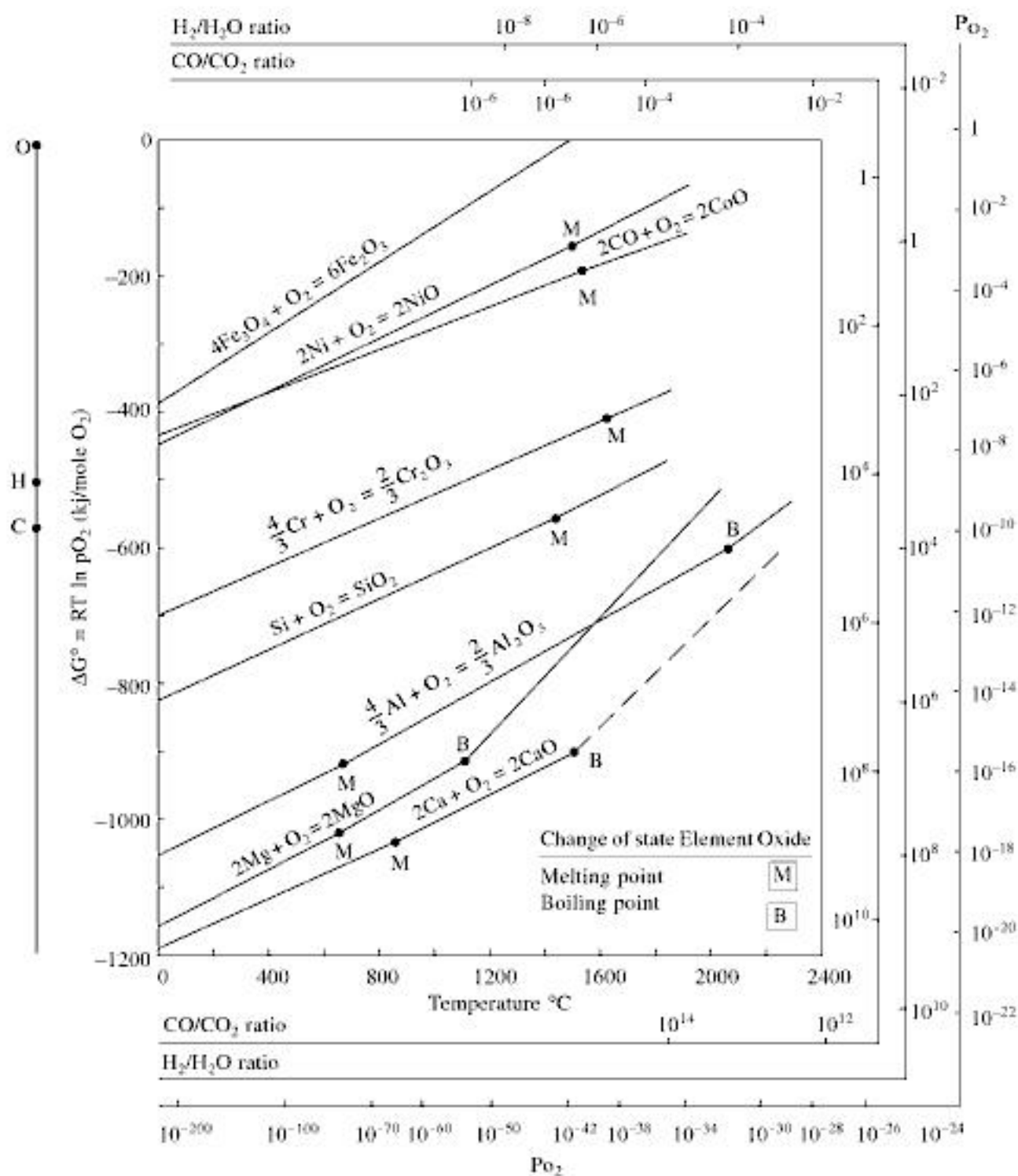


Fig. 1.1 Ellingham diagram, showing the variation of free energy with temperature for various oxides.

silver oxide, which shows a net decrease in entropy as a result of disappearance of gas:



Only in the case of the following two reactions is the entropy not negative:



#### 4 Introduction to High Temperature Oxidation and Corrosion

In Eq. 1.9 one mole of oxygen in the reactants gives one mole of carbon dioxide in the product. Thus the net change in entropy would be insignificant and therefore, the slope of this reaction is near to zero.

In the second case i.e. the formation of carbon monoxide from carbon and oxygen, one mole of oxygen in the reactant gives two moles of carbon monoxide in the product, thus the entropy has increased and therefore the slope is negative.

2. The change in the slope of the lines at certain points indicates a phase change in the metal. This could be melting, boiling or a change in structure, e.g. a change from body centered cubic to face centered cubic for Fe at around 800°C. Such a phase change involves a slight change in entropy due to the latent heat of the phase change and hence causes a small shift in the slope.

3. The most stable oxide has the largest negative value of  $\Delta G^\circ$  and is represented by the lowest line in the diagram. For example, in Fig. 1.1 CaO is the most stable oxide and Cu<sub>2</sub>O, the weakest. A less stable oxide can be reduced by the metal of a more stable oxide. This can be simply deduced from the position of the lines of the oxides in the diagram. Since free energy of formation is considered the value for only one mole of oxygen, the free energy value of the reduction of an oxide by the metal of other, can be obtained simply by the subtraction of their free energy values.

#### 4. Determination of oxidation potential values

One of the most important applications of the Ellingham diagrams is the determination of equilibrium dissociation pressures of oxides at various temperatures. Richardson added a nomographic scale to the Ellingham diagrams. The scale is constructed as follows. At any temperature  $T$ , the standard free energy for a reaction is given by Eq. 1.3 as  $\Delta G^\circ = RT \ln p(\text{O}_2)$ .

The free energy change of a reaction in terms of the partial pressure of the gas is written as

$$\Delta G = \Delta G^\circ + RT \ln p(\text{O}_2) \quad (1.11)$$

which is numerically equal to the decrease in the free energy of one mole of oxygen when its partial pressure is decreased from 1 atmosphere to  $p\text{O}_2$  at the temperature  $T$ . Now considering the variation of  $\Delta G^\circ$  with temperature in Eq. 1.11, for a given pressure, the free energy decrease of 1 mole of an ideal gas,  $\Delta G$  is a linear function of temperature, i.e.  $\Delta G^\circ$  becomes increasingly negative with increasing temperature, and the slope of the  $\Delta G^\circ$ - $T$  line is given as  $R \ln p$ , (which, with  $p < 1$ , is a negative number). Similarly, for a given increase in pressure,  $\Delta G^\circ$  becomes increasingly positive with increasing temperature. Thus a series of lines can be drawn for a given pressure change (always from  $p = 1$  atm to  $p = p$  atm) as a function of temperature. These lines indicate divergence from  $\Delta G^\circ = 0$ ,  $T = 0$  as shown in Fig. 1.2. Superimposition of Fig. 1.2 on the Ellingham diagram as given in Fig.1.1, is shown in Fig. 1.3.

- At  $T_1$ ,  $\Delta G^\circ = ab$  = the free energy decrease at  $T_1$  when  $p\text{O}_2$  decreases from 1 to  $10^{-20}$  atm. Thus  $p\text{O}_2 = 10^{-20}$  atm. For A/AO<sub>2</sub> equilibrium at  $T_1$ .

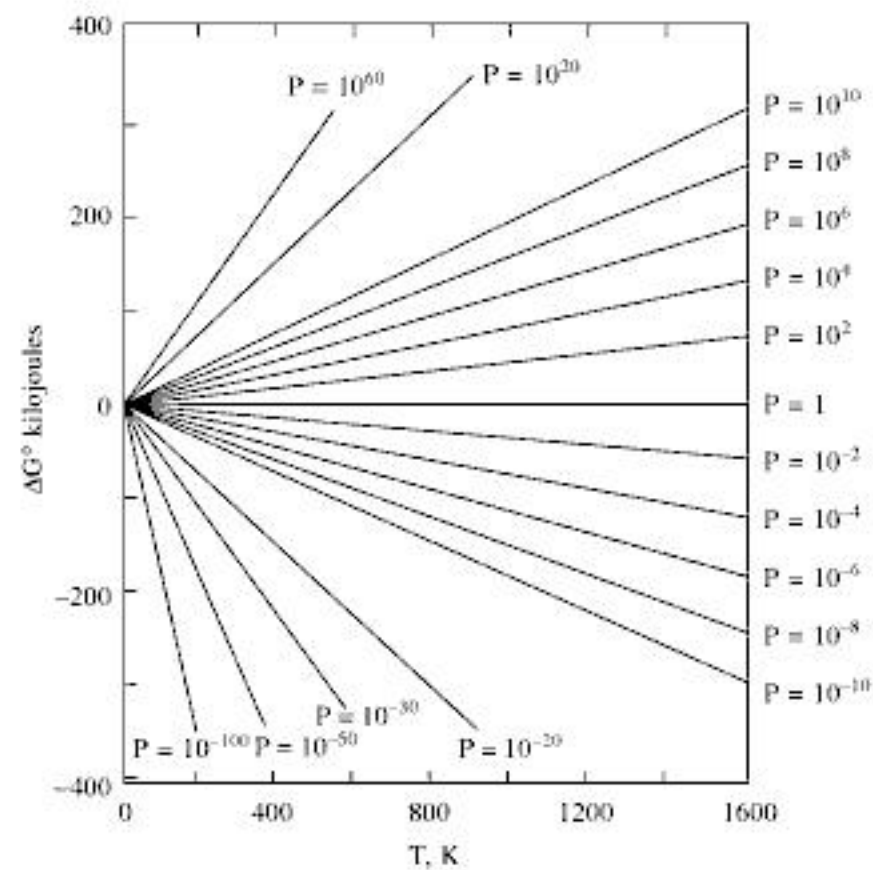


Fig. 1.2 The variation with temperature of the Gibbs free energy difference between 1 mole of ideal gas in the state ( $P = P, T$ ) and in the state ( $P = 1, T$ ).

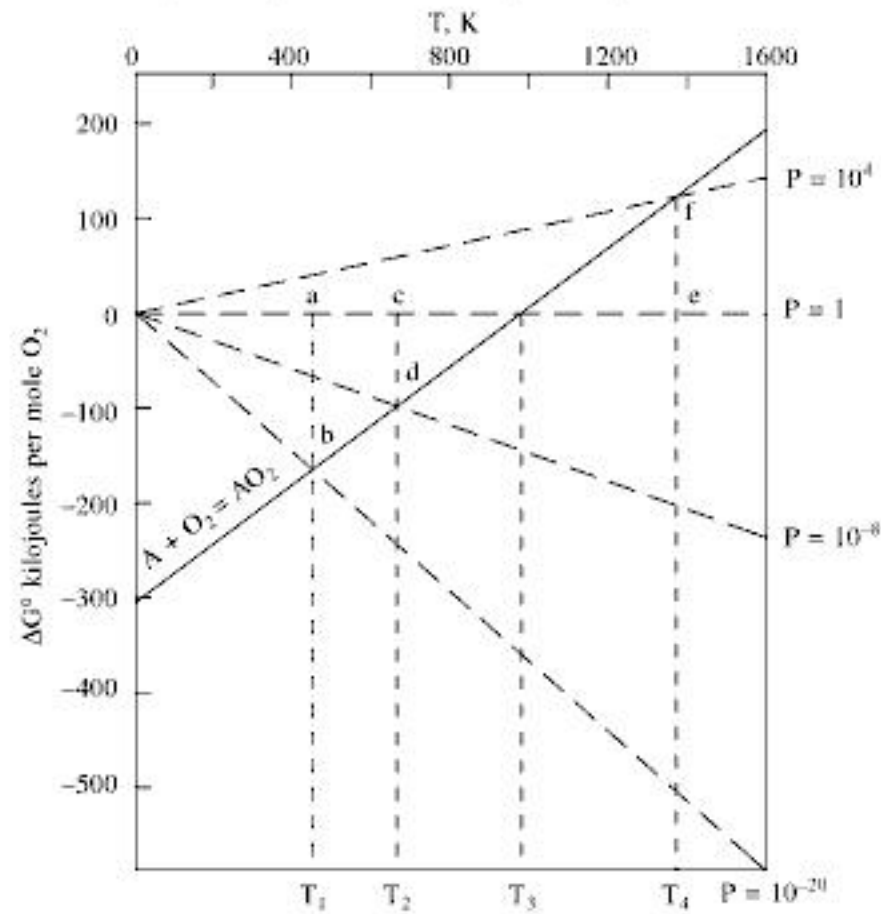


Fig. 1.3 Superimposition of Fig. 1.2 on an Ellingham diagram.

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- At  $T_2$ ,  $\Delta G^\circ = cd$  = the free energy decrease at  $T_2$  when  $pO_2$  decreased from 1 to  $10^{-8}$ . Thus  $pO_2 = 10^{-8}$  atm. For A/AO<sub>2</sub> equilibrium at  $T_2$ .
- At  $T_3$ ,  $\Delta G^\circ = 0$ , which corresponds to change from 1 to  $pO_2$  and therefore  $pO_2 = 1$  atm. For A/AO<sub>2</sub> equilibrium at  $T_3$ .
- At  $T_4$ ,  $\Delta G^\circ = ef$  = the free energy increase at  $T_4$  when  $pO_2$  is increased from 1 to  $10^4$  and therefore  $pO_2 = 10^4$  atm. For A/AO<sub>2</sub> equilibrium at  $T_4$ .

The  $pO_2$  as a function of temperature is thus added as a nomographic scale along the right side and the bottom edge.

The equilibrium partial pressure of any metal/metal oxide can now be obtained by starting from the point 'O' marked on the line on the left of the diagram in Fig. 1.1 (this corresponds to the equilibrium partial pressure of 1 atm.) and intersecting the  $\Delta G^\circ$ - $T$  line at a point corresponding to the desired temperature and extending it to the nomographic scale at the right or bottom edge, which will give the corresponding equilibrium partial pressure of the metal oxide at the selected temperature. For chromium oxide for example at 1000°C, the value of the equilibrium partial pressure of oxygen is  $10^{-21}$  atm. This implies that formation of Cr<sub>2</sub>O<sub>3</sub> is favoured thermodynamically at 1000°C in an environment with the oxygen potential greater than  $10^{-21}$ . Similarly oxygen partial pressure for Ni is  $10^{-10}$  atm. at 1000°C and those of Co, and Al are about  $10^{-12}$  and  $10^{-37}$  respectively. In practice, these low partial pressures of oxygen in ambient gases are achieved from a mixture of gases in which oxygen is one of the components. Such an environment contains no measurable molecular oxygen. The oxidation potential is controlled by either the  $pH_2/pH_2O$  or  $pCO/pCO_2$ . For  $pH_2/pH_2O$ , the oxidation potential is determined by the following reaction:



The standard free energy of formation is related to the partial pressures of hydrogen, oxygen and water by:

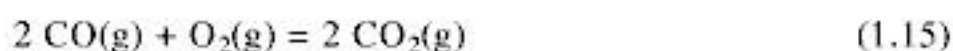
$$\Delta G^\circ = - RT \ln (p_{H_2O}^2 / p_{H_2}^2 p_{O_2}) \quad (1.13)$$

Rearranging the equation gives:

$$pO_2 = \exp (\Delta G^\circ / RT) / (pH_2 / pH_2O)^2 \quad (1.14)$$

Thus the partial pressure of oxygen at various temperatures can be determined as a function of  $pH_2/pH_2O$ . The  $pH_2/pH_2O$  value in equilibrium with the oxide can also be read from Fig. 1.1, using the method discussed earlier for reading equilibrium dissociation pressures of oxides. The starting point for the  $H_2/H_2O$  equilibrium in Fig. 1.1 is the point 'H' instead of point 'O' on the reference line, which is determined from the free energy value of Eq. 1.12. One can see that the  $\Delta G^\circ$  for the combustion reaction of hydrogen (Eq. 1.12), at  $T = 0$  is -511 kJ/mole, where the point 'H' is marked on the reference line at the left of Fig. 1.1. The  $pH_2/pH_2O$  value is read from the  $H_2/H_2O$  scale, which surrounds the upper, right and bottom of the Ellingham diagram. For example, from Fig. 1.1 it is seen that the oxygen potential, in terms of  $pH_2/pH_2O$ , in equilibrium with Cr<sub>2</sub>O<sub>3</sub> at 1000°C is about  $5 \times 10^3$ . Thus Cr<sub>2</sub>O<sub>3</sub> is likely to form at 1000°C when the  $pH_2/pH_2O$  ratio in the environment is less than  $5 \times 10^3$ .

Similarly, the equilibrium reaction in an environment whose oxidation potential is controlled by  $p\text{CO}/p\text{CO}_2$  is:



The above reaction (Eq. 1.15) can be obtained from the reactions given in Eq. 1.9 and 1.10, that is by subtracting the Eq. 1.10 from Eq. 1.9. Therefore, the standard free energy for this reaction at  $T = 0$  would be  $-564.8 \text{ kJ/mole}$ . It can be seen that the corresponding reference point 'C' appears at this value on the reference line.

From Eq. 1.13, one can now re-arrange and write the oxidation potential as:

$$p\text{O}_2 = \exp (\Delta G^\circ/RT) / (p\text{CO}/p\text{CO}_2)^2 \quad (1.16)$$

The  $p\text{CO}/p\text{CO}_2$  value can be read from the  $\text{CO}/\text{CO}_2$  scale by matching it with a reference point 'C' in the same way as in the case of  $\text{H}_2/\text{H}_2\text{O}$ .

Thus it is possible to obtain the oxygen potential of the environment in terms of  $p\text{O}_2$ ,  $p\text{H}_2/p\text{H}_2\text{O}$  or  $p\text{CO}/p\text{CO}_2$  and the oxygen partial pressure in equilibrium with the metal/metal oxide of interest from Fig. 1.1 in order to determine whether or not the oxide is likely to form thermodynamically. Important information for designing industrial alloys can also be obtained from such diagrams. For example, it is clear from Ellingham diagrams that oxides of iron, nickel and cobalt which are the alloy bases for the majority of engineering alloys, are significantly less stable than the oxides of some of the solutes (e.g. Cr, Al, Si etc.) in these alloys. When one of these solute elements is added to iron, nickel or cobalt in a reasonable concentration, the base alloy is protected due to formation of stable oxide on the surface. This is the basis of protection of most of the engineering alloys. Most of the high temperature alloys either form alumina or chromia protective scales on oxidation, or coatings of these elements are applied, which on oxidation form one or more of these oxides.

Similar diagrams for sulphide and carbide systems have also been made. One such diagram for a few metal sulphides is given in Fig. 1.4. Free energy of formation refers here for interaction of metal with one mole of sulphur gas,  $\text{S}_2$ . Dissociation pressures for metal sulphides can be obtained in a similar way in terms of  $p\text{S}_2$  or in the form of ratio of the  $\text{H}_2/\text{H}_2\text{S}$ . Nomograms have been drawn in a similar fashion as for oxide systems. As can be seen  $\text{CaS}$  is the stablest sulphide and  $\text{Co}_9\text{S}_8$  the weakest.

The Ellingham diagram for a few important carbides is given in Fig. 1.5. The most stable carbides are those of chromium, titanium and niobium.

## KINETICS OF OXIDATION

One of the limitations of Ellingham diagrams is that they do not take into account the kinetics of reaction. These equilibrium diagrams only tell us whether under certain conditions of temperature and partial pressure of oxygen, oxide formation is possible or not. Sometimes it is possible that the kinetics of the process are so slow that even if there is a possibility of the reaction to occur thermodynamically, it will take very long to form. Thus it appears that the oxidation reaction has not occurred. Therefore, it is imperative to know about the

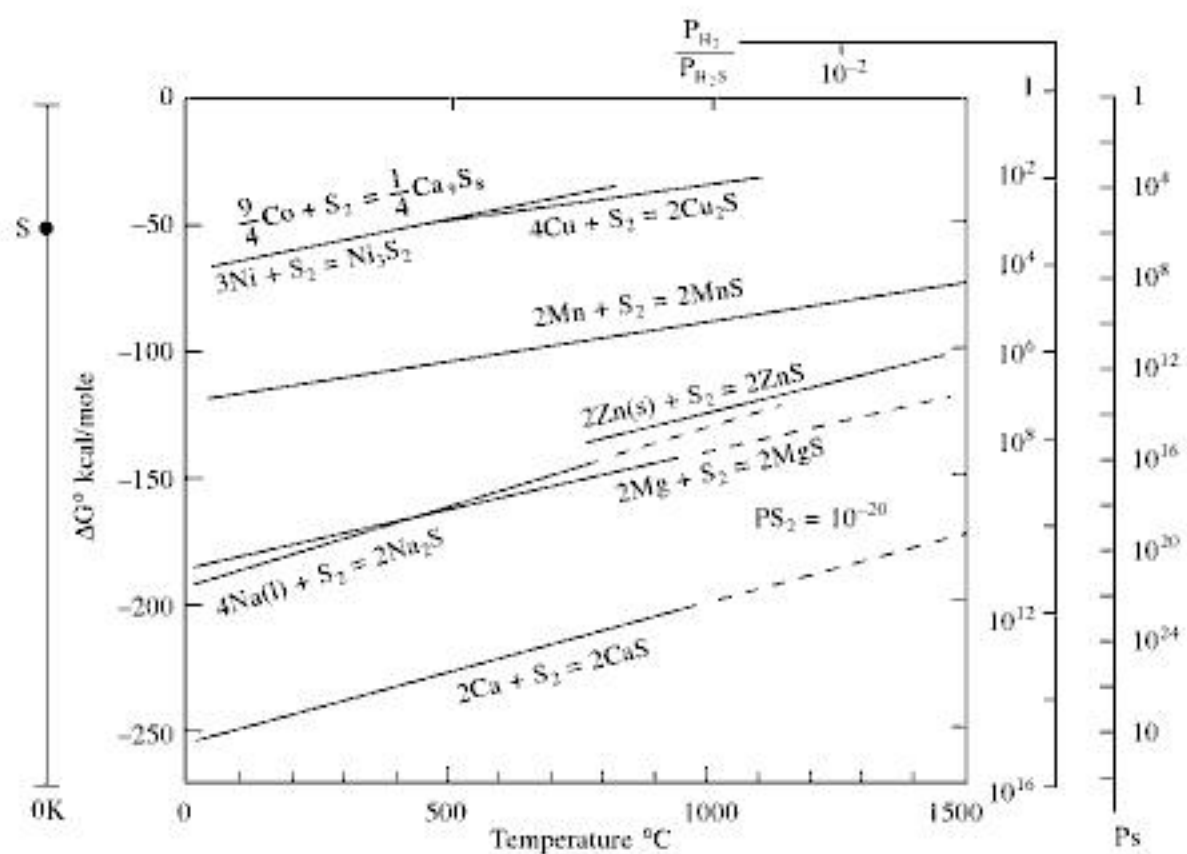


Fig. 1.4 Ellingham diagram for various sulphides.

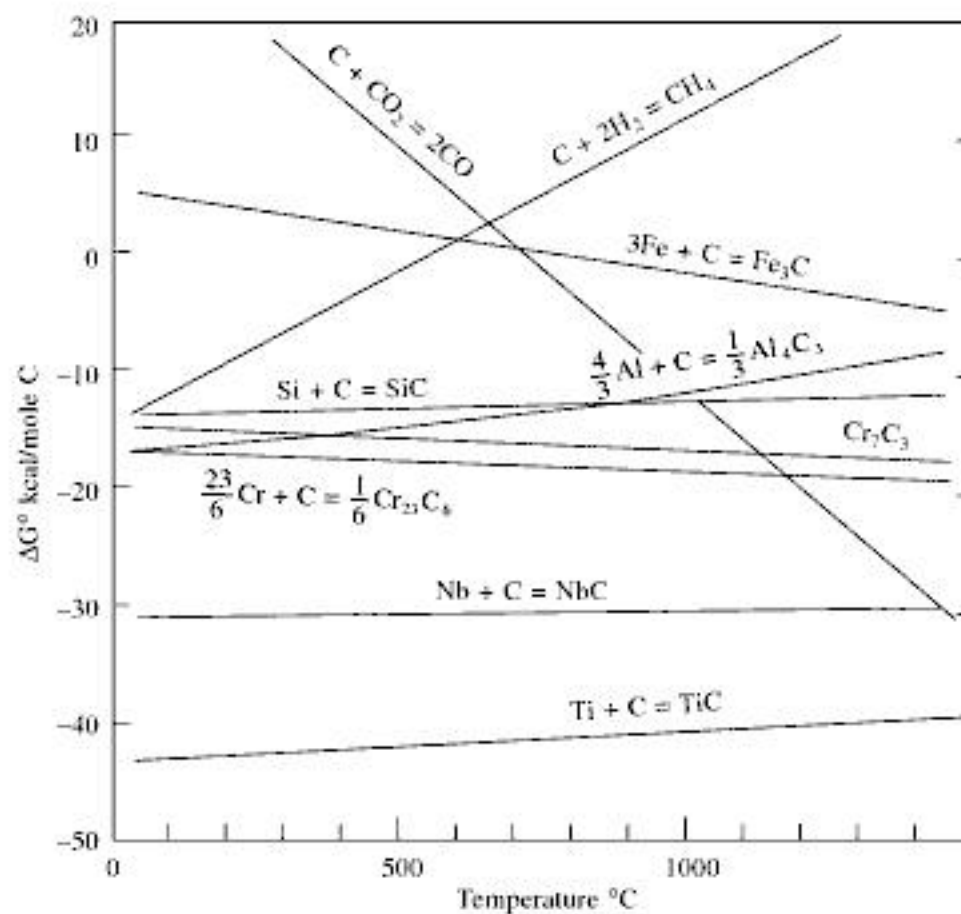


Fig. 1.5 Ellingham diagram for some important carbides.

kinetics of oxidation reactions. Further, if formation of more than one oxide is possible, the diagrams cannot *a priori* tell us what oxide will form in the given environment. The reaction kinetics of formation of different oxides need to be considered. A combination of thermodynamic and kinetic information can give a better understanding about the behaviour of the oxide. Moreover, knowledge of reaction rates is an important basis for elucidation of reaction mechanism.

Rates of the reactions and the corresponding rate equations for the oxidation of a metal depend upon a number of factors. The most important are: temperature, oxygen pressure, surface preparation and pre-treatment of the metal. For engineering design, kinetics of the oxidation is very important as it gives an estimate of the design life of the metal to be used as a particular component at a specific temperature and environment.

The following different rate laws are commonly encountered : linear, parabolic, logarithmic and combinations of them such as paralinear (combination of linear and parabolic) etc.

### Logarithmic Law

It usually represents oxidation in thin layer regime. In the case of most metals heated at low temperatures, the kinetics usually obey logarithmic behaviour. The rate of reaction rises very fast in the beginning and then slows down, either following a direct or inverse logarithmic law:

$$\text{Direct logarithmic law} \quad x = K \log t + A \quad (1.17)$$

and

$$\text{Inverse logarithmic law} \quad 1/x = B + K' \log t \quad (1.18)$$

where  $x$  can be the change in weight as a result of oxidation, thickness of the oxide formed, the amount of oxygen consumed per unit surface area of the metal or the amount of metal transformed to oxide,  $t$  denotes the time and  $K$  and  $K'$  are the rate constants for logarithmic and inverse logarithmic process,  $A$  and  $B$  are the integration constants. The variation of  $x$  with time is shown in Fig. 1.6.

There are a number of theories to explain the two logarithmic laws. These are based on the transport of either ions or electrons. These are discussed in a subsequent chapter dealing with the oxidation in thin layer regime.

### Parabolic Oxidation

From the standpoint of oxidation of engineering alloys, the parabolic law is of great importance. As per this law, the oxide growth occurs with a continuing decreasing oxidation rate. The rate of the reaction is therefore inversely proportional to the scale thickness or the weight of oxide formed. This is represented as:

$$dx/dt = K_p/x \quad (1.19)$$

or after integrating:

$$x^2 = 2K_p t + C \quad (1.20)$$



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a reaction chamber which is exposed to a furnace. In addition to these essential components, a sophisticated balance can have a vacuum system so that oxidation is carried out in a vacuum or at various pressures and a gas inlet and outlet system to carry out the tests in different atmospheres. It is also possible to have special modifications of the balance to carry out tests even in corrosive atmospheres, such as water vapour, steam, sulphur dioxide, chlorine etc. Schematic of a bottom loading balance is shown in Fig. 1.8.

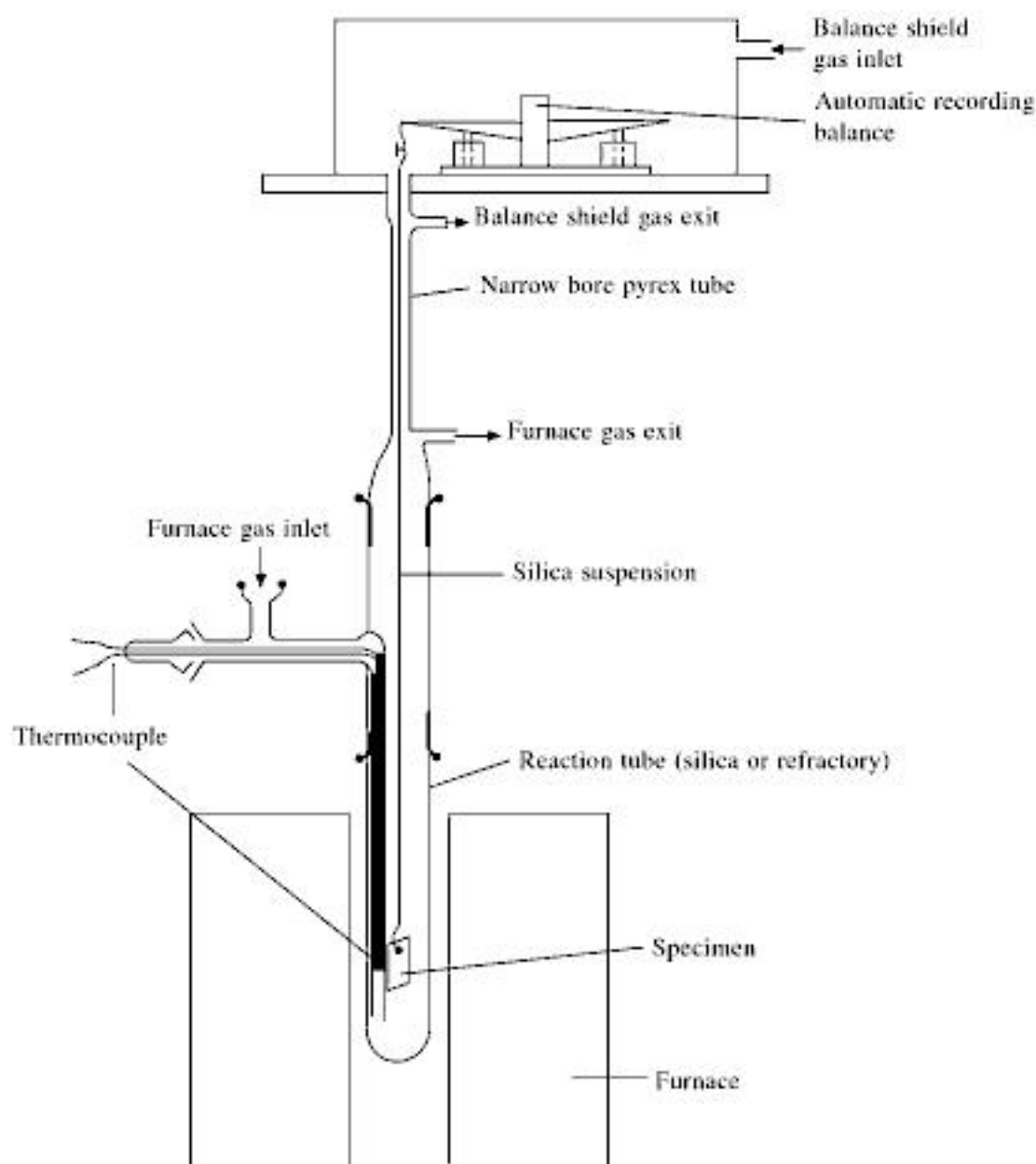


Fig. 1.8 Schematic of a bottom loading balance.

The most important part of a thermobalance is the balance itself. In principle, various types of balances may be employed. Spring balances with quartz or metal helices may serve as inexpensive and reliable balances (Fig. 1.9). Reaction rates in these are measured by measuring the change in the elongation of the helix with a cathetometer. Torsion and other types of balances of varied design and sensitivity are also used. Most of the commercial

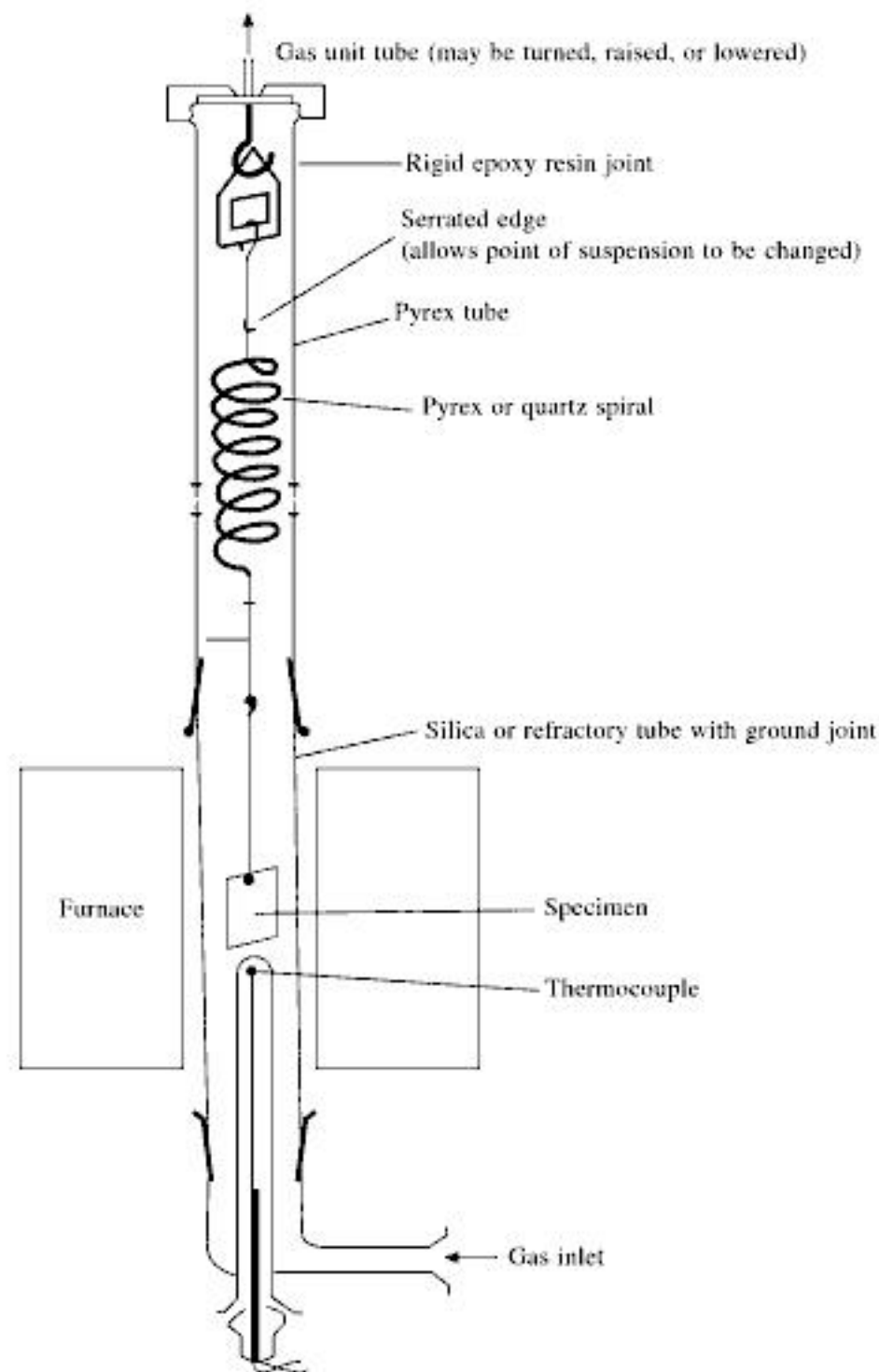


Fig. 1.9 Schematic of a bottom loading continuous recording spring thermobalance.

balances such as the Cahn balances are of the electromagnetic type, where deflection of the beam as a result of weight change is balanced by generating a magnetic field which in turn generates a current equivalent to the force required to bring the beam back to the original or null position. The current required to do so is a measure of weight change and is amplified and recorded in terms of the voltage generated. Balances with various sensitivities are available. Measurement of weight change to an accuracy of  $10^{-6}$  g/cm<sup>2</sup> is usually adequate for oxidation studies and many commercial balances are available with such sensitivity.

Figure 1.8 is a schematic of a simple continuous recording thermobalance. As can be seen the equipment consists of a balance attached to a chamber, which goes into a furnace. In order to carry out test under full isothermal conditions, the furnace can be heated separately and then raised around the sample chamber. Also the inlet and outlet in the reaction chamber provide facilities to carry out tests in any atmosphere.

A versatile thermobalance for high temperature corrosion studies was made by Mettler, of Switzerland. Here the sample is loaded in an upright position. The main advantage of this system is that one can carry out tests in a vacuum, or other gases. There is also a special arrangement to carry out tests in steam or corrosive gases by modifying the chamber. The view of the balance is shown in Fig. 1.10 and the special chamber for steam oxidation in Fig. 1.11. The steam is made by boiling water and is carried to the chamber by a carrier gas such as nitrogen. In order that the steam does not enter the balance chamber, another gas of higher density and at a higher flow rate is passed through the sample chamber which keeps the steam limited to the special chamber only. Any steam which comes down is converted to water and is collected in the reservoir. A similar system with a slight modification is used to carry out tests in corrosive gases, such as sulphur dioxide and chlorine. A similar technique to that used in the case of steam is applied to restrict the corrosive gas in the reaction chamber, i.e. by passing a protective gas from the reaction chamber. There are arrangements to attach the

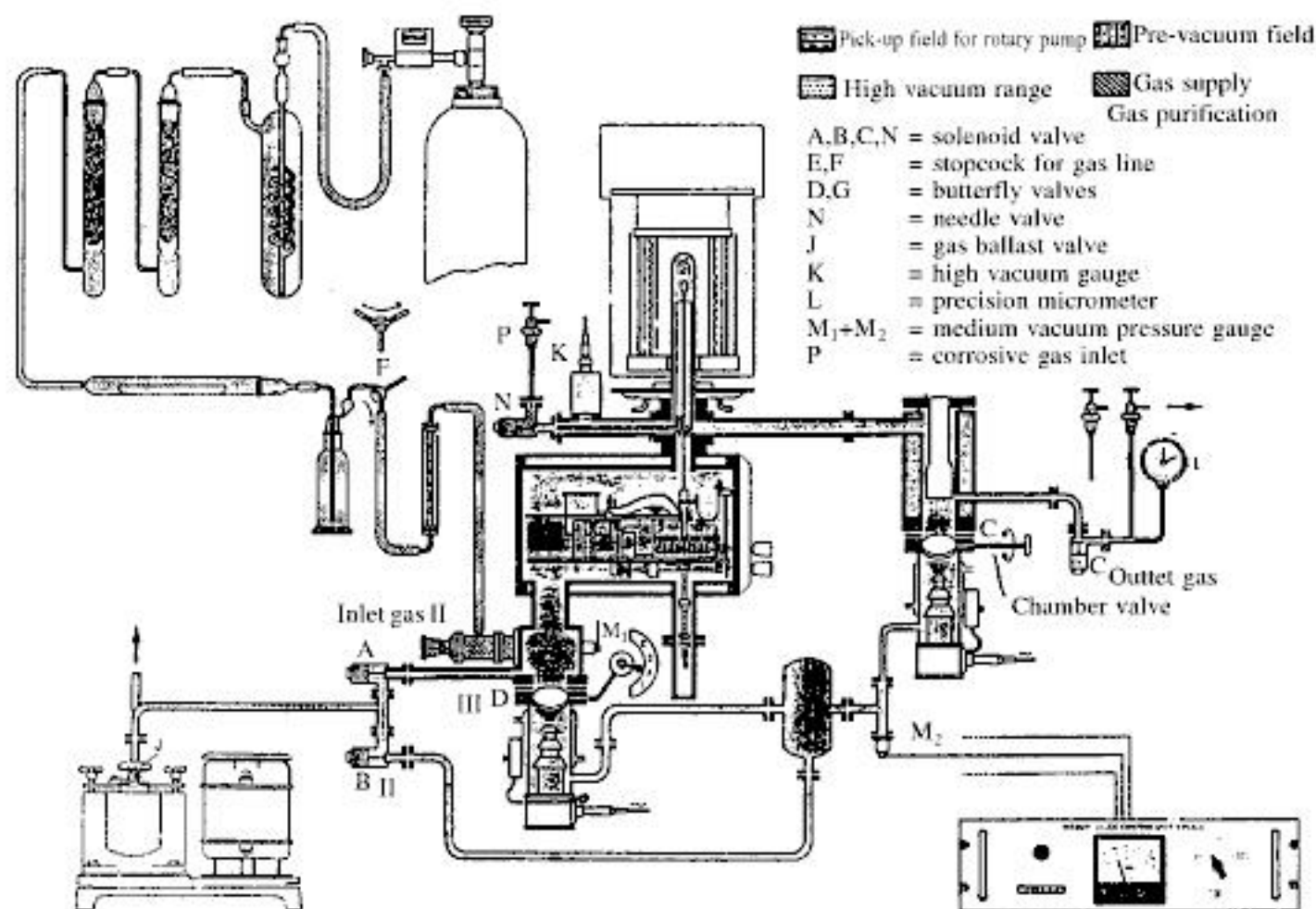
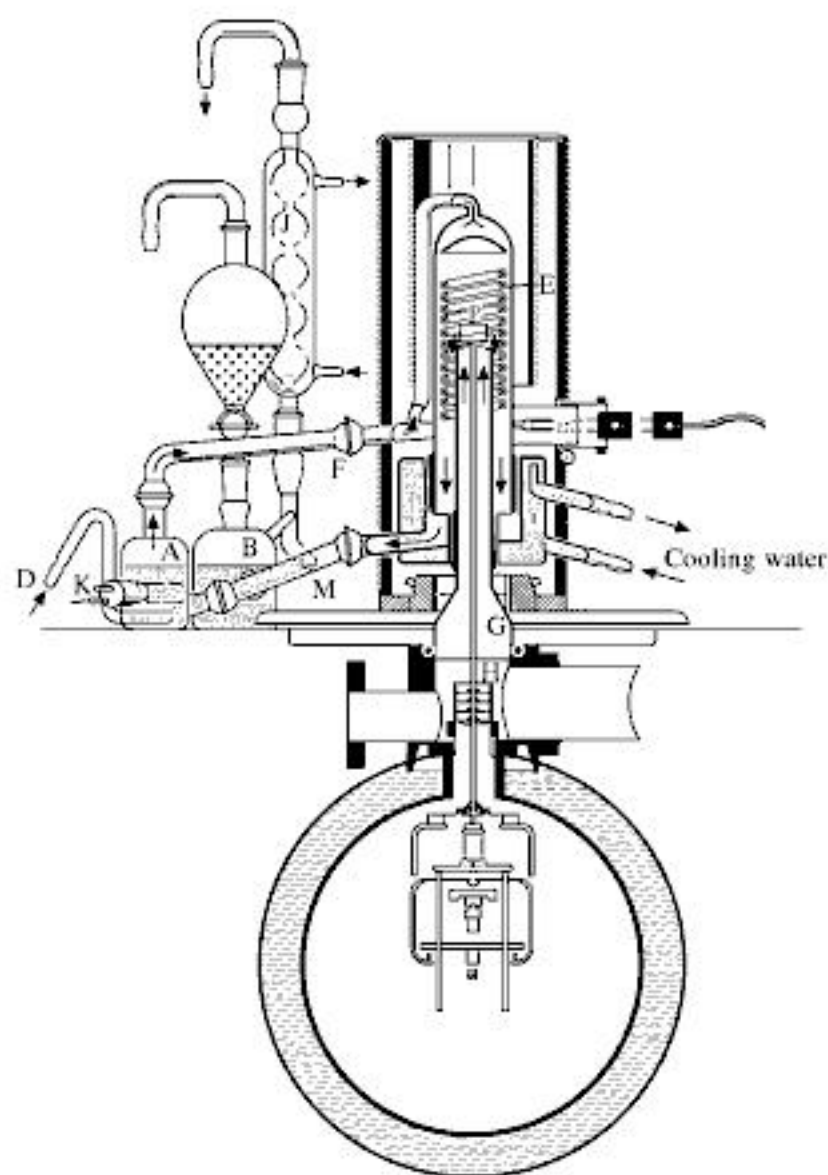


Fig. 1.10 Schematic of a Mettler thermobalance.

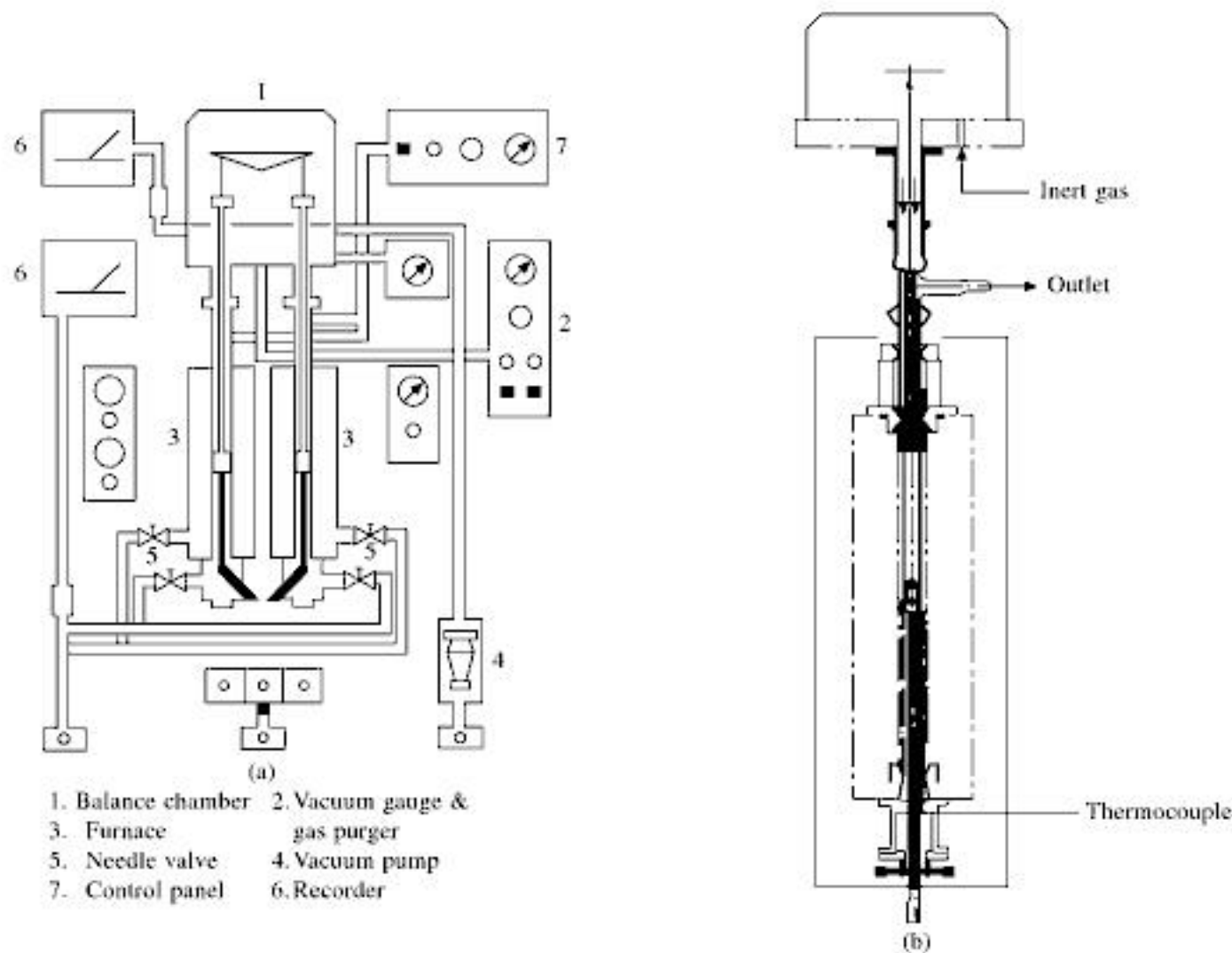


**Fig. 1.11** Schematic of a special atmospheric furnace for oxidation in steam.

system to a gas chromatography analyser or to a mass spectrometer to analyse the gaseous products.

Another versatile system now available in the market is from Setaram, France, Fig. 1.12. Two types of balance are available, symmetrical (a) and single pan (b). In the symmetrical balance, the sample is suspended in one pan and the other is balanced by counter weights. The balance has special features like an automatic gas changing system. Tests in vacuum and under high pressures and in other gaseous environments can be carried out. The balance promises high accuracy and reproducible results.

Another way of measuring oxidation kinetics of alloys in closer industrial environments, such as a simulating combustion environment in gas turbines, is by *burner rigs*. The test environment is produced by combustion of fuel with air. An example of such a system is shown in Fig. 1.13. This burner rig system produces a high velocity gas stream and it is also possible to carry out test in thermal cycling conditions. Samples are loaded in a carousel, rotating at a constant speed to ensure similar test conditions to all the samples. These are then



**Fig. 1.12** (a) A symmetrical thermobalance which provides the best accuracy in scanning and horizontal modes, maximum temperature 1500°C with gas purging facility, (b) Single pan asymmetric balance to carry out test in air, inert gas or corrosive gas.

withdrawn automatically after a definite period from the hot zone, cooled, weighed and replaced. Burner rig tests can also be used to carry out hot corrosion tests by injection of salts in desired amounts and of desired composition.

## Other Methods of Measuring Oxidation Kinetics

### *Oxygen consumption measurement*

The consumption of oxygen during oxidation may also be followed by volumetric and manometric methods. The equipment consists of a reaction chamber connected to a reservoir of reacting gas. The reaction rate is measured by measuring the pressure drop in the system or by measuring the volume of the gas consumed. Oxygen consumption can be measured by measuring the position of an indicator (mercury or diethylphthalate), stored in a long capillary, connected to the reservoir. In both these techniques of volumetric or manometric analysis, the apparatus should be fully thermo-stat. These methods should also be used preferably for



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to silvery; and yellow to brown-red-blue-green in the second order. The compositions of the oxide are close to NiO and PbO. The films formed on heating iron at 250°C, for example, consist of rhombohedral  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, with magnetite underneath it. Magnetite is fairly opaque and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which is responsible for producing colours, is less transparent than NiO, so that the later colours are weak or missing. The sequence in first order is yellow-brown-mauve-blue-silvery grey and in the second order is pinkish blue-blue-greenish blue. The invisible film formed on iron exposed to dry air at 18°C consists of cubic oxide  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

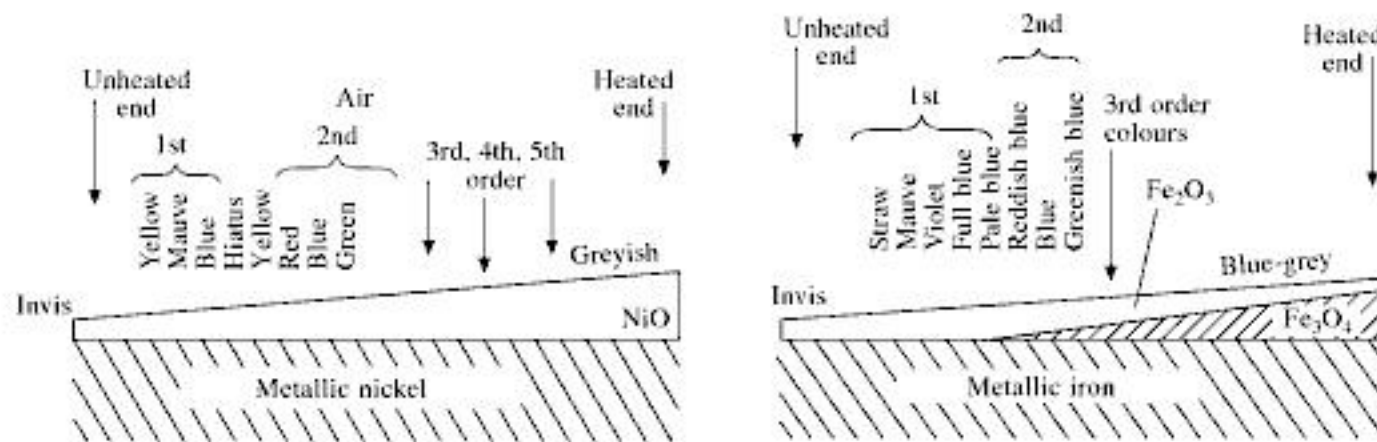


Fig. 1.16 Interference colours obtained on pure nickel and iron when they are heated.

## IDENTIFICATION AND CHARACTERIZATION OF SCALES

Reaction kinetics gives information regarding how fast the oxidation will occur or how long a metal will survive in an atmosphere at a particular temperature. If the aim is to understand the mechanism of oxidation, so that the oxidation behaviour of the metal or alloy can be improved, then detailed information about the scale constituents, scale structure, and composition must be known. There are now a number of techniques which can be used to obtain this information. The simplest is visual and stereo-microscopic analysis which give information about the scale cracks, spallation, exfoliation etc. The scale is then subjected to either X-Ray diffraction analysis to identify the various oxides formed during oxidation or subjected to Scanning Electron Microscopy coupled with Energy Dispersive X-ray Analysis (EDAX) for surface topography, surface morphology and surface composition. Information such as nodule formation, convoluted layers, and type of oxide, whether it is crystalline or amorphous, can be obtained from SEM.

### Scale Cross-section Gives Important Information About:

1. Different oxide layers formed and the sequence in which they are formed.
2. The composition of different layers.
3. Scale adherence, scale porosity, adherence between various oxide layers.
4. Distribution of various elements in the scale—using X-ray mapping.
5. Concentration profiles of various elements.



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lattice are described by a symbol followed by a subscript. For an oxide, the various defects are written as:

- $V_o$  — oxygen vacancy
- $V_m$  — metal vacancy
- $O_i$  — oxygen interstitial
- $M_i$  — metal interstitial

In principle, all types of defects are possible in a solid. However, the free energy of the formation of different types of defects has widely different values, and correspondingly one type of defect structure commonly predominates in a particular solid. The relative concentration of different types of defects is a function of temperature and other variables which influence the state and composition of the solid.

Point defects may be neutral or charged. The charge of a defect is always indicated as the effective charge, i.e. the charge expressed with reference to the charge normally present in the same position in the host lattice. In the Kroeger Vink notation, the effective charge is indicated by a superscript: a dot (.) for each unit of positive charge, a prime (') for each unit of negative charge and a cross (x) for a neutral defect (effective charge of zero). For example:

- $O_O^x$  — represents an oxygen atom on its normal lattice position;
- $O_O''$  — represents an oxygen vacancy with an effective charge of +2;
- $O_m'$  — represents a metal vacancy with an effective charge of -1;
- $O_i''$  — represents an interstitial oxygen ion;
- $O_i^x$  — represents an interstitial metal ion with valance +2;
- $O_{fm}^x$  — represents a foreign cation of valance +2 on  $M^{4+}$  site.

An electron in the lattice is represented by  $e [M_m']$  and electron hole as  $h [M_m']$ .

Concentration of defects are written in square brackets e.g.  $[V_o'']$  indicates the concentration of doubly charged oxygen vacancies. In the case of electrons and holes, the concentrations are written as  $n$  and  $p$  instead of  $e$  or  $h$  respectively.

Figure 2.1 illustrates the two most common defects, found in solids: the Frenkel defect, a cation vacancy, and an interstitial and Schottky defect, a pair of cation and anion vacancy.

In addition to Schottky and Frenkel disorders, other possible defects can be:

|                                  |                 |
|----------------------------------|-----------------|
| A pair of interstitial atoms,    | $O_i'' + M_i^x$ |
| Displaced atoms                  | $O_m + M_o$     |
| Vacancy and misplaced atoms      | $V_m'' + M_o$   |
| Interstitial and misplaced atoms | $M_i^x + O_m$   |

However, these defects are found to be of little importance in comparison to the most common Schottky and Frenkel disorders.

## NONSTOICHIOMETRY

For a long time, it was believed that inorganic compounds had a definite composition,



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1. If the valence of the substituting cation is lower than the valence of the host lattice, cation defects will be created in the cation sublattice of the type  $M_{fm}$ , where  $M_{fm}$  designates the foreign cation. In order to maintain electrical neutrality, this will lead to the formation of an oxygen vacancy on the oxygen sublattice. A typical example is CaO-doped  $ZrO_2$  which is a good oxygen conductor due to the presence of oxygen vacancies formed by Zr doping.
2. If the substituted cations have the same valence as the host lattice cations, no point defect will be created, but the ability to form electronic defects might be changed.
3. When the substituting cation has a higher valence than the host lattice cation, a defect of the type inferior will be formed. In order to compensate for the extra charge, interstitial oxygen  $O_i''$  will be formed. This behaviour has been observed in  $ZrO_2$ -doped  $Y_2O_3$ , which due to the presence of  $O_i''$  shows some oxygen conduction.

### CALCULATION OF DEFECT CONCENTRATION

Concentration of point defects is usually expressed as site fraction, whereas electronic defects are more conveniently expressed as number per unit volume.

The site fraction of a given defect is directly related to the deviation from stoichiometry and can be derived as follows:

Let  $N_o$  = total number of lattice oxygen sites,  
 $N_m$  = total number of lattice metal sites,  
 $N_{v,o}$  = number of oxygen vacancies,  
 $N_{v,m}$  = number of metal vacancies,  
 $n_o$  = number of oxygen ions interstitial sites,

then for an oxygen-deficient oxide with the composition  $MO_{2-x}$ ,

$$\frac{O}{M} = \frac{2-x}{1} = \frac{(N_o - N_{v,o})}{N_m} \quad (2.12)$$

for an oxide of type  $MO_2$

$$N_o = 2N_m \quad (2.13)$$

thus

$$\frac{2-x}{1} = \frac{2(N_o - N_{v,o})}{N_o} = 2 \left( 1 - \frac{N_{v,o}}{N_o} \right) \quad (2.14)$$

which gives

$$\frac{N_{v,o}}{N_o} = [V_o^{\bullet}] = \frac{x}{2} \quad (2.15)$$

Thus oxygen vacancy concentration of an oxide of type  $MO_{2-x}$  is equal to half of its deviation from stoichiometry ( $x$ ).



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Application of the law of mass action to this reaction gives

$$K_{(V_m'')} = [V_m''] [M_m']^2 p(O_2)^{-1/2} \quad (2.33)$$

after insertion of the neutrality condition:

$$2M_m' = V_m'' \quad (2.34)$$

Eq. 2.33 becomes

$$K_{(V_m'')} = 4[V_m'']^3 p(O_2)^{-1/2} \quad (2.35)$$

Thus for these oxides

$$[V_m''] = 1/4 K_{(V_m'')}^{2/3} p(O_2)^{1/6}$$

$$[V_m''] = K'_{(V_m'')} p(O_2)^{1/6} \quad (2.36)$$

and a plot of  $\log [V_m'']$  vs  $\log p(O_2)$  will give a straight line with a slope of 1/6. This is given in Fig. 2.2 along with the behaviour of other defects.

### Oxides with Both Vacancy and Interstitial Defects

So far we have considered such oxides which had only one type of defect, vacancy or interstitial. There are certain oxides which have both types of defects. For example, it can exist as a substoichiometric oxide  $UO_{2-x}$ , (e.g. at high pressures), in which  $V_O^\cdot$  are the main defects while at low pressures, it can exist as  $UO_{2+x}$  which has  $O_i''$  as the dominant defects. Possible defect equilibria for two cases are:

(a) Formation of  $V_O^\cdot$



$$K_{(V_O^\cdot)} = [V_O^\cdot] n^2 p(O_2)^{1/2} \quad (2.38)$$

(b) Formation of  $O_i''$



$$K_{(O_i'')} = [O_i''] p^2 p(O_2)^{-1/2} \quad (2.40)$$

(c) Intrinsic ionisation

$$\text{Neutral Lattice} = e' + h' \quad (2.41)$$

$$K = np \quad (2.42)$$

This reaction becomes predominant at low defect concentration, i.e. at near stoichiometric compositions.



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the conductivity has a positive temperature dependence. This is in contrast to the case for metallic conductors, for which the conductivity decreases with temperature. The conductivity of nonstoichiometric oxides also lies between that of metals and insulators, and these oxides belong to a group of compounds or elements called semiconductors.

The total conductivity ( $\sigma_{\text{total}}$ ) in an oxide is given by the sum of the electronic ( $\sigma_{\text{electronic}}$ ) and ionic ( $\sigma_{\text{ionic}}$ ) conductivities:

$$\sigma_{\text{total}} = \sigma_{\text{ionic}} + \sigma_{\text{electronic}} = \sigma_{\text{total}} (t_i + t_e)$$

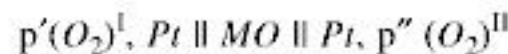
where  $t_i$  and  $t_e$  are the transport numbers of ion and electron respectively.

The mobility of the electronic defects is very much higher than that of point defects, and nonstoichiometric oxides which contain an equivalent number of electronic defects and charged point defects are essentially electronic conductors. When the current is carried out by electron holes, as in metal deficient oxides  $M_{1-x}O$ , or oxides with excess oxygen, the oxide is called a *p*-conductor, on the other hand in the case of oxygen deficient oxide  $MO_{1-x}$  or oxide containing excess metal ( $M_{1+x}O$ ), the oxides are called *n*-conductors.

Information on the defect structure is obtained by measuring the electrical conductivity as a function of oxygen pressure. When the conductivity increases with oxygen pressure, the oxide is a *p*-type conductor, and if it decreases with oxygen pressure, it represents an *n*-type of conductor. Oxygen pressure dependence can be obtained by measuring the value of exponent '*n*' (see Fig. 2.2 and Eqns. 2.31 and 2.32), which gives information about defects and their charge. If the conductivity is independent of oxygen pressure, the oxide may be an electronic conductor.

### Ionic Conductivity

Ionic conductivity is measured by electrochemical cells. The oxide is made electrolyte and is connected to two platinum electrodes at two different sites of the electrolyte. Both these electrodes are maintained at two different oxygen pressures and the cell appears as:



The charge transfer through the cell may be reduced to an equivalent circuit (Fig. 2.4) and is determined by the electronic and ionic conductivities of the oxide. *E* denotes the electrical potential which is given as:

$$E = 2.3RT/4F \log p''O_2^I / p'O_2(g)^{II}$$

where *R* is the gas constant, *T* is absolute temperature, and *F* is the Faraday constant. The potential difference due to the separation of ionic charges  $E_m$  is related to *E* through

$$E_m = t_i E$$

where  $t_i$  is the transference number of the charged species. When the oxide is an ionic conductor,  $E_m = E$ . For an electronic conductor  $E_m = 0$ .

$p'$  and  $p''$  may be fixed by establishing different gas partial pressures or by equilibrating with metal + oxide mixtures on either side of the oxide crystal.

Wagner was the first to establish that  $ZrO_2$  could be stabilized by addition of other oxides,



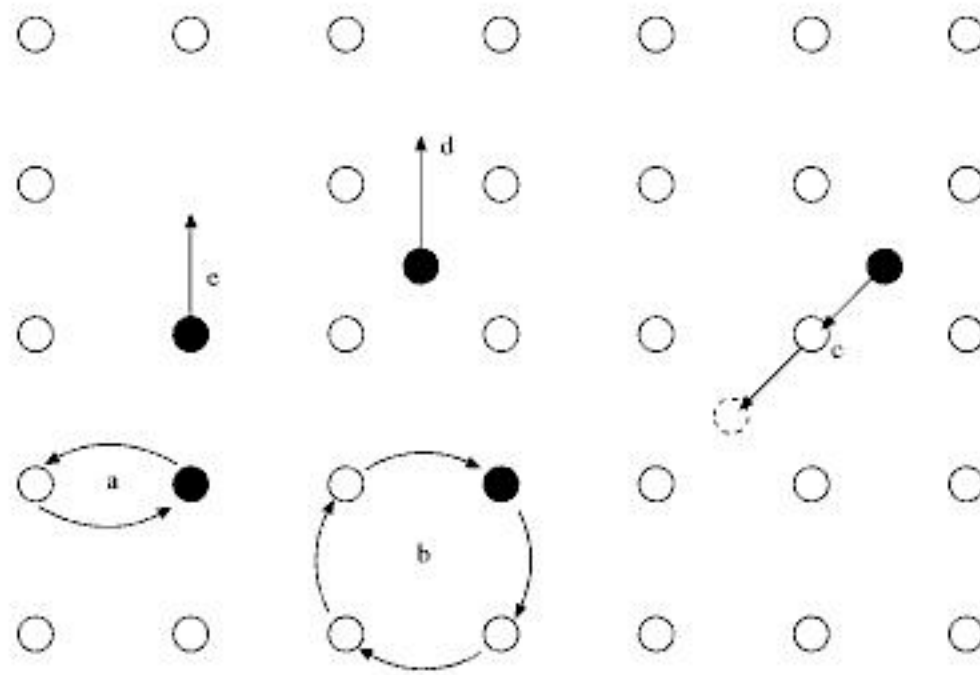
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**Fig. 3.1** The various displacement mechanisms of diffusion: (a) place exchange; (b) ring mechanism; (c) interstitialcy mechanism; (d) interstitial atom movement; and (e) vacancy mechanism.

another common mechanism such as jumping into a vacancy. Therefore, it is not a very important mechanism of diffusion in metals.

**(b) Ring mechanism:** where the exchange takes place between four neighbouring atoms in a ring. This was first suggested by Zener. It is assumed that thermal vibrations are sufficient to cause a number of atoms, which form a natural ring in a crystal, to jump simultaneously in a synchronised manner such that each atom in the ring advances by one position around the ring.

**(c) Interstitialcy mechanism:** when the interstitial atom moves to a regular lattice site, forcing the atom at the regular site to the next interstitial position.

**(d) Interstitial atom movement:** where the atoms move from one interstitial position to the next.

**(e) Vacancy mechanism:** when the atom moves from its regular site to the nearest vacant site. This is the most important mechanism by which large atoms, when substituted at the normal lattice position, move in a lattice.

The Mechanisms (a) and (b) are possible in perfect crystals, while (c), (d) and (e) can occur in imperfect crystals. Vacancy diffusion, for example, is possible in crystals with Schottky defects, while interstitial movement of atoms occurs in crystals with Frenkel defects.

Diffusion in perfect crystals such as described above, is usually called volume diffusion. It is also referred as lattice diffusion or bulk diffusion. In practice, diffusion can also occur in other regions of a crystal, such as jumps along the surface, grain boundary, dislocation or cracks. Diffusion through these paths is termed as short circuit diffusion. Since the lattice at these paths is relatively less densely packed than the bulk lattice, jumping of atoms is relatively easier, leading to faster diffusion of atoms. As a result, diffusion in polycrystalline materials often proceeds much faster than in single crystals.



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using Fick's first law (Eq. 3.3), this can be written as

$$J - J' = - \frac{d}{dx} \left( -D \frac{\partial c}{\partial x} \right) dx \quad (3.9)$$

The accumulated flux per second,  $J - J'$ , is nothing but the rate of change in concentration,  $dc/dt$ , therefore

$$\begin{aligned} \frac{dc}{dt} &= \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \\ &= D^2 \frac{\partial^2 c}{\partial x^2} \end{aligned} \quad (3.10)$$

is Fick's second law when diffusion is considered in only one direction. When diffusion is considered in three dimensions, Eq. 3.10 becomes:

$$\begin{aligned} \frac{dc}{dt} &= D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) \\ &= D \nabla^2 c \end{aligned} \quad (3.11)$$

## SOLUTION OF DIFFUSION EQUATION

Fick's two laws of diffusion Eq. 3.3 and Eq. 3.10 are differential equations and must be solved to obtain algebraic equations describing the variation of concentration as a function of distance and time.

Since Fick's first law,  $J = -D dc/dx$ , does not explicitly consider the change of concentration with time, its use is limited to steady state diffusion, in which the concentration remains constant at each point. This can be illustrated with a diaphragm type of experiment used in measuring the rate of diffusion of a gas through a metal. The gas is maintained at a higher pressure  $p_1$  on one side of the diaphragm and at lower pressure  $p_0$  on the other side. After sufficient time, a steady state will be reached, i.e. the rate at which the gas enters the metal diaphragm on the high pressure side becomes equal to the rate at which it leaves the metal on the low pressure side. Also, the concentration of dissolved gas at each point within the diaphragm does not change with time. This therefore implies that the concentration gradient  $dc/dx$  is constant and therefore can be written as  $(C_0 - C_1)/\Delta x$ , where  $C_0$  and  $C_1$  are the concentrations on either side of diaphragm and  $x$  is the thickness of the diaphragm. The relation between concentration of diffusing gas and distance, therefore becomes linear as shown in Fig. 3.4.

Differential equation (3.10) for Fick's second law can be solved, provided the boundary conditions are known. This will be exemplified by a tracer diffusion experiment to determine the self-diffusion of a diffusing species e.g. determining the self diffusion of Zn in ZnO. A thin layer of  $^{65}\text{Zn}$  can be deposited on one end of a ZnO rod by evaporation or by other



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$$2\sqrt{Dt} (C - C_0) \int_0^\infty (1 - \operatorname{erf}) d(x/\sqrt{Dt})$$

The definite integral has a value  $1/\pi$ ; thus the total amount of diffusing substance which has crossed unit area of the bounded surface up to time  $t$  is  $1.1284 \sqrt{Dt} (C_s - C_0)$ .

### KIRKENDALL EFFECT

When two metals with a large difference in their diffusion coefficients interdiffuse, there is a net transport of material across the plane that initially separated them. This phenomenon is known as the *Kirkendall effect* and can be demonstrated by an experiment shown in Fig. 3.6. A diffusion couple is made by joining a gold and nickel bar so that diffusion occurs across the marked interface. An inert metal such as tungsten can be used as a marker and can be placed in the plane of joining. Such a couple is subjected for annealing at a sufficiently high temperature, e.g.  $1000^\circ\text{C}$  or more for a long time so that interdiffusion of gold and nickel will occur, resulting in a change in concentration distribution as shown in the figure. However, since,  $D_{\text{Au}} > D_{\text{Ni}}$ , more gold atoms than nickel atoms will have diffused past the inert markers. Consequently, the inert markers will no longer be at their original positions but will have moved toward the gold end of the specimen. This movement is known as the *Kirkendall shift*.

The fact that the flux of gold is greater than that of nickel, means that a net flux of vacancies occurs across the Kirkendall interface. In the absence of reactions involving the

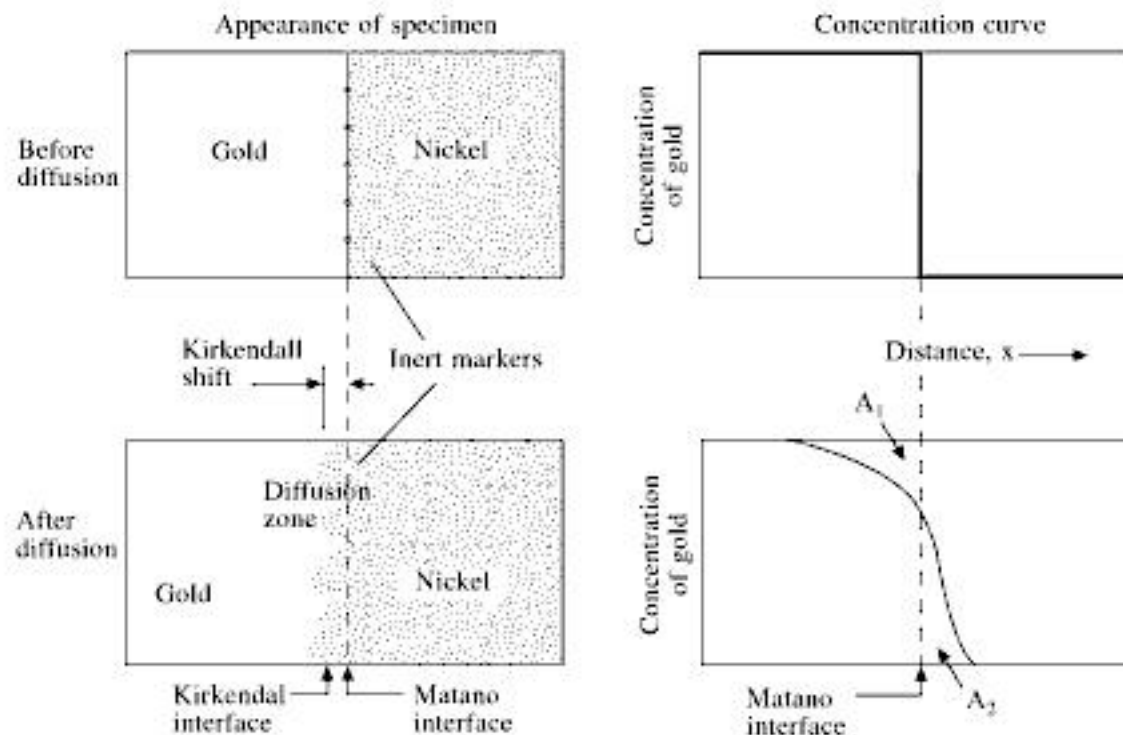


Fig. 3.6 Schematic of Kirkendall effect.



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much lower value of activation energy for the grain boundary diffusion. Fig. 3.8 shows that the apparent diffusion co-efficient,  $D_{app}$ , begins to deviate from  $D_v$  at sufficiently low temperatures because of the increasing contribution of grain boundary diffusion.

### TEMPERATURE DEPENDENCE OF DIFFUSION

Two factors mainly account for the large increase in the rate of diffusion with an increase in temperature: the increase in the jump frequency of the atoms, and the increase in the equilibrium concentration  $N_v$  of the vacancies (or other defects), thus increasing the number of atom/vacancy pairs for jumping. We will first consider the case of a crystal in which diffusion occurs by interstitial mechanism as it does not involve  $N_v$ . However, the same type of reasoning also applies to jumping by vacancy mechanism.

*Interstitial diffusion:* An interstitial atom must possess an exceptional amount of energy before it can jump out of its interstice. The energetics of an interstitial atom are shown in Fig. 3.9. The interstitial atom at its initial site can be represented by position 1 which is confined to the bottom of the potential energy valley. The average thermal energy  $kT$  of the atom is far too small to permit it to jump to the neighbouring site. However, due to statistical

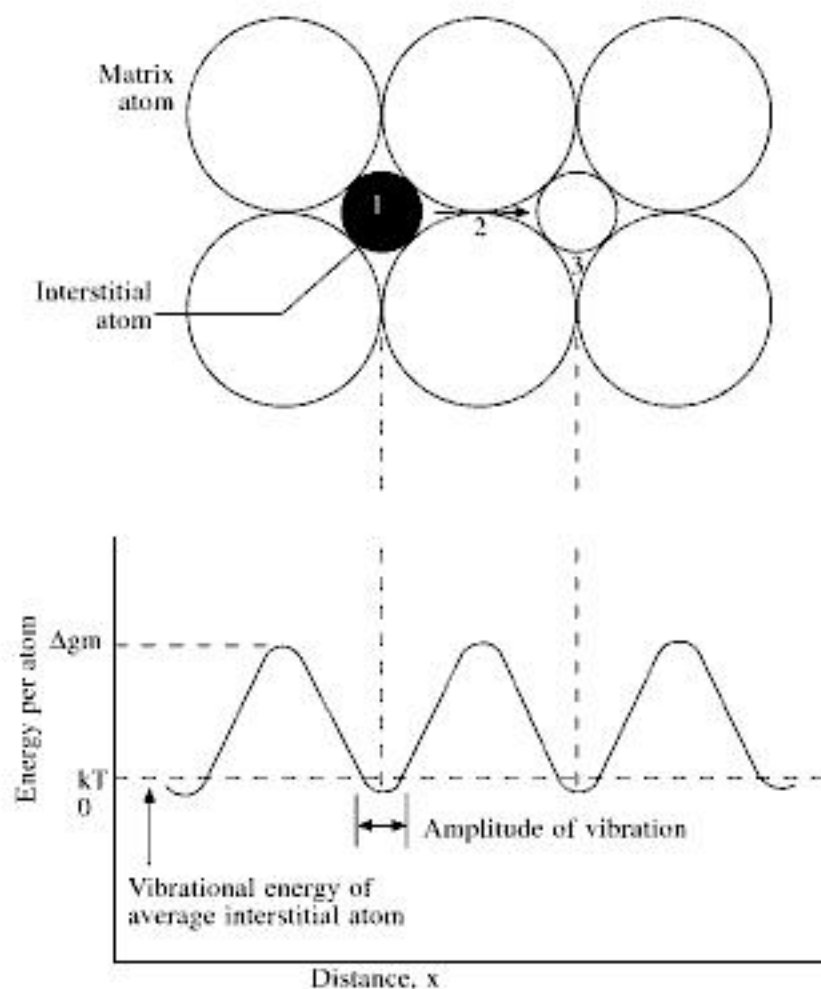


Fig. 3.9 Energetics of the jumping of interstitial atom from its position to the next interstitial position.



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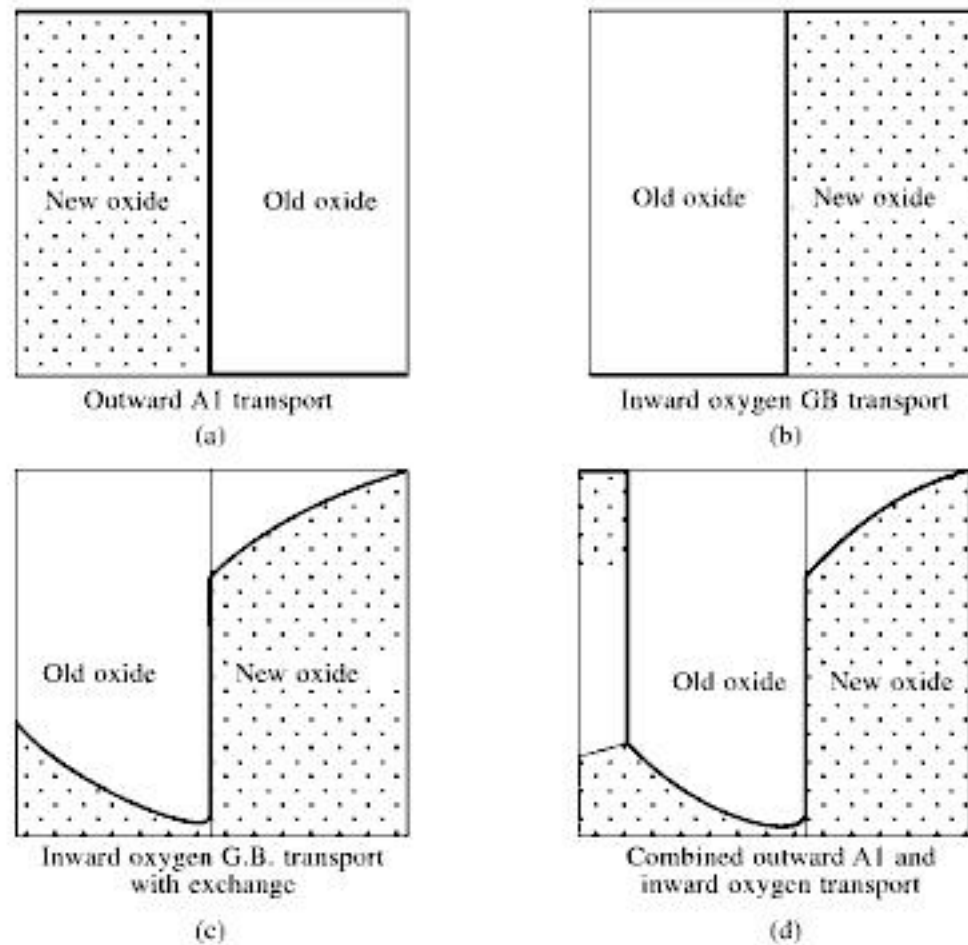


Fig. 3.12 Oxygen tracer profiles of oxides formed.

without disturbing the old oxide formed under natural oxygen (Fig. 3.12a). In case the mechanism is dominated by inward transport of oxygen ions, the new oxide will appear next to the metal/oxide interface, while the old oxide at the gas/oxide interface appears as shown in Fig. 3.12b. In these ideal cases, no exchange of tracers occurs with natural oxygen. When exchange occurs, the inward diffusion profile is slightly modified to account for this exchange process and is shown in Fig. 3.12c. Finally, if the diffusion mechanism is a combination of the outward movement of metal ions and the inward movement of oxygen ion the profile appears as shown in Fig. 3.12d.

### Mass Balance

Once an experimental tracer profile, as discussed above, is obtained, it is possible to conduct a mass balance test to determine the actual growth mechanism. As given in Fig. 3.13, a normalized concentration profile can be plotted in which the  $X$ -axis depicts the fraction of the total scale thickness, while the  $Y$ -axis depicts concentration of the tracer, as a fraction of the maximum tracer concentration in the scale.

Since every atom of  $^{18}\text{O}$  in the oxide entered in when the sample was exposed to the  $^{18}\text{O}$  environment, the number of the lattice sites occupied by tracer atoms in the oxide scale must be the same as the number of oxygen lattice sites, created in the oxide during tracer oxidation. This concept can be used to calculate the thickness of the new oxide  $Y_{\text{new}}$  as shown in Fig. 3.13b. The amount of  $^{18}\text{O}$  in the total oxide is equal to the area B in Fig. 3.13b. Having



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# 4

## Initial Oxidation

The study of initial oxidation is the most important as it is the first step of metal reaction, when exposed to an aggressive environment. At high temperatures, the reaction is so fast that it is difficult to estimate the gas/metal interactions in the initial stages. Thus, in order to know the mechanism of oxidation at the initial stages, experiments are conducted at either low temperatures or low pressures at high temperatures. In both these cases, the high temperature oxidation process is viewed at a slow speed in a manner similar to observing a movie in slow motion. The rate of reaction and hence the kinetics are quite different under these conditions and sometimes these match the kinetics of noble metals which usually exhibit very low oxidation rates.

Before talking about initial oxidation, it is important to first define a clean surface. According to the kinetic theory of gases, for  $1 \text{ cm}^2$  of clean surface, which has about  $10^{15}$  sites, it will take less than a second to form a monolayer of the oxide at room temperature and at a pressure of  $\approx 10^{-9}$  atm. This means that to keep the surface of an active metal clean, it must be kept in an environment with a pressure much lower than  $10^{-9}$  atm. Thus a totally clean metal surface is seldom, if ever found in nature and must be prepared if needed for experimental work. This is the reason, why sophisticated surface analysis techniques, such as Auger Electron Spectroscopy (AES), X-ray Photo Electron (XPS), Scanning Ion Mass Spectroscopy (SIMS), Low Energy Electron Diffraction (LEED) etc. require a pressure of the order of  $10^{-10}$  atm. At normal atmospheric pressure and temperature, most of the metal surfaces have an oxide layer which must be cleaned prior to using the metal for early oxidation studies. Techniques such as *in situ* sputter cleaning of the surface or reducing the oxide by heating in hydrogen, are usually employed to remove the existing scales.

The initial scale formation involves adsorption of oxygen and finally leading to an oxide scale, a few monolayers thick. The entire discussion on the formation of an initial oxide scale is to describe how the phenomenon of adsorption takes place and under what conditions the scale grows laterally to form a thin layer, covering the metal and what are the growth kinetics and structure of this scale. The processes that occur when a clean surface is exposed to oxygen are summarized as follows:

1. Oxygen is adsorbed on the clean metal surface to form a chemisorbed layer.
2. Additional layers of the oxide build up, usually via island growth, possibly through a process of exchange mechanism.



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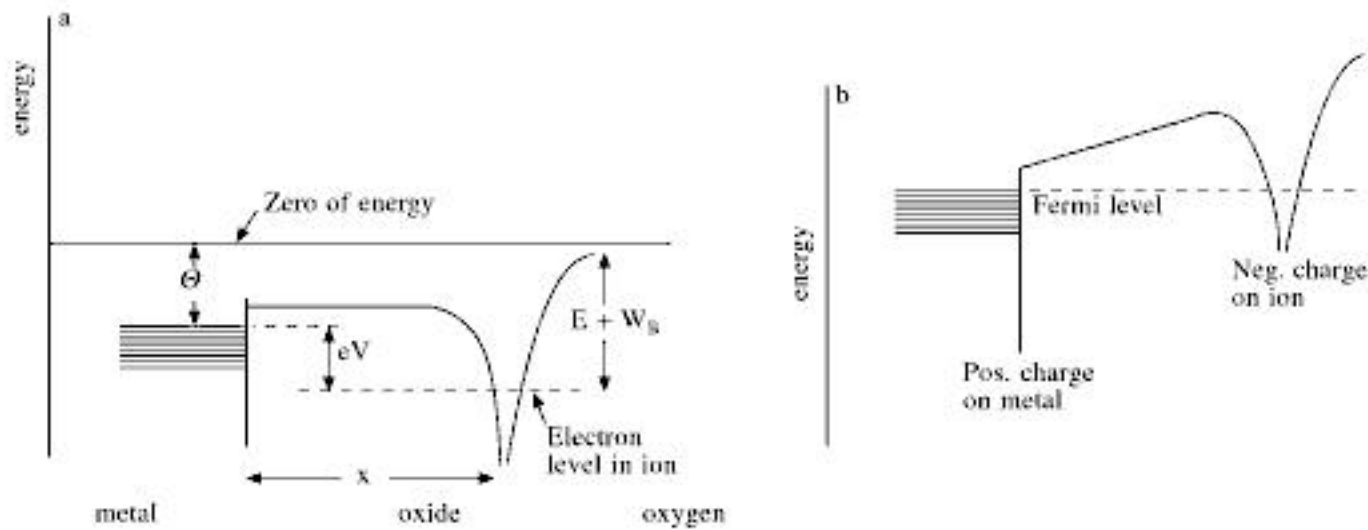


Fig. 4.2 Fermi level of a metal.

the oxide levels below zero is assumed to be given by  $E + W_B$  where  $E$  is the electron affinity of oxygen and  $W_B$  is the energy due to the image force of an electron at a distance  $r$  from an oxide of dielectric constant  $K$ .  $W_B$  is given as:

$$W_B = e^2 (K - 1)/4r (K + 1)$$

We find that  $eV = E + W_B - \phi$ , where  $\phi$  is the work function of the metal. In the above equation, however,  $W_B$  has little significance.

### ELY AND WILKINSIN'S THEORY OF LOGARITHMIC LAW

According to Ely and Wilkinsin, irrespective of the mechanism of ion movement, the activation energy might be of the form

$$W_A = W_O + \mu x$$

where  $\mu$  is a constant and is dependent on the film structure. As a matter of fact many oxides formed at low temperatures have amorphous or glassy structures. Depending upon their bond strength, there have been two main categories in which these oxides can be divided: network formers and network modifiers. The former have a high covalent bond strength of the order of 75 kcal/mole, while the latter are bonded ionically in the network and usually have a bond strength 50 kcal/mole. A few oxides of intermediate bond strength can modify a glass-forming network by becoming part of the network or by bonding ionically with anions in the network.

$\text{SiO}_2$  is an example of the network former. It has a three dimensional random network, having five or six members ring structure as shown in Fig. 4.3. Most of the valence states are saturated and cations are tightly bonded. Such a three dimensional network structure would produce channels extending through the glassy network. In such types of channels, a large ion can move more easily than a small ion, because it is bound less tightly to the glassy network. Therefore, transport by anions is expected in the network former.



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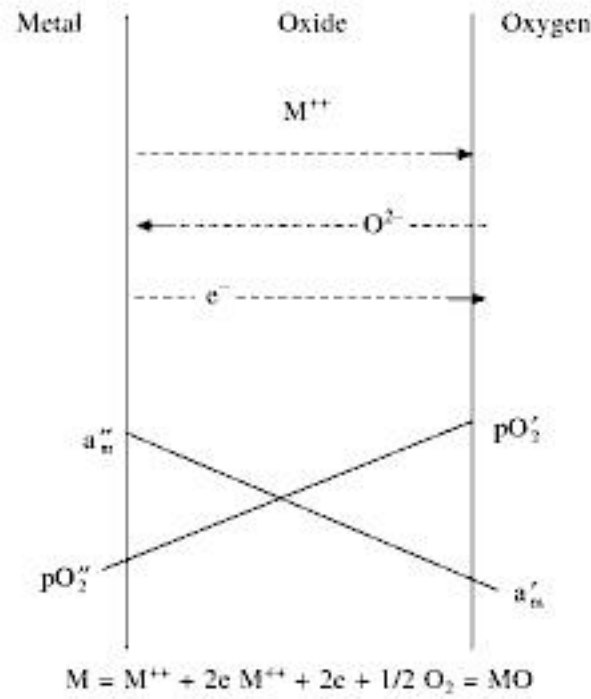


Fig. 5.1 Schematic of scale formation according to Wagner's model.

which together provide the net driving force for ionic migration. Thus a particle  $i$  carrying a charge  $Z_i$  in a position where the chemical potential gradient is  $\partial\mu_i/\partial x$  and electrical potential gradient is  $\partial\phi/\partial x$  is acted upon by force of

$$\partial\mu_i/\partial x + Z_i F (\partial\phi/\partial x) \text{ Joules/mole.cm} \quad (5.1)$$

or by

$$1/N_A(\partial\mu_i/\partial x) + Z_i F (\partial\phi/\partial x) \text{ Joules/particle.cm} \quad (5.2)$$

where  $N_A$  = Avogadro's number

$F$  = Charge in coulombs/mol.

Now, moving through an ionic lattice under a constant force, an ion rapidly assumes a constant velocity known as the terminal drift velocity. The value of the terminal drift velocity, when the ion is acted upon by a unit force is known as the mobility  $B_i$  of that species. Therefore, the flux of the particles moving with a terminal drift velocity  $B_i$  is:

$$\begin{aligned} J_i &= C_i B_i 1/N_A (\partial\mu_i/\partial x) + Z_i F (\partial\phi/\partial x) \text{ particles cm}^2 \text{ sec.} \\ &= C_i B_i (\partial\mu_i/\partial x) + Z_i F (\partial\phi/\partial x) \text{ moles cm}^2 \text{ sec.} \end{aligned} \quad (5.3)$$

where  $C_i$  = concentration in  $\text{cm}^3$

There is a relationship of mobility with the conductivity of that species and this is given by

$$C_i B_i = \sigma_i / Z_i^2 e^2 \quad (5.4)$$

where  $\sigma_i$  = partial conductivity of species  $i$

$e$  = electronic charge



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on integration this gives

$$K_{ZnO} = \text{const}' [(1/pO_2')^{1/6} - (1/pO_2'')^{1/6}] \quad (5.32)$$

Generally  $pO_2''$  is  $\gg pO_2'$  i.e. the partial pressure at the metal/oxide interspace is much smaller. Thus the parabolic rate constant can be assumed to be virtually independent of the pressure of the gas.

Let us take another example—oxidation of Cobalt CoO. It is a metal deficient oxide having cation vacancies and electron holes as per the following equation:



so 
$$K = C_{V_{Co}}' h pO_2^{1/2} \quad (5.34)$$

thus because of electroneutrality  $C_{V_{Co}}' = C_h$

or

$$C_{V_{Co}}' \propto pO_2^{1/4} \quad (5.35)$$

i.e. the conductivity of Columnar vacancies would be proportional to  $1/4$  of the pressure of the gas i.e.

$$\sigma_{co} \propto pO_2^{1/4} \quad (5.36)$$

or 
$$K_{Co}' = \text{const} \int_{pO_2'}^{pO_2''} pO_2^{1/4} d \ln pO_2 \quad (5.37)$$

$$= \text{const} \int_{pO_2'}^{pO_2''} pO_2^{-3/4} d \ln pO_2 \quad (5.38)$$

On integration

$$K_{Co}' = \text{const} [(pO_2)^{1/4} - (pO_2')^{1/4}] \quad (5.39)$$

Thus by knowing the variation of the rate constant with pressure one can determine whether the vacancy mechanism is correct or not. For example in the case of CoO oxidation, the pressure dependence is  $pO_2^{1/4}$  until  $pO_2 = 10^{-5}$  atm. After that the pressure dependence changes to  $pO_2^{1/6}$ . This shows that up to  $pO_2 = 10^{-5}$ , singly charged  $V_{Co}'$  determines the diffusion but after  $10^{-5}$  atm, it is doubly charged  $V_{Co}''$  which determines the oxidation.

## DEVIATION FROM WAGNER'S MODEL

There are only a few oxides which strictly follow Wagner's law. The reasons for this are the basic assumptions. The assumptions that the oxide scale is compact and adherent is not



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Based upon the knowledge of the structure and the diffusion of iron oxides, the mechanism of three layer oxide on pure iron above 570°C is shown in Fig. 6.3.

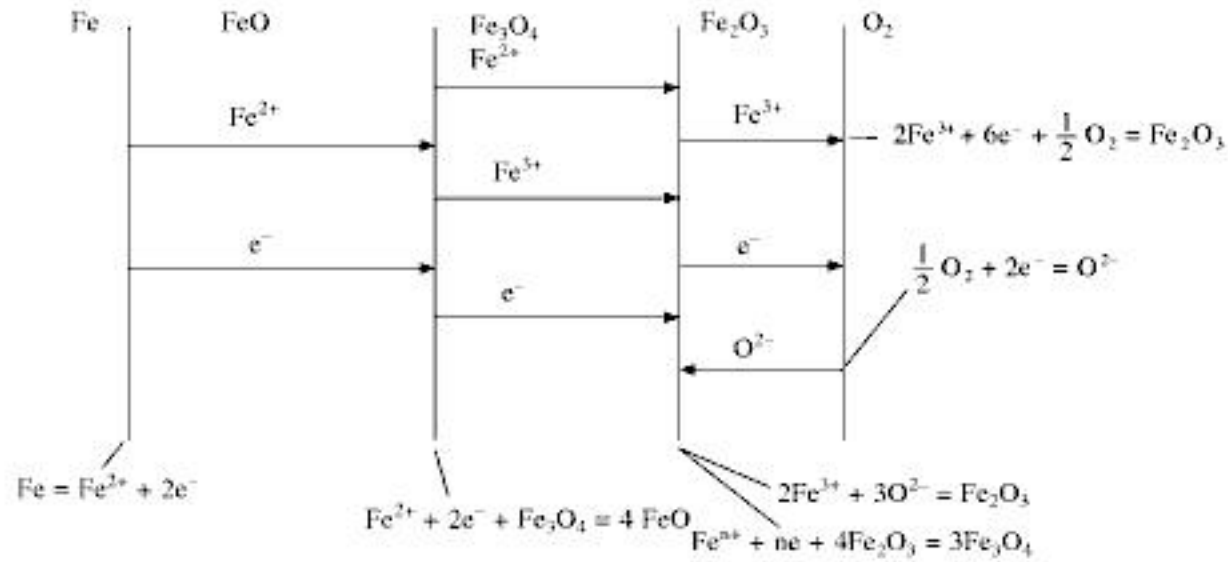


Fig. 6.3 Mechanism of oxidation of iron showing the diffusion of various ionic species.

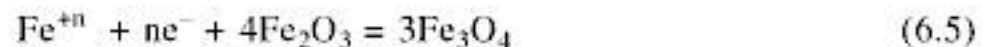
At the iron-wustite interface, iron ionises in the following way:



The iron ions and electrons migrate outwards through the FeO layer over iron vacancies and electron holes respectively. At the wustite-magnetite interface, magnetite is reduced by iron and electrons according to the reaction:

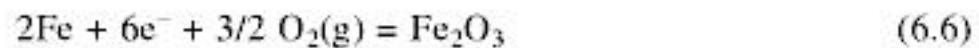


Iron ions and electrons surplus to this reaction proceed outward through the magnetite layer, over iron vacancies on the tetrahedral and octahedral sites and over electron holes and excess electrons respectively. At the magnetite-haematite interface, magnetite is formed according to reaction



The value of  $n$  being two and three for  $\text{Fe}^{+2}$  or  $\text{Fe}^{+3}$  ions, respectively.

If the iron ions are mobile in the haematite, they will migrate through this phase over iron ion vacancies  $V_{\text{Fe}}$  together with electrons, and new haematite will form at the  $\text{Fe}_2\text{O}_3$ , gas interface according to reaction



At this interface oxygen also ionises according to the reaction:



If the oxygen ions are mobile in the haematite layer, the iron ions and electrons, in excess



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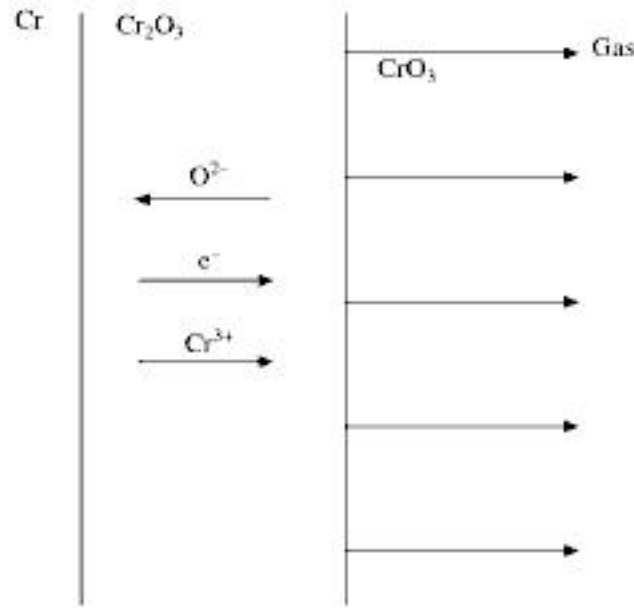


Fig. 6.8 Simultaneous thinning of protective chromia oxide scale as a result of decomposition of chromia to Cr (VI) oxide following evaporation.

$$\frac{dx}{dt} = \frac{k'_d}{x} - k'_s \quad (6.28)$$

where  $k'_d$  is a constant describing the diffusive process and  $k'_s$  describes the rate of volatilisation. This equation can be re-arranged to yield

$$\frac{dx}{\frac{k'_d}{x} - k'_s} = dt \quad (6.29)$$

which upon integration yields:

$$\frac{-x}{k'_s} - \frac{k'_d}{k'^2_s} \ln(k'_d - k'_s x) + C = t \quad (6.30)$$

where  $C$  is the integration constant to be evaluated from the initial conditions. Taking  $x = 0$  at  $t = 0$

$$t = \frac{k'_d}{k'^2_s} - \frac{k'_s}{k'_d} x - \ln\left(1 - \frac{k'_s}{k'_d} x\right) \quad (6.31)$$

Initially, when the diffusion through a thin scale is rapid, the effect of  $\text{CrO}_3$  volatilisation is not significant, but as the scale thickens, the rate of volatilisation becomes comparable to and then becomes equal to the rate of diffusive growth. This situation results in a parabolic oxidation to a limiting scale thickness,  $x_0 = 0$  for which  $dx/dt = 0$  which is shown schematically in Fig. 6.9. Setting this condition in Eq. 6.28 yields:

$$x_0 = \frac{k'_d}{k'_s} \quad (6.32)$$



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$$W = w_1 + w_2 = (K_p t)^{1/2} \quad (6.38)$$

where  $K_p$  is the parabolic rate constant for the overall reaction and can be expressed in terms of the rate constant of individual reactions as

$$K_p^{1/2} = k_1^{1/2} + k_2^{1/2} \quad (6.39)$$

The model describing such simultaneous oxidation rate was proposed by Wagner and is shown schematically in Fig. 6.11. It is assumed that oxygen diffuses inwards through the oxide scale and is consumed by the oxide growth and oxygen dissolution at the metal oxide interface. The metal is to be considered semi-infinite. According to this model the rate of oxygen uptake per unit area is given by

$$\begin{aligned} \frac{dW}{dt} &= -D_2 \left( \frac{dc}{dx} \right) \quad x < \xi \\ &= (c_2 - c_1) \frac{d\xi}{dt} - D_1 \left( \frac{dc}{dx} \right) \quad x > \xi \end{aligned} \quad (6.40)$$

where  $c_2$  and  $c_1$  represent respectively, the oxygen concentration in the oxide and in the metal at the metal/oxide interface,  $\xi$  is the instantaneous thickness of the oxide and  $D_2$  and  $D_1$  are the oxygen diffusion co-efficients in the oxide and metal respectively. The oxygen concentration in the metal at a distance  $x$  is given by the relation

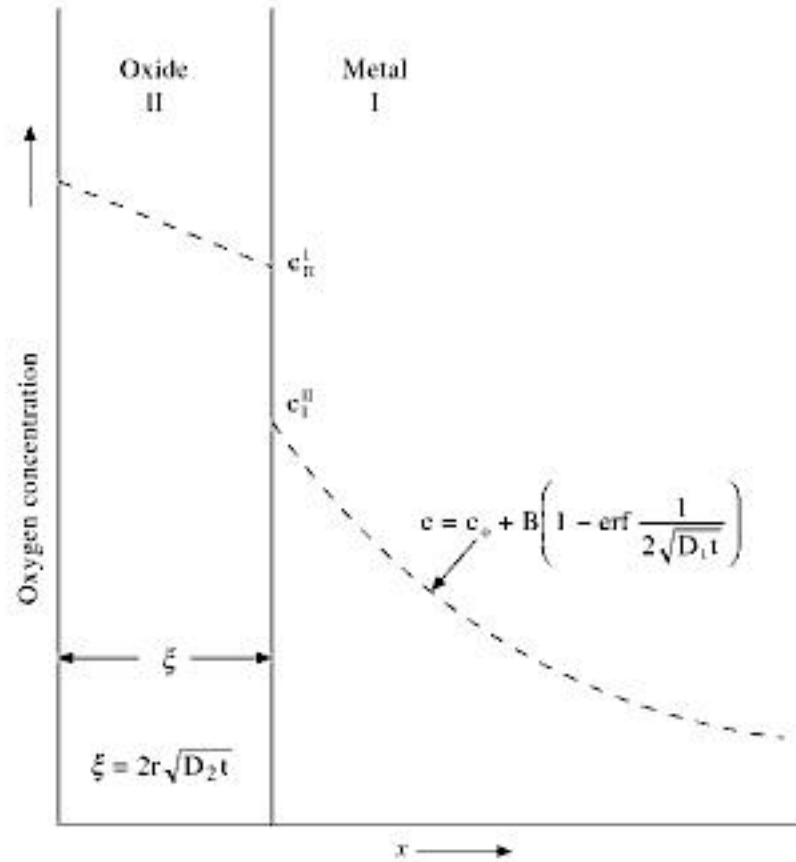


Fig. 6.11 Showing the model for oxide growth process with simultaneous dissolution of oxygen.



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mainly an increased rate of oxide formation, while the dissolution continues at a rate determined by oxygen gradient and diffusion co-efficient of oxygen in metal. During linear oxidation, the oxide has a lamellar structure, parallel to the metal surface, and the colour of the thick oxide ranges from yellow to white. The uniformly light colour of the entire scale suggests that there is no change in the stoichiometry, and this part of the scale is non protective and porous to oxygen.

The linear rate may reflect a reaction controlled by diffusion through a thin, inner layer of the scale which remains approximately constant with time due to repetitive exfoliation. Alternatively, it may reflect a phase boundary reaction such as nucleation and growth of the oxide.

The breakdown of the scale might be explained on two counts. One on the basis of growth stresses and the other due to excessive oxygen dissolution when the lattice parameter undergoes severe change. This happens when dissolution leads to the formation of  $\text{TiO}_{0.35}$  at which large stresses and strains in the metal lead to cracking and exfoliation of the outer layer.

At still more extended periods of oxidation, the linear rate starts decreasing with time. Kofstad has suggested that sintering and grain growth of oxides lead to this decrease in the rate. This growth results in a compact layer of the oxide which probably acts as a solid-state diffusion barrier and causes a decrease in reaction rate.

### Oxygen Dissolution in Titanium

At 650 and 700°C, oxygen dissolves more readily in titanium up to a concentration of 14–15 at.% than at higher temperatures. 14 to 15 at.% corresponds to a composition of  $\text{Ti}_6\text{O}$  at which order disorder transformation may start. It is also indicated by Kofstad that the concentration in the outer layer of the titanium metal tends towards the limiting value of  $\text{TiO}_{0.35}$  during oxidation at 900°C.

In order to determine the oxygen dissolution rates at various temperatures, Fick's second law was used with the following assumptions: the oxygen concentration at the metal/scale interface is about 30 at. %, and the value of the diffusion co-efficient in  $\alpha$ -Ti is:

$$D_o = 8.9 \exp (-220 \text{ (kJ/mole)}/RT) \quad (6.48)$$

The plot at various concentrations is given in Fig. 6.14. The calculated values apply only to temperatures below 882°C, below the  $\beta$  transition temperature. At higher temperatures, the dissolution process involves both dissolution in  $\beta$  phase and growth of  $\alpha$  phase. Oxygen dissolution in the  $\beta$  phase has lower activation energy, about 115 kJ/mole and is faster than in the  $\alpha$  phase. However, since the solubility of oxygen is lower in this phase, a major part of oxygen consumed in the dissolution process results in formation of the  $\alpha$  phase.

## OXIDATION OF ZIRCONIUM

Zirconium and its alloys are important materials for nuclear reactors. Because of their constant use as cladding materials, their oxidation behaviour, especially in steam and water has been widely studied. Interaction of zirconium with oxygen, like titanium, involves both oxygen



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Cracks are also possible to originate in the oxygen rich zone of the metal. At higher concentrations of dissolved oxygen, it is possible to form ordered structure in the metal. Such an ordered structure formation in the metal at oxygen rich zones may give rise to local stresses which may conceivably cause cracking of both, an outer oxide layer of the metal as well as the oxide film. Formation of ordered structure in zirconium metal has been observed in an *in situ* study using electron microscope.

## OXIDATION OF TANTALUM

The oxidation behaviour of tantalum, a group VA metal is quite similar to the IVA metals discussed above in terms of simultaneous formation of oxide and oxygen dissolution. It differs in terms that the solubility of oxygen in the metal is quite low. The maximum solubility of oxygen in tantalum in equilibrium with  $Ta_2O_5$  is about 5 at.% at  $1500^\circ\text{C}$  and reduces to 2 at.% at  $1000^\circ\text{C}$ . The oxygen solubility in Ta and Nb at various temperatures is given in Fig. 6.18. The presence of a few atomic percent of oxygen in tantalum increases electrical resistivity, hardness, tensile strength and modulus of elasticity but causes reduction in percentage elongation and magnetic susceptibility.

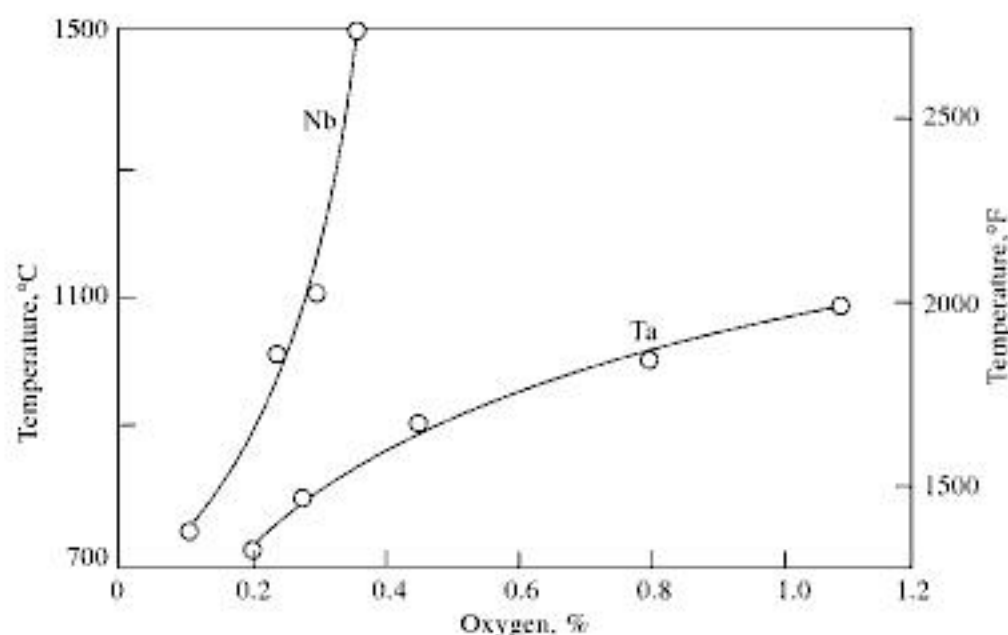


Fig. 6.18 Solubility of oxygen in Ta and Nb as a function of temperature.

Tantalum forms one stable oxide  $Ta_2O_5$ . Various rate laws that the metal follows during oxidation between  $300$ – $1300^\circ\text{C}$  are summarized in Fig. 6.19. During low temperature oxidation when the oxygen dissolution is not significant, the kinetics are logarithmic in nature and the scale formed is amorphous  $Ta_2O_5$ . Above  $300^\circ\text{C}$ , the oxygen dissolution is rather large and here a series of metastable lower oxides ( $Ta_6O$ ,  $Ta_4O$  and  $Ta_2O$ ) are formed as platlets along with the logarithmic growth rate.



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## Oxidation of Alloys

Oxidation of pure metals has been discussed in the previous chapter. In actual practice, alloys, rather than pure metals are used in various high temperature applications. The oxidation behaviour of metals is generally modified by the alloying addition which renders them suitable for a particular high temperature application. Though oxidation of alloys follows the same general phenomenon as that presented earlier for pure metals, the presence of more than one element in the alloy necessitates consideration of a number of additional factors to describe the alloy oxidation behaviour. This renders the mechanism of oxidation of alloys relatively complex compared to that of a pure metal. Several factors determine the effect of alloying additions on the oxidation process:

1. The nature of the alloying addition; i.e., whether it is more or less noble than the parent metal.
2. Solubility in the parent metal.
3. Affinity for oxygen and thermodynamic stability of its oxide.
4. Mobility or diffusion of the metal in the oxide phase.

Depending upon these, the scale formed in an alloy may be:

- (i) A mixture of oxides formed from various alloying elements.
- (ii) A single oxide formed of a specific alloying element.
- (iii) A single or mixed external oxide scale with internal oxides of certain elements.

The first case would be the case of general oxidation, in which oxides of all the elements may form in the initial stage (transient oxidation), followed by the growth of the most stable oxide. In the second case, conditions for selective oxidation of a particular constituent of the alloy would result. Though this would protect the alloy from further oxidation, the selective oxidation can result in the depletion of this element from the underlying matrix, which, in case of any scale damage, cracking or spalling, may result in excessive scale growth rate, resulting in breakaway oxidation. In the third case, due to very high activity of certain elements, inward diffusion of oxygen can cause precipitation of oxides within the matrix, well below the external scale in the alloy. This type of internal oxide can be beneficial in some cases, for example, they can strengthen the base alloy and if formed at grain boundaries in the alloy, restrict grain boundary sliding. But a large amount of internal oxide is deleterious to the alloy; for the grains, completely surrounded by oxidized matter, may be loosened and finally dislodged.



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where  $\Delta G_{(BO_v)}^\circ$  is the standard gibbs free energy of the formation of  $BO_v$ ,  $a_B$  is the activity of  $B$  in the alloy phase and  $a_{BO_v}$  is the activity of the oxide. Assuming  $BO_v$  is formed as pure oxide particles,  $a_{BO_v} = 1$ . Thus in order to calculate the critical oxygen activity, it is necessary to know the activity of the alloying constituent  $B$ , i.e.  $a_B$ .

The necessary condition for the formation of  $BO_v$  can also be formulated in terms of the solubility product  $K_{sp}$  as

$$(a_B)(a_o)^v = K_{sp} \quad (7.4)$$

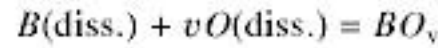
$a_o$  is the activity of oxygen in the alloy. When the product  $(a_B)(a_o)^v > K_{sp}$ , internal precipitation of  $BO_v$  will occur. The internally oxidized zone extends to a depth at which the activity of the dissolved oxygen becomes too small for the formation of the oxide.

To summarize, the conditions required for internal oxide formation are:

- (i) Lower free energy of formation of the internal oxide  $BO_v$  as compared to the base metal oxide.

$$(\Delta G^\circ \text{ for } BO_v < \Delta G^\circ \text{ for } AO)$$

- (ii) Large negative value of  $\Delta G^\circ$  for the reaction



- (iii) Low concentration of the alloying elements.

### Kinetics of Internal Oxidation

Like the oxidation process which forms an external scale, the internal oxidation also follows a particular kinetic law. Its growth with time is an important parameter which can give information about the internal damage of the alloy. Several treatments are available in literature and it is not the purpose of this book to review them. Instead, the kinetics will be first derived for a simplified case, where it is assumed that the counter diffusion of element  $B$  in an alloy  $AB$  is negligible. Then a more general treatment would be given where inward diffusion of oxygen ions and outward diffusion of  $B$  atoms are considered.

### Simplified Treatment

Let us consider a planar binary alloy  $A-B$  in which  $B$  is the less noble alloying element and under the oxidation conditions of low  $pO_2$ , only  $B$  oxidises and no  $AO$  is formed (Fig. 7.2).

Assuming a quasi steady state condition, the dissolved oxygen concentration varies linearly across the zone of internal oxidation. Therefore, the oxygen flux through the internal oxidation zone can be given by Fick's second law as:

$$J = dm/dt = D_o N_o^s / x V_m \text{ (moles cm}^{-2} \text{s}^{-1}) \quad (7.5)$$

where  $N_o^s$  is the oxygen solubility in  $A$  (in atom fraction),  $V_m$  is molar volume of  $A$  ( $\text{cm}^3 \text{mole}^{-1}$ ) and  $D_o$  is the diffusivity of oxygen in  $A$  ( $\text{cm}^2 \text{s}^{-1}$ ). As we have assumed that counter diffusion of  $B$  atoms is negligible, the amount of oxygen accumulated in the internal oxidation zone per unit area of the reaction front is given by:



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By combining Eqs. 7.14, 7.17 and 7.18 one obtains

$$\frac{N_o^s}{N_B^o} = \frac{v \exp(\gamma^2 \operatorname{erf}(\gamma))}{\phi^{1/2} \exp(\gamma^2 \phi) \operatorname{erf}(\gamma \phi^{1/2})} \quad (7.20)$$

From this equation, the values of the parameter  $\gamma$  may be obtained by either a graphical or a numerical solution.

There are two limiting cases of Eq. 7.20

(a) When  $\gamma \gg 1$  and when  $\gamma \phi^{1/2} \gg 1$ , which is equivalent to  $D_o N_o \gg D_B N_B$  i.e. the oxygen diffusion predominates then Eq. 7.20 is simplified to

$$\gamma = \left( \frac{N_o^s}{2v N_B^o} \right)^{1/2} \quad (7.21)$$

when the value of  $\gamma$  is introduced in Eq. 7.11 the thickness of the internally oxidized zone is given by

$$X = \left( \frac{2}{v} \frac{D_o N_o^s}{N_B^o} \right)^{1/2} \quad (7.22)$$

This is the same equation as Eq. 7.10, which was derived for the simplified case, where it was assumed that counter diffusion of  $B$  atoms was negligible.

(b) When  $\gamma \ll 1$  but  $\gamma \phi^{1/2} \ll 1$  equivalent to  $N_o/N_o \ll D_B/D_o \ll 1$

Eq. 7.20 simplifies to

$$\gamma = \frac{\pi^{1/2} \phi^{1/2} N_o^s}{2v N_B^o} \quad (7.23)$$

In this case, the thickness of the internal oxidation zone is dependent on both  $D_o$  and  $D_B$  and an appreciable amount of enrichment of  $B$  as  $BO_v$  takes place in the internal oxide zone due to outward diffusion of  $B$ . The enrichment may be described by a factor which is the ratio of the mole fraction of  $B$  as  $BO_v$  in the internal oxidation zone to the mole fraction in the bulk alloy  $N_B^o$ .

For case (a), the enrichment is negligible. When enrichment takes place it is constant throughout the internally oxidised zone.

### Morphological Details of Internal Oxides

Oxide precipitates at the sub layer are formed by nucleation and growth processes. In general, the oxide particle size is determined by a competition between the rate of nucleation as the reaction front passes and the subsequent growth and coarsening rates of the particles. The longer the time a nucleated particle has to spend between the arrival of oxygen and the oxide forming element, the larger it will grow. Therefore, those factors which favour high nucleation rates will decrease the particle size and those which favour a high growth rate will increase the particle size.



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The delineation between the three regions should not be considered as absolute and can be influenced by temperature and other alloying additions. In addition, as discussed above, the transition to selective oxidation will depend upon various other parameters, such as pretreatments, grain size and specimen geometry.

### Effect of Other Alloying Elements

High temperature alloys, in general contain several other elements which are either added intentionally to reduce oxidation or are present for several other reasons. It is not our aim here to summarize the effect of each individual element on the oxidation process. However, it is worth mentioning here, how the deliberate addition of rare earth and other oxygen active elements improves the oxidation behaviour. Addition of rare earth elements in small concentrations, improves not only the oxidation resistance but also enhances the scale adherence and reduces scale spallation. The mechanism relating to the additions of *Y*, *Ce*, *La* etc., will be treated in a subsequent chapter.

There are certain other elements such as *Mn*, *Mo*, *V*, *Ta*, etc. which are present in several high temperature alloys, to improve their mechanical properties. However, they can have a deleterious effect from the standpoint of the oxidation resistance of the alloy. Manganese which is generally present in most of the Fe-base alloys, has no pronounced effect on the oxidation rate. In fact a mild detrimental effect on oxidation has been reported for the 200 and 300 series stainless steels. *Mo* and *V* if present in large quantities have a deleterious effect as they can form low melting oxides,  $MoO_2$  and  $V_2O_5$  and can lead to catastrophic oxidation.

The effect of certain tramp elements, such as sulphur, phosphorus, boron etc. has also been found to be detrimental to the scale adherence and its spallation resistance. Hence, where good scale adherence is required, these impurities have to be reduced to very low (part per million) levels. Boron, however is added to many superalloys for grain boundary strengthening.

## OXIDATION BEHAVIOUR OF SOME COMMERCIAL ALLOYS

### Carbon Steels and Low Alloy Ferritic Steels

Carbon steel is probably the most widely used engineering material. It is extensively used for high temperature applications in power plants, chemical, and petrochemical industries, oil refining, and in many other industries. Boiler tubes in power plants, reactor vessels in process industries, heat treating fixtures and exhaust train piping are examples of a few components made out of mild steel.

The oxidation behaviour of mild steels is very similar to that of iron, as discussed in the previous chapter. Carbon steels have negligible oxidation in air up to temperatures of about 250-300°C. Oxidation attack is less than about 20 mg/cm<sup>2</sup> up to 450°C. Above this temperature, the oxidation rate increases rapidly, following linear kinetics, especially above 600°C. High Strength Low Alloy (HSLA) steels which contain minor additions of alloying elements, such as manganese, silicon, chromium and nickel have a lower oxidation rate.

Chromium-molybdenum steels are considered to be a better choice for moderate temperature



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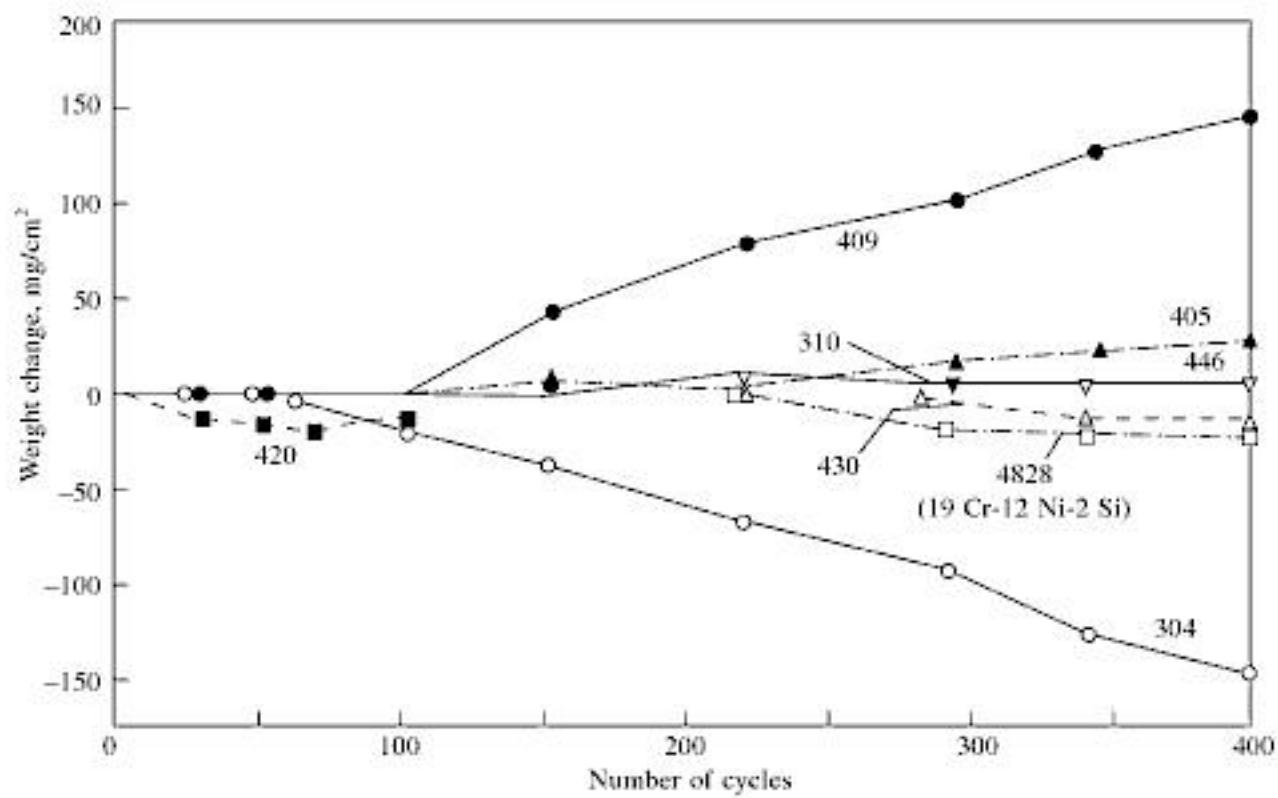


Fig. 7.12 Cyclic oxidation resistance of several ferritic and austenitic stainless steels in air at 1000°C.

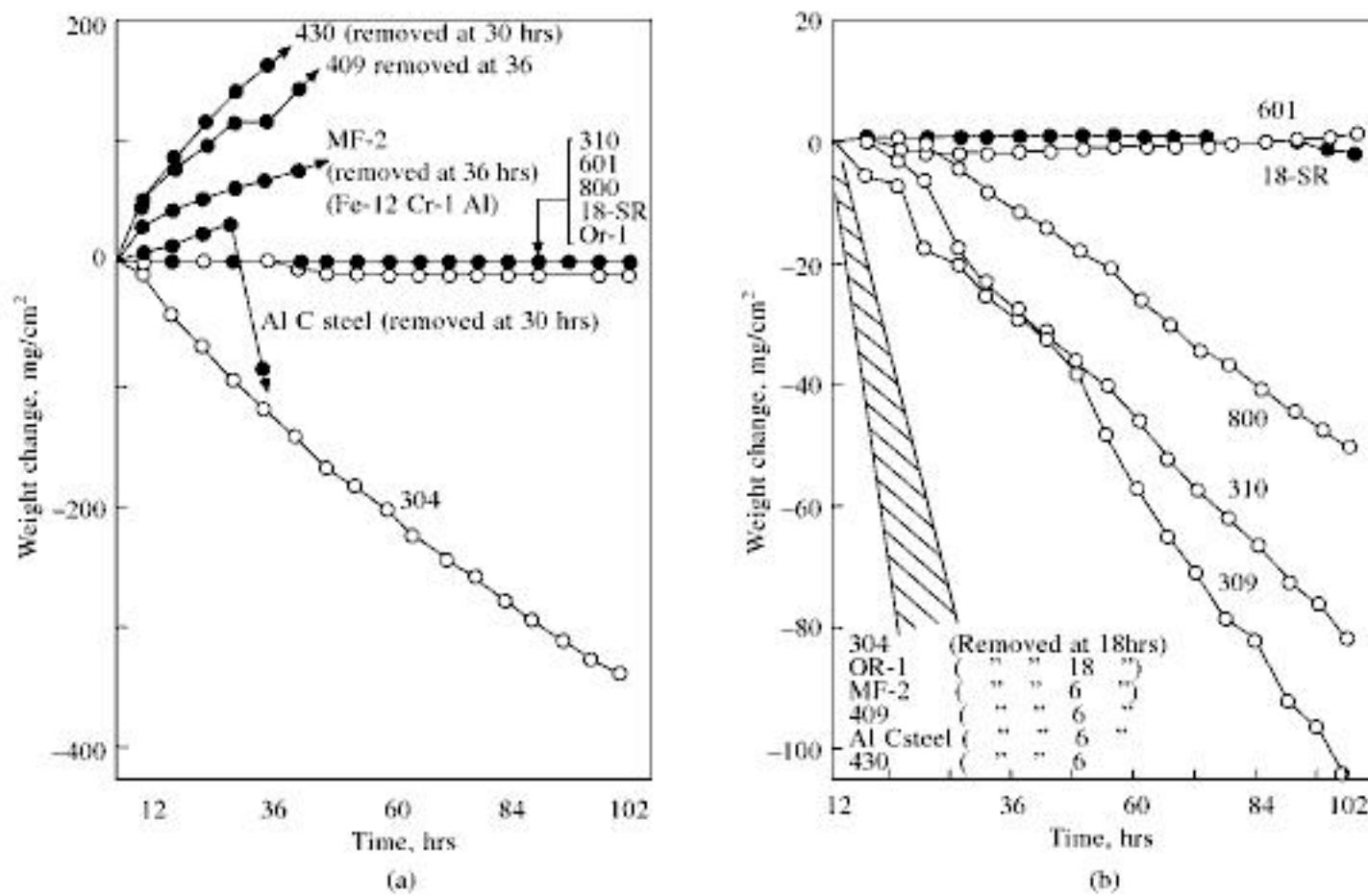


Fig. 7.13 Cyclic oxidation resistance of several ferritic and austenitic stainless steels in (a) air + 10% water vapour and (b) gasoline exhaust at 980°C.



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strength for a longer time period at relatively higher temperatures. Their environmental performance is also better than that of conventional superalloys from the standpoint of resistance to cyclic oxidation and scale spallation resistance.

Table 7.4 Composition of a few common ODS alloys

| Type       | Cr    | Ni  | Fe   | Ti      | Al   | Co   | Mo  | Others                                                                     |
|------------|-------|-----|------|---------|------|------|-----|----------------------------------------------------------------------------|
| MA 956     | 20.0  | —   | Bal  | 0.5     | 4.5  | —    | —   | 0.5Y <sub>2</sub> O <sub>3</sub>                                           |
| MA 754     | 20.0  | Bal | 1.0  | 0.5     | 0.3  | —    | —   | 0.6Y <sub>2</sub> O <sub>3</sub>                                           |
| MA 6000    | 15.0  | Bal | 0.75 | 2.88    | 4.38 | 16.0 | 2.0 | 2Ta, 4W,<br>1.13Y <sub>2</sub> O <sub>3</sub>                              |
| NiCr8020   | 19-21 | Bal | 2.0  | —       | —    | —    | —   | 1Mn, <2Si                                                                  |
| Nimonic 75 | 18-21 | Bal | 5.0  | 0.2-0.6 | —    | 2.0  | 0.3 | 1Mn, 1Si                                                                   |
| DS-Ni      | —     | Bal | —    | —       | —    | —    | —   | 2ThO <sub>2</sub>                                                          |
| MA956      | 20    | Bal | —    | 0.5     | 0.3  | —    | —   | 0.5Y <sub>2</sub> O <sub>3</sub>                                           |
| TMO-2      | 6.0   | Bal | —    | 0.8     | 4.2  | 9.7  | 2.0 | 12.4W, 4.7Ta,<br>0.01B, 0.05Zr,<br>0.05C, 1.1Y <sub>2</sub> O <sub>3</sub> |

## CATASTROPHIC OXIDATION

The rate of oxidation of metals and alloys generally increases with an increase in temperature. When the exposure temperature is very high, several metals and alloys suffer catastrophic oxidation. Carbon steel, for example, suffers catastrophic oxidation when exposed to temperatures above 1000°C in air. Type 316 stainless steel suffers catastrophic oxidation, when exposed to air at 1150°C.

The behaviour described above is not abnormal, as deterioration of materials is expected upon exposure to increasingly high temperatures. However, several metals and alloys undergo rapid oxidation even at much lower temperatures. This type of oxidation is referred to as *catastrophic oxidation* and it occurs with the formation of a liquid oxide. The liquid oxide can dissolve the protective scale or can enhance the transport of the diffusing species, thereby increasing the oxidation rate catastrophically. A few examples where catastrophic oxidation was noticed are given below.

1. Unusual rapid oxidation of Fe-25Ni-16Cr alloy containing 6% Mo at 900°C in static air. However, the same alloy, when heated in flowing air, exhibited good oxidation resistance. It was postulated that in static air, the MoO<sub>3</sub> that is formed due to oxidation is accumulated on the metal surface. MoO<sub>3</sub>, which has a melting point of 795°C, melts and accelerates the oxidation rate. It has been reported that 19Cr-9Ni steel suffered a catastrophic attack at 770°C in air in the presence of MoO<sub>3</sub>. This temperature was very close to the eutectic temperature of MoO<sub>2</sub>-MoO<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>.
2. Catastrophic oxidation of metals and alloys is also noticed in the presence of PbO and V<sub>2</sub>O<sub>5</sub>, when heated in the intermediate temperature range of 700 to 900°C. The lead



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interesting to consider the basic difference between the oxidation and sulphidation processes and the difference in the characteristics of oxides and sulphides in terms of their defect structure and transport behaviour. This will be followed by a description of phase stability diagrams and their use in prediction of scales formed in mixed gas environments. Oxidation and sulphidation of some pure metals will be considered in detail followed by examples of a few commercial alloys.

## OXIDATION VS SULPHIDATION

In this section, we will consider how sulphidation differs from oxidation. The reactions of metals and alloys with sulphur are governed by same principles as discussed for metal oxygen reactions. But for many metals sulphur is much more aggressive than oxygen. The stability of various metal sulphides as a function of temperature, is given by the Ellingham diagram for the sulphides. As shown in Fig. 8.1, the plot of free energy vs temperature for various metal vs metal sulphide reactions. There is very little difference in the stability of sulphides, formed by iron, nickel and cobalt. Chromium, however, forms a relatively stable sulphide, compared to iron, cobalt and nickel. The corresponding sulphur vapour pressure

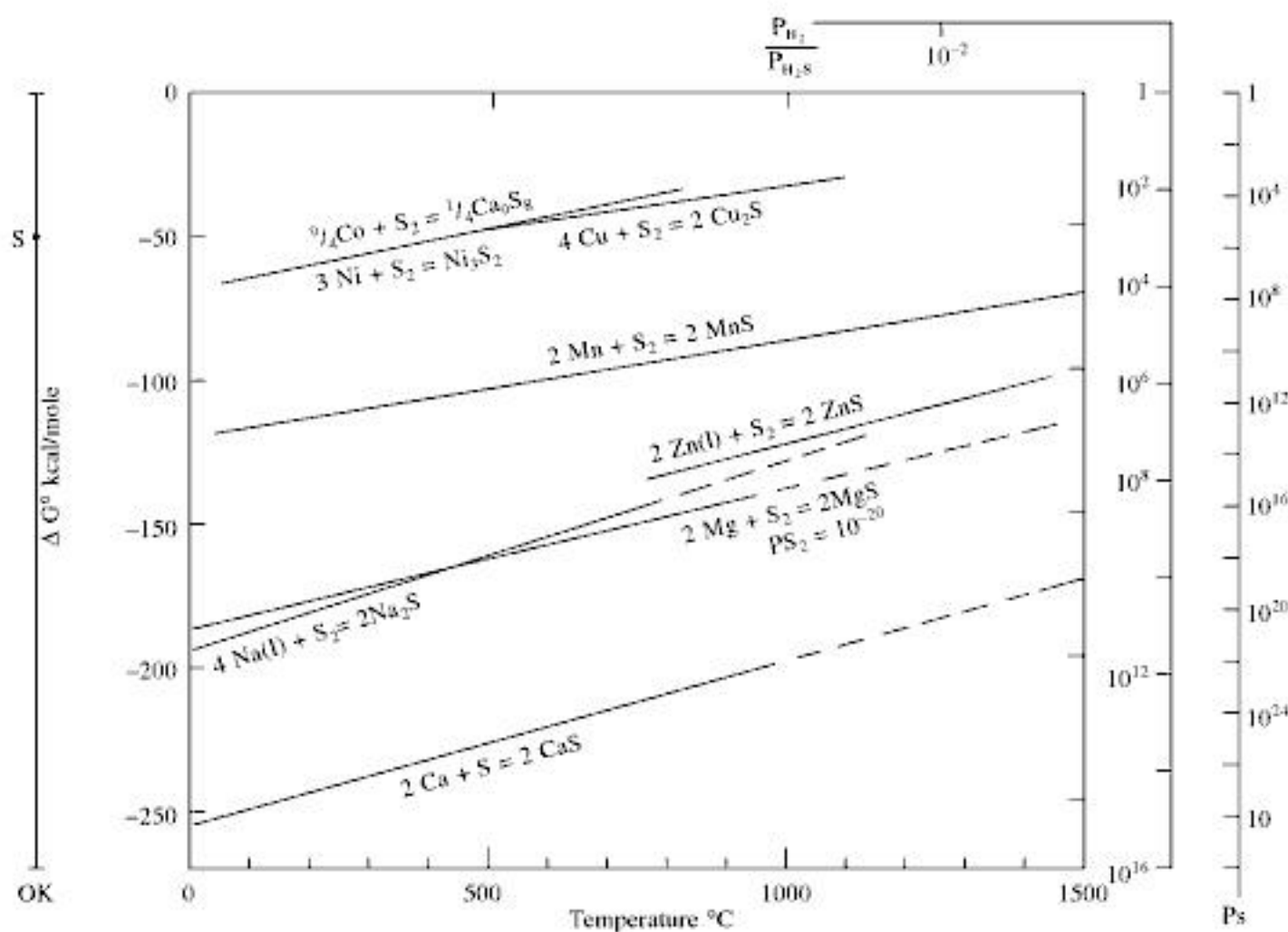


Fig. 8.1 Ellingham diagram for the sulphidation of various metals.



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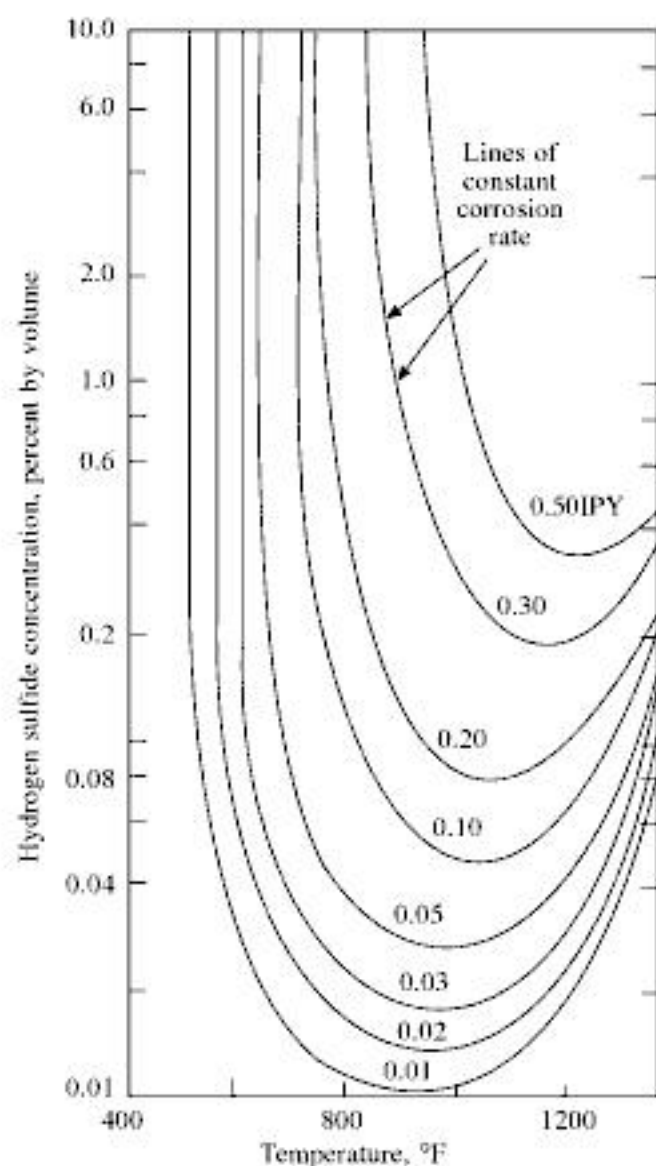
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Ni-Cr-Al alloys, however, behave differently. Addition of Al to Ni-25Cr up to 10%, showed very erratic behavior, when tested in sulphur vapour from 600 to 950°C. The kinetics were found to vary from parabolic to linear. This might be due to the formation of low melting nickel sulphide, as discussed above.

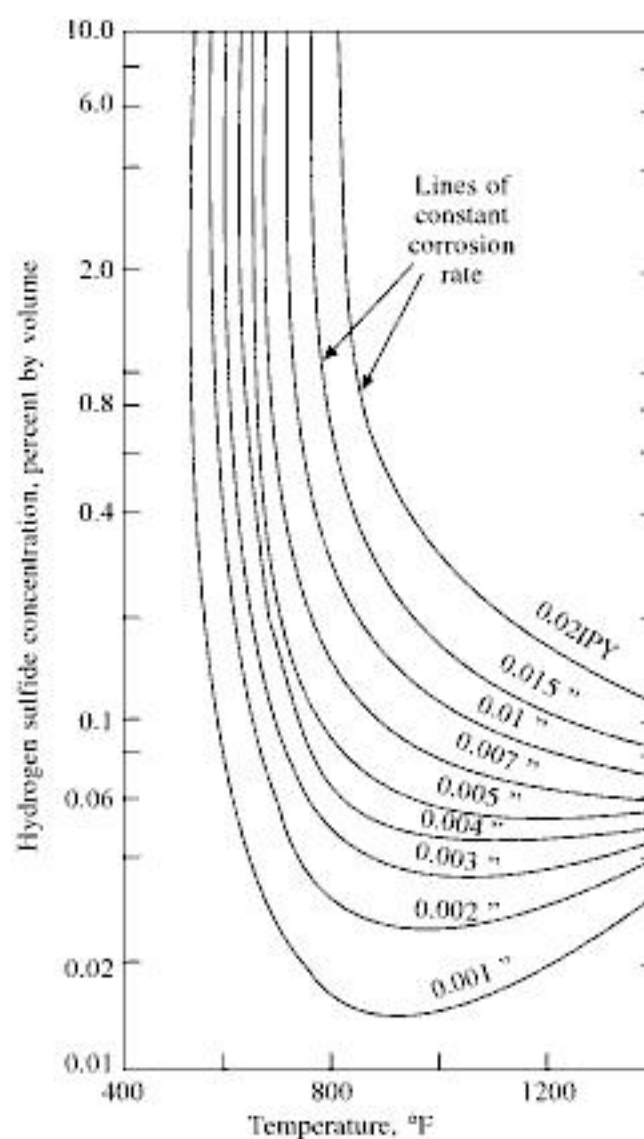
Sulphidation of alloys in an  $H_2/H_2S$  mixture has been described by isocorrosion rate curves for various steels and stainless steels as a function of  $H_2S$  concentration and temperature. These are given in Figs. 8.3 and 8.4 for steels and stainless steels respectively.

### Thermodynamic Aspects of Reaction in Mixed Oxidants

When materials are exposed to multicomponent gas environments or mixed oxidants, several of the fundamental processes mentioned above can occur simultaneously. Furthermore, the second reactant may either modify or degrade the corrosion-product layers that form by



**Fig. 8.3** Isocorrosion rate curves for steels at various temperatures and partial pressures of  $H_2S$ .



**Fig. 8.4** Isocorrosion rate curves for stainless steels at various temperatures and partial pressures of  $H_2S$ .



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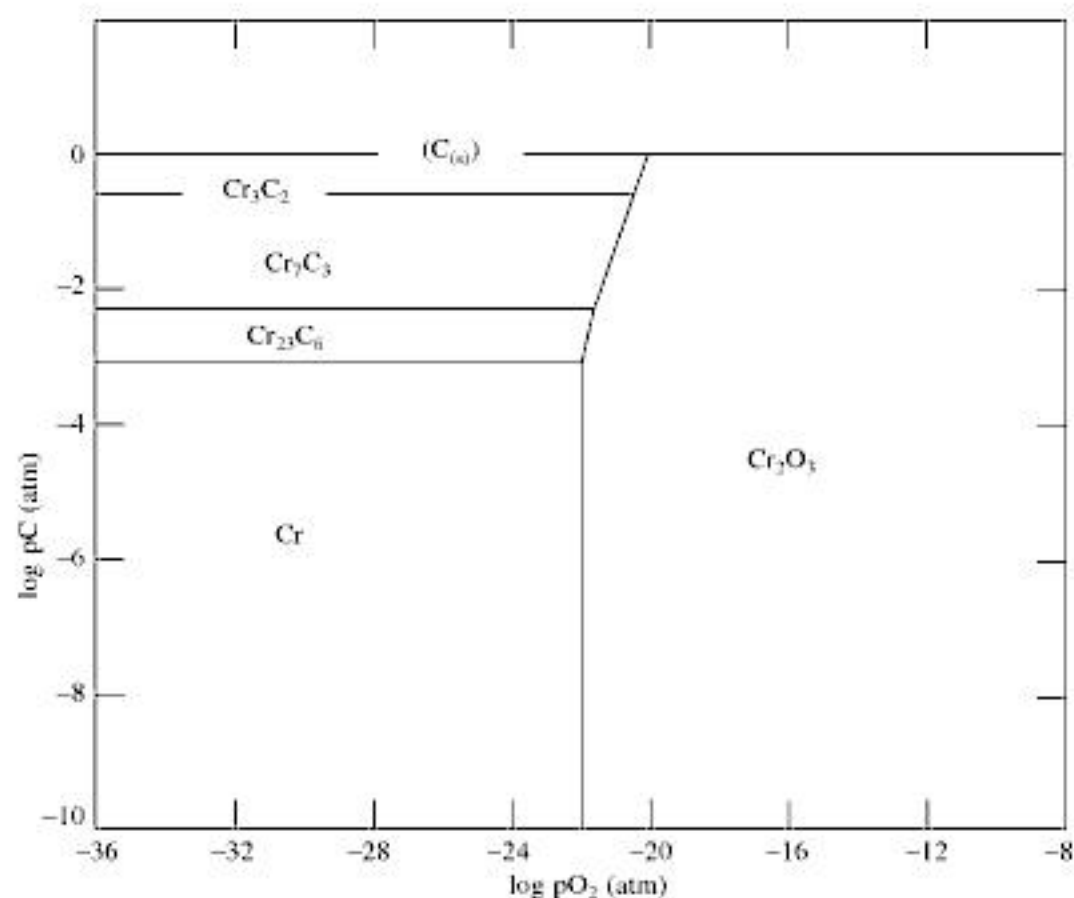


Fig. 8.6 Thermochemical stability diagram for the chromium-carbon-oxygen system developed for a temperature of 982°C.

of Cr oxide scales at 1127°C; however, the formation of Ni/Ni sulphide eutectic with a melting temperature of 635°C is a distinct possibility at lower temperatures.

### Scaling of Alloys in H<sub>2</sub>S-containing Atmospheres

The formation and maintenance of protective surface oxide scales are essential in preventing rapid degradation of structural alloys used in elevated-temperature applications. In principle, one of the three oxides ( $Cr_2O_3$ ,  $Al_2O_3$  or  $SiO_2$ ) constitutes the major component of a thermally formed surface scale. In order to understand the development of protective oxide scales on a given alloy, it is essential to establish the influence of  $pO_2$  variation in the gas environment on the morphology of corrosion-product layers. The inter relationships among partial pressures of oxygen and of the second reactant such as sulphur, carbon, nitrogen or halide in the gas phase, the alloy chemistry, and the test temperature and pressure are of considerable interest in establishing the critical oxygen pressures (if any) that are required to achieve a stable, adherent oxide scale on the metal surface.

### Behaviour of $Cr_2O_3$ -Forming Alloys

$Cr_2O_3$  is the predominant constituent of surface scales formed on heat-resistant austenitic Fe-Cr-Ni alloys. Under isothermal conditions, alloys containing a minimum of about 14 wt.% Cr can be expected to form protective Cr-rich oxide scales in oxygen-rich (single-



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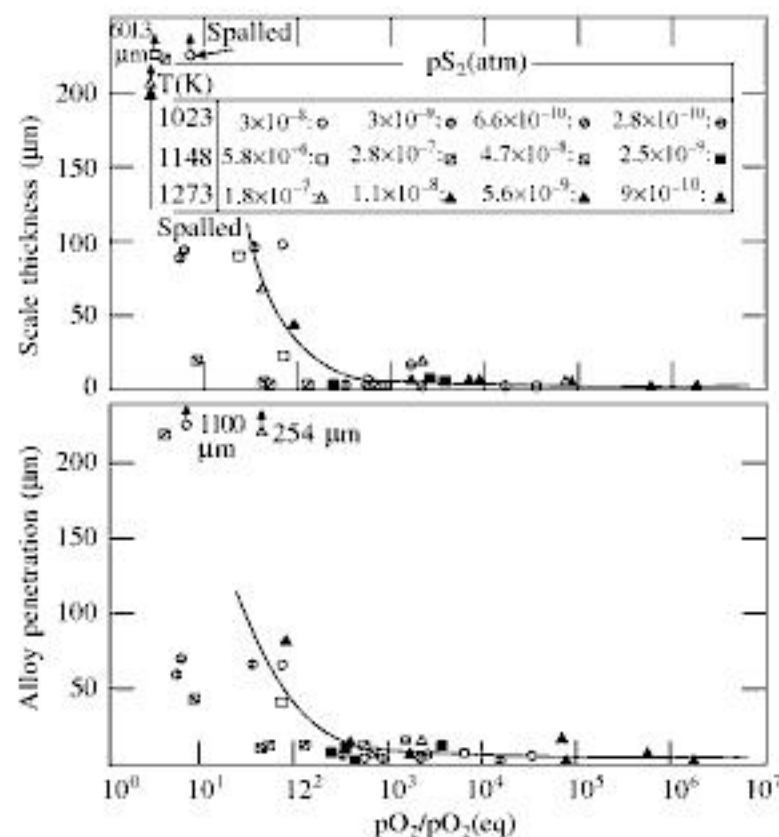


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respectively. Figure 8.10 shows the effect of variation in the  $pO_2/pO_2(eq)$  ratio on the scale thickness and penetration depth for the alloy after a 25-h exposure, at temperatures between 750 and 950 °C, to gas mixtures with a wide range in oxygen and sulphur partial pressures. Results from these tests also indicate that the “transition” or “kinetic” boundary for oxide formation in the high-chromium alloys is at a threshold  $pO_2 = 10^3$  times the  $pO_2$  values for the Cr oxide/Cr sulphide equilibrium.

Transition from nonprotective oxidation of pure chromium takes place at oxygen partial pressures 30 and 42 times that for Cr oxide/Cr sulphide equilibrium. Such a large deviation in  $pO_2$  cannot be explained in terms of solid solution effects or a reduction in activity of sulphide to values below unity. Furthermore, the effect of lowering the exposure temperature is to increase the threshold  $pO_2$  for oxide formation. For example, the absolute values of  $pO_2$  for protective oxide formation are approximately five orders of magnitude higher than the thermodynamic equilibrium value at 65°C. The consequences of oxygen pressures lower than the threshold value in the environment are increased rates of scale growth and substantially deeper penetration of sulphur into the alloy substrate.

In contrast with the corrosion processes that lead to predominantly solid and sometimes liquid (at elevated temperatures) corrosion-product phases upon exposure of metallic alloys to oxygen/sulphur atmospheres, exposure of alloys to environments such as oxygen/chlorine



**Fig. 8.10** Variation in scale thickness and alloy penetration depth as a function of an excess oxygen parameter for Alloy 800 exposed to complex gas environments. The abscissa is a ratio of oxygen pressure in the experiment to that corresponding to Cr sulfide/Cr oxide equilibrium. Conversion factor: 1 atm = 0.101356 MPa.



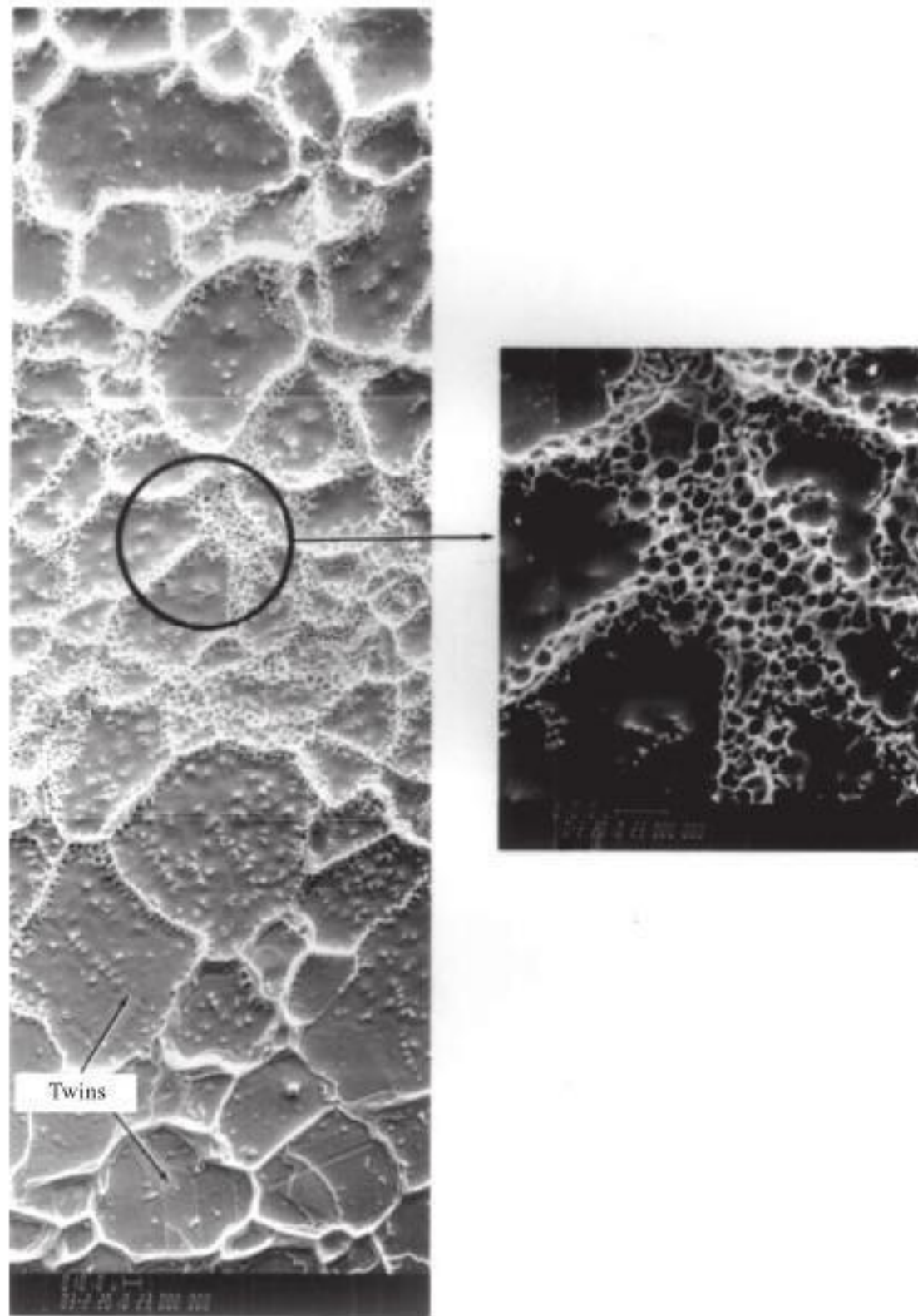
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**Fig. 8.15** Scanning electron microscopy photographs of different magnifications of the metal side of a scale/metal interface on an Fe-25 Cr-20 Ni (wt.%) ternary alloy after exposure to a low-oxygen, high-sulphur environment.

additions of Nb and Zr. Detailed analyses of gas/scale and scale/metal interfaces indicate that the additions of Nb or Zr minimize or eliminate the voids at the scale/metal interface, thereby improving the adhesion of the chromia scale to the substrate. Figures 8.15 and 8.16 show



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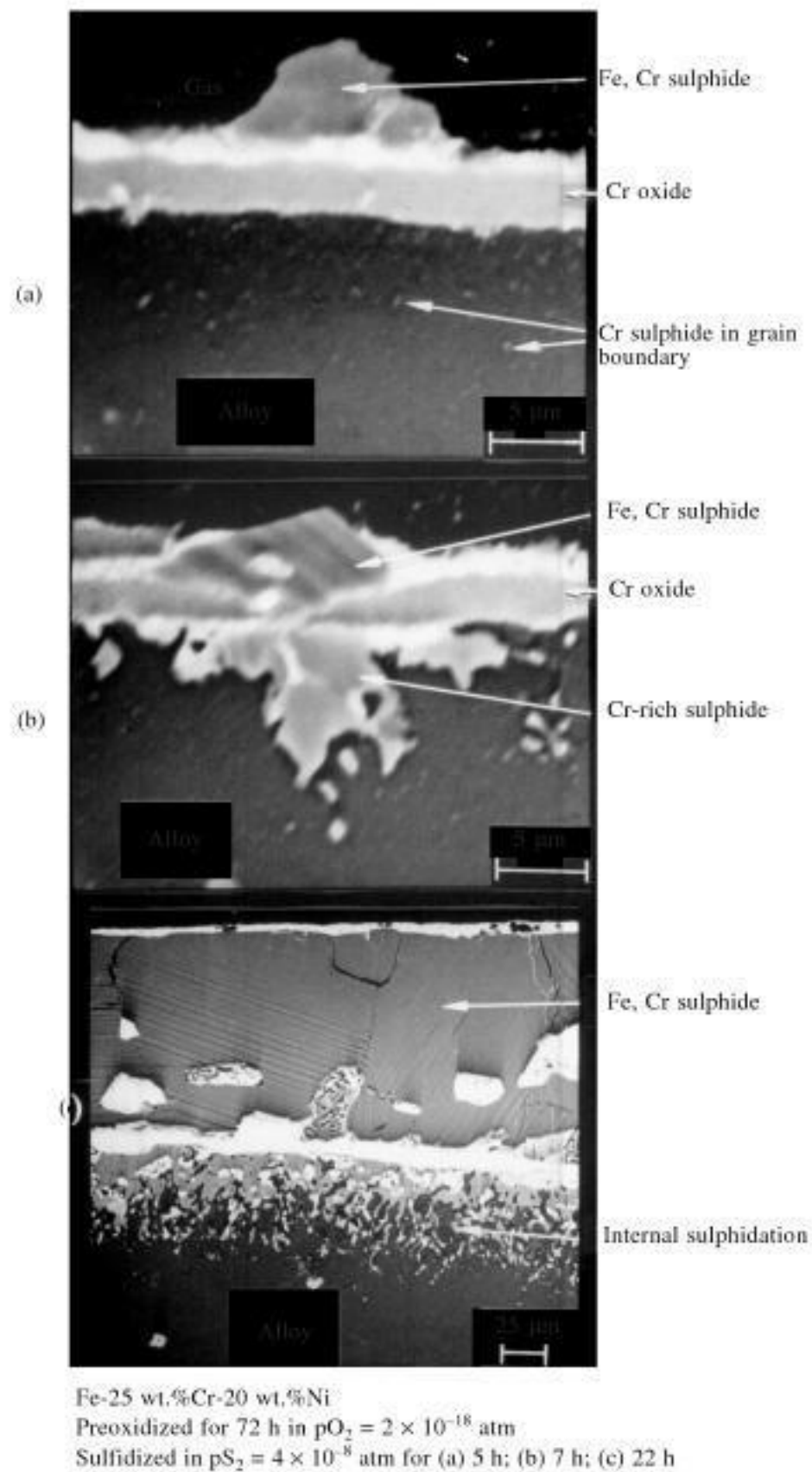


Fig. 8.17 Morphological changes observed in an Fe-25 Cr-20Ni alloy preoxidized in low- $pO_2$  atmosphere and subsequently exposed to  $H_2$ - $H_2S$  atmosphere for different times at 875°C.

formation of aluminum sulphide particles in the  $\text{Al}_2\text{O}_3$  scale in the vicinity of the gas/scale interface.

### Scaling of Alloys in $\text{SO}_2$ -containing Atmospheres

A mixed environment such as  $\text{SO}_2$  and  $\text{O}_2$  exhibits both sulphur and oxygen activities. Thus in order to characterize the corrosion behavior in such an atmosphere, it is necessary to construct the so called stability diagrams. Stability diagrams allow one to predict the stable phases likely to form on pure metals. Metal-sulphur-oxygen stability diagrams are given in Figures 8.19 – 8.22 for Fe, Ni, Cr and Co respectively.

Let us explain the various regions using the Ni-S-O phase diagram as an example. The large rectangular area in Fig. 8.20 represents no reaction with nickel. In this region, both oxygen and sulphur activities are too low to form either oxide or sulphide. Hence, this region is the stable region with no attack. As the oxygen partial pressure increases beyond  $10^{-12}$  atm., the nickel changes to NiO. In a similar way, increasing sulphur partial pressure above  $10^{-8}$  atm. would result in the formation of nickel sulphide or sulphides. When both  $p_{\text{S}_2}$  and  $p_{\text{O}_2}$  are high,  $p_{\text{S}_2}$  beyond  $10^{-6}$  atm. and  $p_{\text{O}_2}$  more than  $10^{-5}$  atm.,  $\text{NiSO}_4$  would be the most stable phase. Thus, depending upon the partial pressures of sulphur vapour and oxygen gas, the scale can be oxide, sulphide or sulphate.

Most of the oxidising environments do not have a direct sulphur vapour pressure, instead, sulphur activity is in the form of the partial pressure of  $\text{SO}_2$ . Therefore it is converted into the corresponding  $p_{\text{S}_2}$  by the following equilibrium reaction:

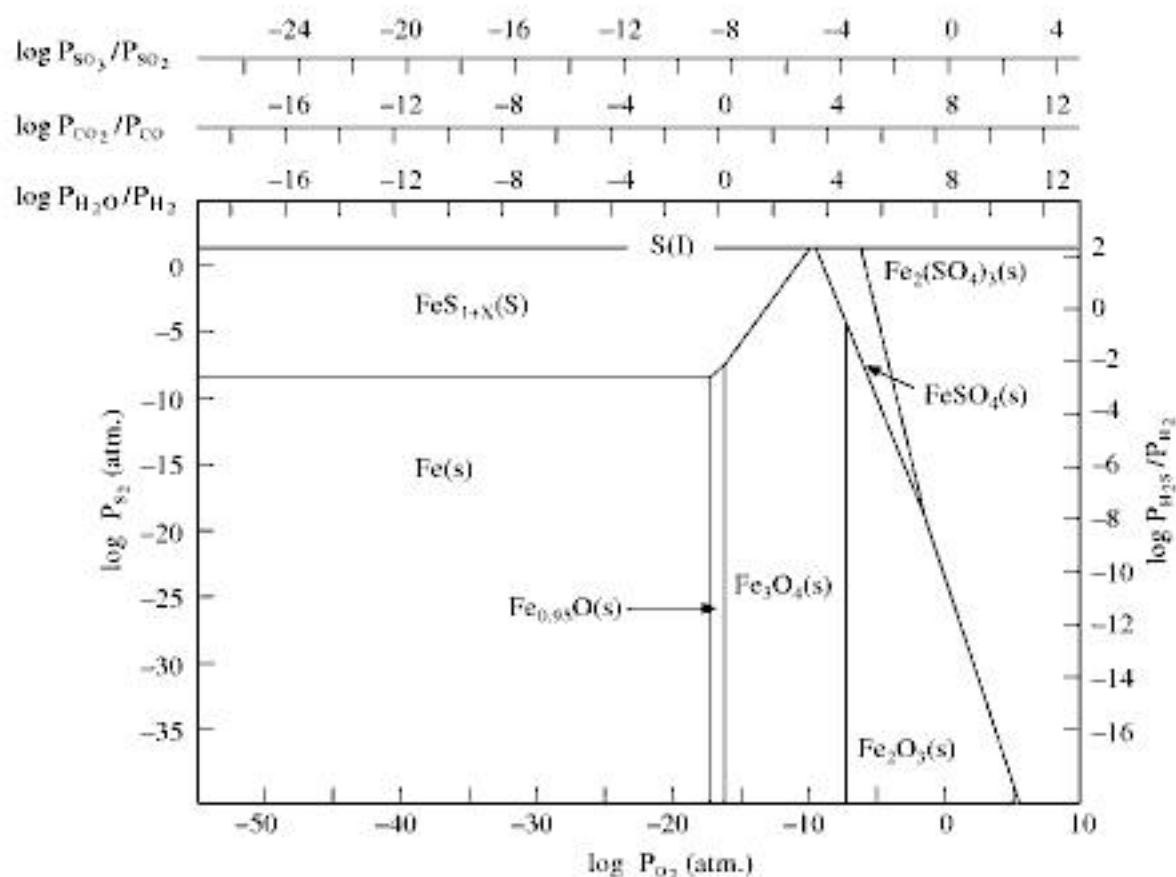


Fig. 8.19 Phase stability diagram of Fe-S-O at 870°C.

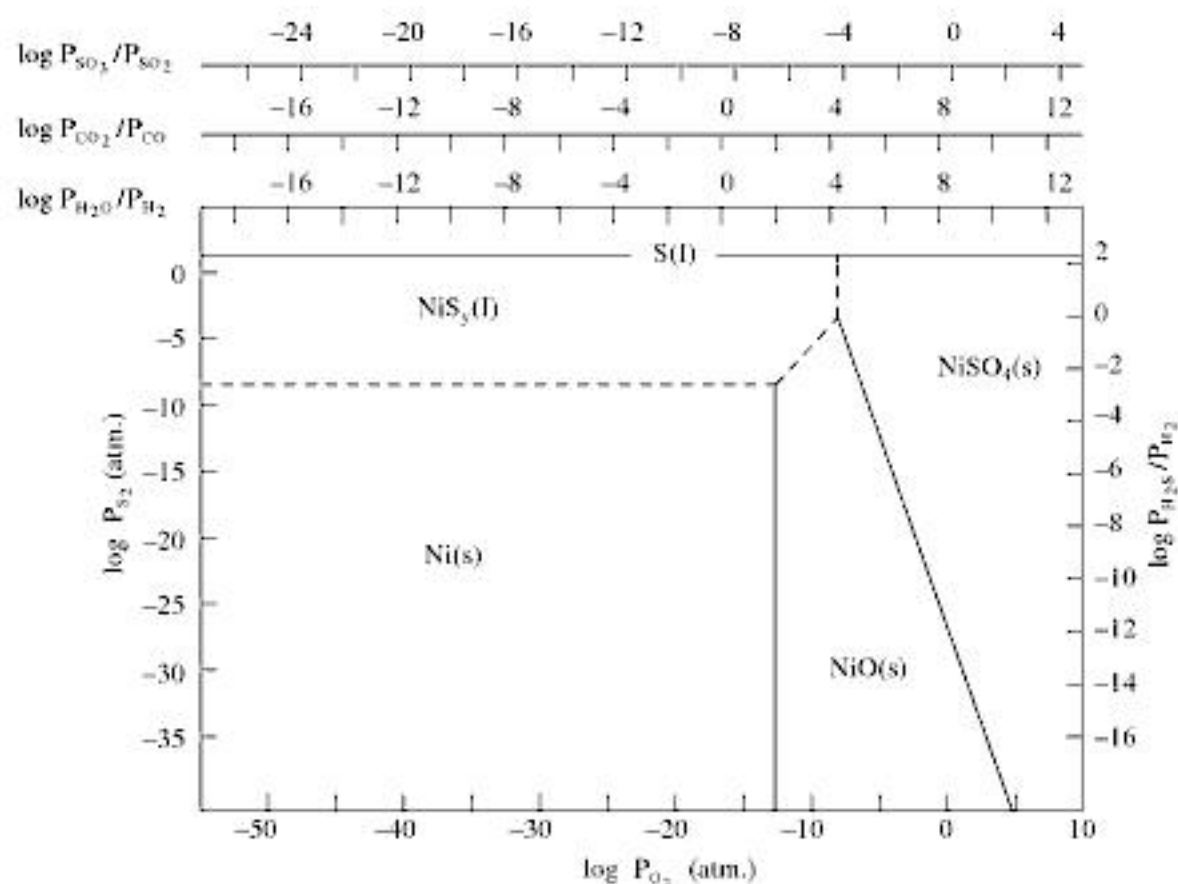


Fig. 8.20 Phase stability diagram of Ni-S-O at 870°C.

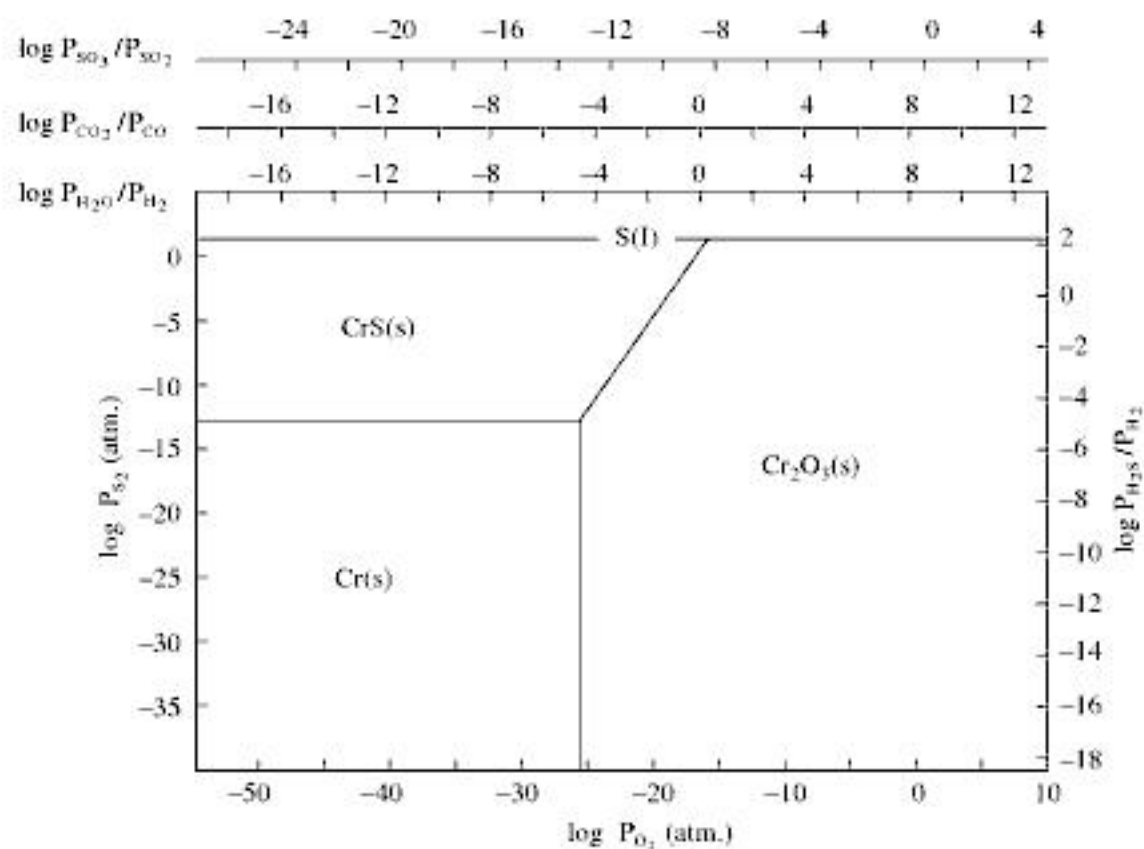


Fig. 8.21 Phase stability diagram of Cr in oxidizing and sulphidizing environments at 870°C.

temperatures for cobalt has been shifted towards the higher temperature side, shifting the temperature of maximum reaction from 600°C for Ni to 920°C for cobalt. This shift is due to two reasons: a higher stabilization temperature of cobalt sulphide  $\text{Co}_3\text{S}_2$  (780-930°C) and higher stability of Co-S liquid solution (about 880°C).

The reaction of iron with  $\text{SO}_2$  is slightly different than that for Co and Ni. Reaction of iron measured at 700°C mainly formed FeO as the outer scale. The sulphide FeS was found enriched in the inner part of the scale next to oxide metal interface. The rate of reaction in  $\text{SO}_2$  was not very different than in air as shown in Fig. 8.28. The reason for this was that both FeO and FeS are equally highly defective oxides. Hence, the diffusion of metal ions does not differ significantly. The reaction of Fe in  $\text{SO}_2$  becomes explosive after a temperature of 940°C, as this is the temperature when a eutectic mixture of FeO+FeS is formed.

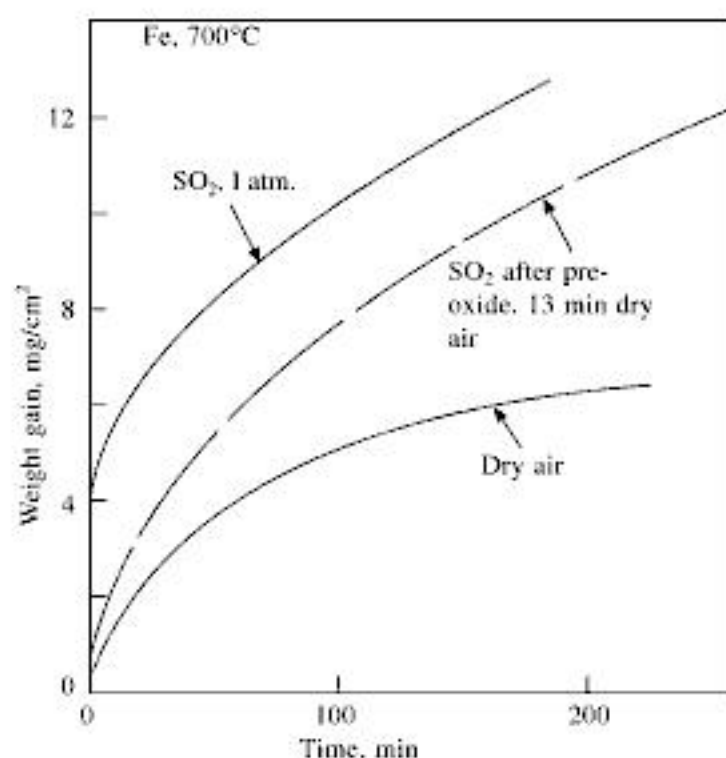


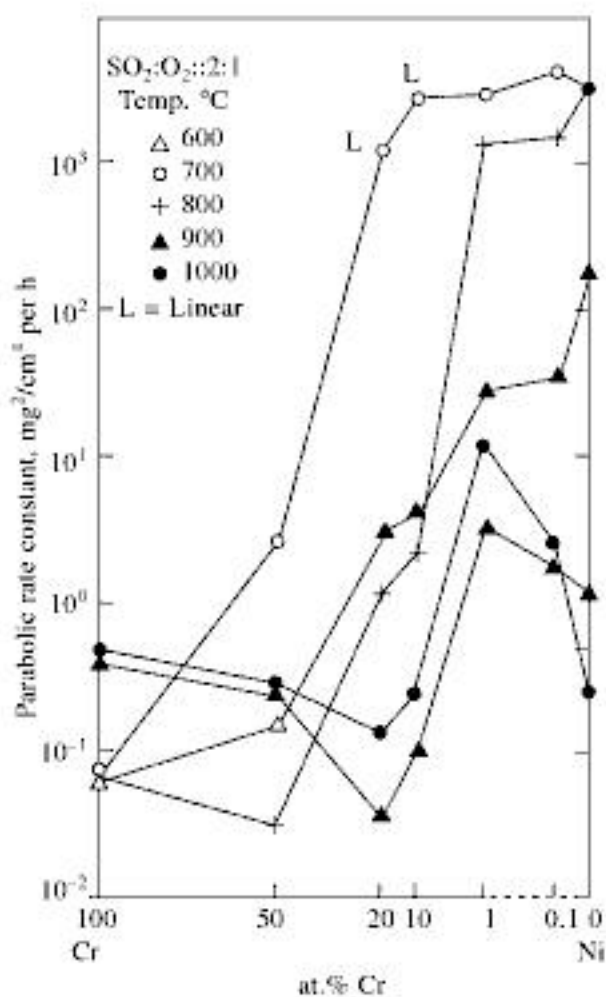
Fig. 8.28 Effect of pre-oxidation on the sulphidation of iron at 700°C.

Chromium, when reacted with  $\text{SO}_2$  at temperatures between 700 to 1000°C, resulted into the formation of chromia scales. No sulphide was detected. However, extensive blistering of the surface was detected in a manner similar to that in oxygen.

### Corrosion of Binary Alloys in $\text{SO}_2/\text{SO}_2\text{-O}_2$ Atmospheres

Reaction of nickel chromium alloys in  $\text{SO}_2$  bearing environments is dependent upon temperature, and the partial pressure of  $\text{SO}_2$ . In 1 atm. pressure of  $\text{SO}_2$ , the reaction is very similar to that of pure nickel with the rate of corrosion increasing with temperature from 600 to 800°C; above this the rate of reaction is much lower. This is because of the formation of a duplex NiO and  $\text{Ni}_3\text{S}_2$  scale at these temperatures, however the nickel sulphide melts after 635°C

and the rate increases up to 800°C. Above 800°C, the nickel sulphide is not stable and also at these temperatures, a protective chromia scale starts forming. The reaction in an SO<sub>2</sub> and O<sub>2</sub> atmosphere also has a similar trend. For an SO<sub>2</sub>:O<sub>2</sub> ratio of 2:1, the effect of addition of chromium to nickel is shown in Fig. 8.29.



**Fig. 8.29** Effect of Cr concentration on the oxidation of Ni in SO<sub>2</sub> and O<sub>2</sub> at various temperatures.

The reaction is quite different when SO<sub>2</sub> pressure is very low. It has been found that the reaction of a Ni-15Cr alloy is faster in 0.2% SO<sub>2</sub> (balance nitrogen), than in pure SO<sub>2</sub>. The reason is obvious, as in 0.2% SO<sub>2</sub> the oxygen concentration is so low that there is no chance for the chromia scale to form. The atmosphere is more reducing, and therefore the reaction takes place as a sulphidation reaction rather than oxidation and sulphidation, which, as has been discussed above is more severe.

Cobalt chromium alloys are expected to behave better than the Ni-Cr alloys as the sulphides of Co are stable up to much higher temperatures (no Co-S liquid below 880°C). Above temperatures of 880°C the chromia layer is more stable and would form first in either pure SO<sub>2</sub> or SO<sub>2</sub>+O<sub>2</sub> atmospheres, this protecting the alloy from further reaction.

Fe-Cr alloys should also behave better than Ni-Cr alloys because of reasons similar to



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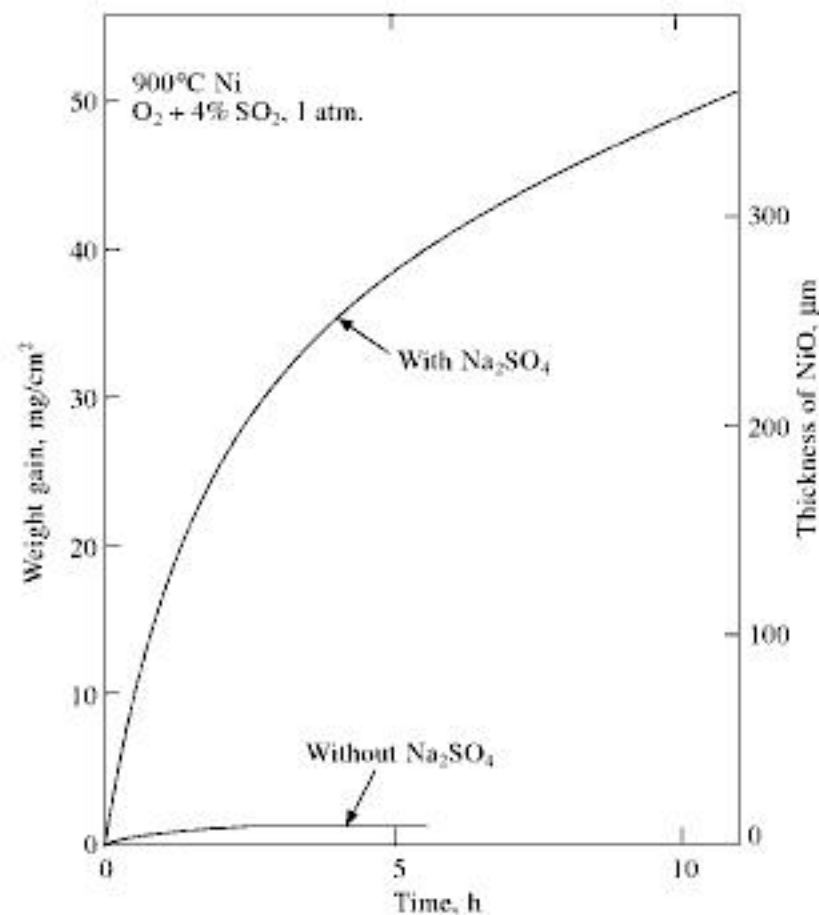


Fig. 9.1 Corrosion of nickel, with and without the presence of the salt  $\text{Na}_2\text{SO}_4$  in 1 atm.  $\text{O}_2 + 4\% \text{SO}_2$  at  $900^\circ\text{C}$ .

slow, till at a certain point, the rate increases suddenly and follows linear kinetics. In other words, there is an incubation period before corrosion rate rises with fast linear kinetics. This type of hot corrosion usually occurs at low temperatures, i.e. the temperature is lower than the melting temperature of the deposited salt. During the initial stages of oxidation, kinetics are just the oxidation of the base metal. As the oxidation progresses, the oxidation products react with the salt deposits and form a complex mixture of salts which has a lower melting point than the original salt. At this stage, the corrosion reaction suddenly rises. Fig. 9.2, for example, shows the corrosion of nickel at  $700^\circ\text{C}$  with  $\text{Na}_2\text{SO}_4$  as a deposit. In the initial stages,  $\text{Na}_2\text{SO}_4$  is solid and the corrosion reaction involves the oxidation of nickel to form  $\text{NiO}$ , which in the presence of  $\text{SO}_2$ , forms  $\text{NiSO}_4$ . It is the mixture of  $\text{Na}_2\text{SO}_4$  and  $\text{NiSO}_4$  which melts at  $671^\circ\text{C}$  and at this stage the reaction rate increases.

In coal based power plants, fireside corrosion involves hot corrosion of type II.  $\text{Na}_2\text{SO}_4$  or  $\text{K}_2\text{SO}_4$ , formed from the reaction of  $\text{SO}_2$  with  $\text{NaCl}$  or  $\text{KCl}$ , present in the coal are the principle salt deposits in the ash. As the maximum outer wall temperature of steam generating tubes ranges from  $550$  to  $650^\circ\text{C}$ , the hot corrosion does not take place till the sulphates deposits react with  $\text{SO}_3$  to form pyrosulphates. For the reaction



about 150 ppm of  $\text{SO}_3$  is required and for a similar reaction with  $\text{Na}_2\text{SO}_4$ , the requirement



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Thus a continuous nickel sulphide formation consumes the alloy. The reaction may continue for a longer duration even with the original amount of sodium sulphate, as the sulphate is being continually formed by the  $\text{SO}_2$  reaction with oxide.

Thus a major difference in the reaction mechanism between acid fluxing and basic fluxing is that in the latter, the melt gradually consumes the salt and becomes saturated with  $\text{NaNiO}_2$  and the reaction subsides. In acidic conditions, molten  $\text{Na}_2\text{SO}_4$  can be considered as a solvent for  $\text{NiSO}_4$  which reacts with nickel migrating outwards through the inner layer with a continuous sulphide net work. In these terms,  $\text{Na}_2\text{SO}_4$  is not consumed and the reaction continues for extended periods of time.

The hot corrosion process, especially with acidic fluxing mechanism, depends very heavily on the temperatures. As described earlier, if the temperature of exposure is lower than the melting point of the melt, the corrosion would not occur unless a complex mixture of salts is formed. In the case of nickel, a mixture of nickel sulphate and sodium sulphate is formed which according to the phase diagram given in Fig. 9.7, has eutectic temperature of  $671^\circ\text{C}$ . Thus at temperatures lower than  $884^\circ\text{C}$ , the melting point of sodium sulphate, hot corrosion would result only when the eutectic mixture is formed. Formation of the eutectic mixture depends upon the temperature and partial pressure of  $\text{SO}_3$ . Fig. 9.8 gives the hot corrosion rate from  $670^\circ\text{C}$  to  $884^\circ\text{C}$ . It can be clearly seen that the reaction is maximum at a temperature where the partial pressure of  $\text{SO}_3$  is maximum. After this temperature the pressure of  $\text{SO}_3$  decreases because of the lower stability of  $\text{SO}_3$ .

The temperature dependence of hot corrosion of Ni in  $\text{O}_2 + 4\%\text{SO}_2$  is summarized in Fig. 9.9, which shows that the reaction is maximum at  $700^\circ\text{C}$ . It then decreases at  $800^\circ\text{C}$  and

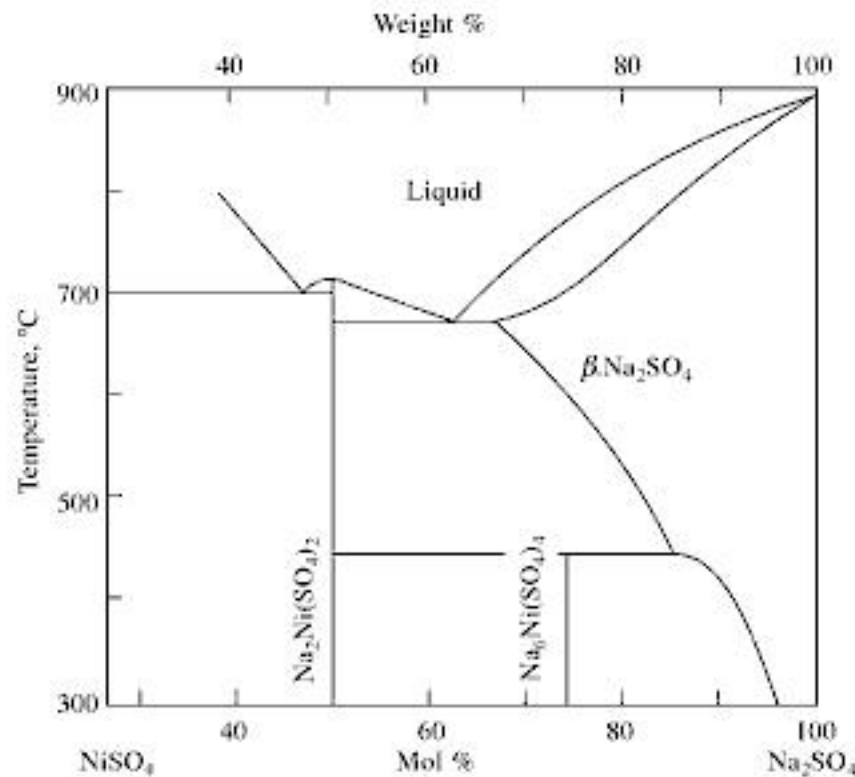


Fig. 9.7  $\text{Na}_2\text{SO}_4$  -  $\text{NiSO}_4$  phase diagram, showing the eutectic temperature of  $671^\circ\text{C}$ .



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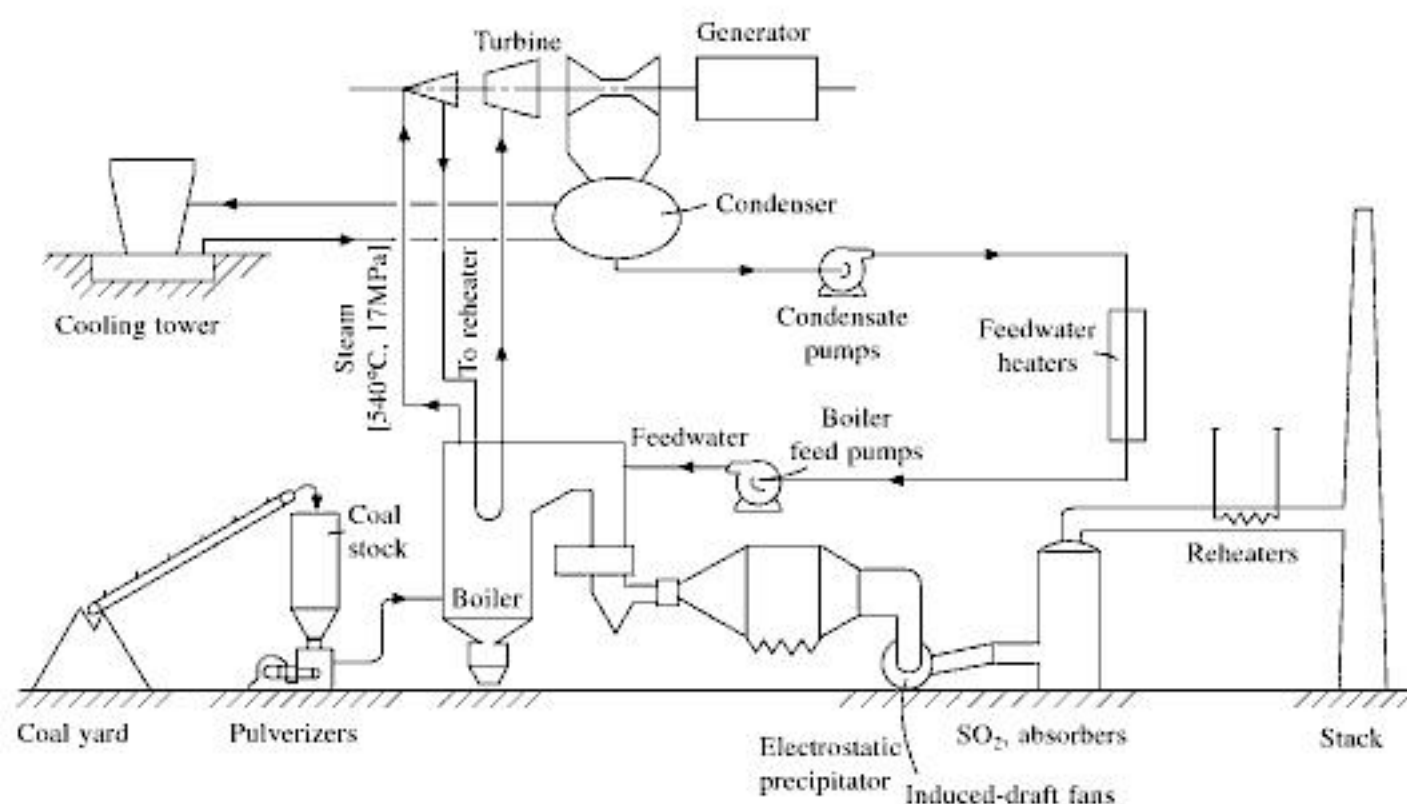


Fig. 14.1 Schematic of a coal-fired power plant.

can lead to the formation of non-protective scales or can disrupt normally protective oxide scales. The principal threats are oxidation and hot corrosion.

Water wall fire-side corrosion generally occurs in regions around the burners. The thick, hard external scales formed may be quite smooth, but often exhibit cracks or grooves (Fig. 14.2), which resemble an alligator hide. The major causes of corrosion of the water wall tubes are: the reducing (substoichiometric) conditions caused by impingement of incompletely combusted coal particles, and molten salt or slag-related attack.

Reducing atmosphere corrosion can be a result of direct reaction of the water wall tubes with a substoichiometric gaseous environment containing sulphur or partially combusted char containing iron pyrites, which gives rise to a very localized corrosive environment. Reducing conditions have two main effects on corrosion. First, they tend to lower the melting temperature of any deposited slag, which increases its ability to dissolve the normal oxide scales on the tubes, and second, the  $H_2S$  is stable which is considerably more corrosive than the  $SO_2$  predominating under oxidizing conditions. In presence of  $H_2S$ , iron sulphide is the expected corrosion product on iron, rather than the oxides ( $Fe_3O_4$  and  $Fe_2O_3$ ). Sulphide scales are less protective as diffusion of iron cations is much faster through sulphides than oxides.  $Cr_2O_3$  forming alloys such as AISI 310 SS, Inconel 671 or chromized coatings exhibit good corrosion resistance in this application.

#### **Molten salt corrosion**

Local disruption of the normal oxide film on the wall tubes by molten slag can lead to accelerated oxidation or to sulphidation-oxidation (if sulphur species are present in the slag).



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105(Ni-20Co-15Cr-5Mo-4.5Al-1.4Ti) and GMR-235 (Ni-15.5Cr-10Fe-5.25Mo-3Al-2Ti). This corrosive deterioration was called black plague. An example of hot corrosion in the rotating blades (made of IN 738) of an aircraft power plant is shown in Fig. 14.5. The creep failure of these blades, which are also called buckets, was initiated by sulphidation. Hot corrosion problems are also encountered in stationary vanes of gas turbines, which cause the deterioration that appears as cracking, swelling or spalling.

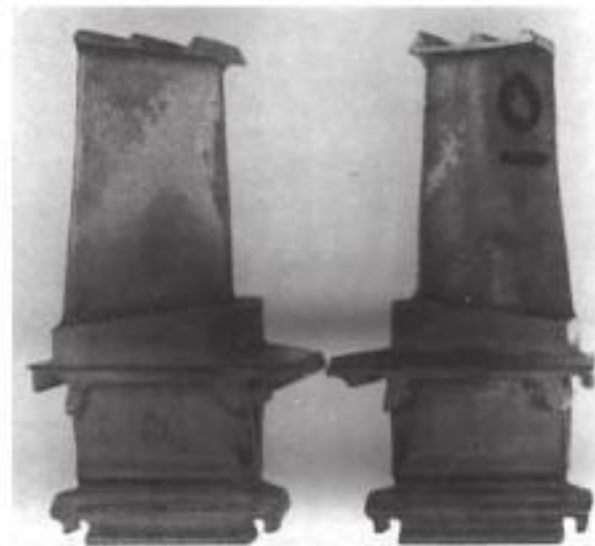
The dynamic nature of the environment in aircraft power plants promotes this type of high temperature oxidation/sulphidation of the main burner components and of downstream parts, such as turbine blades, vanes, and seals. Very high thermal and mechanical strains are produced on these parts because of power plant operation at elevated temperatures. The corrosive ash usually present in this dynamic-oxidation environment is  $\text{Na}_2\text{SO}_4$ , which reacts with power plant materials and causes a depletion of the alloying elements required to form a protective oxide film on the surfaces of these parts. The formation of a protective scale can also be inhibited by the consumption of the alloying elements by means of either acidic or basic fluxing reactions.

### Hot-Salt SCC

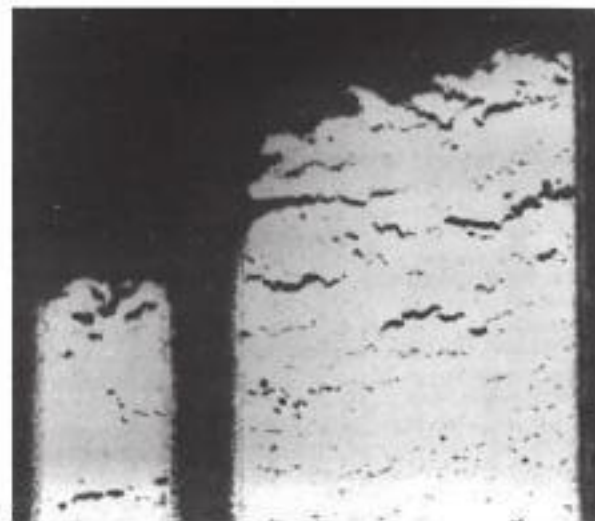
Hot-salt SCC has been observed mainly in components made of titanium alloys, such as the compressor blades. A combination of the following is required to induce this type of failure:

- High stress
- High temperature (approx. 345°C)
- Exposure to high concentration of chloride salts

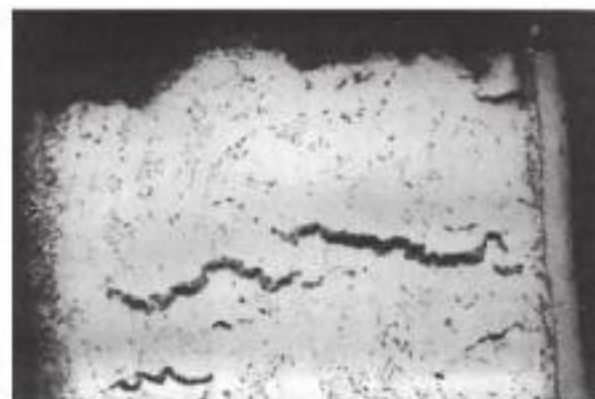
Hot-salt SCC occurs when titanium alloy



(a)



(b)



(c)

**Fig. 14.5** Aircraft power plant turbine blades (a) that were damaged by hot corrosion. (b) Higher magnification view of corrosion, 35 x. (c) Corroded turbine blades, 55 x.



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***Sulphidic corrosion***

Corrosion by various sulphur compounds at temperatures between 260 and 540°C is a common problem in many petroleum refinery processes and occasionally in petrochemical processes. Sulphur compounds from crude oils include polysulphides, hydrogen sulphide, mercaptans, aliphatic sulphides, disulphides and thiophenes. With the exception of thiophenes, sulphur compounds react with metal surfaces at elevated temperatures, forming metal sulphides, certain organic molecules and hydrogen sulphide. The relative corrosivity of sulphur compounds generally increases with temperature. Corrosion is in the form of uniform thinning, localized attack, or erosion-corrosion, depending on the process parameters. Corrosion control depends on the formation of protective metal sulphide scales that exhibit a parabolic growth. In general, nickel alloys are rapidly attacked by sulphur compounds at elevated temperatures, while chromium containing steels provide excellent corrosion resistance (as does aluminium). The combination of hydrogen sulphide and hydrogen can be particularly corrosive, and as a rule, austenitic stainless steels are required for effective corrosion control.

***Sulphidic corrosion in the absence of hydrogen***

This type of corrosion occurs mainly in various components of crude distillation units, catalytic cracking units, and hydrotreating and hydrocracking units. Crude distillation units that process sweet crude oils (less than 0.6 % total sulphur) experience relatively few corrosion problems. However, the distillation units, which process mostly sour crude oil require additional protection against high temperature sulphidic corrosion. For example, low-alloy steels containing a minimum amount of 5% Cr are used in furnace tubes, headers and U-bends, and elbows and tees in transfer lines. The high processing temperatures encountered in the reaction and catalyst regeneration section of catalytic cracking units require extensive use of refractory linings to protect all carbon steel components from oxidation and sulphidic corrosion.

The so-called McConomy curves can be used to predict the relative corrosivity of crude oils and their various fractions. Although this method relates corrosivity to total sulphur content, and thus does not take into account the variable effects of different sulphur compounds, it can provide reliable corrosion trends if certain corrections are applied. Plant experience has shown that the original McConomy curves tend to predict excessively high corrosion rates. Over the years, it has been found that corrosion rates predicted by the original McConomy curves should be decreased by a factor of roughly 2.5, resulting into modified curves as shown in Fig. 14.8. The curves demonstrate the beneficial effects of alloying steel with chromium in order to reduce corrosion rates.

Correction factors for process streams with various total sulphur contents, averages of those proposed originally by McConomy, are shown in Fig. 14.9. As can be seen, doubling the sulphur content can increase corrosion rates by approximately 30%.

***Sulphidic corrosion in the presence of hydrogen***

The presence of hydrogen in hydrotreating and hydrocracking operations increases the severity of high temperature sulphidic corrosion. Hydrogen converts organic sulphur compounds in



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4. Determine defect equilibria for an oxide of type  $\text{MO}_{2-x}$ .
5. What would be the pressure dependence for the defect concentrations for an oxide of type  $\text{M}_{1+x}\text{O}$ ?
6. State the type of defect in an oxide of type  $\text{MO}_{2+x}$ . Derive an expression for the relationship of defect concentration with the partial pressure of oxygen. Also show this relation graphically. What is the name of such a graphical relationship between pressure and defect concentration?
7. Can an oxide show different kinds of defects as a function of pressure? Explain using Brouwer's diagrams.
8. What are Wagner Hauffe's rules? How do they explain the oxidation behaviour of various oxides?
9. Show whether the oxidation rate of the following oxides will increase or decrease by doping Li or Cr into their metal before oxidation.  $\text{ZnO}$ ,  $\text{CaO}$ ,  $\text{FeO}$ ,  $\text{ZrO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$ .

### Chapter 3

1. Why is oxidation through short circuit diffusion paths faster compared to that of volume diffusion?
2. The parabolic rate constant for the oxidation of Ni at  $500^\circ\text{C}$  is several orders of magnitude greater than the calculated one, however, there is complete agreement of the two at  $1000^\circ\text{C}$ . Give reasons.
3. State the various diffusion mechanisms in oxides. Which of these diffusion mechanisms has the lowest, and which has the highest activation energy for diffusing ions?
4. What is the Kirkendall effect? State its importance, giving an example of the oxidation of a particular oxide.
5. What is the interdiffusion co-efficient?
6. How does grain size influence the oxidation rate? Explain why smaller grain size is beneficial for the oxidation of an alloy, but is detrimental to the oxidation of a pure metal.
7. What is the limitation of the marker method to determine the mechanism of transporting species in an oxide?
8. State the principle of the tracer method for determining the mechanism of transport of oxidising species.
9. What is the role of diffusion in secondary creep?
10. Carburization of pure iron is carried out at  $950^\circ\text{C}$ . It is desirable to achieve a carbon content of 0.9% at a depth of 0.1 mm, assuming that the carbon content of the surface is maintained at 1.20% and the diffusion coefficient  $D_{\text{r}}(\text{iron}) = 10^{-10} \text{ m}^2/\text{s}$ . Calculate the time necessary for this process.
11. Two binary alloys containing the elements A and B were intimately joined together by welding. The composition of the alloy to the right of the weld is 40% A and that to the left of the weld, 60% A. The couple is heated very rapidly to a temperature  $T_1$  and held there for 20h. After cooling to room temperature it was found that at a distance of 1.0 mm to the right of the weld the alloy contains 55.0% A. Estimate the



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4. Why are CVD coatings called diffusion coatings? Explain with a specific example.
5. What are the main limitations of CVD coatings?
6. Under what conditions does one get low activity coatings and high activity coatings? Which of the two is better, and why?
7. Differentiate between the properties of flame spray and HVOF coatings?
8. Do atmospheric plasma coatings have sufficient porosity and bond strength? If not how is it rectified?
9. What are the advantages of the transferred arc process over atmospheric plasma spray?
10. How is the IBA method different from other ion beam based techniques?

### Chapter 13

1. What is numerical aperture? How is it related to resolution? What is the maximum resolution obtained from an optical microscope?
2. What is polarized light? What additional information can be obtained using polarized light?
3. Using optical microscopy, what information can be obtained about oxide scales?
4. What are the main features of scanning electron microscopy? Which signals are used for topography and morphology of oxide scales? How is surface composition determined using SEM?
5. What is the main difference between EDAX and EPMA?
6. What information is obtained from back scattered electrons?
7. What are area scan maps? What information do they give about oxide scales?
8. How can TEM be used to get information about oxide scales?
9. How is the information obtained by EDAX different from X-ray diffraction?
10. Describe the principle of AES and XPS. Up to what range of thickness can AES and XPS be used?
11. What is chemical shift? What information does it provide about oxide scales?
12. How is  $^{18}\text{O}$  analysis conducted using SIMS to determine the mechanism of transporting species in the oxide layer?

### Chapter 14

1. Describe the fireside corrosion problems of heat exchanger tubes in coal based power plants?
2. How does the presence of chlorides in coal affect the corrosion behaviour?
3. What are the reducing and oxidising conditions in power plants? How do they affect the corrosion of boiler tubes?
4. Explain how hot corrosion occurs in a gas turbine?
5. How is hot corrosion avoided in gas turbines?
6. What is titanium fire? How does it affect the aircraft power plant?
7. What is the main cause of corrosion in municipal incinerators? What kind of materials are recommended to overcome this problem?
8. What is sulphidic corrosion? How does it differ when hydrogen is present?
9. What is the main effect of a high temperature hydrogen attack?



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# Appendix 4

## IMPORTANT TABLES

Table 1. Some of the SI derived units

| <i>Quantity</i>                            | <i>Name</i>              | <i>Formula</i>                   | <i>Special symbol*</i> |
|--------------------------------------------|--------------------------|----------------------------------|------------------------|
| Area                                       | Square meter             | $m^2$                            | —                      |
| Volume                                     | Cubic meter              | $m^3$                            | —                      |
| Velocity                                   | Meter per second         | $m/sec$                          | —                      |
| Density                                    | Kilogram per cubic meter | $kg/m^3$                         | —                      |
| Concentration                              | Moles per cubic meter    | $mole/m^3$                       | —                      |
| Force                                      | Newton                   | $kg\cdot m/sec^2$                | <i>N</i>               |
| Energy                                     | Joule                    | $kg\cdot m^2/sec^2$ , $N\cdot m$ | <i>J</i>               |
| Stress                                     | Pascal                   | $kg/m\cdot sec^2$ , $N/m^2$      | <i>Pa</i>              |
| Strain                                     | —                        | $m/m$                            | —                      |
| Power, radiant flux                        | Watt                     | $kg\cdot m^2/sec^3$ , $J/sec$    | <i>W</i>               |
| Viscosity                                  | Pascal-second            | $kg/m\cdot sec$                  | <i>Pa-sec</i>          |
| Frequency<br>(of a periodic<br>phenomenon) | Hertz                    | $sec^{-1}$ ( $s^{-1}$ )          | <i>Hz</i>              |
| Electric charge                            | Coulomb                  | $A\cdot sec$                     | <i>Coul (C)</i>        |
| Electric potential                         | Volt                     | $kg\cdot m^2/sec^2\cdot coul$    | <i>V</i>               |
| Capacitance                                | Farad                    | $sec^2\cdot coul^2/kg\cdot m^2$  | <i>(F)</i>             |
| Electric resistance                        | Ohm                      | $kg\cdot m^2/sec\cdot coul^2$    | <i>(Ω)</i>             |
| Magnetic flux                              | Weber                    | $kg\cdot m^2/sec\cdot coul$      | <i>Wb</i>              |
| Magnetic flux density                      | Tesla                    | $kg/sec\cdot coul$ , $Wb/m^2$    | <i>(T)</i>             |

\*Special symbols in parentheses are approved in the SI but not used in this text here, either the name or unparenthesized symbol is used.



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Table 8. Chemical tests and reactions for some common metals

| Reagents                          | Carbon steel            | Stainless Steels                        |                                  |                                                |                    | Aluminum                                          | Magnesium                          | Nickel                          | Monel                            | Inconel     |
|-----------------------------------|-------------------------|-----------------------------------------|----------------------------------|------------------------------------------------|--------------------|---------------------------------------------------|------------------------------------|---------------------------------|----------------------------------|-------------|
|                                   |                         | Types 302,204                           | Types 316,317                    | Types 304,321, 347                             | Types 303,414 430F |                                                   |                                    |                                 |                                  |             |
| Nital-10% nitric acid in methanol | Blackens surface        | No reaction                             |                                  |                                                |                    |                                                   | Cleans surface or turns gray       | Slow reaction turns blue, green | *Slow reaction turns blue, green | No reaction |
| Hydrochloric acid                 | Reacts to clean surface | No reaction                             | Attacks, releasing gas           | Attacks, leaving black smudge, rotten egg odor | Blackens surface   | Blackens surface                                  | Cleans surface                     | Cleans surface                  | No reaction                      |             |
| Copper sulphate solution          | Leaves copper color     | No reaction                             |                                  |                                                |                    |                                                   | Reacts, leaving heavy black smudge | No reaction                     |                                  |             |
| Sodium hydroxide                  |                         | No reaction                             |                                  |                                                |                    | Reacts, leaves gray smudge                        | No reaction                        |                                 |                                  |             |
| Sulphuric acid                    | Cleans surface          | Leaves dark surface with green crystals | Slow attack, leaving tan surface | No reaction                                    |                    | Strongly, reacts, foams, and leaves clean surface | No reaction                        |                                 |                                  |             |
| Zinc chloride in water            |                         | No reaction                             |                                  |                                                |                    |                                                   | Reacts and turns black             | No reaction                     |                                  |             |
| Ferrous chlorides                 |                         | No reaction                             |                                  |                                                |                    |                                                   | Reacts and turns black             | No reaction                     |                                  |             |

\*Note: Monel may be distinguished from nickel which looks alike by the following test. Place a few drops of nital on the surface of the specimen. It will turn blue green if it is either monel or nickel. Then place a small piece of soft iron (a nail will do) in the solution on the sample. If there is no reaction, the metal is nickel, but if the iron turns copper coloured, copper ions have been transferred from the copper in the metal, and it can be assumed that it is monel, which contains copper, zinc and tin and will react with so many acids to turn them black, that chemical tests would be of no value for them. Silver will turn black in sulphuric acid.



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| Temperature               |      | Tensile strength |            | Yield strength |            | Elongation |
|---------------------------|------|------------------|------------|----------------|------------|------------|
| °C                        | °F   | MPa              | ksi        | MPa            | ksi        | %          |
| <b>Nickel-base alloys</b> |      |                  |            |                |            |            |
| <b>Astroloy, bar</b>      |      |                  |            |                |            |            |
| <u>21</u>                 | 70   | 1410             | 205        | 1050           | 152        | <u>16</u>  |
| 540                       | 1000 | 1240             | 180        | 965            | 140        | <u>16</u>  |
| 650                       | 1200 | 1310             | 190        | 965            | 140        | 18         |
| 760                       | 1400 | 1160             | <u>168</u> | 910            | 132        | <u>21</u>  |
| 870                       | 1600 | 770              | 112        | 690            | 100        | <u>25</u>  |
| <b>D-979, bar</b>         |      |                  |            |                |            |            |
| <u>21</u>                 | 70   | 1410             | 204        | 1010           | 146        | <u>15</u>  |
| 540                       | 1000 | 1300             | 188        | 925            | 134        | <u>15</u>  |
| 650                       | 1200 | 1100             | <u>160</u> | 860            | <u>129</u> | <u>21</u>  |
| 760                       | 1400 | <u>2</u>         | 104        | 655            | 95         | <u>17</u>  |
| 870                       | 1600 | 345              | 50         | <u>305</u>     | 44         | 18         |
| <b>Hastelloy X, sheet</b> |      |                  |            |                |            |            |
| <u>21</u>                 | 70   | 785              | 114        | 360            | 52         | 43         |
| 540                       | 1000 | 650              | 94         | 290            | 42         | <u>45</u>  |
| 650                       | 1200 | 570              | 83         | 275            | 40         | <u>37</u>  |
| 760                       | 1400 | 435              | 63         | 260            | 38         | <u>37</u>  |
| 870                       | 1600 | 255              | <u>37</u>  | 180            | 26         | 50         |
| <b>IN-102, bar</b>        |      |                  |            |                |            |            |
| <u>21</u>                 | 70   | 960              | 139        | 505            | <u>73</u>  | 47         |
| 540                       | 1000 | 825              | 120        | 400            | 58         | 48         |
| 650                       | 1200 | 710              | 103        | 400            | 58         | 64         |
| 760                       | 1400 | 440              | 64         | 385            | 56         | 110        |
| 870                       | 1600 | 215              | 31         | 200            | <u>29</u>  | 110        |
| <b>Nimonic 75, bar</b>    |      |                  |            |                |            |            |
| <u>21</u>                 | 70   | 750              | <u>109</u> | —              | —          | <u>41</u>  |
| 540                       | 1000 | 635              | 92         | —              | —          | <u>41</u>  |
| 650                       | 1200 | 538              | 78         | —              | —          | 42         |
| 760                       | 1400 | 290              | 42         | —              | —          | 70         |
| 870                       | 1600 | <u>145</u>       | <u>21</u>  | —              | —          | 68         |
| <b>Nimonic 80A, bar</b>   |      |                  |            |                |            |            |
| <u>21</u>                 | 70   | 1240             | <u>179</u> | 620            | 90         | 24         |
| 540                       | 1000 | 1100             | <u>160</u> | 530            | <u>77</u>  | 24         |
| 650                       | 1200 | 1000             | <u>145</u> | 550            | 80         | 18         |
| 760                       | 1400 | 760              | 110        | 505            | <u>73</u>  | 20         |
| 870                       | 1600 | 400              | 58         | 260            | 38         | 34         |

(Contd)

| Temperature                    |      | Tensile strength |            | Yield strength |            | Elongation |
|--------------------------------|------|------------------|------------|----------------|------------|------------|
| °C                             | °F   | MPa              | ksi        | MPa            | ksi        | %          |
| <b>Nimonic 90, bar</b>         |      |                  |            |                |            |            |
| <u>21</u>                      | 70   | 1240             | 180        | 805            | <u>117</u> | 23         |
| 540                            | 1000 | 1100             | <u>160</u> | 725            | <u>105</u> | 23         |
| 650                            | 1200 | 1030             | 150        | 685            | 99         | 20         |
| 760                            | 1400 | 825              | 120        | 540            | 78         | 10         |
| 870                            | 1600 | 430              | 62         | 260            | 38         | <u>16</u>  |
| <b>Nimonic <u>105</u>, bar</b> |      |                  |            |                |            |            |
| <u>21</u>                      | 70   | 1140             | 166        | 815            | 118        | 12         |
| 540                            | 1000 | 1100             | <u>160</u> | 775            | 112        | 18         |
| 650                            | 1200 | 1080             | 156        | 800            | 116        | 24         |
| 760                            | 1400 | 965              | 140        | 655            | 95         | 22         |
| 870                            | 1600 | 605              | 88         | 365            | <u>53</u>  | <u>25</u>  |
| <b>Nimonic 115, bar</b>        |      |                  |            |                |            |            |
| <u>21</u>                      | 70   | 1240             | 180        | 860            | <u>125</u> | <u>25</u>  |
| 540                            | 1000 | 1090             | <u>158</u> | 795            | 115        | 26         |
| 650                            | 1200 | 1120             | 163        | 815            | 118        | <u>25</u>  |
| 760                            | 1400 | 1080             | 157        | 800            | 116        | 22         |
| 870                            | 1600 | 825              | 120        | 550            | 80         | 18         |
| <b>Pyromet 860, bar</b>        |      |                  |            |                |            |            |
| <u>21</u>                      | 70   | 1300             | 188        | 835            | <u>121</u> | 22         |
| 540                            | 1000 | 1250             | 182        | 840            | 122        | <u>15</u>  |
| 650                            | 1200 | 1110             | <u>161</u> | 850            | 123        | <u>17</u>  |
| 760                            | 1400 | 910              | 132        | 835            | <u>121</u> | 18         |
| <b>Rene <u>41</u>, bar</b>     |      |                  |            |                |            |            |
| <u>21</u>                      | 70   | 1420             | 206        | 1060           | 154        | <u>14</u>  |
| 540                            | 1000 | 1400             | 203        | 1010           | 147        | <u>14</u>  |
| 650                            | 1200 | 1340             | 194        | 1000           | <u>145</u> | <u>14</u>  |
| 760                            | 1400 | 1100             | <u>160</u> | 940            | 136        | 11         |
| 870                            | 1600 | 620              | 90         | 550            | 80         | 19         |
| <b>Rene 95, bar</b>            |      |                  |            |                |            |            |
| <u>21</u>                      | 70   | 1620             | 235        | 1310           | 190        | <u>15</u>  |
| 540                            | 1000 | 1540             | 224        | 1250           | 182        | 12         |
| 650                            | 1200 | 1460             | 212        | 1220           | 177        | <u>14</u>  |
| 760                            | 1400 | 1170             | 170        | 1100           | <u>160</u> | <u>15</u>  |
| <b>Inconel 600, bar</b>        |      |                  |            |                |            |            |
| <u>21</u>                      | 70   | 620              | 90         | 250            | 36         | 47         |
| 540                            | 1000 | 580              | 84         | 195            | 28         | 47         |
| 650                            | 1200 | 450              | <u>65</u>  | 180            | 26         | 39         |
| 760                            | 1400 | 185              | 27         | 115            | <u>17</u>  | 46         |
| 870                            | 1600 | <u>105</u>       | <u>15</u>  | 62             | <u>9</u>   | 80         |

(Contd)

| Temperature               |      | Tensile strength |            | Yield strength |            | Elongation |
|---------------------------|------|------------------|------------|----------------|------------|------------|
| °C                        | °F   | MPa              | ksi        | MPa            | ksi        | %          |
| <b>Inconel 601, sheet</b> |      |                  |            |                |            |            |
| <u>21</u>                 | 70   | 740              | 107        | 340            | <u>49</u>  | <u>45</u>  |
| 540                       | 1000 | 725              | <u>105</u> | 150            | <u>2</u>   | 38         |
| 650                       | 1200 | 525              | 76         | 180            | 26         | <u>45</u>  |
| 760                       | 1400 | 290              | 42         | 200            | <u>29</u>  | <u>73</u>  |
| 870                       | 1600 | <u>160</u>       | 23         | 140            | 20         | 92         |
| <b>Inconel 625, bar</b>   |      |                  |            |                |            |            |
| <u>21</u>                 | 70   | 855              | 124        | 490            | 71         | 50         |
| 540                       | 1000 | 745              | 108        | 405            | 59         | 50         |
| 650                       | 1200 | 710              | 103        | 420            | <u>61</u>  | 35         |
| 760                       | 1400 | 505              | <u>73</u>  | 420            | <u>61</u>  | 42         |
| 870                       | 1600 | 285              | <u>41</u>  | 475            | 40         | <u>125</u> |
| <b>Inconel 706, bar</b>   |      |                  |            |                |            |            |
| <u>21</u>                 | 70   | 1300             | 188        | 980            | 142        | 19         |
| 540                       | 1000 | 1120             | 163        | 895            | 130        | 19         |
| 650                       | 1200 | 1010             | 147        | 825            | 120        | <u>21</u>  |
| 760                       | 1400 | 690              | 100        | 675            | 98         | 32         |
| <b>Inconel 718, bar</b>   |      |                  |            |                |            |            |
| <u>21</u>                 | 70   | 1430             | 208        | 1190           | 172        | <u>21</u>  |
| 540                       | 1000 | 1280             | 185        | 1060           | 154        | 18         |
| 650                       | 1200 | 1230             | 178        | 1020           | 148        | 19         |
| 760                       | 1400 | 950              | 138        | 740            | 102        | <u>25</u>  |
| 870                       | 1600 | 340              | <u>49</u>  | 330            | 48         | 88         |
| <b>Inconel 718, sheet</b> |      |                  |            |                |            |            |
| <u>21</u>                 | 70   | 1280             | 185        | 1050           | <u>153</u> | 22         |
| 540                       | 1000 | 1140             | 166        | 945            | <u>137</u> | 26         |
| 650                       | 1200 | 1030             | 150        | 870            | 126        | <u>15</u>  |
| 760                       | 1400 | 675              | 98         | 625            | 91         | <u>8</u>   |
| <b>Inconel X 750, bar</b> |      |                  |            |                |            |            |
| <u>21</u>                 | 70   | 1120             | 162        | 635            | 92         | 24         |
| 540                       | 1000 | 965              | 140        | 580            | 84         | 22         |
| 650                       | 1200 | 825              | 120        | 565            | 82         | <u>9</u>   |
| 760                       | 1400 | 485              | 70         | 455            | 66         | <u>9</u>   |
| 870                       | 1600 | 235              | 34         | 165            | 24         | 47         |
| <b>M-252, bar</b>         |      |                  |            |                |            |            |
| <u>21</u>                 | 70   | 1240             | 180        | 840            | 122        | <u>16</u>  |
| 540                       | 1000 | 1230             | 178        | 765            | 111        | <u>15</u>  |
| 650                       | 1200 | 1160             | <u>168</u> | 745            | 108        | 11         |
| 760                       | 1400 | 945              | <u>137</u> | 715            | 104        | 10         |
| 870                       | 1600 | 510              | 74         | 485            | 70         | 18         |

(Contd)

| Temperature                 |      | Tensile strength |                     | Yield strength |                     | Elongation         |
|-----------------------------|------|------------------|---------------------|----------------|---------------------|--------------------|
| °C                          | °F   | MPa              | ksi                 | MPa            | ksi                 | %                  |
| <b>Udimet 500, bar</b>      |      |                  |                     |                |                     |                    |
| <a href="#">21</a>          | 70   | 1310             | 190                 | 840            | 122                 | 32                 |
| 540                         | 1000 | 1240             | 180                 | 795            | 115                 | 28                 |
| 650                         | 1200 | 1210             | 176                 | 760            | 110                 | 28                 |
| 760                         | 1400 | 1040             | 151                 | 730            | 106                 | 39                 |
| 870                         | 1600 | 640              | <a href="#">93</a>  | 495            | 72                  | 20                 |
| <b>Udimet 520, bar</b>      |      |                  |                     |                |                     |                    |
| <a href="#">21</a>          | 70   | 1310             | 190                 | 860            | <a href="#">125</a> | <a href="#">21</a> |
| 540                         | 1000 | 1240             | 180                 | 825            | 120                 | 20                 |
| 650                         | 1200 | 1170             | 170                 | 795            | 115                 | <a href="#">17</a> |
| 760                         | 1400 | 725              | <a href="#">105</a> | 725            | <a href="#">105</a> | <a href="#">15</a> |
| 870                         | 1600 | 515              | 75                  | 515            | 75                  | 20                 |
| <b>Udimet 700, bar</b>      |      |                  |                     |                |                     |                    |
| <a href="#">21</a>          | 70   | 1410             | 204                 | 965            | 140                 | <a href="#">17</a> |
| 540                         | 1000 | 1280             | 185                 | 895            | 130                 | <a href="#">16</a> |
| 650                         | 1200 | 1240             | 180                 | 855            | 124                 | <a href="#">16</a> |
| 760                         | 1400 | 1030             | 150                 | 825            | 120                 | 20                 |
| 870                         | 1600 | 690              | 100                 | 635            | 92                  | 27                 |
| <b>Udimet 710, bar</b>      |      |                  |                     |                |                     |                    |
| <a href="#">21</a>          | 70   | 1190             | 172                 | 910            | 132                 | <a href="#">7</a>  |
| 540                         | 1000 | 1150             | <a href="#">167</a> | 850            | 123                 | 10                 |
| 650                         | 1200 | 1290             | 187                 | 860            | <a href="#">125</a> | <a href="#">15</a> |
| 760                         | 1400 | 1020             | 148                 | 815            | 118                 | <a href="#">25</a> |
| 870                         | 1600 | 705              | 102                 | 635            | 92                  | <a href="#">29</a> |
| <b>Unitemp AF2-1DA, bar</b> |      |                  |                     |                |                     |                    |
| <a href="#">21</a>          | 70   | 1290             | 187                 | 1050           | 152                 | 10                 |
| 540                         | 1000 | 1340             | 194                 | 1080           | 157                 | <a href="#">13</a> |
| 650                         | 1200 | 1360             | 197                 | 1080           | 157                 | <a href="#">13</a> |
| 760                         | 1400 | 1150             | <a href="#">167</a> | 1010           | 146                 | <a href="#">8</a>  |
| 870                         | 1600 | 830              | 120                 | 715            | 104                 | <a href="#">8</a>  |
| <b>Waspaloy, bar</b>        |      |                  |                     |                |                     |                    |
| <a href="#">21</a>          | 70   | 1280             | 185                 | 795            | 115                 | <a href="#">25</a> |
| 540                         | 1000 | 1170             | 170                 | 725            | <a href="#">105</a> | 23                 |
| 650                         | 1200 | 1120             | 162                 | 690            | 100                 | 34                 |
| 760                         | 1400 | 1400             | 115                 | 675            | 98                  | 28                 |
| 870                         | 1600 | 525              | 76                  | 515            | 75                  | 35                 |

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