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**Organic and Inorganic Coatings for
Corrosion Prevention –
Research and Experiences**

Papers from EUROCORR '96

Edited by
L. FEDRIZZI & P. L. BONORA

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European Federation of Corrosion Publications Series Introduction

The EFC, incorporated in Belgium, was founded in 1955 with the purpose of promoting European co-operation in the fields of research into corrosion and corrosion prevention.

Membership is based upon participation by corrosion societies and committees in technical Working Parties. Member societies appoint delegates to Working Parties, whose membership is expanded by personal corresponding membership.

The activities of the Working Parties cover corrosion topics associated with inhibition, education, reinforcement in concrete, microbial effects, hot gases and combustion products, environment sensitive fracture, marine environments, surface science, physico-chemical methods of measurement, the nuclear industry, computer based information systems, the oil and gas industry, the petrochemical industry and coatings. Working Parties on other topics are established as required.

The Working Parties function in various ways, e.g. by preparing reports, organising symposia, conducting intensive courses and producing instructional material, including films. The activities of the Working Parties are co-ordinated, through a Science and Technology Advisory Committee, by the Scientific Secretary.

The administration of the EFC is handled by three Secretariats: DEHEMA e. V. in Germany, the Société de Chimie Industrielle in France, and The Institute of Materials in the United Kingdom. These three Secretariats meet at the Board of Administrators of the EFC. There is an annual General Assembly at which delegates from all member societies meet to determine and approve EFC policy. News of EFC activities, forthcoming conferences, courses etc. is published in a range of accredited corrosion and certain other journals throughout Europe. More detailed descriptions of activities are given in a Newsletter prepared by the Scientific Secretary.

The output of the EFC takes various forms. Papers on particular topics, for example, reviews or results of experimental work, may be published in scientific and technical journals in one or more countries in Europe. Conference proceedings are often published by the organisation responsible for the conference.

In 1987 the, then, Institute of Metals was appointed as the official EFC publisher. Although the arrangement is non-exclusive and other routes for publication are still available, it is expected that the Working Parties of the EFC will use The Institute of Materials for publication of reports, proceedings etc. wherever possible.

The name of The Institute of Metals was changed to The Institute of Materials with effect from 1 January 1992.

A. D. Mercer

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Preface

The environment at the present time is becoming more and more aggressive with respect to artefacts. The protection of building structures, high voltage towers, off-shore constructions, bridges, chemical plants, electrical equipment and even art objects, monuments etc. is almost always achieved by means of the best method available to separate the object from the environment, i.e. the application of a coating.

Apart from aesthetic considerations, the use of protective coatings is receiving significant attention both in the scientific and in the marketing fields, being driven, on the one hand by the increasing demand for total quality, outstanding performance, long and reliable service life, and on the other hand, by the need for low prices, easier application techniques and environmentally friendly components.

Most coatings are multilayer systems and include a metal layer (zinc, aluminium or other metals or alloys), a chemical pretreatment (phosphate layers and/or adhesion promoters), a set of organic (polymer) layers (primer, intermediate, top-coat) each one characterised by specific duties and related features and components. Moreover, many of the commonly used dangerous components (chromium, lead, organic solvents, cadmium, ...) are no longer acceptable in environmental awareness terms, although their performances are acknowledged to be outstanding. There is a need for substitutes (or alternative techniques) with both comparably reliable performances and environmental acceptability.

In the session on Coatings held during EUROCORR' 96 the following topics were much discussed:

- Life-time prediction of organic coatings;
- Environmentally friendly coatings;
- Testing; and
- Surface preparation techniques.

This book contains a selection of the scientific work presented in the Conference with the aim of focusing on the research developments in the frame of corrosion protection coatings for industrial use.

The book is in four sections describing, respectively, organic coatings, zinc coatings, other metallic coatings and ceramic coatings.

Electrochemical techniques such as Electrochemical Impedance Spectroscopy (EIS) or Electrochemical Noise Analysis proved to be very effective in the testing of organic coatings. Attention was also paid to metal surface preparation and to coating adhesion.

Ceramic coatings including oxides and nitrides produced using spraying or physical vapour deposition techniques, were studied in various aggressive environments, with care taken to obtain corrosion resistance data in conditions of mechano-chemical attack (wear-corrosion, erosion corrosion).

Surface modification by laser treatments is described in some detail.

Various metal deposition techniques are described — including hot-dip, electrodeposition, spray or sol-gel — for the production of corrosion resistant coatings of nickel, aluminium or zinc alloy.

P. L. Bonora

Chairman of EFC Working Party on Coatings

L. Fedrizzi

Volume Editor

Part 1

Organic Coatings

Laboratory Corrosion Monitoring of Zinc-Rich Paint Coatings on Naval Steel in Seawater by Electrochemical Methods

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ABSTRACT

Laboratory assessment of the performance of zinc-rich paint (ZRP) coatings on naval steel in seawater has been carried out using electrochemical impedance spectroscopy (EIS) combined with cathodic protection potential measurements. Different formulations of painted naval steel samples were investigated during exposure times up to 50 days. ZRP coating formulations included those with the zinc pigment content covering a wide w/w-concentration range as well as those with different organic/inorganic binders based on chlorinated-rubber, epoxy-polyamide, ethyl-silicate and alkyd-resins. Experimental impedance diagrams have been quantitatively explained in terms of a transfer function analysis using identification procedures and non-linear fit routines. Information concerning the influence of both binder type and zinc pigment concentration on the corrosion protection behaviour of these ZRP coatings was obtained from the exposure time dependence of the system parameters, which were derived from the fitting procedure.

Characteristics and properties of the different naval steel/ZRP coating/seawater systems have been determined according to the application of an impedance transfer function model which describes the reactions taking place at the metal/film and film/solution interfaces as well as the diffusion processes through the active ZRP film. The kinetic parameters correlate well with gradual system deterioration and reflect the way in which the galvanic effect and barrier-action properties of the ZRP employed as primers progressively diminished. The whole set of results can be interpreted in terms of corrosion processes going on extensively through pores and cracks of these coatings.

1. Introduction

In modern technology, the use of coatings with organic and inorganic compounds provides a widespread method for the corrosion protection that is necessary to improve the durability of engineering metallic structures. In these industrial applications the corrosion protection properties are determined by a complex mechanism which includes the effects of factors such as coating formulation, chemical composition and pre-treatment of the metallic surface, environmental prevailing conditions, as well as electrochemical reactions occurring during the corrosion process

either inside the coating itself and/or at the metal/coating interface during and after water uptake and oxygen permeation, respectively. Therefore, the protective properties of the coating can be attributed to an electrochemical action and/or a barrier-type effect. Due to the great diversity of products necessary to best serve the large number of specific purposes for which coatings are applied, the technology of protective organic/inorganic coatings has expanded tremendously in the course of the last decades. It is worth noting that high-performance coatings were developed as need for them arose and as materials became available which allowed their application.

The *in situ* deterioration of protective coatings during exposure to corrosive media can be explained by considering the typical service situations. Localised corrosion processes caused by inhomogeneities within the protective film applied on active metals are the most frequent reasons for damage of metallic surfaces which are covered by relatively thin organic/inorganic coatings. Even in the case of a high solid content in the coating, its inner structure will exhibit an inhomogeneous nature which becomes more so with penetration of aggressive electrolyte and with accumulation of corrosion products. Thus, the corrosion of polymer coated metals involves a gradual formation of defects followed by the penetration of corrosive species which promote progressive adhesion loss and subsequent attack of the underlying base metal [1]. Both electrical and electrochemical methods have been in general use for a long time to detect and evaluate the early degradation of coatings on steel [2].

The application of fast electrochemical transient methods for an appropriate evaluation of the relative ability of a painting scheme to provide anticorrosive protection to metallic substrates has generally not been available until recently. The situation appears to be changing, particularly with the advent of modern a.c. electrochemical techniques. There are now many examples in the literature describing the use of electrochemical impedance spectroscopy for investigations concerning protective coatings [3–16]. In the field of polymer coated metals, this technique has mainly been employed to study the reaction kinetics and mass transport processes at electrodes with restricted diffusion to the polymer film structure [3,4], and to characterise the barrier properties of unpigmented organic polymer coatings [5].

In recent years, primers heavily pigmented with zinc dust have been extensively used as protective coatings of naval steels exposed to seawater environments. Zinc rich paints (ZRP) including binders based on epoxy, alkaline metal silicates or alkyd silicates gained initially similar acceptance. In the particular case of iron-based metallic substrates exposed to either industrial or saline atmospheres, paints containing a high content of pure zinc particles homogeneously dispersed in both organic and inorganic binders are currently employed in corrosion protective ZRP coatings. In the case of inorganic binders, the use of ethyl-silicate appears to be predominant. It is interesting to note that the formulation of commercial ZRP coatings which are currently applied, includes various types of organic binders, such as those based on chlorinated-rubber, epoxy-polyamide, epoxy-esters, polyesters, polyurethanes, and alkyd resins [1,17,18]. A high pigmentation level is required for improved electrical contact between adjacent zinc particles and between them and the steel substrate so that when the electrolyte solution reaches the steel/paint interface the dissolution reaction of the metallic zinc active fraction will provide cathodic protection to the steel substrate for a certain time.

Inorganic zinc primers are highly adherent, reacting to form a chemical bond with the steel substrate. This prevents undercutting of the organic topcoats so that any coating breaks do not expand. The inorganic zinc coatings can be used either alone or as a permanent primer over which topcoats may be applied. On the other hand, although organic ZRP coatings protect in a similar manner, provided the zinc is in particle-to-particle electrical contact, the organic binders are not chemically reacted to the substrate. Likewise, the physicochemical properties of ZRP are affected by the content of zinc in the dry film as well as by the type and nature of the binder selected to provide uniformity and coherence to the coating system. Therefore, the ability of the binder to produce a compact surface layer is closely related to its molecular size and complexity.

Data obtained from impedance spectroscopy techniques, open circuit corrosion potential (E_{corr}) measurements, steady-state polarisation curves and visual assessments have been used in attempting to evaluate the performance of ZRP coatings based on different binders during exposure to corrosive media [19–36]. Impedance spectra have been interpreted in terms of appropriate system models [32–36] and the corresponding kinetic parameters correlated with corrosion processes taking place extensively through pores and cracks in the ZRP coatings, which thus behave like porous electrodes due to the presence of such voids. Electrochemical impedance spectroscopy (EIS) has previously been applied to corrosion studies of the protective behaviour of these coatings [19–21,27–29], but until recently [33–36] system models failed to simulate the whole frequency response taking into account the gradual development of a porous structure during the corrosion process. Therefore, a complete interpretation of changes in the impedance spectrum at different exposure times to an aggressive environment, that would account for variations in the active zinc area of the coating, was also lacking.

This paper aims to discuss the systematic application of a.c. electrochemical techniques combined with corrosion potential measurements, to gain a deeper insight concerning the characterisation of effects related to ZRP coating composition on the corrosion resistance of steels at different immersion times in seawater. Data obtained from accelerated tests which were carried out using painted steel surfaces, are also taken into account in assessing the degree of rusting and blistering.

2. Characteristics and Properties of ZRP Coatings

2.1. Binders

The effect of corrosion inhibition due to many currently used ZRP coatings involves the contribution of all the zinc dust particles as active species and, additionally, the improvement of the binder matrix resistance [37–39]. This allows the binders to behave as an effective barrier to the corrosion process promoted by the aggressive environment by acting as a high resistance located between the anodic and cathodic areas where corrosion reactions are already taking place. The barrier layer properties of ZRP coatings are determined by the rate of transport of water, electrolyte ions and molecular oxygen through the polymeric matrix of the surface film. Likewise, a good adhesion of the coating to the substrate improves the corrosion protection. To gain

knowledge on the barrier action of ZRP coatings it is necessary to analyse their dielectric characteristics, which rarely exhibit ideal behaviour in terms of conventional equivalent circuits [6]. Thus, investigations performed to characterise the influence of binders by using electrochemical impedance spectroscopy, have clearly shown deviations from ideality of either capacitive or resistive components. These deviations have, in principle, been attributed to effects arising from surface roughness at the corroding metal/coating interface.

The ideal dielectric behaviour of barrier coatings is significantly affected by the type of binder, curing process and solvent content. Furthermore, it is also influenced by water up-take of the ZRP structure. The corrosion processes at the steel substrate can be detected by examining the dependence of the capacitance value at high frequencies on exposure time [7]. Experimental results are usually analysed from graphical techniques in which coating parameters can be directly estimated from the frequency response of Bode plots or Nyquist diagrams [10–16]; alternatively, the set of impedance spectra data can be simulated using non-linear least-squares fit procedures [16, 40–43].

2.2. Zinc Pigment Particles

The performance of primers is related to the size, distribution and morphology of the zinc particles distributed in the applied coating [1]. Generally, the particle size lies within the range 0.1–40 μm , the typical morphology being either spherical, foil or fibre shaped. An appropriate particle-size distribution is required to obtain the best arrangement to generate a highly resistive compact film. As far as the particle size is concerned, high corrosion protection can be achieved by including spherical granules with a mean diameter of about 2–9 μm , since larger values promote the gradual sedimentation of particles.

Controlled mixtures of both spherical and foil shaped particles are found to improve the corrosion protection effect, to diminish the sedimentation process, and to enhance the adhesive characteristics of ZRP coatings. It is noteworthy that highly pure zinc dust must be employed in order to avoid impurities that have a detrimental influence on the long-time coating performance. Usually the accepted zinc oxide content in the manufacture process of zinc particles is lower than 5% w/w, a limit which is fixed taking into account that when this concentration value is exceeded the large amount of oxidised zinc particles affects the quality of electrical contacts between them that is required for an effective cathodic protection of the steel substrate.

2.3. ZRP Coating Thickness

The value of the dry film thickness is an important factor affecting the corrosion protection of steels in aggressive environments during the serviceable life of ZRP coatings [1]. A properly selected film thickness value will depend to some extent on the type of binder when ZRP primers are applied, as is usually the case, to a blasted metallic surface with an average roughness about 40–60 μm . This means that a ZRP thickness exceeding 60 μm of dry film must be used just to cover the complete substrate profile topography, but even under these circumstances a long-life protection effect cannot be assured as substrate uncovered surface peaks may

protrude. For long time protection a total thickness of the final ZRP coating should be about 100–200 μm , the upper limit requiring at least two pack primer applications. A single pack primer cannot generally be applied to yield a total film thickness higher than 100 μm .

3. ZRP Coating Uses

Zinc represents the most common corrosion protection coating material for iron type metallic substrates [1,37]. In a chromate converted condition, it provides satisfactory corrosion protection in industrial atmospheres as well as in salt spray testing. However, non-converted zinc exhibits a very high electrochemical reactivity in practical conditions [38]. Furthermore, some of the high performance organic coatings which have been used for many years for the corrosion protection of metallic structures, cannot be employed nowadays because formulations of these coatings mostly contain active corrosion inhibitors like chromates and lead based pigments having a strong detrimental environmental influence. It is worth noting that the inclusion of these substances is clearly limited by the advanced legislative restrictions. Thus, the use of new binders and anticorrosive pigments are now being considered for the development of green coating formulations. The volatile solvent content of ZRP coatings must also be diminished. This can be partly achieved by replacing the organic solvent with water. Corrosion mechanisms of novel coating systems are open to kinetic analysis by modern experimental techniques.

The ability of zinc dust paints to provide corrosion protection where small scratches extend through the coating to the metal can be associated with the fact that zinc particles are often smeared over the surface so that further active zinc areas appear freshly exposed over the scratch. The excellent anticorrosive properties of zinc dust paints have been attributed [23,39] to two fundamental protection mechanisms (i) the galvanic protection stage, which requires good electrical contact among the zinc particles themselves as well as between them and the steel substrate, and (ii) the barrier-like behaviour stage, which is reinforced by the amount and nature of zinc corrosion products leading to promotion of the stable formation of a dielectric surface film. In the case of the most important polymeric binders (i.e. chlorinated rubber, ethyl-silicate, epoxy polyamide, and alkyd resins) used in the formulation of ZRP coatings, the content of the zinc particles is about 75–90% w/w in the dry film.

Zinc dust primers are widely used in almost all steel applications [44,45]. In shipbuilding the applications of ZRP began with those based on inorganic binders which were developed and employed by navies during the Second World War. Nevertheless, subsequent demand has mainly grown in the field of organic based materials and, in particular, ZRP coatings based on epoxy resins have become firmly established as shop primers for replacement of wash primers in shipyard works. Epoxy zinc primers were later specified, because of their excellent corrosion prevention properties as well as their suitability for shipbuilding practice. Present day painting procedures use a low zinc-content epoxy primer which can be overcoated using non-saponifiable materials such as epoxy or chlorinated rubber.

ZRP coatings applied on steel bridges represent an early successful use of these materials. They provide outstanding corrosion protection to bridge structures located

in almost every set of prevailing climate conditions. When ZRP coating performance is compared with that given by a sprayed zinc layer covered with a conventional topcoat, the ZRP has the advantage of easier application control. In those cases where a long-time corrosion protection is needed, or where engineering structures become practically inaccessible in service operation, the use of ZRP systems will be largely justified on an economic basis. In applications where topcoats are needed for improved protection of the bridge structure the inner layer containing the inorganic zinc species can accept various possible paint compositions for incorporation in the outer layer of the coating. Thus, vinyl compounds have been frequently used as well as alkyd compounds, although when alkyds are employed a special bonding tiecoat should be applied over the inorganic zinc surface to ensure a satisfactory adhesion during service operation.

The demand for ZRP coatings for corrosion protection in marine cargo containers has increased remarkably during the last decades. Both galvanised steel and zinc rich painted steel are specified, the latter is particularly employed for stand frames and pillars.

Railways have successfully adopted epoxy-ester based ZRP for sleepers, e.g. rail holders, although galvanising was used for some sections near the coast. Because of the good performance of these structures, ZRP is expected to be increasingly applied in similar fields. Likewise, railways have also specified inorganic ZRP coatings to protect the buffers of good wagons which are heat treated after coating. They are also employed to protect the inside of both refrigerator wagons and petroleum tanks.

From the point of view of pollution and environmental hygiene, ZRP coatings are finding extensive applications in different fields and further uses are also expected. It is interesting to note that certain problems still remain open to discussion concerning zinc fumes. Large and medium sized shipyards have overcome these difficulties, having the painting and welding processes carried out with proper safeguards as well as good ventilation. Corrosion problems in engineering applications are greater now than at any time and, accordingly, effective practical solutions are in great demand. In the near future it will be necessary to reduce dramatically the use of those volatile organic compounds or solvents, which have been major components in the formulation of protective coatings. Present researches on high-performance coatings are in the area of high solids and near 100% solids coatings, and towards water-based or water-dispersed coating materials.

4. Corrosion Studies of ZRP Coating Performance

4.1. Conventional Electrochemical Techniques

The main function of a coating is related to the physical separation of two highly reactive materials, the environment and substrate. Consequently, the effect of aggressive ions and species on the essential primer properties should be carefully analysed. Changes of adhesion, cohesion, intercoat bond, resistance to corrosion and chemicals, and protection as single coat during exposure to a particular environment are all factors that are associated with the coating performance.

ZRP are usually applied as anticorrosion primers in multilayer coating systems and not as single protective layers. The outstanding performance of these coatings

can be mainly associated with the cathodic protection of the steel substrate when the critical volume concentration of metallic zinc pigments is exceeded in the paint composition, bearing in mind that a high content of zinc dust is required to provide a good electrical connection between the pigment particles as well as between particles and the metallic substrate. The classical work of Mayne [39] has demonstrated the importance of the zinc content in the coating for it to behave like a sacrificial anode. However, this mode of action becomes time-limited because of the tendency of the zinc particles to be oxidised, losing their mutual electrical contact.

It should be pointed out that in the absence of anticorrosive pigments, the main mechanism of corrosion protection consists in blocking the diffusion of corrosive species like water, ions and/or oxygen through the polymeric matrix. However, because of the heterogeneous character of paint films the corrosion process will occur, with the anodic reaction being generally initiated at coating defects and the cathodic reaction taking place in adjacent regions [46]. This fact has given support to investigations concerning the composition and structure of corrosion product films formed beneath the paint in order to gain a better understanding of the mechanism of corrosion protection provided either by organic or by inorganic ZRP coatings.

Various techniques have been used to detect and evaluate the degradation of ZRP coatings [47,48]. Early works used polarisation resistance measurements and looked at zinc binder wetting properties [24] or measurements of the equivalent capacitance at a constant frequency using a bridge method [49,50].

4.2. Applications of Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is becoming of increasing importance in corrosion studies [51–58] and it has been also used to evaluate the protective behaviour of ZRP coatings [19–21,23–36]. Mézáros and Linqvist [25] employed a porous electrode model to explain the impedance response characteristics, whereas Szauer and Brandt [19] used an impedance technique to examine the cathodic protection and zinc deposition processes. Real *et al.* [33] have recently attempted to model and fit the impedance response according to a transmission line model to interpret the system parameters obtained using various film thicknesses of ethyl-silicate coatings at different immersion times in seawater.

In most electrochemical systems steady-state current–potential (E – I) relationships are easily measured at either constant current or constant potential. The dynamic response of the system can be obtained by perturbing with a small electrical signal superimposed on the constant d.c. potential or current signal the steady state conditions obtaining. The estimation of the transfer function impedance, $Z(j\omega)$, can be derived from the experimental data set. The complex impedance diagrams provide the experimental information which requires to be transformed in a quantitative mathematical expression to analyse the dynamics of the corrosion process [59–68]. Digital signal processing allows the use of perturbation signals of different profiles and Laplace and Fourier transform algorithms to determine the impedance from time-domain procedures by spectral analysis. The dynamic characteristics of the metal/coating/electrolyte system are represented by its transfer function impedance, which can be calculated by the relationship between a deterministic (input signal) perturbation and the corresponding (output signal) response according to

$$Z(j\omega) = \Delta E(j\omega) / \Delta I(j\omega) = L[\Delta E(t)] / L[\Delta I(t)] = F[\Delta E(t)] / F[\Delta I(t)] \quad (1)$$

where ω is the angular frequency, j $(-1)^{1/2}$, $Lf(t)$ and $Ff(t)$ the Laplace and Fourier transforms of a time-domain function, respectively. Another possibility is to estimate the impedance results by spectral analysis, in which both deterministic and random/pseudo-random signal perturbations can be applied. In this case:

$$Z(j\omega) = G_{EI}(j\omega) / G_{II}(j\omega) \quad (2)$$

where $G_{II}(j\omega)$ is the auto-power spectrum of the input signal (in this case, for instance, a current excitation) and $G_{EI}(j\omega)$ the cross-power spectrum of input and output (electrode potential transient) signals. In order to determine the transfer function impedance by spectral analysis, the spectral density functions can be estimated either through finite Fourier transform of correlation functions or through finite Fourier transform of the original time history records [59–64].

Thus, EIS has proven to be a powerful tool to obtain the specific parameters of these complex corrosion systems [32–36]. Using a proper transfer function analysis and identification procedures it is possible to obtain an optimal correlation between the experimental and theoretical data in order to interpret the whole set of impedance spectra recorded for the steel substrate/ZRP coating/aggressive electrolyte interfaces at different exposure times [32–36,69–71].

In the case of the application of the transmission line model, ZRP samples with ethyl-silicate matrix and different coating thicknesses have been tested using electrochemical impedance spectroscopy [33]. The Nyquist diagrams, after ohmic drop corrections exhibit in the high-frequency domain a constant phase angle of about -45° . This behaviour is typical for porous systems and can be explained using the cylindrical pore theory [7,9,12, 72–74]. The appropriate algorithm, based on a transmission line model [75,76] for n cylindrical pores linked in parallel, was developed to account for variations of the electrochemically active area by estimating the characteristic geometrical parameters of the porous structure. Each R_k , C_k and $R_{t,k}$ element of the transmission line associated with a single pore of radius r_p and length l is given by :

$$R_k = R_0 N^{-1} \quad (3)$$

$$C_k = 2 \pi r_p l C_d N^{-1} \quad (4)$$

and

$$R_{t,k} = N R_t (2\pi r_p l)^{-1} \quad (5)$$

where $R_0 = l (\pi K r_p^2)^{-1}$ corresponds to the electrolyte resistance of a single pore between its aperture and the bottom, K is the electrolyte conductivity and C_d and R_t are the specific interfacial capacitance and the charge transfer resistance, respectively. The impedance contribution associated with each $(k-1)$ element of a pore is expressed as:

$$Z_{k-1} = R_{k-1} + [j\omega C_{k-1} + (R_{t,k-1})^{-1} + (Z_k)^{-1}]^{-1} \quad (6)$$

Thus, the impedance of a single pore Z_p can be calculated taking into account N units of the transmission line. Consequently, the calculated impedance Z_T related to n pores is given by:

$$Z_T = Z_p n^{-1} \quad (7)$$

The parameters derived from the fitting procedure, r_p , l , and n number of pores, suggest that the electrochemically active area $A = n(2 \pi r_p l)$, diminishes markedly with increasing immersion time. Independently of the coating thickness, this time-dependence was found to be mainly brought about by a decrease of the pore radius with increasing exposure time due to the accumulation of corrosion products as confirmed by SEM micrographs [33,35].

The impedance spectrum of each particular ZRP coating whose composition is depicted in Table 1, was strongly affected by the exposure time in the aggressive electrolyte. The dependence of the open circuit corrosion potential (E_{corr}) on the exposure time in seawater has been successfully applied as a simple tool for the evaluation of corrosion protection by ZRP coatings due to their conductive nature (Fig. 1). The change of E_{corr} for the tested samples illustrates the corresponding galvanic protection supplied by the ZRP layer. Thus, the gradual shift of E_{corr} to more positive potentials with rising immersion time reveals a progressive loss in the galvanic protection effect. After prolonged exposure time E_{corr} reaches the typical value corresponding to the corrosion potential of steel in seawater that lies close to -0.65 V (SCE). The analysis of results presented in Fig. 1 yields first indications on the influence of ZRP coating composition on the expected period of durability.

For the sake of comparison, Figs 2–8 show typical Nyquist and Bode plots for

Table 1. Composition of the various ZRP that were used

Type of ZRP							
Components	1	2	3	4	5	6	7
Alkyd-resin	13.5	14.2	21.5	12.3			
Ethyl-silicate						19.0	
Chlorinated-rubber	9.6						20.1
Epoxy-polyamide					22.2		
Zinc	76.9	85.8	78.5	87.7	77.8	81.0	79.9
Total solid	83.6	89.9	86.4	90.8	85.1	86.4	88.1
Zinc (%) in the dry film	91.9	95.4	90.8	96.6	91.5	93.7	90.8

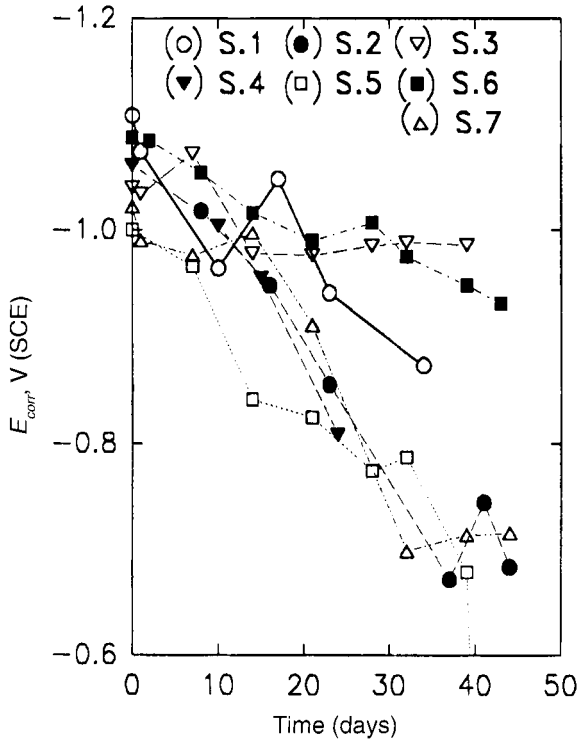


Fig. 1 Dependence of E_{corr} on exposure time in artificial seawater for the various tested samples.

impedance measurements carried out at the corresponding corrosion potential with 10 mV peak to peak sine wave perturbation in the frequency range $3 \text{ mHz} \leq f \leq 65 \text{ kHz}$. Samples 1–7 (geometrical area 17.8 cm^2) with ZRP coating thicknesses close to $60 \mu\text{m}$ were tested in artificial seawater after different exposure times. SAE 1020 (UNS G10200) steel plates were used as the metallic substrate. Impedance diagrams exhibit at low frequencies a Warburg diffusion impedance tail. A slightly distorted capacitive contribution with a constant phase angle of about -45° was observed in the high frequency range. This behaviour may be attributed to the porous nature of the ZRP.

The set of impedance diagrams recorded at different exposure times in the aggressive electrolyte contain valuable information related to the characteristics of the coating parameters as well as to the transfer kinetics of corrosion process going on extensively through pores and cracks in the paint. Impedance spectra were analysed using a non-linear fit routine according to the following transfer function:

$$Z(j\omega) = R_\Omega + \left\{ \frac{R_C + R_{D0}(jS)^{-0.5} \tanh(jS)^{0.5} + R_A}{R_A [R_{D0}(jS)^{-0.5} \tanh(jS)^{0.5} + R_C]} + [CPE]^{-1} \right\}^{-1} \quad (8)$$

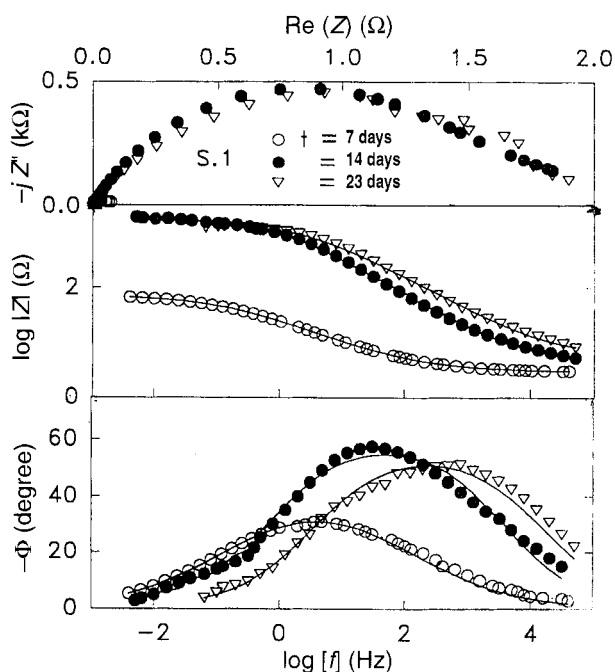


Fig. 2 Dependence of both Nyquist and Bode plots obtained using alkyd-resin and chlorinated-rubber containing ZRP coating formulation (sample 1) on exposure time in seawater. Bode plots include simulated curves according to theoretical transfer function given in eqn (8).

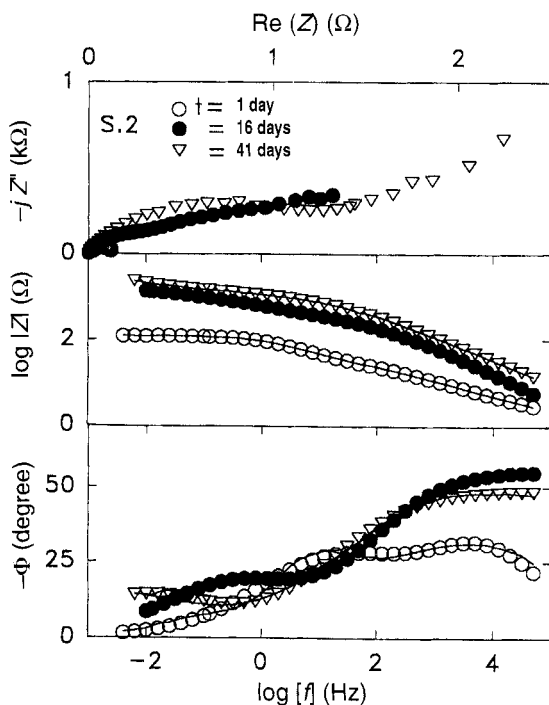


Fig. 3 Dependence of both Nyquist and Bode plots obtained using 14.2% alkyd-resin ZRP coating formulation (sample 2) on exposure time in seawater. Bode plots include simulated curves according to theoretical transfer function given in eqn (8).

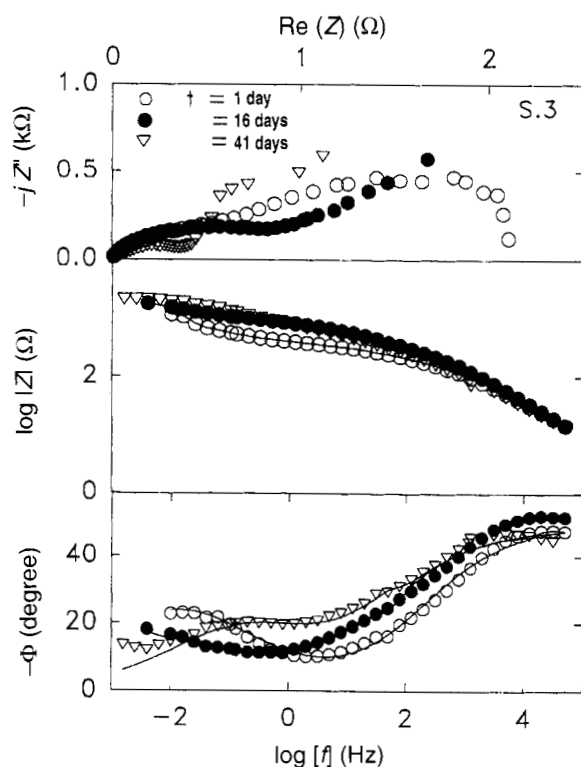


Fig. 4 Dependence of both Nyquist and Bode plots obtained using 21.5% alkyd-resin ZRP coating formulation (sample 3) on exposure time in seawater. Bode plots include simulated curves according to theoretical transfer function given in eqn (8).

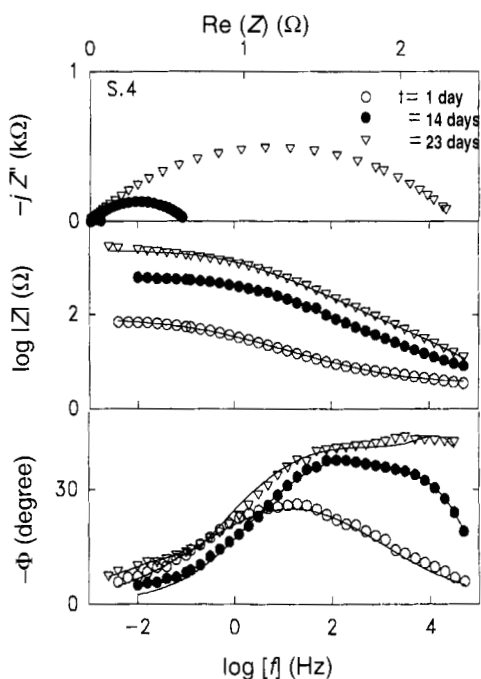


Fig. 5 Dependence of both Nyquist and Bode plots obtained using 12.3% alkyd-resin ZRP coating formulation (sample 4) on exposure time in seawater. Bode plots include simulated curves according to theoretical transfer function given in eqn (8).

Fig. 6 Dependence of both Nyquist and Bode plots obtained using epoxy-polyamide-containing ZRP coating formulation (sample 5) on exposure time in seawater. Bode plots include simulated curves according to theoretical transfer function given in eqn (8).

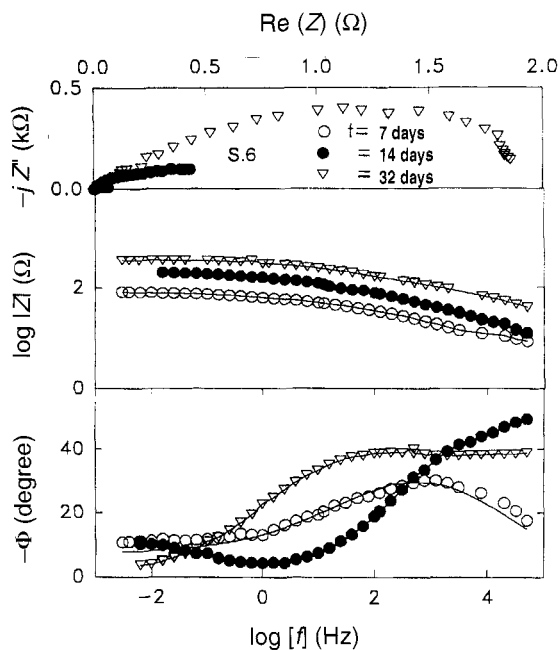
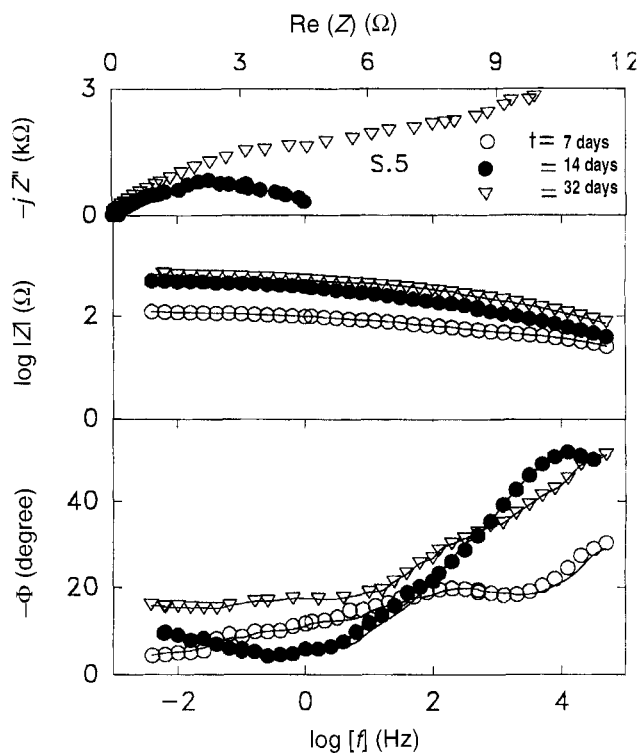


Fig. 7 Dependence of both Nyquist and Bode plots obtained using ethyl-silicate-containing ZRP coating formulation (sample 6) on exposure time in seawater. Bode plots include simulated curves according to theoretical transfer function given in eqn (8).

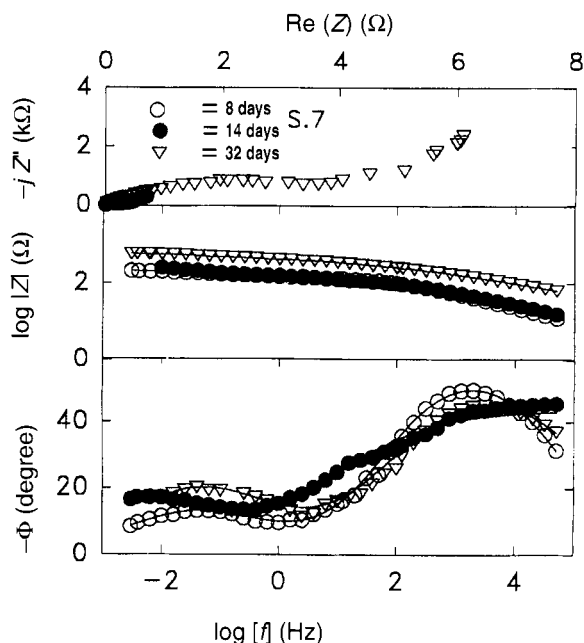


Fig. 8 Dependence of both Nyquist and Bode plots obtained using chlorinated-rubber containing ZRP coating formulation (sample 7) on exposure time in seawater. Bode plots include simulated curves according to theoretical transfer function given in eqn (8).

where R_{Ω} is the uncompensated electrolyte resistance, the constant phase element, CPE, involves a parameter α which was found to lie within the 0.4 to 0.6 range in all the experiments. It should be noted that $\alpha = 0.5$ corresponds to the special case of an active porous electrode. The increase in α can be associated with modifications of the porous structure arising from the formation of a complex corrosion product layer which is mainly attributed to the interaction of pure zinc with carbon dioxide and oxygen dissolved in the aggressive electrolyte to form zinc carbonate or zinc oxide. The resistance R_A related to the anodic partial contribution to the corrosion process, accounts for the charge transfer resistance of the zinc dissolution reaction. On the other hand, the resistance R_C includes the series combination of the electrolyte resistance inside the pores and the charge transfer resistance of the oxygen reduction reaction. Furthermore, a finite diffusion impedance was considered in order to account for the transport process involved in the cathodic partial reaction through the coating. The diffusion resistance, R_{D0} , is the $\omega \rightarrow 0$ limit of a finite length Warburg impedance contribution $Z_W = R_{D0} (jS)^{-1/2} \tanh(jS)^{1/2}$, where $S = d^2 \omega / D$, d and D being the diffusion length and diffusion coefficient, respectively. Accordingly, the lower the value of $d / D^{1/2}$ the sooner the diffusion tail will curve at decreasing frequencies towards the real axis.

The dependences of fit parameters on immersion time in artificial seawater for different ZRP coating formulations are collected in Figs 9–15. At $\omega \rightarrow 0$ the real component of the impedance can be described as the polarisation resistance, R_p , which includes the sum of R_C and R_{D0} contributions in parallel with that of R_A . The good agreement between experimental and fitted results is depicted in Figs 2–8, for comparable immersion times. The decrease of the capacitance as well as the increase of the resistance R_A can be attributed to a progressive decrease of the electrochemically

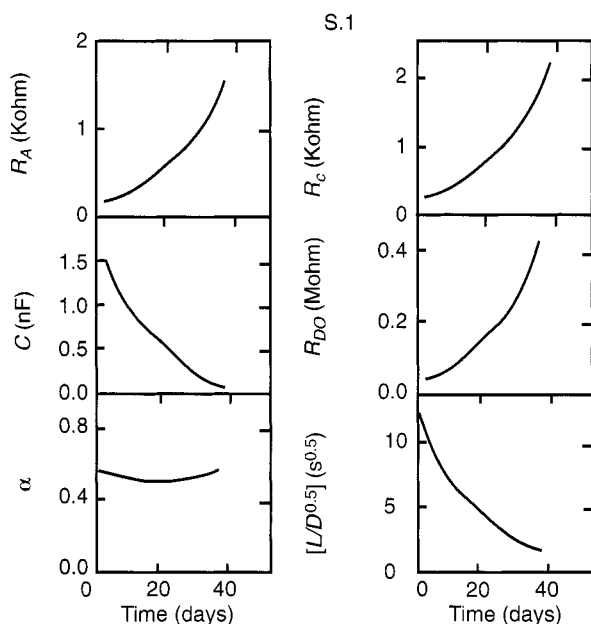


Fig. 9 Dependence of the fitting parameters on exposure time in seawater using the transfer function (eqn (8)) for sample 1.

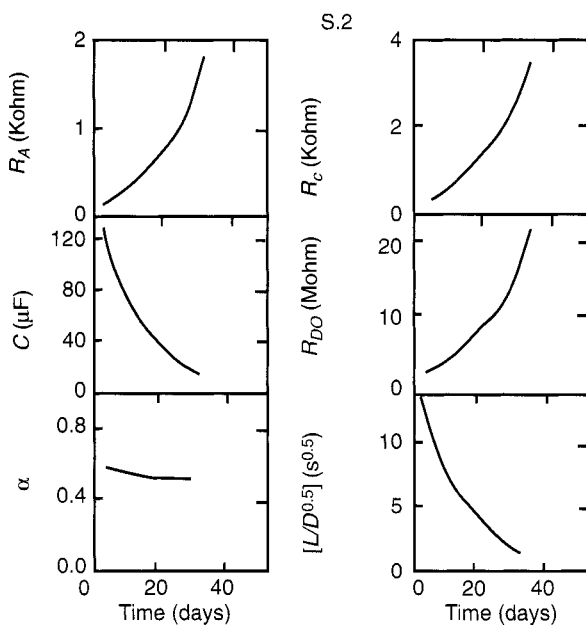


Fig. 10 Dependence of the fitting parameters on exposure time in seawater using the transfer function (eqn (8)) for sample 2.

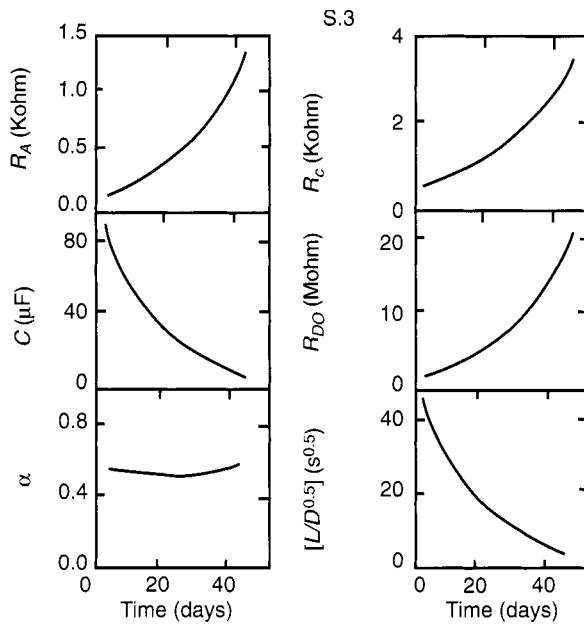


Fig. 11 Dependence of the fitting parameters on exposure time in seawater using the transfer function (eqn (8)) for sample 3.

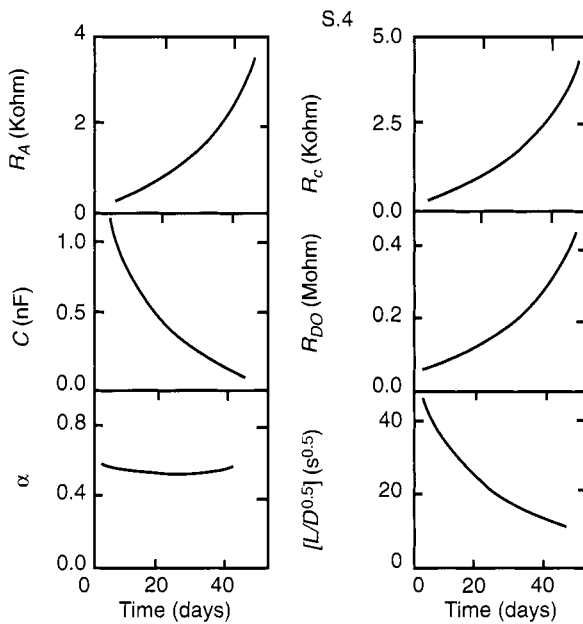


Fig. 12 Dependence of the fitting parameters on exposure time in seawater using the transfer function (eqn (8)) for sample 4.

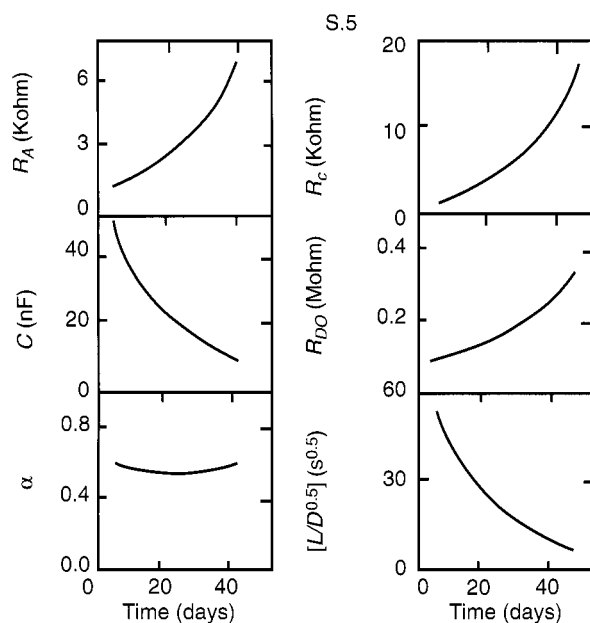


Fig. 13 Dependence of the fitting parameters on exposure time in seawater using the transfer function (8) for sample 5.

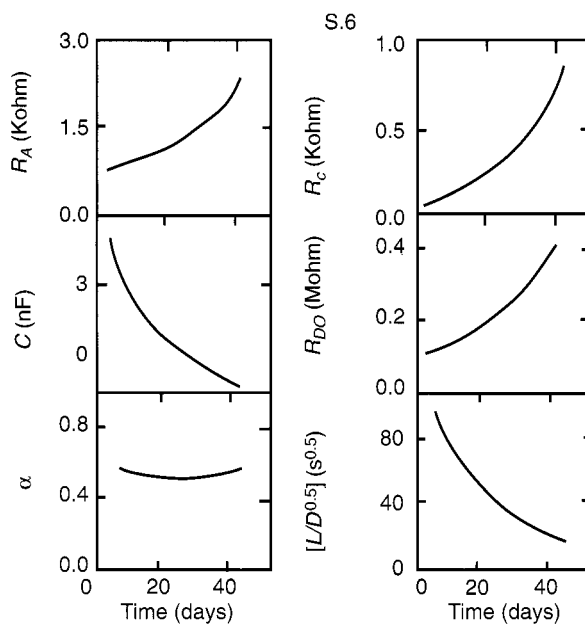


Fig. 14 Dependence of the fitting parameters on exposure time in seawater using the transfer function (8) for sample 6.

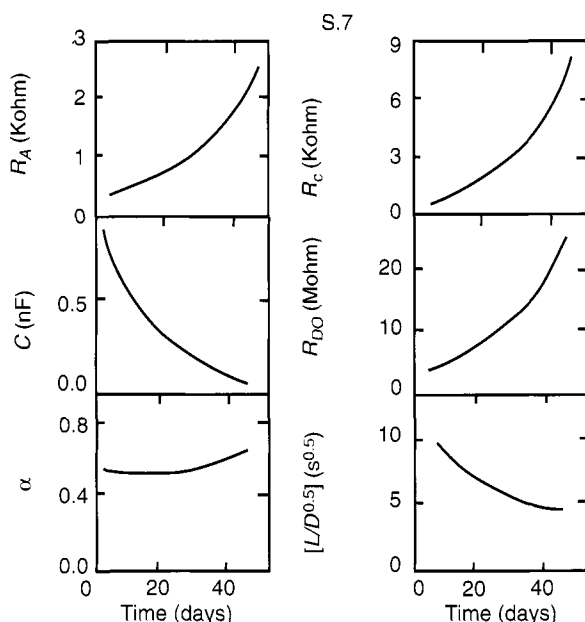


Fig. 15 Dependence of the fitting parameters on exposure time in seawater using the transfer function (8) for sample 7.

active area of active zinc due to the accumulation of corrosion products in the porous structure.

In order to evaluate the corrosion protection effect of different ZRP, a comparison of R_p values was carried out. According to this, samples 3 and 6 present the smallest R_p values, only exhibit the best protective properties for the steel substrate, whereas sample 7, with the largest R_p parameter exhibits the worst protective behaviour. Taking into account that the ZRP coating thickness is about 60 μm , from the values of d^2/D obtained for the different sample formulations presented in Table 1 one can estimate $D \approx (9 \pm 3) \times 10^{-6} \text{ cm}^2\text{s}^{-1}$, a diffusion coefficient value which suggests that the mass transport phenomenon takes place in the solution within pores in the ZRP coating. This diffusion process can be associated with the transport of dissolved oxygen from the coating/seawater interface to the bottom of pores, preceding the cathodic partial reaction of oxygen reduction. It is interesting to note that the diffusion coefficient of molecular oxygen in base media at 25°C calculated from the Levich, Gregory and Riddiford and Newman equations yielded a value of about $1.1 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ [77].

5. Conclusions

The EIS method has proved to be a powerful tool in the assessment of the protective behaviour of either organic or inorganic ZRP coatings applied on a metallic substrate and exposed to an aqueous medium. Experimental impedance spectra have been interpreted using a non-linear fit routine according to a transfer function analysis. Corrosion reaction parameters derived from the fitting procedures and their

dependence on exposure time in an aggressive media suggest that, through an initial cathodic protective period and a final barrier layer type protection, the type of binder as well as the zinc pigment content are variables of paramount importance as far as the relative anticorrosive properties are concerned.

The changes of the capacitance values, the increase of the resistances R_A and R_C , and the appearance of diffusion process were related to the progressive disconnection of the pigment particles taking place along with the thickening of the zinc corrosion product layer on these particles. Moreover, the transmission line model approach can account for changes of the electrochemically active area of zinc particles due to the accumulation of corrosion products. Dynamic system analysis employing small signal perturbation facilitates the determination of system specific parameters which characterise the gradual deterioration of ZRP coating performance with increasing immersion time in seawater.

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Factors Affecting the Electrochemical Behaviour of Zinc-Rich Epoxy Paints

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ABSTRACT

The behaviour of zinc-rich epoxy paints in 3% NaCl solution has been studied with respect to the effect of grain size of the zinc particles using Electrochemical Impedance Spectroscopy (EIS) and electrode potential measurements. Results show that the size and distribution of the zinc particles play an important role in the cathodic protection period of the system. It was concluded that film thickness, contact impedance and electrolyte resistivity are the significant parameters involved in an efficient cathodic protection of the steel substrate.

1. Introduction

Zinc-rich paints (ZRP) are used mainly as primers to protect steel against corrosion. Their protective effect is based on the galvanic action between the steel substrate and the zinc particles in the film. Because of this galvanic action, ZRP protect the steel substrate even when small mechanical damages or holidays are present in the film. For the galvanic action to work properly, a high pigment concentration (typically >60% by volume) is necessary to ensure a good electrical contact between zinc particles in the film and between the film and the steel substrate. Hence, ZRP can be defined as coatings having high pigment (zinc dust) concentration [1].

The galvanic effect is the most important mechanism for ZRP in the protection of the steel, but it is not the only one. It is well known that a certain barrier effect has also a contribution to the steel protection. During the early stages of exposure, the main protection mechanism is galvanic, but this effect decays with time and gradually changes to a barrier effect [2–4]. While the former mechanism depends on the galvanic action of zinc particles, the latter is enhanced by the accumulation of zinc corrosion products. Obviously, it is desirable to extend the galvanic protection period as long as possible in order to guarantee the main characteristic of the film, i.e. its ability to protect steel even with small holidays in the film.

The behaviour of ZRP has been extensively studied using visual inspection, corrosion potential measurements, steady-state polarisation curves and, more recently, impedance spectroscopy [5–7]. Most of these studies, carried out in saline solutions, concern the type of binder (i.e. organic, inorganic) or the pigment volume concentration (PVC). However, little attention has been paid to the particle-to-particle electrical contact which determines the galvanic effect of these protective paints. Another aspect which is lacking in the literature is the effect of the grain size of the

zinc particles on the protecting properties. The influence of these two factors in the electrochemical properties of the protecting film will be discussed in this paper using corrosion potential measurements and Electrochemical Impedance Spectroscopy (EIS).

Although the range of ZRP types is very large, they can nevertheless be classified in two main groups [1], relating to the chemical nature of the binder: organic and inorganic zinc-rich paints. The present paper deals with the behaviour of organic ZRP having an epoxy resin as binder, i.e. zinc-rich epoxy paints (ZREP).

2. Experimental

Commercial ZREP were applied by a roll bar to carbon steel plates previously cleaned and degreased. Once cured, the samples were stored in a desiccator until the moment of testing. The thickness of the prepared films was 60 μm and the zinc content was 62% of the volume of the dry film. Four series (A to D in Table 1) of samples were prepared with different sizes of the zinc dust particles in the films, according to the data in Table 1. The relative grain sizes can be seen in Fig. 1.

For testing, samples were immersed in 3% NaCl solution at the open circuit potential. Periodically, measurements of corrosion potential and EIS were made at this potential. The typical three electrode arrangement was chosen for impedance measurements. The electrolyte was confined in a glass tube which was fixed to the painted surface by an O-ring. Figure 2 illustrates the electrolytic cell design. The total tested area was 9 cm^2 . A saturated calomel electrode (SCE) was used as reference electrode. The EIS measurements were performed using a frequency response analyser (Solartron 1255) and a potentiostat (Solartron 1286). A filter (Kemo VBF8) was also used to improve the signal to noise ratio. The impedance domain covered was 100 kHz to 1 mHz. The measurements were made at the open circuit potential and at different immersion times. The impedance data were analysed using the simplex method described elsewhere [8].

3. Results and Discussion

Figure 3 presents the corrosion potential–time behaviour of Series C paints up to 10 000 h immersion in 3%NaCl solution. According to this figure, four periods can be distinguished in the lifetime* of the ZREP.

Table 1. Diameter of the zinc dust particles used in the tested paints. Note that the standard deviation of the particles size is higher for Series C and D than for A and B

Series of Samples	A	B	C	D
Diameter (μm)	2.5–3.5	3.5–4.5	4.5–6.0	6.0–9.0

*The 'lifetime' of the paint is here the length of the test, which is chosen as the time necessary to visually observe iron rust spots at the electrolyte side of the film.

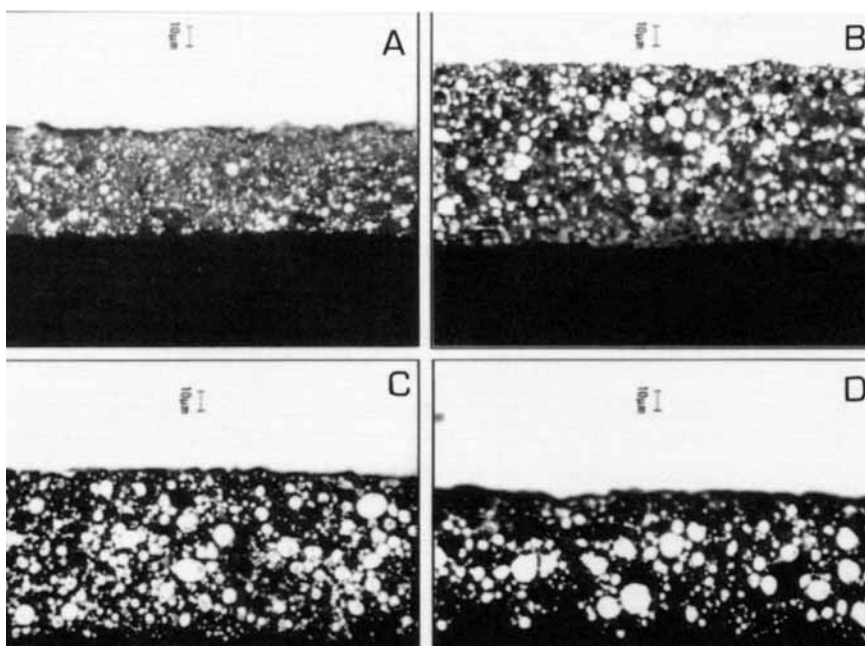


Fig. 1 Cross-section of the studied ZREP prior to exposure. Series A, B, C and D. The observed black vacancies are due to the zinc particles leaving the binder when cutting and polishing the sample.

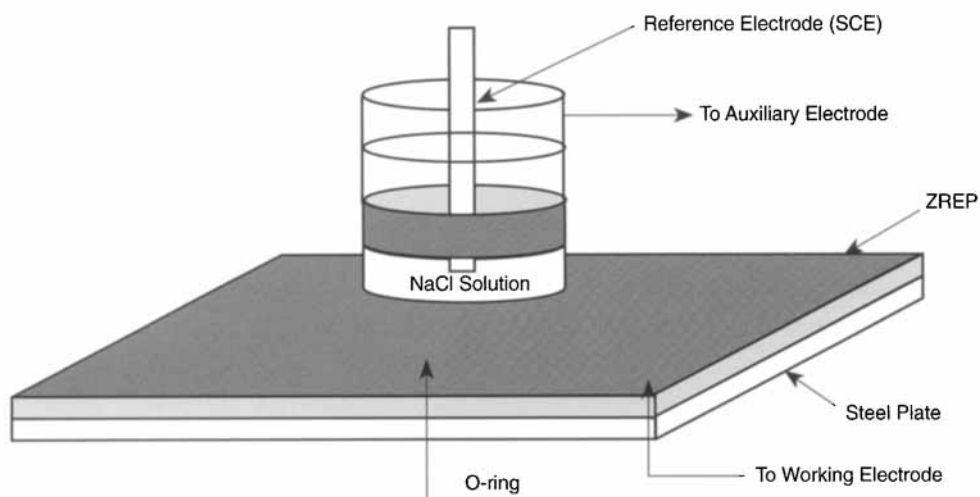


Fig. 2 Cell design for EIS measurements on ZREP.

- Period 0* The corrosion potential shifts in the noble direction to reach, in some cases, values in the range of steel in this medium.
- Period 1* The corrosion potential shifts in the cathodic direction to reach values close to those corresponding to a zinc specimen in this medium. This shift occurs with two different slopes (sub-periods 1A and 1B).
- Period 2* The corrosion potential increases to about -0.9V vs SCE where a short stabilisation is reached. This stabilisation is called the 'transition' period.
- Period 3* The corrosion potential rises again reaching the potential over which cathodic protection is no longer efficient (according to the literature [5], potentials more anodic than -0.86V vs SCE indicate the end of the cathodic protection of the steel). In this period the corrosion potential starts to fluctuate and some rust spots are visible on the film surface. The paint no longer protects the steel substrate.

These general features have been interpreted in a previous paper [8] in terms of the evolution of the zinc particle-to-particle contact impedance. Prior to immersion in the electrolyte, the ZREP has a dielectric behaviour associated with the presence of the native (natural) zinc oxide layer which electrically insulates the zinc particles. When the sample is immersed in the electrolyte, two phenomena occur in parallel: the native oxide starts to dissolve, enabling electrical contact between zinc particles to be established (activation of zinc particles), and the surface of the steel substrate begins to be wetted. As the kinetics of the former process are not fast, the active zinc-to-steel area ratio decreases, which leads to an increase in the potential of the galvanic couple. This is the behaviour observed in Period 0 (Fig. 3). After about 9 min of immersion, the active steel surface does not increase any more because it is completely wetted. However new zinc particles, having thicker native oxide layers, which continue to activate, cause the zinc-to-steel area ratio to increase and hence the potential of the galvanic couple shifts to cathodic values. This is the behaviour observed in Period 1 (Fig. 3).

The difference in slopes between periods 1A and 1B can be interpreted using the concept of contact impedance between zinc particles. The corrosion products formed due to zinc corrosion start to block the film pores and tend to isolate each zinc particle thus partially compensating the effect of particle activation. From the point of view of the film impedance, this behaviour can be modelled using the equivalent circuit shown in Fig. 4, for which the impedance is given in eqn (1), where L is the thickness of the film, $\gamma = (Z_m + R_e)/Z_1$, Z_m the contact impedance between zinc particles along the transmission line, Z_1 the interfacial impedance of a small segment between zinc particles and the electrolyte inside the pores (parallel to the steel surface), and R_e is the resistance of the electrolyte inside the film.

$$Z = \frac{Z_m R_e L}{Z_m + R_e} + \frac{(Z_m^2 + R_e^2) \cosh(L\sqrt{\gamma}) + 2Z_m R_e}{(Z_m + R_e)\sqrt{\gamma} \sinh(L\sqrt{\gamma})} \quad (1)$$

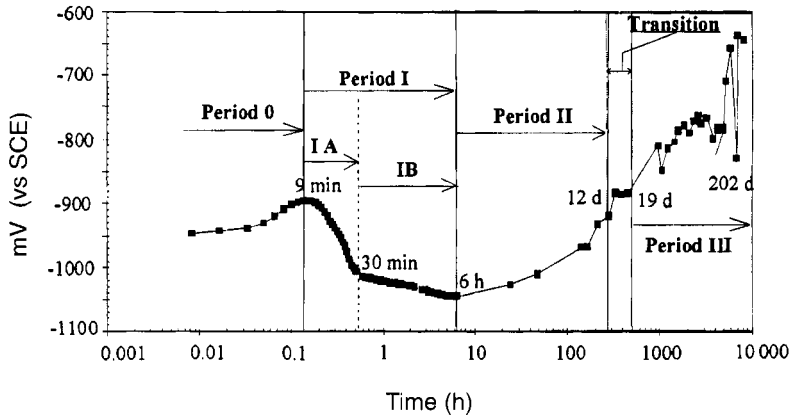


Fig. 3 Development with immersion time of the corrosion potential of the ZREP Series C/steel plate system.

The contact impedance, Z_m , is given in eqn (2), where α_m accounts for the dispersion of the contact impedance along the transmission line.

$$Z_m = \frac{R_m}{1 + (j\omega R_m C_m)^{\alpha_m}} \quad (2)$$

The interfacial impedance, Z_1 , is obtained by considering the double layer capacitance, C_1 , and the faradaic resistance, R_1 , associated with the zinc dissolution.

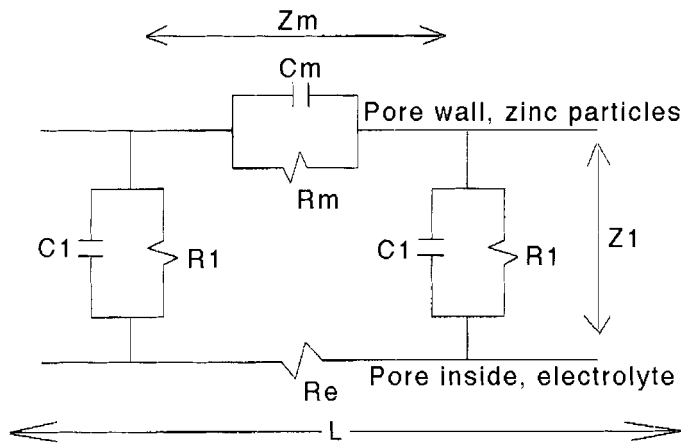


Fig. 4 Scheme of the transmission line used to model the behaviour of a ZREP/steel system. Z_m is the contact impedance between zinc particles, Z_1 the interfacial impedance and R_e the resistance through the binder.

Hence, one can write eqn (3) where the parameter α_1 accounts for the distribution of the R_1C_1 time constant.

$$Z_1 = \frac{R_1}{1 + (j\omega R_1 C_1)^{\alpha_1}} \quad (3)$$

This model assumes that the cathodic reaction (oxygen reduction) occurs at the steel surface under cathodic control, hence the measured impedance corresponds to the film impedance [8].

Figure 5 corresponds to the impedance spectrum for Series C samples at one day immersion in the electrolyte. A good agreement can be observed between experimental and calculated data. The high frequency loop in the spectrum corresponds to the contact impedance between zinc particles in the film. As this contact impedance defines most of the film properties, it is interesting to analyse here one of the factors which affect it, i.e. the size of the zinc particles.

The data in Fig. 6 give information about the effect of the zinc grain size in the galvanic protection provided by the film. Although the overall behaviour is as described in Fig. 3, some differences between the different series can be noticed. Thus, in the early stages of immersion, the corrosion potential of series A and C varies by several tens of millivolts, while in systems B and D the corrosion potential always remains in the range of $-1V$ vs SCE. After the first hour of immersion, all

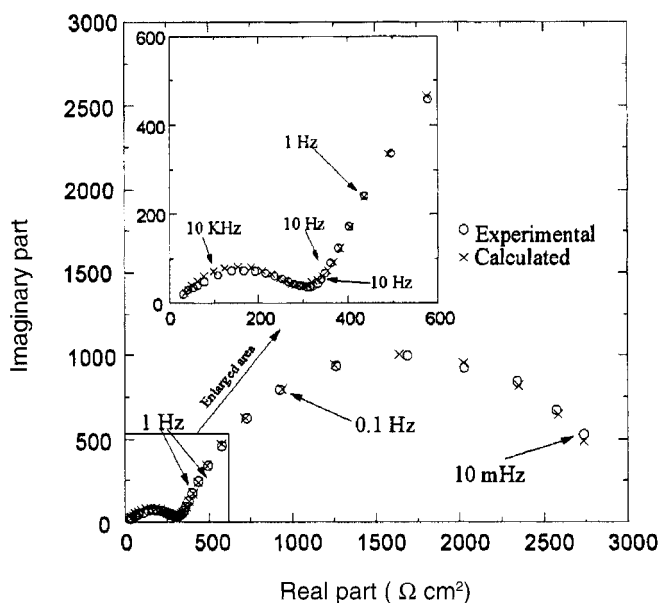


Fig. 5 Impedance spectrum for ZREP type C at one day immersion in the electrolyte. The corrosion potential was -1028 mV vs SCE. The calculated values have been obtained using eqn (1) using the following parameters: $R_{sol} = 21 \Omega.cm^2$, $R_m = 82.4 k\Omega.cm$, $C_m = 1.25 nF.cm^{-1}$, $\alpha_m = 0.717$, $R_1 = 15.8 \Omega.cm^{-3}$, $C_1 = 0.165 F.cm$, $\alpha_1 = 0.832$, $R_e = 8.37 k\Omega.cm$, $L = 0.006$ cm. The R_{sol} value accounts for the solution resistance between the reference electrode and the film/electrolyte interface.

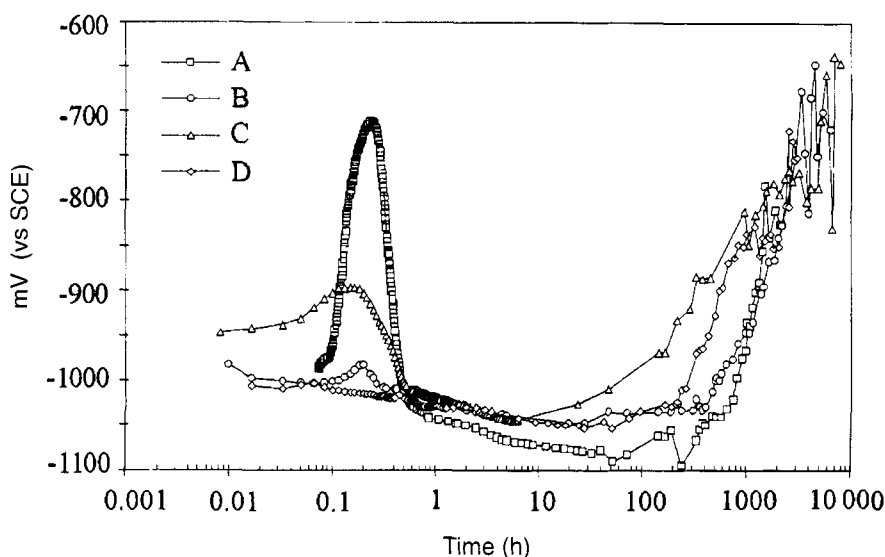


Fig. 6 Change with immersion time of the corrosion potential for the studied ZREP (series A, B, C, and D).

potentials shift to the cathodic direction for about 30 h, except systems B and C, for which the corrosion potential starts to rise in the anodic direction after about 6 h of immersion. From Fig. 6, it is clear that systems A and B cathodically protect the substrate for longer times than systems C and D. This behaviour can be interpreted using the film electrical model depicted in Fig. 4.

The impedance spectra obtained for periods 1 and 2 can be modelled using eqn (1). However, at the transition period, the cathodic reaction starts to develop at the film/solution interface. This leads to a new time constant appearing in the high frequency region of the impedance spectrum [8]. If eqn (1) is modified accordingly, it can be used to obtain the significant parameters describing the evolution of the ohmic resistance of the tested ZREP with immersion time. The fitted values for these significant parameters are summarised in Figs 7 and 8.

According to the data depicted in Fig. 3, the ohmic resistance through the film, R_e in Fig. 4, is higher for systems C and D than for A and B. As this resistance hinders the galvanic current flow between the zinc particles and the steel substrate, the galvanic current involved in steel protection will be lower for systems C and D, which have the bigger zinc particles. An interpretation for this difference in resistance can be given in terms of the pore tortuosity in the film, which is higher for systems C and D because of the difference between the sizes of their zinc particles (see Table 1) which permits a better packing of the zinc dust. As the four paints tested have the same thickness, the resulting differences in R_e can only be attributed to the tortuosity factor.

Figure 8 displays the change with immersion time of the resistance between zinc particles which is smaller for systems A and B than for C and D. This can be explained again as a function of the grain size. For systems A and B the number of particles is higher which means a higher number of electrical contacts, i.e. lower R_m values.

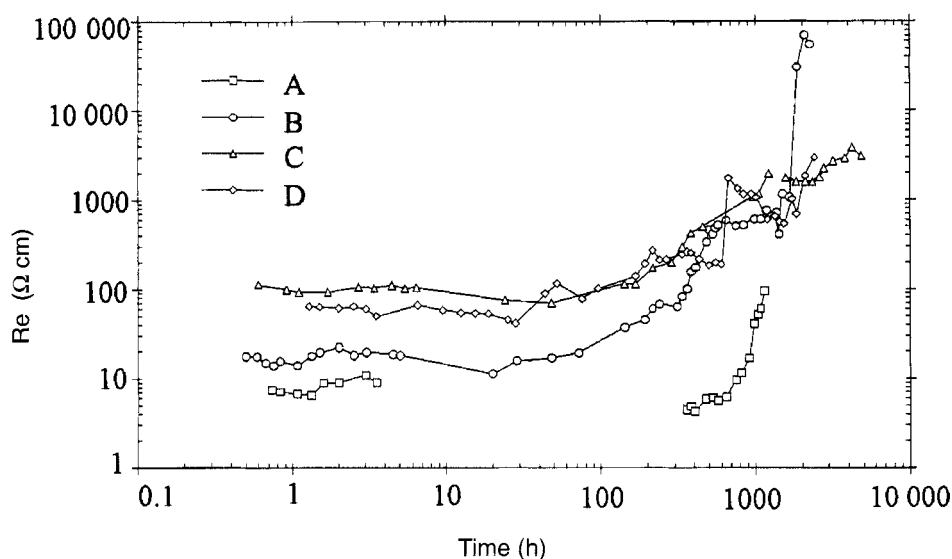


Fig. 7 Change with immersion time of the ohmic resistance through the binder.

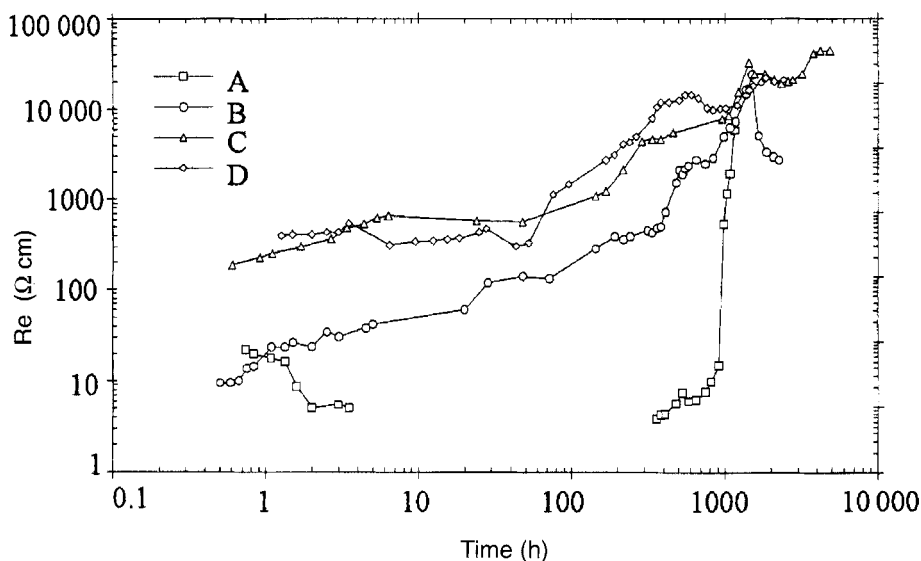


Fig. 8 Change with immersion time of the resistance between zinc particles.

With increase in immersion time R_m gradually increases due to zinc dissolution. The zinc corrosion products make the zinc particles move away from each other which leads to an increase in R_m . Furthermore, it is interesting to note that some data are lacking for system A in Figs 7 and 8. This is due to the fact that the behaviour of this

system cannot be interpreted using the circuit model depicted in Fig. 4 and, therefore, the fitted data are omitted. In this case, the electrode presents the typical behaviour of a flat electrode indicating that the penetration depth of the electric signal in the film pores is higher than the pore length (i.e. film thickness times pore tortuosity). This fact proves also that the pore tortuosity in the film increases as the average zinc particles size increases.

The behaviour of system A as a flat electrode means that all the zinc particles participate in the galvanic protection of the steel substrate. This does not occur in the rest of systems for which the behaviour corresponds to a porous electrode. In these cases, a part of the zinc in the film does not contribute to the galvanic action and is consumed in a self-corrosion process.

As the resistance in the film increases, the zinc particles close to the film/solution interface lose electrical contact with the steel substrate. The corrosion of these particles then starts to take place without galvanic coupling with the steel substrate. The reduction of dissolved oxygen at the film surface makes the neighbouring solution more alkaline and this has a twofold effect. First, zinc passivation starts to occur, the zinc corrosion products change to hydroxide [9] thereby increasing the contact impedance and, secondly, ions in solution precipitate, so making the solution through the film more resistive, i.e. R_p increases. All these changes in significant parameters indicate the end of the cathodic protection period. According to Figs 6, 7 and 8, the system for which all zinc particles are involved in the cathodic protection of the steel substrate maintains this protection for the longer period of time.

4. Conclusions

The grain size of zinc particles plays an important role in the cathodic protection effect of zinc-rich epoxy paints.

The film thickness as well as the nature of the zinc corrosion products are also factors defining the galvanic effect in these systems because their relative values define the penetration depth of the electric signal in the film and therefore whether the film behaves as a flat or porous electrode, i.e. either all or only part of the zinc particles participate in the galvanic action.

For the optimum formulation of a paint composition, all the above mentioned significant parameters must be considered. The nature of the zinc corrosion products, i.e. as affected by the chemistry of the environment, will be a factor of importance in decreasing the overall resistance through the film.

5. Acknowledgement

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Sorption Characteristics of Cathodically Deposited Epoxy Films

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ABSTRACT

Epoxy coatings on steel were formed by cathodic electrodeposition of an epoxy resin modified by an amine and isocyanate using the constant voltage method (resin concentration 10 wt%, temperature 26°C, applied voltage 250 V). The corrosion behaviour of these protective coatings was investigated during exposure to different corrosive agents (H_2O , 3% NaCl, 3% Na_2SO_4 , 3% sodium salt of 2-naphthol-3,6 disulfonic acid) using a.c. impedance measurements (EIS), gravimetric liquid sorption experiments, differential scanning calorimetry (DSC) and potential-time measurements.

The time required to saturate the coating with pure water, obtained from sorption data, coincided with the initial increase in coating capacitance and relative permittivity and the initial decrease in pore resistance, obtained from a.c. impedance measurements, denoting the entry of electrolyte into the coating. The closely similar values of diffusion coefficient for water across an epoxy coating and for the energy of activation of water diffusion, obtained in the different corrosive agents, suggest that the first step of electrolyte penetration through the coating is related to water uptake and that it is independent of the type and dimensions of ions in the electrolyte. The closely similar values of enthalpy of vaporisation of different volatile electrolytes and the quantity of water inside the coating, obtained from DSC measurements, provide additional confirmation for the proposed mechanism. The time dependence of potential is in accordance with results obtained from EIS.

1. Introduction

It is generally accepted that organic coatings applied to metal surfaces provide corrosion protection by introducing a barrier to ionic transport and electrical conduction, in situations where the sorption and transport of charged (ions) and uncharged (water, oxygen) species affect the corrosion behaviour of a polymer/metal system [1–6]. Thus when a polymer coated metal is exposed to an electrolyte, there will be a gradual reduction in barrier protection as water, oxygen and ions penetrate the coating. It has been shown that the water uptake and ion penetration of a coating are important factors in determining the corrosion stability of organic coatings and that diffusion is the major process responsible for the transport of water and other species through a coating [7–10].

2. Experimental

Protective coatings were formed during cathodic electrodeposition of an epoxy resin modified by amine and isocyanate on steel using a constant voltage method. The resin concentration in the electrodeposition bath was 10 wt% solid dispersion in water at pH 5.7, the temperature was 26°C and the applied voltage was 250 V. The test panels were pretreated by mechanical cleaning (polishing), degreasing in a saturated solution of sodium hydroxide in ethyl alcohol, pickling with a hydrochloric acid solution at 1:1 dilution (30 s) and rinsing with distilled water. After coating for 3 min, rinsing and baking at 180°C for 30 min, the film thickness, measured by a Dermatron thickness tester, was 17 μm . For a.c. impedance measurements the coated samples were exposed to 3% NaCl in distilled water for periods of 45 days. A three-electrode cell arrangement was used in the experiments. The working electrode was a coated steel panel (steel T-57, ISO standard) situated in a special Teflon holder. The counter electrode was a platinum mesh with a surface area considerably greater than that of the working electrode and the reference electrode was a saturated calomel electrode. A.C. impedance data were obtained at the open-circuit potential using a PAR 273 potentiostat and PAR 5301 lock-in amplifier. The impedance measurements in all cases were carried out over a frequency range of 100 kHz–10 mHz using a 5 mV amplitude of sinusoidal voltage. The impedance spectra were analysed using a suitable fitting procedure [11].

Gravimetric liquid sorption experiments were performed by weighing samples on a balance with accuracy of 1×10^{-5} g following immersion in different corrosive agents (H_2O , 3% NaCl, 3% Na_2SO_4 , 3% sodium salt of 2-naphthol-3,6 disulfonic acid) at different temperatures (25, 40, 50 and 60°C). The samples were periodically removed from the electrolyte and weighed. Sorption curves were used to evaluate the diffusion coefficient for water across an epoxy coating. From the diffusion coefficient values at different temperatures, the energy of activation of water diffusion through the epoxy coating was calculated.

The DSC (differential scanning calorimetry) measurements were carried out over a temperature range of 18–110°C at a heating rate of 5°C/min, using a Perkin-Elmer DSC-2 instrument with nitrogen as a purging gas. Each sample, weighing about 5 mg, was placed in the volatile sample pan with a pin hole in the cover [12] and analysed as follows: heated from 18 to 110°C at a 5°C/min rate and at a range of 1 mcal s⁻¹ (run 1), after 5 min on 110°C cooled to 18°C at 40°C/min rate and rescanned at 5°C/min (run 2). The temperature scale was calibrated with high purity indium standards. The enthalpy of vaporisation of volatile electrolyte and quantity of water inside the epoxy coating were determined from DSC measurements.

3. Results and Discussion

Figure 1(a) presents the Nyquist complex plane plots and Fig. 1(b) presents the Bode plots for the impedance of an epoxy coating electrodeposited on steel after various exposure times in 3% NaCl solution. A general equivalent electrical circuit model for the behaviour of polymer-coated metals in corrosive environments has been developed (Fig. 2a) [13–15], where R_Ω is the resistance of the electrolyte, R_p is the

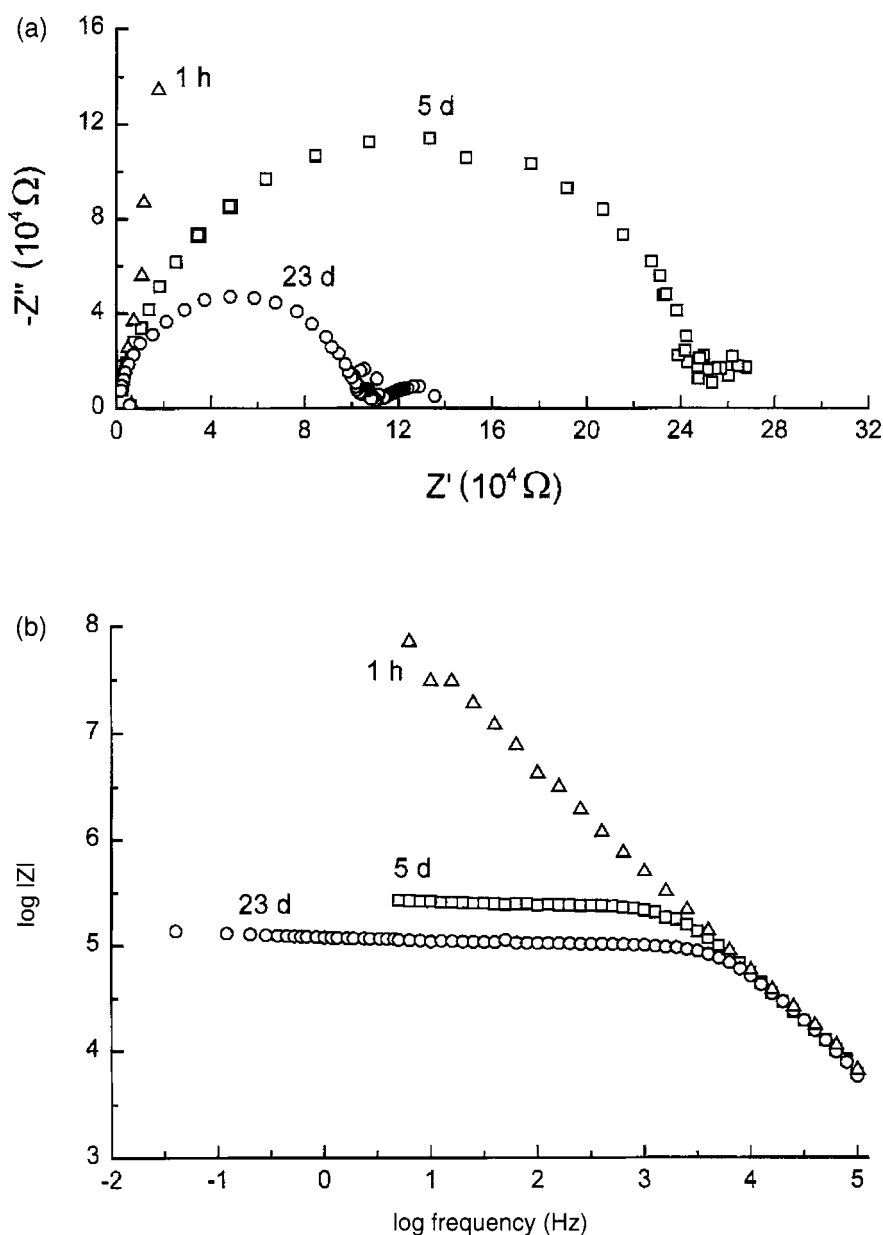


Fig. 1 Complex plane plots (a) and Bode plots (b) for epoxy coating electrodeposited on steel after various exposure times in 3% NaCl.

coating pore resistance due to electrolyte penetration, C_c is the capacitance of the film and Z_f is the impedance related to the faradaic reaction at the metal/solution interface. Different equivalent electrical circuits have been proposed for Z_f . One of these consists of a resistance (the charge-transfer resistance R_f) in parallel with a

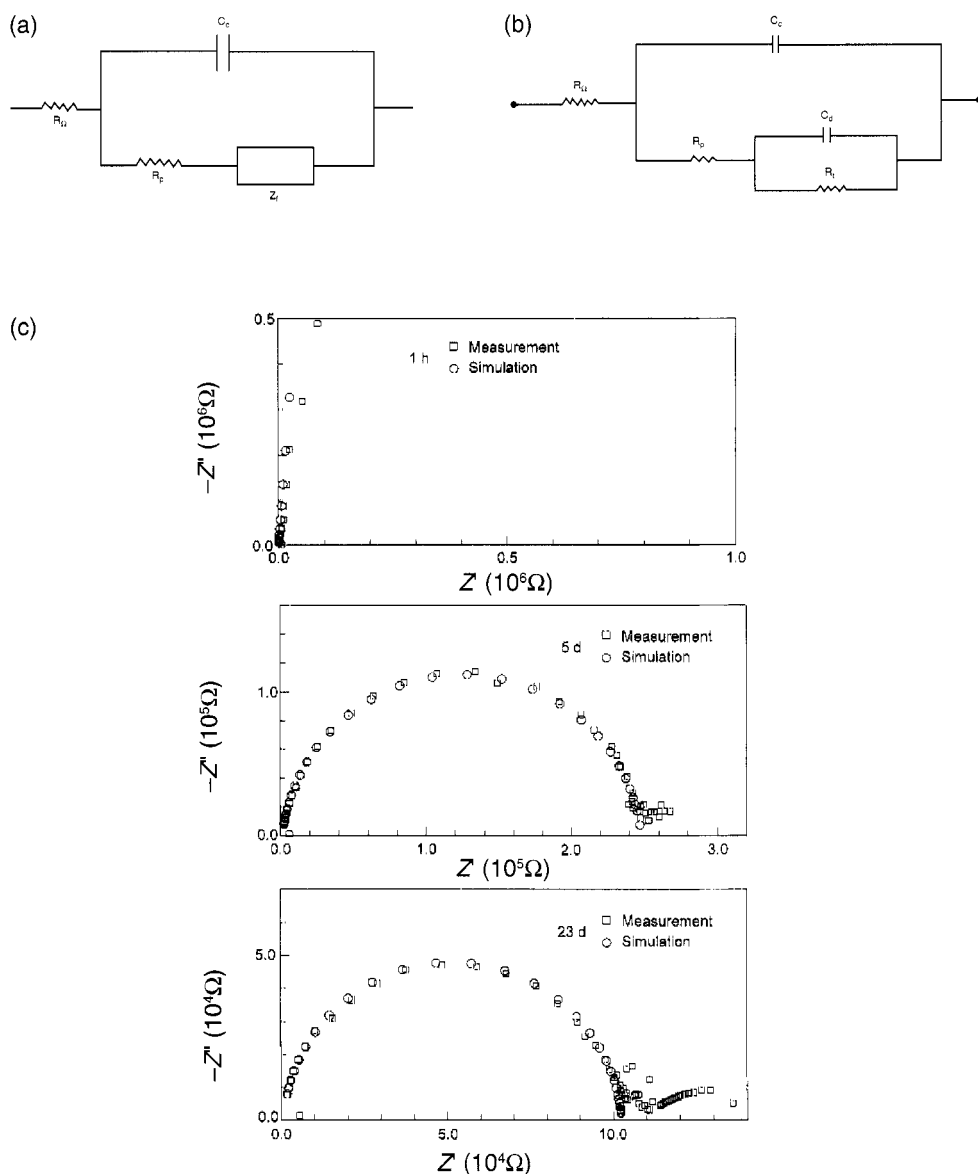


Fig. 2 (a), (b) Equivalent electrical circuits of a polymer-coated metal and (c) fitting of experimental data from Fig. 1(a).

double-layer capacitance C_d , as shown in Fig. 2(b). The fitting of experimental data in Fig. 1(a), using the program of Boukamp [11], shows (Fig. 2c) that impedance plots correspond well to the model in Fig. 2(b). From the impedance plots in the complex plane, the coating capacitance, C_c and pore resistance, R_p were obtained and are plotted as a function of time in Figs 3 and 4, respectively. The relative permittivity of the epoxy coating, ϵ_r , was calculated from the film thickness and coating capacitance using the equation:

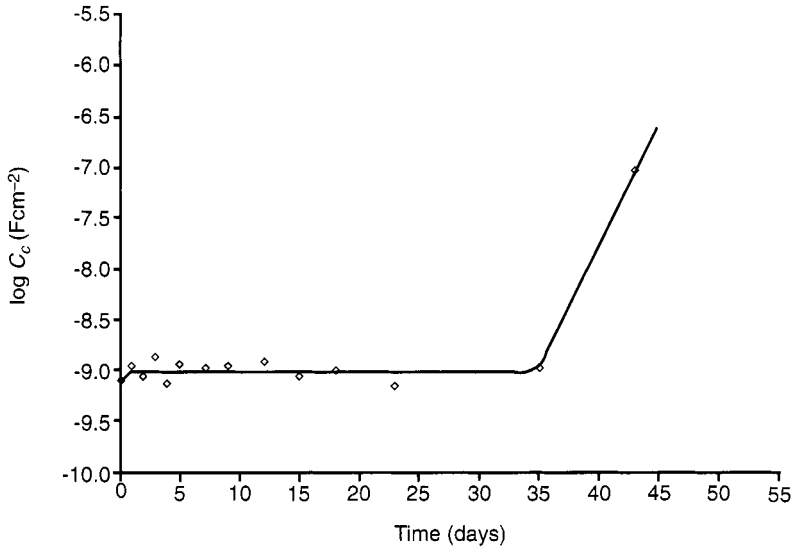


Fig. 3 The time dependence of coating capacitance for epoxy coating during exposure to 3% NaCl.

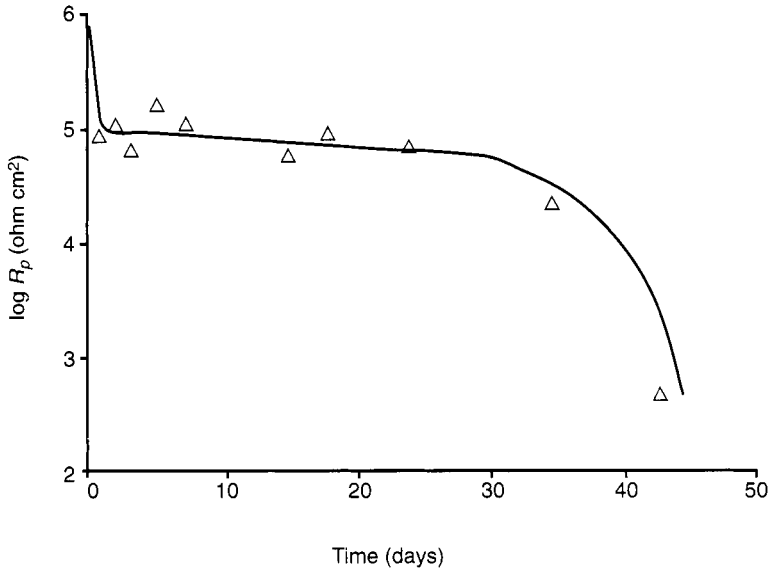


Fig. 4 The time dependence of pore resistance for epoxy coating during exposure to 3% NaCl.

$$\epsilon_r = \frac{C_c \delta}{\epsilon_0} \quad (1)$$

where $\epsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$, the permittivity of the vacuum. The time dependence of relative permittivity is presented in Fig. 5. The initial value for ϵ_r of 15 is somewhat

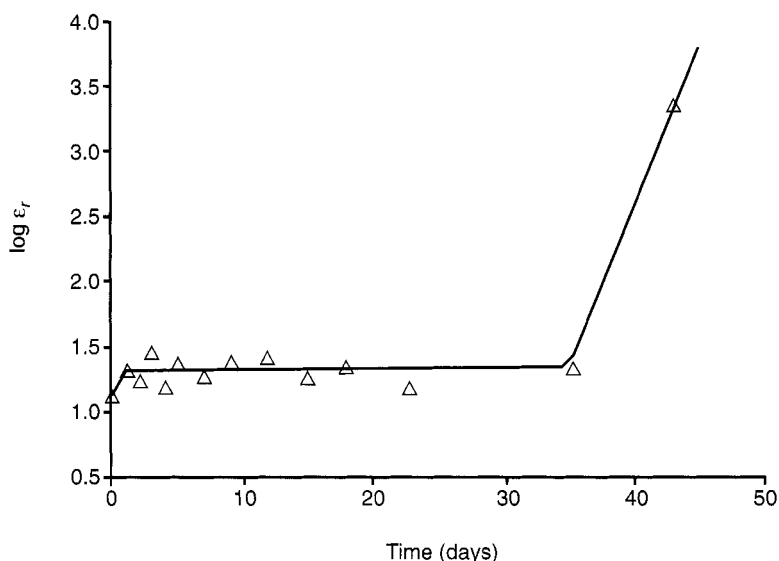


Fig. 5 The time dependence of relative permittivity ϵ_r for epoxy coating during exposure to 3% NaCl.

higher than the usually referred values for epoxy resins of $\epsilon_r \approx 5$. Bearing in mind that the film was obtained by electrodeposition from a water-containing solution, this might be due to some incorporation of water molecules in the deposited film. Three time domains may be distinguished in Fig. 3. The initial increase in coating capacitance, which coincides with the initial decrease in pore resistance (Fig. 4) and initial increase in relative permittivity (Fig. 5), denote the entry of electrolyte into the coating [4,8,16,17]. In the second domain the coating is already saturated with electrolyte and the values of coating capacitance (Fig. 3) and relative permittivity (Fig. 5) are constant over a longer time period, coinciding with the plateau in the $\log R_p$ - t plot (Fig. 4). The value of the relative permittivity during this period was calculated to be 20 and comparison with the relative permittivity of the epoxy coating before exposure to corrosive agent 3–5 [18], indicates that the coating is already saturated with electrolyte after the first time domain. Finally, there is a rapid change in C_c over the third time domain (Fig. 3) where increase in coating capacitance after a longer period means the beginning of detachment of coating from the substrate as a result of adhesion loss and the onset of underfilm corrosion reactions following the contact between the electrolyte and the metal surface. This period corresponds to the final drop of the pore resistance (Fig. 4) and the final increase in relative permittivity (Fig. 5). It should be noted that $\epsilon_r \approx 2000$ after 40 days of exposure has no physical meaning but is merely, a calculated value using the fitting procedure for a model corresponding to the presence of the epoxy film. The large jump of a calculated ϵ_r is simply an indicator of the destruction of the epoxy film.

Liquid sorption experiments were conducted to investigate the mechanism of electrolyte penetration through an epoxy coating and to explain the three time domains observed for the time dependencies of pore resistance, coating capacitance and relative permittivity, since it is known that the first domain depends on the

sorption characteristics of the coating. Initially, distilled water was used as corrosive agent. The gravimetric sorption liquid data are reported as a plot of the amount of absorbed water at time t , m_t , against $t^{1/2}$ (Fig. 6a, sorption curve). The water uptake is linear with $t^{1/2}$ until steady-state is reached. The observed initial linear behaviour suggests that the sorption is controlled by Fickian diffusion. Assuming Fickian behaviour with a constant diffusion coefficient D , the sorption data should obey the equation [19]:

$$\frac{m_t}{m_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{D(2n+1)^2 \pi^2}{\delta^2} t\right] \quad (2)$$

where m_∞ is the amount of absorbed water at equilibrium and δ is the film thickness. By series expansion of eqn (2) for small values of t , one obtains:

$$\frac{m_t}{m_\infty} = \frac{4D^{1/2}}{\delta\pi^{1/2}} t^{1/2} \quad (3)$$

Using eqn (3), the ratio m_t/m_∞ was plotted against $t^{1/2}/\delta$ (Fig. 6b, reduced sorption curve) and from the initial slope of the linear region, the diffusion coefficient for water across a non-pigmented epoxy coating was calculated to be $3.16 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$. The time required to saturate the film with pure water coincided with the initial decrease in pore resistance (Fig. 4) and the initial increase in coating capacitance (Fig. 3) and relative permittivity (Fig. 5) with time, during exposure to 3% NaCl. On the other hand, the diffusion coefficient of Cl^- ions across an epoxy coating has been reported [7] as $4.7 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, i.e. one order of magnitude smaller than the diffusion coefficient of water. This suggests that the first step in electrolyte penetration through the coating is related to water uptake in the micropores of the polymer net, which occurs according to Fick's law [10]. Indeed, a plateau in the $\log C_c-t$ plot (Fig. 3), $\log R_p-t$ plot (Fig. 4) and $\log \epsilon_r-t$ plot (Fig. 5) was observed after 1 day of immersion, which is comparable with the time required to saturate the film with pure water (Fig. 6a).

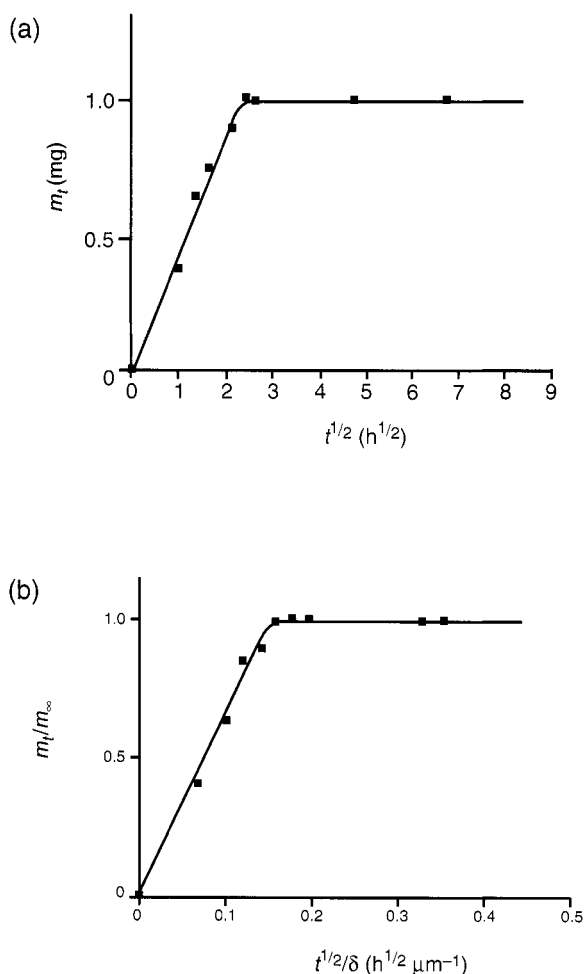
In order to confirm this assumption, gravimetric liquid sorption experiments in the different corrosive agents (3% NaCl, 3% Na_2SO_4 , 3% sodium salt of 2-naphthol-3,6 disulfonic acid) were conducted. It can be seen from the sorption curves obtained (Fig. 7a for 3% NaCl and Fig. 8a for 3% Na_2SO_4) that the time required to saturate the coating with different electrolytes was the same as for saturation with pure water, independently of the type and dimensions of ions in the electrolyte (Cl^- , SO_4^{2-} , $\text{C}_{10}\text{H}_{13}\text{OH}(\text{SO}_3)_2^{2-}$) and coincided with the initial increase in coating capacitance and relative permittivity and the initial decrease in pore resistance.

From reduced sorption curves at different temperatures (Fig. 7b, for 3% NaCl and 8b for 3% Na_2SO_4), the values of diffusion coefficient for water, $D(\text{H}_2\text{O})$, during exposure to different corrosive agents were determined (Table 1). Using the Arrhenius equation for temperature dependence of the diffusion coefficient:

$$D = A \exp(-E_a/RT) \quad (4)$$

Table 1. The values of diffusion coefficient for water, $D(\text{H}_2\text{O})$, at 25 °C and energy of activation of water diffusion across the epoxy coating in different corrosive agents

Electrolyte	H_2O	3% NaCl	3% Na_2SO_4	3% Na salt of 2-naphthol-3,6 disulfonic acid
$D(\text{H}_2\text{O}) \times 10^{11}$ (cm^2s^{-1})	3.16	2.83	3.85	3.85
E_a (kJ mol^{-1})	14.3	12.0	12.5	13.7

**Fig. 6** A plot of the amount of absorbed water at time t , m_t , against the square root of time (a) and the reduced sorption curve (b), at 25 °C for epoxy coating during exposure to distilled H_2O .

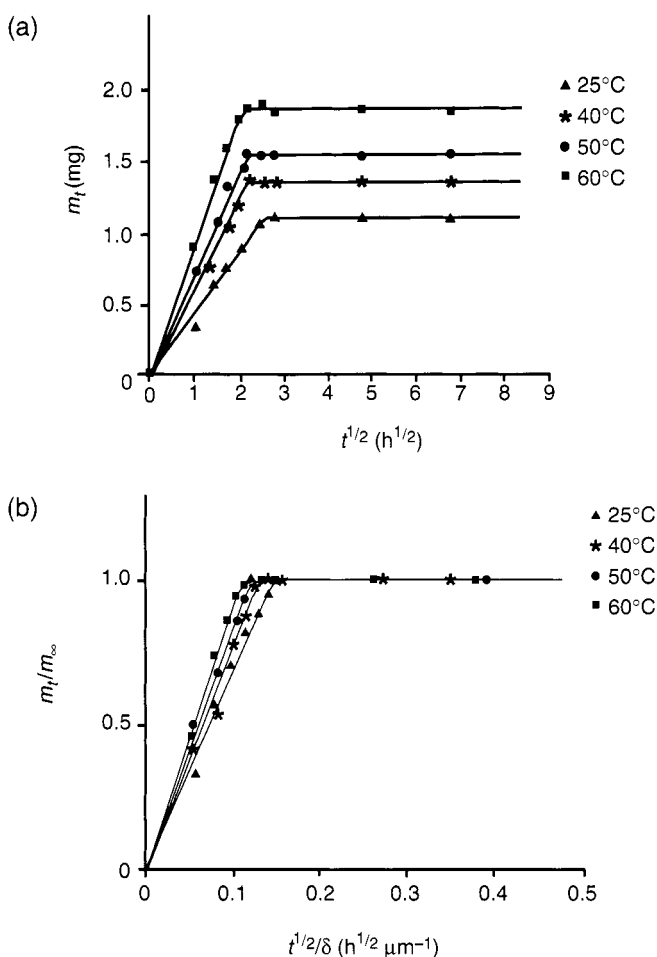


Fig. 7 A plot of the amount of absorbed water at time t , m_t , against the square root of time (a) and the reduced sorption curves (b), at different temperatures for epoxy coating during exposure to 3% NaCl.

the energy of activation of water diffusion through the epoxy coating, E_a , was calculated (Fig. 9, for 3% NaCl and Table 1).

The closely similar values of diffusion coefficient for water and for the activation energy of water diffusion through the epoxy coating obtained in the three different corrosive agents, confirm the proposed model of electrolyte penetration [10], in which the first step is related to water uptake when molecules of pure water diffuse into the micropores of the polymer net according to Fick's law and is independent of the type and dimensions of ions in the electrolyte.

Differential scanning calorimetry was used to measure the enthalpy of vaporisation of the volatile electrolyte as a function of increasing temperature (between 18 and 110°C). From DSC thermograms obtained for the epoxy coating after 7 days of exposure to the various corrosive agents (Fig. 10, p.44), the enthalpies of vaporisation

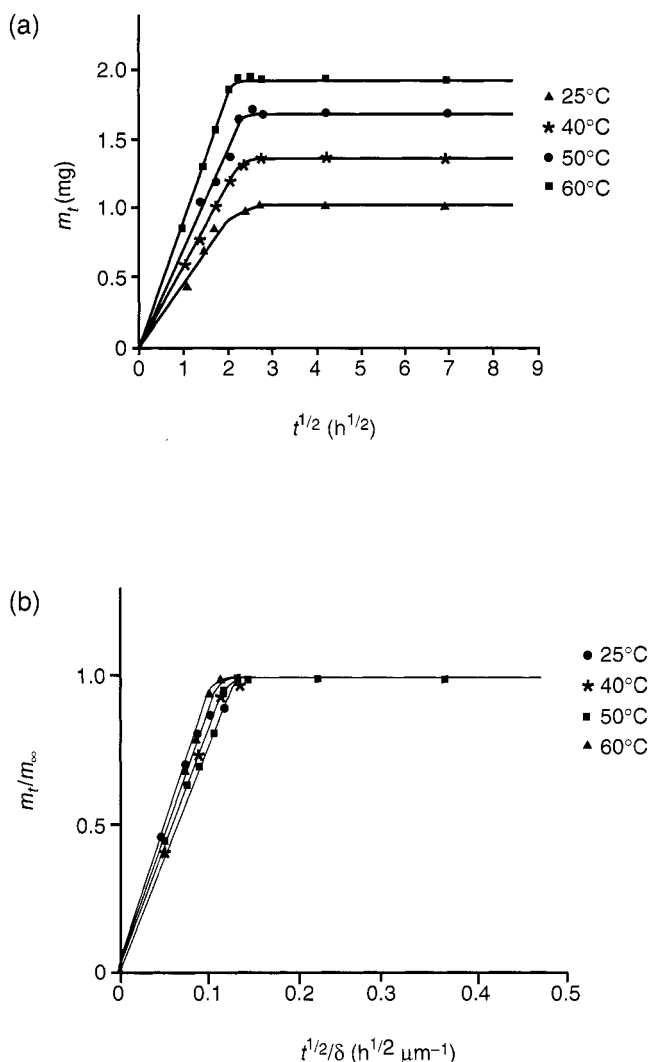


Fig. 8 A plot of the amount of absorbed water at time t , m_t , against the square root of time (a) and the reduced sorption curves (b), at different temperatures for epoxy coating during exposure to 3% Na₂SO₄.

of different volatile electrolytes were calculated from the area under the endothermic trace: results are presented in Table 2. From the obtained values of enthalpy of vaporisation, the quantity of water inside the coating was calculated for the different corrosive agents (Table 2) knowing the average value of enthalpy of vaporisation of pure water between 20°C and 110°C ($\Delta_{vap}H = 2342.9 \text{ J g}^{-1}$) [20].

The closeness of the values of enthalpy of vaporisation of the different volatile electrolytes and of the quantity of water inside the coating, provide additional confirmation for the first step of the proposed mechanism of electrolyte penetration through the coating.

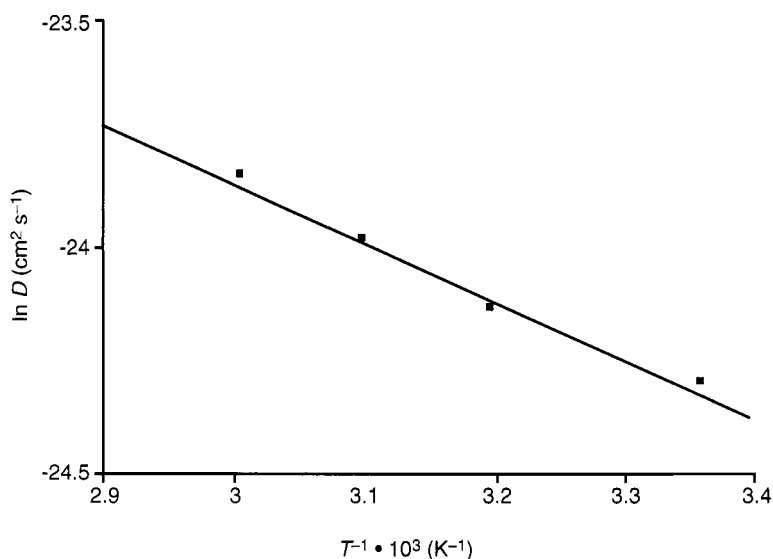


Fig. 9 Arrhenius temperature dependence of diffusion coefficient for water during exposure to 3% NaCl.

The second step of electrolyte penetration, which corresponds to the plateau in $\log C_c-t$ (Fig. 3), $\log R_p-t$ (Fig. 4) and $\log \epsilon_r-t$ (Fig. 5) plots, is related to penetration of water and ions through the macropores which, with time, become deeper and finally penetrate the coating [10]. This leads to contact between the electrolyte and the metal surface and to the beginning of electrochemical processes at the metallic interface as can be concluded from the final increase in coating capacitance and relative permittivity and the final drop in pore resistance.

Since it is well known that the movement of the corrosion potential of a polymer-coated steel with time is related to its corrosion behaviour, potential-time measurements were conducted. The potential-time curve for the epoxy coating during exposure to 3% NaCl is shown in Fig. 11. The period taken to reach the peak potential before its gradual decline represents the useful life of the film [21,22]. After

Table 2. The values of enthalpy of vaporisation, $\Delta_{vap}H$ and water content during exposure to different corrosive agents

Electrolyte	$\Delta_{vap}H \text{ (J g}^{-1}\text{)}$	Water content (wt%)
H ₂ O	18.8	0.80
3% NaCl	23.3	1.0
3% Na ₂ SO ₄	24.7	1.1
3% Na salt of 2-naphthol-3,6 disulfonic acid	21.8	0.93

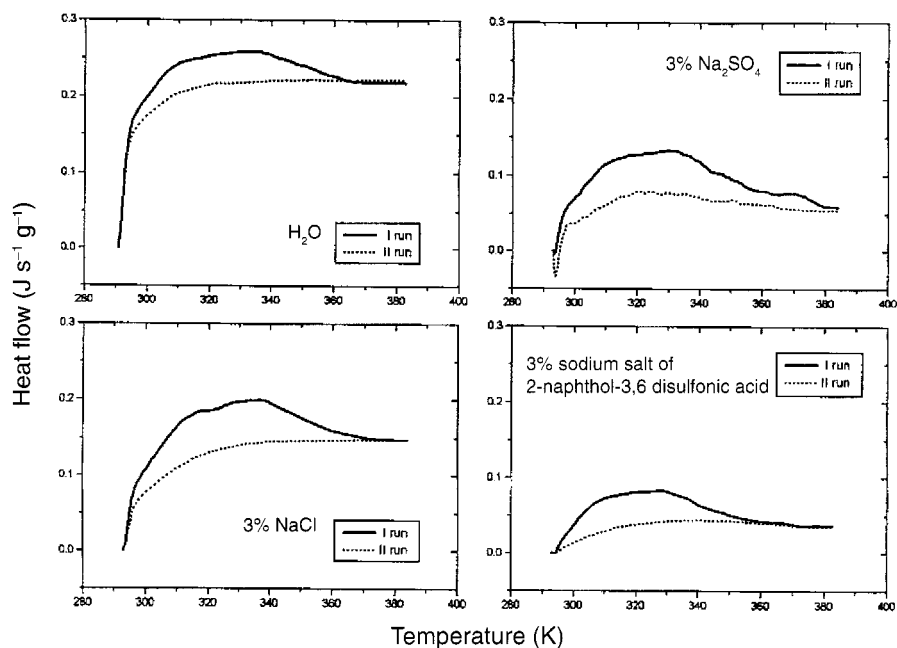


Fig. 10 Differential scanning calorimetry thermograms for epoxy coating after 7 days of exposure to various corrosive agents.

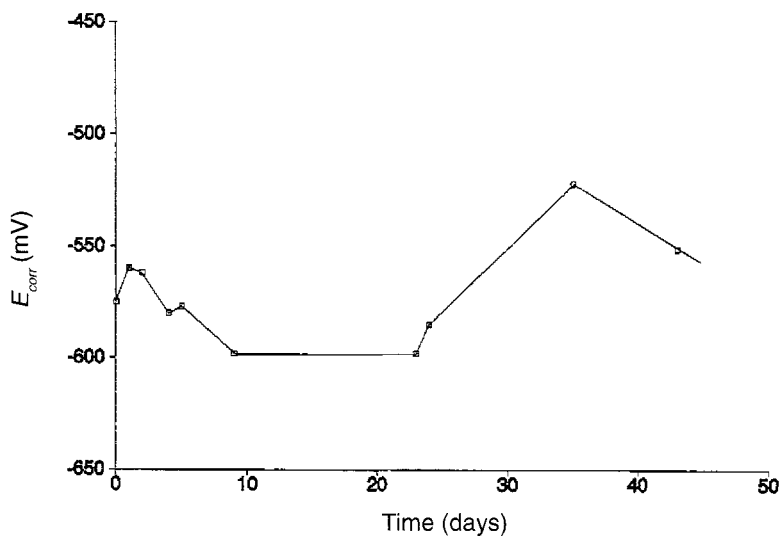


Fig. 11 Potential as a function of immersion time for epoxy coating during exposure to 3% NaCl.

this period (about 35 days) contact between the electrolyte and the metal surface occurred as the macropores in the coating became deeper and finally penetrated the coating.

4. Conclusions

Using a.c. impedance measurements, gravimetric liquid sorption experiments, differential scanning calorimetry and potential-time measurements, it is suggested that electrolyte penetration through an organic coating occurs in two steps. The first step is related to water uptake, when molecules of pure water diffuse into the micropores of polymer net according to Fick's law and is independent of the type and dimensions of ions in the corrosive electrolyte. The proposed mechanism was confirmed by the near agreement of the values of diffusion coefficient for water, energy of activation of water diffusion, enthalpy of vaporisation of volatile electrolyte and quantity of water inside the coating obtained during exposure to different corrosive solutions. The second step is related to penetration of water and ions through the macropores which leads to contact between electrolyte and metal surface and the beginning of electrochemical processes at the metallic interface. This was confirmed by the existence of a peak in the potential-time behaviour followed by a steady decline, corresponding to the final increases in coating capacitance and relative permittivity and the final decrease in pore resistance.

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EIS – Studies of Commercially Available Coatings on Steel

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ABSTRACT

Using impedance spectra series the swelling of four coatings was investigated with respect to water uptake and changes of diffusion in the coatings. For the interpretation of the measured data a fitting algorithm with some physical models was applied to represent the measured data. The results were compared to obtain a suitable and understandable physical model. Models with more than four parameters were found to be not useful because of the limited frequency range and sometimes physically meaningless values. Therefore, a model with only four adjustable parameters was used to describe the swelling of the coatings. The comparison of the parameters from the different coatings showed significant effects such as increased water uptake of a coating pigmented with micaceous iron oxide. This finding is in contradiction to the widely used term 'barrier type pigment'. Thus, in this case, the correlation that is often postulated between water uptake and corrosion protection performance is not valid, although this coating material is reliable in industrial practice.

1. Introduction

Electrochemical impedance spectroscopy (EIS) is widely used to investigate polymer coatings on metallic substrates [1,2]. Many papers are published dealing with thin clear coats, of which only two are cited here [3,4]. Measurements of the effects of carefully applied defects can also be found in the literature [4]. EIS is also used for investigation of coating properties of commercially applied powder coatings or cathodic dip coatings, but only for thin layers of 10–25 μm thickness [5]. Much pure research work has been carried out with electrochemical experiments to study the influence of delamination of coatings [6–8].

The technology of application of heavy duty corrosion protective coating materials is different from that of the above materials. Spraying, brushing-on or roller coating are the types of applications most used in the protection of large steel structures like energy transmission towers or bridges. The coating thicknesses which are usually of more than one layer have values above 200 μm and sometimes up to 1000 μm . Only a few papers deal with coatings which are used for protection from severe corrosion attack, that is, coatings with more than one layer and higher thicknesses, e.g. 100 μm each.

If an organic coating works well it will have an extremely high electrical resistance associated with typical capacitor properties [9,10]. In the case of high resistance

coatings with nearly perfect barrier properties, i.e. without any defects, it will not be possible to measure the potential of the steel interface. However, it is possible to measure the coating capacity or, better, the constant phase element (CPE) behaviour of the coating [11]. The barrier properties are easily determined by making measurements in the range of 10–10⁴ Hz and analysing the data with an RC model based curve fitting algorithm. Using EIS it is also easy to see whether or not the coating has defects since with defects a more complicated impedance spectrum will be obtained. Pores and broken blisters give access to the steel interface where corrosion can occur. Using active anti-corrosion pigments the steel surface at these defects could still remain passive — if the pigments are effective.

To approach realistic systems, we started our work with highly pigmented coatings (e.g. high solids) which are commercially available and are used in practice. Our aim was to study the early hours of swelling, because under atmospheric conditions the water uptake should be an important factor for the performance of an organic coating. Both oxygen and water are required at the steel interface for corrosion to occur once the adhesion of the coating is partly lost.

The first step was to investigate the water uptake of four coating materials which usually are applied as top coats.

The change in the CPE during swelling will show differences between the coatings with respect to the chemical nature of their binders. The influence of pigmentation is also not negligible [12]. In particular, the effect of micaceous iron oxide (MIO) should be discussed in more detail. Generally speaking MIO is called a barrier type pigment which should increase the path length for water and oxygen to the steel substrate. But new results have given reason to believe that MIO increases the water uptake of these type of coatings [12,13].

The analysis of the data obtained from EIS is not very simple and sometimes misinterpretations can occur. The usual method is to select a model which is in good agreement with some physical aspects of the particular problem.

2. Experimental

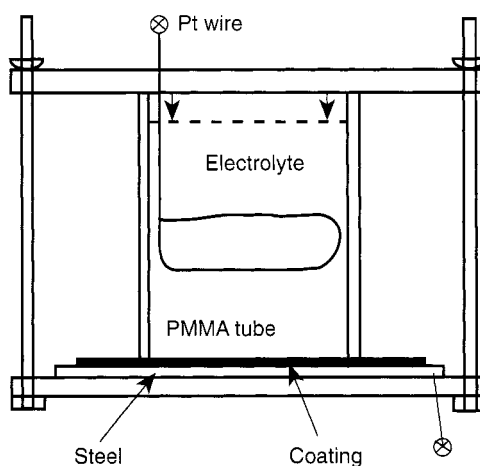
A drag down blade (film applicator) was used to apply one layer only, of *ca.* 200 μm thickness to ground mild steel plates. Varying dry film thicknesses could occur as a result of slight variations in the individual total residue contents. The four coating materials were formulated with three types of binder systems (physically drying alkyd resin, two component polyurethane and moisture curing polyisocyanate). A short description of the materials is given in Table 1.

To measure the water uptake and the first 12 h of swelling the samples were immersed in an electrolyte solution. The coated steel panels were mounted in a sample holder as shown in Fig. 1. The polymethylmethacrylate (PMMA) tube was filled with 0.01M KNO₃ or KCl solutions. A concentration of 1M was sometimes used.

At the beginning and after each hour of immersion an impedance spectrum was recorded from 10 to 10 000 Hz — unless indicated otherwise. The measuring device was a two electrode equipment fitted in a Faraday cage with the Zahner IM 6 electrochemical impedance spectrometer including all types of measuring and analysis software. A two electrode cell was used because it was not always possible

Table 1. List and characterisation of coating materials coating

Coating	Description
A	moisture curing polyisocyanate, one component additionally pigmented with micaceous iron oxide
B	moisture curing polyisocyanate, one component regular pigmentation
C	physically drying PVC–alkyd resin regular pigmentation
D	two component polyurethane coating regular pigmentation

**Fig. 1** Measuring cell for coated steel samples.

to detect the working electrode potential because of the very high coating resistance. The a.c. amplitude was 10 mV for coatings A and B because of pronounced changes in their spectra and their lower resistance after 12 h. For coatings C and D the a.c. amplitude was 100 mV, because of their longer lasting high resistance. The sampling area was 4.9 cm². As the frequency range was limited to 10 to 10 000 Hz the recording of each spectrum required 24 s, including 5 times sampling of each frequency. This short period was necessary because of non-stationary states during the first hours of immersion [12]. Each sample was measured at three different points to avoid artefacts, for example pores, which could give difficulties in the interpretation of the spectra.

3. Results and Discussion

3.1. Data Modelling

The spectra series of the four coatings are shown in Fig. 2. All measurements in Fig. 2 were carried out with 0.01 molar KNO₃ solution.

All plots show more or less the same behaviour, thus, the later curves have lower

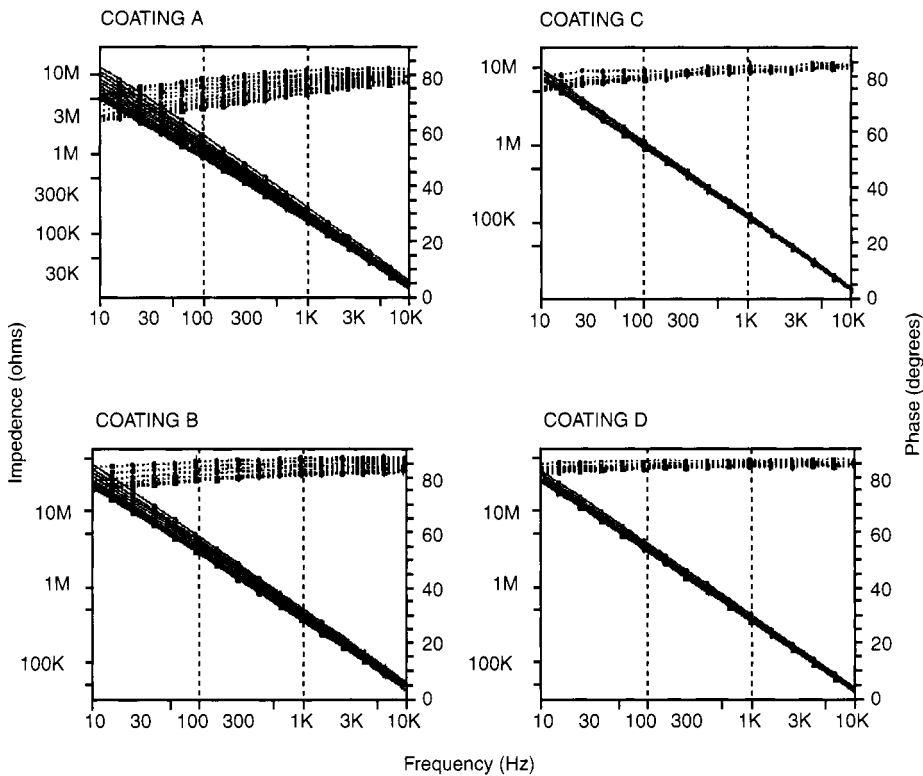


Fig. 2 Impedance series measurement of coatings A–D; 1 spectrum per hour.

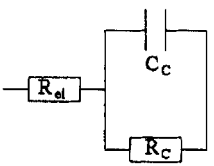
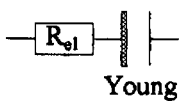
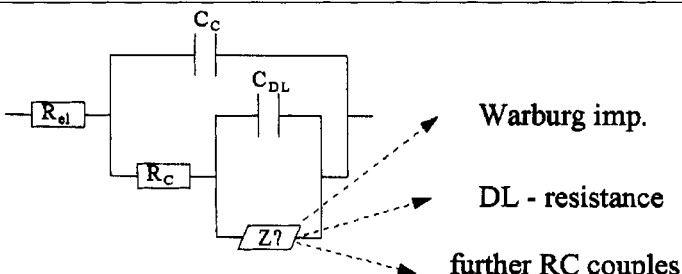
impedance and phase angle than the curve measured immediately after immersion — a result that can be explained by an increase in the capacitance due to water uptake.

As can be seen, even without further data processing, coatings A and B show much more change in phase and impedance spectra during the measurement period than coatings C or D. In addition, this effect is more pronounced for coating A. The interpretation of the data with transfer functions or equivalent circuits provides parameters of the physical model which form the basis for the derivation of both methods. The results using the transfer function method or equivalent circuit method are identical but the equivalent circuit method is more illustrative.

Some of the published equivalent circuits, which might be appropriate for this problem, are listed below (Table 2a).

However, these models are not really appropriate to cover all experiments. In Fig. 3(a–c) the fit (solid line) and measured points are shown for model 1–3. For curve fitting the unspecified impedance element in model 3 was set to be a resistor. The measured curves in Fig. 3 or Fig. 4 are only examples for two different types. After 24 h swelling the Nyquist plot of coating B is shown in Fig. 3, and similarly coating A is shown in Fig. 4. The x-axis is the real part of the impedance and the y-axis the imaginary part (Mohm). The aim of both figures is to show the accuracy of the fits and to demonstrate the problems with the significance of the whole fit or with the number of fitting parameters.

Table 2a. Equivalent circuits used in literature for the description of EIS experiments after immersion (CPE as capacitor)

model 1	
model 2	
model 3	

The Nyquist plot amplifies smaller deviations which can be hardly recognised in the Bode plot (see Fig. 2). However, a disadvantage of the Nyquist plot is, that it is not always possible to judge the whole shape of the curve, because of the linear scale of the axis, which suppresses the high frequency RC couples. Since the models in Table 2(a) do not represent the measured curves sufficiently, some other models were considered (Table 2b, p.53).

In addition the χ^2 values of the models in Tables 2(a) and (b) are given in Table 3 for the two example measurements. It can be seen that there is no universal model for both measurements. Model 6 with its nine parameters fits quite well, but this fact is not surprising.

In Figs 3(h) and 4(h) model 6 was fitted with two different sets of starting parameters. The resulting parameters are given in Table 4. The fitting procedure showed that not all of these parameters are significant — those with low significance are printed in italics.

It turned out that for coatings with high thicknesses and high contents of pigments and fillers all the models shown here, as well as some others, do not fit the measured data well. There are some quite distinct problems, e. g. not enough significant parameters because of the limited frequency range and there is no consistency in the model, i.e. one model fits the measurement using one coating but not the other.

The significance of the fits is questionable if too many parameters are involved. Model 6, for example, needs nine parameters if the capacitors are treated as CPE. Additionally, the CPE exponent n_{DL} is out of the range for capacitors (0.9–1) or Warburg-impedance (0.5). The physical meaning of this element then becomes

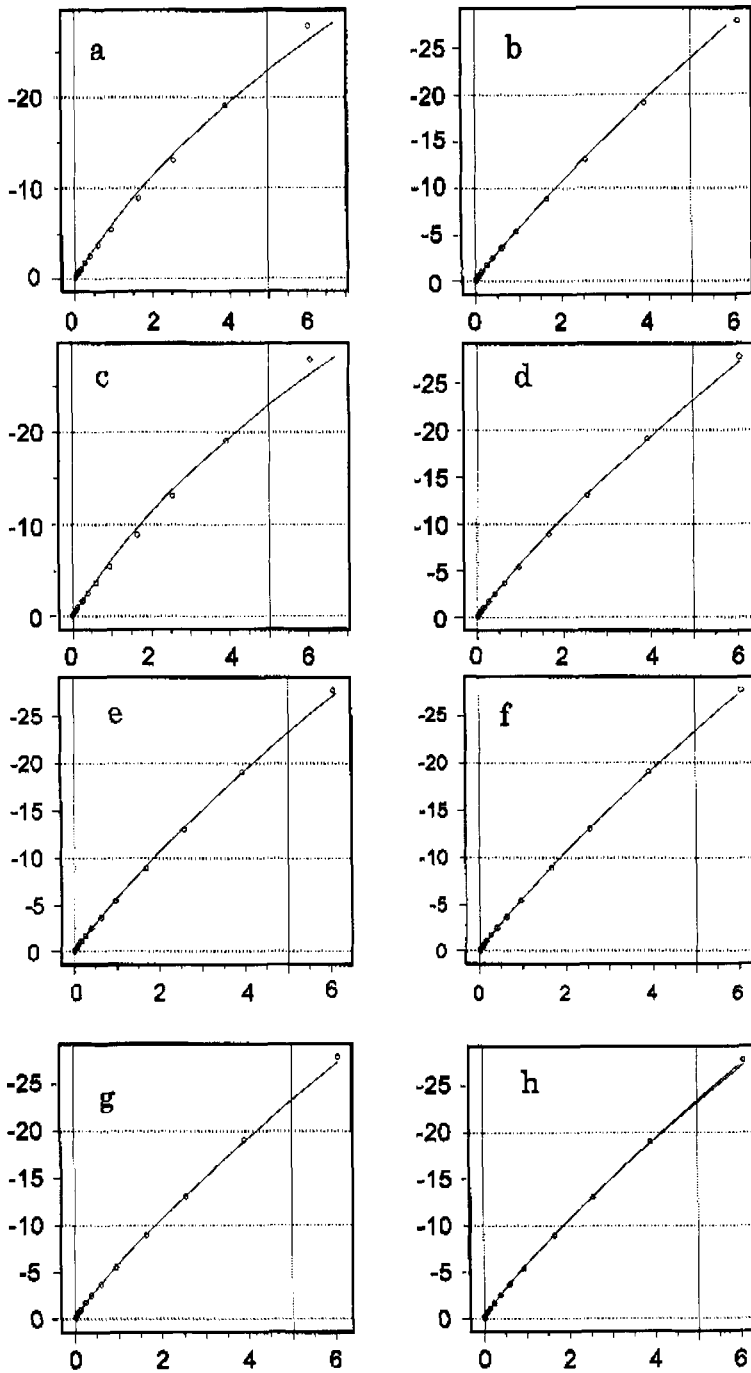


Fig. 3 Spectrum of coating B: (a) fit with model 1; (b) fit with model 2; (c) fit with model 3; (d) fit with model 4; (e) fit with model 5; (f) and (g) fits with 2 sets of starting parameters for model 6; (h) comparison of (f) and (g). Nyquist plots: x and y axes the real and imaginary parts of the impedance.

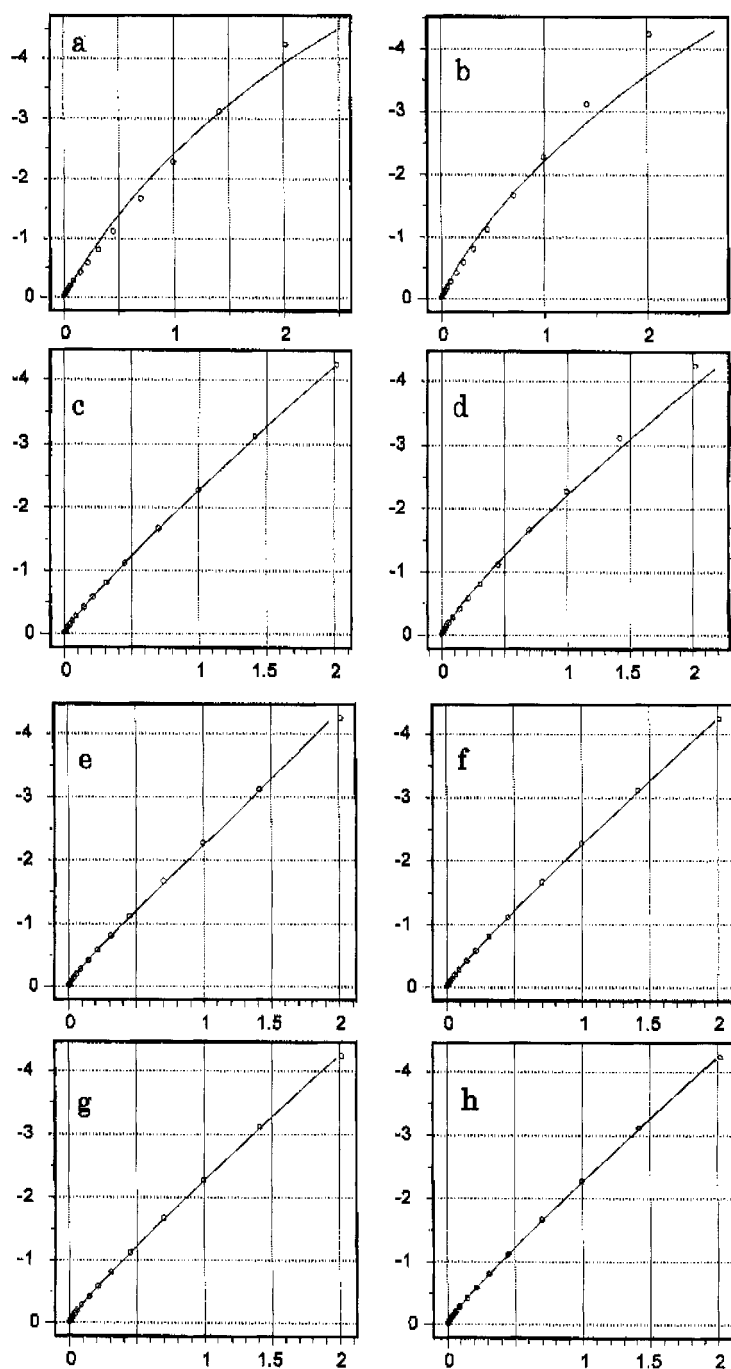
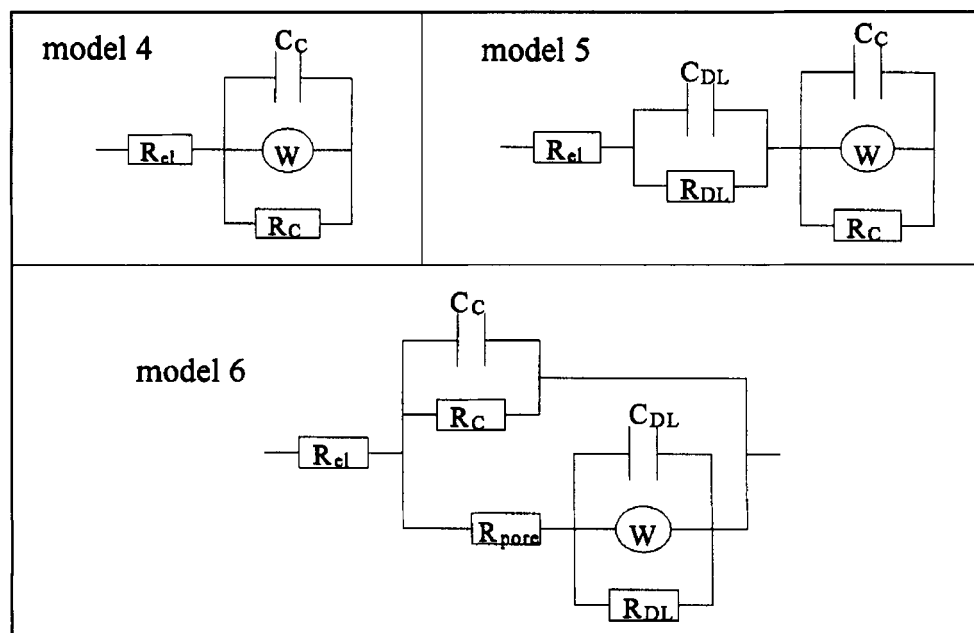


Fig. 4 Spectrum of coating A: (a) fit with model 1; (b) fit with model 2; (c) fit with model 3; (d) fit with model 4; (e) fit with model 5; (f) and (g) fits with 2 sets of starting parameters for model 6; (h) comparison of (f) and (g).

Table 2b. Equivalent circuits for EIS data representation (CPE as capacitor)

Table 3. Chi square values, CHI_Q , after curve fitting using model 1–6 for two different measurements

Model	CHI_Q of fit Curve A (see Fig. 3)	CHI_Q of fit Curve B (see Fig. 4)
1.	0.0193	0.1741
2.	0.0074	0.1268
3.	0.0192	0.0002
4.	0.0126	0.0176
5.	0.0112	0.0031
6.	0.0071	0.0003

somewhat questionable, as does the entire model (see also discussion of Table 6, model 3). n_c denotes the exponent of C_c as CPE.

In Table 5 the chi square values (χ^2) for the fits are shown together with the number of parameters required for each model.

So an obvious decision would be to use a simple model probably omitting the lowest χ^2 values and with only few free adjustable parameters of high significance. Model 4 meets these demands.

The physical meaning of model 4 is easy to explain: the water uptake of the coating can be seen in the change of the capacity of the CPE as well as in a change in the

Table 4. Fit of model 6 using two different sets of starting parameters

Parameter	Curve A Fit 1	Curve A Fit 2	Curve B Fit 1	Curve B Fit 2
χ^2	0.0071	0.0073	0.0003	0.0003
C_c (pF)	188.2	233	612	600.5
n_c	0.9842	0.9632	1.002	1.01
R_c (TΩ)	112.7	8.65	87.81	150.4
R_{pore} (kΩ)	8.9	14	6.162	7.262
C_{DL} (pF)	165	118.9	601.8	621
n_{DL}	0.8618	0.8598	0.6723	0.673
DW (GΩ)	1.795	1.546	0.739	1.025
R_{DL} (TΩ)	1.558	0.12	1.213	2.083
R_{el} (Ω)	65.54	195	47.41	53.74

Table 5. Number of parameters required for each model and chi square value obtained for coating A–D

Model	Number of Parameters	Coating A	Coating B	Coating C	Coating D
1	4	0.183	1.2437	1.2047	1.2521
2	4	0.0147	0.0431	0.0368	0.4501
3	7	0.0005	0.0012	0.0011	0.0035
4	5	0.014	0.1209	0.0949	0.0492
5	8	0.0043	0.0386	0.0238	0.0582
6	9	0.0001	0.0002	0.0032	0.0359

Table 6. Values for the parameters obtained for coating A–D by curve fitting of model 3

Model 3	Coating A	Coating B	Coating C	Coating D
C_C/F	713p	372p	452p	422p
n_C	0.9542	0.982	0.9557	0.9768
R_C/Ω	224k	183k	9.61M	670k
C_{dl}/F	223.5p	98p	30.7p	15.4p
n_{dl}	0.5851	0.7188	0.6294	0.652
R_{dl}/Ω	4.4G	2.8G	1.73G	34G
R_{el}/Ω	26	32	304	68

exponent n . The Warburg impedance describes the resistance to diffusion, a high impedance value means a low diffusion rate and vice versa. The coating resistance is very high if the coating is in service without pores and defects ($>100\text{ G}\Omega$) or below $100\text{ M}\Omega$ if the coating is porous or delaminated and probably having rust spots. Most of the coatings investigated here show values above $10\text{ G}\Omega$.

Model 3 seems to fit best for all coatings after 24 h and over an extended frequency range from 1 Hz to 100 kHz. But, as can be seen in Table 6, the exponent of the double layer capacitance n_{dl} is too low for a capacitor and too high for a Warburg impedance behaviour. If the Warburg impedance is incorporated into model 3 the fit becomes worse. This is the same if Z is replaced by a resistor with series connection to a Warburg impedance or a further introduction of model 1 and its variations (e.g. Warburg impedance instead of resistor connected in parallel). The values printed in italics have only low significance. Furthermore, the C_{dl} values are too small and probably not realistic, because every impedance spectrometer has input capacities and line capacities in that range.

The application of model 4 with its reduced fit quality is only one approach to a discussion about the different behaviour of the coatings A–D, even if the fit is not the best one. But the few parameters involved in model 4 are all understandable. The comparison of the parameters obtained can be carried out independently of their absolute size. When using absolute values conclusions should be drawn carefully. The different shape of the parameter time plots is an important and significant property for each coating. Table 7 shows the parameters of model 4 obtained by fitting the measurements after 24 h of immersion. The frequency range was from 1 Hz to 100 kHz. It becomes clear that differences in the chemical nature of the coatings influence the electrochemical behaviour. Very interesting is the high C_c value of the coating A which was pigmented with MIO (micaceous iron oxide) in a moisture curing binder. The low Warburg impedance of coating A gives a first hint of a specific interaction of MIO resulting from an increased water uptake or mobility — at least with the pigments near to the coating surface.

Table 7. Values for the parameters obtained for coating A–D by curve fitting of model 4

Model 4	Coating A	Coating B	Coating C	Coating D
C_c/F	763p	456p	465p	439p
n_c	0.9177	0.9084	0.9381	0.9612
DW/Ω	99.5M	1.77G	1.47G	4.8G
R_c/Ω	57G	3.2G	1.93G	47G
R_{el}/Ω	7	68	99	95

4.2. EIS Series Measurements

Immersion tests can be readily used to study the swelling or water uptake of coatings. The measured series in Fig. 2 show this swelling and therefore every spectra of the series was fitted to model 4 to get a more mathematical description of the behaviour of coatings under immersion conditions.

Model 4 was used because it has only 5 free adjustable parameters, even if the quality of the fits is not absolutely the best, i.e. compared to models with an increased number of electrical elements. As shown in section 3.1. it is easily possible to fit models with a higher number of free parameters to get excellent fitting quality, but the significance of each parameter will be reduced. Model 4 consists of the coating resistance R_c and the coating capacity C_c as a CPE with n_c . The Warburg impedance DW describes the diffusion processes in the coating and R_{el} the resistance of the electrolyte. This model was checked to be suitable over a frequency range of 1 Hz to 100 kHz, after 24 h of immersion (the parameters are shown in Table 7). There, DW was a significant and exactly determinable parameter, in contradicstinction to R_c , which was not always exactly measurable because it had the same order of magnitude as the input resistance of the spectrometer. Therefore, discussion of R_c time plots is not useful. To improve the accuracy of the measurement the frequency range was limited as described in the experimental section, to obtain short measuring periods of only 24 s. This was necessary to obtain stationary state conditions, which are required for EIS measurements and interpretation of fitting data.

The curve fitting of each of the spectra delivers a time resolved set of fitting parameters. Each parameter can be plotted vs time. These plots demonstrate clearly the different behaviour of the coatings in the early period of immersion. For example the exponent n_c of the CPE shows a very different behaviour, depending of the coating involved (Fig. 5). Also the water uptake, which can be seen by an increase of the capacity (Fig. 6), is significantly different. The capacity time plots are normalised to improve the comparison.

In accordance with the above results coating A shows a higher increase in capacity compared to the other coatings. This fact cannot be explained only by variations in the dry film thickness of the samples. Furthermore, the magnitude of the effect is

much bigger than the variations in the dry film thickness. As known from earlier work [12,13], MIO pigments increase the water uptake and decrease the Warburg-impedance. This result was obtained in the first part of the present paper when discussing the modelling of the data. A ranking for the degree of cross-linking can be derived from the nature of the binders in the coatings. The degree of cross-linking decreases as follows: $D > A \sim B > C$. Coating C has only physical drying. This ranking list can also be seen in the Warburg impedance–time plots in Fig. 7, with exception of coating A. Again A shows the lowest impedance which is equivalent to the highest diffusion coefficient.

Figures 5–7 show clearly that after 15–20 h the coatings are in a steady state with only minor changes occurring. Therefore, it might be sufficient to reduce the measuring time to 10–20 h. With the ranking established for that time of immersion, it must be pointed out that none of the samples was rusting or blistering after 70 h, i.e. none of the coatings could be seen to fail by that time.

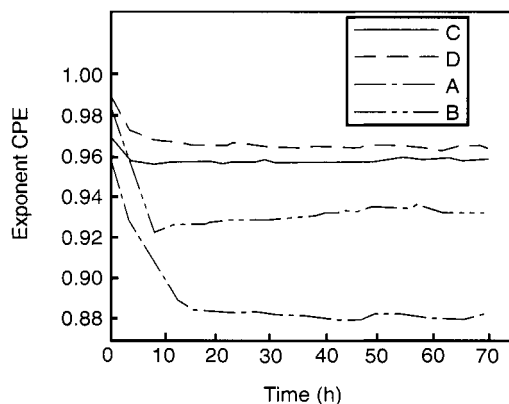


Fig. 5 Exponent n_C of model 4 during 70 h of immersion.

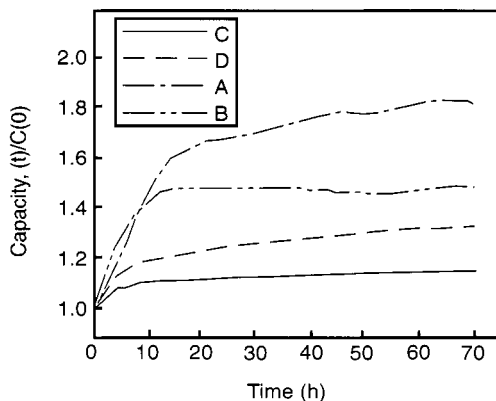


Fig. 6 Ratio of the capacity $Y(t)$ to the starting capacity C_0 , relative change of the capacity.

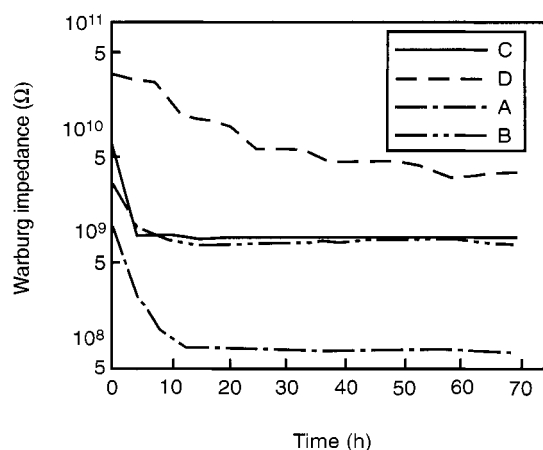


Fig. 7 Warburg impedance from model 4 during 70 h of immersion.

5. Conclusions

It has been shown that it is almost impossible to find a suitable physical model to explain the processes during immersion of more than one type of coating. Sometimes the fit of one set of curves is not possible with one model so that it might be recommended to change the model within a set of related models. But if a proper model could be found, this change should not be necessary. Furthermore, the results from some of the other models have given questionable parameters which have led to problems of interpretation. A compromise model was found that although without pronounced fitting success nevertheless gave good significance to each parameter. Each spectrum of impedance spectra series obtained from four paints was fitted to this model. This curve fitting procedure delivers time resolved parameters of the model. The model could be kept unchanged for all coatings and all series because it fitted fairly well every spectrum. For some cases another model may fit a little better, but then more than 5 fitting parameters would be required. The parameters obtained from our model can be compared directly. It was found that the parameter time plots describe the individual behaviour for each coating and that these results can be explained in relation to the nature of the polymer component of the coating material and, in one case, to pigmentation using micaceous iron oxide.

Finally, it is evident, that differences in the water uptake are common and cannot be correlated with corrosion protection properties of the coatings, since all the coatings in this work gave excellent corrosion protection (e.g. 10 years guarantee). Furthermore, there are explanations why MIO gives an increase in corrosion protection properties even if the coating shows a higher water uptake [14]. The use of MIO in coatings results in a high permeability, allowing water to leave and to enter the coating rapidly — without damage — through the micro fogging process, i.e. the formation of small water clusters in the polymer part or in the pigment binder interface from condensation of water vapour. The experimental results and the considerations about the nature of the polymeric backbone of the coating are in fair agreement and so further possibilities for checking these need to be sought.

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Natural and Chlorosulfonated Polyethylene Rubber Coatings for Anticorrosion Protection in Reducing and Oxidising Chemicals, and in Natural and Industrial Conditions

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ABSTRACT

The corrosion behaviour of a natural rubber of TM type, of a compound with 25% natural rubber and 75% chlorosulfonated polyethylene (CSPE) of PR-7 type and of two CSPE rubbers of CSPE-E (cross linked with epoxy resin) and of CSPE-L (cross linked with litharge) type as simple vulcanising sheets and as coatings (linings) on carbon steel was studied in laboratory, natural and industrial conditions. The experimental results enabled the usefulness of these materials to be defined in terms of corrosion media, temperature range and duration of effectiveness. The performances of rubbers both in reducing and in oxidising chemicals increase with increasing CSPE rubber content and the content of ingredients, the best resistance being shown by the CSPE-L type rubber. (Symbols are the commercial symbols of the manufacturer.)

1. Introduction

In order to slow down or halt the corrosion process, elastomeric coatings can be applied to a metal surface. Each elastomer has a certain environmental versatility and chemical tolerance [1–5]. Therefore, the development of new elastomers to fulfil industrial needs is a continuing process.

In this paper the behaviour in laboratory, natural and industrial conditions of some natural rubbers with additions of chlorosulfonated polyethylene (CSPE) rubber and of CSPE rubbers (formulated to resist attack in oxidising chemicals) is reported.

2. Experimental

The rubbers were manufactured by the Anticorosiv S.A. Co., Romania and were tested as simple sheets and as coatings (linings) applied to carbon steel. The compositions are given in Table 1 from which it can be seen that the rubbers differ both in their composition and in their cross linking systems.

The studies were carried out on simple elastomer vulcanising sheets (2 mm thick

Table 1. The composition of the materials

Type*	Content (wt%)		Cross linking system
	Natural rubber	CSPE rubber	
TM	100	–	–
PR-7	25	75	litharge
CSPE-E	–	100	epoxy resin
CSPE-L	–	100	litharge

* commercial symbols of manufacturer.

from which were cut the samples for the experimental tests) and on sheets applied to carbon steel with a special adhesive (Anticorrosiv S.A. Co.) after the removal of all foreign material and rust from the surface by sandblasting to bright metal with immediate application of a phosphating primer; the thickness of the coatings was approximately 2 mm. For laboratory experiments the following corrosion media were used: 5, 10, 20, 30 and 50% H_2SO_4 , 5, 10, 20 and 30% HCl , 5, 10 and 20% HF , 30, 50 and 60% H_3PO_4 , 5 and 10% HNO_3 , 5, 10, 20, 30 and 50% NaOH , sodium hypochlorite NaOCl with 12–13% active Cl , sea water, at various temperatures: 23, 40, 60 and 80°C. Furthermore, salt spray tests at 40°C (ASTM B 117-73, continuous tests) were conducted in a I.A.U.C. type room (Romanian production) and tests at –4, –12, –20°C (Romanian standard STAS 6828-63, STAS 8393/2-71) in Feutron 3001 type rooms (German production).

Tests were also conducted in some typical natural and industrial conditions. These included an urban environment (Bucharest), immersed (Black Sea) and atmospheric (Romanian coast) marine environments, an industrial atmosphere (products of coal distillation at a coal plant, including carbon, sulfur, nitrogen oxides, coal, tars) and some corrosive media from the chemical industry, e.g. tanks containing 70–80% H_2SO_4 and chlorine, 30–34% HCl , 150 g L^{-1} NaOH , 20% NaOH and chlorine traces etc. at ambient temperature and in a reaction vessel containing 240 g L^{-1} NaOH and chlorine at 30°C.

The immersed specimens in the laboratory corrosive solutions and those exposed to salt spray and at low temperatures were examined after 350, 700, 1400, 2100, 4200, 8400 h (1 year) exposure. Those exposed in urban, marine and industrial atmospheres and those immersed in chemical equipment were examined after 1, 3, 6, 12, 24 months (2 years).

Estimates of the protective properties were made from qualitative (visual assessment) and quantitative measurements: percentage change of weight ΔW (%), weight loss W_l (%), liquid absorption A (%), hardness, tractional-tearing resistance ΔR_t (%), tractional-tearing length ΔL_t (%) (following ISO 62-80, ISO 175-81, and ASTM D 453-78 for gravimetric parameters and ISO R 462-65, ASTM D 412-80 for mechanical properties). The performances of the studied coatings were estimated as good (G), moderate (M) and poor (P), obtained by correlation of the results for sheet samples

with those for sheets applied to carbon steel. These performances include the following limits [6,7]:

- good (G) for a maximum variation of the gravimetric parameters of 5% and of the mechanical properties of 25%;
- moderate (M) for a variation of the gravimetric parameters between 5 and 10% and mechanical properties between 25 and 35%; and
- poor (P) for a variation of the gravimetric parameters over the limit of 10% and of mechanical properties over the limit of 35%.

3. Results and Discussion

3.1. Accelerated Tests in Laboratory Conditions

For estimating the performances of the rubbers it was necessary to correlate the variations of all the six quantitative assessment parameters mentioned above with time and with concentration and temperature of the environments. The change in weight ΔW offers only general information about the effect of corrosion media towards the rubbers but if this characteristic is correlated with the loss in weight W_t and with liquid absorption, A , it should be possible to obtain data on the mode of deterioration, for example, dissolution W_t , swelling A or both. Then from the variations of mechanical characteristics ΔR_t and ΔL_t we can determine if the attack affects the elasticity properties of the materials.

The variations of the main characteristics properties were as follows:

(a) In the case of good performance all properties show slow variations (within acceptable limits) with small slope which tend to a constant level after a certain period of time thus reflecting a reduced reactivity of the material to the aggressive media; the slopes of the plots become steeper with increasing temperature, but the plots themselves still tend to a constant level denoting good stability. The concentration of the corrosion media affects to only a small degree the variations of the characteristic properties.

(b) For poor performances the variations of the main properties with time exceed acceptable limits and have steeper slopes which do not tend to a constant level; this fact reflects an increased reactivity; the temperature effect is more noticeable than in the case of good performances being higher for 60 and 80°C. All properties are affected by the concentration of the corrosive media the slopes of the dependencies being very steep thus denoting the degree of deterioration.

CSPE-L type rubber has good resistance in 50 wt% H_2SO_4 (Fig. 1) with slow variations of all properties at 23, 40 and 60°C; in 30 wt% HCl this material is poor at 40, 60 and 80°C because the absorption A and the mechanical properties ΔR_t and ΔL_t show very high variations with time, and do not tend to a constant level. The material was deteriorated by swelling.

Figure 2 illustrates the time variations of the quantitative characteristics for PR-7 type rubber. In 50 wt% H_2SO_4 at 23°C, all properties show slow variations which are

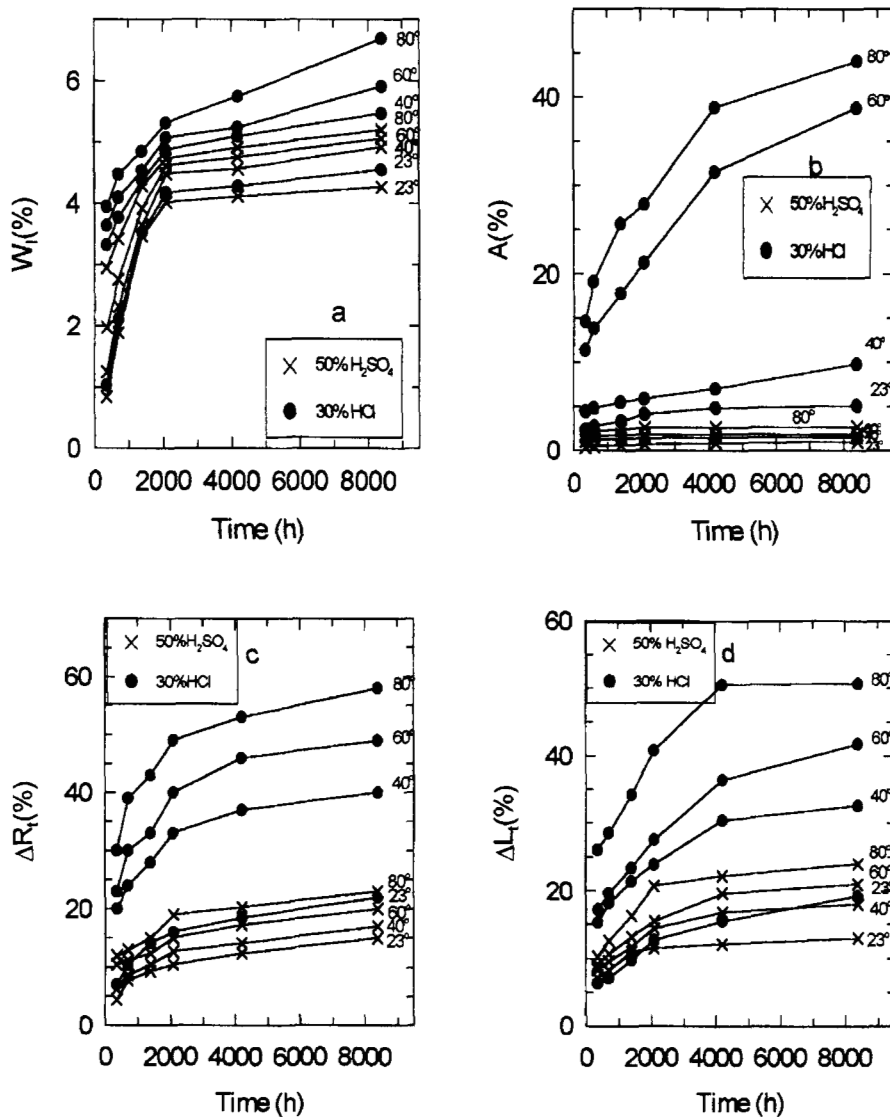


Fig. 1 Variations of the main properties with time for CSPE-L type rubber: 50% H_2SO_4 (x) and 30% HCl (•); (a) weight loss W_l ; (b) liquid absorption A ; (c) tractional-tearing resistance ΔR_t ; (d) tractional-tearing length ΔL_t .

within acceptable limits and tend to a constant level, indicating good behaviour. In 50 wt% H_2SO_4 at 40, 60 and 80°C and in 30 wt% HCl at 23 and 40°C, the mechanical properties exceed the acceptable limits in respect to swelling and increase of the dimensions thus indicating poor behaviour. In 30 wt% HCl at 60 and 80°C, all properties exceed the limits; they do not tend to a constant level and, in fact, the slopes of the property-time curves are very steep.

The effects of the concentration of HCl and NaOH solution are shown in Fig. 3 (p.65) and 4 (p.66). In the case of CSPE-E type rubber (Fig. 3) in NaOH solutions at

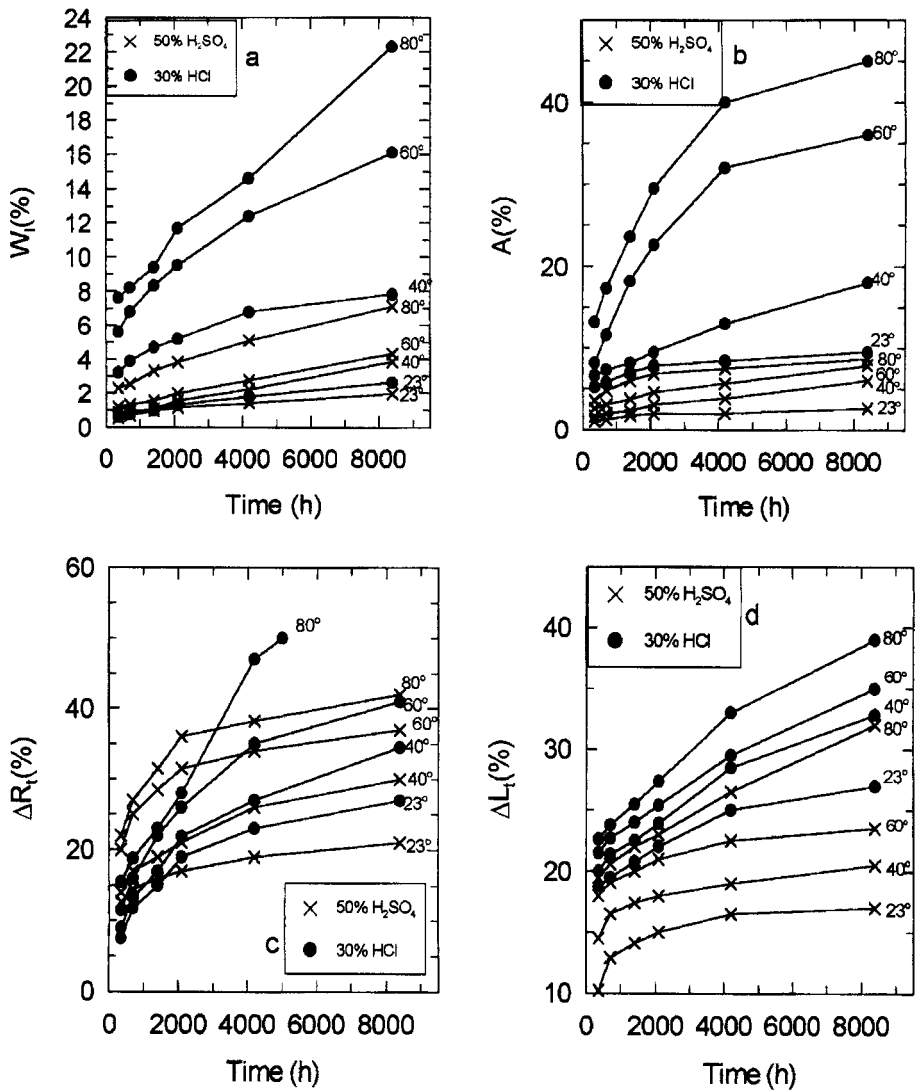


Fig. 2 Variations of the main properties with time for PR-7 type rubber: 50% H₂SO₄ (×) and 30% HCl (●); (a) weight loss W_l ; (b) liquid absorption A ; (c) tractional-tearing resistance ΔR_t ; (d) tractional-tearing length ΔL_t .

60° and 80°C, the mechanical properties change significantly but weight loss and absorption only to a small degree thus revealing poor behaviour. In HCl solutions at 40, 60 and 80°C the absorption and mechanical properties change markedly. For PR-7 type rubber (Fig. 4) only the mechanical properties are significantly influenced in NaOH solutions at 40, 60 and 80°C but in HCl solutions at 40, 60 and 80°C all the properties increase very much and exceed the acceptable limits.

Figure 5 (p.67) shows the performances of all rubbers in reducing and oxidising chemicals after 8400 exposure hours. The higher resistance of CSPE-L and CSPE-E

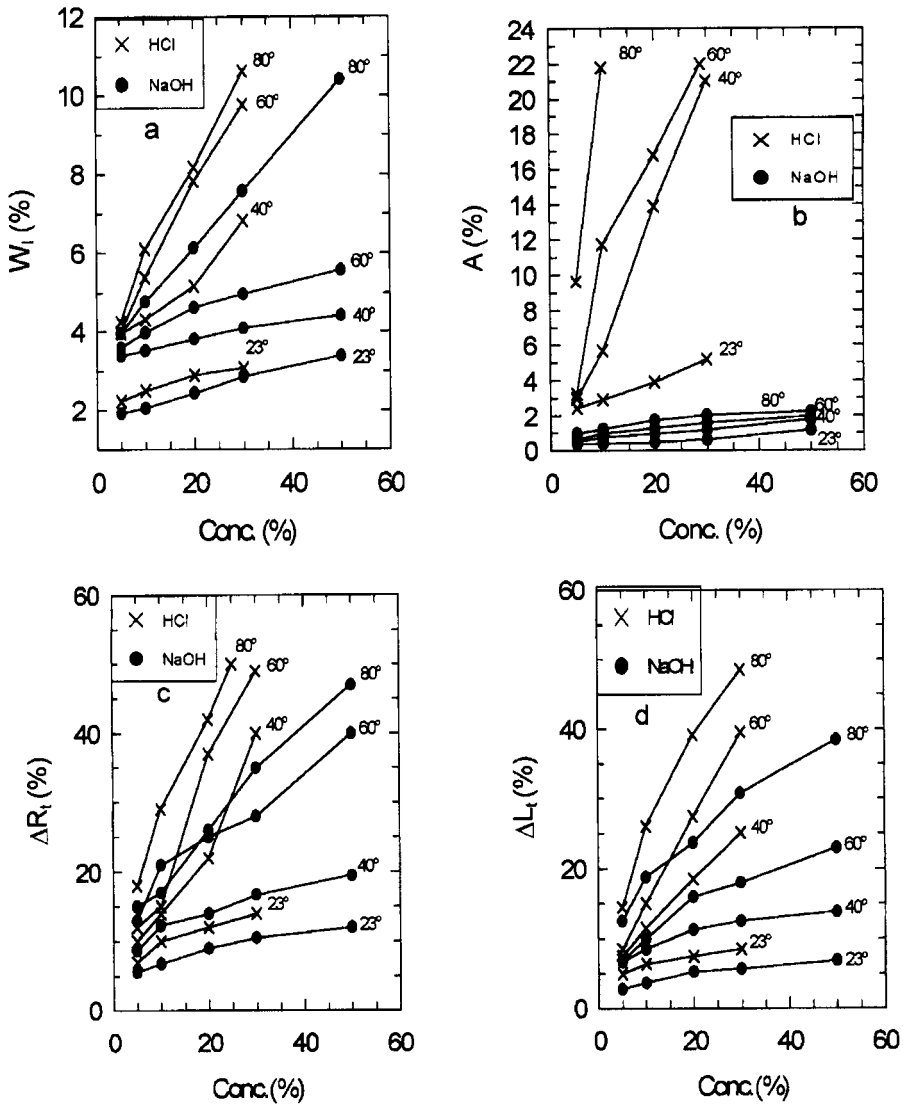


Fig. 3 Variations of the main properties vs concentration for CSPE-E type rubber in HCl (x) and in NaOH (•); (a) weight loss W_l ; (b) liquid absorption A ; (c) tractional-tearing resistance ΔR_t ; (d) tractional-tearing length ΔL_t .

type rubbers (created specially to resist such media) can be seen as well as the limited resistance for the TM type natural rubber and for the compound with 25% natural rubber, PR-7 type rubber. The performances of rubber increase with increasing CSPE rubber content and with content of additives.

Table 2 presents the protective properties of elastomers under laboratory conditions after 8400 exposure hours. It follows from this table that the usefulness of these materials is defined by the corrosion media, temperature range and period of effectiveness. The best performances of the four types of rubbers that were tested

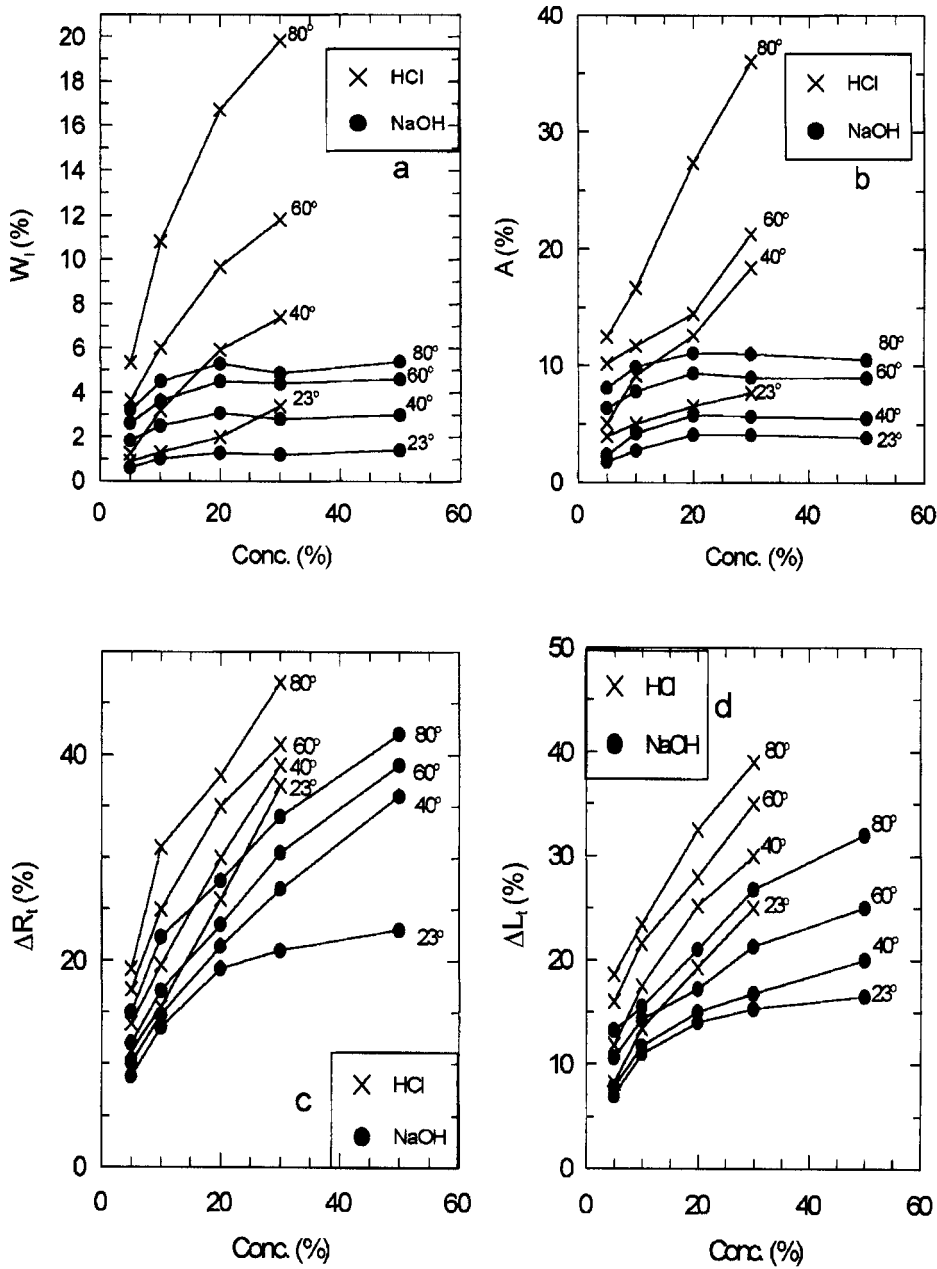


Fig. 4 Variations of the main properties vs concentration for PR-7 type rubber in HCl (x) and NaOH (•); (a) weight loss W_l ; (b) liquid absorption A ; (c) tractional-tearing resistance ΔR_t ; (d) tractional-tearing length ΔL_t .

were shown by CSPE-L type rubber with the highest CSPE rubber content and with the litharge cross linked system.

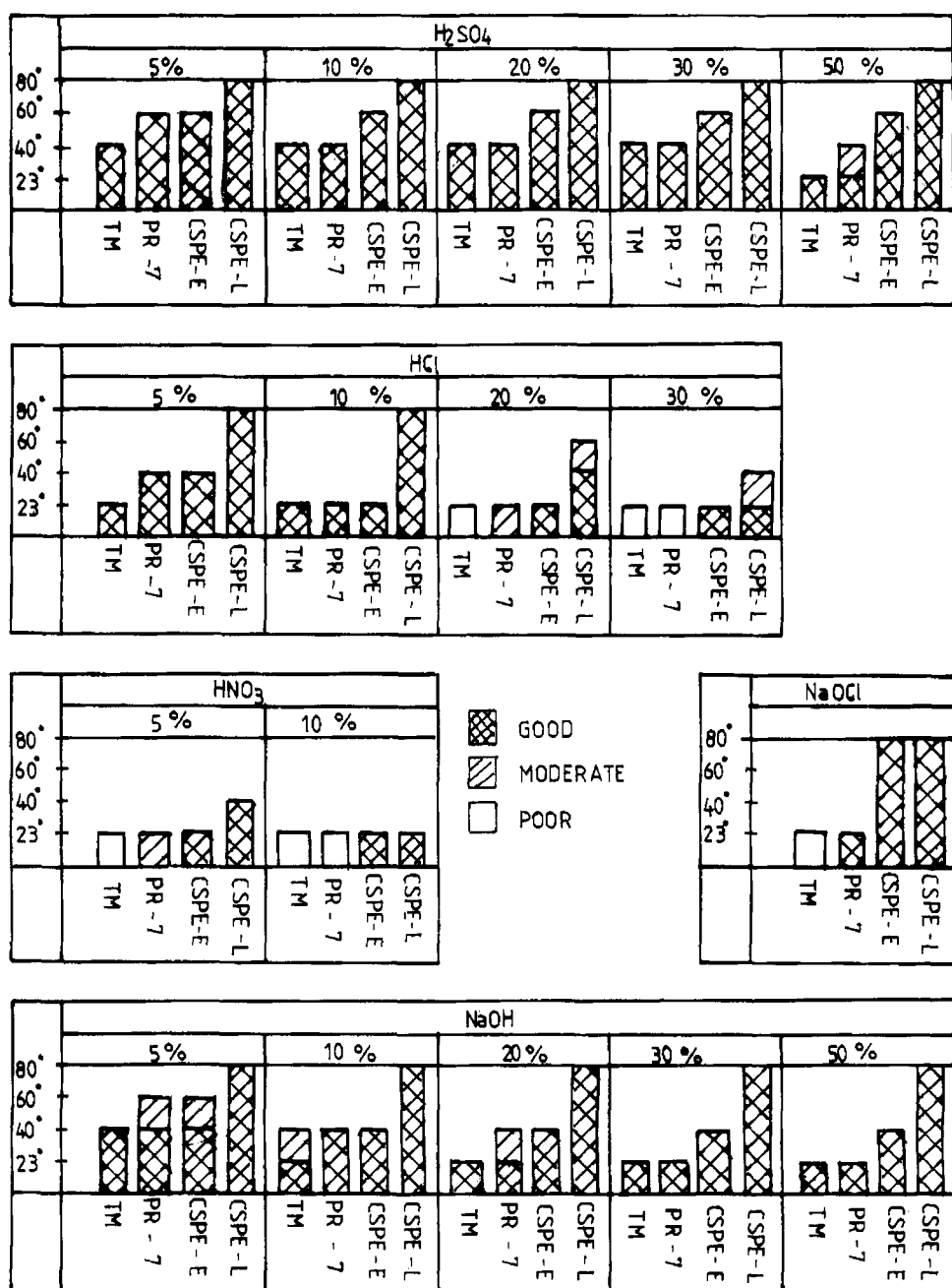


Fig. 5 Performance of rubbers in reducing and oxidising chemicals after 8400 h of exposure.

Table 2. *Protective capacity of the studied materials, under laboratory conditions for 12 months*

Corrosion media		Rubbers			
		TM	PR-7	CSPE-E	CSPE-L
H ₂ SO ₄	5%	M ₁ *G**	M ₁ G*	G ₁ G*	G
	10%	M ₁ *G**	G ₁ *G**	G ₁ G*	G
	20%	G**	M ₁ *G**	M ₁ G*	G
	30%	G**	G**	G*	G
	50%	G†	G+M**	G*	G
HCl	5%	M ₁ **G†	G**	G ₁ *G**	G
	10%	G†	G†	M ₁ **G†	G
	20%	G ₁ +M†	G ₁ +M†	G†	G**M*
	30%	M ₁ +P	M ₁ +P	G†	G†M**
HF	5%	G ₁ +P	G†	M ₁ **G†	G**
	10%	M ₁ +P	G†	G†	G**
	20%	P	G ₁ +M†	G ₁ +P	G**
H ₃ PO ₄	30%	G ₁ *G**	G*	G ₁ G*	G
	50%	G+M**	G*	M ₁ G*	G
	60%	G+M**	G**	G**	G
HNO ₃	5%	G ₁ +P	G ₁ +M†	G†	G**
	10%	M ₁ +P	M ₁ +P	G†	G†
NaOH	5%	M ₁ *G**	G**M*	G ₁ *G**	G
	10%	G+M**	G**	G**M*	G
	20%	G†	G+M**	G**	G
	30%	G†	G†	G**	G
	50%	G†	G†	G**	G
NaOCl		G ₁ +P	G†	G	G
Sea water		G*	G*	M ₁ G*	G
Salt spray		G	G	G	G
Tests at: -4°C; -12°C; -20°C		G [§]	G [§]	G [§]	G [§]

All test results at 12 months except with subscript 1 for 6 months.

G = good.

M = moderate.

P = poor.

No asterisk = up to 80°C inclusive; * = up to 80°C inclusive; ** = up to 40° inclusive; † = up to 23°C; § = up to -20°C inclusive.

3.2. Tests in Typical Natural and Industrial Conditions

Table 3 presents the performances of the elastomer coatings in natural and industrial environments after 2 years exposure. CSPE-L and CSPE-E type rubbers again show high resistance. A good correlation in the same environment and temperature conditions is seen on comparing the results in natural and industrial environments with the studies under laboratory conditions.

The changes of the quantitative characteristics over time and with the concentration of the corrosion media are similar to those which were observed under laboratory conditions.

Table 3. Protective capacities of the studied coatings, under typical natural and industrial conditions for 24 months

Corrosion Media	Rubbers			
	TM	PR-7	CSPE-E	CSPE-L
Black Sea Water	G	G	G	G
Black Sea Atmosphere	G	G	G	G
Urban Atmosphere (Bucharest)	G	G	G	G
Industrial Atmosphere (Coaling Plant)	G	G	G	G
Storage vessel: 70–80% H ₂ SO ₄ with chlorine	G ₁ P	G ₁ P	G	G
Storage vessel: 30–34% HCl	G ₂ M ₁ P	G ₁ P	G ₁ M	G
Storage vessel: 150 gL ⁻¹ NaOH	G	G	G	G
Storage vessel: 20% NaOH with traces of chlorine	G ₁ P	G	G	G
Filtration Vessel: 7–10% HCl and water jets	G	G	G	G
Filtration Vessel: 7–10% KOH and water jets	G	G	G	G
Reaction Vessel: 240 gL ⁻¹ NaOH with chlorine at 30°C	G ₂ M ₁ P	G ₁ P	G	G

G = good; M = moderate; P = poor.
no subscript up to 24 months; ¹ up to 12 months; ² up to 6 months.

However, the experiments need to be continued for a longer periods under typical industrial conditions, because the degradation process is rather slow.

4. Conclusions

The experimental results have established the protective capacities of a natural rubber of TM type, of a compound of PR-7 type (with 25% natural rubber and 75% CSPE rubber), of two CSPE rubbers of CSPE-E and CSPE-L types, in terms of corrosive media, temperature range and period of effectiveness.

The replacement of natural rubber by CSPE rubber and the changes in the additives content do not affect the protective properties of the natural rubber. On the contrary, these increase with the best resistance to reducing and oxidising chemicals being shown by CSPE-L type rubber with the highest CSPE rubber content and with the litharge cross linked system.

A comparison of the results from natural and industrial environments with the studies under laboratory conditions shows good correlation for the same environment and temperature conditions.

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Study of Electrolyte Penetration in Thin Paint Films

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ABSTRACT

The electrochemical techniques of electrochemical impedance and stepwise polarisation have been used to study the permeation of NaCl solution through thin (20–25 μm) paint films (of the acryl, alkyd, epoxy and nitro types). Coating capacitance and pore resistance were monitored with immersion time (up to 60 days) in 3% NaCl solution and their trends evaluated; the water uptake and the conductive pathways in the paint films were determined. Polarisation curves were recorded for bare and painted electrodes; the percentage decrease in the dissolution current of the steel substrate and the porosity of the protective films were calculated. The results were interpreted in terms of a model in which at first the solution rapidly penetrates the fissures and the capillaries existing as defects in the coating followed by a diffusion of solution into the polymer. All experimental results were correlated with the protective properties of paint coatings.

1. Introduction

The mechanism by which a polymer coating protects a metal substrate against corrosion is very important. It is generally accepted that an organic polymer coating reduces the corrosion of a metal substrate immersed in an electrolyte in two ways [1]. First, the organic coating acts as a membrane to oxygen, water and ions; the sorption and transport of charged (ions) and uncharged (water, oxygen) species then affect the corrosion behaviour of the polymer/metal system [1–5]. The general view is that the rate of water and oxygen diffusion cannot be the rate controlling factor and that the movement of ions across the film is the rate determining step. Secondly, the organic coatings can contain inhibitive pigments or corrosion inhibitors, which may modify the anodic reaction of metal corrosion.

A better evaluation and understanding of the metallic substrate corrosion process under organic films could be provided by electrochemical techniques [1–8]. Impedance, resistance, capacitance and polarisation curves have therefore been used in the present paper to study the permeation of NaCl solution through thin paint films.

2. Experimental Details

The coatings (acryl, alkyd, epoxy and nitro types – without pigments) were applied by brush to carbon steel test samples (discs) previously polished and degreased (no primer was used). Dry film thicknesses in the range 20–25 μm were obtained. The discs were placed and cemented in special glass sample holders. Tests were carried out by immersion (after a curing period of 14 days) in a solution of naturally aerated 3% NaCl. The test methods included electrochemical impedance measurements, stepwise polarisation measurements and visual assessment.

The electrochemical impedance measurements were conducted at the open circuit potential in the 0.1 Hz–100 kHz frequency range. The time dependence of the coating capacitance and of the pore resistance were determined for immersion periods of up to 60 days; simultaneously visual observations were made of the coating degradation (appearance of corroded and delaminated areas) and correlated with coating capacitance and pore resistance values.

The volume fraction of water taken up in the coatings (Φ_t) was calculated following the Brasher and Kingsbury formula [3]:

$$\Phi_t = (\log C_t / C_0) / \log 80 \quad (1)$$

where C_t is the capacitance of the protective film at time t , C_0 is the capacitance of the protective film at time $t = 0$ and 80 is the relative permittivity of water.

The total area of conductive pathways (A_t) which develop in the protective film (1 cm^2 area) between the substrate and the bulk electrolyte was calculated using Walter's formula [6]:

$$A_t = l / (k \cdot R) \quad (2)$$

where l is the average length of the pathways ($\approx$ protective film thickness), k is the conductivity of the pathways ($\approx$ the conductivity of the bulk solution) and R is the resistance of the protective film.

Anodic polarisation curves were recorded for bare and coated electrodes by stepwise polarisation (50 mV / 5 min step). The efficiency of the protective films [7], E , (the percentage decrease of dissolution current density) and the porosity of the protective films [8], P (connected with the conductive pathways) were determined by comparing the dissolution current density of the coated substrate (i_c) with the dissolution current density of the bare substrate (i_b):

$$E = [(i_b - i_c) / i_c] \cdot 100\% \quad (3)$$

$$P = (i_c / i_b) \cdot 100\% \quad (4)$$

3. Results and Discussions

3.1. Evaluation of the Trends of the Coating Capacitance and Pore Resistance

Touhsaent and Leidheiser [4] proposed a model for electrolyte penetration into paint

films. At first, the electrolyte solution enters into coating defects (fissures and capillaries). This is termed the capillary phase and is considered to be a separate phase from the polymer coating. The resistance of this aqueous phase is that of the electrolyte solution. Secondly, the polymer is partially penetrated by the electrolyte solution and this phase is denoted as the 'into polymer solution' phase. Afterwards, if the paint film detaches from the substrate due to adhesion loss then electrolyte enters under the film. All these changes in the paint film are reflected in coating capacitance and pore resistance values; penetration of the electrolyte solution is responsible for an increase in coating capacitance and a decrease in pore resistance.

Figure 1 presents Nyquist impedance plots for alkyd painted carbon steel after some immersion periods in NaCl solution.

The electrochemical impedance study used the equivalent circuit shown in Fig. 2. The equivalent circuit contains: the solution resistance (R_{Ω}), the coating capacitance (C_c), the pore resistance (R_p), the charge transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}).

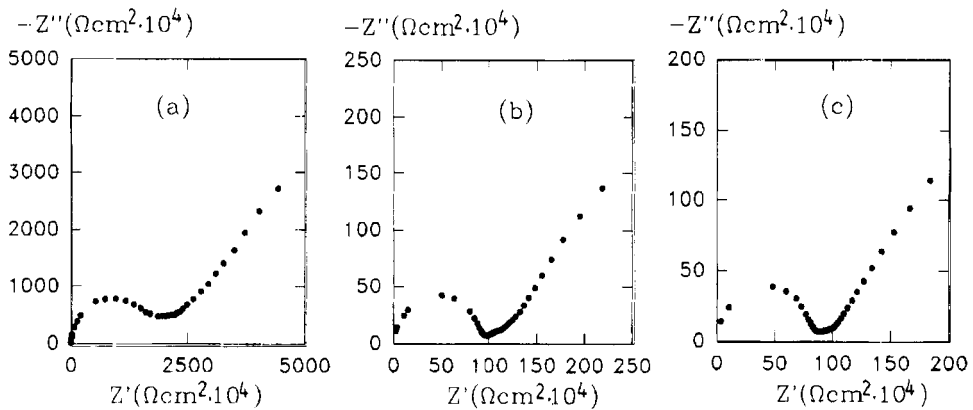


Fig. 1 Nyquist impedance plots for alkyd painted carbon steel after: (a) 24 h; (b) 100 h; and (c) 200 h immersion in 3% NaCl solution.

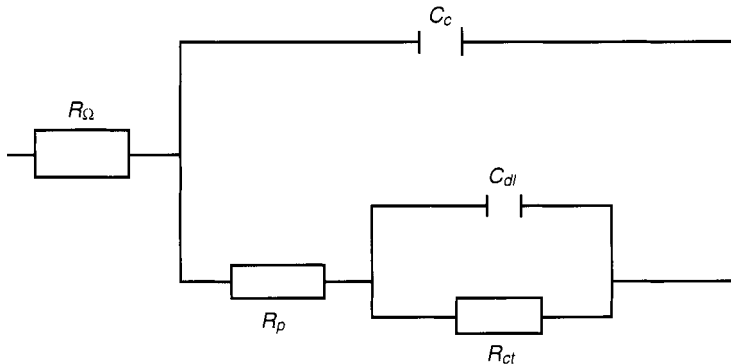


Fig. 2 Equivalent electrical circuit of paint coating on metal.

The developments of coating capacitance and pore resistance as a function of immersion time in 3% NaCl solution for the tested painted samples are presented in Figs 3–6.

The range of values and the variation of the coating capacitance and pore resistance over time differed for the tested organic films as follows.

3.1.1. Alkyd paint film

As can be seen from Fig. 3(a) the coating capacitance shows a slow increase during the first three days of immersion, followed by an insignificant linear increase and tending towards a constant level. The pore resistance decreases in a similar manner. (Fig. 3b).

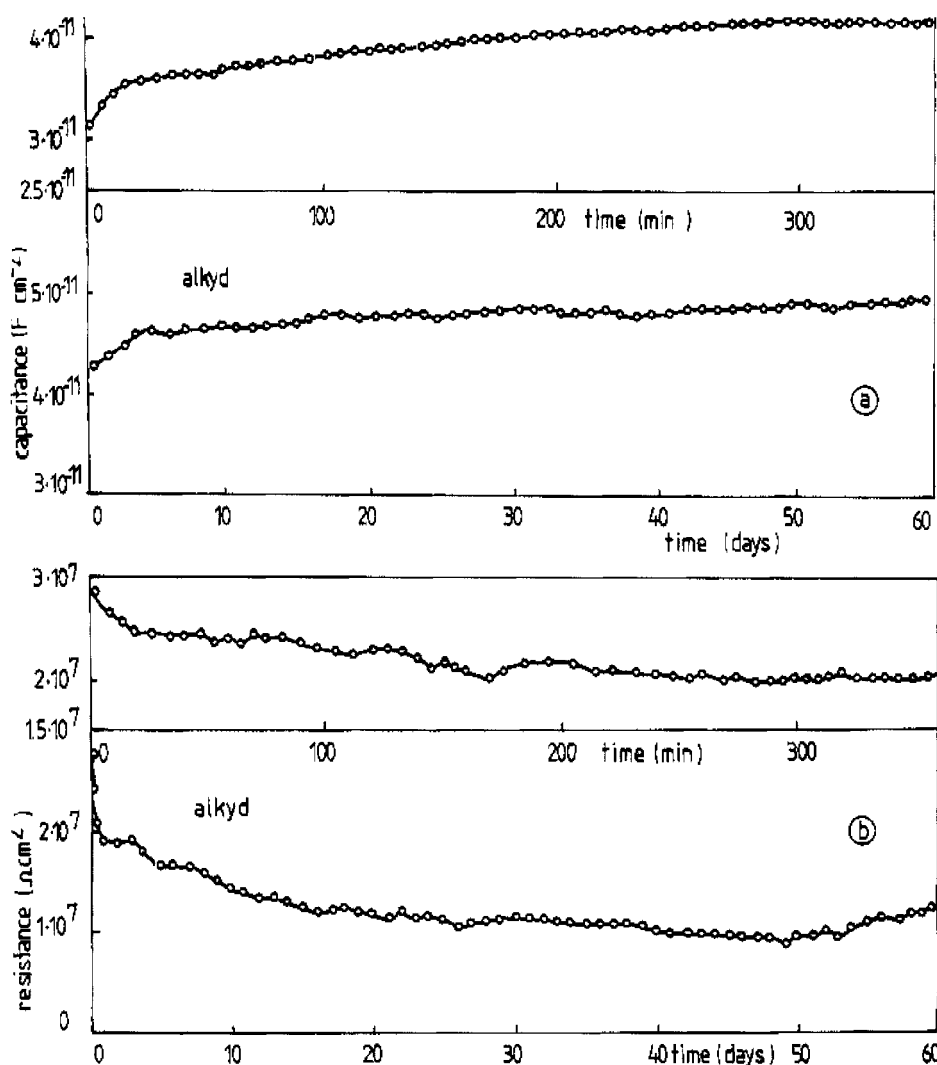


Fig. 3 Time dependence of coating capacitance (a) and pore resistance (b) for alkyd painted carbon steel in 3% NaCl solution.

For all exposure periods in the test solution, the capacitance and resistance values did not change their order of magnitude.

3.1.2. Epoxy paint film

The variations of coating capacitance and pore resistance for epoxy painted samples are plotted in Fig. 4.

As can be seen in this Figure, large changes take place during the first days immersion with the coating capacitance values increasing by one order of magnitude

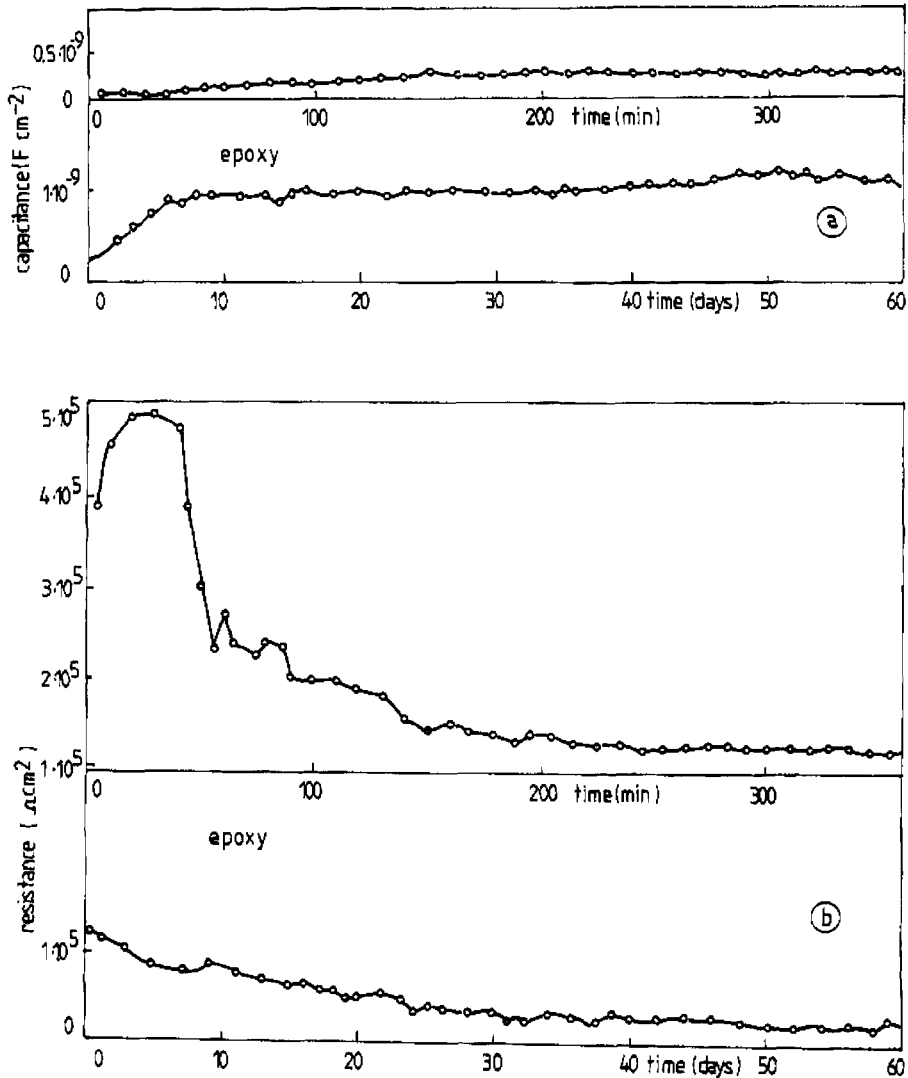


Fig. 4 Time dependence of coating capacitance (a) and pore resistance (b) for epoxy painted carbon steel in 3% NaCl solution.

and the pore resistance values decreasing similarly. These changes are followed by slower modifications, which with time tend to a constant level.

3.1.3. Nitro paint film

Figure 5 presents the time dependence of the coating capacitance and pore resistance for nitro painted carbon steel, and shows a similar development and values of coating capacitance and pore resistance to that of the epoxy film.

3.1.4. Acryl paint film

The plots for the acryl painted samples are illustrated in Fig. 6. For the acryl film, the

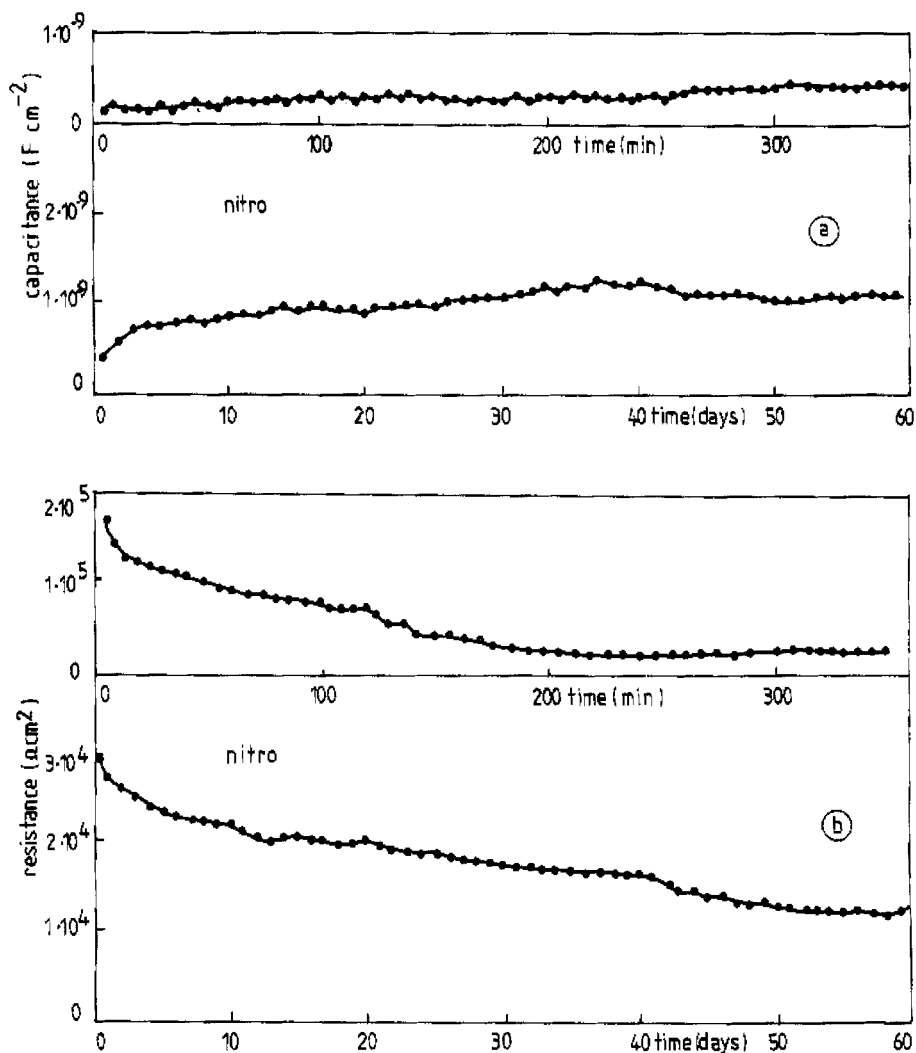


Fig. 5 Time dependence of coating capacitance (a) and pore resistance (b) for nitro painted carbon steel in 3% NaCl solution.

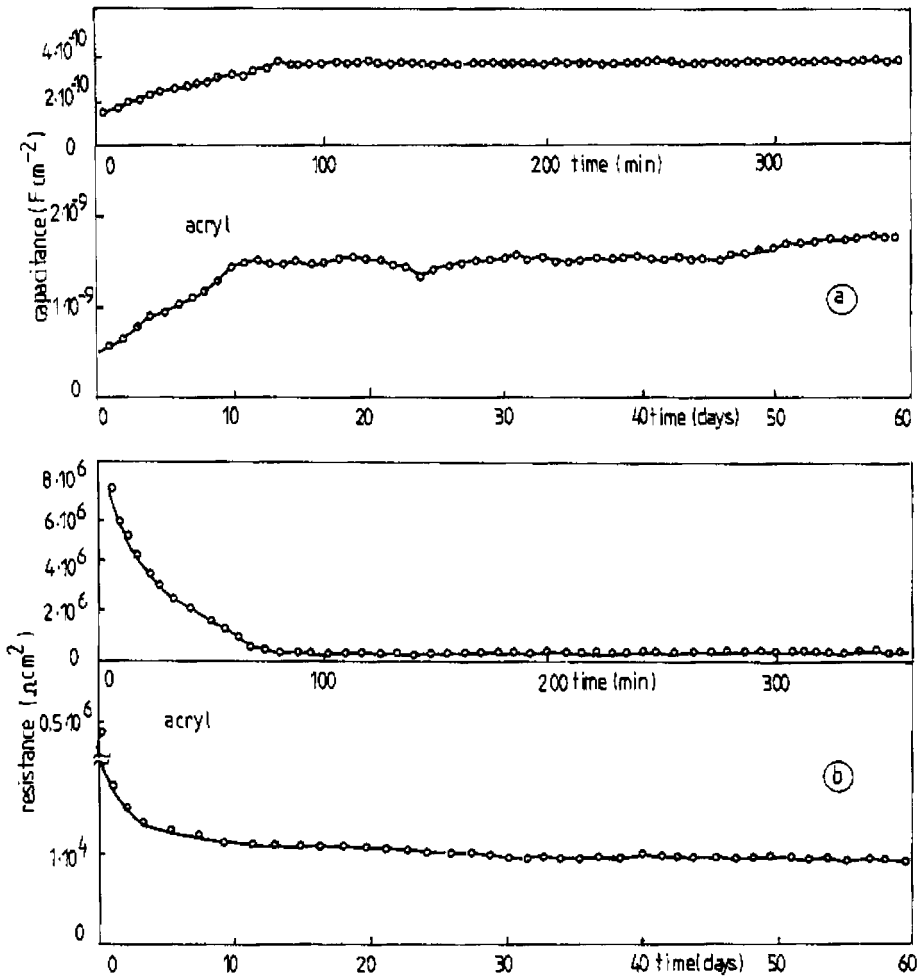


Fig. 6 Time dependence of coating capacitance (a) and pore resistance (b) for acryl painted carbon steel in 3% NaCl solution.

evolution of coating capacitance and pore resistance over time showed sharp modifications during the first days immersion.

These were followed by slower changes leading finally to constant values.

The values of the coating capacitance and pore resistance vary with the paint type. The lowest capacitance ($\approx 4.5 \times 10^{-11}$ F cm⁻²) and the highest resistance ($\approx 10^7$ Ω cm²) were shown by the alkyd film for all immersion periods in the test solution; the other paint films had capacitance values of $1\text{--}1.5 \times 10^{-9}$ F cm⁻² and resistance values about 10^4 Ω cm².

The variation of the coating capacitance differs (depending on the film type) only in the first days of immersion. Thus, there was a slow increase for the alkyd film, a large increase for the epoxy and nitro films and a sharp increase for the acryl film.

In the proposed model, three time ranges may be distinguished as in Figs 3–6. The first shows an increase in coating capacitance and a decrease in pore resistance

and corresponds to the entry of NaCl solution into capillaries of the paint films and lasts three to ten days depending on the paint type. The second range with the slow linear changes, more easily seen in some cases than in others, may be attributed to solution diffusion into the polymer. The third range, where the values of the coating capacitance and pore resistance are constant over time, shows that the paint films are now saturated with solution. No subsequent changes in coating capacitance and in pore resistance appear and this emphasises that the paint films do not detach from the substrate.

The calculated water uptake using eqn (1) shows a low water permeability of the alkyd paint and a high water uptake for the other three paints (Fig. 7). The curve for the alkyd film indicates a low water uptake into capillaries (few defects) and no water into the polymer with time. The other films show a high uptake of water into capillaries (more defects) during the first days of immersion and after that a slow increase of water uptake which corresponds to diffusion into the polymer.

The total area of the conductive pathways calculated using eqn (2) indicates the lowest values for the alkyd paint (Fig. 8). This shows that the corrosion process of the metallic substrate under the alkyd film progresses with difficulty and is easier under the other paint films.

The results of these various measurements show that evaluation of trends of coating capacitance and pore resistance will provide information about the performance of coatings.

3.2. Evaluation of the Polarisation Curves

The paint films (without primer coat) were applied by brush and therefore contained pores so that it was possible to obtain polarisation curves after two hours immersion.

Figure 9 illustrates the anodic polarisation curves for bare and coated carbon steel recorded after two hours immersion in the test solution.

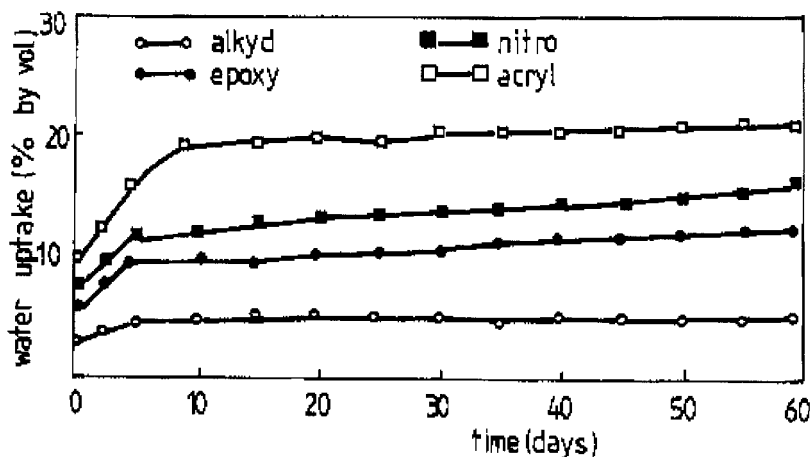


Fig. 7 Water uptake of paint on carbon steel in 3% NaCl solution vs time.

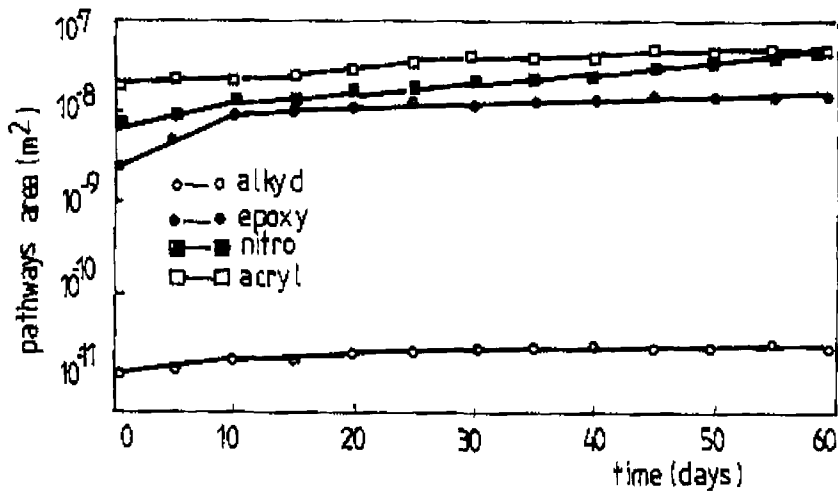


Fig. 8 Total area of conductive pathways in the protective films vs time in 3% NaCl.

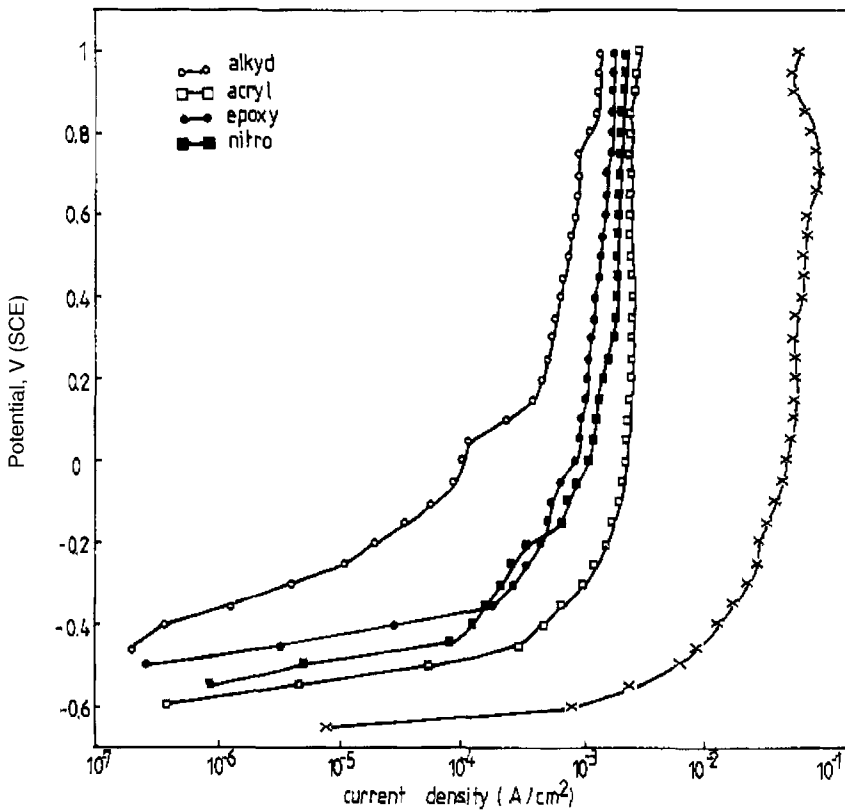


Fig. 9 Anodic polarisation curves of bare and coated carbon steel in 3% NaCl solution, after 2 h immersion.

The polarisation curves offer supplementary information about the corrosion behaviour of the tested painted samples. Thus, they show a decrease of dissolution current density of painted steel in comparison with that of bare steel and a shift of corrosion potentials in the noble direction; these changes become more prominent with decrease in paint capacitance, water uptake and area of the conductive pathways and with increase of paint resistance (Table 1 and 2).

The results show that the polarisation curves offer information about the corrosion behaviour of painted carbon steel only at the time at which they are recorded. The data that are obtained depend on the exposure time in the aggressive solution before the polarisation and consequently on the degradation state of the paint film. Therefore the polarisation curves cannot estimate the paint performances over time.

The efficiency and porosity of the protective films (as calculated from the decrease in dissolution current density) change with the increase in exposure time in the test solution before the polarisation. As can be seen in Figs. 10 and 11 only the alkyd paint shows insignificant modifications; this paint type provides a good barrier to the NaCl solution.

The results of polarisation curves are in good agreement with the capacitance and resistance measurements.

3.3. Visual Assessment

The visual assessments confirm the results of the electrochemical measurements, with good performance of the alkyd film (the samples did not show corroded or delaminated areas after the total exposure period) and a decrease of protective properties for the other tested paints (one or two rust spots appearing on the sample surface by the end of the exposure period).

Table 1. *The characteristics of tested paint films after 2 h immersion*

Characteristic	Paint film				Bare steel
	Alkyd	Epoxy	Nitro	Acryl	
Corrosion potential (mV/SCE)	-450	-530	-560	-620	-720
Maximum dissolution current density (Acm^{-2})	1.4×10^{-4}	0.5×10^{-3}	1.5×10^{-3}	3×10^{-3}	7×10^{-2}
Capacitance (Fcm^{-2})	3.9×10^{-11}	2.5×10^{-10}	3.5×10^{-10}	3.8×10^{-10}	0.3×10^{-6}
Water uptake (%)	2.5	6	8.2	9	–
Resistance (Ωcm^2)	2.2×10^7	1.8×10^5	0.6×10^5	1.5×10^5	27
Area of pathways (m^2)	0.8×10^{-11}	2×10^{-9}	8×10^{-9}	2×10^{-8}	–

Table 2. The characteristics of tested paint films after 60 days immersion

Characteristic	Paint film				Bare steel
	Alkyd	Epoxy	Nitro	Acryl	
Corrosion potential (mV/SCE)	-475	-550	-590	-650	-700
Maximum dissolution current density (Acm^{-2})	3.3×10^{-4}	1×10^{-2}	1.3×10^{-2}	2.2×10^{-2}	6.5×10^{-2}
Capacitance (Fcm^{-2})	4.8×10^{-11}	1×10^{-9}	1.2×10^{-9}	1.8×10^{-9}	1.2×10^{-6}
Water uptake (%)	5	12	16.5	19	–
Resistance ($\Omega \text{ cm}^2$)	1.2×10^7	2.5×10^4	1.2×10^4	1×10^4	38
Area of pathways (m^2)	1×10^{-11}	1×10^{-8}	4.1×10^{-8}	4×10^{-8}	–

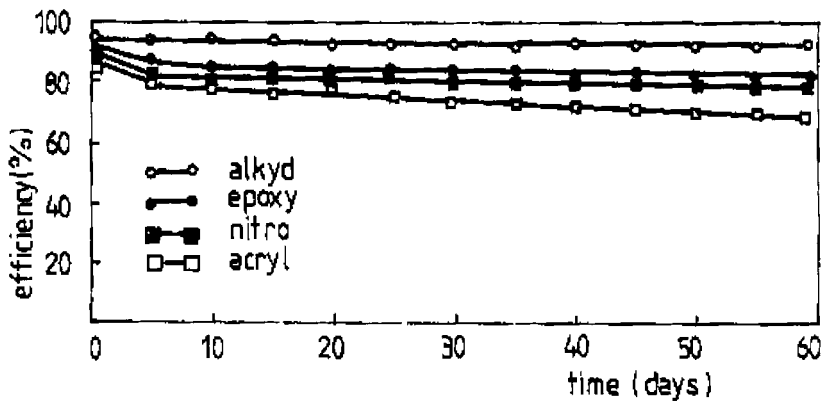


Fig. 10 Efficiency of paint films vs immersion time in 3% NaCl solution.

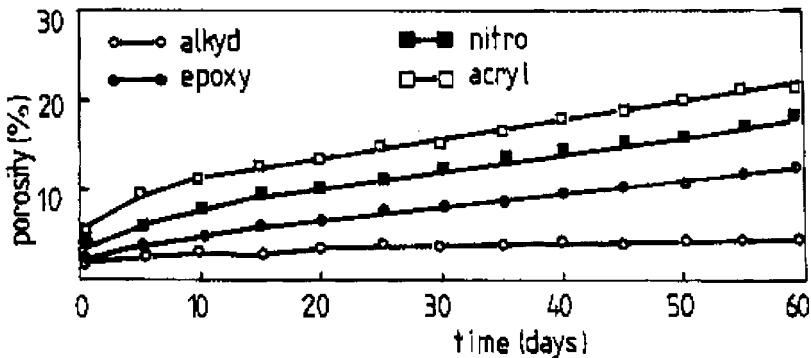


Fig. 11 Porosity of paint films vs immersion time in 3% NaCl solution.

4. Conclusions

The NaCl solution penetration in four thin (20–25 μm) paint films (acryl, alkyd, epoxy, nitro type) on a carbon steel substrate has been investigated by using electrochemical impedance and stepwise polarisation measurements. It was established that the permeation of NaCl solution into paint films follows the model proposed by Touhsaent and Leidheiser [4].

The water uptake shows a low permeability of the alkyd film and a high permeability of the other film types.

The total area of conductive pathways had minimum values for the alkyd paint, which did not change over time; these values point to a reduced movement of ions through the film and consequently good protective properties.

The evolution over the first 14 exposure days and the orders of magnitude of the coating capacitance and pore resistance of paint films can be used as a relative measure of their protective performances.

The values of efficiency and porosity of the alkyd film are consistent with the good protective performance and the polarisation curves and correlate well with the capacitance and resistance measurements and the visual assessment.

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Electrochemical Noise Measurement in the Study of Surface Coatings

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ABSTRACT

The Electrochemical Noise Method (ENM) was used to investigate the protection afforded by coatings to steel and aluminium. This method uses the tiny voltage and current fluctuations emitted naturally by materials in a conducting environment. From these the parameter Resistance Noise (R_n) is calculated. R_n has been found to relate to general corrosion rates of metal. Previous work on coatings has shown R_n to be approximately equivalent to the low frequency impedance of the coating/metal system. ENM affords a non-intrusive alternative to the more standard d.c. resistance method to assess coating performance. Results for two waterborne coatings on steel and aluminium are presented. The electrochemical noise values were similar to the d.c. resistance values for the higher resistance coating, with differences being attributable to the lower sensitivity of the noise equipment at high resistances. The less protective film gave higher R_n than d.c. values; the former related better to observed protection.

Application of the noise method for evaluating detached coatings was investigated as it allows variation of temperature and external solution to be studied which are established methods for accelerating coating degradation. Results show ENM to be a promising method for continuous monitoring, assisting formulation (screening paints) in the laboratory, for quality control purposes and investigating degradation mechanisms.

1. Introduction

Producers and users of anti-corrosive coatings need to assess quickly and accurately the degree of protection being afforded to the underlying metal. The normal approach is visual assessment using standards such as ASTM D610 (corrosion) and D714 (blistering) after exposure to accelerated tests. In some investigations these scales are extended to include an assessment of the corrosion at a scratch. Sometimes the paint is stripped from the substrate before assessment and occasionally weight loss is measured. A more sophisticated method which is nonetheless fairly similar is to use infra-red radiation as described by McKnight and Martin [1].

Corrosion is essentially an electrochemical process. Hence, where a conducting environment is naturally present or can be introduced outside the coating then an electrochemical measurement of some kind should give useful information. With paint films work is made more difficult because of the high electrical resistance of the coating so all measuring equipment has to have very high impedance ($>1 \times 10^{10} \Omega$). Also, any attempt to measure corrosion rate directly through the film (e.g. using the Linear Polarisation Resistance method, LPR) is likely to fail because one of the

important criteria for application of the LPR method is that the ionic resistance should be low. In most cases with paints it is very high and thus a direct measurement of the corrosion rate under the film will not normally be possible (the use of segmented electrodes may get round this to some extent).

Measuring a simple through-film d.c. resistance value has proved most useful and for traditional paint systems it has been shown to be, at least qualitatively, a good guide to the protection afforded by the coating system to the substrate. In 1948, Bacon, Smith and Rugg [2] measured the *in situ* d.c. resistance of over 300 paint systems in sea water and established the following criteria. A d.c. resistance of $> 1 \times 10^8 \Omega \text{ cm}^{-2}$ indicated good protection, a resistance lower than $10^6 \Omega \text{ cm}^{-2}$ resulted in poor protection and a resistance of between 1×10^6 – $1 \times 10^8 \Omega \text{ cm}^{-2}$ meant the degree of protection was borderline. It was concluded that this method, for all but the very lowest resistance paints, is measuring the resistance of the paint coating to the movement of ions. It has been postulated that one of the main ways in which a coating reduces or stops corrosion is by providing an ionic barrier between anodes and cathodes. Mayne *et al.* [3–5] investigated quite thoroughly the ionic resistance characteristics of paint and varnish films. The work showed that for varnish films the correlation between corrosion and ionic resistance was excellent [4]. Thus it is generally accepted that in the case of the solvent-containing systems the ionic barrier mechanism is paramount.

However, in recent times it has been found that the d.c. method, although still an excellent way to obtain maximum information from a relatively simple measurement, does have some limitations. Thus, it has been observed that some paints, particularly modern waterborne primers, may prevent corrosion while having *in situ* through-film resistances below $1 \times 10^8 \Omega \text{ cm}^{-2}$. This could be because the main way they protect is not through their ability to act as a barrier to external ions. With any paint there is also the situation where the through-film d.c. resistance is high but the paint has lost adhesion and corrosion may be occurring perhaps because of salts present on the surface or aggressive ions leached out by water and arriving at the paint metal interface.

What is required then is an electrochemical method which will indicate what is happening at this interface. To investigate this, attempts have been made to apply more sophisticated electrochemical methods such as a.c. impedance and the d.c. transient method. Two recent papers using the former method are those by Thompson [6] in the UK and Tait [7] in the USA. However, although in theory these methods should allow separation of the paint part of the resistance from the interface part, in practice this has proved possible only in a handful of cases.

All the above methods have a major disadvantage. They apply an external voltage which can disturb the system under test. Hence for continuous monitoring they are all unsuitable, i.e. any monitoring has to be intermittent.

Recently [8,9], an electrochemical method has come to the fore which shows great promise for investigating anti-corrosive coatings. This is the electrochemical noise method. No external source of current or voltage is needed. Hence monitoring can be continuous. The most useful parameter to obtain is the Resistance Noise (R_n) derived as the standard deviation of the voltage noise divided by the standard deviation of the current noise. However, there is also the possibility of obtaining a low frequency impedance spectrum from noise data. One difficulty with a.c.

impedance is that because corrosion is a d.c. process the most relevant information is that gathered at the low end of the frequency spectrum (e.g. below 1 Hz). However it is the gathering of the information that takes a long time and most disturbs the system. In a noise measurement one can apply MEM (Maximum Entropy Method) or FFT (Fast Fourier Transform) to obtain a low frequency impedance spectrum which will cover the range from the speed of frequency of measurement, e.g. two a second (0.5 Hz) up to the reciprocal of the time taken to get a measurement — if it takes 16 min (1000 s), this would be equivalent to 1×10^{-3} Hz. Results were reported for bare metal corrosion recently by workers from UMIST [10].

There are a number of applications for the electrochemical noise method in the investigation of coatings on metal substrates. In this paper several of these are introduced but significant results are only given for two situations. One is the quite commonly investigated situation of an intact organic coating on a metal substrate. Recent work at North Dakota State University [11–14] used the noise method to study mainly solvent borne systems. Hence, for this investigation it was decided to look at waterborne coatings. The second is the investigation of detached coatings. Some comments on application of the noise method in other situations (e.g. to metallic coatings and to scratched coatings) are included.

2. Experimental

Substrates were aluminium and steel panels (Q panelsTM). These were used in the as-received state but were degreased before application of the coating. The coatings were two waterborne primers supplied by Zeneca: a black vinylidene (Haloflex) and a grey acrylic (Neocryl). They were applied by spreader bar to give a total thickness of 150 μm (3 Coats – Haloflex) and 90 μm (2 coats – Neocryl). Exposure was to diluted Harrison's solution (0.35% ammonium sulphate, 0.05% NaCl) in PVC cells attached by silicone glue to the substrate so that an area of 11.8 cm^2 was exposed. Both electrochemical noise and d.c. resistance were measured as a function of time at room temperature (18–22°C).

Electrochemical Noise was measured using equipment supplied by ACM, Cumbria, UK. The essential component of this is a zero-resistance ammeter (ZRA) data logger. The set-up is shown in Fig. 1 and is similar to the original method used by Skerry [8]. A pair of nominally identical panels is required. Every 2 s, for a period of 512 s, the current between them is monitored and at the same time the voltage of the pair is measured with respect to the reference electrode. A typical noise plot is shown in Fig. 2. From the standard deviations of the resultant 256 data points, the voltage noise and current noise are calculated and by dividing the former by the latter, the resistance noise R_n is derived. A total of six cells (three pairs) were examined for each system. To make noise measurements on detached pieces of coating a modification of the method was employed as shown in Fig. 3.

The d.c. resistance was measured using a Keithley Electrometer which has a high input impedance ($1 \times 10^{15} \Omega$). Note that the *in situ* d.c. resistance of individual panels can be obtained. Also by mounting a piece of coating in a glass cell and using two reference electrodes, the same instrument can be used to measure the d.c. resistance of detached film.

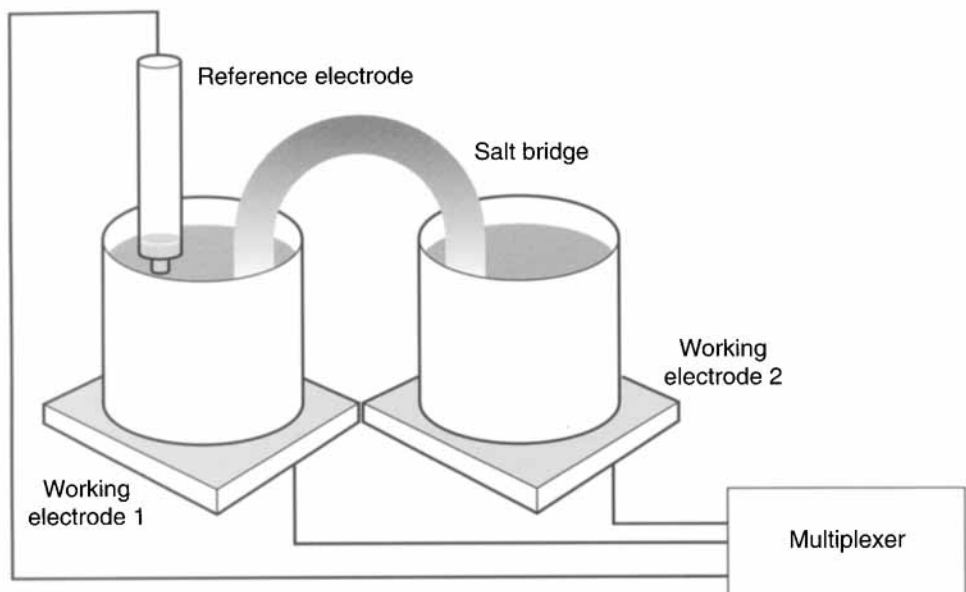


Fig. 1 Set-up for noise measurements (bridge method).

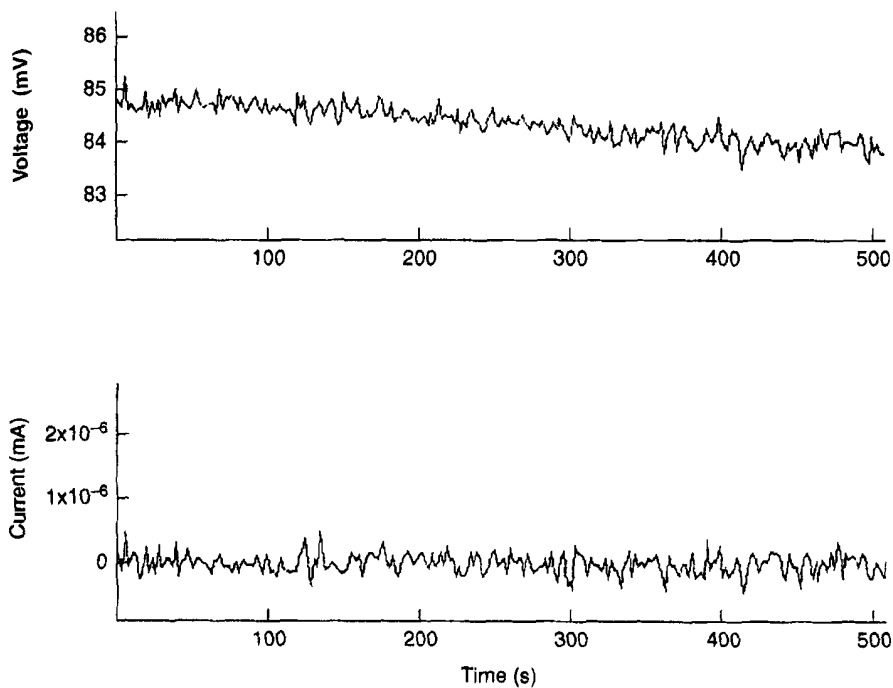


Fig. 2 A typical noise plot.

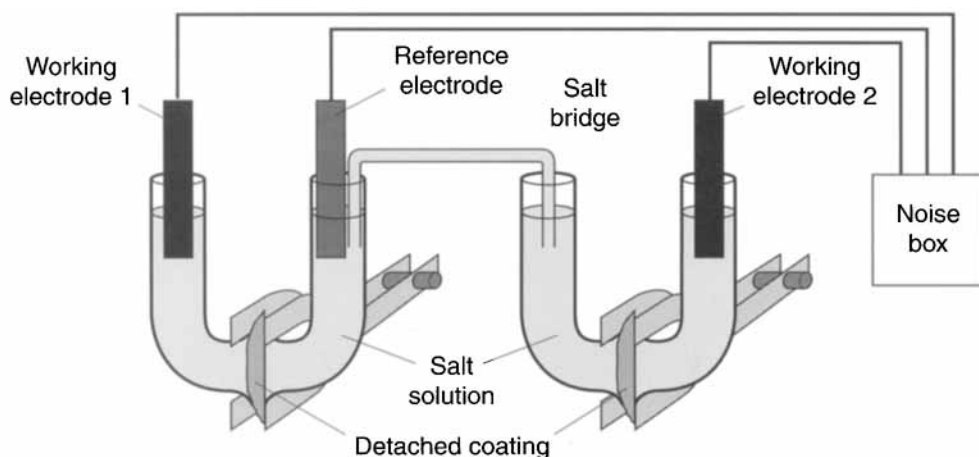


Fig. 3 Set-up for noise measurement of detached coating.

3. Results and Discussion

3.1. Attached Coatings

Although the ENM method is suitable for continuous monitoring as reported in work by the author in the USA [11], lack of equipment availability meant that in these experiments electrochemical noise was only measured after one day, one week, one month and two months. These measurements were sufficient to give a good indication of how the coating was performing and allow comparison with the d.c. resistance. The two systems behaved quite differently but quite reproducibly.

A plot of d.c. resistance as a function of time for all six cells of the Neocryl is shown in Fig. 4. There is very close grouping of the results particularly in the early stages. High initial d.c. resistance ($> 1 \times 10^8 \Omega$) was maintained in five/six samples throughout the six weeks and no corrosion was observed. The sixth sample had a lower resistance ($1 \times 10^7 \Omega$) and a small rust spot was eventually observed. The R_{ii} value was also high but not as high as the d.c. resistance.

The Haloflex at $150 \mu\text{m}$ had a much lower initial d.c. resistance of about $1 \times 10^6 \Omega\text{cm}^{-2}$ which fell with time to below 1×10^5 . Reproducibility among the six samples was excellent as shown in Fig. 5. Not much corrosion was seen even after six weeks but there was blistering although the blisters were small. It appears that there is an inhibitor in this primer (probably phosphate) which was quite effective in stopping rusting although it was not effective in preventing loss of adhesion. The latter problem was 'picked up' by the low d.c. resistance. The resistance noise value was fairly low but not as low as the d.c. resistance.

Results showing the difference between the aluminium and steel substrate after 24, 190 and 512 h are shown in Figs 6 and 7 for d.c. resistance and resistance noise respectively. Another paper [15] has looked specifically at the effect of the substrate on the electrochemical response. In that paper these results are compared with those

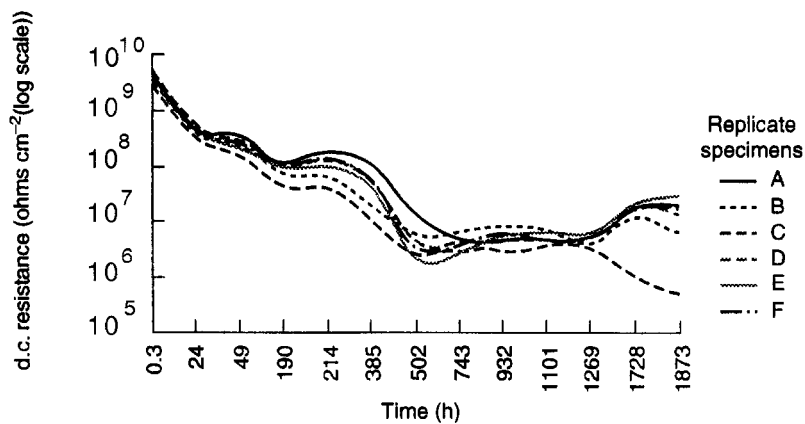


Fig. 4 Performance comparison of large area Neocryl cells.

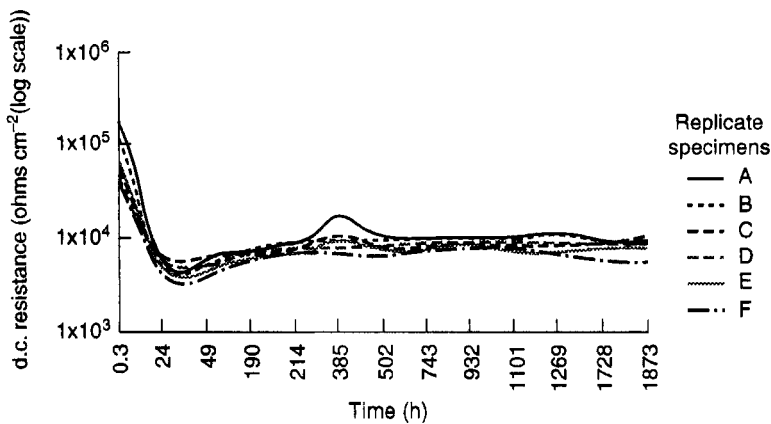


Fig. 5 Performance comparison of large area Haloflex cells.

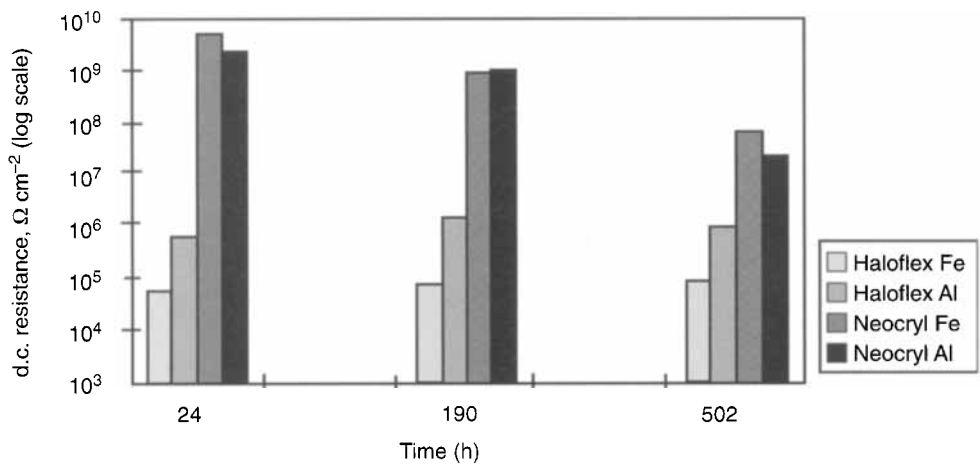


Fig. 6 Effect of time on R_{dc} with Fe and Al substrates.

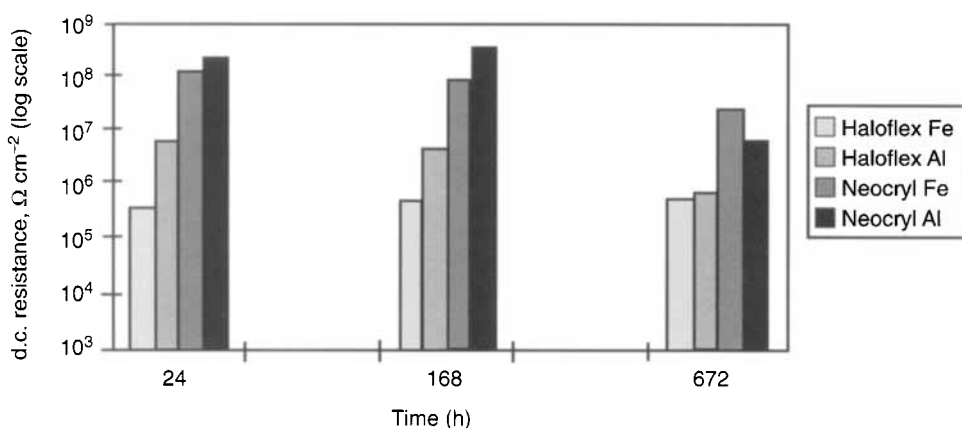


Fig. 7 Effect of time on R_n with Fe and Al substrates.

for several solvent based coatings on steel and aluminium and electrocoat applied to zinc and phosphated zinc, iron and phosphated iron. Here we will just note that there is very little difference between steel and aluminium when they were coated with Neocryl but considerably more difference when they were coated with the Haloflex (which had an overall lower resistance). This was explained by the relative corrodibility of the two substrates in relation to the protection afforded by the two paints, i.e. both the steel and the aluminium substrate were equally well protected by the Neocryl but the Haloflex was unable to protect the steel as effectively as the aluminium and hence a lower resistance on the steel was observed.

Some results comparing the electrochemical noise R_n value and the d.c. resistance value for both the Neocryl (higher set of values) and Haloflex (lower set of values) are shown in Fig. 8. These values were obtained after 4 weeks on test for triplicate samples. The d.c. values are straight averages of the two samples (there is some

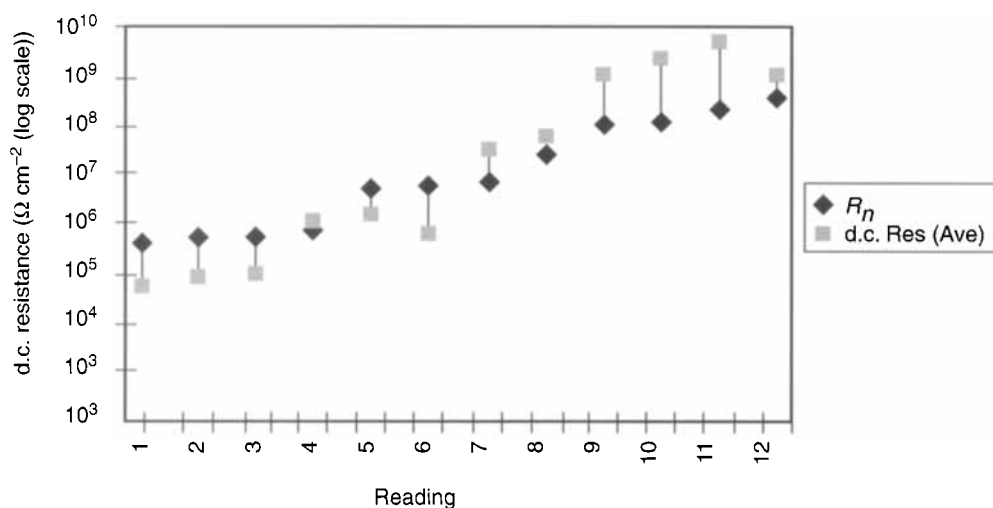


Fig. 8 Comparison between R_{dc} and R_n (points plotted in ascending value of R_n).

evidence [13] that where the values are very different it is better to take the geometric mean) but in this case the values were very close so a simple arithmetic mean was justified. This graph shows that there is a correlation between R_n measurement and the average d.c. resistance of any individual sample. However, the range of the d.c. resistance values is greater than the range of electrochemical noise R_n values. The explanation for this in the case of the higher set of results (Neocryl) is probably an equipment limitation. It has previously been observed that the electrochemical noise method is unable to measure accurately high resistance values and this is attributed to its difficulty in measuring very small current signals (limit about 1×10^{-10} A). What is more interesting is the fact that for the lower resistance system (Haloflex) the noise R_n value is considerably higher than the d.c. value. This has not been seen before: in fact in previous work when corrosion is occurring it was observed that R_n values were close to d.c. resistance values. The higher resistance noise value observed in this case appears to correlate with the observed lack of corrosion in the case of the Haloflex paint. The low d.c. resistance value is consistent with some adhesion failure (blistering was observed).

3.2. Detached Coatings

Direct Current resistance measurements have often been made on detached solvent-borne coatings [3–5] and that work showed the measurements to be a good guide to the subsequent protection afforded when the coating is applied to a metal substrate. Some detached pieces of the waterborne coatings have been examined using both electrochemical noise method and the d.c. resistance method. The set-up for noise measurements is shown in Fig. 3. Some results after 0.5 and 2 h (Haloflex) and 0.5 and 168 h Neocryl are shown in Fig. 9. There is excellent agreement between the noise value and the d.c. resistance value. Note that the area exposed in these experiments was 2.5 cm^2 and the d.c. value was (as in the attached experiments) obtained as the arithmetic mean of the two individual pieces of coating both of which had similar resistance values.

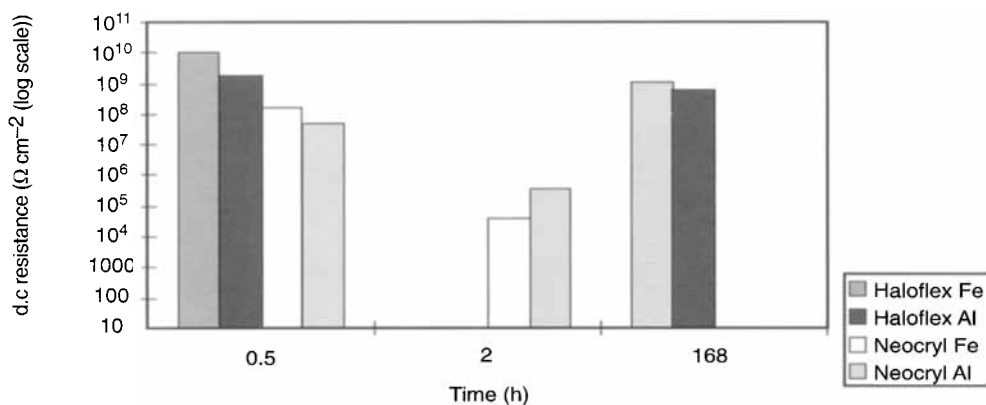


Fig. 9 Comparison of DC and R_n values for detached coatings.

3.3. Comparison between Attached and Detached d.c. Resistances

The way the d.c. resistance falls with time for both attached (to steel) and detached coatings is shown in Fig. 10. There is a close parallel between the two. This indicates that, as with solvent-borne systems, measuring the resistance of detached films for these types of waterborne coatings is a useful method of predicting their behaviour on a steel substrate. It is appreciated that the nature of the substrate will have some influence e.g. on the time it takes to reach an equilibrium value or the rate of fall of the resistance.

Measurements on detached films particularly using the noise set-up shown in Fig. 3 also has the potential ability to assist with mechanistic studies. Apart from varying the paint film (thickness, type of binder, pigment loading degree of cure etc.) one can also vary:

- (i) the solution — e.g. simulate the solution under the film on one side and the external solution on the other side;
- (ii) the size of the electrode — e.g. make the two working electrodes very small to simulate the effect of a very small active area; and
- (iii) the type of electrode — e.g. type of metal, passivating treatment before the paint is applied, the surface finish etc.

Note that for this approach to give useful information it has to be assumed that there has been minimal chemical interaction between the paint and the binder during application and curing of the paint. There will be some physical interaction (adhesion by mainly secondary bonding) but for all paints applied at room temperature this assumption is probably justified. For paint coatings which are stoved during application, particularly those at high (200°C) temperatures chemical interaction may need to be taken into consideration, e.g. by pre-treating the metal and allowing it to react with a small quantity of paint at the appropriate temperature.

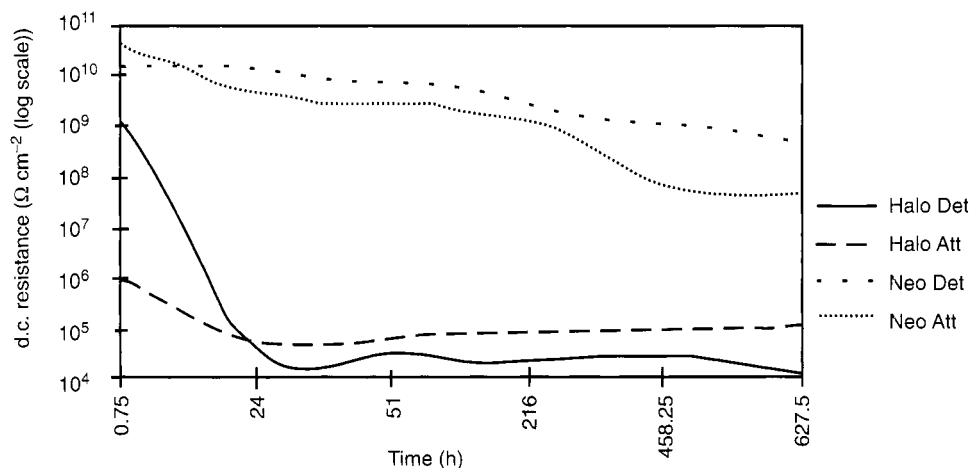


Fig. 10 Comparison of detached and attached film.

4. Other applications of the Noise method

Several other applications of electrochemical noise method have also been investigated in a preliminary way.

4.1. Scratched Organic Coatings

The performance of a coating at a scratch is very important. Electrochemical measurements have been applied much less frequently to this situation. Some quite recent work [15] with electrocoat on a variety of substrates showed that the d.c. resistance of the scratch did relate quite well to the protection afforded although in that case the resistance was much lower (between 1×10^3 and $1 \times 10^5 \Omega\text{cm}^{-2}$). Some preliminary work is in progress using the electrochemical noise method to investigate the effect on a scratch of an organic waterborne coating. These results show that the noise value is often considerably higher than the d.c. resistance in the early stages of exposure but after a time they settle to the same level. This work is on-going and will be reported subsequently.

4.2. Metallic Coatings

In the past the standard d.c. linear polarisation resistance (LPR) method has been used to obtain the corrosion rate of these types of coating material. Work elsewhere [16] has shown that R_n often correlates quite well with R_p . The non-intrusive nature of the electrochemical noise method should make it very useful for this application. More interesting is to investigate whether, as occurs with scratched organic coatings, measurement of R_n (or d.c. resistance) can be used to investigate a break in the metallic coating. When attempts were made to investigate scratched zinc coatings the response was heavily dominated by the relatively large area of active zinc metal. To take this work further, ways of isolating the scratch area either by physical or chemical means need to be found. These are currently being developed.

5. Conclusion

The applicability and usefulness of the electrochemical noise method has been demonstrated for the situation of intact waterborne primers on steel and aluminium. Good correlation has been obtained between the d.c. resistance and R_n values. It appears that with the Haloflex paint the higher R_n value reflects a low level of corrosion whereas the lower d.c. resistance value indicates some degree of adhesion loss. The electrochemical noise method has also been extended to study detached coatings and preliminary results again show its applicability to this situation. The R_n relates to the more established d.c. resistance value. This work together with previous work [8–14] has established beyond reasonable doubt the usefulness of the R_n value for monitoring protection afforded by anti-corrosive coatings. With regard to future work, the time has now come when spectral analysis of noise data can be expected to yield useful information. This technique has great promise for mechanism investigation particularly what is occurring at the metal-polymer interface by

comparing noise spectra obtained on the substrate with those obtained off the substrate. The method also looks promising for investigating scratched organic coatings and intact and scratched metallic coatings.

6. Acknowledgements

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Comparison of the Results of Different Adhesion Tests Carried Out on Hot-Dip Galvanised Steel

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ABSTRACT

Investigations on the adhesion of a two-component-epoxy on a zinc surface (usual hot-dipped galvanised) are described. The pretreatment of the zinc surface was varied, to determine its influence on adhesion. Similarly, the measurement of adhesion was carried out with wet and dry coatings to assess the influence of water content in the paint film on this property.

The results of different kinds of adhesion tests were compared to find the correlation between these methods.

1. Introduction

Adhesion is a very important characteristic of a paint system. It is well-known that paint systems with poor adhesion after weathering will result in poor performance.

Adhesion is based on the chemical and physical forces between the top side of the zinc layer and the underside of the paint film which covers the zinc surface.

To understand more about the forces between these two phases — the zinc substrate and the paint film — these forces should be measured. Many adhesion tests exist to solve this problem, but all these destroy the interfacial zone. Therefore, the result obtained is mainly influenced by the resistance to mechanical damage. Furthermore, the results are also determined by paint properties such as elasticity and hardness.

Different adhesion tests employ different principles of measuring. Thus, it is inevitable that different results will be obtained when different adhesion tests are used. We have therefore applied different adhesion tests, on a ranking basis, to come to a reliable decision as to which kind of pretreatment provides the best adhesion between the top side of the zinc layer and the underside of the paint film.

Adhesion forces depend on both the behaviour of the underside of the paint film and the properties of the topside of the zinc layer. Thus, the state of the zinc surface before applying the organic coating is very important in affecting the amount of adhesion in the interfacial zone.

The pretreatment of the zinc surface will strongly influence its physical and chemical behaviour. Therefore, it is very important to determine the adhesion forces on that pretreated zinc substrate which is intended to be used in practice.

In these investigations we employed galvanised plates without weathering before

applying the paint. The paint application on weathered galvanised surfaces under on-site conditions involves higher costs than when applied in-house. For that reason in-house application will increase in future.

As there is less experience in choosing the best process for treating an unweathered galvanised surface, we investigated the adhesion forces in relation to various applied pretreatments.

We used the usual pretreatments for weathered galvanised surfaces to determine whether there is also an effect on adhesion on unweathered galvanised surfaces, and if so, to what extent.

The pretreatment procedure to be selected for preparing weathered galvanised surfaces depends largely on the weathering period, the type of atmosphere and the expected life of the construction. Furthermore, the choice of pretreatment will be influenced by the size of the construction to be painted. Chemical treatments are used as well as mechanical.

2. Experimental

2.1. Pretreatments

Various pretreatment methods were used as applied in practice and under the usual conditions. Before carrying out the treatments all surfaces were degreased.

The conventional procedures, used in this study, were as follows.

2.1.1. Degreased surface

Surfaces that were only degreased were used in comparing results of adhesion measurement on zinc galvanised surfaces with the various pretreatments. Surfaces were degreased with acetone.

2.1.2. Treatment with an ammonia solution

A solution of 1.25% ammonia in water containing a wetting agent was applied to the galvanised surface. During this procedure a cleaning pad (Scotch Brite™) was used to scour the galvanised surface. After a period of 10 min, the solution, which formed a foam during this process, was rinsed off with water. In practice, different workers use different quantities of water because there is no specification for the required quantity. We therefore investigated the effect of the quantity of water used during rinsing. In one case we used a large quantity of water which reached a pH-value of 7 after rinsing from the zinc surface. In the second case, by using only a little quantity, a pH-value of 9 was obtained. The pH-value of the applied ammonia solution was 10.

2.1.3. Sweep-Blasting

Sweep-Blasting is a special form of blasting and widely used in practice. Careful conditions during the blasting procedure were used to avoid local flaking of the zinc layer.

In this investigation the galvanised surface was blasted with a mineral slag by choosing a pressure of 0.3 MPa, a distance between the nozzle and the galvanised surface of 0.3 m and an angle of 30°.

2.1.4. Grinding

The galvanised surface was ground by using a grinding machine and an emery paper P 120.

2.2. Adhesion Tests

Different methods were used to determine if and to what extent the adhesion of the coatings varied in relation to the pretreatment of the galvanised surface. In addition, the results of the various methods (pull-off test, torsion test and cross-cut test) were compared to find out whether they showed the same tendency. In this investigation it was of special interest to determine the adhesion at the interphase coating/substrate. Therefore only results where these adhesion failures occurred, were of interest.

2.2.1. Pull-off test

All pull-off tests described in this paper were conducted by applying a one side pull-off test by using plates of a thickness of 2 mm, i.e. a variation from DIN EN 24624 that specifies a two side pull-off test in the case of thin plates. To avoid bending of the plates the dolly diameter that was used was only 7 mm. Earlier investigations showed that by using a dolly with a reduced diameter in the one-side test we obtained the same results as in the two side pull-off test with 20 mm dollies (see Table 1).

The dolly was fixed by an epoxy resin-based glue in the case of measuring dry adhesion and, in the case of wet adhesion by a cyanoacrylate adhesive. It was necessary to use these different types of adhesives for dry and wet adhesion measuring. Thus, the application of an epoxy resin-based glue on the dry coating top side guaranteed that breaking did not occur in the interface between the dolly and the coating. With the wet paint coating, breaking in the paint film/zinc coating interface could be obtained only by using a cyanoacrylate-based glue.

It was necessary to investigate a number of glues so that types could be used that would guarantee that breaking would not occur in the glue/coating interface, while ensuring, that no chemical reactions took place.

Table 1. Comparison of the results of the pull-off test by using different measuring parameters (Thickness of plates: 2 mm; pretreatment: Sweep-Blasting)

Coating system based on	One side pull-off; dolly dia.: 20 mm mean value/s.d. (MPa)	One side pull-off; dolly dia.: 7 mm mean value/s.d. (MPa)	Two side pull-off; dolly dia.: 20 mm mean value/s.d. (MPa)
Epoxy I	0.84 / 0.09	8.67 / 0.84	11.76 / 1.33
Epoxy II	1.38 / 0.18	11.62 / 1.14	13.31 / 2.14
Epoxy ester	0.60 / 0.14	7.78 / 0.87	7.45 / 1.40
Alkyd resin	0.68 / 0.27	8.05 / 0.54	11.30 / 1.51

The dolly was pulled off vertically by applying increasing forces with a tensile strength testing machine (Instron Company).

To compare the influence of pretreatment procedures on adhesion only those results were of interest in which the fracture occurred within the interfacial zone between the underside of the paint film and the topside of the zinc layer.

The calculated results based on the relation between the pull-off force and the area of the dolly were expressed as MPa.

2.2.2. Torsion test

The torsion test was performed by applying a so called Twist-O-Meter of Epprecht Instruments and Controls. The principle of this measuring method is similar to that of the pull-off test. The dolly was again fixed by an epoxy resin-based glue when measuring dry adhesion and, in the case of wet adhesion, by a cyanoacrylate adhesive.

In this test a continuously increasing torsion force acts on the dolly until delamination of the paint film and fracture occurs within the duplex (coating/galvanised) system. The calculated results are based on the relation between the torsion force and the area of the dolly and expressed by MPa.

2.2.3. Cross-cut test

The cross-cut test is used widely in practice even though it is no longer recommended as an adhesion test. The test was performed in accordance with DIN EN ISO 2409.

2.3. Adhesion Measuring after Different Exposure Conditions

The adhesion test on a coating without exposure is of less importance since it is only in the presence of moisture that the conditions can be simulated which occur in practical conditions. These are: swelling of the coating, interaction of the moisture in the interfacial zone between the underside of the paint film and the top side of the galvanised surface and reconditioning. The adhesion was therefore tested as follows:

- Without exposure (after complete drying and hardening).
- After exposure to moisture in wet film condition (performed in accordance with the so called HAAGEN test, a special condensation test developed for duplex systems, similar to that described in ISO 6270).
- After reconditioning (drying), 4 weeks under controlled conditions of 23°C and a relative humidity of 50% after performing the HAAGEN test).

3. Applied Materials

3.1. Type of Coatings Used

The coatings were based on the two-component-epoxy Beckopox EP 301, 75% in xylol and on the curing agent Versamid V 115 70% in xylol.

An unpigmented paint was used in studying the effect of pretreatment on adhesion since this ensured that failure would occur in the interfacial zone. With a pigmented paint failure occurs within the paint film and only the cohesion forces of the paint film itself are characterised.

3.2. Galvanised Steel Plates

Steel sheets $100 \times 200 \times 2$ mm of steel St 37 were used. A normal hot-dip galvanising process was carried out under practical conditions. The temperature of the zinc bath was 450°C . The thickness of the zinc layer ranged from 40 to $60\text{ }\mu\text{m}$.

4. Results and Discussion

The results of adhesion tests are shown in Figs 1–3 for the pull-off test, in Figs 4–6 for the torsion test and in Figures 7–9 for the cross cut test. The vertical columns represent the mean values of 10 to 12 single values and the standard deviation is indicated. The abbreviations used for the pretreatment procedures are:

- Degreas. = zinc surface that is only degreased
- Amm.th = thorough rinsing after pretreatment with ammonia solution
- Amm.sl = slight rinsing after pretreatment with ammonia solution
- Sweep. = sweeping
- Grinding = grinding by using a machine and emery paper.

It can be seen that the interphase adhesion depends strongly on the type of pretreatment. With blasted and ground galvanised surfaces high adhesion values were obtained in the case of all the three exposure conditions.

The adhesion to galvanised steel pretreated by the ammonia solution showed high values when thorough rinsing was used. If a small quantity of water was used (slight rinsing) the adhesion values were low. This results proves, that the quantity of water during rinsing is of great importance for the interface adhesion. There are no publications at all on this pretreatment method and the possible chemical reactions between the ammonia solution and the zinc surface. Therefore, the present authors can only speculate on a causal connection between adhesion and the quality of rinsing

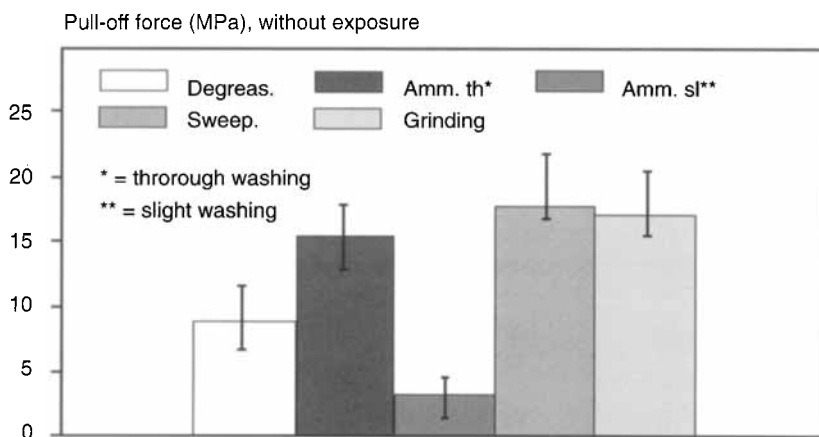


Fig. 1 Pull-off forces — without exposure depending on the pretreatment method.

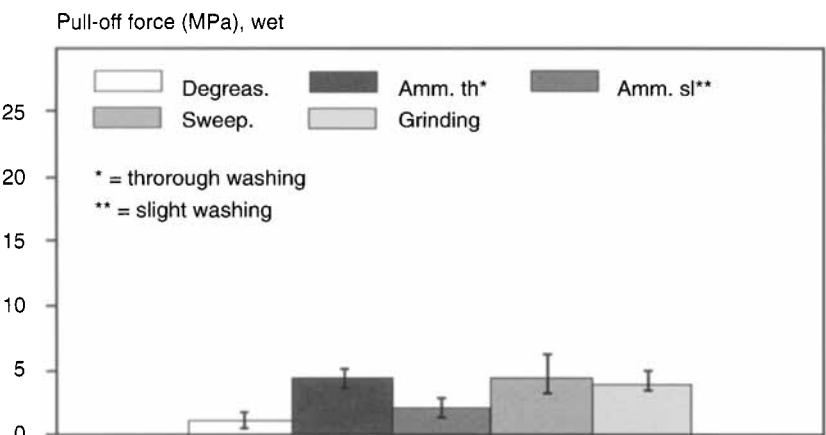


Fig. 2 Pull-off forces — wet condition depending on the pretreatment method.

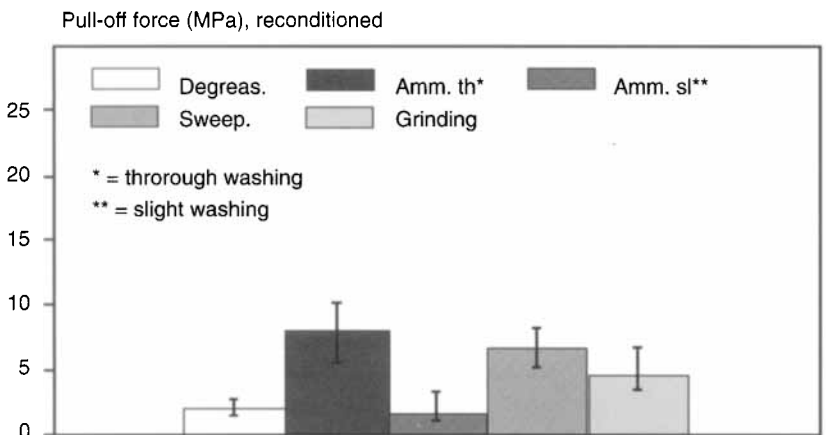


Fig. 3 Pull-off forces — reconditioned depending on the pretreatment method.

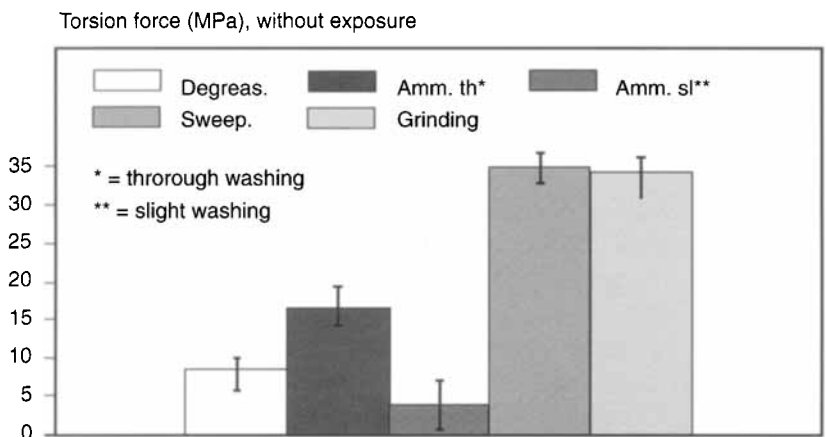


Fig. 4 Torsion forces — without exposure depending on the pretreatment method.

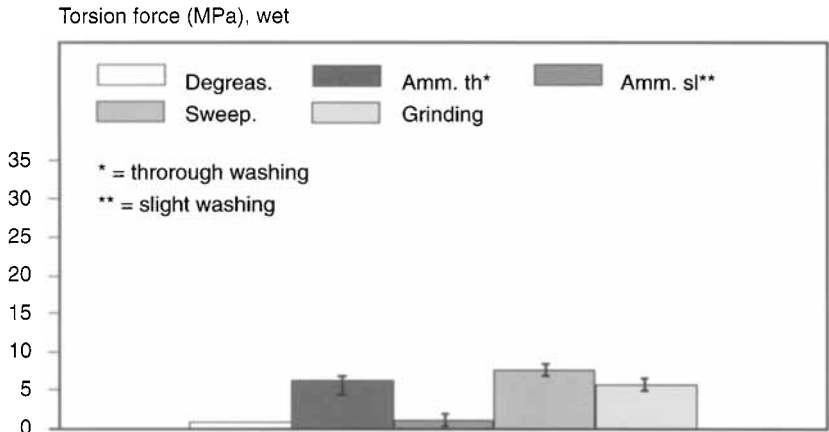


Fig. 5 Torsion forces — wet condition depending on the pretreatment method.

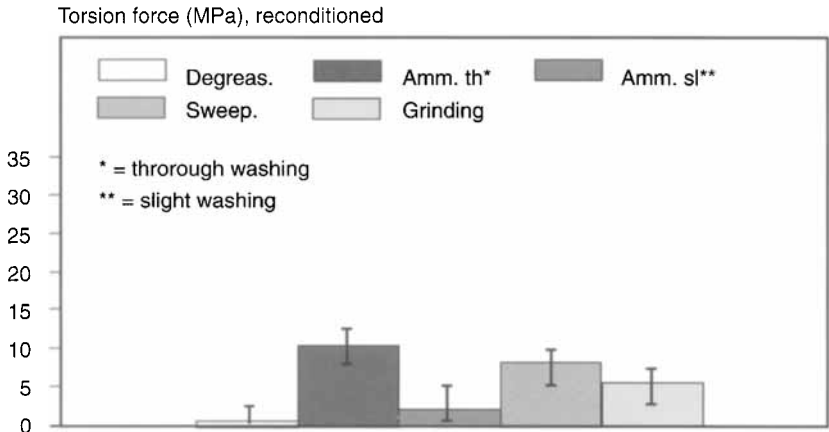


Fig. 6 Torsion forces — reconditioned depending on the pretreatment method.

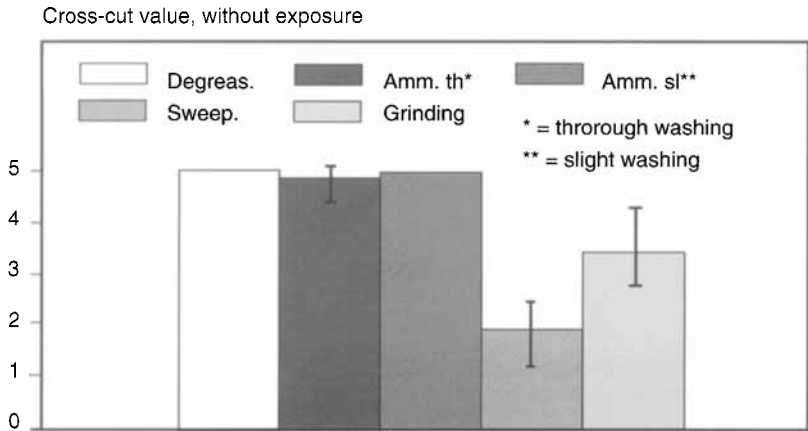


Fig. 7 Cross-cut test — without exposure depending on the pretreatment method.

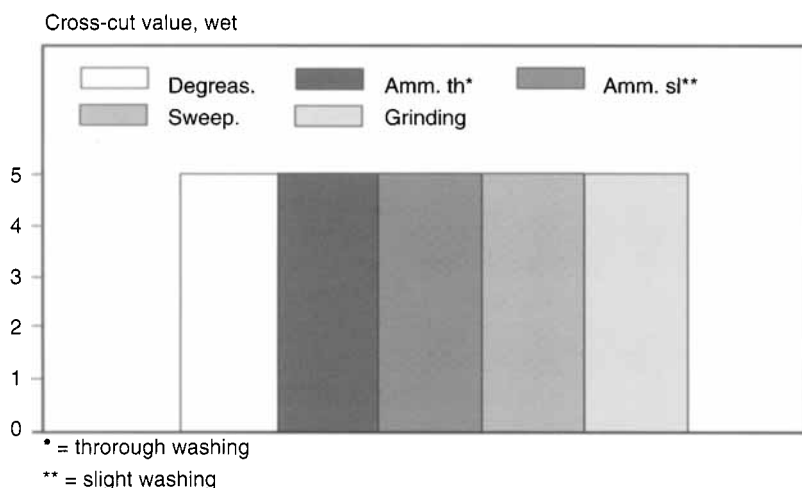


Fig. 8 Cross-cut test — wet condition depending on the pretreatment method.

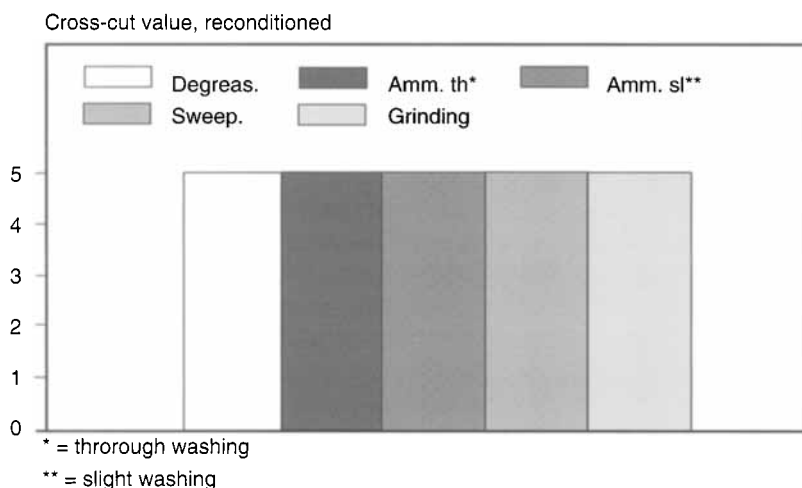


Fig. 9 Cross-cut test — reconditioned depending on the pretreatment method.

after treating with ammonia solution. On the one hand, it is well known that hot dip galvanised zinc coatings form zinc oxide and zinc hydroxide on their surfaces immediately after galvanising. On the other hand, water soluble zinc di- or tetraammine hydroxide can be formed as a result of the reaction between zinc hydroxide and ammonia solution. By rinsing the zinc surface thoroughly after treating it with ammonia solution these soluble products were removed. In the case of slight rinsing these soluble compounds can remain on the zinc surface and lead to lower adhesion of the painted zinc coating.

The zinc surface that was merely degreased showed — as expected — bad adhesion

in all cases. It was used only to provide a comparison with the mechanical or chemical pretreated zinc surfaces.

To assess the performance of the coating the adhesion was determined after different exposure situations. The adhesion value for the coating without exposure is typical for the individual coating and was used for comparing with the value after exposure and reconditioning. For the evaluation of the durability of a coating system under practical conditions the measurement of the wet film adhesion and in a reconditioned state is of importance. The adhesion under wet film conditions shows the extent to which the adhesion in the interfacial zone can be reduced by water. The adhesion values of a reconditioned film show to which extent the adhesion can be restored during the drying process.

5. Conclusions

The comparison of the different adhesion tests showed that the quality of the different surface pretreatments could be distinguished by using the pull-off and the torsion tests.

On the contrary, no differentiation was possible with the cross-cut test. This test is widespread in practice as an adhesion measuring method. But the results of this test are influenced more by the elasticity and the hardness of the organic coating, i.e. as compared with the other adhesion tests. The less elastic an organic coating the lower the adhesion values given by the cross-cut test. Moreover, it is hardly possible to distinguish between different actual adhesion values in the interface. The results of this study confirm the recommendations in the latest edition of DIN EN ISO 2409 not to use this test as an adhesion test.

Characterisation of Pretreatment Processes Applied to Aluminium Alloys to be Coated with Organic Layers

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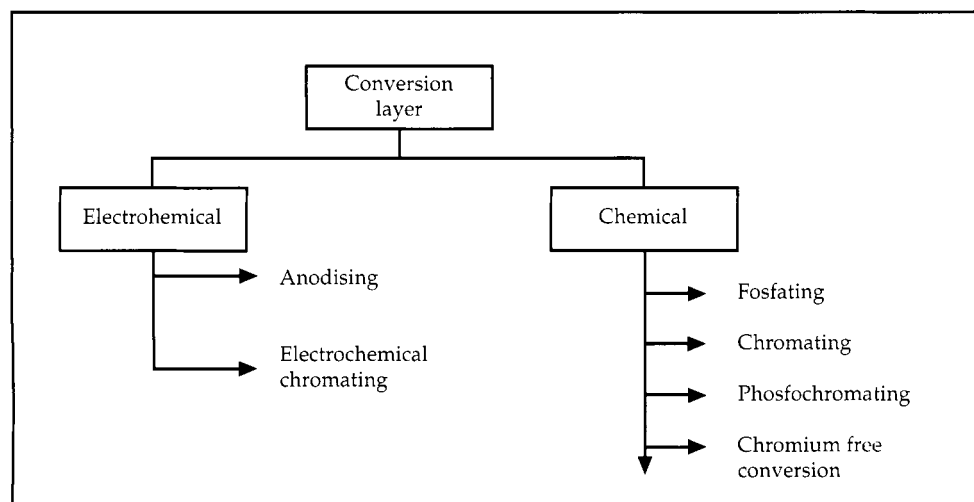
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1. Introduction

It is well known that the natural oxide film which forms when an aluminium surface is exposed to the atmosphere is responsible for the high corrosion resistance of aluminium. This corrosion resistance can be improved by organic finishes such as paints or lacquers. Substrate pretreatments play in this case an important role in the protection behaviour of aluminium alloys. Table 1 gives the main conversion layer treatments.

The purpose of this paper is to show that with complementary experimental techniques (chemical and surface analytical, *ex situ* techniques) the structure and composition of the conversion layers can be determined and also the influence of the process parameters on these characteristics.

Table 1. Conversion layer treatments



2. Anodising

In the anodic oxidation (also called anodising) of aluminium the metal is made the anode in an electrolytic cell containing a suitable electrolyte. Electrochemical aluminium oxidation takes place and the aluminium cations that are formed react with oxygen anions of the aqueous electrolyte to form aluminium oxide.

The structure and composition of the oxide layer depend on the electrolyte (nature, composition and temperature), the electrolysis parameters (current density, potential and process time) and the composition of the treated aluminium surface.

By selecting the proper anodising conditions the layer characteristics can be adapted to the required properties for each specific application. It is therefore necessary to understand the nucleation and growth of the oxide layer [1,2].

2.1. Influence of Electrolysis Conditions

If the natural oxide film is insoluble in the electrolyte (borate and tartrate solutions) only film thickening can occur and this will result in a compact strongly adherent and practically non-conducting film. Due to the field assisted ion migration growth the thickness of the barrier layer ($0.01\ \mu$ to max. $1\ \mu$) varies directly with the forming voltage. The theoretical value ($1.4\ \text{nm V}^{-1}$) is influenced by temperature, electrolyte composition, etc.

Transmission Electron Microscopy (TEM) cross sections of a barrier layer are described in the literature [1] and the layer composition can be analysed by Auger Electron Spectroscopy (AES) [3].

However, to avoid any damage to the specimen that may occur as a result of the preparation method, irradiation or vacuum effects, two complementary methods may be used, namely, Spectroscopic Ellipsometry (SE) and Electrochemical Impedance Spectroscopy (EIS).

The ellipsometry data of a barrier film (Fig. 1a) can be interpreted with the two layer model of Fig. 1(b) [4,5]. The top layer in this model characterises the composition and thickness of the barrier film. The thickness and the aluminium content of the thin interface layer quantify the microscopic substrate roughness. The full lines show the calculated response using the Bruggeman expression.

Figure 2(a) shows the Bode diagram of a barrier layer. These experimental results do not indicate a purely capacitive behaviour and can be interpreted with the equivalent network shown in Fig. 2(b). The resistance R_{el} represents the ohmic drop in the electrolyte and the two parallel components R_b , C_b characterise the barrier film. From the film thicknesses measured at different anodising voltages, the growth rate of the oxide film determined with SE and EIS is established at $1.2\ \text{nmV}^{-1}$ which matches the data obtained with TEM.

In those cases where the electrolyte moderately attacks the oxide layer (chromic, sulfuric, phosphoric and oxalic acid) a second type of surface treatment is obtained. Above the barrier layer a porous layer is formed with a characteristic columnar and hexagonal structure [2]. The growth of the porous oxide layer can be simply described as a competition between oxide film formation and its dissolution. The oxide film formation is promoted by the formation of aluminium ions (proportional to the

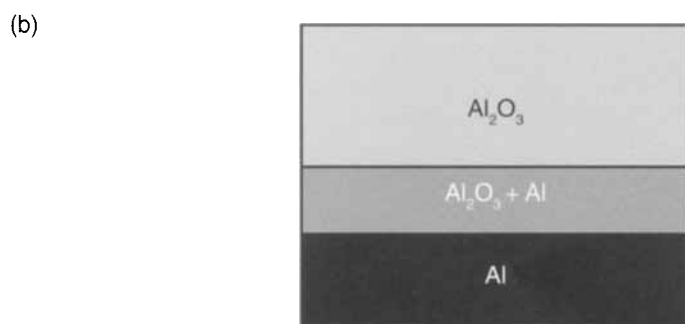
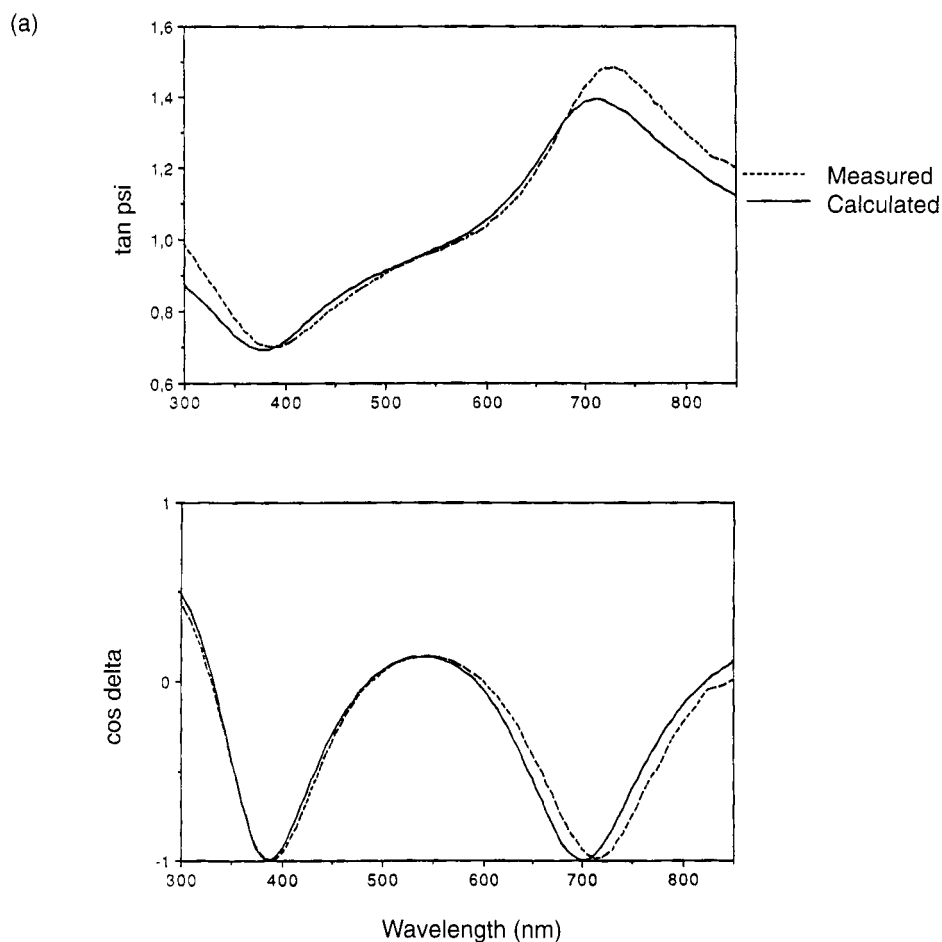
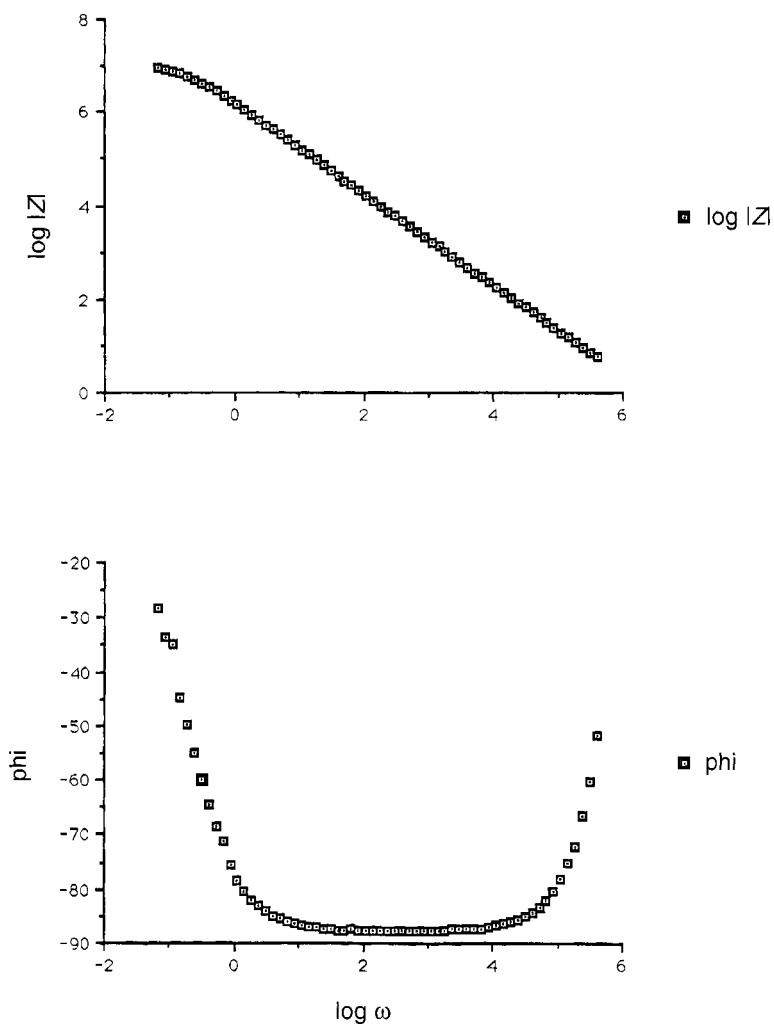


Fig. 1(a) Measured (dashed line) and calculated (full line) ellipsometry spectra of the barrier film, grown at 100 V in a 3% ammonium tartrate solution of pH 5.5 at 22 °C and a current density of 0.81 A dm^{-2} ; (b) Two layer model of the barrier film. The first and second layer represent the barrier film and the film-substrate interface, respectively.

(a)



(b)

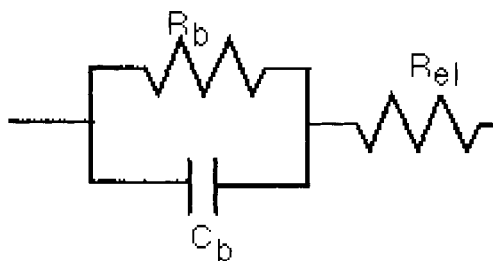


Fig. 2(a) Bode plot of the barrier film, grown at 20 V in a 3% ammonium tartrate solution of pH 5.5 at 22 °C and a current density of 0.81 A dm^{-2} ; **(b)** Equivalent network of the barrier film.

applied current density) and their reaction with oxygen ions. Oxide film dissolution is related to the acid aggressiveness.

This competition is reflected in the shape of the anodising potential under constant current density conditions. Oxidation at constant current density shows an approximately linear increase in voltage from the beginning of anodising (barrier layer formation). After a certain time a maximum is reached, described in terms of non-uniform film growth resulting in pore development. The maximum is followed by a decrease to a steady-state voltage leading to the formation of a relatively regular porous oxide film which thickens according to Faraday's law. Cell, pore and barrier layer dimensions depend on the anodising conditions and are characterised by fixed anodising ratios (nm V^{-1}) (Table 2) and can be calculated from the steady state anodising voltage.

The aluminium substrate plays an enormous role in the growth of the oxide layer. Thus, for example, the electrochemical behaviour of precipitates can be very complex, promoting regions where metal dissolution, gas evolution or other side reactions occur. The initiation of pores, on the other hand, can be influenced by the surface topography (anodising of extruded profiles whether, or not, rolled, grained, ...). A pretreatment such as electrograining [6] can be used to produce a well defined surface morphology.

Ellipsometry spectra of a porous film (Fig. 3), can be interpreted by a two layer model [5,13]. The top layer of this model represents the porous part of the film and consists of an Al_2O_3 -void mixture. The interface layer, modelled as a $\text{Al}_2\text{O}_3/\text{Al}$ composite represents the barrier film part and the scalloped substrate roughness. Using the cell and pore dimensions measured with TEM it is possible to determine the void content of the porous layer and the Al content of the interface layer. The characterisation of the porous film thickness at different anodising times by SE and TEM enables the establishment of a growth rate of 12.4 nm V^{-1} under the applied anodising conditions.

Table 2. Size characterisation of the porous layer

	Measured value (nm)	Ratio (nm/V)
Anodising conditions: 2M sulphuric acid at 232°C, anodising potential 14 V		
Barrier film thickness	15.0	1.1
Pore diameter	10.0	0.7
Cell width	38.0	2.7
Anodising conditions: 0.4M phosphoric acid at 22°C, anodising potential 100 V		
Barrier layer thickness	100.0	1.0
Pore diameter	87.0	0.87
Cell width	250.0	2.5

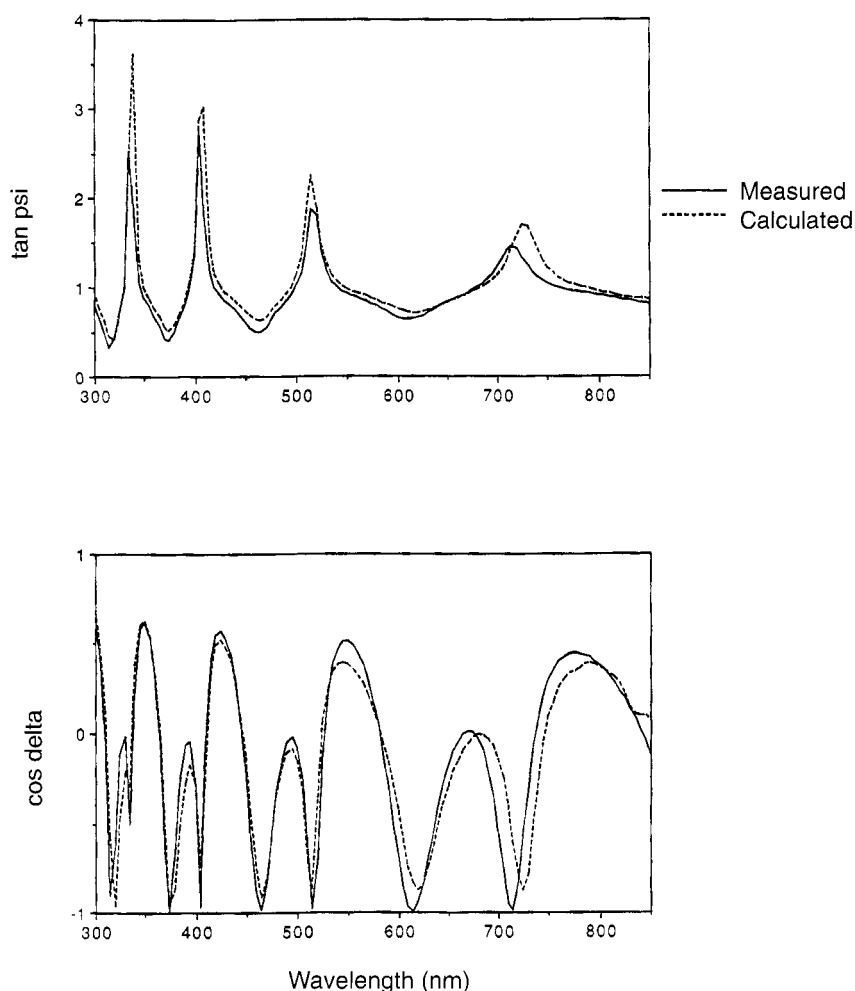


Fig. 3 Measured (dashed line) and calculated (full line) ellipsometry spectra of the porous anodising film, grown in a 20% sulfuric acid solution at 25°C and a current density of 0.81 A dm^{-2} during 60 s.

2.2. Sealing the Porous Layer

In nearly all applications, the porous oxide layer is sealed to improve the corrosion resistance. Among the different processes, sealing in hot water (80–100°C) containing some additives, is used worldwide. The pores are filled due to the reaction of aluminium oxide with hot water and this results in the formation of boehmite.

EIS is a powerful method to characterise the sealing of the porous film [5,7]. The results shown in Fig. 4(a), obtained after different sealing times can be interpreted with the equivalent network of Fig. 4(b). R_{el} is the resistance of the electrolyte, C_b and R_b the capacity and resistance of the barrier film and the sealed porous film and can be characterised by the capacity and resistance C_s and R_s . The decrease of C_s and increase of R_s during the sealing can be explained by the filling of the pores by

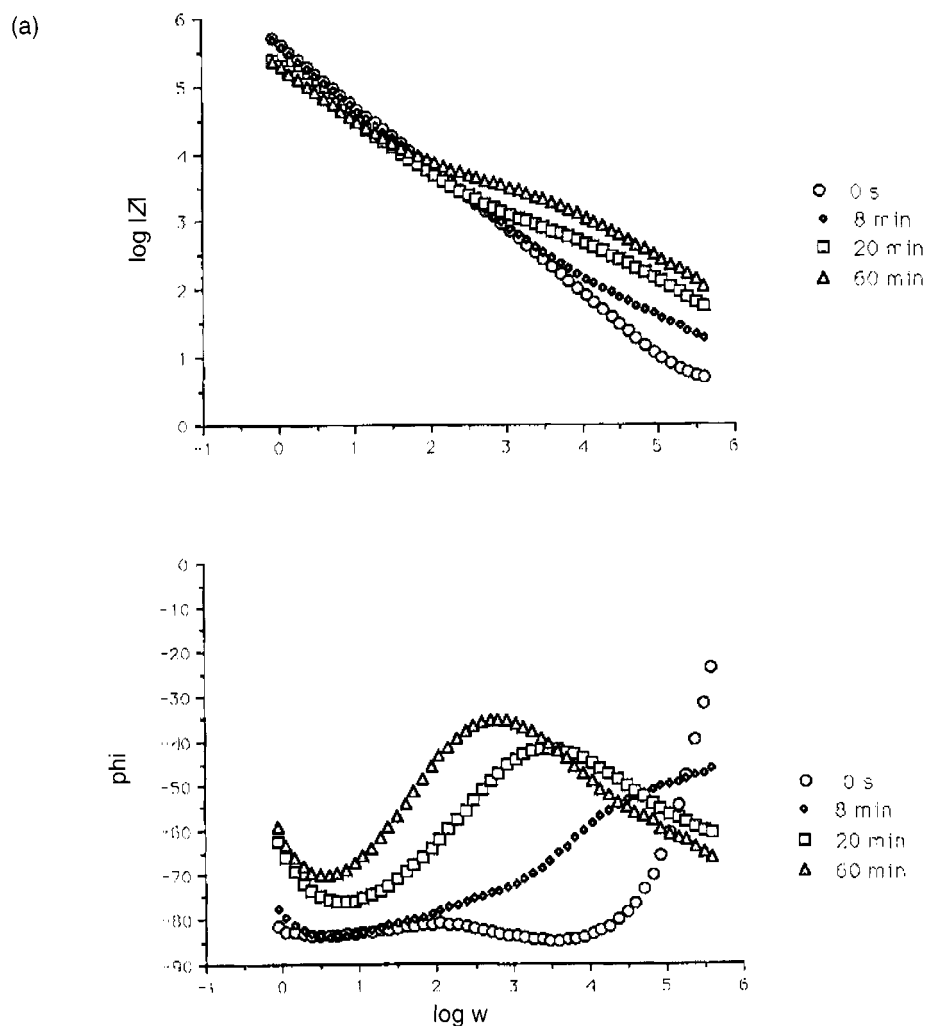


Fig. 4 (a) EIS spectra of the sealed porous film; (b) Equivalent network of the sealed porous film.

hydration products which have a lower permittivity than the electrolyte. It is very important to note that if the impedance is measured *in situ* while sealing the surface layer can only be simulated with the equivalent network of the barrier film. This

means that the conversion reaction and the pore filling do not take place in the sealing bath but outside of it. When the sealed material is put back again in hot water the boehmite dissolves reversibly.

3. Chemical Conversion Treatments

Different bath composition can be used for chemical conversion treatments (Table 1).

3.1. Phosphochromating

Phosphate chromate conversion layers on aluminium alloys are widely used to improve corrosion resistance, for decorative purposes, to lower electrical resistance and improve paint adhesion. First introduced in the aircraft industry, this chemical treatment has performed remarkably well for architectural purpose and beverage cans production. These layers are produced, after degreasing and alkaline etching, in a conversion bath containing chromium trioxide, active fluorine and phosphoric acid.

From depth profiles obtained with Auger spectrometry [8] it can be concluded that a two layer structure is formed after conversion: chromium and phosphorus are present in the outer layer while fluorine and aluminium are found near the substrate surface. The presence of CrPO_4 and AlOF have been detected (Fig. 5) by X-ray Photoelectron Spectroscopy (XPS) [8] and Fourier Transform Infra-red Spectroscopy (FTIS) [10].

EIS data of conversion layers with different process parameters (immersion time, fluorine content and conversion temperature) can be simulated with the equivalent network shown in Fig. 6 [8,11,12]. R_1 represents the electrolyte resistance. The porosity of the conversion film is described by an constant phase element Q_3 in series with R_3 C_3 . This dispersion factor Q_3 can be interpreted in terms of a transmission line describing a network of electrolyte resistances and double layer capacitances in the pores of the conversion layer. If the pore geometry is estimated, a penetration parameter can be deduced from the impedance frequency dispersion. R_2 models a conducting path through the layer, caused by imperfections.

By fitting the EIS measurements, the influence of the process parameters on the electrical components shows that the layer thickness increases linearly with the

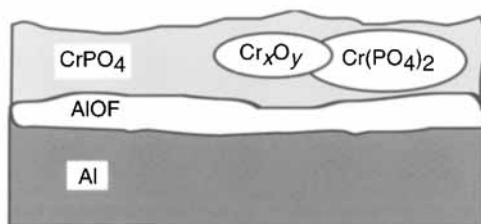


Fig. 5 Model of the conversion layer based on surface analysis.

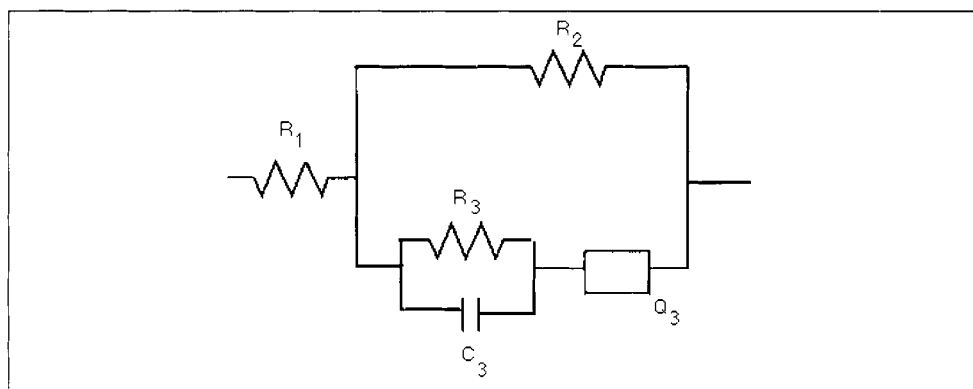


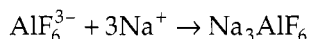
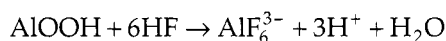
Fig. 6 Impedance model of the conversion layer.

immersion time. A thicker coating is obtained when the fluorine content of the bath or the temperature increase. A relation exists between the influence of the pretreatment time in NaOH and the fluorine content in the conversion solution.

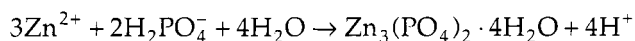
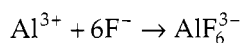
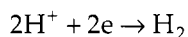
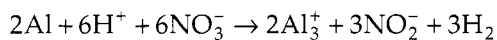
3.2. Phosphating

Phosphating, although already used for a long time on steel sheets, has been introduced only relatively recently for aluminium, particularly for automotive applications. When steel and aluminium are simultaneously treated, zinc phosphating is used or — more precisely — the trications process in which the bath contains zinc, nickel and manganese cations.

In contrast to most other conversion treatments which form amorphous layers, a crystalline zinc phosphate film is produced in this case. After the attack of the existing aluminium oxide layer by fluorides and the formation of cryolite:



the metal surface comes in contact with the phosphating solution and hopeite $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ is formed:



The structure and density of the layer are influenced by the pretreatment process which includes an activation step. The activation of the surface is achieved by the deposition of small titanium phosphate nuclei on the aluminum substrate — although other pretreatments such as a degreasing alkaline etching of the anodised surface can

be used. The composition of the aluminium alloy also plays an important role in the resulting phosphate layer. Figure 7 shows the fine and dense crystal structure of the phosphate layer obtained on AA5754 Al alloy after 240 s alkaline etching (5 % NaOH) [14].

After dipping the aluminium substrate in the activating solution containing colloidal titanium phosphate particles it has been shown by AFM examination that the surface is covered by nuclei of titanium phosphate which are adsorbed flat walled on the aluminium surface (Fig. 8) [15]. X-ray diffraction proved that they are crystalline.

Time of Flight Secondary Ion Mass Spectrometry (TOF SIMS) mappings, taking the Ti mass signal as a tool for measuring the distinction of these nucleation agents, clearly indicates that the initial surface condition plays a major role in the number of centres deposited on the aluminium surface.

When the activated aluminium surface is dipped in the phosphating solution, zinc phosphate crystals are immediately formed which grow in 2 D dimension leading

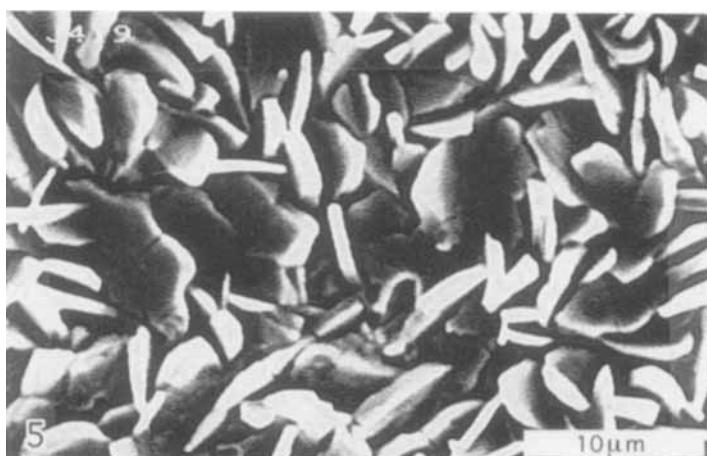


Fig. 7 Structure of the phosphate layer obtained on AA5754 Al alloy after 240 s etching alkaline.

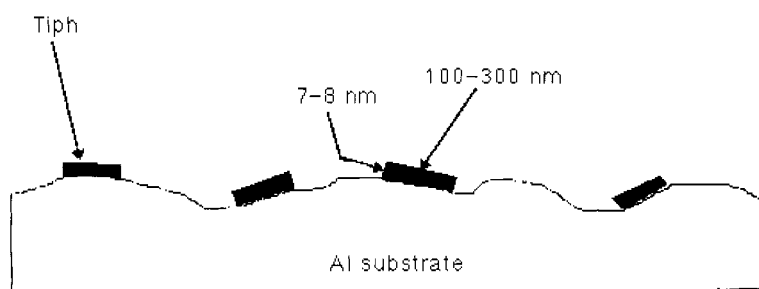


Fig. 8 Schematic drawing of the presence of Ti phosphate (Tiph) nucleation centres on aluminium surface.

to flat crystals in contact with the aluminium surface. A close packed dense layer is obtained, having crystals of a size of about 5–20 μm . It seems that the other parameters of the activating bath (concentration, temperature and process time) are less important; however, ageing of the colloidal solution has an important influence.

3.3. Zirconium Based Chromium-Free Conversion Layer

Conversion baths containing toxic hexavalent chromium compounds will be limited in the future due to ecological and health reasons. Therefore, alternative conversion coatings, also called chromium free conversion coatings are developed. So far, of the alternative processes only those based on zirconium salts have gained wide acceptance. The aqueous solutions used for the zirconium based conversion process contain mainly H_2ZrF_6 , which acts both as source of Zr and a source of F^- . A small amount of HF is frequently added. The most recently developed conversion baths also contain a polymeric compound.

The use of complementary surface analysis techniques (AES, XPS and SIMS) allows the composition of these conversion layers to be determined. The structure is two layered [16], in which the bottom layers contain only Al and O, while the top layer also contains a fluorinated zirconium compound and a polymer (which is located at the outer surface). While the distribution of Zr and F is homogeneous in the top layer, the small amounts of Zr and F that remains in the bottom layer are due to the presence of the elements in the pits, which penetrate the bottom layer. The equivalent network proposed for the study of the chromate conversion layers can be also used for the characterisation of the zirconium based conversion layers. With the variation of the capacity C_3 (of Fig. 6) it can be concluded that the layer thickness is nearly independent of the conversion time and smaller than 10 nm, which is very thin compared to the chromium phosphate conversion layers.

4. Conclusions

This overview of the studies of surface treatment of aluminium alloys carried out in the Department of Metallurgy, Electrochemistry and Materials Science at the Vrije Universiteit Brussel has shown that the use of complementary *ex situ* and *in situ* techniques (surface analytical and electrochemical methods) allows a better understanding to be reached of the mechanism of these surface treatments and to characterise the obtained surface layers.

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Soluble Ion Contamination on Steel Surfaces and its Effect on the Stability of Coatings

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ABSTRACT

The influence of chloride and sulfate ions on the steel surface on the durability of selected paint systems — water- and solvent-borne as well as mixed systems was investigated. The accelerated tests were conducted in salt spray and Prohesion chambers as well as in water and NaCl solution. The systems were also exposed to the natural environment, in rural and urban-industrial atmospheres. The corrosion damage was evaluated visually and by means of impedance spectroscopy. The variable influence of chloride and sulfate on the tested systems was determined. A possible correlation between accelerated tests and the actual damage to systems at corrosion sites is discussed.

1. Introduction

The effect of surface preparation on the stability of coatings is well known and accepted.

Grease, oils, dust, corrosion product residues and remains of old coatings all represent contaminants that have to be removed by careful cleaning of metal surfaces prior to painting. Each of these contaminants is normally easily visible particularly when present in significant amounts and there is no doubt that they have an adverse effect on the performance of coatings [1–3].

However, there is evidence that many components, although properly painted with coatings, such as high quality paints properly tested in the right atmospheric conditions and applied to surfaces prepared to the highest level of cleanliness, nevertheless show significant levels of corrosion damage after only months instead of the years of service that had been predicted [4–6].

The problem has become urgent in the cases of bridges, and in the pulp and paper industry, the electrical supply industry, in shipyards, salt works, plants producing chloroparaffins and fertilisers, in the mining and petroleum industries, in vessels used for storing aqueous media and so on.. This situation has resulted in the initiation of a range of scientific research projects sponsored by industries concerned with these and similar problems [5–9]. Several years of detailed studies have led to the conclusion that the reason for the premature failure of coatings and the consequent accelerated corrosion is the presence of invisible ion surface contamination which can be resistant even to blast cleaning. The problem is becoming yet more serious with the use of the new generation paints that can be applied to surfaces less well prepared than in the past. These surfaces will contain corrosion product residues on

which further ion contamination is likely to gather when renovation painting is considered. Problems can also arise when paints with improved tolerance to salt, for example, those containing lead and chrome pigments, are not acceptable for environmental protection reasons [10,11].

Ion contamination on a metal surface can originate from a number of sources including:

- 'normal' air pollution
- salt treatment of roads in the winter (10M tonnes in the USA in 1970/71 [12];
- air borne industrial products; exhaust gases from combustion of various fuels;
- building construction materials, like gypsum, anhydrite etc.

Ion contamination can also be introduced during blast cleaning when the abrasive itself is contaminated with ions and also from the actual substrate, i.e. from the steel. Chloride ions may also form during the degeneration of the paint binder where this is composed of chlorinated rubber, polyvinyl or other chlorine-containing polymers [13]. Various substances can be found on painted surfaces of which the most frequently occurring are chloride and sulfate ions — with accompanying cations.

The damaging effect of surface ion contamination on coatings has been studied by many researchers. The main consequences of contamination have been found [6,9,14–17] to be as follows:

- salts on the surface absorbing moisture from the atmosphere salts causing osmotic flow of moisture through paint layers;
- salts reducing the electrical resistance of the corrosion cells (increased electrolyte conductivity);
- differing concentrations of salts at different areas of the surface generating differences in potential thereby causing corrosion currents; and
- salts lowering the pH value on the surface, since in the presence of oxygen these salts could act as oxidisers producing HCl or H₂SO₄ and lower the pH to values even as low as 1.5 with resulting corrosion.

As a consequence of these effects, instead of poorly soluble or insoluble iron hydroxides, soluble hydrated iron chlorides and hydroxychlorides or sulfates are formed *in situ*; these diffuse across the surface and lead to widespread corrosion.

In trying to draw up some general recommendations for the avoidance of the detrimental effects of ion impurities it seemed advisable to establish a data base for the various types of paints that are used in different corrosive environments.

2. Studies of Selected Painting Systems on Steel Surfaces Contaminated with Chloride and Sulfate Ions

2.1 Experimental

In the Institute of Precision Mechanics in Warsaw, studies of a range of Polish industrial paint systems have been carried out and the resistance of these to surface ion contamination examined. Results will be presented here for four selected types

Table 1. Generic types of coatings and thicknesses

Number of system	System component	Generic type	Surface preparation ISO 8501-1	Thickness (μm)
1	Primer	Waterborne modified acrylic	Sa 2,5	140–160
	2nd Coat	Waterborne modified acrylic		
2	Primer	Epoxy solvent-borne	St 3	140–160
	2nd Coat	Epoxy solvent-borne		
3	Primer	Polyvinyl solvent-borne		
	2nd Coat	Epoxy solvent-borne		
4	Primer	Water-borne rust converting modified copolymer butyl acetate/dibutyl maleate	Sa 2,5	140–160
	2nd Coat	Polyvinyl solvent-borne		

of paint systems applied to substrates with St3 and St2.5 surface preparations according to ISO 8501-1.

The systems were selected so as to represent different types of paints.

The following corrosion tests were conducted with the selected systems:

(a) *accelerated tests:*

- Tests in a salt chamber (type VSN 20/1000) according to ISO 7253/84 (spraying with 5% NaCl solution, temp. $35\pm 2^\circ\text{C}$) using panels with a diagonal cut;
- Immersion tests in 5% NaCl solution according to ISO 2812/93 Part 1;
- Immersion tests in distilled water, according to ISO 2812/93 Part 2;
- Tests in a Prohesion chamber Q-Fog type (1-h alternate cycles of drying at 35°C and spraying with 0.4% ammonium sulfate + 0.05% sodium chloride solution,

(b) *natural exposure tests at two sites of different corrosion aggressivities:*

- In a rural atmosphere (Masuria Lake district) in one of the cleanest sites in Poland, but with 'imported' atmospheric pollution (acid rain);
- In an industrial-urban atmosphere (Warsaw) with a typical level of industrial pollution.

The degradation of the coatings was evaluated according to ISO 4828/1982. Parts 1–6. The condition of the coatings was assessed, initially and during the tests, by means of:

impedance spectroscopy (EIS) — measurements in 3% NaCl aqueous solution were conducted with an Atlas impedance system (analyser Atlas 9121 FRA, impedance interface Atlas 9181 from 100 kHz to 0.01 Hz, amplitude 10–100 mV). An electrochemical cell of area 10 cm² was used in which the coated panel formed the working electrode and a platinum wire the counter electrode;

- determination of mechanical properties in which adhesion, according to ISO 2409/1992 (Paints and varnishes: Cross cut test) and resistance to impact (according to ISO 6272/ 1993 Paints and varnishes: Falling weight test) were measured.

All tests were conducted with three types of contamination:

- (i) without ion contamination; and
- (ii) with chloride ion contamination at ~10, ~50 and ~100 µgcm⁻² concentration and with sulfate contaminants at ~50, ~100 and ~240 µgcm⁻² concentration.

The contaminants were applied following the procedure described by Flores *et al.* [18].

3. Results

In this paper results are given for one concentration of sulfate ions, ~50 µgcm⁻² and one chloride concentration ~10 µgcm⁻², these being the minimal concentrations above which, according to DIN Standard Draft 55982, the total concentration of sulfates and chlorides becomes harmful to coatings) with discussion of the visual estimates of the corrosion damage.

In most cases the damage occurred earlier and more extensively the higher the ion concentration.

Typical impedance spectra presented as Bode plots before and after exposure for coatings on surfaces contaminated with chloride and sulfate ions are compared with coatings on clean surfaces in Figs 1 and 2 for the water-borne system (1) and the solvent-borne system (3) (the absence of some curves is because the damage of these coatings was such that impedance measurements were impossible).

In Table 2 the minimum times at which the first signs of degradation became visible in the accelerated tests are compared with the results after 7 months natural exposure.

In Table 3 the ranking of the paint systems applied to the ion-free and the sulfate contaminated surfaces is shown for the six test conditions described above.

The results in Table 2 and the rankings in Table 3 are based on visual (ISO) assessments of the coating damage after the corrosion tests and values of the coating resistance measured by EIS for the same conditions.

Table 4 presents the mechanical properties of the various systems that were studied.

The performance of the coatings from the tested systems in the selected corrosion conditions as based on the visual (ISO 4828/1982, Parts 1–6) evaluations after the tests and on the values of the mechanical properties are described below. The duration of the tests was 96 cycles unless degradation occurred prematurely (as indicated).

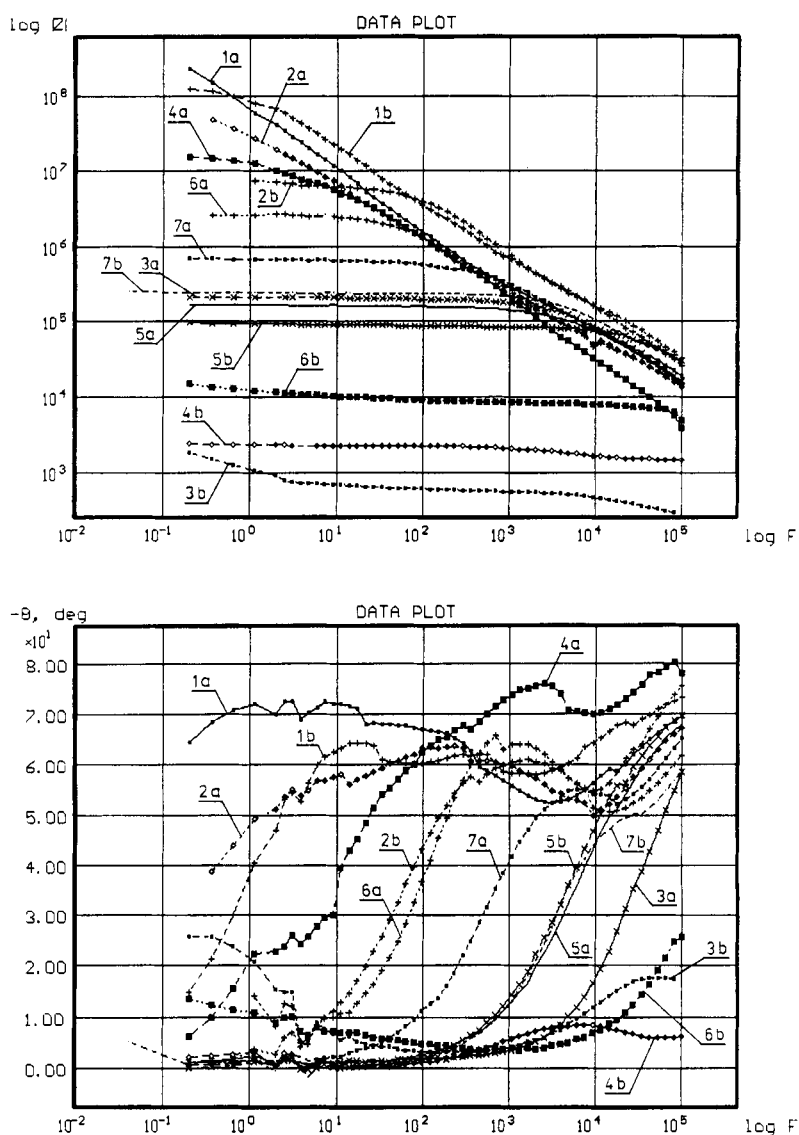


Fig. 1 (a) Bode plots for systems 1: 1a-7a — ion-free surfaces; 1b-7b — surface contaminated with chloride ions; 1 — before tests; 2 — Prohesion chamber; 3 — salt chamber; 4 — immersion in water; 5 — immersion in NaCl; 6 — rural corrosion site; 7 — industrial/urban corrosion site.

(a) Immersion in distilled water.

For the water-borne system (1) the corrosion resistance fell off badly when the substrate was contaminated with either ion; lack of adhesion was observed with sulfate ion contamination. Epoxy system (2) and polyvinyl system (3) showed reduced corrosion resistance when the substrate was contaminated with sulfate ions. There was a complete reduction in impact value for system (3). The corrosion resistance of the mixed system (3) did not appear to be significantly affected by the contaminants.

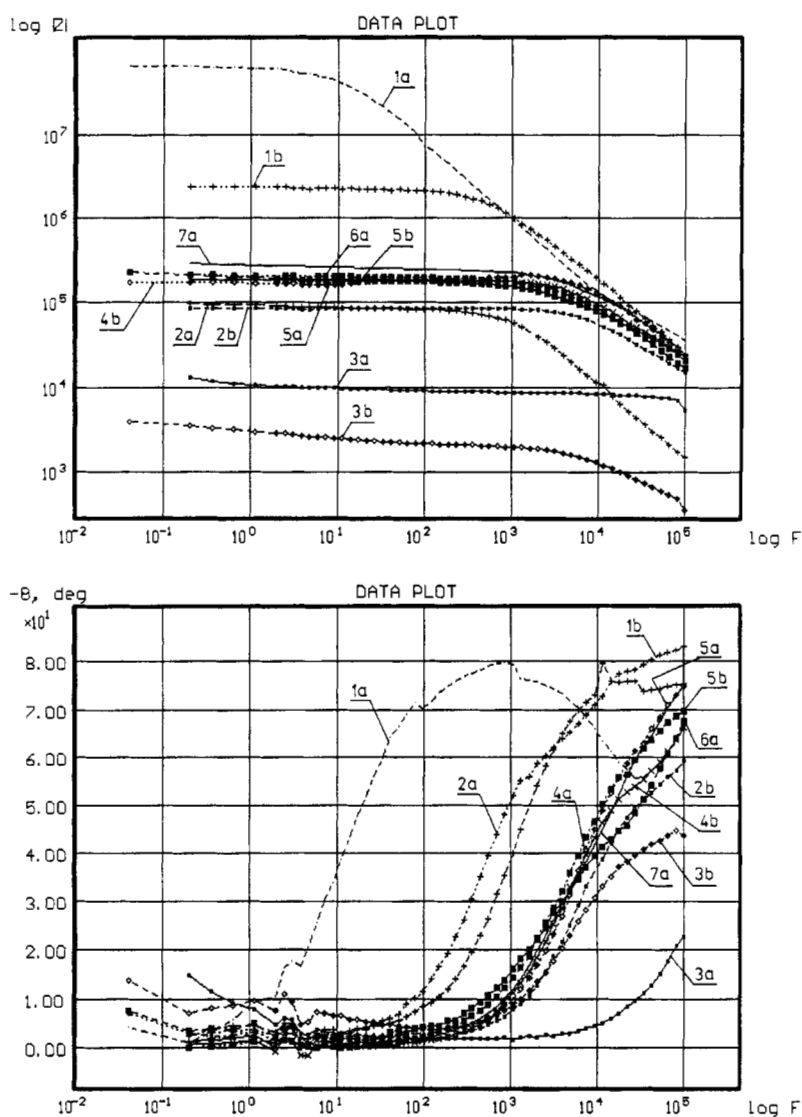


Fig. 1 (b) Bode plots for systems 3: 1a–7a — ion-free surfaces; 1b–7b — surface contaminated with chloride ions; 1 — before tests; 2 — prohesion chamber; 3 — salt chamber; 4 — immersion in water; 5 — immersion in NaCl; 6 — rural corrosion site; 7 — industrial/urban corrosion site.

(b) Immersion in 3% NaCl.

All systems were adversely affected by the presence of sulfate ions and particularly systems (1) and (2) which were also adversely affected by chloride ions. System (4) showed few differences between clean and contaminated surfaces.

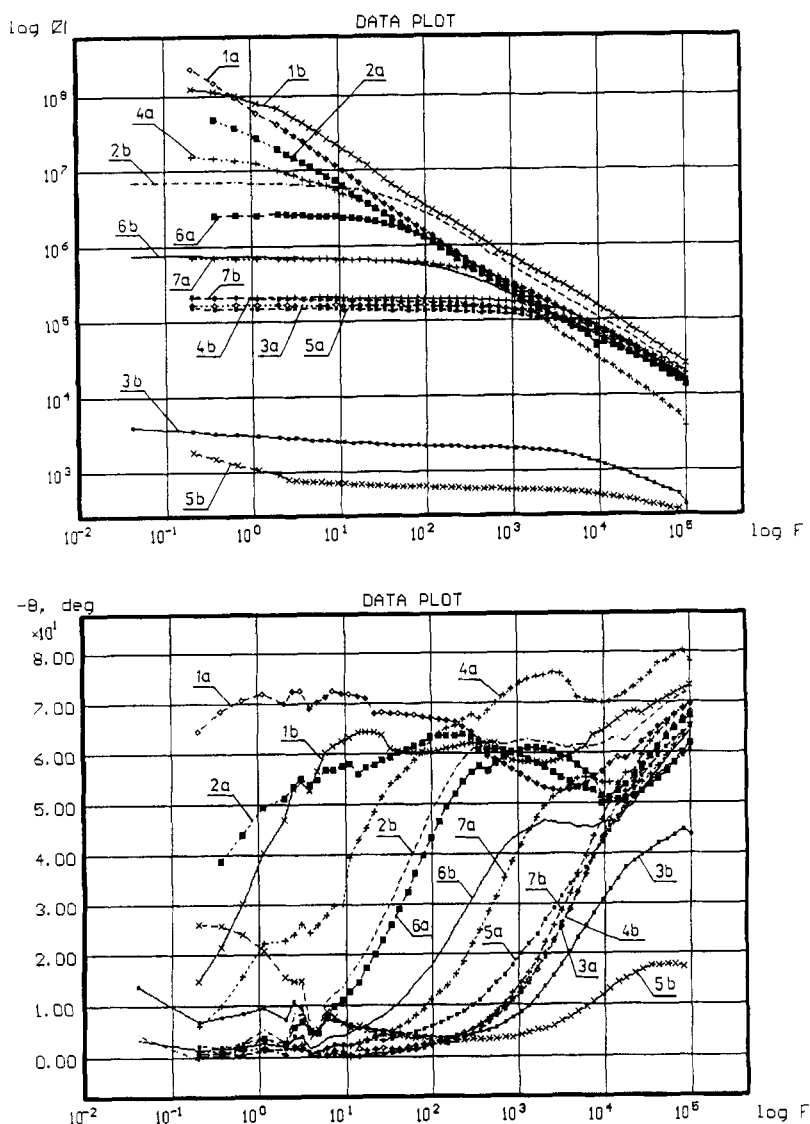


Fig. 2 (a) Bode plots for systems 1: 1a-7a — ion-free surfaces; 1b-7b — surface contaminated with sulfate ions; 1 — before tests; 2 — prohesion chamber; 3 — salt chamber; 4 — immersion in water; 5 — immersion in NaCl; 6 — rural corrosion site; 7 — industrial/urban corrosion site.

(c) Salt chamber.

System (1) immediately showed a high level of degradation for all surfaces and particularly for those with contamination. In fact, because of the degree of degradation the tests with this system were terminated at 16 cycles. For system (2) the behaviour was worse on the ion contaminated surfaces than on the clean surfaces. Thus, there were visible blisters and signs of corrosion but these were not so significant as for

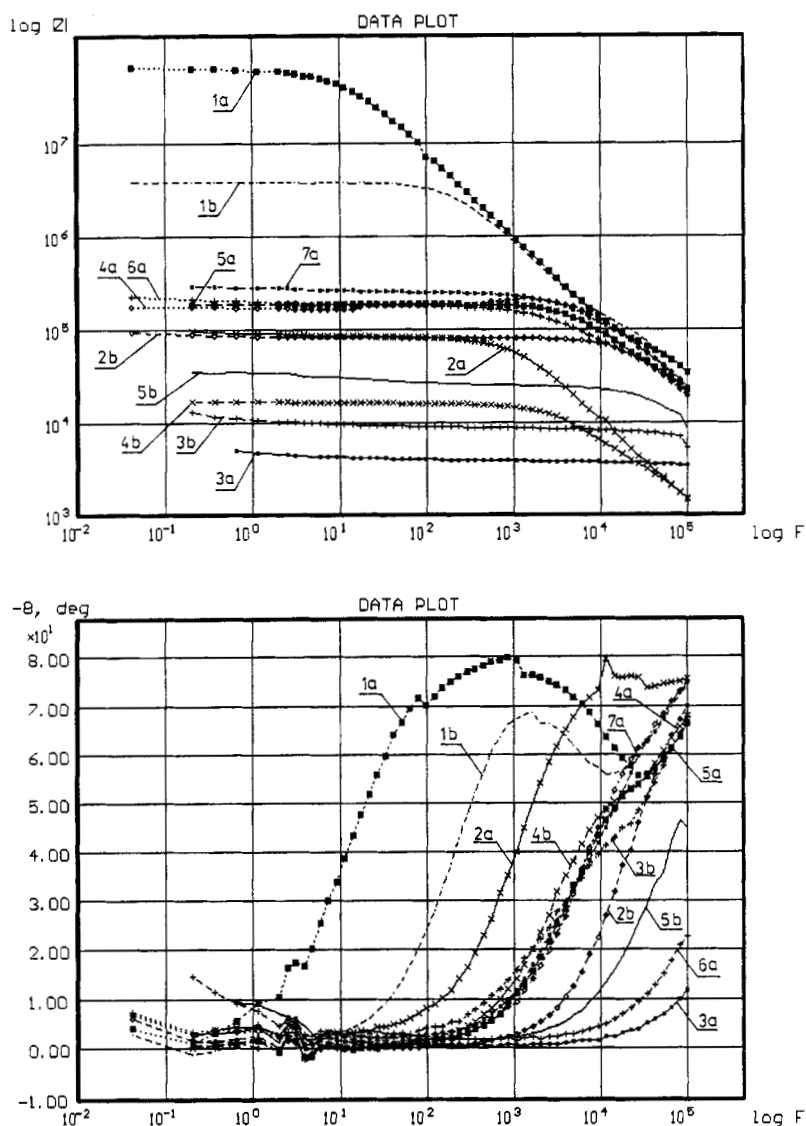


Fig. 2 (b) Bode plots for systems 3: 1a–7a — ion-free surfaces; 1b–7b — surface contaminated with sulfate ions; 1 — before tests; 2 — prohesion chamber; 3 — salt chamber; 4 — immersion in water; 5 — immersion in NaCl; 6 — rural corrosion site; 7 — industrial/urban corrosion site.

system (1). A lack of adhesion developed on surfaces with chloride ion contamination. System (3) was mainly affected by chloride ion contamination. However, for both contaminants the mechanical properties were worse than for the clean surface. System (4) showed the least intensive corrosion which developed weakly in the presence of chloride ions but more so in presence of sulfate.

Table 2. The minimum time (days) for the first evidence of degradation to become visible in accelerated tests and the results after 7 months natural exposure

Number of system (see Table 1)	Salt chamber (cycles)	Prohesion (cycles)	Water immersion (days)	NaCl immersion (days)	Rural atmosphere (7 months)	Industrial atmosphere (7 months)
Without ions						
1	5	34	30	50	nvd	nvd
2	15	16	62	>100	nvd	nvd
3	19	21	>100	>100	vd (blisters 2-S3)	nvd
4	35	34	>100	>100	vd (cracking 2)	vd (cracking 2)
For 15 μgcm^{-2} chloride ions						
1	3	27	6	3	vd (blisters 2 (S3))	nvd
2	3	5	42	45	nvd	nvd
3	5	21	>100	>100	vd (blisters 2	nvd
					(S2), cracking 2)	
4	26	7	>100	>100	vd (cracking 2)	vd (cracking)
For 50 μgcm^{-2} sulfate ions						
1	>3	16	6	1	nvd	nvd
2	10	21	10	6	vd (blisters 1 S4)	vd (Ri3)
3	16	21	10	40	vd (delamination)	vd (delamination)
4	16	21	76	76	nvd	nvd

nvd – no visual damage; vd – visual damage.

(d) Prohesion test.

System (1) showed lower resistance on contaminated than on clean surfaces — as was the case with the immersion tests — but compared to the systems (2) and (3) its resistance in absence of ions was higher and comparable to that of system (4). Systems (2) and (4) were adversely affected by chloride ions. System (3) behaved in a similar manner for all surfaces although its mechanical properties fell when applied to surfaces with both types of ion contamination.

Table 3. Ranking of systems applied to the ion-free and contaminated surfaces after corrosion tests (visual observation)

Type of test	The observed succession from the best to the worst		
	without ions	chlorides	sulfates
Immersion in water	4 = 3 > 2 > 1	4 = 3 > 2 > 1	4 > 2 > 3 >> 1
Immersion in 3% NaCl	2 = 3 = 4 > 1	4 = 3 > 2 > 1	4 > 3 > 2 > 1
Salt spray chamber	4 > 3 = 2 > 1	4 >> 1 = 2 = 3	3 = 4 > 2 > 1
Prohesion chamber	1 > 4 > 3 > 2	1 > 3 > 4 > 2	2 = 3 = 4 > 1
Rural atmosphere	1 = 2 > 3 > 4	1 = 2 >> 3 = 4	1 = 4 > 2 >> 3
Industrial atmosphere	1 = 2 = 3 > 4	1 = 2 >> 3 = 4	1 = 3 > 2 >> 3

Table 4. The results of mechanical testing of the investigated systems (1–4 ion-free; 1a–4a contaminated with sulfate; 1b–4b contaminated with chloride)

System	Before tests		Salt spray		After 16 cycles					
					Prohesion		Immersion in H ₂ O		Immersion in 3% NaCl	
	Imp. cm	Adh.*	Imp.	Adh.*	Imp.	Adh.*	Imp.	Adh.*	Imp.	Adh.*
1	50	1	50	1	50	1	20	1-2	50	1
1a	50	1	50	1	50	1	45	1-2	50	3-4
1b	50	1	50	1	50	1	30	4	15	3-4
2	40	1-2	25	1-2	15	1-2	5	2	5	1-2
2a	30	1-2	15	3-4	20	1-2	15	2	20	2-3
2b	25	1-2	15	1-2	15	1-2	5	2	5	2
3	45	1	30	1-2	15	2	30	1-2	15	1-2
3a	40	2	15	3	5	2	15	2-3	5	2
3b	10	1-2	0	2-3	0	2-3	0	2-3	0	2-3
4	45	1	10	1-2	10	1	10	1	10	1
4a	45	1-2	10	2-3	5	1-2	10	1-2	5	1-2
4b	10	1	10	2-3	10	1	10	1-2	10	1

*Scale according to ISO 2409/1992: from 1 (good) to 4 (bad).

(e) Rural atmosphere (7 month test).

The water-borne system (1) and the mixed system (4) showed no visual damage for clean and sulfate contaminated surfaces but blistered slightly in the case of surfaces contaminated with chloride ions. The epoxy system (2) remained unchanged on uncontaminated surfaces as well as on surfaces contaminated with chloride ions. Blistering occurred on surfaces with sulfate contamination. The polyvinyl system (3) blistered on the clean surface and had cracks when present on contaminated surfaces. The mixed system (4) had cracks on the clean surface and on that contaminated with chloride but not on that with sulfate — the same behaviour as in the rural atmosphere.

4. Discussion

The influence of ion contamination on the tested coatings was manifested mainly as blistering or cracking as a result of increased water osmosis. The sensitivity of the coatings to surface ion contamination differed depending on the coating system and the corrosion environment. On the basis of the results that have been obtained it is not possible to determine whether the degree of required surface cleanliness should be higher in some environments than in others. Thus, the significant differences in surface cleanliness dependence that were found in immersion tests with sulfate ion contamination were not so clearly marked with chloride ion contamination.

It should be pointed out that the ranking of the durability of the coating systems could be completely different if other types of tests were conducted. This is equally true for ion-free and for contaminated surfaces as the ranking is quite different in these two cases. The ranking for these systems therefore depends on the methods chosen (Tables 1 and 2).

For the majority of the tested systems the influence of surface contamination by sulfate ions was quite different from that of chloride ions. Thus, the epoxy system (2) which was insensitive to chloride ions, both in accelerated and field tests, experienced significant damage when surfaces were contaminated with sulfate ions.

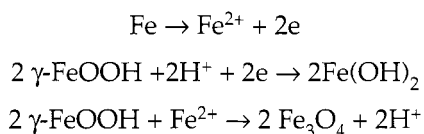
In the case of systems (1) and (3) which, in the majority of tests, presented the highest sensitivity to surface contamination, it appeared that the changes in coating resistance measured by EIS generally correlated with the visual assessment of coatings although there were some exceptions, i.e. in the salt chamber and water immersion results.

There was also no clear correlation between the results of the traditional accelerated tests that were used in our study and the results of tests at corrosion sites. Thus, the system (1), despite the considerable damage found in accelerated tests did not appear to experience this in a natural environment. Conversely, system (3), which behaved well in accelerated tests, was significantly damaged at both corrosion test sites.

It should also be pointed out that in these studies of ion contamination systematic errors could result either from uneven distribution of the applied ions and/or from corrosion processes starting immediately after their application to the metal surface. Attempts were made to exclude both sources of error in this work but their exclusion was not always possible.

Taking all the data from this work into account leads us to believe that the presence of ion contamination critically influences the mechanism of coating degradation. At present it is difficult to determine the mechanism of the coating damage. It is obvious that processes of osmotic water migration through coatings are of great importance and can lead in many cases to blistering and delamination of the coating. The coating degradation is also dependent on the types of binder, fillers/pigments and other additives and can increase if the substrate is acidified by ions resulting from binder hydrolysis.

The influence of ions, even on the highest quality coatings, as may be used on less well prepared surfaces, is well known and established. According to the following scheme of undercoat corrosion the cathode reaction is the reduction of lepidocrocite instead of the well known oxygen reduction [19].



In this case the corrosion rate does not depend on the rate of oxygen transport through the coating since the oxidising agent (rust) is under the coating where galvanic cells are then produced.

This is possible only when the electrolyte conductivity under the coating is high enough and this, in turn, depends on the level of the ion contamination. A change in the morphology of the rust and especially the production of spinels may explain the loss of adhesion between the coating and the metal surface. Each, or any combination, of these reasons could be the cause of the coating damage but it is necessary to know the sensitivity of different types of paints and their systems, i.e. in respect of their composition and the service environment, to surface contamination with ions.

5. Conclusions

Traditional accelerated tests are inadequate for estimating durability of protection in relation to tests at corrosion sites.

In most cases evaluation of coatings by EIS methods correlates quite well with visual ranking of coatings and may allow the duration of tests to be shortened.

Contamination with sulfate ions at the level of $50 \mu\text{gcm}^{-2}$ and chloride ions at $10 \mu\text{gcm}^{-2}$ adversely affected all the tested systems in this work in all corrosion test environments although the magnitude of the damage depended on the type of painting system.

Surface contamination with ions can lead to a change in the mechanism of the corrosion process with corrosion products at the surface of the metal assuming the role of oxidising agent in the cathodic process.

Widescale statistically significant investigations are necessary to draw proper conclusions on the effect of ion contamination of a metal surface on the performance of paint coatings.

These investigations should consider the effect of different aspects of surface ion contamination on the coating stability and should include:

- the type of ion contamination
- concentration of ions
- simultaneous presence of ions (possible synergism)
- distribution of ions
- the type of covering paint and paint properties
- thickness of coating
- the environment in which the paints are to be used
- the nature and type of surface on which the paint is applied.

These problems are important in the world community of those engaged in corrosion research and are on the agenda of ISO-/TC 35/SC12 sub-committee. The answers to these questions, which will take some years to produce, should form the basis for development of existing ISO standards which, because of their general nature do not fulfil the needs of paint producers and users.

There is, therefore, a need to carry out research of a more detailed character to ensure the optimal application of paints and anti-corrosion protection. In doing this, it is important to consider the overall economic effects, that is, by weighing the expected protection time against the associated costs to achieve this.

6. Acknowledgements

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Part 2

Zinc Coatings

Corrosion Resistance of Zinc Alloy Coatings

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ABSTRACT

The corrosion behaviour of chromated zinc and chromated zinc alloy (Zn-Co, Zn-Fe and Zn-Ni) coatings, obtained from different industrial plants, was studied by means of accelerated corrosion tests (salt spray test and d.c. electrochemical techniques) and field tests. The morphology of corrosion attack in the salt spray tests is also reported. At almost neutral pH values, all the chromated zinc alloy coatings show a better corrosion resistance than the conventional chromated zinc coatings. Acidity causes a decrease in the corrosion resistance of both chromated zinc and chromated zinc alloys; at low pH values the corrosion resistance of zinc coatings is higher compared to the alloy coatings. The results show that the corrosion resistance of Zn-Co and Zn-Fe alloys mainly depends on the formation of a particularly protective chromate conversion layer, while the corrosion resistance of Zn-Ni alloys is due to the particular corrosion mechanism.

1. Introduction

The increase in the guarantee period of vehicles and the requirements for higher corrosion resistance of metallic coatings compared to pure zinc have led to the industrial production of electrodeposits based on zinc alloys with metals of the 8th group (Zn-Ni, Zn-Co, Zn-Fe) [1, 2].

Amongst the zinc alloys, the Zn-Ni (8–15%) has been the most successful [3–5]. The Zn-Ni alloy coatings used on automotive bodies have performed well both in the perforation corrosion test [6], in which salts and muddy water can remain for a long time in hidden zones, and in cosmetic corrosion [10–13] caused by the removal of external paint, such as by pebbles. The corrosion resistance of Zn-Ni alloy essentially depends on the percentage of Ni [11]. With regard to the corrosion mechanism of these materials, many researchers agree with that proposed by Lambert [12]: thus, generally, Zn-Ni alloys are less active than pure zinc, have a lower corrosion rate and offer less galvanic protection to the steel. The preferential dissolution of zinc at the start of corrosion offers good galvanic protection. However, this leads to Ni enrichment of the alloy and a rise of corrosion potential towards more noble values, so that less cathodic protection is offered to the steel. During the preferential corrosion of the zinc phase, internal stresses increase giving rise to cracks over the whole coating, thus leaving the steel substrate exposed to the environment. The rapid increase in pH inside the cracks, due to the cathodic reduction of oxygen, causes precipitation of corrosion products which fill the cracks. The coating assumes a composite-like structure formed of corrosion products and a nickel enriched

alloy layer. This composite coating acts as a protection barrier [12–14]. The superficial enrichment of nickel on the surface of the corroded coatings was demonstrated by Short by scanning electron microscope (SEM) observation and by energy dispersive X-ray analysis (EDXA), after removal of the corrosion products [15].

The Zn–Co alloy coatings (Co <1%) are electrodeposited from chloride-based baths, using existing acid zinc plating plants [16–20]. A full range of compatible passivating baths have been developed to improve the corrosion resistance [15, 21, 22]. A decrease in the corrosion rate for zinc coatings containing 0.3% Co and 0.06% Cr compared to pure zinc in salt spray tests was found by Adaniya *et al.* [24, 25]; this was attributed to the fact that during the initial stages of corrosion, zinc dissolves rapidly, while cobalt and chromium dissolve rather slowly. The dezincification of the surface leads to an improved barrier layer which reduces the corrosion rate. This has been confirmed by Short [15] for Zn–Co alloys containing 1–10% Co.

Zn–Fe alloy coatings, already extensively used in Japan, are now being increasingly used in Europe and in North America. Two kinds of zinc alloy coatings have been developed: one with a low iron content (0.3–0.9 %) and the other with a higher iron content (15–25%). Alloys belonging to the first kind are obtained from free cyanide alkaline baths, using conventional alkaline zinc equipment. For this type of coating, the nonsilver black passivation by chromate treatment is particularly used [26]. The black colour is due to a fine dispersion of metallic iron and iron oxides in the otherwise green chromate coating matrix. In this case the conversion layer has to be considered to be like a composite material. The Zn–Fe alloy coatings with a higher iron content are obtained from acid baths (sulfate or chloride), in plating plants for continuous steel sheet production [9] or from alkaline baths containing triethanolamine as a complexing agent [27].

2. Experimental Details

Zinc and zinc alloy coatings were electrodeposited on mild steel discs (1 mm thick, exposed area 15 cm²) and bolts in rack and barrel industrial plating plants, respectively. After the electrodeposition all the samples were passivated. The experimental details for electrodeposition and passivation processes are reported in Table 1.

The composition of the coatings was determined by means of inductively coupled plasma spectroscopy (ICP); Table 2 shows some physical and chemical characteristics of the zinc alloys obtained from the rack plating plant compared to those of chromated zinc coatings.

The corrosion resistance of the coatings was studied with both field and laboratory tests. For the field tests, the galvanised steel bolts were placed on the underside of cars which were subjected to the 'For Life' test (Fig. 1). The car runs for 10 km on different roads and repeats the cycle 10 times; at the end the panels are removed and stored for 8 h in a humidity chamber followed by a further 8 h at room atmosphere. The whole process was repeated 40 times. The specimens were removed and inspected after a run of 8000 km and 640 h in a humidity chamber (corresponding to 2 cycles 'For Life'). Salt spray tests (NaCl 5%, $T = 38^{\circ}\text{C}$) and d. c. polarisation measurements

Table 1. Conditions of electrodeposition and passivation of zinc and zinc alloy coatings

	Electrodeposition	Passivation
Zn (rack plant)	NaCN 55; NaOH 80; Zn ²⁺ 22 g dm ⁻³ ; addition agent BL 295 J (Unisida Europlating) 18–20 °C; 1–2 A dm ⁻² .	CrO ₃ 2.6 NaCl 5 g dm ⁻³ ; 18–30°C; 10–30 s.
Zn (barrel plant)	ZnCl ₂ , 65; KCl 200; H ₃ BO ₃ 26 g dm ⁻³ ; addition agents Entorbrite (OMI Int.); pH 5.5; 1 A dm ⁻²	CrO ₃ 2.6; NaCl 5g dm ⁻³ ; 18–30°C; 10–30 s.
Zn–Co (rack plant)	ZnCl ₂ 80; KCl 210 ; H ₃ BO ₃ 25; Co ²⁺ 4–7 g dm ⁻³ ; addition agent Zicrolite K (OMI Int.) 28°C; 2 A dm ⁻² .	Udyfin 7748 (OMI Int.) 30mL dm ⁻³ ; 28°C; pH 1.8; 20 s
Zn–Co (barrel plant)	ZnCl ₂ 80; KCl 210; H ₃ BO ₃ 25; Co ²⁺ 4–7 g dm ⁻³ ; addition agent Zicrolite K (OMI Int.) 28°C; 1 A dm ⁻² .	Udyfin 7748 (OMI Int.) 30mL dm ⁻³ ; 28°C pH 1.8; 20 s
Zn–Fe (rack plant)	Zn ²⁺ 10; Fe ³⁺ 0.1; NaOH 130 g dm ⁻³ ; addition agent Zinfer (Unisida Europlating); 25°C; 2 A dm ⁻² .	Unifix Zinfer (Unisida Europlating) 40mL dm ⁻³ ; 20°C; pH 2; 60 s
Zn–Fe (barrel plant)	Zn ²⁺ 15; Fe ³⁺ 0.1; NaOH 130 g dm ⁻³ ; addition agents Zinfer (Unisida Europlating); 22°C; 0.8 A dm ⁻²	Unifix Zinfer (Unisida Europlating) 40mL dm ⁻³ ; 20°C; pH 2; 60 s
Zn–Ni (acid bath, rack plant)	NH ₄ ⁺ 110; Cl ⁻ 260; Zn ²⁺ 39; Ni ²⁺ 24 g dm ⁻³ ; addition agent: Zinni N (Unisida Europlating); 38°C; 2.5 A dm ⁻² .	Zinnifix (Unisida Europlating) 90 g dm ⁻³ ; 35°C; pH 1.9; 60 s
Zn–Ni (acid bath, barrel plant)	NH ₄ ⁺ 110; Cl ⁻ 260; Zn ²⁺ 39 ³ ; Ni ²⁺ 24 g dm ⁻³ ; addition agent: Zinni N (Unisida Europlating); 38°C; 1 A dm ⁻² .	Zinnifix (Unisida Europlating) 90 g dm ⁻³ ; 35°C; pH 1.9; 60 s.
Zn–Ni (alkaline bath rack plant)	Zn ²⁺ 10; Ni ²⁺ 1.5; NaOH 130 g dm ⁻³ ; addition agent: Zinni-Al (Unisida Europlating) 25°C; 2 A dm ⁻² .	Zinnifix (Unisida Europlating) 90 g dm ⁻³ ; 35°C; pH 1.9; 60 s

Table 2. Composition, chromium content and thickness of the studied coatings

Coating	Thickness (μm)	Composition (%)	Cr (mg cm^{-2})
Zn	18	Zn	0.03
Zn-Co	9	Zn-Co 0.8	0.02
Zn-Fe	10	Zn-Fe 1.1	0.08
Zn-Ni (acid bath)	12	Zn-Ni 9.9	0.05
Zn-Ni (alkaline bath)	8	Zn-Ni 12.3	0.07

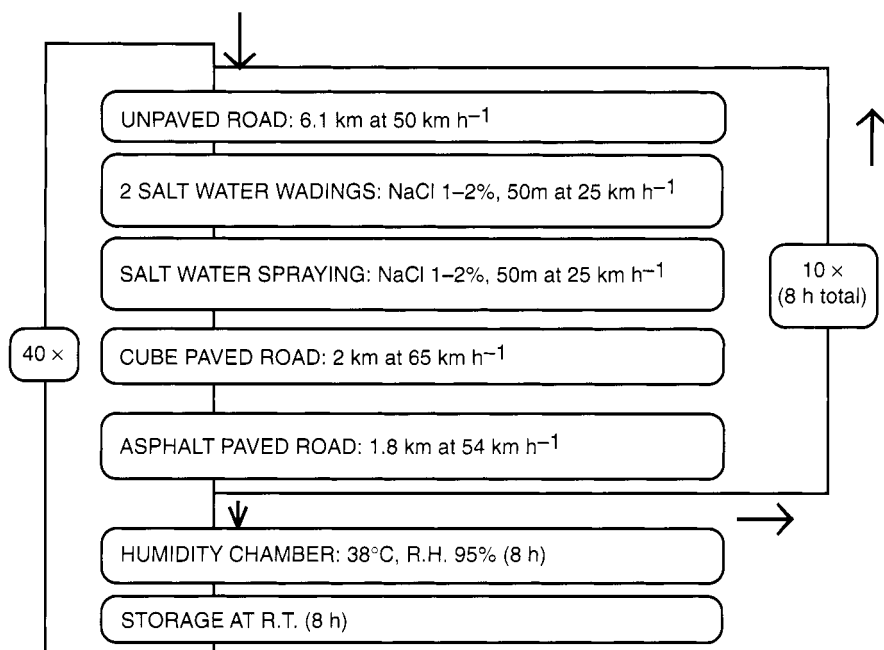


Fig. 1 Schematic diagram of the 'For Life' test procedure: total length of time in humidity chamber 320 h; length of an elementary daily cycle (10 km repeated ten times) 100 km; total length of test 4000 km; total duration of test 40 working days, with storage in a shed at room temperature during weekends and holidays.

at $25 \pm 1^\circ\text{C}$ in quiescent aerated 0.6M NaCl solution were conducted on the samples obtained from the rack plant. The electrochemical cell, the electrodes and the equipment used have been described elsewhere [4].

The microstructural characterisation was carried out using a scanning electron microscope (SEM) and surface microanalysis was performed by energy dispersive X-ray analysis (EDXA).

3. Results and Discussion

3.1. Morphology

Table 3 shows the preferential crystallographic orientation of the studied coatings obtained by X-ray analysis. The Zn–Co and Zn–Fe alloy coatings have the same structure as Zn, but with different crystallographic orientation, associated with the low cobalt and iron content respectively. As previously noted [11], the structure of Zn–Ni coatings mainly depends on the Ni content in the alloy; electrodeposits with about 10% of Ni have both η phase (pure zinc) and γ phase ($\text{Ni}_5\text{Zn}_{21}$), while those with 12% or more of Ni have only the γ phase.

Figures 2–6 show, by SEM observations, the microstructure of the coatings obtained. The chromated zinc shows a homogeneous and smooth structure with a thin network of cracks related to the chromated layer only (Fig. 2). The chromated Zn–Co coating appears smooth and very homogeneous (Fig. 3). The chromated Zn–Fe alloy coatings show a homogeneous surface, characterised by a network of cracks limited to the chromate layer [28] (Fig. 4). The chromated Zn–Ni alloy coatings (Figs 5 and 6) are both similar and show mamillar formations, surrounded by a dense network of cracks, present throughout the whole alloy layer [29].

3.2. Corrosion Resistance

In the ‘For Life’ test, as well as in circulating vehicles, the corrosion of the metallic components of cars is mainly caused by exposure to an aggressive environment. Figure 7 shows the surface morphology of some galvanised steel bolts removed from the underside of the car at the end of the test. On the bolts coated by chromated zinc with organic sealant, general corrosion with rusting at the steel substrate was observed (Fig. 7a). The chromated zinc coated bolts were protected with an organic sealant (generally used for automotive components, thickness 4 (μm) to reduce the reactivity

Table 3. Preferential chrystallographic orientation of the studied coatings obtained by X-ray analysis

Coating	Zn (002)	Zn (100)	Zn (411) (330)	γ (101)	Zn (102)	Zn (422) (600)	γ (103)	Zn Phases Present
Zn	—	100	—	12	—	—	—	Zn
Zn–Co	—	17	—	6	1	—	100	Zn
Zn–Fe	—	11	—	6	—	—	100	Zn
Zn–Ni (acid bath)	13	—	100	—	2	53	δ +Zn	
Zn–Ni (alkaline bath)	—	—	100	—	—	14	—	δ

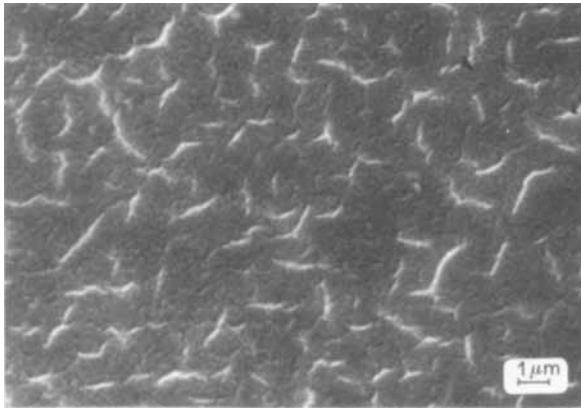


Fig. 2 Microstructure of chromated zinc.

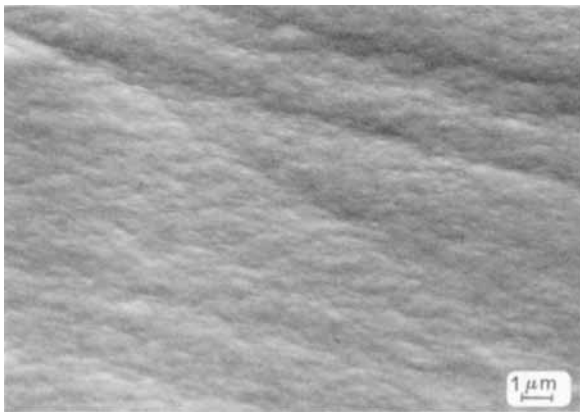


Fig. 3 Microstructure of chromated Zn-Co alloy.

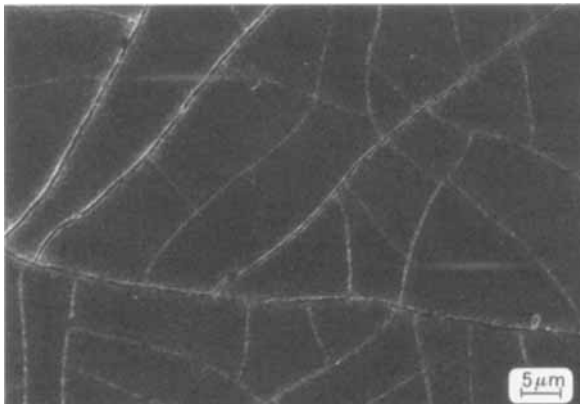


Fig. 4 Microstructure of chromated Zn-Fe alloy.

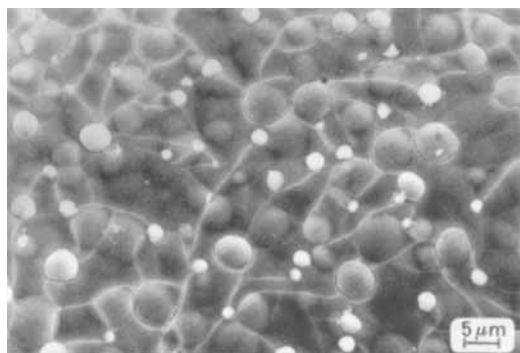


Fig. 5 Microstructure of chromated Zn–Ni alloy (acid bath).

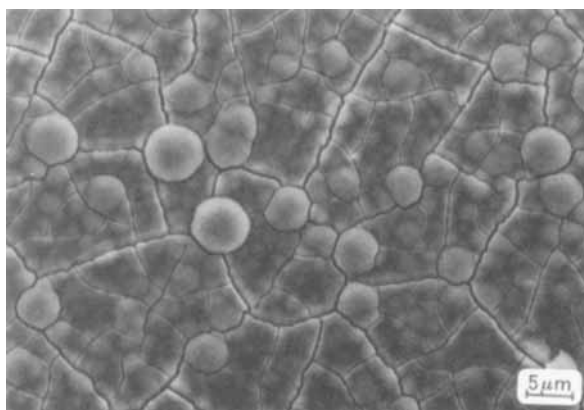


Fig. 6 Microstructure of chromated Zn–Ni alloy (alkaline bath).

of the coating by the strong effect of the barrier layer. All the alloy coatings studied show a considerable improvement in corrosion resistance (Figs 7b–d); corrosion products were almost exclusively white and only a slight red rust were observed.

Figure 8 shows the increase in white rust versus time during the salt spray exposure of chromated zinc and zinc alloy coatings obtained from the rack plant. To evaluate the effects of heat treatment on the corrosion resistance, some samples were heated at 120° for 1 h before testing. This treatment is thought to simulate the corrosion conditions which some zinc electroplated components are subjected to, for example in the car engine compartment. All the alloys show better corrosion resistance than Zn, both in the length of time up to the initial formation of white rust and the propagation rate. The best results were obtained with alkaline Zn–Ni and Zn–Fe alloys (curves e and g). The chromated zinc coatings subjected to heat treatment, show a remarkable decrease in corrosion resistance (curve a); no differences were observed in both Zn–Ni alloys while a slight worsening was observed for the Zn–Fe one (curve f). X-ray analyses carried out after exposure in the salt spray chamber, showed that for all coatings the main corrosion product was $\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2$.

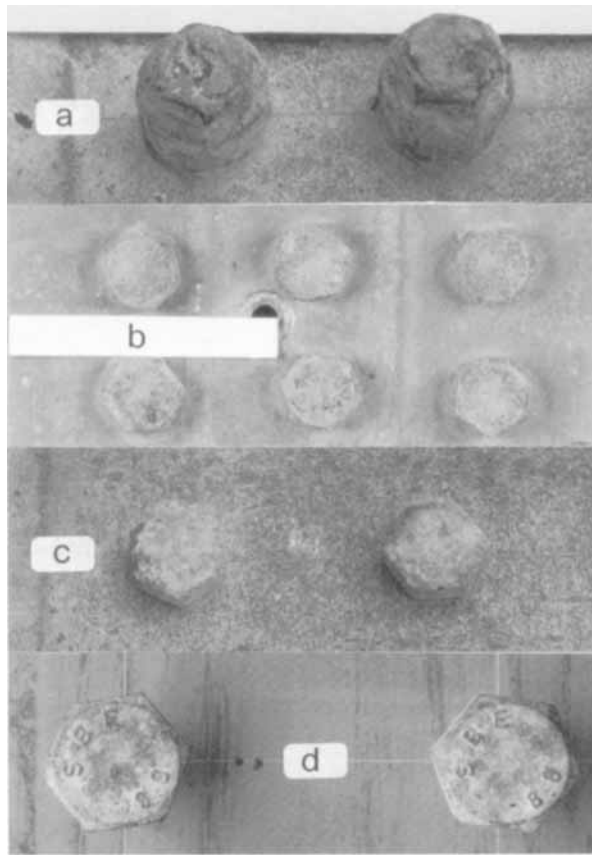


Fig. 7 Chromated zinc and zinc alloy coated bolts after the 'For Life' test. (a) bolts coated by chromated zinc with organic sealant; (b) chromated Zn–Co alloy coated bolts; (c) chromated Zn–Fe alloy coated bolts; (d) chromated Zn–Ni alloy coated bolts. All the samples were obtained by barrel plants.

The E_{corr} and R_p values obtained in aerated 0.6 M NaCl solution are reported in Table 4. Both E_{corr} and R_p values of Zn–Ni alloy obtained from alkaline bath are higher than the other coatings, as a result of the high Ni content; the values related to Zn–Fe coating, although better than for the zinc, are worse when compared to the other alloys, as opposed to what would be expected from the results obtained by salt spray tests. This is probably due to the different interaction between the chromating conversion layer of Zn–Fe coating with the two environments. In fact, the salt spray test simulates atmospheric corrosion with a high oxygen availability, while in the NaCl solution corrosion occurs in conditions of oxygen diffusion. Table 4 also shows the E_{corr} and the R_p values in slightly acidic 0.6 M NaCl solutions. The increase in acidity leads to a drop in corrosion resistance for all types of coating: at pH 3.0 the corrosion potential and the polarisation resistance values become almost similar for all coatings and the zinc alloys are less efficient with respect to zinc. This inversion of the R_p values is due to a rapid destruction of the chromated layer at low pH values

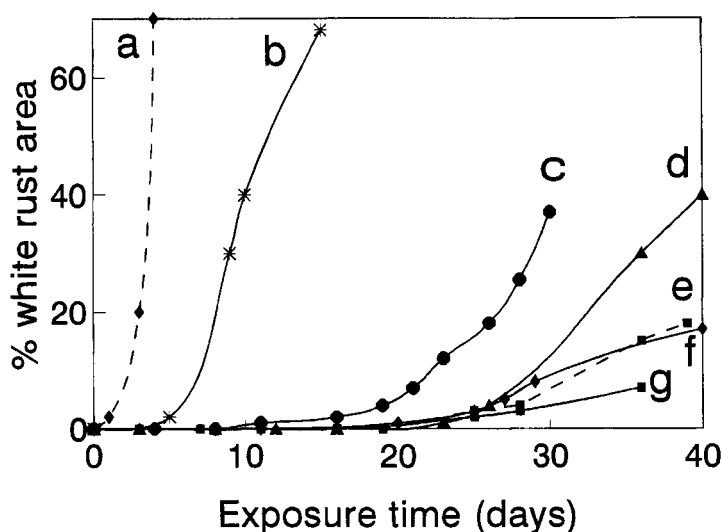


Fig. 8 Propagation of white rust during the salt-spray test on: (a) chromated zinc after heat treatment (1 h at 120 °C); (b) chromated zinc; (c) chromated Zn–Co alloy; (d) chromated Zn–Ni alloy (acid bath) with and without heat treatment; (e) chromated Zn–Ni alloy (alkaline bath) with and without heat treatment; (f) chromated Zn–Fe alloy after heat treatment (1 h at 120 °C); (g) chromated Zn–Fe alloy. The coatings were obtained in the rack plating plant.

and to the depolarisation of the hydrogen reduction, favoured by the presence in the alloys of metals more noble than zinc.

Figure 9 shows the anodic and cathodic polarisation curves, obtained in aerated 0.6M NaCl solution on chromated zinc and zinc alloy coatings. The slopes of the anodic curves of zinc and zinc alloys differ one from the other and to explain this

Table 4. E_{corr} and R_p values of the studied coatings in aerated 0.6M NaCl solutions at various pH

Coating	pH 6.4		pH 4.5		pH 3.0	
	E_{corr} (Ag/AgCl) (mV)	R_p (k Ω cm ²)	E_{corr} (Ag/AgCl) (mV)	R_p (k Ω cm ²)	E_{corr} (Ag/AgCl) (mV)	R_p (k Ω cm ²)
Zn	-979	37	-994	8	-1027	0.8
Zn–Co	-916	77	-970	15	-1011	1.0
Zn–Fe	-975	56	-982	10	-1019	0.5
Zn–Ni (acid bath)	-925	66	-930	18	-998	0.4
Zn–Ni (alkaline bath)	-765	147	—	—	—	—

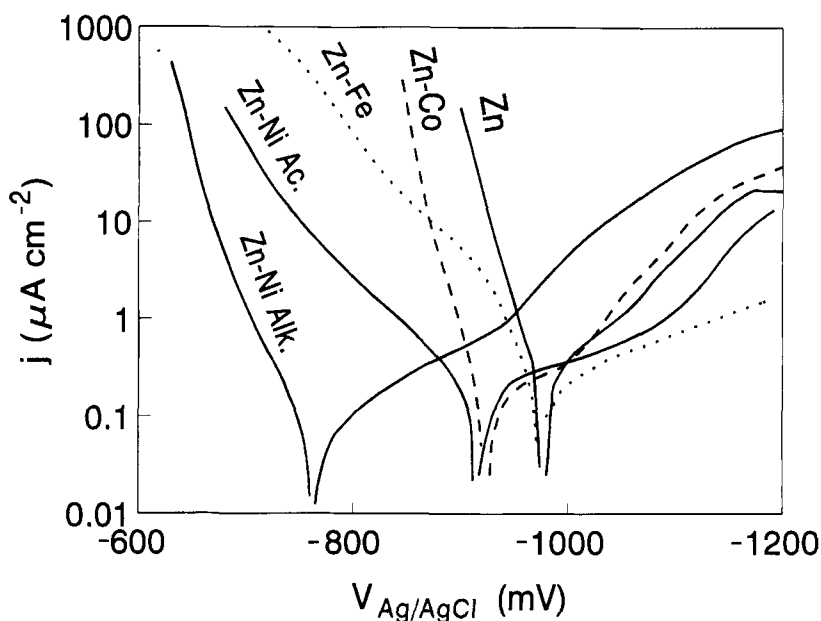


Fig. 9 Polarisation curves in aerated 0.6M NaCl solution (pH 6.4) for zinc and zinc alloy coatings obtained by rack plating plant.

behaviour further experimentation is necessary. In fact, the anodic trend of the curves depends principally on the breakdown of the chromated conversion layer which in some cases (such as in Zn-Fe alloy) has to be considered to be like a composite material since it contains a fine dispersion of metallic and oxide particles. The cathodic polarisation curves are characterised by a first region where the current density rises slowly before reaching the limiting current related to oxygen diffusion (about $15 \mu\text{A cm}^{-2}$); this behaviour is attributed to the barrier effect exerted by the chromate layers and depends therefore on the thickness and efficiency of the chromate layer [1, 2, 4]. The Tafel curves confirm the trend of R_p and E_{corr} values reported in Table 4: the Zn-Ni coatings obtained by the alkaline bath method behave better and correspondingly have a more noble free corrosion potential and a polarisation resistance higher than all the other coatings.

Figures 10–13 show SEM images of Zn and zinc alloy coatings after exposure to salt spray. The corrosion of the chromated zinc coatings proceeds by localised attack with rupture of the chromated layer and corrosion of the zinc. The corrosion products are voluminous (Fig. 10). Also, on the chromated Zn-Co alloy coatings, corrosion proceeds by localised attack with rupture of the chromate layer. The film breaks off from the Zn-Co substrate causing new cracks through which the aggressive solution can penetrate. On prolonging the exposure time, corrosion proceeds under the chromate layer and the corrosion products are far less voluminous than those formed on chromated zinc (Fig. 11). Figure 12 shows the surface of the Zn-Fe alloy coating after exposure in the salt spray chamber. As in the case of chromated Zn-Co, the corrosion products start to form at the cracks and at points where defects in the

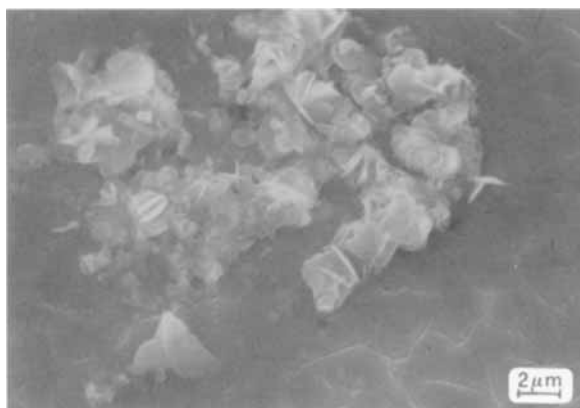


Fig. 10 Chromated zinc coating after 96 h of salt spray test.

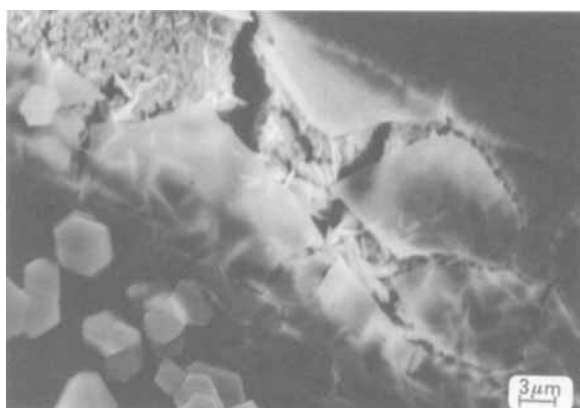


Fig. 11 Chromated Zn-Co alloy coating after 600 h of salt spray test.

chromate layer are present. As the products become more voluminous, the surrounding passivation layer is broken off and corrosion spreads by attacking the underlying material. On the chromated Zn–Ni alloys, the attack proceeds with the formation of a network of rather deep cracks which entirely cut through the zinc coating; during exposure, these cracks become wider and corrosion products deposit in their inner surfaces (Fig. 13). The corrosion products are thin and predominately localised at the cracks, because the inner surfaces are not protected by the chromates. Subsequently, corrosion expands to the external surfaces. These observations confirm the corrosion mechanism proposed by Lambert [12].

4. Conclusions

All the chromated zinc alloy coatings studied (Zn–Co, Zn–Fe and Zn–Ni), electrodeposited in industrial barrel or rack plants, show better corrosion resistance than conventional chromated zinc in both field and laboratory tests.

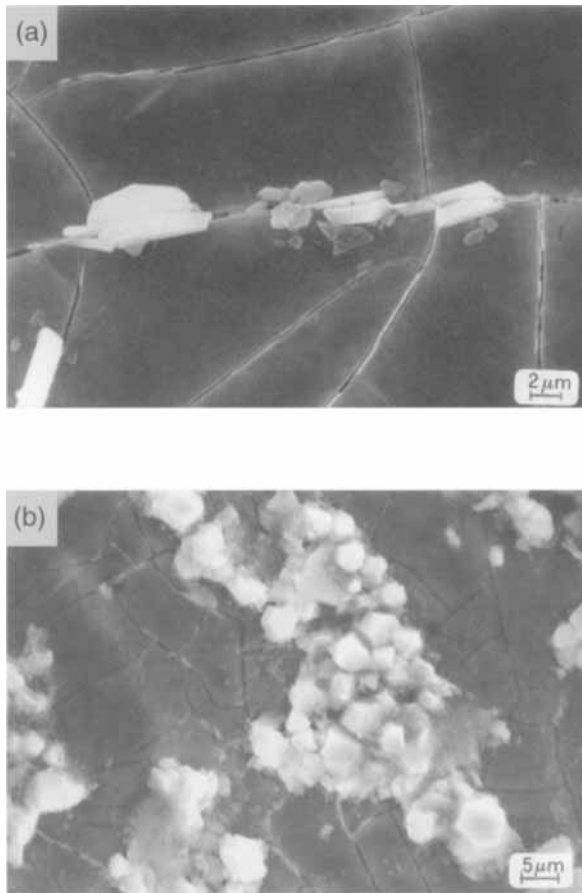


Fig. 12 Zn-Fe alloy coating after salt spray test. (a) 360 h; (b) 600 h, sample submitted to heat treatment (120°C for 1 h) before testing.

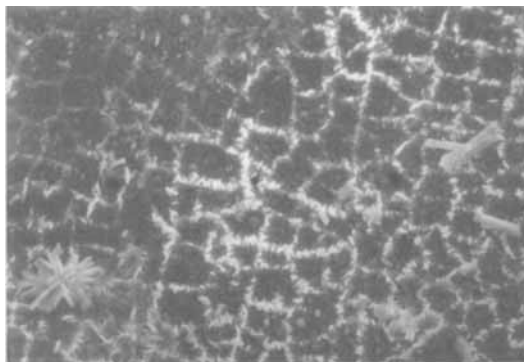


Fig. 13 Chromated Zn-Ni alloy coating after 960 h of salt spray test.

The corrosion resistance of chromated Zn–Co and Zn–Fe alloys is mainly due to the formation of a particularly protective chromate conversion layer, which increases the cathodic overvoltage. The presence of defects in, or low thickness of, the chromate layer decreases the corrosion resistance. The corrosion attack is triggered where there are cracks in the chromate layer and then proceeds by a breaking-off of the chromate layer. The corrosion resistance of the Zn–Ni alloys is generally attributed to the γ phase. The observations carried out by SEM confirm the corrosion mechanism proposed by Lambert, which proposes the formation of a composite formed of corrosion products and of a nickel enriched alloy layer. This composite coating acts as a protection barrier.

An increase in acidity leads to a decrease in the corrosion resistance of both chromated zinc and chromated zinc alloy coatings which become less efficient than chromated zinc at low pH values. The negative influence of acidic media can be attributed to the rapid destruction of the chromate layer and to the depolarisation of the cathodic reaction of hydrogen reduction. This occurs particularly on Zn–Ni alloys due to the lower overvoltage of hydrogen reduction on nickel

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Corrosion Protection of Sintered Metal Parts by Zinc Coatings

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ABSTRACT

Corrosion resistance of zinc coated sintered steel parts was studied by using electrochemical methods. A wide range of industrially produced coatings, including electroplated and hot dip zinc as well as Dacromet® and cold or hot zinc dust deposition treatments, were investigated.

Conventional corrosion tests were employed to compare corrosion resistance, whereas electrochemical test methods were used, to obtain a better understanding of the mechanisms which control corrosion processes and the corrosion rate.

The experimental results of this study showed protection of sintered steel by coatings is possible when the process is very well controlled; however, defects in the coating can always be present due to the substrate porosity, and these will be of different types and extents depending on the kind of deposition treatment employed. The proposed treatments are also discussed on the basis of some economical and technological parameters such as costs, tolerance requirements, chemical composition and density of the sintered parts.

With these facts in mind the use of sacrificial coatings can be recommended because of the possibility of cathodic protection operating at coating defects.

1. Introduction

The production of metal sintered components has increased greatly for many applications in circumstances where corrosion resistance is also required (e.g. in the engine compartments of cars, for pumping systems etc.). The mechanism of corrosion and protection of sintered metal powders reveals that the role of surface pores is an unusual and incompletely understood characteristic; the corrosion behaviour of sintered metal parts is mainly determined by the presence of the interconnected porosity which can act as pre-existing crevices [1].

Our previous work [2–4] has shown that the corrosion behaviour of sintered stainless steel can be improved by the optimisation of the process parameters (sintering time, atmosphere, etc.) or of the alloy composition (addition of copper [5], tin [6] etc.), but, nevertheless the performance of massive stainless steel is still noticeably better. Some further improvements can only be reached by closure of surface pores, for example, by a shot peening treatment [7].

The corrosion protection of less noble steels is traditionally obtained by various surface treatment methods such as painting, electroplating, dipping or spraying, which cannot always be easily transposed to sintered metal parts. In fact, because of the presence of the porosity, the usual cleaning or pickling pretreatments must be applied with particular care [8], and the treatment electrolytes for electroplating must

not be aggressive since they may remain entrapped in the porosity — alkaline baths generally being preferable [1].

However, a well-established practice exists for the protection of sintered Powder Metallurgy (PM) parts and several alternative methods are available, although little systematic work has been reported which considers in detail some of the important characteristics of these methods.

In order to reduce porosity, steam treatment has been used but has given only short term resistance to corrosion [9]. Copper electroplating, using an alkaline cyanide solution, has proved to be effective as a thin underlayer to seal porosity; when used before electroless nickel deposition it was shown to be the most effective treatment with respect to other pretreatments used [10]. Electroless nickel has been proposed by many authors but the corrosion resistance results are not always as good as expected, and some problems can arise from the cost [8,11]. Finally, cathaphoretic painting, epoxy powder coating or zinc coating obtained by dipping were also recently indicated as interesting methods of protecting sintered parts [8,12].

The aim of the present work is to study in detail a wide range of industrially produced zinc coatings, covering all the main proposed treatments, to evaluate the microstructural characteristics of these and, in particular, to point out the structural defects which can affect the corrosion behaviour of protected sintered metal parts. Zinc electroplating is one technique that can be proposed, possibly after impregnation of pores with resin or another appropriate sealant. Sherardising and mechanically deposited zinc (mechanical galvanising) can be applied to sintered pieces with unsealed open porosity. Another way for zinc deposition is by hot dipping and in this case pore impregnation is also not necessary.

2. Experimental

The samples studied in this work were obtained from industrial production; both the sintered substrates and the corrosion protection treatments were carried out by specialised factories. The sintered substrates used were:

- (A) Distaloy AE (4%Ni, 1.5%Cu, 0.5%Mo, 0.8%C, Fe bal.), nominal density 7 gcm^{-3} ;
- (B) atomised iron alloyed with 2%Cu and 1%C; nominal density 6.4, 6.6 and 6.8 gcm^{-3} ;
- (C) atomised iron alloyed with 0.3%C; nominal density 7 gcm^{-3} .

The samples were compacted using an uniaxial press and sintered in an endogas atmosphere following the usual sintering procedures. The following types of zinc coatings were studied:

- (a) zinc electroplated with a coating thickness of 13–15 μm ;
- (b) zinc hot dipped with a coating thickness of 40–55 μm ;
- (c) inorganic zinc in a chromate vehicle (Dacromet®), with a coating thickness of about 12 μm ;

- (d) zinc coating obtained by Sherardising with a thickness of about 12 μm ; and
- (e) mechanically deposited zinc with a coating thickness ranging between 12 and 18 μm .

Zinc electroplating is quite an involved process due to the porous structure of sintered iron parts. To avoid entrapment of plating bath constituents in the interconnected porosity, an impregnation pretreatment was conducted using a polyester resin, thus sealing the open porosity. Furthermore, to ensure the electrical conductivity necessary for the electrodeposition, the surfaces of the samples were polished by tumbling. To obtain an improved corrosion resistance, the zinc electroplated samples were submitted to a conventional 'yellow' chromatising treatment and then painted with a very thin varnish film.

For zinc deposition by hot dipping the substrates were treated by fluxing at 40°C and pH = 3 and then immersed in molten zinc at 460°C for 1 min. After zinc deposition the samples were centrifuged to homogenise the thickness.

Dacromet® is an aqueous dispersion of zinc flake in chromic acid. The zinc flake is in the shape of platelets, about 0.2 μm thick and 20–40 μm wide [12]. The coating method used for the small parts, after proper cleaning, was to bulk dip-spin. The parts were placed in a metal basket, dipped into the bath solution, then spun to remove excess coating material. No resin impregnation was necessary prior to coating. The coated parts were then heated in air to a peak metal temperature of about 300°C to achieve a good cure. To ensure full coverage and to cover marks caused by parts touching during bulk processing, three consecutive cycles of coat and cure were needed.

In the Sherardising process, the components, precleaned by shotblasting, were placed in sealed containers with zinc dust and an inert medium. The containers were rotated in a furnace for 2 h at 350°C. The coating obtained in this way consisted of iron-zinc alloys. The samples were then passivated by a chromate treatment.

Zinc was mechanically deposited after a thorough cleaning by shot blasting and a deposition of a thin layer of electroless copper. The sintered parts were then tumbled in a bath containing metallic zinc in powder form, impact media (glass or other chemically inert substances) and water. They were then separated from the liquid media, rinsed and dried. After zinc deposition some samples were submitted to a bronze coloured chromate conversion treatment.

The samples were studied by optical observations using both light and scanning electron microscopes; some observations were also carried out on fractured sections obtained by breaking the samples in liquid nitrogen.

All the produced samples were submitted to conventional industrial corrosion tests, such as salt spray and total immersion tests.

The salt spray test was carried out following the DIN 50021 standard at 35°C and using a 5% NaCl brine. For the total immersion test, a 3.5% NaCl solution was used. The samples were immersed for 30 days. The time to the first appearance of corrosion on the substrate was evaluated together with the percentage of corroded area at the end of the test.

The electrochemical tests were conducted in a conventional three electrode electrochemical cell, using a calomel electrode as reference and a platinum wire as counter-electrode.

Polarisation measurements were made in aerated 0.1M sodium chloride solution by using a PAR 273 potentiostat. Electrochemical Impedance measurements were obtained as a function of immersion time in an aerated 3.5% sodium chloride solution. The tests were performed using a Solartron 1255 Frequency Response Analyser and a PAR 273 potentiostat in the 100 kHz–1 mHz frequency range with a 10 mV amplitude of the sinusoidal voltage signal.

3. Results and Discussion

The zinc electroplated samples showed a homogeneous surface structure with an almost constant thickness. The quality of the coating is also well defined at the edge of the samples [13].

The ideal situation is when impregnation is effective: the resin seals the pore and the electrodeposited coating appears as a compact and continuous layer homogeneously covering the substrate (Fig. 1). Moreover, the coating/substrate interface appears well defined without pronounced discontinuities, which accounts for the effectiveness of the tumbling process in polishing the metal surface and consequently for a good coating substrate adhesion. The growth of the zinc coating is not always possible over the sealed pores (Fig. 2), particularly when the pore size is too large; in this case the formation of a zinc bridge over the pore is hindered due to the presence of a large non-conducting zone. The porosity of the substrate is not always completely filled by the impregnation treatment. In such cases it is possible to obtain an almost complete filling by the zinc coating, thus maintaining a good surface finish, or an incomplete filling. In the latter case the coating continuity can be compromised.

The samples coated with hot dipped zinc are characterised by a good coating substrate adhesion; the coating thickness is higher than the electrodeposited coatings

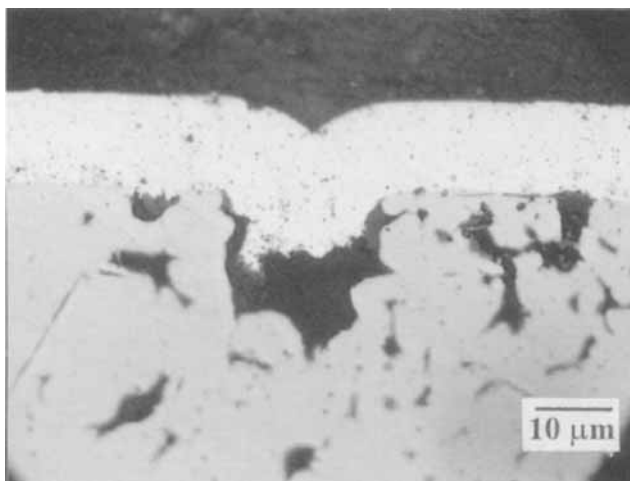


Fig. 1 Optical micrograph of the metallographic section of a zinc electroplated sample.

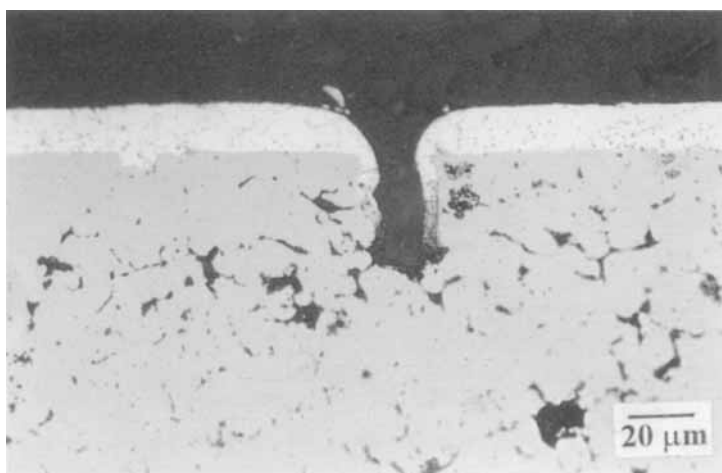


Fig. 2 Zinc coating discontinuities at sites of large size pores.

and ranges from 35 to 55 μm. Frequently the coating is thicker near the edges. Everywhere the coating is sufficiently uniform and defect-free.

The open surface porosity appears sealed (Fig. 3) and the coating level appears to be not completely flat, as shown in Fig. 4. In this optical micrograph, obtained after Nital 3% metallographic attack, the various zinc-iron alloys are evident.

Dacromet® coatings appear sufficiently well distributed, compact and continuous. Figure 5 shows the microstructure of the coating with the zinc flakes oriented parallel

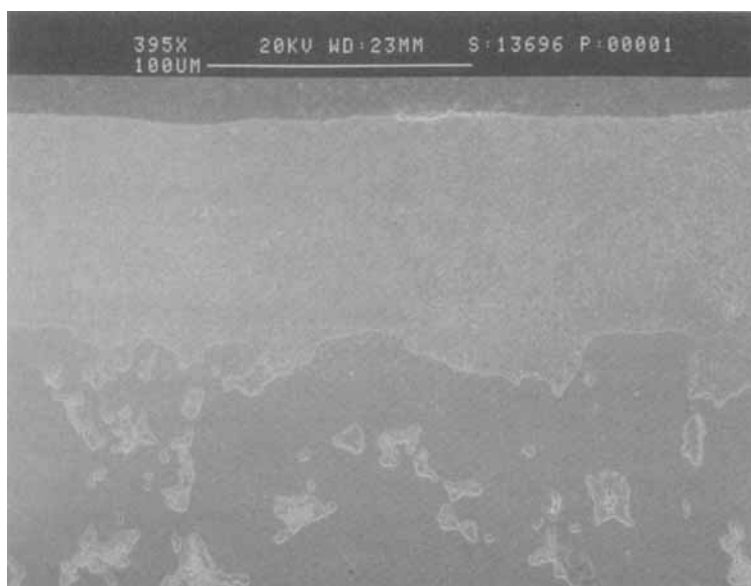


Fig. 3 SEM micrograph of the metallographic section of a hot dip zinc deposited sample.

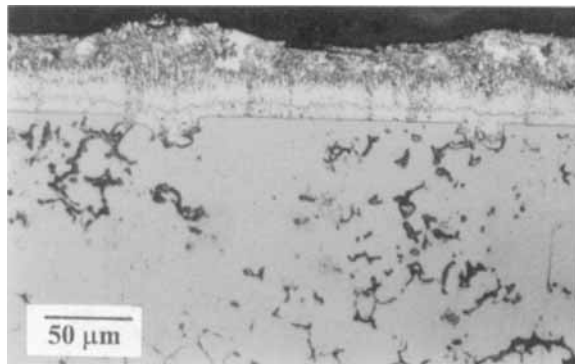


Fig. 4 Optical micrograph, obtained after Nital 3% metallographic attack, showing the various zinc-iron alloys in the hot dip zinc coating.

to the substrate surface. The coating substrate interface does not show the presence of any defects that would account for some adhesion loss. In fact adhesion tests performed using a pull-off technique showed good results, although sometimes giving problems of coating decohesion.

The homogeneity of the coating thickness is not as good as for electroplated and hot dip samples. In particular some problems can arise at the edges [13] where the coating can be completely absent. Hence, the effectiveness of this type of treatment is closely linked to the geometry of the metal parts which have to be protected. The Dacromet® coating can fill some large open surface pores, but it is more usual for it to cover the porosity like a bridge [13], leaving a flat surface aspect. Finding a coating defect, such as uncovered open porosity, remote from the sample edges is unlikely.

The coating obtained by the Sherardising process does not appear continuous

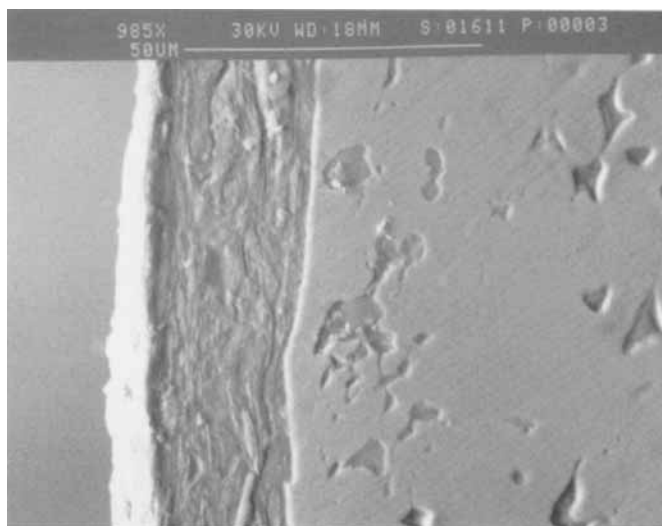


Fig. 5 SEM micrograph of the metallographic section of a Dacromet® coating.

and homogeneous over the whole surface. Some areas are unprotected, particularly at the sample edges [13] as observed for the previous coating. Figures 6 and 7 show the coating microstructure in two different zones. In the first, the zinc grains appear to be sufficiently compacted and sintered by the thermo-mechanical treatment; the EDXS analysis indicates that the coating is composed of an iron–zinc alloy as is usual for this type of treatment. On the other hand, in the second zone the zinc grains are only partially sintered showing large discontinuities between each other. The surface microanalysis in such a zone indicates a weak presence of the iron–zinc alloy. The frequent presence of the defects in this coating is thus due to the presence of this last type of microstructure which is explained by an incorrect Sherardising process (short treatment time, non-homogeneous temperature distribution). As observed for the Dacromet® coating, the large pores can in this case also be filled by zinc grains, but more frequently, the coating creates bridges over the surface porosity.

Coatings of mechanically deposited zinc appear very similar to sherardising coatings. In general the coating thickness is sufficiently uniform (Fig. 8) and open porosity of the substrate is sufficiently sealed. In some zones coating defects are evident. Thus, zinc powder appears to be badly compacted (Fig. 9) or the substrate is uncoated, especially at the sample edges.

4. Conventional Corrosion Tests

All the conventional tests were performed on a large number of samples for each type of surface treatment considered in this work. Whatever the type of test, the experimental data showed a small dispersion of the corrosion behaviour of the samples belonging to a certain type of coating and such behaviour was particularly uniform for the zinc electroplated samples. This result is accounted for by a good

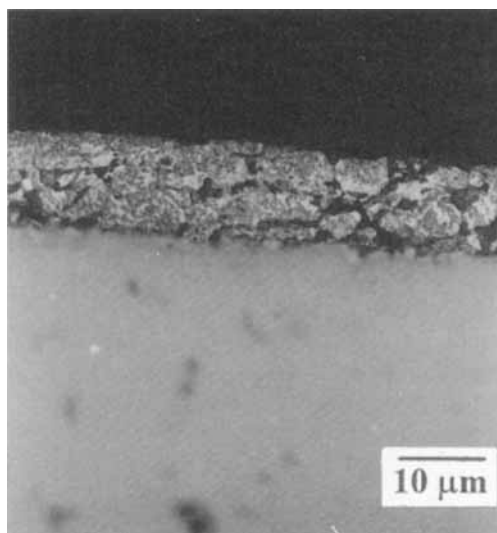


Fig. 6 Zone of a sufficiently good sintering of the Sherardising coating; sample etched with Nital 2%.

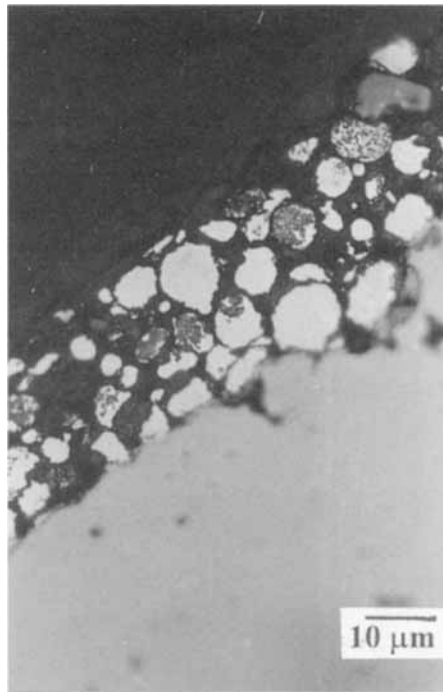


Fig. 7 Bad sintering of the zinc particles of the Sherardising coating; sample etched with Nital 2%.

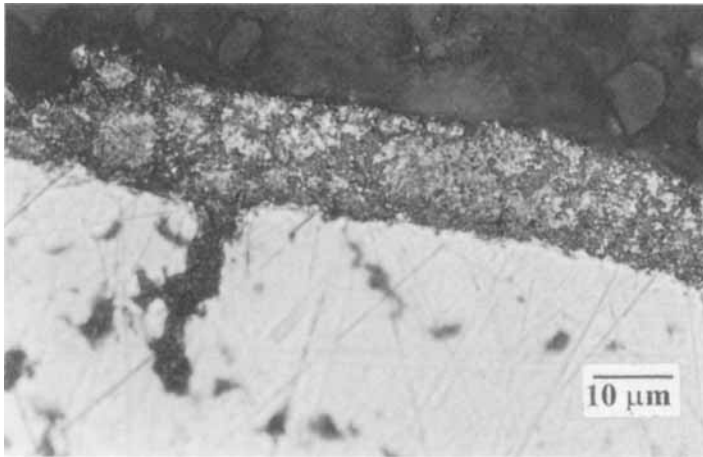


Fig. 8 Optical micrograph of mechanically deposited zinc coating corresponding to open porosity of the substrate.

homogeneity of the studied samples, which indicates a good control of the technological process. Only hot dip treated samples showed a large dispersion covering both the worst and the best results.

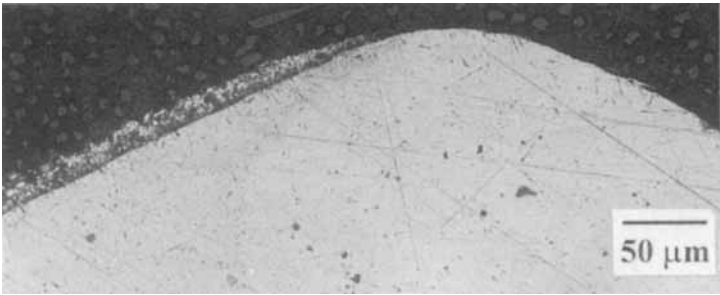


Fig. 9 Mechanically deposited zinc; absence of the coating on the sample edge.

The averaged results of the salt spray test are shown in Fig.10. Two clearly different behaviours can be noted. Electroplated and Dacromet® coated samples offer good resistance to salt spray test (in the range of 600–700 h or more). Among the electroplated samples only that with a reduced zinc thickness already showed corrosion after 600 h of test, but no differences were found as a function of the substrate steel. In general the electroplated samples had a better behaviour than that of Dacromet® samples; this can be attributed to the presence of the chromate layer which for some hours also hinders the formation of white rust. Some tests performed on sintered metal substrates containing various amounts of copper coated with Dacromet® treatment showed a reduced corrosion resistance on increasing the copper content in the substrate.

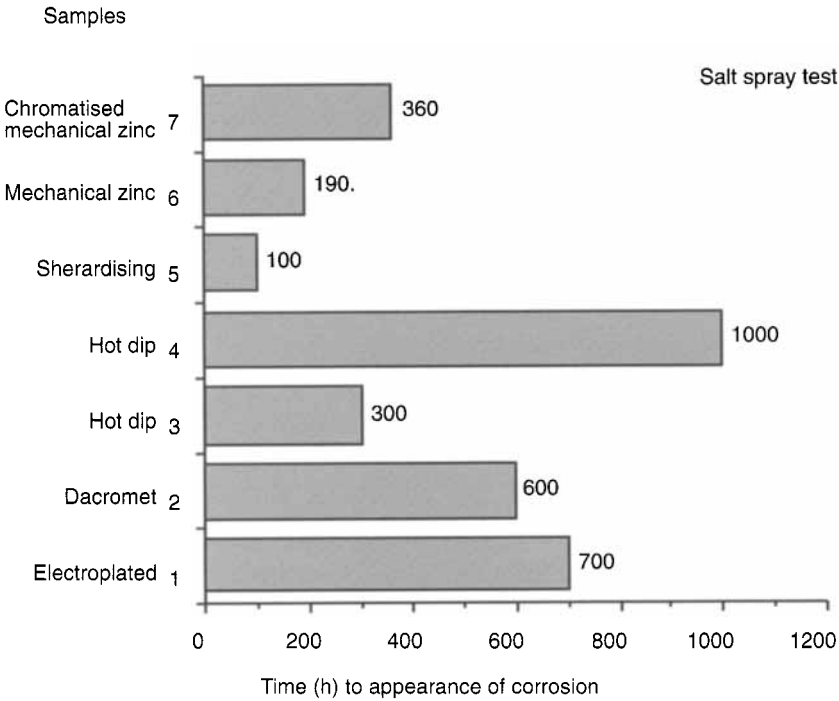


Fig. 10 Results of the salt spray test.

The sherardising and mechanically deposited zinc treatments clearly show the worst behaviour (less than 200 h resistance). The samples treated using the hot dip method show a variable behaviour which is accounted for by a non complete optimisation of the treatment procedures. In fact, due to the low density of the sintered pieces they can float over the melted zinc bath and sometimes can stick to each other.

The total immersion test results are in general agreement with the salt spray data (Table 1). In particular, the differences between different treatments are still evident, electroplated and Dacromet® samples behaving better than the other samples, apart from the variable behaviour of hot dip zinc. In order to justify the particularly good behaviour of samples treated in this way, it must be remembered that the coating thickness of these samples is about twice the thickness of the other samples. This type of test highlights the different corrosion behaviour of Dacromet® coating with respect to electroplated zinc; the presence of defects at the sample edges stimulates the corrosion in the former.

5. Electrochemical Tests

Only the treatments showing the best behaviour were studied with electrochemical techniques [14].

Figure 11 shows the anodic polarisation curves of electroplated zinc, hot dip zinc and Dacromet® samples, obtained in a 0.1M NaCl solution. The anodic behaviour of the different samples is similar showing the activation of the zinc anodic processes. Dacromet® coated samples show higher currents which can be due to a wider microscopic surface resulting from the high surface roughness. However, the polarisation curve of the Dacromet® coating shows at the higher polarisation a current, which is remarkably lower than that with a zinc electroplated coating; this trend can be attributed to the chromate component of such a coating which probably becomes more significant during anodic dissolution.

Table 1. Experimental data from the total immersion test. Column two shows the time of first attack on the substrate; column three shows the percentage of rusted area after 30 days of immersion

Sample	Rusting time (h)	% After 30 days
Zinc electroplated	360	3
Hot dip zinc	80	30
Hot dip zinc	700	2
Dacromet	205	7
Mechanical zinc	150	22
Sherardising	160	25

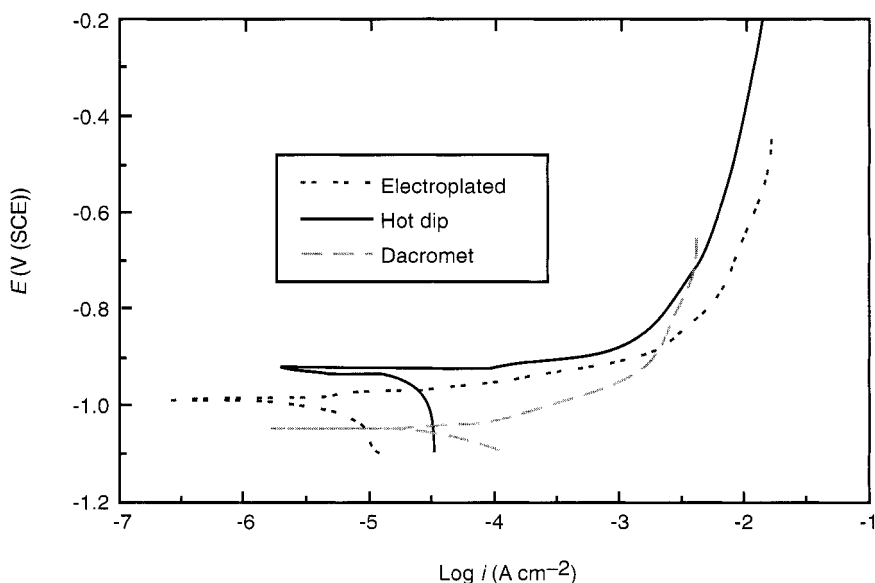


Fig. 11 Anodic polarisation curves of electroplated zinc, hot dip zinc and Dacromet® samples, obtained in a 0.1M NaCl solution.

The electrochemical behaviour of zinc electroplated sintered steels is represented, as a function of time, in Fig.12. The impedance diagram at the first hours shows two capacitive loops: the high frequency one can be related to the chromated layer which acts as a protection barrier, the low frequency is related to the faradaic impedance.

The impedance diagram changes with the immersion time. At first, the spectrum shape remains constant and decreases the impedance. The real component of the impedance at the lowest frequencies becomes $600 \Omega\text{cm}^2$ after 1 day. After 7 days the diagram shape changes; the first capacitive loop disappears almost completely because of the almost complete detachment of the chromate coating, whereas a diffusion tail appears related to the presence of voluminous corrosion products. The total impedance remains very low, showing an active dissolution of the zinc coating which exerts a good cathodic protection to the steel substrate at some defects associated with the substrate porosity. After about 17 days the impedance diagram changes further; only one rather depressed capacitive loop being present. The continuous deterioration of the coating leads to a very complicated surface situation with a simultaneous presence of zinc and zinc corrosion products, part of the chromate layer and an increasing substrate steel area. Starting from about 15 days of immersion, the total impedance begins to increase and after about 30 days reaches $1200 \Omega\text{cm}^2$; in the same time the corrosion potential shifts towards more noble values. The explanation of such a change in the impedance data is the increasing exposure of the steel substrate which contributes to the electrode electrochemical reactions. Starting from about 15 days some small rusted points appear highlighting the beginning of the steel corrosion in the more defective zones of the coating [14].

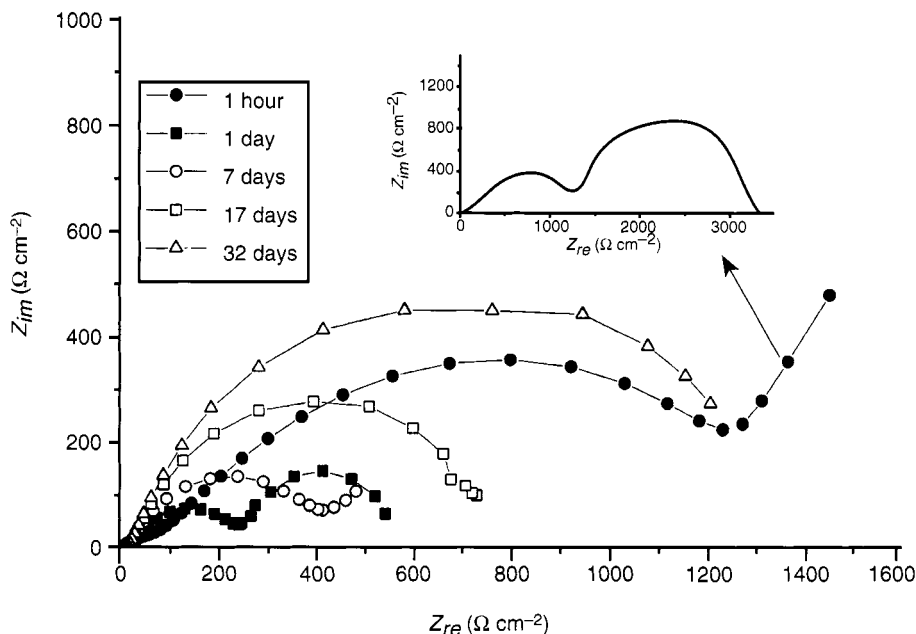


Fig. 12 Nyquist impedance plots of a zinc electroplated sintered steel during immersion in a sodium chloride solution.

The electrochemical behaviour of zinc hot dipped sintered steels is represented in Fig.13. In this case the impedance diagram shows one capacitive loop which is related to the faradic impedance. On initial immersion the real component of impedance is very low at about $200 \Omega \text{cm}^2$, showing the active dissolution of zinc. After 1 day a diffusion tail appears related to the presence of zinc corrosion products. With increase in the immersion time the total impedance begins slowly to increase but it remains very low. After 14 days the impedance reaches $1000 \Omega \text{cm}^2$ as a result of the presence of more protective corrosion products. After 28 days of immersion rusted points are not present and the coating is still protective. The corrosion potential remains at the typical value of zinc.

Figure14 shows the development of the impedance diagrams as a function of the immersion time for Dacromet[®] treated samples. The shape of the diagram after a few hours is quite complex, showing at least four time constants. The protective coating is, in fact, composed of the chromated zinc flakes and also, aluminium compounds which are present [13]. The total impedance at the lowest frequencies is very low ($100\text{--}200 \Omega \text{cm}^2$) and indicates rapid zinc dissolution, which can be further enhanced by the very rough surface morphology and by the presence of some defects on the surface — as observed by microscopical analysis.

The impedance diagram changes rapidly in the following days with two main features. The various time constants which characterise the system become more and more indistinguishable and the total impedance at the lowest frequencies increases noticeably: $1000 \Omega \text{cm}^2$ after 1 day, $5000 \Omega \text{cm}^2$ after 6 days, more than $10\,000 \Omega \text{cm}^2$ after 22 days. After 8 days of immersion it is already possible to observe some localised attack on the steel substrate, probably at coating defects as shown in the microstructural characterisation.

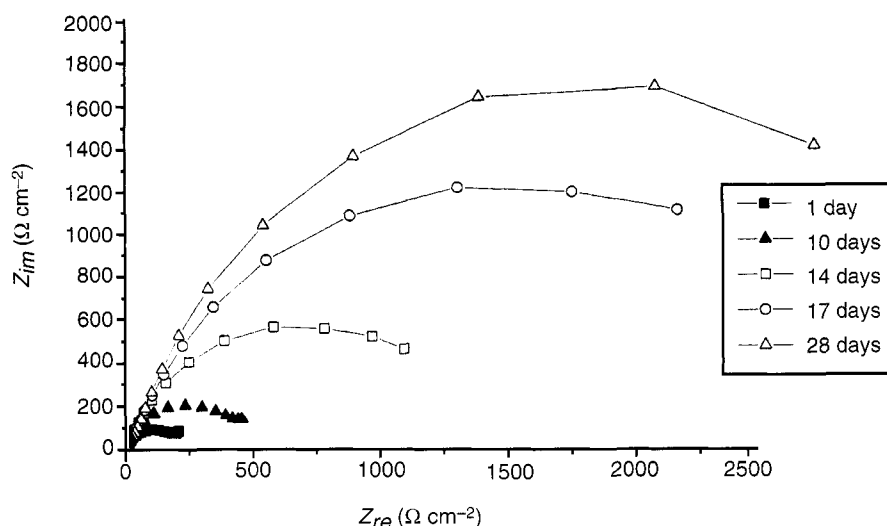


Fig. 13 Nyquist impedance plots of a hot dip zinc coated sintered steel during immersion in a sodium chloride solution.

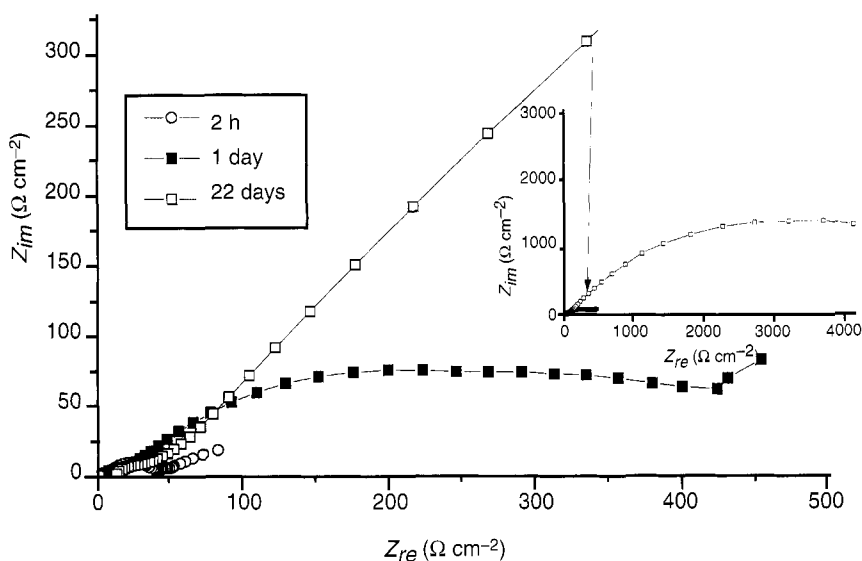


Fig. 14 Nyquist impedance plots of a Dacromet® coated sintered steel during immersion in a sodium chloride solution.

The impedance characterisation was shown to be very effective in determining the quality of the various zinc coatings.

With electroplated samples the corrosion behaviour is firstly determined by the barrier protection of the chromated layer. The high impedance data and the presence of two capacitive loops account for the effectiveness of such a layer; the cathodic protection of the zinc coating can then be evaluated from the changes in the impedance diagram, which is sensitive to the exposure of steel substrate areas. Different kinetics

of this development can be associated with coating thickness or the presence of a high defect density related to non-satisfactory pore impregnation or resin tumbling.

For the hot dipped samples the impedance is very low immediately after immersion, because the zinc is not protected by a chromated layer; however the presence of more and more protective corrosion products causes a total impedance increase with immersion time. The zinc hot dipped coatings appear to be more protective than the electrodeposited; such behaviour can be also due to the greater thickness of the hot dipped coatings.

6. Conclusions

The corrosion behaviour of the various coatings on sintered steel components depends strictly on the coating microstructure and on the presence of defects.

In particular, coatings obtained by electrodeposition show a better structure at the edges of components and better protect all those zones which are difficult to reach as a result of the component geometry. Sintered parts protected by dipping or by Sherardizing proved to be more defective at edges.

The presence of defects in the coated sintered part is mainly due to the effects of the substrate porosity on the coating growth. The zinc electroplated samples after impregnation were less defective both as a result of the absence of open pores and the absence of coating discontinuity at the edges. On the other hand, some problems may derive from impregnation by resin if the sample surface is not well cleaned by the removal of the resin from the external reactive surface.

The corrosion behaviour of the Dacromet® coated samples was determined both by the zinc flakes and by the chromate component with, the substrate preparation being of particular importance. Moreover, the cathodic protection can sometimes be insufficient to protect small defects.

The zinc electroplated samples showed good performances which are very similar to those of zinc coatings obtained on non-porous steel substrates. The process of producing this type of coating is quite complex and the use of the electrochemical impedance technique allows us to distinguish the effectiveness of the different stages of production, i.e. impregnation, tumbling, zinc plating and chromating.

Even the zinc hot dipped coating is good in the absence of defects and with good sealing by zinc of the pores. However, the coating thickness is not very uniform and can induce problems if the samples require a very strict tolerance.

Some further comments on the treatments considered in this work are summarised in Table 2 (overleaf).

7. Acknowledgements

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Table 2. Main features of the studied treatments

	ADVANTAGES	DISADVANTAGES	CRITICAL ASPECTS
ELECTROPLATED	• good thickness control • surface homogeneity • possibility of surface treatments	• involved process • costs • density of components • hydrogen embrittlement	• impregnation • tumbling • handling of components
HOT DIP	• thick thickness • no need of impregnation • treatment time	• not homogeneous thickness • strict tolerances • Fe-Zn phases control • geometry of component	• fluxing • floating of components • bath temperature • treatment time
SHERARDIZING	• low cost • easy process • no need of impregnation	• poor edge coverage • poor corrosion protection • inclusion of inert compound	• sintering • surface cleaning
MECHANICAL PLATING	• low cost • easy process • no need of impregnation	• poor edge coverage • poor corrosion protection • inclusion of inert compound	• tumbling • surface cleaning
DACROMET	• easy process • no need of impregnation • thickness control	• poor edge coverage • poor cathodic protection • chemical composition of the substrate (copper)	• surface cleaning • bath cleaning • multi step coating

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Electrocrystallisation of Zinc from Ammonium Chloride Solution in the Presence of an Additive

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ABSTRACT

Zinc electrocrystallisation, in presence of a commercial additive used in zinc plating, was used to determine the mechanism by which the additive acts. Before studying zinc electrocrystallisation, the mechanism of hydrogen evolution from a zinc-free solution with or without additive was studied in order to determine the electrode coverage by the additive. The zinc deposition process can be summarised as (i) hydrogen evolution on the bare steel substrate, rapidly stopped by a zinc underpotential deposition; (ii) a first zinc layer deposition without any influence of the additive, in the free holes of the adsorbed layer; (iii) zinc deposition under the influence of the additive.

1.1 Introduction

Although it is recognised that smooth and fine grain zinc deposits can only be obtained from additive-containing solutions, little is known about the mechanism by which they act, and, more precisely, how they modify the nucleation and growth of metal electrocrystallisation. However, some reviews on the mechanism of the action of additives are available [1–4]. They have shown that three mechanisms can be proposed. These can be described as (i) a blocking effect; (ii) a reactive adsorption and (iii) a complex formation. The main features of these mechanisms are as follows:

(i) In the blocking effect, the additive is strongly adsorbed on the surface and completely inhibits some sites available for charge transfer. The deposition mechanism is not modified and the reduction of the active surface depends on the relative coverage θ . Thus, if the adsorption simply results in the blocking of the electron source areas the extent of the active sites available for reaction decreases and the average rate of the reaction reduces in direct proportion. Changes in electrochemical parameters are not observed.

(ii) With reactive adsorption, the adsorbed species may enter the electrical double layer, displacing the potential and hence influencing the electrochemical reaction, which will usually be reflected in the change of the Tafel slope. The adsorbate is not inert but active. The adsorption must be of the chemical type resulting in a strong bonding. The moiety covered by the additive does not suppress the charge transfer but modifies the kinetic process. Two kinetic factors intervene: k for charge transfer

on the free moiety $(1-\theta)$ and k' on the moiety θ , covered by the additive, with two possibilities: $k > k'$ or $k < k'$.

(iii) With complex formation in solution, the ligand must be removed before the formation of adatoms and both the kinetics and the mechanism of electrodeposition are modified. It has been shown experimentally that the Tafel slope is higher when complexing agents are present in solution. A last possibility that is sometimes involved, could be the formation of a three-dimensional film which modifies the substrate.

Adsorption, even in the simplest case, is a displacement reaction, the adsorbate displacing molecules of solvent or ions of the base electrolyte from the surface. The surface coverage is therefore a result of a competition between several species for sites on the electrode surface. The water-metal interactions are influenced not only by the nature of the metal (the difference in hydrophilicity of metals is well known) but by the mono-crystal faces. In the case of chemisorption a strong dependence on surface crystallography is observed. On polycrystalline metals, the result is a non-uniform distribution of the adsorbed molecules that can result in holes in the adsorbed layer.

This paper reports on a study of the action of a commercially available additive on the mechanism of zinc deposition on steel. It is impossible to accept the rate of proton discharge being independent of an adsorbed organic layer, and recent results have shown that the hydrogen evolution reaction (h.e.r.) on steel is rapidly stopped by a zinc Under Potential Deposition (UPD) [5], suggesting that the same active sites are used for cation (H^+ or Zn^{2+}) reduction. These results substantiate the possibility of making a first approach to the role of an additive on zinc plating by studying the influence of this additive on the h.e.r. from a zinc-free solution. Several electrochemical methods were therefore used for studying hydrogen evolution and zinc electrocrystallisation. For hydrogen evolution three procedures were used: (i) potentiodynamic polarisation curves at two different scan rates to prove the effect of the additive on the h.e.r.; the results have shown the effect of the potential scan rate on the cathodic polarisation curves; (ii) from that, Tafel lines were determined potentiostatically by holding the potential until a steady state current was obtained; the duration of each polarisation was of several minutes, and sometimes hours; (iii) electrochemical impedance spectroscopy measurements were run to determine the double layer capacitance C_{dl} . For zinc electrocrystallisation the potential sweep method was employed using baths with and without the additive.

2. Experimental

A classic three-electrode cell was used and all the potentials were recorded with respect to a saturated calomel electrode (SCE). The blank solutions consisted of 5M NH_4Cl in absence or presence of an additive. The additive, Zeta-plus, referred further to as Zeta, was provided by the Continental Parker Society and was used at a concentration of 40 mL L^{-1} . The additive is a mixture of several organic compounds (polyethylene glycol, sodium benzoate, benzaldehyde compound, etc.). The zinc electrocrystallisation was studied from a solution containing 0.5M $ZnCl_2$ in 5M NH_4Cl in absence or in the presence of Zeta. All solutions were prepared in water treated by

a Millipore system. During zinc deposition, additive adsorption must be considered first on the steel substrate and then on the new zinc crystallites. Therefore, steel and a 10 μm zinc layer electrodeposited on steel were used as substrates. The steel substrate (35CD4) was polished with emery paper to a grade 1200 finish.

The equipment consisted of a EG&G-PAR Model 273 potentiostat and a microcomputer system capable of controlling the experiments, collecting data, and plotting them. The potential sweep experiments started from the rest potential of the substrate in solution and continued in the cathodic direction. Impedance measurements were made by superimposing a 2 mV sinusoidal voltage in the frequency range of $50 \text{ mHz} < f < 10 \text{ kHz}$ on the open circuit potential after 20 min in free immersion. Modelling was done using the Equivalent Circuit program of Boukamp. The capacitance change as a function of immersion times was tested at a significant high frequency (1 kHz) to obtain a capacitive circuit.

3. Results

3.1. Hydrogen Evolution Reaction

3.1.1. Cathodic polarisation curves and Tafel lines

The adsorption of organic molecules is relatively slow, except on mercury, and the adsorption steady state can be reached in several minutes. This time factor is seen in Fig. 1 which shows, for a solution with additive, the effect of the sweep rate on the hydrogen evolution kinetics on steel. Curve (b) from a bath with additive, obtained at 20 mV s^{-1} is similar to curve (a) without Zeta, but with a slightly lower current. Curve (b') was recorded at 0.5 mV s^{-1} from an additive containing solution and shows a strong inhibiting effect on h.e.r. From that the Tafel lines were determined by the potential-step method. At each potential the system was held for a time long enough to reach a steady state. Figure 2 presents the Tafel plots with (curve b) and without (curve a) Zeta, on steel. The straight lines are parallel and exhibit a slope of 0.247 V/decade , but the current decreases significantly in the presence of Zeta. These results suggest that there is a strong inhibiting effect without changing the hydrogen evolution mechanism. Since the h.e.r mechanism does not change, the inhibiting effect is merely due to a blocking process of the metal electrode. The coverage can be therefore determined by the simple relationship: $\theta = 1 - J_{\text{add}}/J$ (where J and J_{add} are the current densities for the Zeta-free solution and for the Zeta containing solution respectively), which gives $\theta = 0.75$.

Figure 3 shows the results of h.e.r on zinc with (b) and without (a) Zeta. The slope of the Tafel line for the additive free solution is 0.115 V/decade . For Zeta containing solution, the slope of the Tafel line was 0.195 V/decade , and the line intersects the other without Zeta at about -1500 mV . The change in the Tafel slope indicates a change of the mechanism, and the additive effect is not a blocking effect of the active sites. Therefore, the coverage cannot be determined by the above relationship between the current obtained with and without Zeta.

3.1.2. Electrochemical Impedance Spectroscopy (EIS)

Capacitance measurements were run only at the rest potential. The spectra for steel

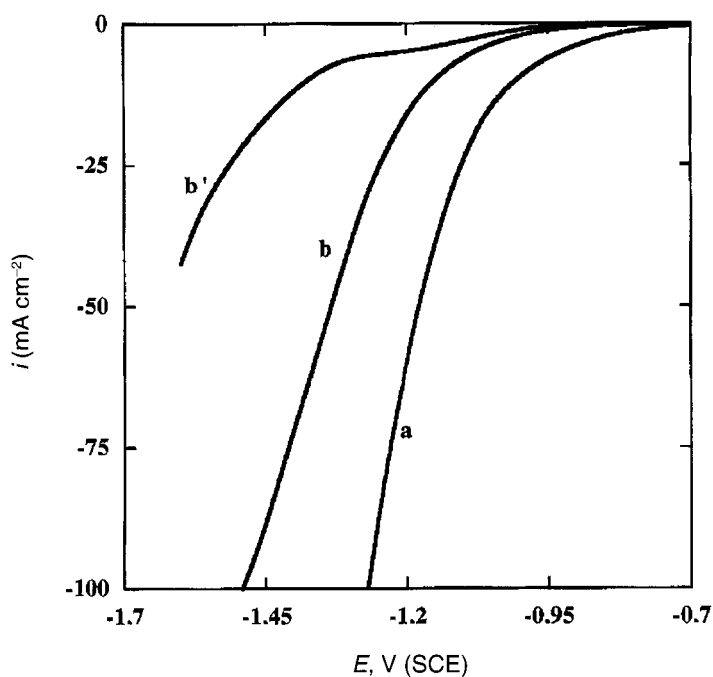


Fig. 1 Linear sweep polarisations on steel from 5M NH_4Cl with Zeta (b and b') and without Zeta (a). Curves a and b were obtained at 20 mV s^{-1} , a' and b' at 0.5 mV s^{-1} .

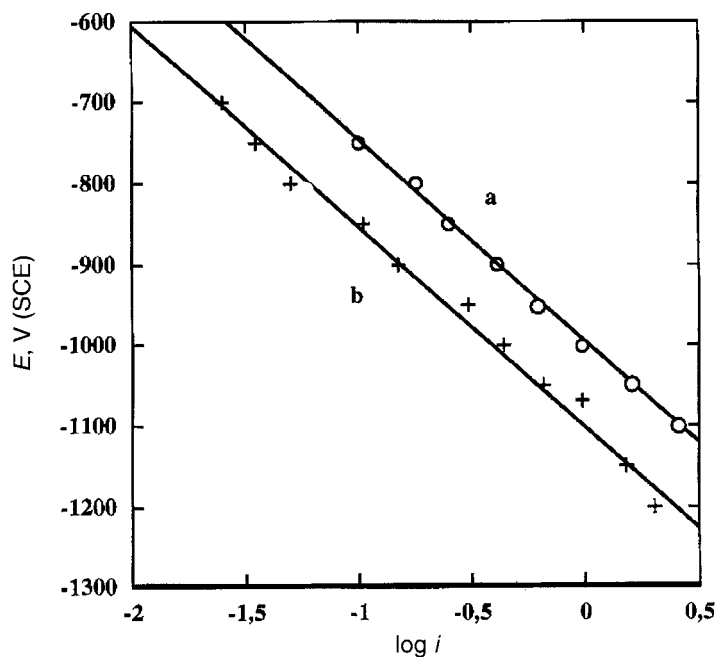


Fig. 2 Tafel line on steel in 5M NH_4Cl with (b) and without (a) additive.

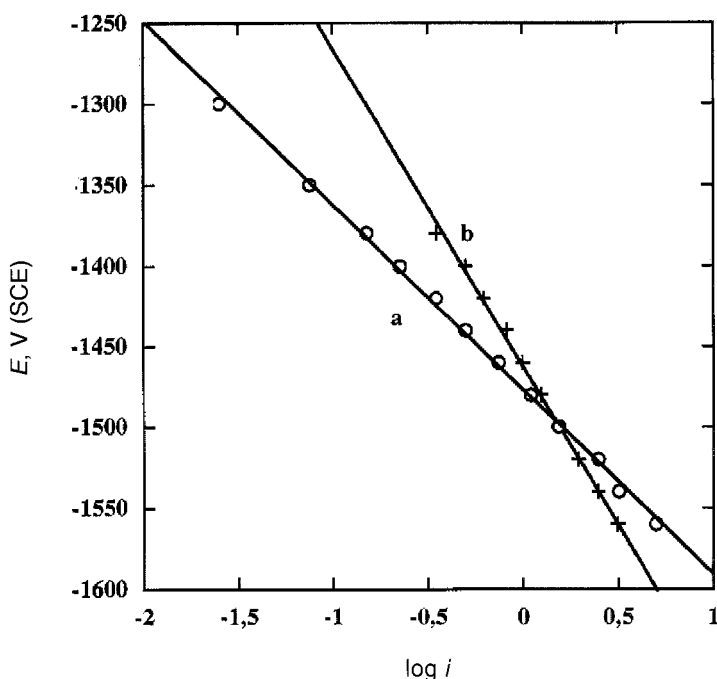


Fig. 3 Tafel line on zinc in 5M NH_4Cl with (b) and without (a) additive.

and zinc are dominated on a Nyquist plot by a semi-circle (Figs. 4 and 5), and the real data fitted with the simulated data for a chemisorption model, which is the Randles-type circuit with an impedance element added in series with the charge transfer resistance. In Fig. 6 the capacitances of steel and zinc versus the immersion time are reported for baths without and with Zeta. On steel, the capacitance in the additive-free solution (curve a) increases with time, which is likely due to a corrosion reaction that increases the active surface of the substrate. In the solution with additive (curve a'), the capacitance was lower and this value could be related to an adsorption of the additive on the electrode surface [6]. The determination of the surface coverage of the electrode was calculated by the relation:

$$\theta = 1 - C_{add}/C_{dl}$$

where C_{add} is the capacitance obtained from an additive-containing solution and C_{dl} the capacitance from additive-free solution. The result, $\theta = 68\%$ gives about the same value as determined from the Tafel plots. In the case of a zinc substrate (curves b and b') the effect of the additive is less important than on steel, nevertheless a decrease of the capacitance occurs which could indicate an adsorption process but, as reflected by the Tafel lines, it should be an active adsorption. To determine the kinetics of the adsorption process on steel the following experiment was run (Fig. 7 — curve 3): after immersing the electrode for 220 s in an additive-free bath, Zeta was added to the bath and the capacitance determined until its stabilisation. First, the capacitance decreased rapidly and then slowly until stabilisation which took more than 600 s,

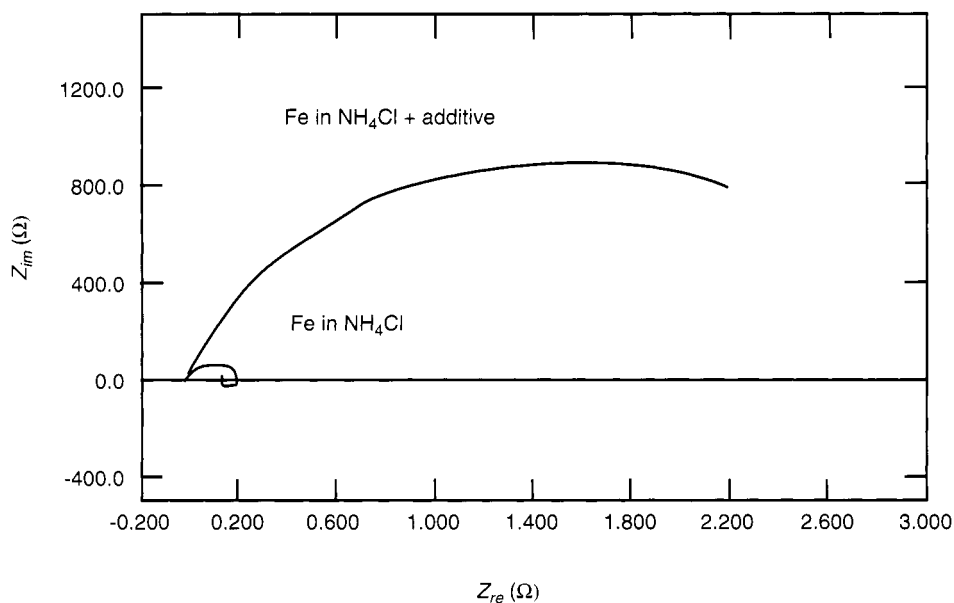


Fig. 4 Nyquist plot on steel at corrosion potential in 5M NH_4Cl with and without additive.

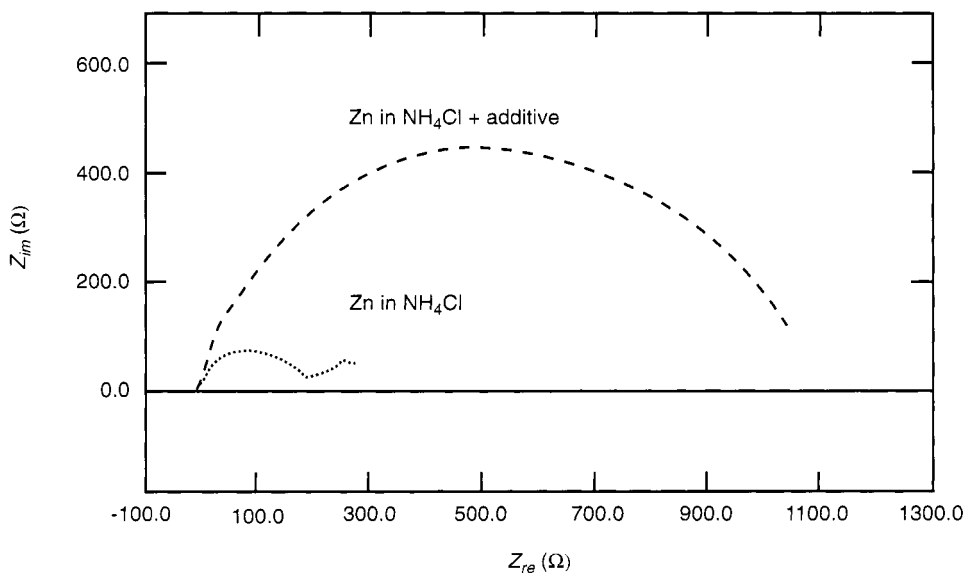


Fig. 5 Nyquist plot on zinc at corrosion potential in 5M NH_4Cl with and without additive.

showing that the adsorption on steel is a relatively slow process. The same behaviour was observed for a zinc substrate but the adsorption was relatively faster.

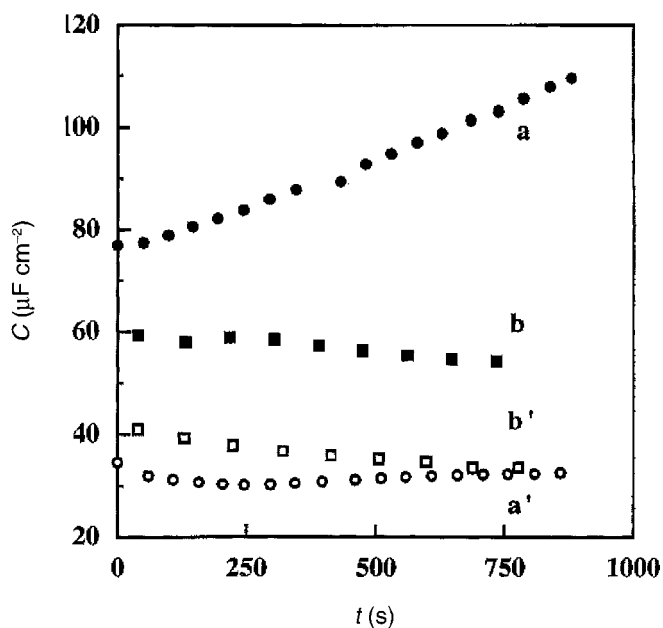


Fig. 6 Capacitance vs immersion time in 5M NH_4Cl on steel (a and a') and zinc (b and b') with (a' and b') and without (a and b) Zeta.

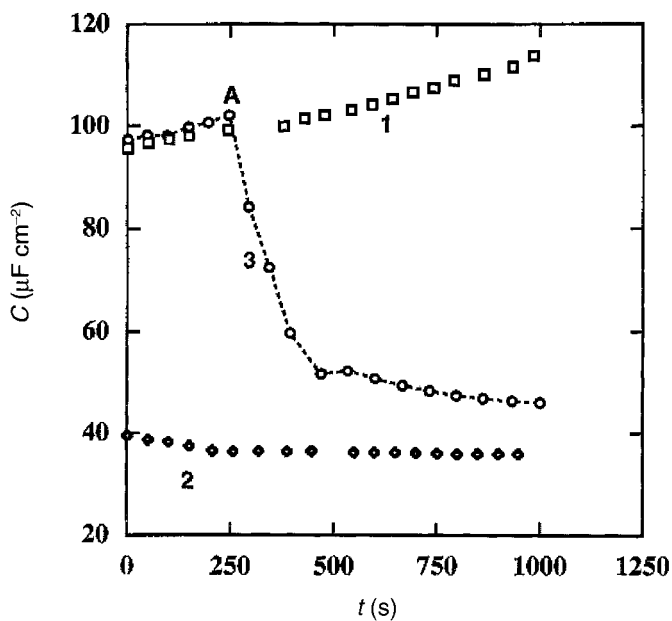


Fig. 7 Capacitance vs immersion time in 5M NH_4Cl , on steel, with (2) and without (1) additive. Curve 3: effect of the additive; 'A' indicates the additive addition to the NH_4Cl solution.

3.2. Zinc Electrocrystallisation

Figure 8 shows the cathodic part of the voltammogram for additive-free zinc ammonium chloride solution on steel (curve a). The curve shows an increase in current until $E = -1200$ mV, due to the zinc crystallisation, followed by a current plateau, at about 100 mA cm^{-2} , indicating a mass transfer control of the process. Then hydrogen evolution on the zinc crystallites caused a new increase in current. In the same figure, the influence of Zeta on the zinc electrocrystallisation on steel (curve b) and on zinc (curve c) substrates is also shown. The cathodic current increases from the same overpotential ($E = -1300$ mV), on the two substrates until a peak current at about -1700 mV, and the potential–current slope is similar for both the substrates. The main feature of these curves is that they are similar, with apparently no influence of the substrate on the crystallisation overpotential. It is unlikely that the substrates, which present a completely different behaviour towards hydrogen evolution, present a similar behaviour towards zinc deposition as shown in this figure. This fact leads to the hypothesis that the zinc crystallisation occurred on a substrate modified by a preliminary reaction.

Figure 9 shows the same experiments, only on steel, using a current density scale of 5 mA cm^{-2} . Curve (a), without additive, in the potential region before the Zn^{2+}/Zn equilibrium potential, shows a small peak. This peak is due to hydrogen evolution on steel rapidly stopped by a zinc Under Potential Deposition (UPD) [5]. When Zeta was added to the bath (curve b), before the steep increase in current at about -1300 mV shown in Fig. 8, two small waves were observed. The first one is in the potential

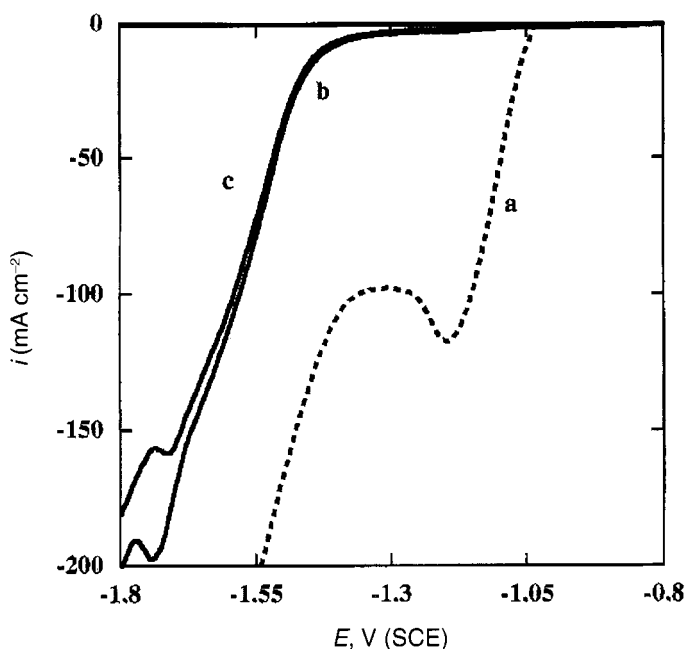


Fig. 8 Linear sweep polarisations on steel (a and b) and on zinc (c) in $0.5\text{M ZnCl}_2 + 5\text{M NH}_4\text{Cl}$ solution, with (b and c) and without (a) additive. Scan rate 20 mV s^{-1} .

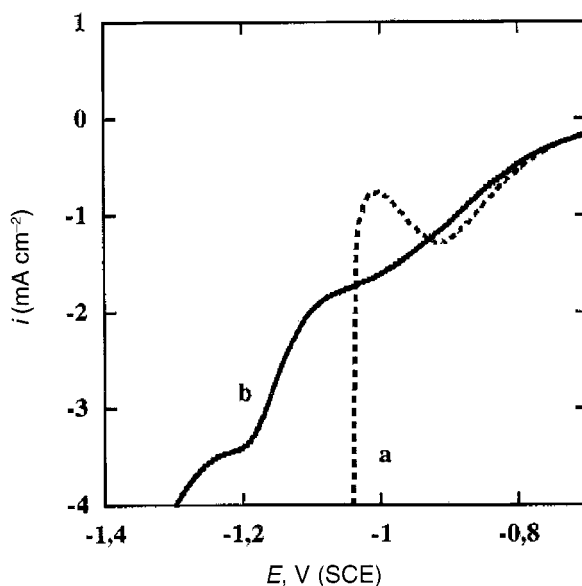


Fig. 9 Linear sweep polarisations on steel in 0.5M ZnCl_2 + 5M NH_4Cl solution, with (b) and without (a) additive. Scan rate 20 mV s^{-1} .

region anodic to the potential at zero current (-1024 mV). This wave also appeared in the curve in absence of additive (curve a), and in that case it was attributed to hydrogen evolution on steel, rapidly stopped by a zinc UPD. It is worth noticing that the shape of the curves (a) and (b) is not exactly the same, probably because in the case of an additive-containing bath, an adsorption process of the additive hinders the hydrogen evolution reaction. This result is in good agreement with those obtained for blank electrolytes. The second wave, with current up to 3.7 mA cm^{-2} , is in the same potential region as zinc deposition from Zeta-free bath. In order to check whether this peak really corresponds to a zinc deposit, a voltammogram was run in the potential range -700 to -1300 mV (Fig.10). On the reversed scan an anodic peak commences at -1024 mV , which is the free potential of zinc in this solution. This peak is related to the dissolution of zinc deposited, without any influence of the additive, under the second small cathodic peak. The charge under this peak was 27 mC cm^{-2} , which indicates that more than 50 monolayers were deposited.

4. Conclusions

The additive affects the hydrogen evolution on steel and on zinc, in a different way. On steel, the adsorption of the additive affects h.e.r. by blocking the active sites. The Tafel lines obtained in presence and in absence of additive are parallel, which indicates that the kinetics were not modified so that the surface coverage by the additive can be determined. On zinc, even if an adsorption process was proved by the capacitance measurements at the rest potential, no modification of the Tafel line was observed in presence of the additive at low overpotential. For higher overpotentials, a catalytic

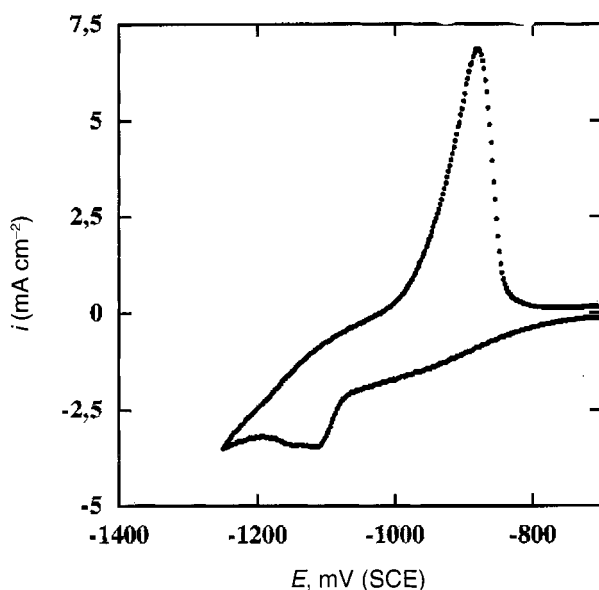


Fig. 10 Influence of the scan reversing potential in the potential region of the second peak: cyclic voltammogram at 20 mV s^{-1} on steel in $0.5\text{M ZnCl}_2 + 5\text{M NH}_4\text{Cl}$ solution with additive.

effect on h.e.r. was observed and was reflected by a modified Tafel slope. Zinc deposition on steel from the additive-containing solution can be explained on the basis of hydrogen evolution. The steel electrode was not completely covered by the additive, and zinc can be deposited on additive-free sites before being deposited under the influence of the additive. The zinc deposition process can be summarised as follows:

1. Hydrogen evolution on the bare steel substrate, rapidly stopped by zinc UPD.
2. First zinc deposition without any influence of the additive, i.e. in the holes left free by the adsorbed layer.
3. Zinc deposition under the influence of the additive.

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Effects of the Microstructure of Zinc on the Corrosion Behaviour of Galvanised Steel in 3.5% Sodium Chloride

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ABSTRACT

The corrosion behaviour of Zn hot-dip galvanised steel and Zn galvanized steel in 3.5% NaCl (to represent a marine environment) was studied with electrochemical and free corrosion tests. Potentiodynamic polarisation, electrochemical impedance and weight loss measurements were carried out on specimens after different immersion times at 25°C, in 3.5% NaCl solutions with a dissolved oxygen concentration of 6.5 ppm and a pH = 5.8.

XPS analysis was also made on different specimens before and after immersion in the corrosive solutions. The following were observed:

- (i) Zn galvanized coatings (GA) have a lower average corrosion rate than hot dip galvanised Zn (HD) because of their more noble electrode potential;
- (ii) during the first corrosion steps, the average corrosion rate of both GA and HD coatings is increased by microstructural heterogeneity;
- (iii) the corrosion layer on HD and GA specimens is mainly formed by Zn oxidation compounds, having an atomic percentage of $\geq 90\%$ in both specimens.

Al and Fe compounds are present as minor components in the surface layers; they could act as 'dopants' in the passive films by changing their chemical-physical properties and, hence, their passivating power.

1. Introduction

Zn coatings offer sacrificial steel protection because of their lower electrode potential compared with iron [1,2]. Because of the porosity of the zinc corrosion products formed from zinc dissolution, a continuous diffusion of zinc ions is possible through the corrosion layer, thus favouring sacrificial zinc dissolution. However, when zinc corrosion compounds are formed with lattice size greater than that of the zinc matrix [3], coating adhesion to the metallic substrate will decrease somewhat and could even lead to spalling of the coating.

Iron-zinc alloys, whose oxidation products may have smaller lattice size and hence lower coating spalling effects, show a good corrosion resistance [4] (higher than that of a pure zinc layer) and sacrificial steel protection at the same time, despite their higher electrode potential. Iron-zinc alloys are obtained with hot-annealing treatment of zinc hot-dip galvanised steel. With this treatment, several Fe-Zn intermetallic compounds are obtained [5] (FeZn_{13} , ζ phase, Zn rich; FeZn_{11} , δ_1 phase; FeZn_3 , Γ

phase with the lowest Zn content) with different structures, elemental compositions and electrode potentials. This may create a non-homogeneous coating structure in which microgalvanic cells are likely to form between Fe-rich islands (cathodic sites) and Zn-rich zones (anodic sites) with subsequent decrease in the Fe–Zn coating corrosion resistance. Pure zinc corrosion resistance can be affected by several factors, namely:

- (1) segregations at grain boundaries (e.g. Pb intermetallic compounds) or non-metallic inclusions like Al_2O_3 , which, being cathodic to the metallic matrix, stimulate localised corrosion [6,7];
- (2) plane preferential orientation: metallic materials with hexagonal lattice and preferential orientation on the 001 plane [8,9] show a very high corrosion resistance which increases when corrosion products are formed on metallic surfaces with the same 001 plane preferential orientation and decreases when the passive films are arranged on the $hk0$ plane.

The aim of this work was to study the corrosion behaviour of zinc or iron–zinc coatings in NaCl solution to assess whether iron–zinc coating corrosion resistance is affected, just like that of a pure zinc coating, by microstructure (which changes significantly because of the presence of different Fe–Zn intermetallic compounds) and by non-metallic inclusions.

2. Methods and Materials

Specimens were cut from sheets of hot-dip Zn galvanised steel (HD1 and HD2) and of Zn galvannealed steel (GA1 and GA2).

The thickness of the Zn layer in HD specimens was 11 μm ; some HD specimens were annealed to obtain GA specimens with unchanged Zn content (79 gm^{-2}).

The preferential plane orientation was on the 001 plane for HD1 and HD2 specimens and hkl plane for GA1 and GA2 specimens.

A heterogeneous structure was observed by X-ray microdiffractometry (Rigaku DC-1 Max, Cu $K\alpha$ radiation). In both GA1 and GA2 specimen surfaces, two intermetallic Fe–Zn compounds were found: ζ (ASTM 34-1314 card) with preferential orientation on the hkl plane and δ_1 (ASTM 13-578 card), dispersed in ζ phase, with preferential orientation on the $h00$ plane.

GA2 specimens showed a more homogeneous microstructure because of their smaller grain size (10–30 μm GA2 and 60–100 μm GA1, referred to X-Y plane) and a lower amount of δ_1 phase particles in the ζ phase. Surface layer composition before and after corrosion was assessed with X-ray photoelectron spectroscopy (XPS). Before corrosion, aluminum oxides, iron and lead compounds were found (Table 1).

HD1 and GA1 specimens showed a higher surface concentration of aluminium present as non-metallic macro inclusions (HD1) as well as surface oxide micro-dispersions in the metallic matrix.

Corrosion experiments were carried out at 25°C in quiescent NaCl 3.5% aqueous solution with dissolved oxygen content (DO) of 6.5 ppm.

Table 1. Atomic ratio of some surface elements referred to Zn 2p₃ unitary atomic ratio

Specimen	Al	Fe	Pb
HD1	9.73	0.80	2.02
HD2	0.12	0.19	1.36
GA1	4.44	0.04	0.01
GA2	0.52	0.07	0.00

Potentiodynamic polarisation tests were carried out with a scanning rate of 100 μVs^{-1} on previously free-corroded specimens for 2 and 144 h. Corrosion current density and polarisation resistance were calculated from the polarisation curves. Starting from the equilibrium potential in the anodic and cathodic direction, a domain (25 mV) in which $\log i$ vs E shows a linear relationship was selected to calculate polarisation resistance [10].

Then, in this domain corrosion current density and polarisation resistance were calculated following the Stern and Geary method [11].

Electrode impedance measurements were carried out on previously free-corroded specimens for 2 and 144 h by perturbing the equilibrium potential of the specimens with 10 mV a.c. with decreasing frequency from 60 kHz to 10 mHz.

The impedance diagrams were plotted as Nyquist plots and deconvolved by using ZPlot W Schlumberger program. Free corrosion experiments were carried out for periods ranging from 120 to 360 h. From these tests, the total weight loss of corroded specimens was calculated as the sum of the amount of Zn present in insoluble corrosion products (adhering to the corroded surfaces) plus the amount of Zn present in solution as soluble corrosion products.

A suitable chemical attack with a glycine saturated aqueous solution was used on corroded specimens to dissolve oxidation compounds. Zinc concentration was then measured using an atomic absorption spectrophotometer.

Corrosion layer characterisation was made with XPS spectroscopy.

The X-ray photoelectron spectrometer used for the investigation was a VG Escalab 210 with a spherical sector analyser and unmonochromatised Mg K α ($E = 1253.6$ eV) as excitation source. Spectra were obtained at a vacuum better than 10^{-7} mbar with a normal detection angle to the surface; the C1s binding energy, 284.8 eV of hydrocarbon contamination, was used to compensate charging effects. Spectrum data were recorded and processed using a Digital PDP 11/53 computer interfaced with the system.

3. Results and Discussion

3.1. Electrochemical Tests

Potentiodynamic polarisation curves show that HD specimens have the highest corrosion current density (i_{corr}) and the lowest polarisation resistance (R_p) for shorter

(Table 2) as well as longer pre-immersion times. This is consistent with the different metallic coating composition: the HD specimen coating is pure zinc, with a lower electrode potential and hence more active, whereas the GA specimen coating consists of Fe–Zn alloys, with higher electrode potential and hence less active.

HD1 and HD2 specimens show similar corrosion rates throughout immersion time range (Table 2), despite their different impurity concentrations (Table 1), which could stimulate general and localised corrosion [6,7]. This may suggest that the microamount of such impurities has no significant impact on the corrosion process of pure zinc. For shorter immersion times, polarisation resistance values of GA1 specimens are lower (Table 2). This may be due to δ_1 phase isles, cathodic to phase matrix, which form microgalvanic cells that stimulate matrix dissolution (ζ phase). For longer exposure times, polarisation resistance values of GA specimens are similar: this could suggest that with increasing immersion times GA1 and GA2 surface microstructures become similar because of selective Zn dissolution.

The impedance measurements confirmed the higher corrodibility of HD specimens.

All impedance curves, plotted as Nyquist diagrams, show a depletion semicircle; an example of this trend is shown in Fig.1. This could be correlated with the microscopic metal–solution interface roughness arising from surface modifications from the onset of localised corrosion [12, 13], or with multiple redox reactions due to the presence of intermediate species [14, 15].

Literature data show that two electrical equivalent circuit models could be used to deconvolve impedance spectra. The first model [16], which supports the existence of a two step anodic dissolution mechanism involving the presence of intermediate species, disregards the contribution of the cathodic reaction, because it concerns the anodic reaction only: hence it does not fit a specimen corrosion process, simultaneously fed by both anodic and cathodic reactions. Conversely, the second model (Fig. 2), involving anodic and cathodic reactions and used to deconvolve EIS

Table 2. Electrochemical parameters from polarisation curves of HD and GA specimens after different pre-immersion times in NaCl solution. Mean values from three measurements

Specimen	Imm. time (h)	b_a (mV/dec)	b_c (mV/dec)	i_{corr} ($\mu\text{A cm}^{-2}$)	E_{corr} (mV, (SCE))	R_p ($\text{k}\Omega \cdot \text{cm}^2$)
HD1	2	15.1	–21.3	4.00	–1045	1.0
	144	19.5	–23.0	1.06	–1048	4.3
HD2	2	17.2	–20.2	3.99	–1040	1.0
	144	22.3	–32.0	1.19	–1040	4.8
GA1	2	23.2	–32.0	1.13	–871	5.1
	144	22.6	–50.8	0.31	–862	21.9
GA2	2	22.6	–32.0	0.71	–861	8.1
	144	28.0	–41.4	0.38	–864	19.1

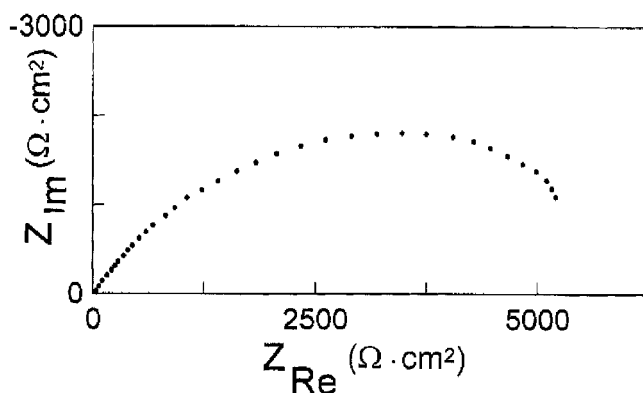


Fig. 1 Nyquist diagram of GA2 specimens after 144 h in NaCl solution.

spectra of Zn–Al coatings free corroded in Na_2SO_4 solutions [17], was satisfactorily applied to deconvolve the impedance spectra, notwithstanding the limit of the one step anodic zinc dissolution that excludes the presence of intermediate species.

In Fig. 2, C represents the double layer capacitance, R_a the charge transfer resistance of the anodic process, in parallel with the contribution of the cathodic reaction resistances R_c (charge transfer resistance of the oxygen and hydrogen reduction) and Q (accounting for the diffusion control of the cathodic reaction).

Simulated spectra obtained with this last model revealed a very good fit with experimental results (Fig. 3); the calculated values of the electrical circuit model components are shown in Table 3.

R_a , representing the charge transfer resistance of the dissolution process may be taken to correspond, as a rough approximation, to polarisation resistance (R_p ; Table 2) obtained from polarisation curves. R_a just like R_p , shows:

- an increase with increase of pre-exposure time in all specimens.

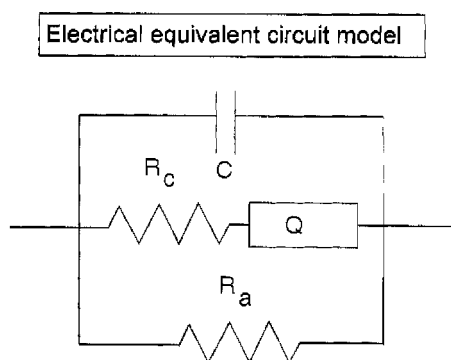


Fig. 2 Model of the electrical equivalent circuit for a continuous oxide layer used to deconvolve EIS spectra of both HD and GA specimens.

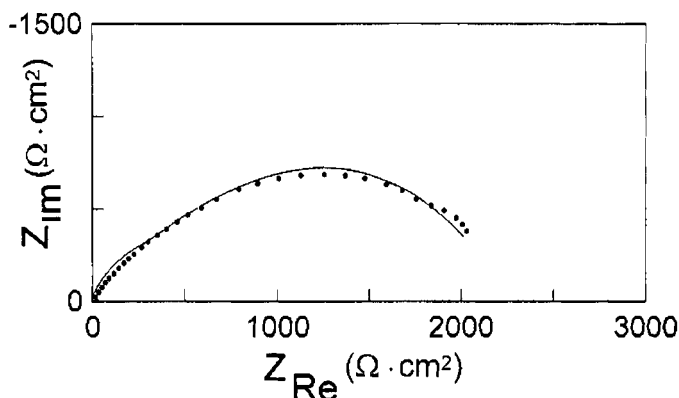


Fig. 3 Experimental (points) and simulated (solid line) Nyquist diagram of GA2 specimens after 2 h in NaCl solution.

- in agreement with Table 2, similar values in HD1 and HD2 specimens for short as well as for long pre-exposure times notwithstanding different impurity concentration (Table 1) of the specimens, which could stimulate general and localised corrosion [6,7]. (This would suggest the presence of impurities does not significantly influence the corrosion process).
- for long pre-immersion times, values of GA specimens higher than those of HD specimens: this may be consistent with an enrichment in iron on metallic surfaces that inhibits metal dissolution.

Table 3. Values of the electrical circuit model components of Fig. 2 calculated from impedance spectra of HD and GA specimens after different pre-immersion times in NaCl solution

Specimen	Imm. time (h)	R_a ($\Omega \text{ cm}^2$)	R_c ($\Omega \text{ cm}^2$)	Q ($\Omega \text{ (rad s}^{-1}\text{)}^{-n} \text{ cm}^2$)	C (F cm^{-2})
HD1	2	1800	100	2800	1×10^{-5}
	144	2000	100	2900	1×10^{-5}
HD2	2	2000	100	2000	1×10^{-6}
	144	3000	50	2000	1×10^{-6}
GA1	2	2300	100	5300	1×10^{-5}
	144	12000	100	28000	2×10^{-7}
GA2	2	7000	100	3000	3×10^{-5}
	144	8500	300	18000	2.5×10^{-6}

The value of n , in the constant phase element (Q), ranges from 0.42 to 0.50; this element (a Warburg resistance) can be linked with the diffusion resistance of the cathodic species through the passive film.

- for short pre-immersion times, a low value for GA1 specimens – this may be linked to the high amount and large size of δ_1 phase islands (cathodic to ζ phase) that can form microgalvanic cells stimulating ζ phase matrix dissolution.

R_c , representing the charge transfer resistance of the cathodic process remains unchanged for all specimens and does not change significantly with the pre-exposure time.

Conversely, the diffusion resistance of the cathodic species through the passive film, designated Q , shows higher values for GA specimens, mainly for longer pre-immersion times: this could be linked to the different compositions of the passive film.

The capacitance values range from 3×10^{-5} to 2×10^{-7} F cm⁻², thus indicating that oxides are the main components of the passive layer. With increasing immersion time, these values remain unchanged for HD specimens whereas they decrease for GA specimens. This could be correlated with the higher corrosion resistance of GA specimens leading to lower concentration of Zn⁺ ions on the metallic surface and hence to lower amounts of intermediate Zn oxidation compounds (having a higher percentage of ionic bonds and higher capacitance).

3.2. Weight Loss Tests

Weight loss experiments (Fig. 4) show that HD specimens have an average corrosion rate higher than GA specimens throughout the exposure time, thus confirming electrochemical test results; i_{corr} values were calculated from weight loss measurements using Faraday's law and then compared with those obtained from potentiodynamic polarisation (Table 2) and impedance tests (Table 4). The corrosion rate from these latest tests was estimated from resistance R (Table 3) by using the equation [18]:

$$i_{corr} = B/R \quad (1)$$

From literature data for metal corrosion in aqueous environment, the B value was assumed to be a constant of 0.025 V.

Table 4 shows a good agreement between i_{corr} obtained from weight loss and impedance tests; conversely, the values from polarisation tests are lower. This means that impedance tests lead to a more reliable corrosion rate measurement. The weight loss test confirms the results obtained from electrochemical tests, since the corrosion rates of:

- HD1 specimens are higher than HD2 specimens throughout the immersion time range. (This could be consistent with the higher percentage (Table 1) and larger size of impurities in HD specimens. These impurities, present as surface oxides (undermined together with the first layers of the metallic matrix after short exposure times) as well as non-metallic inclusions (remaining in the metallic matrix), can affect the corrosion process by stimulating corrosion, according to literature data [6,7]);

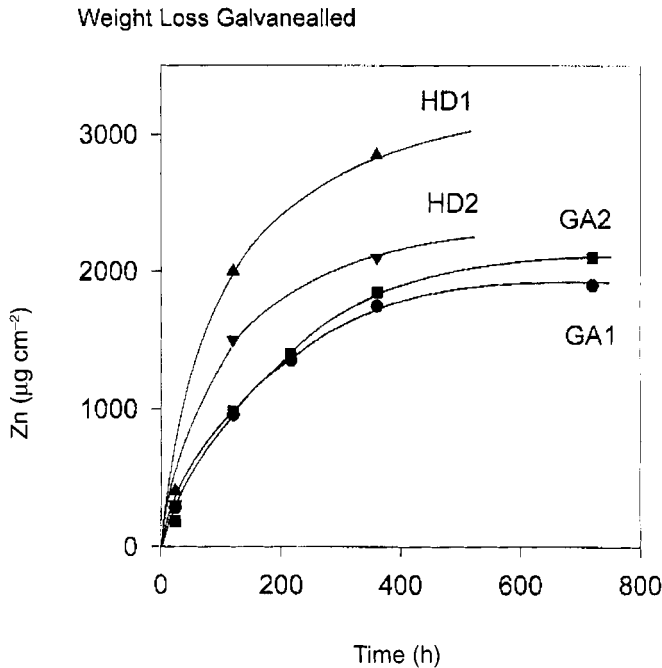


Fig. 4 HD and GA specimen weight loss vs immersion time.

- GA1 specimens for shorter immersion times are lower than that of GA2 specimens, whereas they are higher for longer immersion times. (This may be linked to the presence in GA1 specimens of δ_1 Fe–Zn phase, cathodic to the matrix, which enhances Zn dissolution during the first corrosion steps. By increasing the immersion time, because of the different concentration in impurities of GA1 specimens, a ‘doped’, more protective, corrosion layer of mixed oxides could be formed).

Table 4. i_{corr} (μAcm^{-2}) values of HD and GA specimens after 144 h immersion time, obtained from: potentiodynamic polarisation (column 1), electrochemical impedance (column 2) and weight loss tests (column 3)

Specimen	1	2	3
HD1	1.06	11.4	11.4
HD2	1.19	10.2	10.2
GA1	0.31	4.5	4.6
GA2	0.38	6.2	5.1

3.3. Surface Analysis

XPS analysis shows that after 144 hours of exposure, the corrosion layer formed on HD and GA specimens mainly consists of Zn oxidation compounds, with an atomic percentage of $\geq 90\%$ in both specimens. ZnO and Zn(OH)₂ (Fig. 5) are Zn oxidation compounds in all specimens. Fe and Al oxides are the other components of the passive films. Thus, Fe (Fig. 6) is present as iron oxide (Fe₂O₃, BE = 710.7 eV) with an atomic percentage lower than $\leq 0.3\%$ in HD and ranging from 3% in GA2 to 5% in GA1 corrosion products: Al (Fig. 7) is probably present as Al₂O₃ with an atomic percentage ranging from 5% in GA1 specimens to 0.3% in HD2 specimens. As is known, the different aluminum oxides cannot be discriminated with XPS analysis because the hydrated forms of aluminum oxide (Al(OH)₃) are decomposed to Al₂O₃ and H₂O in the high vacuum chamber during XPS analysis [19].

As shown by surface analysis, Al and Fe compounds are present as minor components in the surface layers. However, they could act as 'dopants' in the passive films by changing their chemical-physical properties and hence their passivating power. For this reason, the corrosion rate of GA1 specimens with higher surface Al atomic percentage may become lower than that of GA2 specimens, with lower Al.

4. Conclusions

- Zn galvanized coatings (GA) have a lower average corrosion rate than hot dip galvanised (HD) because of their more noble electrode potential.

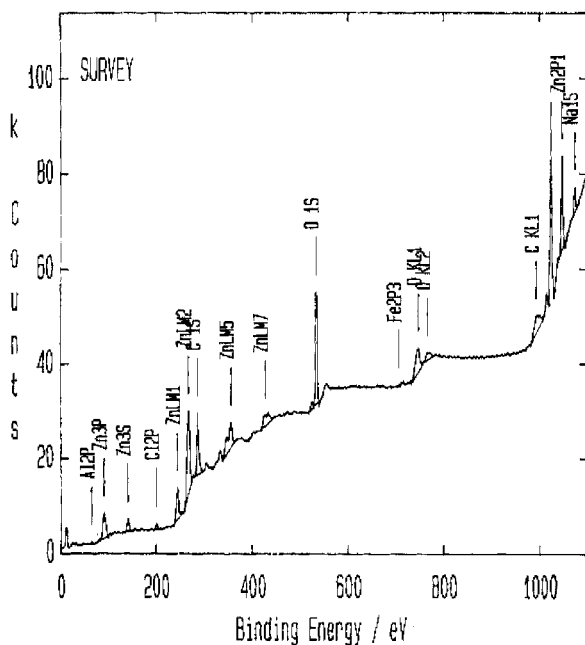


Fig. 5 XPS survey spectrum of GA1 specimens exposed for 144 h in NaCl solution.

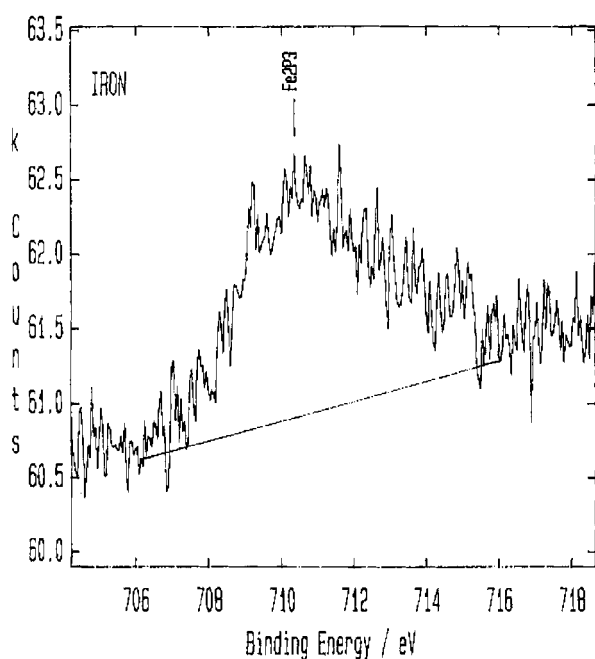


Fig. 6 XPS region of Fe 2p₃ from GA1 specimens exposed for 144 h in NaCl solution.

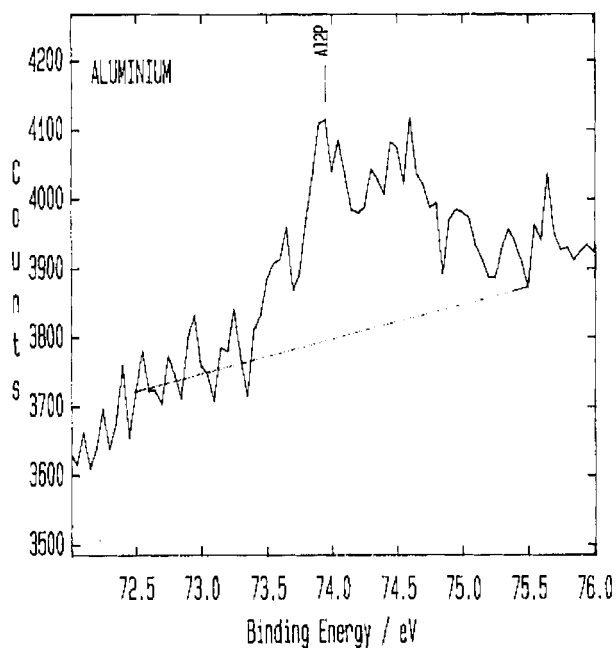


Fig. 7 XPS region of Al 2p from GA1 specimens exposed for 144 h in NaCl solution.

- During the first corrosion steps, the average corrosion rate of both GA and HD coatings is increased by microstructure heterogeneity.
- The corrosion layer formed on HD and GA specimens is mainly formed by Zn oxidation compounds, with an atomic percentage of $\geq 90\%$ in both specimens. Al and Fe compounds are present as minor components in the surface layers.

However, they could act as ‘dopants’ in the passive films by changing their chemical–physical properties and hence their passivating power. For this reason, the corrosion rate of GA1 specimens with the higher surface Al atomic percentage may be lower than that of GA2 specimens, with lower Al.

5. Acknowledgement

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Structural Characterisation of Silica Coatings Applied on Polished Ferrous Substrates and Derived from Hydrolysis and Condensation of Ethylsilicates

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ABSTRACT

Since the 1930s the ethyl-polysilicates have been used in prehydrolysed forms as binders for zinc-rich paints. They lead to the formation, but only on sand-blasted ferrous substrates, of inorganic coatings that provide a high protection against corrosion. The characterisation, by means of appropriate physico-chemical analytical techniques, of sol gel derived coatings, not zinc-loaded, has led us to propose a process allowing the formation of thick and adherent silica coatings even on polished supports. Despite the adhesion properties of coatings obtained by this process, it appears that they systematically suffer from cracking after ageing. Vibrational analysis by Raman microspectrometry of the starting solutions of the silicates and of their derived coatings has provided evidence of the considerable importance of the effect of the initial sol composition on the evolution of the morphology of the coatings with time.

1. Introduction

The fabrication of coating films starting from metal alkoxides is a promising application of the solgel technique. We are interested in silica-based glass coatings (loaded or not loaded with zinc dust) of thicknesses in the range [2–50 μm] for application, in corrosion prevention, on bare ferrous substrates, i.e. non sand-blasted supports. The characterisation of sol-gel derived coatings [1] has led us to develop a technique [2] to form such coatings, from a polyethylsilicate prehydrolysate ($\text{Si}_n\text{O}_{n-1}(\text{OC}_2\text{H}_5)_{n+2}$; $n \leq 4$), that are adherent even to polished substrates. The prehydrolysate we used was ethyl silicate 40 (ETS40), as being the most common organic silicate used in the production of zinc-based anticorrosive paints [3]. Our technique consists of the following steps: (1) chemical surface pretreatment of the ferrous support by an amorphous phosphating to promote adhesion, (2) spray deposition of the prehydrolysate, (3) drying and heat treatment to convert the gel film into a silica glass coating. The results obtained by such a process are very

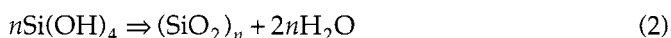
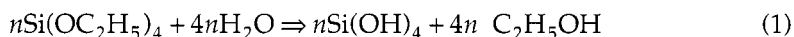
conclusive and lead to highly adherent (non) loaded silica coatings (adhesive strength of 1.3 MPa) that offer electrical insulation ($7 \text{ M}\Omega/50\text{cm}^2$, 15 bars for a non zinc loaded coating $5 \mu\text{m}$ thick) and a good thermal shock strength [3]. Despite the excellent adhesion obtained for these coatings, a solution to the phenomenon of fracture of films needs to be found so as to improve their physico-mechanical characteristics. The physical and chemical processes accompanying film formation will greatly influence the microstructure of the deposited films. Brinker *et al.* have shown that the structure of thin organic modified SiO_2 -films depends, among other factors on the size and structure of the oligomeric precursors [5–7]. Consequently, we have modified the prehydrolysate composition by varying its oligomeric species as obtained by the hydrolysis and condensation process of tetraethylorthosilicate (TEOS). Characterisation of these species has been discussed in previous work [8–10].

In this report, we describe the use of Raman spectroscopy to determine the influence of the prehydrolysate formula on the structural and compositional development of the final coating. The application to the corrosion prevention of steel protected by such coatings, but zinc-loaded, is also presented.

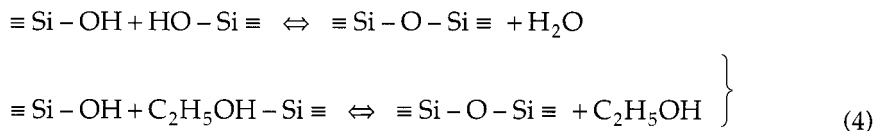
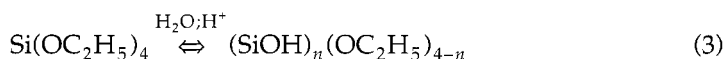
2. Hydrolysis and Condensation of TEOS: General Trends

The sol–gel process starts with liquid precursors and, through hydrolysis and condensation reactions, leads to solid structures.

Under stoichiometric conditions, TEOS theoretically gives rise to pure amorphous silica by the following reactions:



If stoichiometry is not respected, reactions (1) and (2) are respectively replaced by reactions (3) and (4):



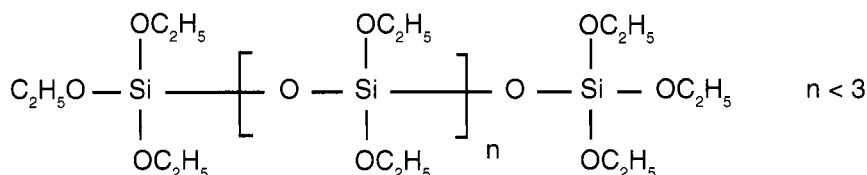
The hydrolysis and condensation of TEOS are, in this paper, acid catalysed. These reactions lead to condensed polysilicate sols or gels. Structure of the polymers obtained in this way (linear, branched or cyclic) depends on several parameters such as, for example, temperature, $\text{H}_2\text{O}/\text{TEOS}$ molar ratio, concentration of the co-solvent or strength and concentration of the acid catalyst.

3. Experimental

3.1. Preparation of the Ethyl Silicate Prehydrolysates

3.1.1. Sol from Ethylsilicate 40

Dynasil40 (Hüls AG), the industrial product we used from the beginning of this study, is a blend of ethyl esters of various polysilicic acids and serves as the starting product for the manufacture of the binder for zinc dust paints. According to the manufacturer's data, it should contain an equivalent of about 40–42 wt% SiO₂. Its average molecular weight is 610. The theoretical formula of this ethylpolysilicate is:



Just before use, the starting sol was prepared by mixing 35 wt% Dynasil40 with 60 wt% water-free ethanol in a reactor; 0.5M HCl was gradually added to the solution under constant stirring, the acid being used as catalyst.

Vibrational analysis by means of Raman spectroscopy showed that this sol is a mixture of condensed oligomeric products ranging from the tetramer to the more highly condensed linear and cyclic structures [3]. This sol is labelled T.

3.1.2. Sols prepared directly from TEOS

These sols are referred to as A, B₁, B₂ and C. These starting solutions were prepared by the hydrolysis and condensation of a pure commercial solution of TEOS (> 98 wt%, Fluka Chemie, Switzerland) with various 'acid catalyst/TEOS', 'H₂O/TEOS' and 'EtOH/TEOS' molar ratios.

Initially TEOS and water are immiscible and an alcohol co-solvent (here ethanol) is usually employed to homogenise the TEOS-H₂O system. However the ethanol generated by the hydrolysis reaction should be sufficient to convert the initial biphasic system to an homogeneous one. Solutions A, B₁, B₂ were prepared without ethanol. The solution C involved dropwise addition of a H₂O–EtOH mixture to the silicon reagent. In all cases the acid (HCl or HNO₃) initially incorporated in the aqueous phase was used as the catalyst.

We have considered in a previous work [10] the effect of the alcohol co-solvent in the initial mixtures: thus, increasing the amount of ethanol leads to a complete consumption of TEOS as well as an improvement in the performance of the acidic catalysis. Consequently, solutions A, B₁, B₂ were allowed to react under reflux (85°C) for 24 h whereas solution C was prepared only by mixing under vigorous stirring. The chemical compositions of these solutions are given in Table 1.

3.2 Substrates and Coatings Preparation

Coatings were produced on polished ferrous substrates. Before coating, ferrous plates

Table 1. Chemical compositions of sols

Sols labels	Chemical compositions	Volume (mL)	Moles	H ₂ O/TEOS*	Acid/TEOS*
A	H ₂ O (HCl 0.03M)	2.8	0.155		
	HCl	---	8.4 10 ⁻⁵		
	TEOS	20	0.089	1.75	0.001
	EtOH	0	0		
B ₁	H ₂ O (HNO ₃ 0.03M)	2.8	0.155		
	HNO ₃	---	8.4 10 ⁻⁵		
	TEOS	20	0.089	1.75	0.001
	EtOH	0	0		
B ₂	H ₂ O (HNO ₃ 0.03M)	2.8	0.155		
	HNO ₃	---	8.4 10 ⁻⁴		
	TEOS	20	0.089	1.75	0.001
	EtOH	0	0		
C	H ₂ O (HNO ₃ 0.03M)	3.2	0.177		
	HNO ₃	---	9.6 10 ⁻⁴	2	0.01
	TEOS	20	0.089		
	EtOH	46.4	0.8		

* Molar ratios.

were chemically pretreated by amorphous phosphating, doubly rinsed with distilled water and water-free ethanol. Films were deposited by spraying the ethylsilicate prehydrolysate (solutions A, B₁, B₂, C or T). Dissolution of the amorphous ferrous phosphate (vivianite Fe₃(PO₄)₂ · 8H₂O) in the ethylsilicate prehydrolysate and consequent release of the crystallisation water of the phosphate, ensure that hydrolysis and condensation reactions start at the 'substrate-coating interface' with formation of a 'substrate-coating' interphase [2, 11].

After the ethylsilicate deposition, drying and heat treatment (100°C) were carried out in an infrared oven (3 steps of 10 s). Each coating was then kept at room temperature and 50% R.H. for 16 months.

3.3. Coatings Characterisation

The surface morphology of all coatings was examined by scanning electron microscopy (SEM).

Structural studies were carried out using Raman microspectrometry analysis. This is an important technique for understanding some aspects of these materials. The Raman spectra were recorded by means of a multichannel spectrometer (DILOR XY) using the 514.53 nm radiation from an argon ion laser for excitation. The spectral resolution was 4 cm^{-1} and the band positions were accurate to $\pm 1\text{ cm}^{-1}$. The 100 to 4000 cm^{-1} spectral range was analysed. Samples were placed in the laser beam with a 90° observation geometry.

Corrosion resistance of samples was examined with the classical salt spray test (NF 41002) and with impedance and corrosion potential measurements. A three-electrode electrochemical cell was used comprising the specimen working electrode ($S = 5.75\text{ cm}^2$), a calomel reference electrode and a platinum counter electrode. The electrolyte was deaerated 3 wt% NaCl solution ($\text{pH} = 7.5$). Impedance measurements were regularly made with a Z Tacussel processor. The amplitude of the sinusoidal signal was 10 mV close to the corrosion potential and the frequency ranged from 10^{-2} to 10^5 Hz .

4. Results and Discussion

4.1. Formation and Morphological Development of Coatings

With HCl as acid catalyst and with molar $\text{H}_2\text{O}/\text{TEOS}$ ratios below 1.5, it has been impossible to form successful coatings because of the direct evaporation of the prehydrolysate during the drying stage in the infrared oven. Solution A ($\text{H}_2\text{O}/\text{TEOS} = 1.75$; $\text{HCl}/\text{TEOS} = 0.001$) led to a coating that remained sticky whereas solution T evolved toward a thick, adherent crack-free but soft coating.

On the other hand, under HNO_3 catalysis and with the same molar ratios (solution B_1), the final coating appeared as adherent, crack-free and soft. Presence of ethanol and an increase of the acid concentration (solutions B_2 and C) allowed the similar coating to form while promoting the polymerisation rate.

These first established facts emphasise the basic influence of $\text{H}_2\text{O}/\text{TEOS}$ molar ratio, of the acid catalyst and consequently of the oligomeric composition of the starting sols. The characterisation of these oligomeric species has been discussed in other work [3,9]: we have shown that HCl catalysis promotes hydrolysis (reaction 3) at the expense of condensation (reaction 4). Table 2 summarises the oligomeric composition of the prehydrolysates.

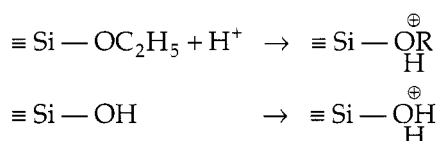
Macroscopic and microscopic examinations of the coatings before and after ageing during 16 months at room temperature and 50% R.H. are given in Table 3 and strengthen the hypothesis that chemical and physico-mechanical properties of the final coating depend on the degree of oligomerisation within the starting sol. Thus, contrary to the sols containing high condensed oligomers (sols A and T), the sols B_1 , and B_2 and C that contain mainly trimer species, formed adherent, transparent and crack-free coatings that kept their initial morphology after ageing.

Furthermore, it appears that the presence of silanols (Si-OH units) in the starting solution (sol A) significantly influences the formation and development of the film. While the sol T coating remained adherent (but not crack-free) after ageing, the sticky film of sol A systematically warped and flaked after ageing. Based on comparison of the composition of sols A and T it would appear that only the silanols enrichment of sol A may cause a low polymerisation rate and consequent loss of adhesion.

Table 2. Oligomeric composition of the starting sols

Sols	Raman and ^{29}Si RMN characterisation [9,11]
A	Species with three non bridging oxygen atoms. Linear partially hydrolysed tetramers
B ₁ , B ₂ and C	Dimers and trimers
T	Tetramers and more highly condensed linear species

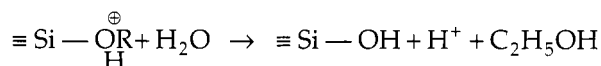
The low condensation rate is explainable if one considers the acid catalysed hydrolysis – condensation mechanism: the acid serves to protonate negatively charged ethoxy (or hydroxy) groups making alcohol (or water) a better leaving group:

**Table 3.** Coatings morphology before and after ageing

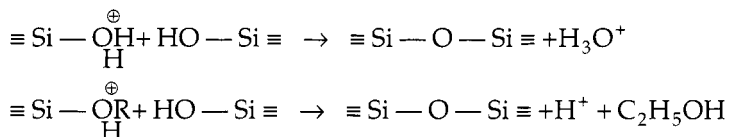
Sols	Catalyst	Initial morphology	Morphology after ageing	Thickness*
A	HCl (0.03M)	sticky film	non adherent flaking	<5 μm
B ₁	HNO ₃ (0.03M)	soft transparent adherent crack free	hard transparent adherent crack free	$\approx 5 \mu\text{m}$
B ₂	HNO ₃ (0.3M)	hard transparent adherent crack free	hard transparent adherent crack free	$\approx 5 \mu\text{m}$
C	HNO ₃ (0.3M) + ethanol adherent	hard transparent adherent crack free	hard transparent crack free	$\approx 15 \mu\text{m}$
T	HCl	hard transparent adherent crack free	hard transparent adherent flaking	$\approx 15 \mu\text{m}$

*Using a Permascope thickness tester.

During the hydrolysis reaction, a water molecule attacks the electrophilic silicon and the proton is regenerated:



The condensation mechanism is given by:



However, the substitution of OH for OC₂H₅ (hydrolysis) and the substitution of OSi for OH or OC₂H₅ (condensation) decrease the electron density on the silicon atom. Consequently, extensive hydrolysis and condensation in the starting solution (solution A) should retard the polycondensation kinetics.

With regard to the loss of adhesion of the sol A derived coating after ageing, it appears that the extensive initial ratio of partially hydrolysed oligomeric species prevents the creation of the 'substrate-coating' interphase as discussed (Section 3.2).

4.2. Structural Characterisation of Coatings

Because of the incomplete polymerisation of the sol A derived coating and its alteration after ageing with a total loss of adhesion, the corresponding Raman spectrum could not be obtained.

In order to show the influence of starting sol oligomer composition on the structure of the final coating, we have specially studied the Raman spectra of coatings C and T. These Raman spectra were recorded just after the drying stage and heat treatment of the coatings. The Raman spectrum corresponding to the sol T derived coating, which suffers cracking after ageing, is shown on Fig. 1. Figure 2 corresponds to the Raman spectrum of coating C that keeps its initial perfect morphology with time. Figures 3 and 4 are representative of the microstructures of these coatings deduced from the Raman spectra analysis.

Assignments for Raman bands are listed in Table 4 (p.190). The major features of the Raman spectra associated with the silicate network vibrational modes are the 440, 490, 600, 800, 1090 and 1180 cm⁻¹ bands; the broad asymmetric band in the 200–500 cm⁻¹ region provides evidence for a three dimensional polymerised silicate network. The distinct peaks in the 2800–3000 cm⁻¹ region and the bands at *ca.* 1455 and 880 cm⁻¹ are related to ethoxy species. The bands at *ca.* 960 cm⁻¹ and in the 3500–3750 cm⁻¹ region are evidence of the presence of silanol groups.

Despite an overall similarity, the spectrum of the sol C derived coating differs from that of the sol T derived coating.

At first, at *ca.* 600 cm⁻¹ the spectrum of sample C has a weakly D₂ band which indicates the presence, at the surface or in the bulk of the coating, of three-membered (SiO–) rings. The spectrum of coating T does not have a detectable D₂ band.

A second difference is displayed at *ca.* 490 cm⁻¹; this band has a larger intensity

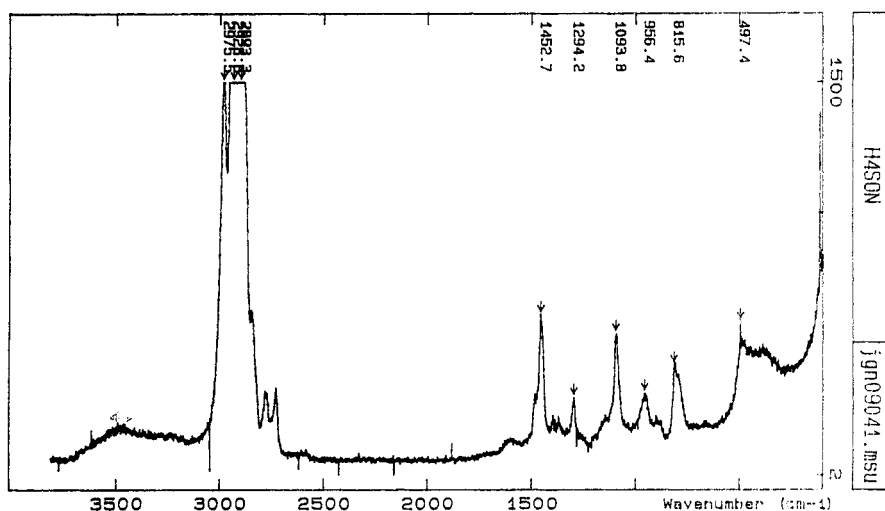


Fig. 1 Raman spectrum of the sol T derived coating.

LASIR C.N.R.S. U.P.R. 2631 L LILLE DILOR XY	OPERATOR	jgn	EXCITATION (nm)	514.53	SPECT.SLIT WIDTH (cm⁻¹)	/
	DATE	05-25-1992	LASER POW. (mW)	300	DETECTOR (nbr of diodes)	1024
	SAMPLE	ph amo	FOREMONO. (cm⁻¹)	/	FILTER	
	GRATING	1800	SPECTRO. (cm⁻¹)	/	INTEGRATION TIME (s)	
	MODE	MULTICHANNEL	SLIT WIDTH (μm)	200	NUMBER OF ACCUMULATIONS	
REMARK: OBJX80 phosp am (100292)						

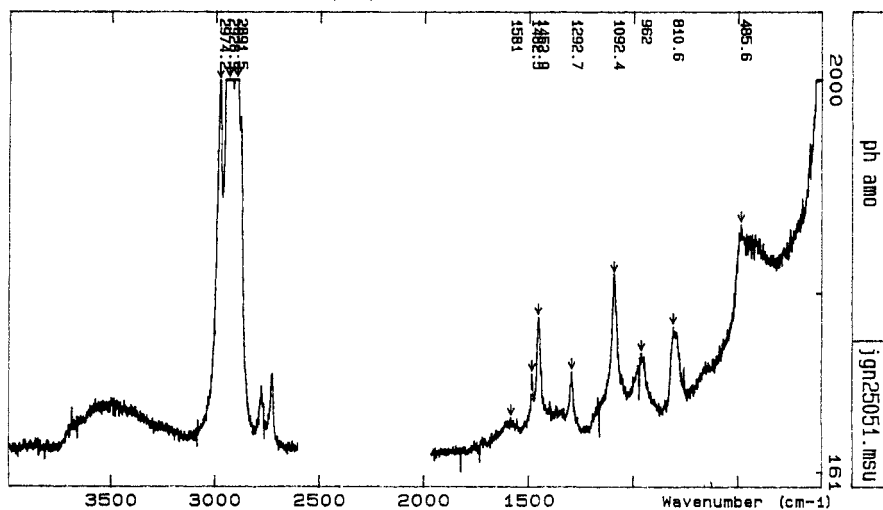


Fig. 2 Raman spectrum of the sol C derived coating.

for sample C compared with that of sample T. This band has been assigned to the breathing mode of four membered rings isolated by a non-bridging oxygen preferentially linked to an hydrogen. Thus this band is both characteristic of a polycondensation process and of the silanol Si–OH density. The difference in hydroxyl

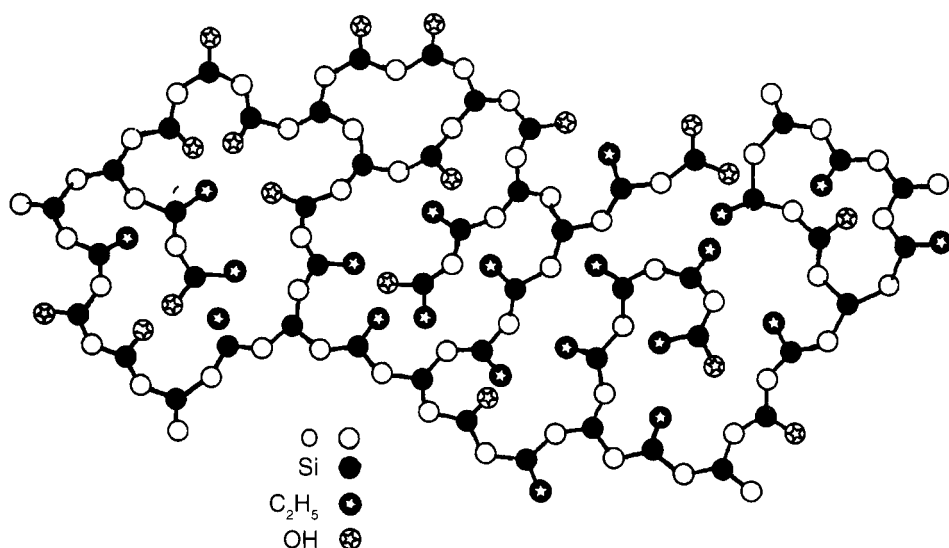


Fig. 3 Polymeric microstructure of coating T (ground plane).

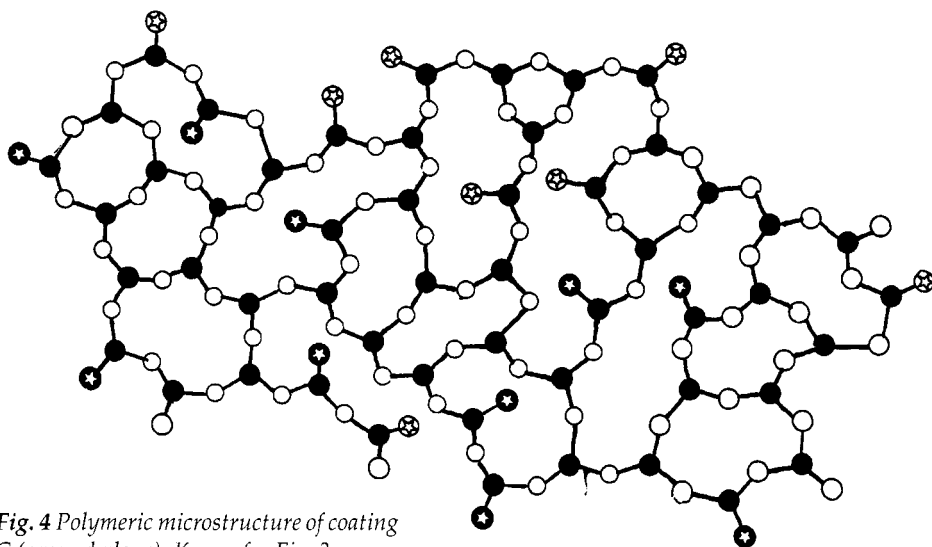


Fig. 4 Polymeric microstructure of coating C (ground plane). Key as for Fig. 3.

density is also displayed in the Raman spectra by the difference in the intensities of the band at *ca.* 960 cm⁻¹ assigned to the Si-OH stretching mode. Furthermore, Raman bands in the 3200–3750 cm⁻¹ region are indicative of the type of these silanol groups. So, the existence of isolated, i.e. non-hydrogen bonded silanol groups, is only established for sample C by the emergent narrow band at *ca.* 3750 cm⁻¹. For sample T, only hydrogen bonded SiO-H or water (broad band in the 3200–3500 cm⁻¹ region with two maxima at *ca.* 3200 and 3450 cm⁻¹) are clearly shown.

Table 4. Assignment of Raman bands

cm ⁻¹	Assignment
3750	Free SiO–H groups
3500	Hydrogen bonded SiO–H
3200–3450	Absorbed water
2800–3000	Ethoxy groups, C–H stretching mode
1455	Ethoxy groups, H–C–H deformation
1290	Ethoxy groups, CH ₂ twist
1090–1180	LO and TO Si–O–Si asymmetric stretching modes
950–960	Si–OH stretching mode
882	Ethoxy groups, C–C–O symmetric stretching modes
810–815	Symmetric Si–O–Si stretching mode
600	D ₂ band, three-membered rings breathing mode
490	D ₁ band, four-membered rings with a non bridging oxygen breathing mode
440	Vibrational mode of [SiO ₄] with four silicon atom neighbours

The last, but certainly the most important, difference between the two samples is given by comparison of the relative intensities of the ethoxy groups and silica network characteristic bands, i.e. respectively the bands at 1455 and 1090 cm⁻¹. So, it clearly appears that there is much more retention of organics within sample T. This is confirmed by the presence, only on the Raman spectrum of this coating, of the characteristic weak band at 882 cm⁻¹ assigned to C–C–O symmetric stretching mode.

On the other hand, the Raman spectrum of the best coating C (that remains adherent and crack-free with time) gives evidence of an advanced three dimensional network, and although unhydrolysed ethoxy groups and silanol units are present within the structure, they are sufficiently isolated from each other. This inhibits subsequent condensation and the coating keeps its initial morphology even after ageing.

4.3. Corrosion Resistance of Ferrous Substrates with Zinc-loaded Coatings

With the classical salt spray test (NF41002) we have proved that using our process, no corrosion phenomena of the ferrous support occur in the scratch even after 1000 h of exposure if the zinc weight concentration in the dry coating is greater than 50%.

This good corrosion prevention provided by such coatings has been confirmed by measurements of the electrochemical potential changes with time. Figure 5 shows the potential/time curves obtained for two zinc-loaded coatings C_{40} and C_{90} .

Coatings C_{40} and C_{90} derive from starting sol C that respectively contains 40 and 90 wt % of metallic zinc powder. These coatings have been applied on bare ferrous substrates as explained above (Section 3.2). In both cases, the thickness of these dry, adherent and crack-free coatings was $30\ \mu\text{m} \pm 5\ \mu\text{m}$.

The decrease in potential can be taken as a measure of the coating failure and makes it possible to find out directly whether effective cathodic protection of the steel base is going on. So, it clearly appears (see Fig. 5) that both coatings offer electrochemical protection of the ferrous support for more than 1000 h, the values of the measured potential being the $-1000\ \text{mV/SCE}$ zinc electrode potential throughout this time. Moreover, and contrary to all expectations, the cathodic protection period of the less zinc-loaded coating (C_{40}) is twice as long. Unfortunately, no useful information, concerning the corrosion mechanism that is involved, can be obtained by this potential/time method. Electrochemical impedance spectroscopy combined with electron microprobe microanalysis has made a significant contribution to this corrosion study and results will be discussed elsewhere. In any event, and without going into all the details, it clearly appears that the morphology of the less zinc loaded coating and the chemical structure of the silica binder, both have a direct influence on the diffusion process of corrosive species like O_2 or Cl^- .

5. Conclusion

Both layout and concentration of ethoxy and silanol groups within the coating's silicate structure have a significant influence on the filming properties of sol-gel derived coatings. The best lasting physico-mechanical properties of such coatings are obtained with a three dimensional polycondensation process that induces a silicate

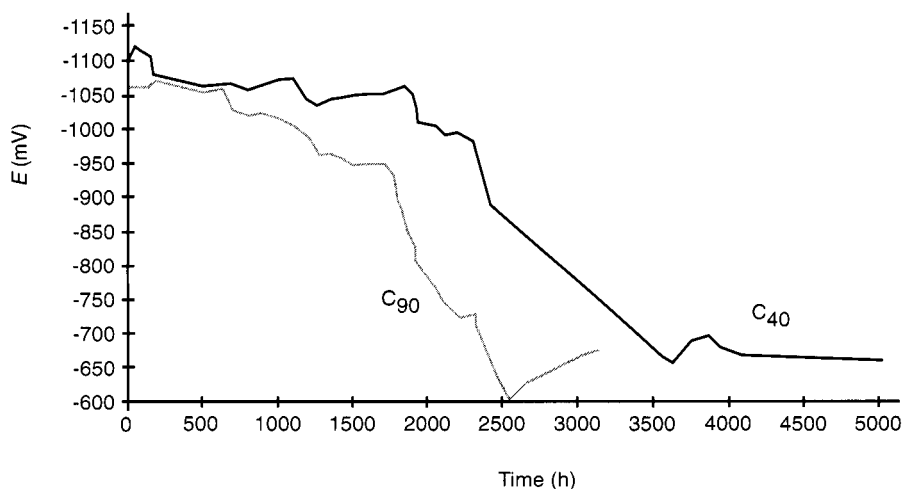


Fig. 5 Potential vs time curves of samples C_{40} and C_{90} .

network containing isolated silanol and ethoxy groups. Application by our process of such zinc-loaded coatings, that do not suffer from cracking, is now possible even on polished ferrous substrates. It was also proved that one can markedly reduce the zinc dust concentration without prejudicing the anticorrosion characteristics of the coating.

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Part 3

Other Metallic Coatings

A Review on Laser Surface Modification for Enhanced Corrosion Resistance

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ABSTRACT

A review of the main results found in the literature of the effect of laser surface modification (including melting, alloying and cladding types of treatments) on the corrosion performance of different metallic materials is presented. This survey as well as the personal experience of the authors that have participated in two EC (European Community) funded programmes related to this topic lead to the conclusion that the success of the treatment depends on the type of process. Thus, surface cladding seems to have stronger potential for industrial applications than the other two types of treatment.

1. Introduction

Laser surface modification is a term used mainly to refer to three procedures: laser surface melting (LSM), laser surface cladding (LSC) and laser surface alloying (LSA). Laser processing uses a high power laser beam that rapidly heats a thin surface layer of the material with very high energy density followed by rapid self-quenching provided by the bulk substrate, acting as a huge heat sink. The cooling rate in the laser process is controlled by the laser processing parameters according to the various requirements. It can be as high as 10^7 deg s^{-1} which is sufficient for some alloys with a deep eutectic to form metallic glasses. In most cases, the cooling rate in the laser surface melting is typically in the order of 10^3 deg s^{-1} and the cooling rate in the laser surface alloying and laser surface cladding ranges from 10^2 – 10^3 deg s^{-1} . Laser surface treatment modifies corrosion behaviour of the materials by altering one or more of the following parameters: surface composition, microstructure, distribution of the alloying elements and impurities or secondary phases.

2. Laser Surface Melting

In laser surface melting, a laser beam melts a thin surface layer and the underlying bulk provides self-quenching, with cooling rates from 10^3 up to 10^7 deg s^{-1} .

The first application of laser processing for improving corrosion resistance of metals appears in the work of Anthony and Cline [1] on surface normalisation (desensitisation) of AISI 304 stainless steel by laser surface melting. Under certain heat treatments or welding practices, 304 stainless steel becomes sensitised and susceptible

to catastrophic intergranular corrosion. Within the sensitisation temperature range, carbon rapidly diffuses to the grain boundaries where it combines with chromium to form chromium carbides (Cr_{23}C_6 or other carbides depending on the temperature), thus depleting chromium in the grain boundaries. Not only do the grain boundaries contain less Cr for passivation, but a galvanic cell is set up between the grain boundaries (small anodic areas) and the unaffected grains (large cathodic areas). The result is rapid electrochemical attack along the grain boundaries and deep penetration of the bulk. Anthony and Cline using a laser beam melted the surface layer of the sensitised AISI 304 stainless steel followed by rapid self quenching. Specimens processed in this manner, due to the refined microstructure and redistribution of chromium in the grain (or subgrain) and grain boundary (or subgrain boundary), were resistant to intergranular corrosion when subjected to a standard Strauss test (a boiling solution of 10% H_2SO_4 and 10% CuSO_4) for 72 h, whereas there was severe intergranular corrosion of the unprocessed (sensitised) surfaces.

Nakao and Nishimoto [2] used laser surface melting to desensitise the heat-affected zone (HAZ) near the welds on AISI 304 stainless steel. After laser melting, the specimens were found to be immune to intergranular corrosion in a standard 10% oxalic acid electrolytic etch test in the HAZ which otherwise suffers 'weld decay'. Recently it has also been found that laser surface melting eliminates the intergranular stress corrosion of sensitised AISI 304 stainless steel in 0.5M sodium thiosulfate solution [3].

McCafferty *et al.* [4] studied the pitting corrosion resistance of the laser surface melted AISI 304 stainless steel in 0.1M NaCl solution. The anodic polarisation curve for the laser surface melted AISI 304 is presented in Fig. 1. For comparison, the anodic polarisation curves for the commercial AISI 304 and AISI 316 were also included in the Figure. Laser surface melting of AISI 304 increases the pitting potential of the steel by at least 200 mV which is more effective than that given by the usual practice of using a Mo-containing stainless steel (AISI 316). Using Auger Electron Spectroscopy

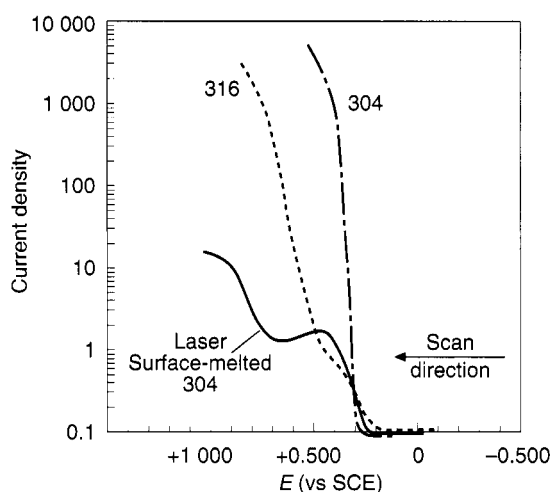


Fig. 1 Effect of laser surface melting on the anodic behaviour of AISI 304 stainless steel in 0.1M NaCl (after ref.[4]).

(AES) analysis no difference was found between the passive films formed on the LSM sample and on its commercial counterpart. With Electron Probe Microanalysis (EPMA), the authors found that the sulfur content in the LSM sample is half of that in the commercial steel. The above analysis results indicate that the improved pitting corrosion resistance by laser surface melting is due to the removal or redistribution of the large sulfide inclusions, which are known to be preferred sites for pit initiation in stainless steels.

The redistribution of these inclusions during the rapid solidification process in the laser surface melting results in a larger number of smaller inclusions which were believed [4] to be less harmful to pitting corrosion resistance. In addition, the high temperature in the laser process probably causes evaporation of these inclusions, thus reducing the amount of inclusions.

Stewart and Williams [5] studied the effect of laser surface melting on the pitting corrosion behaviour of high sulfur (HiS) 304 stainless steel produced in the laboratory and commercial AISI 304 stainless steel in 1000ppm chloride solution with a stochastic method. They found that laser surface melting markedly improved the pitting corrosion resistance of the type 304 stainless steel — the nucleation frequency and life time of micropits were both reduced and the cumulative probability of nucleation of a stable pit was also decreased as a consequence of the laser treatment — as shown in Fig. 2.

The authors also found that the sulfide inclusions in the laser surface melted layer were smaller than $0.5\ \mu\text{m}^2$ and admitted that with this size, the inclusions could not induce damaging pits.

Lumsden *et al.* [6] have also found that laser surface melting of AISI 304 stainless steel raised the pitting corrosion potential in 0.1M NaCl, in agreement with the above results. Laser surface melting also facilitated passivation in 1N H_2SO_4 by decreasing the critical current density for passivation. They suggested that the mechanism for the improvement involves the elimination or refinement of the second-phase inclusions such as sulfides. However, the same authors found that laser surface melting and rapid solidification had different effects on the pitting behaviour of a series of ferritic stainless steels of composition Fe–13Cr– x Mo, where x varies from 0 to 5%. As shown in Table 1, unless the Mo content was at least 3.5%, laser melting had either a deleterious effect or no effect on the pitting potential. An increase in pitting potential was obtained only for the 5% Mo alloy.

Bonora [7] has reported that surface melting of AISI 304 stainless steel with a $5.6\ \text{J cm}^{-2}$ laser pulse promotes the anodic dissolution and pitting nucleation in 0.5M Na_2SO_4 containing Cl^- . In this case, laser melting produced an unfavourable surface finishing consisting of craters and thermal fatigue striations that enhance pit nucleation. An identical effect has also been found in surface melting of Fe–19Cr by Q-switched Nd-YAG laser [8].

Moore *et al.* [9] studied the effect of surface modification by LSM using a CO_2 laser on the pitting behaviour of the Al 2024 aluminium alloy but found no improvement in the pitting resistance because of the cracks and pores that were present in the treated surface.

McCafferty *et al.* [10] studied the corrosion behaviour of Al 3003 (Al–Mn) aluminium alloy with the surface melted by a CO_2 pulse laser with an output of $100\ \text{J cm}^{-2}$ for 1 μs duration in a low vacuum chamber. They measured the uniform

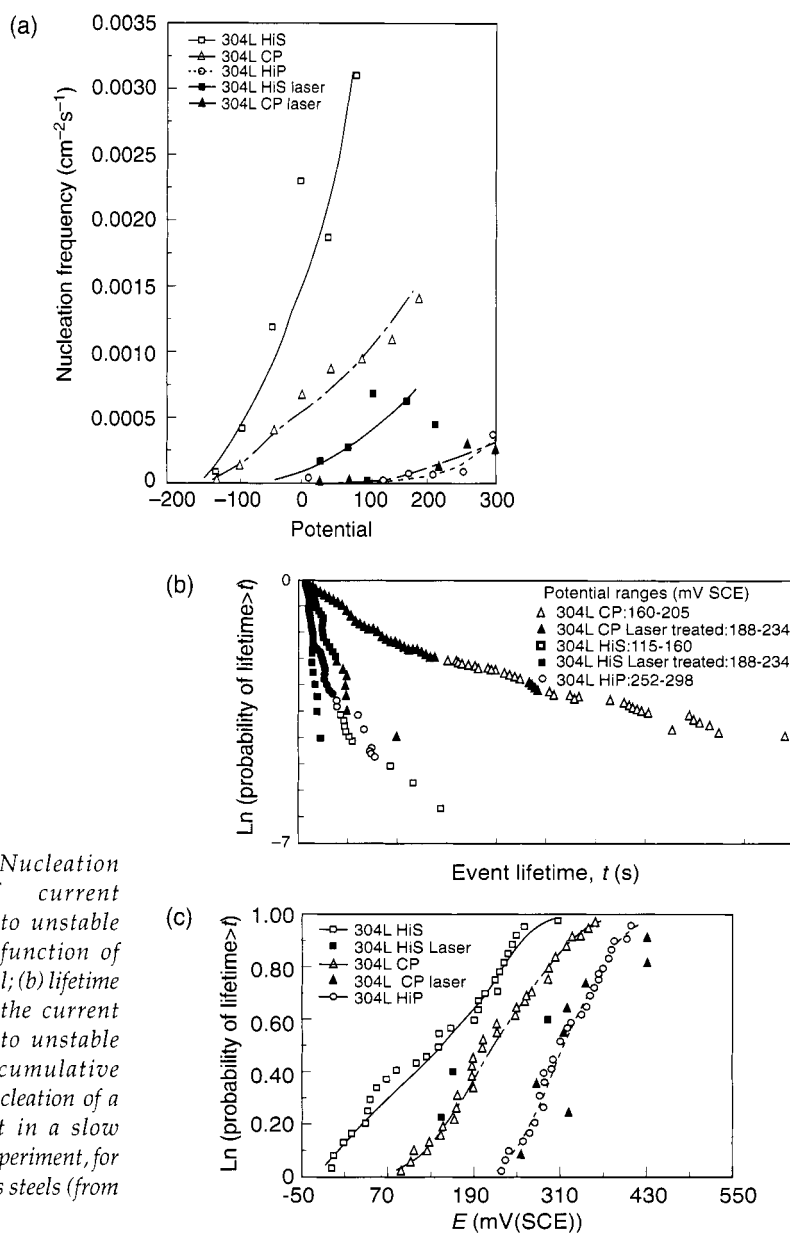


Fig. 2 (a) Nucleation frequency of current transients due to unstable micropits as a function of electrode potential; (b) lifetime distribution of the current transients due to unstable micropits; (c) cumulative probability of nucleation of a propagating pit in a slow potential ramp experiment, for different stainless steels (from ref. [5]).

corrosion rates of the laser surface melted sample and an untreated sample in 0.1M HCl and 0.1M sodium citrate solutions by cathodic polarisation and colorimetric analysis and found that the corrosion rate for the former is about half of that for the latter. However, the pitting potential of the alloy in 0.1M NaCl was unchanged by laser surface melting. Similar results had also been obtained previously for the pitting corrosion of laser surface melted pure aluminium in 0.1M NaCl by Bonora *et al.* [11].

Bonora *et al.* [11] observed the effect of LSM on the corrosion behaviour of pure Al using a Q-switched nanosecond pulsed ruby laser with energy density at the surface

Table 1. Effect of laser surface melting on the pitting potential of ferritic stainless steels in 0.1M NaCl (after ref. [6])

Composition	E_{pit} (mV)/ untreated	E_{pit} (mV)/LSM	Effect of LSM
Fe–13Cr	115	–100±40	Harmful
Fe–13Cr–2Mo	200	–5±5	Harmful
Fe–13Cr–3.5Mo	230	230±20	None
Fe–13Cr–5Mo	280	420±40	Beneficial

between 1 and 5 J cm^{–2}, giving an estimated cooling rate of the order of 10¹¹ K s^{–1}. The pitting potential was unchanged after LSM but the current density was lower on anodic polarisation under both potentiostatic and potentiodynamic control. This effect was also observed by Hagans and Yates [12] for a pure Al surface melted using a Q-switched Nd-YAG laser with 5 ns pulses at 4 mJ/pulse when the material was corrosion tested in a boric–borate solution containing 1 g L^{–1} NaCl.

Opara *et al.* [13] reported that the anodic current density of an Al–Si alloy polarised in 5% NaCl solution at potentials more negative than the breakdown potential is related to the specific energy input of laser treatment.

Virtanen *et al.* [14] have reported that laser surface melting of cast Al–Si (7–12%) alloys significantly refined the microstructure of the alloys. Thus, the dissolution rate of Al–Si alloys at the free corrosion potential in 0.1M NaCl solutions was decreased after laser surface melting and the critical pitting potential was increased for Al containing 7–12% Si significantly, but not for Al–17% Si after LSM.

Draper *et al.* [15] studied the corrosion of a series of laser surface melted aluminium bronzes (Al–Mn–Fe) in acidified chloride solution. Laser surface melting eliminates the Fe-rich phase which is an anodic phase existing in the commercial alloys making the surface more homogeneous, thus improving the corrosion properties. The same group [16] also investigated the effect of laser surface melting on the corrosion behaviour of tin-modified copper–nickel alloy (88.2 Cu–9.5 Ni–2.3 Sn) in humid atmospheres containing H₂S or Cl₂ pollutants. Laser surface melting significantly decreased the thickness of the corrosion product layers.

Recently Li, Ferreira *et al.* [17] found that laser surface melting of 2024-T351 aluminium alloy evaporates Mg selectively from the melted layer, changing the precipitates from CuAl₂Mg to CuAl₂ after solidification. Laser surface melting also refines the microstructure at the subgrain scale. The laser surface melted layer is composed of fine dendrites and continuous CuAl₂ precipitates in the dendrite boundaries (Fig. 3). Laser surface melting eliminates intergranular corrosion in chloride solution — which occurs in commercial 2024-T351 aluminum alloy (Fig. 4) — due to the modification of the microstructure. The same effect is visible on the anodic polarisation curves of the alloy as-received and after laser treatment (Fig. 5). The anodic transient at –652 mV for the as-received sample is indicative of

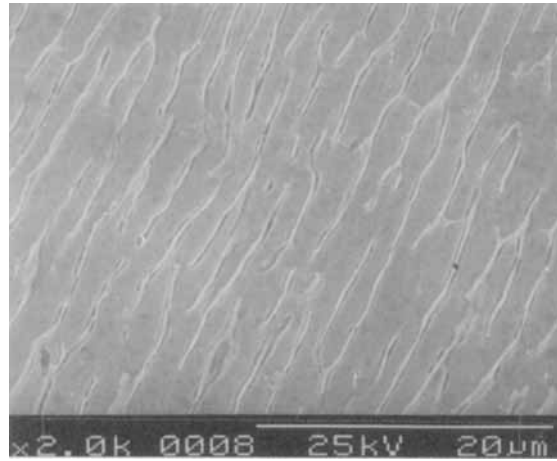


Fig. 3 Microstructure of laser surface melted layer showing CuAl_2 precipitates around the dendrites (after ref. [17]).

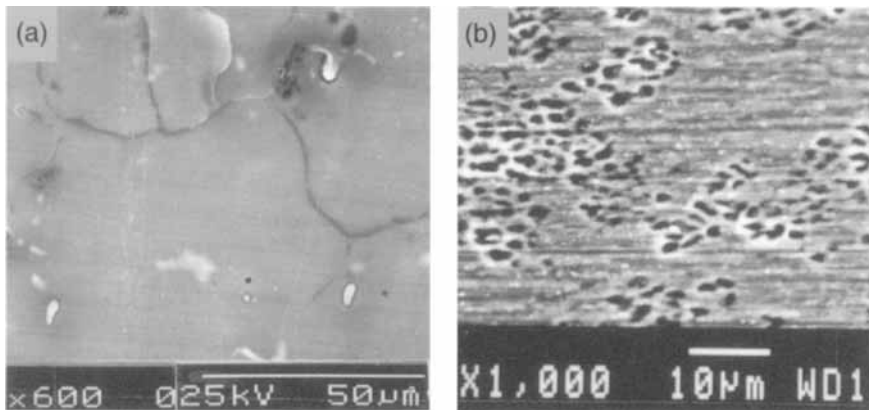


Fig. 4 Localised corrosion morphologies of 2024-T351 after anodic polarisation in deaerated 3% NaCl. (a) As-received showing pitting and intergranular corrosion; (b) after laser treatment showing only pitting corrosion (after ref. [17]).

intergranular corrosion [17]. For the melted sample the transient vanishes, since only pitting corrosion takes place at -635 mV.

Becker *et al.* [18] and Asami *et al.* [19] found that amorphous layers could be produced by laser surface melting of Ni-Nb and Fe-Si-B alloys, respectively, but complications arose due to the fact that partial recrystallisation occurred in regions where there was overlapping of passes during the processing. By decreasing the time for laser irradiation and selecting surface alloy compositions having a longer time for recrystallisation from the amorphous state, Asami *et al.* [19], Yoshioka *et al.* [20,21] and Hashimoto *et al.* [22] were able to prepare amorphous surface alloys of Pd-Cu-Si, Fe-Cr-P-C, Fe-Cr-Mo-P-C and Pd-25Rh-10P-9Si by laser surface

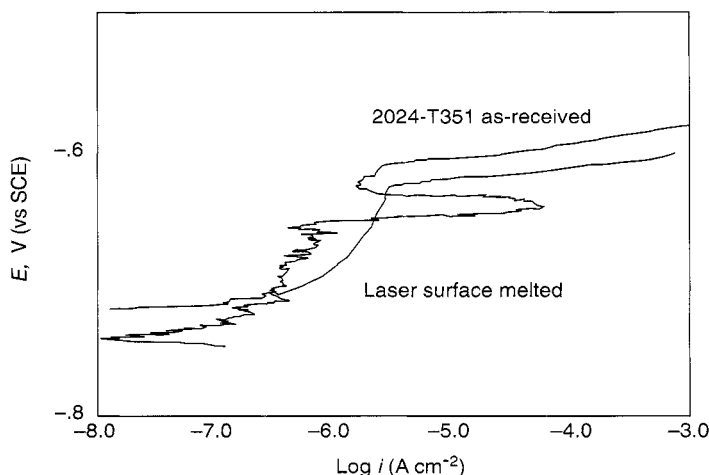


Fig. 5 Anodic polarisation curves of Al2024-T351 as-received and laser surface melted in deaerated 3% NaCl solution (after ref. [17]).

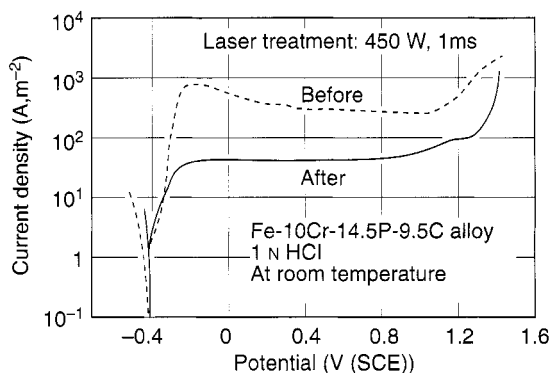


Fig. 6 Anodic polarisation curves of Fe-10Cr-14.5P-9.5C in 1M HCl before and after LSM (after ref. [19]).

melting of the master alloys. Figure 6 shows the effect of laser processing on the anodic polarisation behaviour of Fe-10Cr-14.5P-9.5C alloy in 1M HCl. The laser processed sample is passivated at the free corrosion potential whereas the unprocessed sample undergoes active dissolution. Moreover, the passive current density is reduced by one order of magnitude for the processed sample.

A similar effect has also been found on laser surface melting of Pd-25Rh-10P-9Si alloys as shown in Fig. 7, in which the anodic polarisation curve of the melt-spun amorphous ribbon as well as that of the crystalline cast alloy are also included for comparison. The laser processed amorphous surface alloy presents much better passive behaviour than its crystalline counterpart and slightly better or equivalent passive behaviour to the melt-spun amorphous ribbon in 0.5M NaCl.

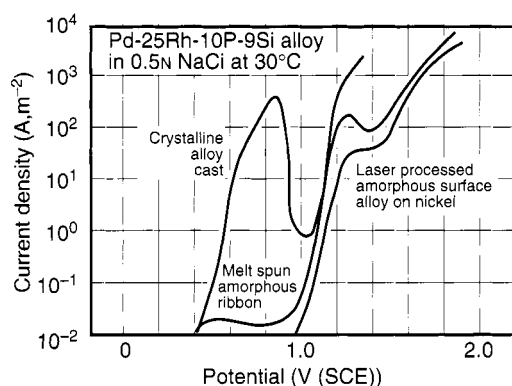


Fig. 7 Anodic polarisation curves of amorphous and crystalline alloys of Pd-25Rh-10P-9Si in 0.5M NaCl (after ref. [22]).

3. Laser Surface Cladding

Laser surface cladding is a process in which the surface of the substrate is melted slightly by a laser beam with simultaneous delivery of foreign materials in the molten pool. After solidification, a coating forms on the substrate with little dilution of the substrate. Laser surface cladding can also be performed by completely melting materials predeposited on the substrate which is only slightly melted by the laser beam.

In the earlier work, laser surface cladding was carried out by laser beam melting of materials predeposited on the surface by flame or plasma spraying, electroplating, etc. Usually the coatings produced by flame or plasma spray have residual porosity and bad adhesion to the substrates. Laser melting can eliminate the porosity and improve the adhesion of the coatings to the substrates thus increasing the corrosion resistance.

Ayers *et al.* [23] studied the effect of laser melting of plasma sprayed Ti coatings on mild steel. Laser melting eliminates the porosity that existed in the coating. Results of immersion tests in natural seawater for 15 days show that the free corrosion potential of the laser melted coating is more similar to that of pure Ti and that of the plasma sprayed coating is more similar to that of the steel substrate.

Bhat *et al.* [24] compared the protectiveness of the laser processed plasma sprayed porous Ni-Cr coating and an untreated coating in various HCl solutions in short term tests. They found that the laser processed coating was more protective whereas the untreated one suffered rapid corrosion with the corrosive solution penetrating the coating directly and attacking the underlying substrate.

Similar enhancement of corrosion resistance of flame and plasma sprayed coatings was also observed by Yang *et al.* [25], in an investigation of laser melting of Fe-Cr-Si-B and Ni-Cr-Si-B coatings produced by flame and plasma respectively, and is depicted in Fig. 8.

In 0.5M H₂SO₄ + 0.5M NaCl solution, laser melting reduces the active-passive peak current density and the passivation potential of the Fe-Cr-Si-B coating but does not

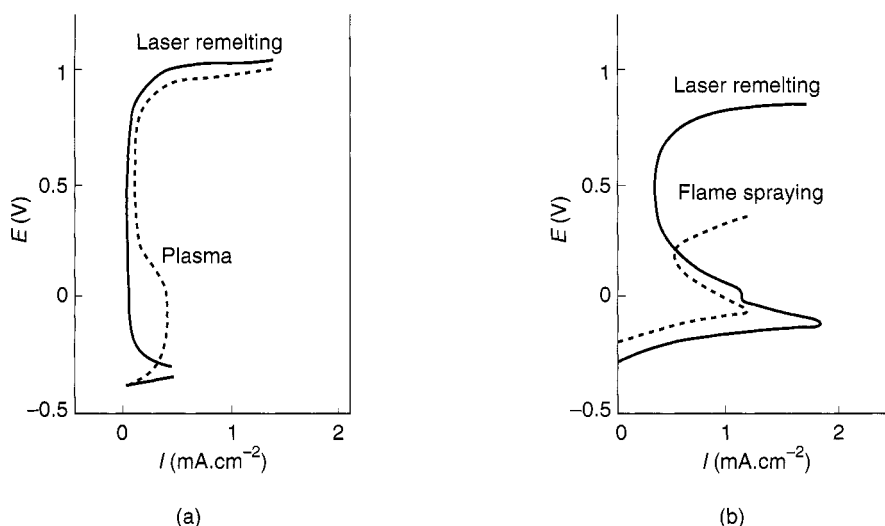


Fig. 8 Anodic polarisation curves of (a) plasma sprayed Fe-Cr-Si-B and (b) flame sprayed Ni-Cr-Si-B coatings, before and after laser processing, in 0.5M H_2SO_4 + 0.5M NaCl solution (after ref. [25]).

much affect the transpassive potential of the coating. In the case of the Ni-Cr-Si-B coating, laser melting increases the pitting potential of the coating by at least 500 mV.

A series of Ni-Cr-P-B amorphous coatings with 14–17Cr, 15–18P, 2–5B, were obtained by laser melting thin strips of master alloys with the above compositions previously bonded to the substrates [26]. The anodic polarisation tests were carried out in 1M HCl solution at 30°C and the results shown in Fig. 9. For comparison, the same tests were also performed on the crystalline master alloys and the melt-spun amorphous alloys and the results are also shown in the same Figure. The laser processed Ni-15Cr-16P-4B and Ni-10Cr-16P-4B alloys present much lower passive current density than their crystalline counterparts (Fig. 9 b,c) and the laser processed Ni-20Cr-16P-4B alloy presents anodic behaviour similar to its crystalline counterpart (Fig. 9a). In some cases, the laser processed coatings display slightly better corrosion resistance than the melt-spun amorphous, but in other cases they are worse. The behaviour strongly depends on the structure and defect character of the coatings. In the Ni-20Cr-16P-4B alloy, the laser treated overlapped area was partially recrystallised due to the heating caused by the processing of the next track that partly overlapped the previous one and there were also small cracks in the surface. Therefore its corrosion resistance is the worst among all the laser processed samples. In the Ni-10Cr-16P-4B alloy, the overlapped area was also partially crystallised but cracks were not present; thus the corrosion resistance of this alloy is better than the 20Cr laser processed sample, but is not as good as its melt-spun amorphous counterpart. In the Ni-15Cr-16P-4B alloy, the coating is totally amorphous, thus displaying the best corrosion resistance among these three laser processed samples and it is even better than its melt-spun amorphous counterpart.

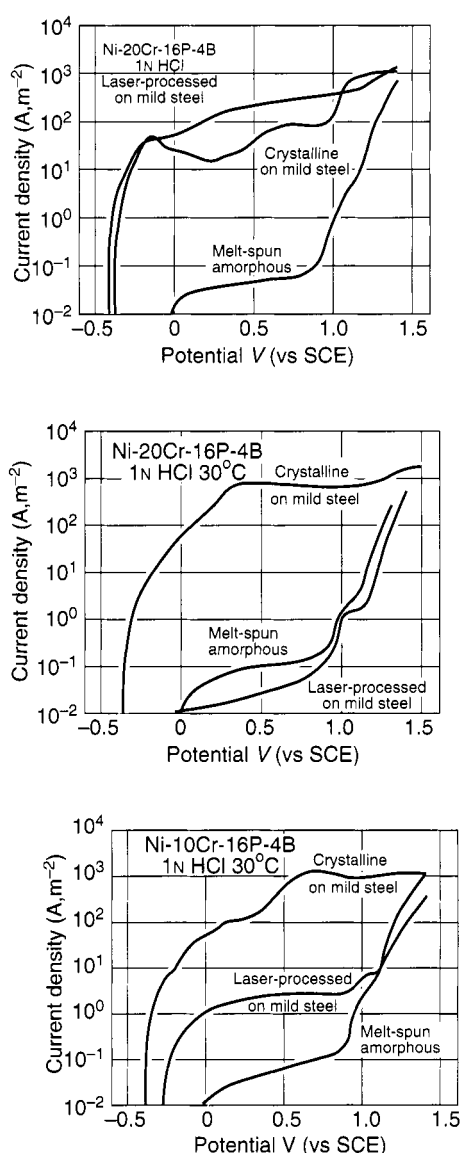


Fig. 9 Anodic polarisation curves for Ni-xCr-16P-4B alloys in 1M HCl at 30°C (after ref. [26]).

Ni-40Nb and Ni-40Nb-10Cr amorphous coatings were also successfully deposited on a copper substrate by laser surface cladding [27]. Figure 10 shows the anodic polarisation curves of the coatings and crystalline Ni-40Nb alloy in 0.5M H_2SO_4 . The critical passivation current density of the amorphous Ni-40Nb is about one order of magnitude lower than that of the crystalline alloy and is further reduced by another half order of magnitude, by the addition of 10Cr. The passive current density of the amorphous Ni-40Nb is one and half orders of magnitude lower than that of its crystalline counterpart and is also further reduced by the addition of 10Cr by another one order of magnitude.

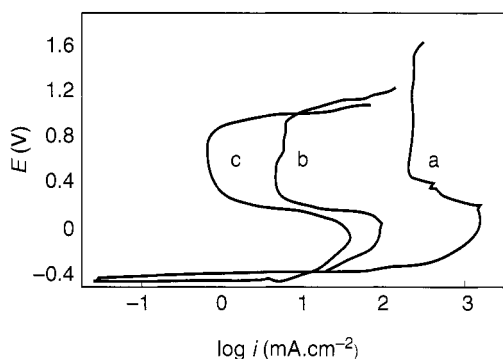


Fig. 10 Anodic polarisation curves of (a) crystalline Ni60Nb40, (b) amorphous Ni60Nb40 and (c) Ni60Nb40Cr10 coatings processed by laser in 0.5M H_2SO_4 (after ref. [27]).

More recently, in order to provide cathodic protection of steels, coatings of Zn–Al were produced, with simultaneous delivery of the powders into the molten pool under the laser irradiation, and corrosion tested [28,29]. The corrosion potentials of the Zn– x Al coatings (x , 0–7 wt%) produced by LSC in 0.5M NaCl are *ca.* –1.025 V(SCE) which is similar to that of the pure zinc and lower than that of steel (*ca.* –0.75V). Therefore the Zn– x Al coatings can provide cathodic protection to the steel. The corrosion rate of Zn–6Al coating is one order of magnitude lower than that of the pure zinc.

Li *et al.* successfully laser clad UNS S44700 (Fe–30Cr–4Mo) superferritic stainless steel [30] and UNS S31254 (Fe–19Cr–18Ni–6Mo–0.2N) superaustenitic stainless steel [31] on mild steel by delivering on the substrate a powder mixture with the alloys' composition and simultaneously laser melting. The surface alloy in both cases consisted of fine dendrites with slight segregation of Cr and Mo in the dendrite boundaries. XRD results showed that the structure of the surface alloy was ferritic in the former case and austenitic in the latter case as were their respective commercial counterparts. From the corrosion resistance point of view both surface alloys behaved similarly to their commercial counterparts, i.e. they did not pit in anodic polarisation tests carried out in NaCl and $FeCl_3$ solutions. After immersion in 1M $FeCl_3$ solution (acidified to pH 0.4) for two months the ferritic surface alloy pitted slightly, whereas the austenitic surface alloy showed a large amount of small pits with a grid pattern, due to the preferential attack of the dendrites depleted in Mo and Cr.

4. Laser Surface Alloying

Laser surface alloying is very similar to laser surface cladding. The only difference is that in laser cladding, the substrate is almost unmelted during the laser processing whereas in laser surface alloying the substrate is melted to a certain extent to form surface alloys with the molten alloying elements that are added.

One of the earliest studies on the corrosion behaviour of laser surface alloyed

steel was performed on 1018 steel (carbon steel) alloyed with Cr by laser melting a pre-sputtered Cr layer on the substrate in deaerated 0.1M Na₂SO₄ [32]. The anodic polarisation curves are presented in Fig. 11. The 1018 steel undergoes extensive active dissolution at all anodic potentials, whereas the three Fe–Cr surface alloys passivate. As seen in Fig. 11, with the increasing Cr content, there is a decrease in both the critical current density for passivation and passive current density.

However, the passive current densities of the laser surface alloyed samples are 100 times larger than for AISI 430 stainless steel (16Cr, 0.4Mn, 0.3Si, 0.05C, balance Fe) in the same solution and 5–50 times larger than for comparable Fe–Cr binary alloys in 1N H₂SO₄ [33,34]. The authors ascribed this difference mainly to local chemical inhomogeneity in the laser surface alloys and also to the existence of small cracks and stresses in the surface.

The decrease of corrosion resistance due to local chemical inhomogeneity was also observed on laser surface alloying of the same steel with Cr and Si in 0.5M NaCl [35].

To obtain a homogeneous composition distribution of alloying elements in the coatings, following laser surface alloying of mild steel with Cr and Ni, laser surface melting was adopted by Chiba *et al.* [36]. They found that with the increase of the number of laser melting cycles, the composition becomes more uniform and the corrosion resistance of the surface alloys increases in 0.5M H₂SO₄ and 0.5M H₂SO₄ + 0.5M NaCl solutions. However, with further increase of the number of laser melting cycles, the corrosion resistance decreases because the chromium concentration in the coating decreases due to its selective evaporation. The effect of the number of the laser melting cycles on the chromium concentration in the coating and corrosion behaviour is displayed in Figs 12 and 13, respectively.

It is usually more difficult to obtain the desired composition in a surface alloy by laser surface alloying than by laser surface cladding, especially in multi-element alloys. To produce a surface alloy with the same composition as AISI 316, different laser processing parameters were tried and several Fe–Cr–Ni–Mo surface alloys, with

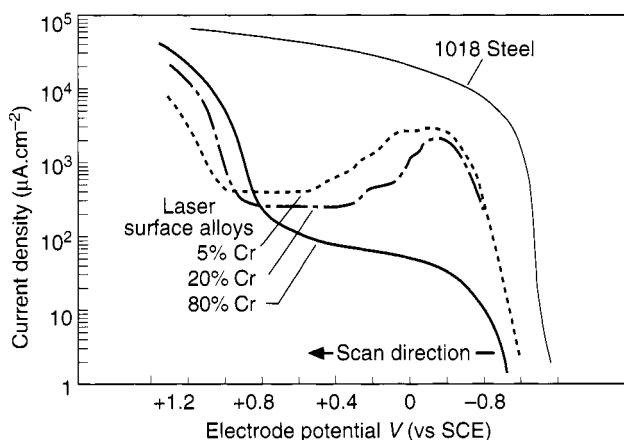


Fig. 11 Anodic polarisation curves of laser alloyed 1018 steel and untreated 1018 steel in 0.1M Na₂SO₄ (after ref. [32]).

different compositions and microstructures, were produced before a surface alloy with similar composition to AISI 316 was obtained [37]. The surface alloy with similar composition to AISI 316 displayed much better passivation behaviour and higher pitting corrosion resistance than its commercial counterpart. The passive current density is more stable and the pitting potential is about 200 mV higher than that of the commercial steel, because the sulfide inclusions, which are generally thought to act as precursors of pits, were eliminated from the surface alloy as indicated by both EPMA and EDX.

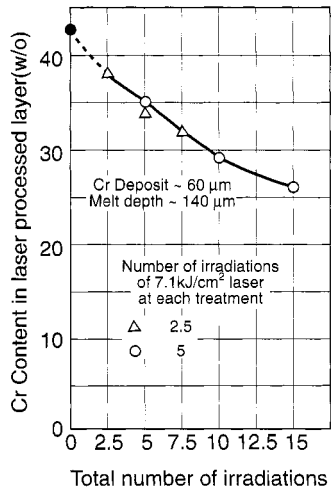


Fig. 12 Effect of the number of laser melting cycles on the chromium concentration in the coating (from ref. [36]).

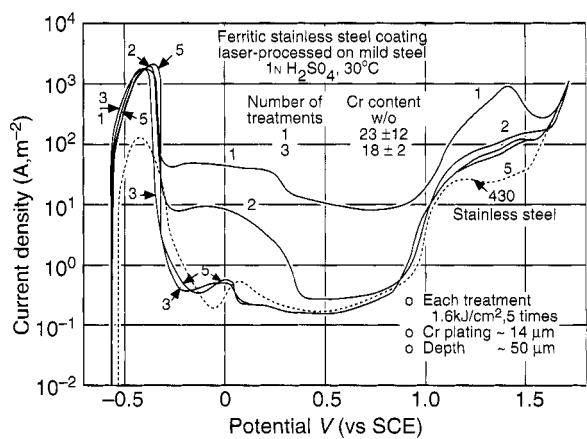


Fig. 13 Effect of the number of laser melting cycles (1–5) on the corrosion behaviour of an iron based surface alloy in 0.5M H₂SO₄ (from ref. [36]).

Using a CO₂ laser with 10kW, Lumsden *et al.* [38] produced Fe–Cr–Ni surface alloys by melting a layer of Ni and Cr powder mixture on steel predeposited as a slurry. Passivation performance of these surface alloys was studied in 1N H₂SO₄. The passivation performance of all Fe–Cr–Ni surface alloys were found to be superior to that of the substrate (AISI 4140), with the critical passivation current density for passivation decreasing in the order: AISI 4140 > Fe–11Cr–4Ni > Fe–19Cr–8Ni > Fe–29Cr–13Ni. The passivation behaviour of the Fe–11Cr–4Ni alloy was found to be inferior to the passivation behaviour of AISI 304 stainless steel, the passivation behaviour of the Fe–19Cr–8Ni alloy comparable, and the passivation behaviour of the Fe–29Cr–13Ni alloy superior.

Fe–Ni–Cr and Fe–Ni–Cr–P surface alloys were also produced by laser melting electroplated Cr and Ni layers for the former surface alloy and electroplated Cr and Ni–P layers for the latter surface alloy [39,40]. Fe–21Ni–24Cr and Fe–24.5Ni–22Cr surface alloys display higher pitting corrosion resistance than AISI 304 in 0.5M NaCl whereas the Fe–17Ni–15Cr–xP (*x* is unknown) alloy suffers rapid dissolution in the same solution due to the formation of a M₃P type intermetallic compound that precipitates in the dendrite boundaries and which probably causes depletion of Cr in the dendrites destroying the passivity of the surface alloy.

Moore *et al.* [41] produced type 300-series stainless steel surface alloys with different amounts of Mo by laser melting Mo, Cr, and Ni layers deposited on AISI 304 substrates. Addition of Cr and Ni here is to maintain the chemical composition in the range of the 300-series. The anodic behaviour of the surface alloys is displayed in Fig.14. In 0.1M NaCl, Fe–18.9Cr–9.1Ni–3.7Mo surface alloy presents comparable corrosion resistance to that of the commercial AISI 316 (16–18Cr, 10–14Ni, 2–3Mo). Moreover, the Fe–19.2Cr–11.7Ni–9.6Mo alloy did not pit.

Laser surface alloying of AISI 304 stainless steel with Si produces a microcrystalline

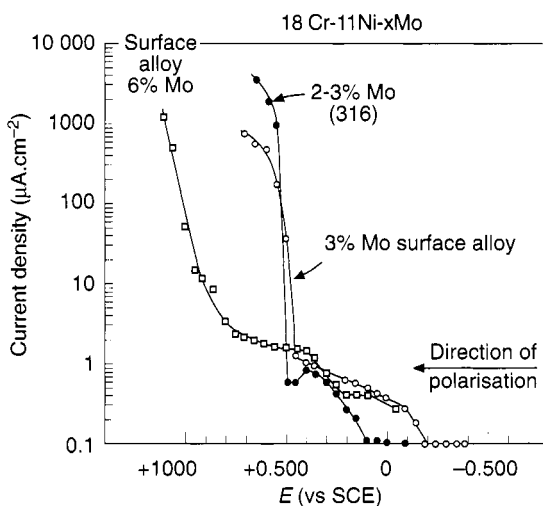


Fig. 14 Anodic polarisation curves of Fe–Cr–Ni–Mo surface alloys produced by LSA in deaerated 0.1M NaCl (from ref. [41]).

intermetallic compound coating with Fe_3Si structure [42]. This coating did not undergo pitting corrosion in $0.5\text{M H}_2\text{SO}_4 + 0.5\text{M NaCl}$ and the passive current density was one order of magnitude lower than for the untreated AISI 304 stainless steel. Moreover, laser surface alloying also greatly increases the wear resistance of the steel.

Incorporation of nitrogen in the surface alloy by laser melting AISI 304 stainless steel in a nitrogen atmosphere gives variable pitting corrosion results [43]. With some laser processing parameters, it increases the pitting potential of the steel in 0.5M NaCl by 80 mV, whereas with other parameters, it decreases the pitting potential. The existence of nitrogen in the surface was confirmed by secondary ion mass spectroscopy (SIMS). However, the state of nitrogen (solute or nitride) in the alloy surfaces which is vitally important for the pitting corrosion resistance of the alloys was not determined.

Recently, it was shown that laser surface alloying of AISI 4135 steel (0.33C, 0.75Mn, 0.3Si, 1.09Cr, 0.185Mo, 0.007P, bal Fe) with noble metals including Pd, Pt and Au effectively retards hydrogen ingress into the steel [44].

Li *et al.* [45] alloyed Al7175-T7351 with chromium producing a microcrystalline surface alloy with extended solubility of chromium in the α -Al phase. An identical result was obtained using pure aluminium as substrate [46]. To homogenise the chemical composition and improve the surface condition of the alloyed layers, they were then laser remelted. In the alloyed and remelted layer the microstructure was very fine showing a cellular equiaxed morphology with intermetallics organised radially around primary cubic particles (Fig. 15a). Underneath this layer in a region that corresponds to the material that was not affected by the remelting treatment, i.e., the structure results only from alloying; the predominant morphology shows long faceted needles of intermetallic compounds dispersed in a matrix of aluminium as observed in Fig. 15(b).

The presence of chromium in Al7175-T7351 laser surface alloy enhances pitting corrosion resistance and hardness of the alloys as shown, respectively, in Figs 16 and 17. The higher the chromium content in the laser alloyed layer the higher is the pitting potential. This improvement is due to the formation of a passive film containing CrOOH and/or Cr_2O_3 which retards the propagation of pitting.

5. Conclusions

- Laser surface treatments are able to modify the microstructure and/or surface composition of substrates, thus changing the corrosion behaviour of the substrate.
- The success of the treatments depends on the effectiveness of the control of the local chemical composition and its homogeneity. The presence of pores, cracks or other irregularities is also usually deleterious for the corrosion behaviour.
- Of the various treatments, laser surface cladding shows comparatively stronger potential for application in industry, since the processing is easier to control.

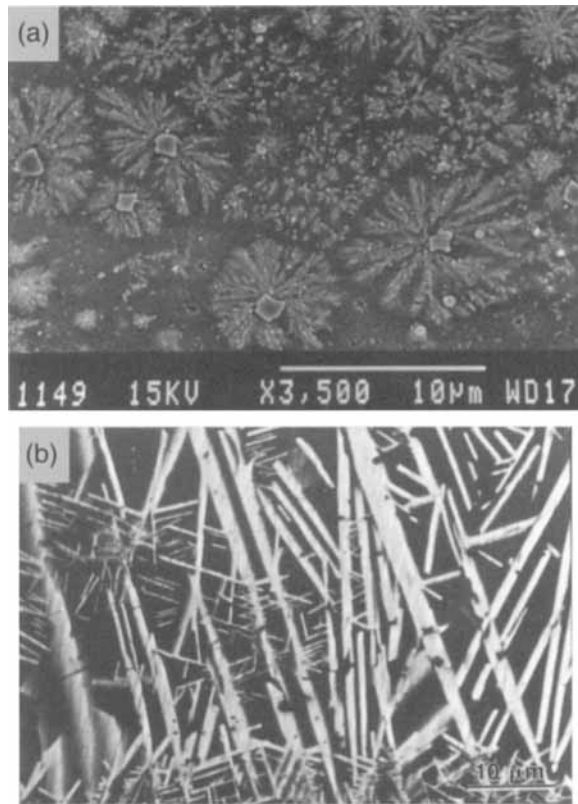


Fig. 15 (a) Cellular structure at the top of aluminium–chromium alloyed and remelted layer showing radial intermetallics around primary cubic particles; (b) needle shaped intermetallics at top of the aluminium–chromium alloyed layer (after ref. [45]).

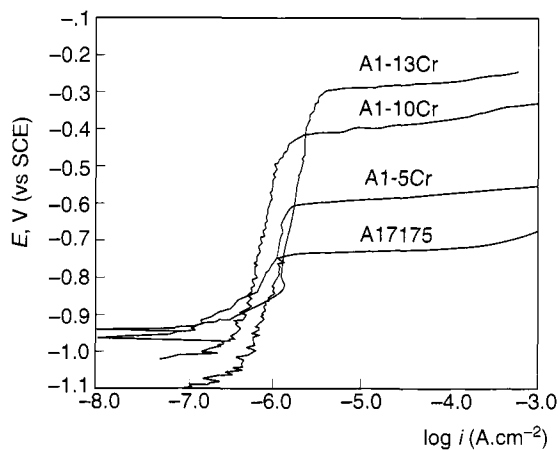


Fig. 16 Anodic polarisation curves of untreated Al7175-T7351 and laser chromium alloyed 7175 alloy in deaerated 3% NaCl solution (after ref. [44]).

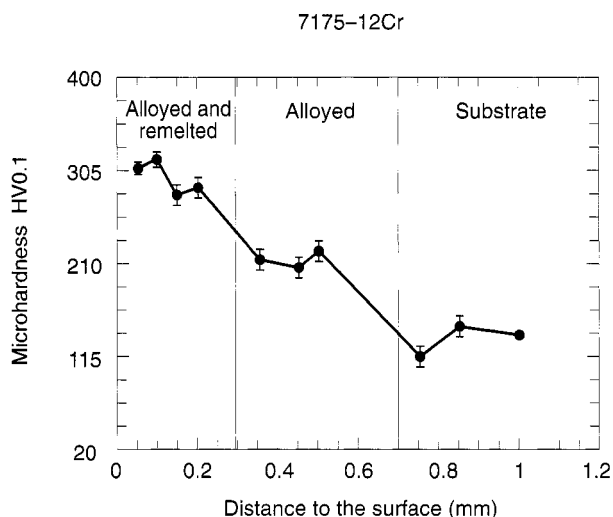


Fig. 17 Microhardness profile of laser alloyed Al7175 alloy with chromium (12Cr) (after ref. [45]).

- Laser surface modification could be a good alternative to other surface modification processes to enhance corrosion (and wear resistance) since adherence to the substrate is very good and the process is environmentally friendly. However, careful attention must be given to processing aspects. It must also be recognised that laser surface treatments are only feasible for small areas of materials.

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Protection of Steel Structures in Marine Applications against Corrosion Using Aluminium Spray Coatings

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ABSTRACT

Long-life and maintenance free anti-corrosion coatings are eagerly pursued, both by environmentalists as well as by those responsible for maintenance of steel structures. Traditional organic systems often do not meet these requirements. An obvious alternative is offered by using metal spray coatings: zinc for atmospheric applications, aluminium for sea water environment. For the latter, literature reports a service life exceeding 20 years. An extensive literature survey concluded the use of aluminium spray coatings for the protection of steel surfaces in marine applications to be 'very promising', nonetheless their actual use in The Netherlands is almost non existent. A possible explanation would be the poor documentation of practical experience in literature, combined with a lack of understanding of the protective mechanisms involved, resulting in little acceptance of aluminium coatings for corrosion protection. Therefore, commissioned by the Dutch Ministry of Transport, Public Works and Water Management, a series of laboratory experiments has been used to evaluate the protective properties of aluminium spray coatings on structural steel in sea water. Techniques included are cyclic polarisation, immersion exposure continuous and cyclic, current monitoring at artificial defects, tribological and mechanical testing toughness, flexibility and adhesion strength together with the influence of fouling organisms. It is concluded that aluminium based spray coatings appear to provide a suitable protection for steel structures in sea water.

1. Introduction

In many countries, including The Netherlands, metal spray coatings are more and more being considered as a promising alternative for heavy duty anti-corrosion paint systems. Nonetheless, the amount of available research data on the performance of these systems for moderate temperature corrosion protection can be classed as modest. Perhaps for this reason the actual use of metal spray coatings for corrosion protection does not seem to reflect the expected performance of these systems; the general conclusions of reported case studies [1–13] and electrochemical investigations [14–22] are almost unanimous about the protective ability of sprayed metal coatings.

Following a request from the Dutch Ministry of Transport, Public Works and Water Management several of the most pressing design uncertainties regarding the use of metal spray coatings have been addressed. This work was directed specifically towards reducing the risks for a large scale application by systematic research. The selected systems consisted of both flame and electric arc sprayed aluminium based coatings on mild steel in natural sea water.

The research areas included the following main topics. The first was an examination of the paradox of the protective mechanism of an aluminium coated steel which depends on the formation of a passive layer for general corrosion protection, but also needs to provide cathodic protection at pores and defects that expose the underlying steel. A second main area of interest was the role of a sealer coating. Most coating suppliers appear to recommend the use of an organic sealer to be applied on top of the metallic spray coating [23,24]. The suggested reason is generally to 'block pores... and to extend the service life of the metallic coating'. This also invokes a paradox since, generally, organic coatings cannot be expected to last longer than, perhaps half the service life of an uncoated metallic spray coating [25–29]. The use of a sealant would then effectively halve the 'time to first maintenance' which would consist of removing the deteriorated sealer and re-applying a new layer. And, although the steel substrate would undoubtedly be adequately protected, the thermal spray coating would be reduced to a very expensive primer. The third concern of coating sceptics is that metallic thermal spray coatings would be too brittle to be applied on large structures that are subjected to a dynamic load and consecutively show elastic strain during service. The thermal spray coating is suspected to be unable to support this movement and crack at the stressed areas.

Furthermore, as a fourth subject, there is the possibility of using thermal spray aluminium as a sliding surface for moving parts in sluices or other sliding-gate systems. The counter surface in such a system would typically be a high performance polymer as for instance, ultra-high molecular weight polyethylene UHMWPE. Although this application would not be expected to remove the spray coating by friction, it could affect the integrity of the passive layer, or cause conditions for crevice corrosion, that could drastically limit the service life of the thermal spray coating.

Finally, since aluminium is known to be sensitive to micro environment changes in pH or dissolved ions [30–32], the behaviour in presence of biological fouling organisms was investigated. Barnacle growth on aluminium coatings could create pH differences underneath the organism, and the animal's shell could create de-aeration and crevice corrosion phenomena which would cause rapid attack of the coating layer.

This broad range of subjects involves many protective/failure mechanisms which in turn demand the use of a wide variety of experimental techniques to address the specific problems. To minimise the risk of introducing other failure mechanisms in the tests, the laboratory experiments were designed to be as close as possible to the actual in-service situation. The techniques used consisted of mechanical characterisation, electrochemical characterisation and monitoring during exposure experiments, supported with electron microscopy studies.

2. Experimental

2.1. Materials

Since the coating should be suitable for large surface area/low cost use, the only realistic spray techniques are autogenic flame spray and electric arc spray. Plasma, HVOF or detonation spraying will be either too limited regarding surface area and geometry, too expensive, or both.

The sprayed metals were: Al wire 99.7 %, flame spray; AlMg5 wire, arc spray.

Both systems were sprayed on a freshly grit-blasted SA3, aluminium oxide, mild steel panels of 150 mm × 100 mm × 4 mm. The target layer thickness for both metallic coatings was 100 μm . The Al99.7 coatings were applied in the laboratory, the AlMg5 were applied by a commercial thermal spray application company.

Since most literature reports the use of metal spray coatings combined with either an organic sealer non-pigmented high viscous resin or a full organic paint system, the test was extended with the following systems: Al99.7 + paint brush applied; Al99.7 + sealer brush applied; AlMg5 + paint spray applied.

The target layer thickness for both paint and sealer was 50 μm . All coating application was carried out in full accordance with the suppliers recommendations.

Figures 1 and 2 gives an impression of the cross section of the systems.

The first conclusion from this investigation is clearly illustrated by these figures. It proved very difficult to meet the target thicknesses of both the coating layers. Although the average thickness of the Al99.7 coating was indeed 100 μm , the organic

Fig. 1 Al99.7 plus full organic paint system. Magnification ca. 60 $\times$.

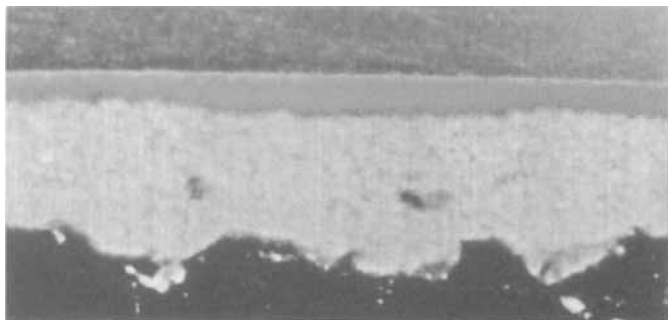
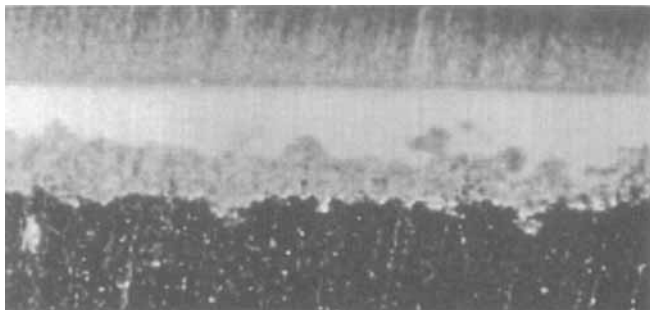


Fig. 2 AlMg5 plus full organic paint system. Magnification ca. 60 $\times$.

coating on these panels was only 30 μm . The coatings on the AlMg5 sprayed panels were both too thick: the AlMg5 coating itself was 250 μm and the organic coating had an average thickness of 75 μm . These values should be considered significant when evaluating the corrosion protection performance of the various systems. All used organic coatings showed good wetting of the thermal spray layer. No macroscopic pores could be detected.

2.2. Mechanical Characterisation

Since metallic coatings will be competing with organic systems used for corrosion protection, some typical mechanical paint tests have been used on the metal coatings to see how the results compare. The selected tests to determine the mechanical properties of the aluminium coated steel panels were the following:

- flexibility, by means of a three-point bending test;
- adhesion, by means of a dolly pull-off test; and
- relative toughness by means of the pencil hardness test and the pendulum damping test.

To evaluate the effect of ageing during exposure, the mechanical properties flexibility, adhesion and toughness were investigated before and after 3000 h of immersion in natural sea water.

2.2.1. Flexibility

Flexibility was tested using a three-point bending arrangement, as illustrated by Fig. 3. The flexibility is expressed as the amount of bending sag in millimetres until cracking of the coating was observed. After the test, the bending load was removed and specimens were prepared for microscopic evaluation of the amount and nature of any cracks present. This test was carried out on the steel panels with a metallic coating only. No organic sealer or paint was applied since this was not expected to influence the flexibility of the system. In fact, the presence of a perhaps more flexible, organic coating would make the observation of cracks in the thermal spray layer impossible.

Table 1 lists the results of this investigation. The measurements were replicated four times.

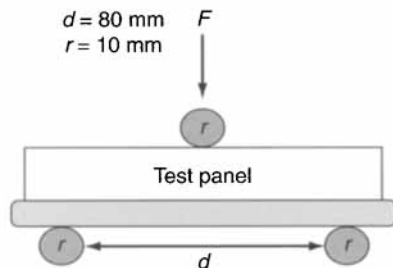


Fig. 3 Three-point bending test arrangement.

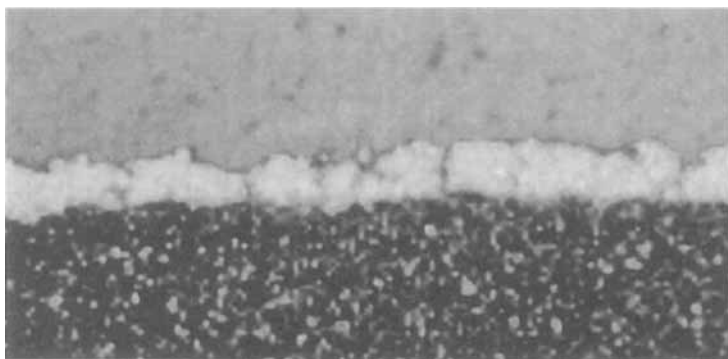
Table 1. Results of flexibility test using the three-point bending arrangement

	Immersion	Meas. 1 (mm)	Meas. 2 (mm)	Meas. 3 (mm)	Meas. 4 (mm)	Avg. (mm)	s.d. (mm)
Flame spray Al99.7	before	20.40	17.40	17.35	19.90	18.80	1.60
	after	21.25	12.40	10.20	9.70	13.38	5.37
Arc spray AlMg5	before	5.30	8.55	6.90	7.10	7.00	1.30
	after	8.40	5.40	4.70	4.70	5.80	1.76
High-build epoxy (nominal value)						3–9	

The panels that were aged in sea water before the test, generally displayed a lower bending value at cracking of the coating. It should be stated that this is partially explained by the method of evaluation, since the aged coating was considerably darker than the original coating. This increased the contrast between the cracks and the coating and made the observation of small cracks easier. The decreased flexibility after exposure is still significant, although a quantitative value for this decrease cannot be taken from these results.

Cross-section analysis showed that all cracks at the end of the experiment went through to the steel substrate. The Al99.7 generally showed a large number of narrow, small cracks whereas the AlMg5 coating displayed fewer, but considerably wider cracks as illustrated by Figs 4 and 5.

Based on these results it can be concluded that the values of the aluminium based spray coatings are either comparable or more flexible than a standard high build epoxy coating. It should be noted that much higher values can be obtained by using special flexible polyurethane based paints.

Fig. 4 Al99.7 after bending test. Magnification ca. 60 $\times$.



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partly on the dolly/adhesive interface, which indicates an even greater adhesion value for the coating than could be measured using this test arrangement.

A completely independent adhesion test carried out as a routine check by the thermal spray company that applied the AlMg5 coating yielded an average adhesion strength of 15.7 Nmm^{-2} . This value lies within the range of the listed test results.

No significant effect on the coating adherence could be detected after 3000 hours immersion in natural sea water. For comparison, adherence strength of typical heavy-duty organic anti corrosion paints range from 6 to 14 Nmm^{-2} . This leads to the conclusion that the adhesion of Al based thermal spray coatings is either comparable to, or better than, traditional organic coatings.

2.2.3. Toughness

The relative surface toughness of the thermal spray coatings was determined using two techniques typically used for surface toughness measurements on organic paints. The selected methods were the pendulum method and the NEN 5350 pencil-hardness test. Both are qualitative tests by definition, but even so the results should be treated very carefully since the surface roughness of the sprayed coatings will influence the measured values.

The pencil hardness measurement according to NEN Dutch standard 5350 uses 17 normalised pencils ranging from hardness 6B to 9H. The outcome of the experiment is defined as the toughest pencil that does not leave a permanent mark when pressed at an angle of 45° and with a pressure of 750 grams onto the coating surface.

The pendulum hardness test, as schematically represented in Fig. 6, determines the amount of damping of the pendulum motion, i.e. the dissipated energy in the coating due to deformation.

Two metal spheres support the frame of the pendulum and press on to the coated surface. The time in seconds required to stop the pendulum motion after a specific amplitude was applied is a measure of the damping toughness.

A soft coating will generally damp the motion more which will result in a low surface toughness value.

The results of the surface toughness tests are listed in Table 3. The pendulum tests were in triplicate.

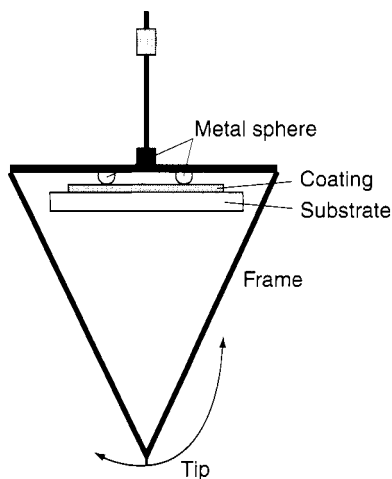


Fig. 6 Pendulum surface toughness arrangement.

Table 3. Results of the surface toughness tests

	Immer- sion	Pencil test	Pendulum test (s)			avg.
			#1	#2	#3	
Flame spray Al99.7	before	3–4H	5.6	89.6	16.8	37.3
	after	5–6H	89.6	103.6	88.2	93.8
Arc spray AlMg5	before	>9H	147.0	133.0	142.8	140.9
	after	>9H	173.6	144.2	170.8	162.9
Traditional organic heavy-duty anti-corrosion coating (nominal value)		HB–1H				35–60

The surface roughness of the thermal spray coatings has a large influence on the results. The arc spray coating is relatively more smooth than the flame spray coating, resulting in a much higher pendulum surface toughness. Also, the results indicate an increase in coating toughness after 3000 hours of immersion. This may well be explained by the relative ‘flattening’ of the surface due to corrosion of roughness peaks during the exposure. Nonetheless, the comparison with nominal value for organic systems shows clearly that an aluminium based thermal spray coating will exhibit a significantly tougher outer surface. The measured values however, should not be used in a quantitative analysis.

2.3. Tribological Tests

Since the success of aluminium based coatings in sea water is expected to depend on the build up of a protective oxide layer, the influence of continuous abrasion of this layer, as occurs in tribology applications, is investigated. An example of this situation would be the protection of slip planes on sluices or bridges etc. A common counter surface in these applications is the ultra-high molecular weight poly ethylene UHMWPE which is also used in the tests.

The aluminium based thermal spray coatings were applied on the outside of a steel ring 12 mm × 75 mm as shown in Figs 7 and 8. The sprayed surfaces were turned and polished to an initial surface roughness of R_a 1.4 µm.

In the first part of the test, the friction factor and possible material loss were measured at a surface pressure of 2.5 Nmm⁻² and a sliding speed of 0.01 ms⁻¹. The coatings were tested consecutively in dry air for 20 h and 20 h in immersion water at ambient temperature. After this test no damage of either the PE or the aluminium surface could be observed. The friction factor for both surfaces remained below the detection limit of 0.6 × 10⁻⁹ mm²N⁻¹.

A second arrangement, as shown in Fig. 9, was used to electrochemically monitor the potential of the sprayed surface during load. Since the monitoring was considered sufficiently sensitive, the sliding speed was increased to 0.1 ms⁻¹. The corrosion

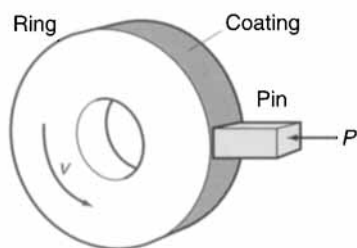


Fig. 7 Tribological test arrangement.

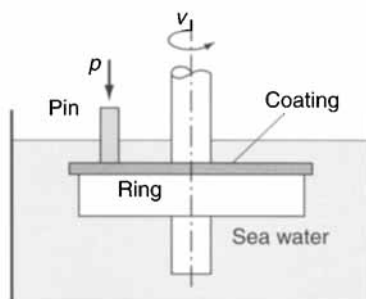


Fig. 8 Tribological/electrochemical test.

potential of the aluminium surface was monitored during the test using a Ag/AgCl reference electrode.

The AlMg5 arc spray coating did not show any effect resulting from the tribological load. The corrosion potential did not change significantly during the test thus

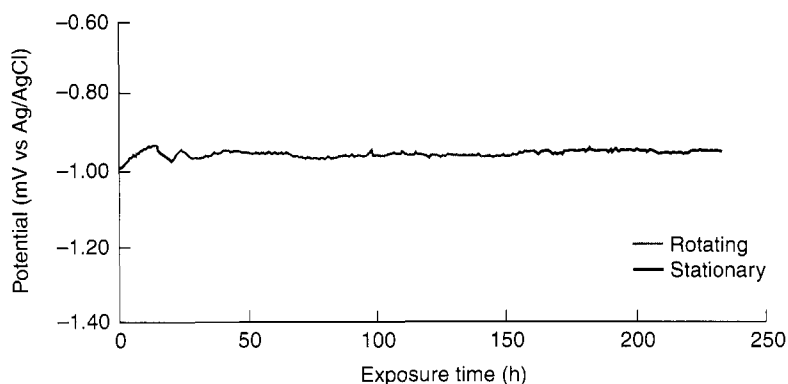


Fig. 9 Corrosion potential of AlMg5 arc spray coating under tribological load in natural sea water.

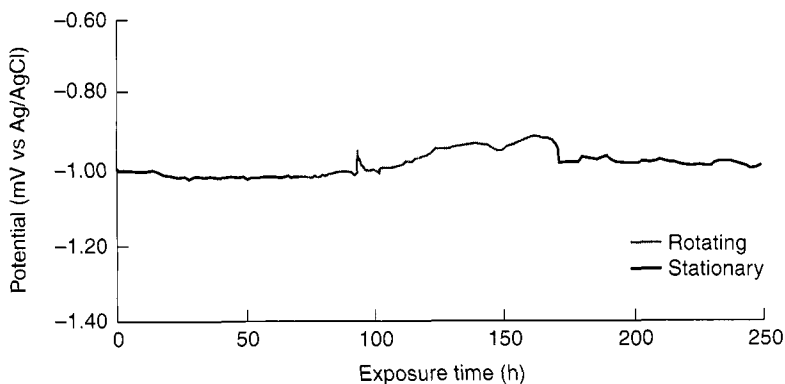


Fig. 10 Corrosion potential of Al99.7 flame spray coating under tribological load in natural seawater.

indicating no sign of activation or break down of the passive layer. The Al99.7 coating however had become too thin after the polishing pretreatment. The thickness was less than 10 μm at various places resulting in a mixed potential during the tribological load. After stopping the rotation of the rings, the potential dropped rapidly into the passive region of the aluminium spray coating. The insoluble corrosion products most probably caused this behaviour by blocking the pores and effectively shielding the steel substrate from the corrosive environment.

2.4. Cyclic Voltammetry

The electrochemical properties of the sprayed materials as reflected by the polarisation curve were investigated using cyclic voltammetry. An evaluation of the effect of the spray process was made by comparing the polarisation curves measured on the coating with the curves measured using the Al99.7 and AlMg5 wire material before spraying as the working electrode.

The curves were measured in natural sea water from -1400 to -300 mV vs Ag/AgCl at 0.2 mVs^{-1} . Four consecutive scans were recorded over this potential range. The volume of the measurement cell was 5 litres and it was actively aerated to minimise changes in the electrolyte during the measurement. A typical example of the measured potential–current relationship on the sprayed panels is given in Fig. 11.

The results of these measurements showed an equilibrium potential of *ca.* -1100 mV for the Al99.7 to *ca.* -1200 mV vs Ag/AgCl for AlMg5 system. No activation on either system occurred below -600 mV and the maximum current density in the passive zone was about 0.5 Am^{-2} .

No significant difference between the behaviour of the materials before (wire material) and after spraying (coating) could be observed. It should be noted that

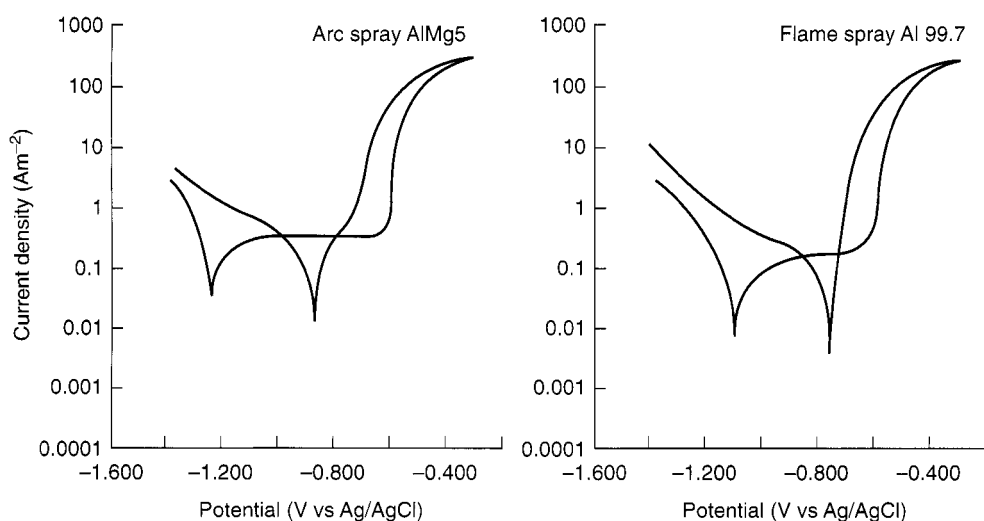


Fig. 11 Typical polarisation curve of Al-based thermal spray coatings on steel in natural sea water; left AlMg5; right, Al99.7.

comparison of current density observations was limited by the accuracy of the surface area measurement on the rough sprayed surface. Other characteristic values determined from the polarisation curves are listed in Table 4.

2.5. Immersion Exposure

The overall behaviour and stability of the aluminium panels in sea water was determined using an immersion experiment. Freshly coated panels were fitted with an electrical connection and partially immersed in natural sea water. Half of the aluminium thermal spray coating was covered with an organic coating to evaluate the effect of the presence of the interface on the corrosion behaviour. Theoretically this interface could cause de-aeration related crevice corrosion phenomena. The test arrangement is schematically shown in Fig. 12. The sea water was continuously refreshed during the experiment at a rate of 0.5 litres per hour. The total volume of the immersion basin was 10 litres.

During 3000 h of immersion in natural sea water the overall appearance and the electrode potential of the aluminium coatings were determined. The potential was measured using Ag/AgCl reference electrodes. The result of the corrosion potential monitoring during exposure is shown in Fig. 13.

The figure shows that the potentials settle at values around -1000 mV vs Ag/AgCl, which are in the centre of the passive region, as seen in Fig. 11.

Table 4. Characteristic values determined from the polarisation curves

		Corrosion current density (Am^{-2})			Passive current density (Am^{-2})			Corrosion potential (mV Ag/AgCl)		
Scan		2	3	4	2	3	4	2	3	4
Flame spray	Wire	0.01	0.07	0.07	0.07	0.11	0.18	-1056	-1166	-1160
Al99.7	Coating	0.16	0.51	0.76	0.21	0.38	0.57	-1098	-1082	-1069
Arc spray	Wire	0.18	0.27	0.48	0.25	0.55	0.50	-1178	-1219	-1229
AlMg5	Coating	0.19	0.35	0.49	0.69	0.59	0.61	-1233	-1208	-1196
		Polarisation resistance (Ohm m^2)			Pitting potential (mV Ag/AgCl)			Anodic hysteresis (kWm^{-2})		
Flame spray	Wire	1.88	0.54	0.46	-654	-630	-684	5.77	5.77	4.95
Al99.7	Coating	0.48	0.19	0.10	-649	-649	-657	3.96	3.46	3.17
Arc spray	Wire	0.19	0.13	0.14	-640	-647	-651	8.42	6.66	5.05
AlMg5	Coating	0.14	0.10	0.10	-682	-698	-665	3.70	4.12	4.59

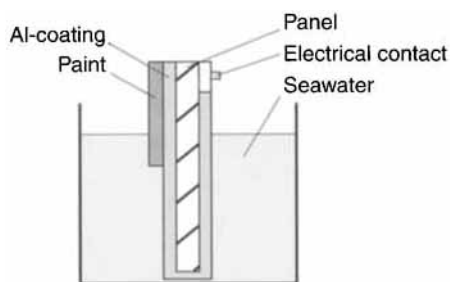


Fig. 12 Test arrangement during immersion exposure.

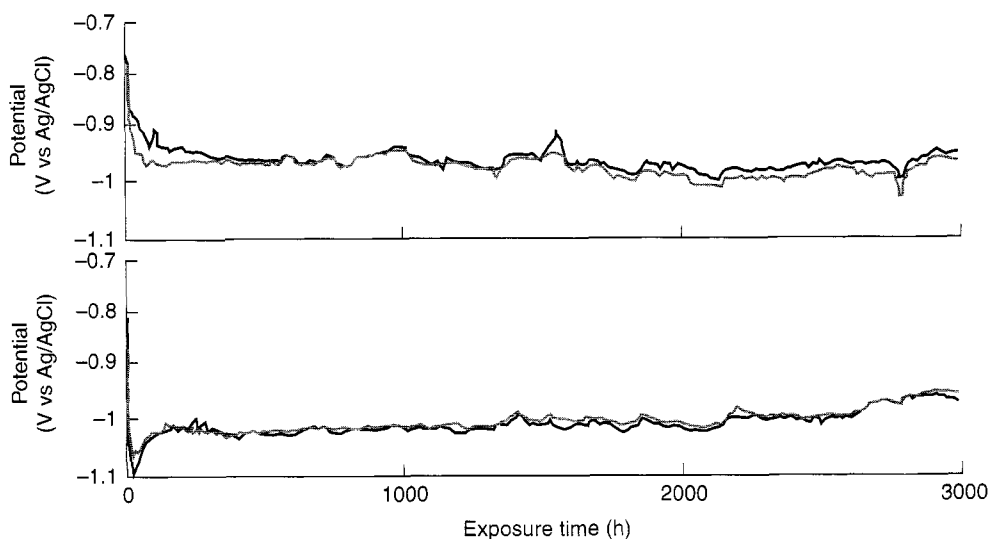


Fig. 13 Corrosion potential during immersion in natural sea water for Al based thermal spray coatings. Dual lines represent replicated measurements (top AlMg5, bottom Al99.7).

Differences between the two systems are only significant in the initial period. These are most probably due to activation by exposure of the steel substrate and subsequent blocking of pores by insoluble corrosion products.

A typical change in appearance during exposure is illustrated by the Figs 14 and 15. After exposure, both systems had changed from a metal gloss appearance to a dull grey, blotchy look. No ferrous corrosion products could be observed. No increased deterioration crevice corrosion on the painted to unpainted interface was visible.

2.6. Galvanic Coupling

Successful use of aluminium based spray coatings will greatly depend on the behaviour of the coating at small defects. The results from cyclic exposure showed that the steel substrate exposed in scratches in the coating with a limited surface area will be cathodically protected by the aluminium. The magnitude of the protection



Fig. 14 Fresh Al99.7 spray coating.

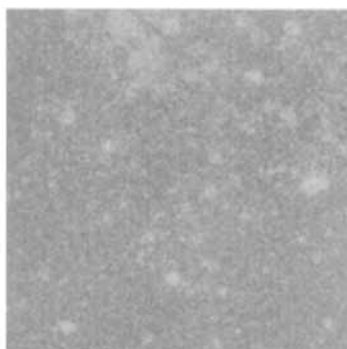


Fig. 15 Al99.7 flame spray coating after 1000 h of exposure in natural sea water.

current in this case will determine the service life of the aluminium coating. To evaluate this, two tests were used.

First, a 'worse case scenario' was simulated by coupling a coated panel with a relatively large area of steel (aluminium/steel: 1/1.5) in natural sea water and measuring the cathodic current. The steel surface consisted of a rotating electrode to ensure optimal transport processes to increase the corrosion current.

It is seen (Fig. 16) that the corrosion current stabilises at about 0.15 A m^{-2} . Assuming uniform corrosion, the corrosion rate calculated using the Faradaic equation is approximately 0.2 mm/year .

Although this value would appear to be a fair estimate of the rate of maximum galvanic corrosion of thermal sprayed aluminium based coatings in sea water, the test situation did feature a relatively large geometrical distance between the aluminium surface and the steel.

A more realistic simulation is represented in Fig. 17. This consists of two identical aluminium coated panels on one of which a 5 mm dia. defect was made. The aluminium to steel ratio now was 1 to 0.0006. This yielded a much lower and, for Al99.7, decreasing current between the two panels, resulting in a value of about

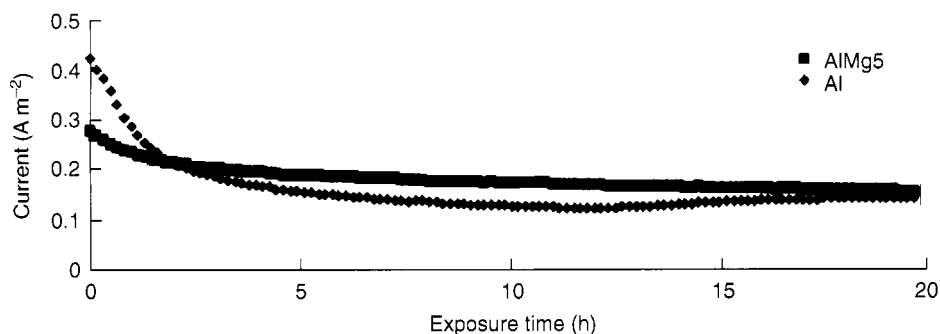


Fig. 16 Galvanic current between Fe and thermal sprayed aluminium coating; approximate surface ratio aluminium/steel:1/1.5.

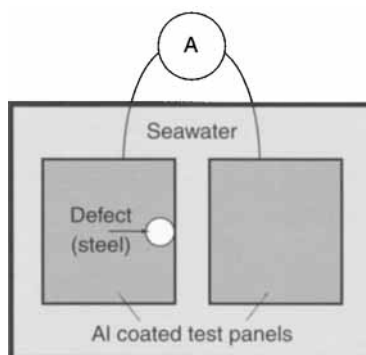


Fig. 17 Galvanic coupling of two identical panels with a defect on one panel.

0.6 μm /year after 600 h. No excessive corrosion of the aluminium coating could be seen and again an insoluble salt deposit was found at the exposed steel surface, effectively blocking the defect.

Further analysis of these deposits using electron microscopy and electron probe micro analysis revealed two main structures, as shown in Figs 18 and 19. In particular, the needle structure shown in Fig. 19 formed a dense, tightly adherent deposit covering the steel surface. The decreasing corrosion current will probably be mainly caused by this deposit, effectively blocking access to the cathodic sites.

2.7. Fouling Test

From the apparent roughness of the metal coating and the non-toxicity of aluminium, the system would appear to provide the ideal surface for growing and sustaining fouling organisms. For this reason, barnacles were grown on the coated metal surface since these species have been reported to damage conventional coatings. Barnacles reproduce by spawning larvae, as shown in Fig. 20, which attach themselves after an initial exploration phase to a suitable surface. After attachment the larvae metamorphose into barnacles. In the TNO laboratories in Den Helder, the barnacle *Balanus amphirite* is cultivated for antifouling experiments.

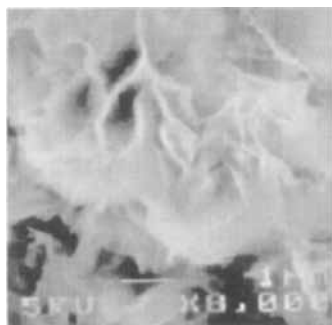


Fig. 18 Mainly Ca-containing form of cathodic deposit.

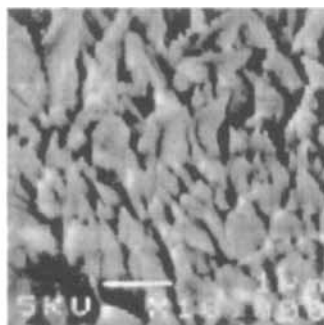


Fig. 19 Mainly Mg-containing form of cathodic deposit.

During the laboratory experiments, the larvae were added to vessels containing the steel panel with the aluminium sprayed coating. Immediately after adding the larvae, they displayed distorted behaviour. Most larvae sank to the bottom of the container, making weak movements of legs and antenna. It is proposed that this behaviour was induced by the high electrochemical activity of the aluminium panels directly after immersion, caused by galvanic effects between pores and the aluminium metal. It has been reported before that metal spray coatings can limit the development of fouling [27]. However, after this initial period which lasted for several hours, the larvae recovered and displayed their normal settlement behaviour. After settlement and the metamorphose, the juvenile barnacles developed normally, indicating no detrimental effect resulting from the aluminium spray coating. Two months after the start of the experiment, 80–90% of the panel was covered with healthy barnacles.

Parallel to the laboratories studies a set of coated panels was exposed outdoors in the Den Helder harbour at a depth of 1 m.

Examination of the panels after three months, revealed that the surfaces were covered for 70–95% with healthy barnacles as shown in Fig. 21.

After 23 months the grown barnacles were removed and the coating was examined. Microscopic studies of cross-sections of the coating directly underneath a barnacle did not reveal any penetration of the base of the organism into the aluminium layer. No significant damage of the aluminium coating or resulting loss of corrosion protection could be seen.



Fig. 20 Cyprid larvae of the barnacle *Balanus amphirite*

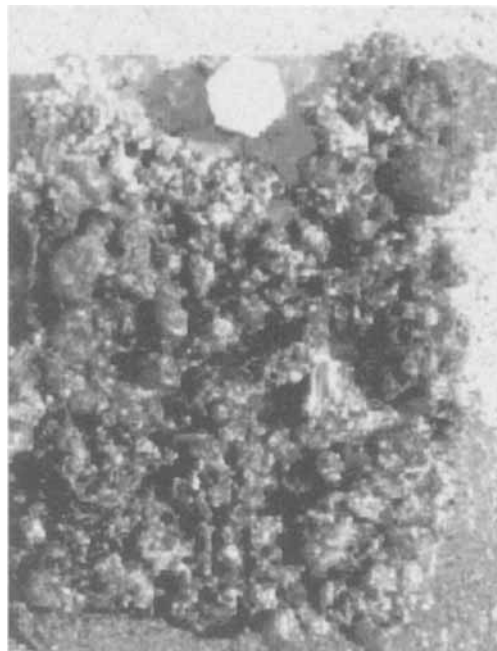


Fig. 21 Al99.7 coated panel, partially coated with an organic paint system, after three months immersion in natural sea water in the Den Helder harbour.

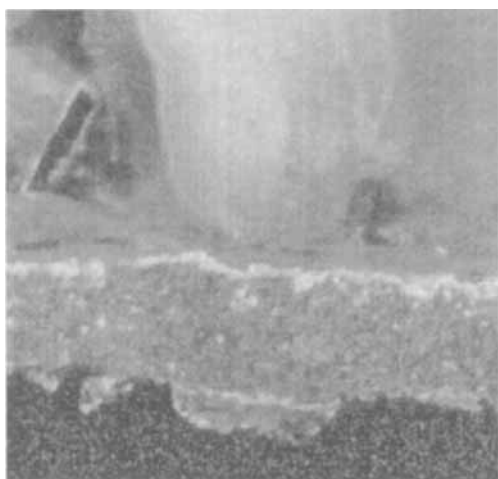


Fig. 22 Close-up of barnacle shell edge on Al-based spray coating cross-section.

3. Discussion

The aluminium based spray coatings Al99.7 and AlMg5 on steel proved to be stable in natural sea water. Using a coating with a nominal thickness of 100 μm ensures no significant corrosion of the aluminium layer. Exposed steel at defects micro/macro pores, cracks, scratches will be cathodically protected and the defects will be eventually blocked with corrosion products and insoluble salt deposits.

Coating thicknesses less than 20 μm will suffer the development of voluminous corrosion products, caused by the many pores through to the steel substrate.

The activated aluminium, as can be observed from the polarisation curves will corrode relatively rapidly in sea water. The corrosion rate, assuming general corrosion, will be in the range of 0.2 mm per year. The circumstances when this may occur are when a small section of aluminium coating is galvanically coupled to a large area of steel. The expected service life of an aluminium coating is under these circumstances extremely short.

The corrosion potential of the aluminium coating will be between -900 and -1000 mV vs Ag/AgCl which is sufficiently negative to ensure cathodic protection of any exposed steel. When the cathodic steel area is sufficiently small a deposit of insoluble salts at the cathode will drastically limit the corrosion rate. These salts mainly consist of Ca and Mg carbonates, in which the Mg compounds appear especially effective in forming a barrier scale on the cathodic surface.

A surface ratio of 1000:1 aluminium to steel and a defect diameter of 5 mm ensured a corrosion rate of less than 1 μm per year. The service life of an intact aluminium coating is expected to be significantly longer.

The use of organic systems (paint, sealer) did not contribute significantly to the corrosion resistance of the aluminium system. It is expected that good barrier paints will have negative effect on the cathodic protection mechanism. The cathodic protection depends on the electrical contact between the electrolyte and the anode material. A high resistive paint will hinder current flow and ionic transport and thus limit the effectiveness of the cathodic protection.

The mechanical properties of aluminium sprayed coatings are generally speaking, superior to the properties of common anti-corrosion paints. For example, the adhesion strength of organic systems will in practice not exceed 10 Nmm^{-2} whereas the Al99.7 system reached values beyond 16 Nmm^{-2} . Flexibility measurements showed the development of cracks through to the steel substrate. However, in view of the cathodic protection mechanism, the risk of corrosion of the steel substrate will remain minimal. The formation of cracks will only occur at the very limit of the bending load for these systems. The magnitude of this maximum load is comparable to the values normally associated with high build organic coatings.

An important fact regarding the mechanical properties of the aluminium based thermal spray coatings is that no significant changes could be measured after 3000 h of immersion in natural sea water.

Polished spray coatings for tribological applications showed very good prospects. The amount of wear expressed as the wear factor versus UHMWPE was not detectable. Continuous friction while immersed in sea water did not have a significant effect on the corrosion potential. Visible examination also could not detect any increase in corrosion activity. Sufficient coating thickness for these applications is absolutely necessary. Pores through the coating will result in voluminous aluminium corrosion products that can be expected to interfere seriously with any tribological application.

The amount of fouling after outdoor immersion exposure in sea water on the coated panels was relatively large. An anti-fouling coating for situations where fouling would be undesirable is therefore necessary. On the other hand, the abundance of biological activity also suggests no harmful effect of the coatings on the environment.

The corrosion protection properties of the spray coatings did not suffer from damage by fouling organisms after 23 months of exposure. Also, the barnacle *Balanus amphirite* could not damage the coating.

When using an antifouling paint in combination with an aluminium based spray coating, care should be taken, as previously discussed for sealers, not to disrupt the inherent cathodic protection mechanisms.

4. Conclusions

Based on the results of the experiments briefly described in this paper, the following can be concluded:

1. Aluminium based spray coatings appear to provide a suitable protection for steel structures in sea water.
2. The aluminium coatings are electrochemically stable (negligible corrosion rate) in natural sea water. Pores in the coating will be effectively blocked with corrosion products.
3. Exposed steel in the vicinity of the coating will be cathodically protected. A sufficiently small defect will be blocked by calcareous deposits, effectively stopping the corrosion reaction

4. The mechanical properties flexibility, adhesion, toughness remained unaffected after 3000 h of immersion in natural sea water.
5. Polished aluminium based thermal spray coatings proved a suitable sliding surface against ultra-high molecular weight polyethylene.
6. The thermal spray surface proved very susceptible to biological fouling organisms but no damage to the aluminium layer could be observed.

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Structure and Corrosion Behaviour of Electroless Ni Coatings Deposited from Differently Stabilised Baths

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ABSTRACT

The influence of Bi, Pb/Cd and Te additions as bath stabilisers on the structure composition and corrosion behaviour of two types of electroless Ni-P coatings was compared. Bi and Te additions seem to be less effective than Pb/Cd towards bath stabilisation, but they have a similar smoothening action on surface topography and a refining effect on coating texture. The presence of these stabilisers up to concentrations of a few ppm leads to a somewhat higher deposition rate and to a slight lowering of P content in the Ni-P coatings. At the open circuit potential, the electroless Ni-P coatings deposited from a series of baths are less resistant to corrosion in a 3.5 wt % NaCl aerated solution than a Ni coating electroplated from a conventional sulphamate bath, but the corrosion rate is lower as the P concentration increases; as a consequence, the coatings deposited from stabilised baths tend to be less corrosion resistant. On the other hand, the refining effect of the stabilisers on the coating texture can be beneficial to the protectiveness of the coating by making it less sensitive to localised corrosion, such as 'tunnelling' or internodular cracking. The Ni-P coatings however, show a greater passivation capability than electroplated Ni owing to the formation at more noble potentials of a thin protective layer rich in phosphate anions.

1. Introduction

The anodic behaviour of electroless Ni coatings in near-neutral chloride solutions depends mainly on composition and microstructure but the attack morphology and its consequences on their protective capacity may be significantly influenced by the growth morphology and by the presence of intrinsic and/or induced defects [1]. Most of these characteristics are determined by the bath components and the deposition pH, but the type of bath stabilisers can also play an important role. Indeed, a very different behaviour between two Ni-P coatings deposited on various substrates from similar baths stabilised, respectively, by Pb (1 μM at pH 4.2) and mercaptobenzothiazole (10 μM at pH 4.8) was recently observed [2].

In the present work, the effect of Bi and Te additions as stabilisers, in place of the more toxic Pb and/or Cd, on corrosion resistance of a medium- and high-P electroless

coatings in a 3.5 wt% NaCl aerated solution at pH 6.3 was studied and compared with that of a Ni coating electroplated from a sulfamate bath.

2. Experimental

The deposition baths were prepared by dissolving reagent grade chemicals in distilled water and worked without replenishment up to a maximum of 3 h. The composition of these baths is reported in Table 1. Pb and Cd were added as nitrates, while Bi and Te were added as $\text{Bi}_2(\text{SO}_4)_3$ and K_2TeO_3 respectively.

The deposition was carried out on polished, degreased and Pd-activated copper discs of 25 mm dia. at $92 \pm 1^\circ\text{C}$ and lasted about 2 h for the SAL bath, and 3 h for the SGMP bath, from which the deposition was slower, to produce a coating thickness greater than 25 μm . The electroplated Ni was deposited at about 60°C from a sulfamate bath with the following composition: Ni sulfamate 450, H_3BO_3 37.5, Na laurylsulfate 0.1 gL^{-1} , pH = 4, c.d. = 5.4 Adm^{-2} , to produce a 50 μm thick layer.

Surface topography and growth morphology were studied by scanning electron microscopy (SEM). The composition was determined by electron probe microanalysis (EPMA), visible absorption spectrophotometry (for P) and atomic absorption spectrophotometry (AAS) (for Pb, Cd, Bi and Te).

The corrosion behaviour was studied by potentiodynamic polarisation tests in a 2L ASTM standard cell using an AMEL corrosion measurement system at a scan rate of 10 mV/min. The specimens were partially masked by spraying on the peripheral zone of the disc a base layer of acrylic lacquer and a top layer of poly-tetrafluoroethylene, thus leaving an inner 2 cm^2 exposed area. The base layer adheres strongly to the metal surface and effectively bonds the top hydrophobic PTFE layer to it, thus reducing all crevice corrosion risks and hindering leakage through the massive poly-tetrafluoroethylene disc holder. The attack morphology and the surface

Table 1. Composition of the deposition baths (SAL = Ni-Sulfate, Na-Acetate and Lactic acid; SGMP = Ni-Sulfate, Glycine, Malic acid and Na-Propionate)

Reagent	SAL bath (pH = 4.5)	SGMP bath (pH = 4.2)
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	26.3 gL^{-1}	26.3 gL^{-1}
NaH_2PO_2	11.3 gL^{-1}	25 gL^{-1}
CH_3COONa	27.2 gL^{-1}	–
$\text{CH}_3\text{CH}_2\text{COONa}$	–	15 gL^{-1}
$\text{CH}_3\text{CHOH-COOH}$	11.1 gL^{-1}	–
$\text{CH}_3\text{CHNH}_2\text{-COOH}$	–	7.5 gL^{-1}
$\text{CH}_2(\text{COOH})\text{CH}(\text{OH})\text{COOH}$	–	9.0 gL^{-1}

composition of the corroded specimens were studied by SEM observations and X-ray photoelectron spectroscopy (XPS). XPS spectra were recorded in a Perkin Elmer PHI 5600ci spectrometer using nonmonochromatised AlK α radiation (1486.6 eV). The working pressure was less than 1×10^{-8} Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au4f $_{7/2}$ line at 83.9 eV with respect to the Fermi level. Ion sputtering was conducted using argon and a beam voltage of 0.7 kV.

3. Results and Discussion

3.1. Effect of Stabilisers on Morphology and Composition

Bi and Te are good stabilisers [3,4] at a concentration level much higher than Pb and Cd, but they have a similar smoothening effect on the surface topography (Fig. 1), and are worthy of consideration also as brightening agents.

This microlevelling effect is well demonstrated by the roughness profiles (Fig. 2) traced by a stylus profilometer (5 μ m tip radius) across the surface of the Ni–P coatings of the SAL series deposited on copper disks ground with a 220 grit emery paper ($R_a = 0.36 \mu$ m). The bath without stabilisers had no microlevelling power, while the stabilised baths led to a significant R_a decrease. Nevertheless, it is very difficult to avoid the formation of small nodules, pits and streaks, resulting from the entrapment of foreign particles and the presence of hydrogen bubbles standing and sweeping on the surface during deposition.

The smoothening effect of the stabilisers is due to their ability to be selectively adsorbed on the surface of the growing Ni–P layer. For the same reason, they have a refining effect on the growth morphology; that is particularly true for Te, as shown in Fig. 3(b).

On the other hand, the presence of stabilisers has a negative effect on the throwing power of the deposition bath, so this effect must be taken into account in cases where complicated substrates are to be coated.

At a concentration corresponding to the best compromise between bath stability and coating appearance, every stabiliser tends to inhibit the H $_2$ development and P codeposition more than Ni $^{2+}$ ions reduction, thus leading to a slightly increased deposition rate and to a lowering of the P content (Table 2, p.237). A small amount of additive (no more than 0.2 wt%) becomes incorporated into the Ni–P alloy.

3.2 Corrosion Potential and Polarisation Resistance

The open-circuit potential E_{corr} of the Ni–P coatings after 1 h immersion is more negative than that of the electroplated Ni and shifts towards more active values as the P content increases. Thus, the effect of the additives can be simply explained on the basis of their influence on the alloy composition. In any case, E_{corr} continues to move towards the positive direction and a true steady-state is reached only after about 48 h.

The polarisation resistance, R_p , was determined by polarising the coatings in the range ± 20 mV around E_{corr} and working out the current vs potential data according

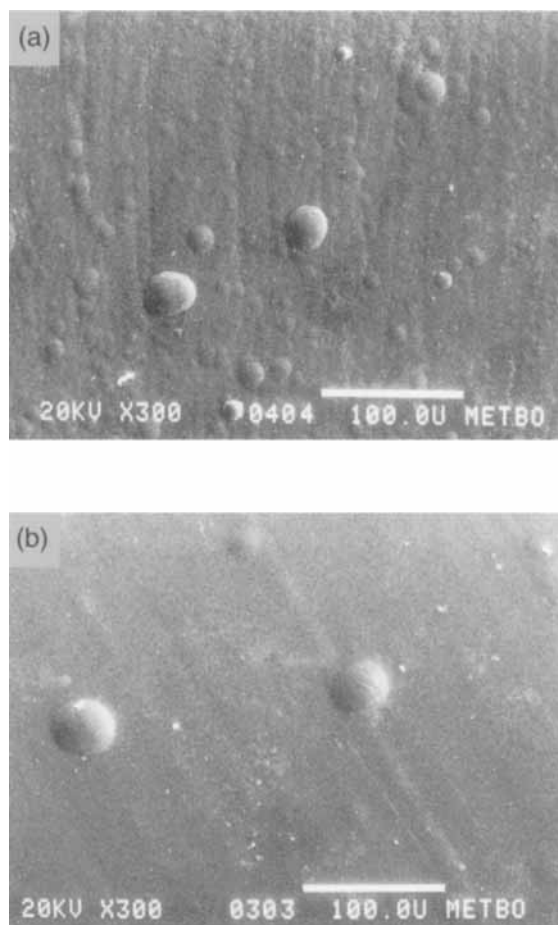


Fig. 1 Surface topography of the Ni-P coatings deposited from the SGMP bath: (a) without stabilisers, (b) with Pb/Cd.

to both a linear approximation and a non-linear fitting program. The results of these tests are compared in Fig. 4. It can be clearly seen that: (a) the R_p of the electroplated Ni is much higher than that of the electroless Ni coatings, (b) the high-P electroless coatings show a higher R_p than the medium-P coatings, and (c) with some exceptions, the stabilisers cause a significant lowering of R_p .

3.3. Corrosion Rate and Morphology

The corrosion current density i_{corr} derived from the fitting program is in good agreement with that determined by extrapolation to E_{corr} of the anodic Tafel slope (Fig. 5). Therefore, the 'linear' polarisation technique proves to be a simple and reliable way for estimating the corrosion resistance. The electroplated Ni is more corrosion resistant at the open-circuit potential but the electroless Ni coatings have a superior

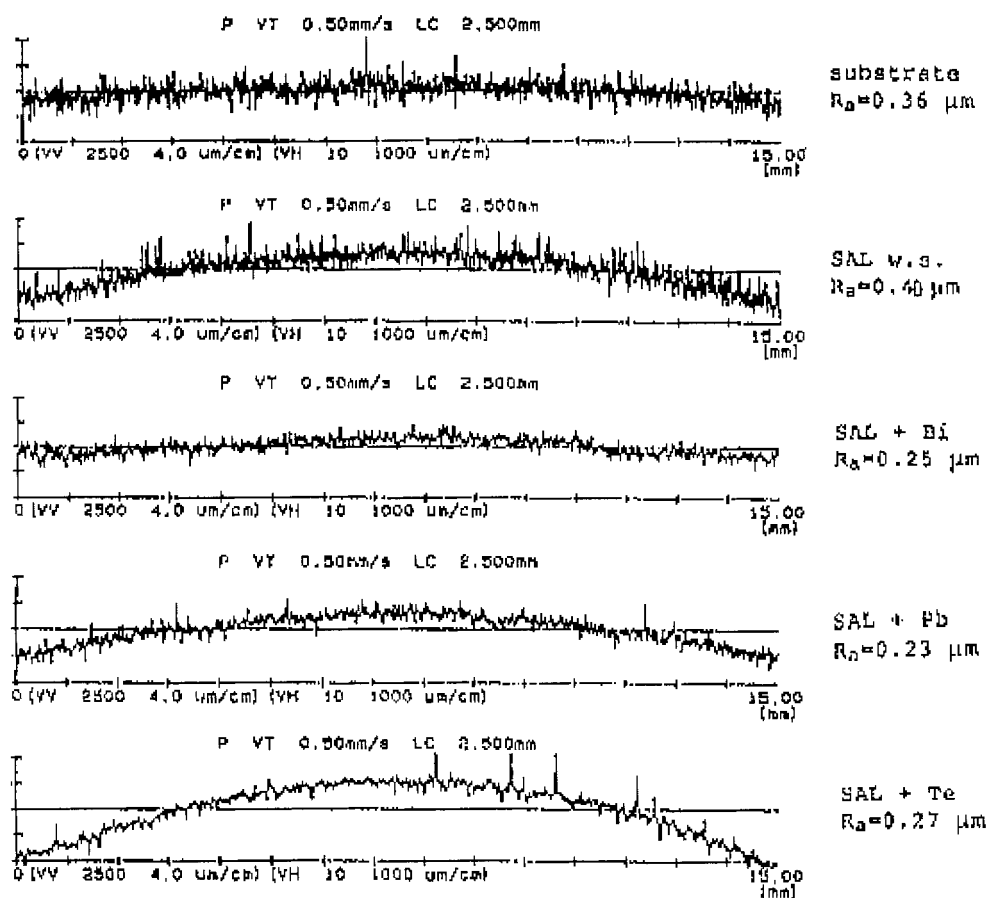


Fig. 2 Roughness profiles on the surface of the Ni-P coatings of the SAL series.

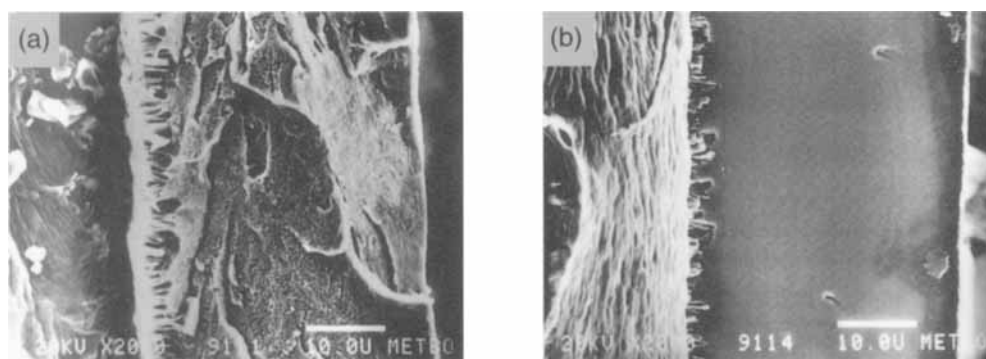


Fig. 3 Fracture sections of the Ni-P coatings deposited from the SGMP bath: (a) without stabilisers, (b) with Te.

Table 2. P content in the coatings (wt%) and H_2/Ni molar ratio (*) after 1 h deposition

Bath type	without stabilisers (w.s)	+ Bi (ppm)			+ Te (ppm)			+Pb/Cd (ppm/ppm)		
		6	2	4.5	8	2.5	4	1/2	0.1/0.3	1/1
SAL (pH 4.5)	8.3	7.4			7.6			7.8		
SGMP (pH 4.2)	10.5		9.6			9.8			9.7	
SGMP (pH 4.2)	2.2*			1.5*			1.9*			1.8*

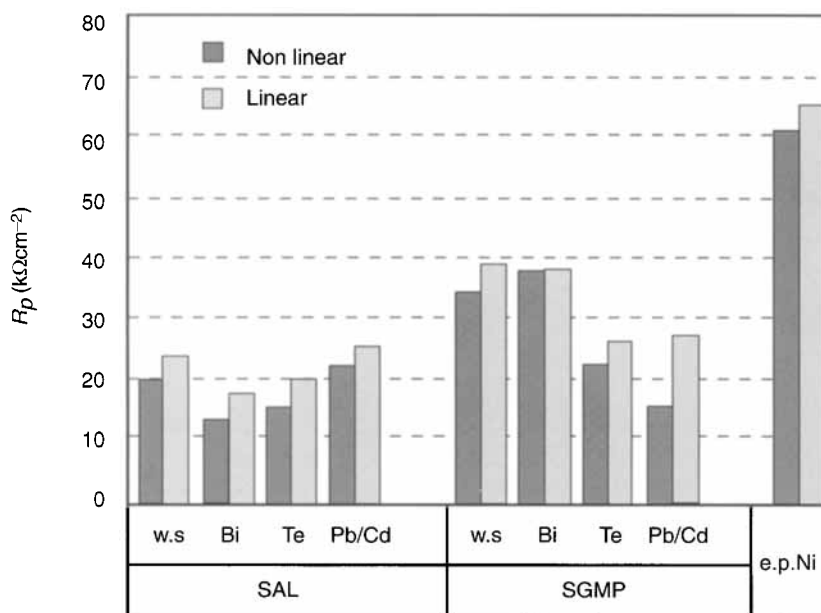


Fig. 4 Polarisation resistance of the electroplated Ni (e.p. Ni) and of the electroless Ni-P coatings of Table 2.

passivation capacity at more noble potentials and the passivation range is wider in the high P alloys (Fig. 6a). The trend and position of potentiodynamic curves are little affected by the addition of stabilisers to the deposition bath (Fig. 6b).

The surface appearance of the tested coatings was not significantly modified by the anodic polarisation and the SEM observations did not provide evidence of any significant sign of localised attack up to the upper limit of the passivation range. At more positive potentials the enhanced corrosion led to a substantial modification of the surface appearance from clear-bright to dark-matt.

A more or less pronounced surface blackening can also be observed on almost all

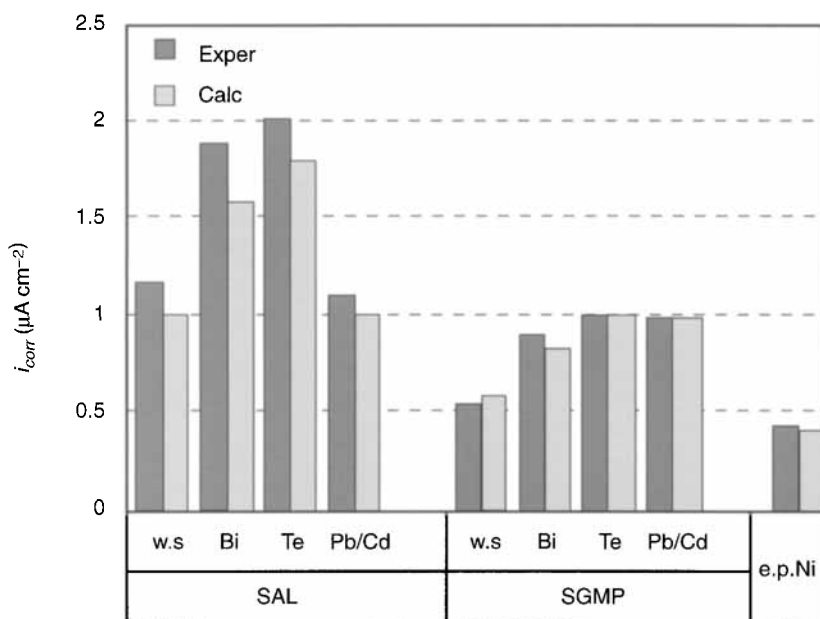


Fig. 5 Corrosion current density i_{corr} derived from the fitting of the polarisation data (calc) and determined by extrapolation of the Tafel plot (exper).

samples after some days of immersion in the chloride solution at the open circuit potential. There are, however, some important differences in the attack morphology, which seems to be controlled more by the growth texture of the coating than by its composition. In fact, a finely fibrous texture such as the texture produced, for example, by the Te stabilised SGMP bath, tends to favour a substantially generalised attack (Fig. 7a), whereas a layered or columnar texture [5,6], such as the typical texture of the coatings of the SAL series or the texture produced by the Pb/Cd stabilised SGMP bath, seems to be more prone to a selective attack at the internodular boundaries (Fig. 7b). The degree of the localisation of corrosive attack is obviously important with respect to the coating protectiveness. In fact, a generalised or micro-localised attack may be much less penetrating than a macro-localised one, which can grow to display 'tunnelling' or 'cracking' phenomena.

3.4. Composition of the Passivating Film

The passivating film that grew on electroless Ni coatings exposed to the NaCl solution was studied by means of XPS analysis. The energy values of the emission bands and their intensity allowed us to identify the species forming the film. The distribution of these species was determined on the basis of the variation of the atomic ratios O/Ni and P/Ni as a function of the incidence angle θ (20°, 45°, 90°) of the X-ray beam and of the sputtering time (0, 2, 4 min). The energy values corresponding to O, P and Ni demonstrate that the film essentially consists of Ni oxide, Ni hydroxide and Ni phosphate.

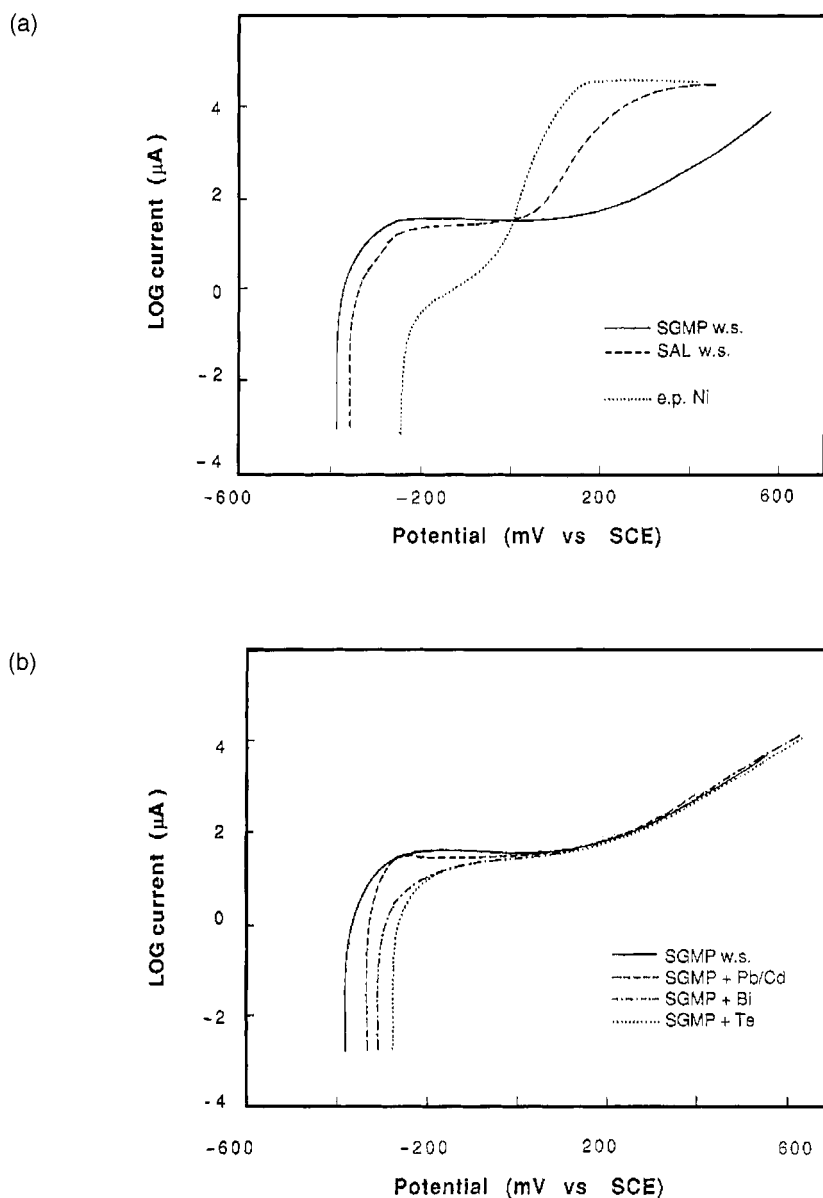


Fig. 6 Anodic polarisation curves of: (a) *e.p.* Ni and the two Ni-P electroless coatings deposited from unstabilised baths; (b) the Ni-P coatings deposited from differently stabilised SGMP baths.

From the variation of the O/Ni and P/Ni atomic ratios as a function of $\sin \theta$ after 0, 2 and 4 min of sputtering (Fig. 8) it can be argued that the film is composed of an inner layer of NiO and an outer layer of Ni(OH)₂. In the electroless Ni-P coatings both layers also contain significant amounts of Ni phosphate (Fig. 9). In the high-P coatings the phosphate concentration is particularly high at the interface between the film and the substrate.

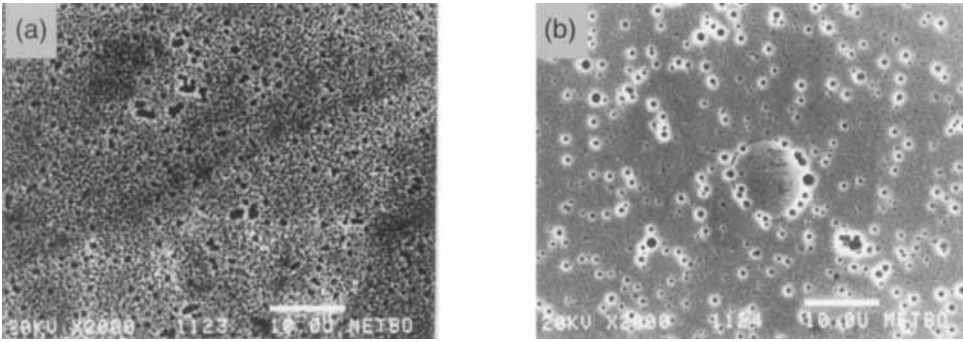


Fig. 7 different types of attack morphology on Ni-P coatings: (a) SGMP + Te, (b) SGMP without stabilisers.

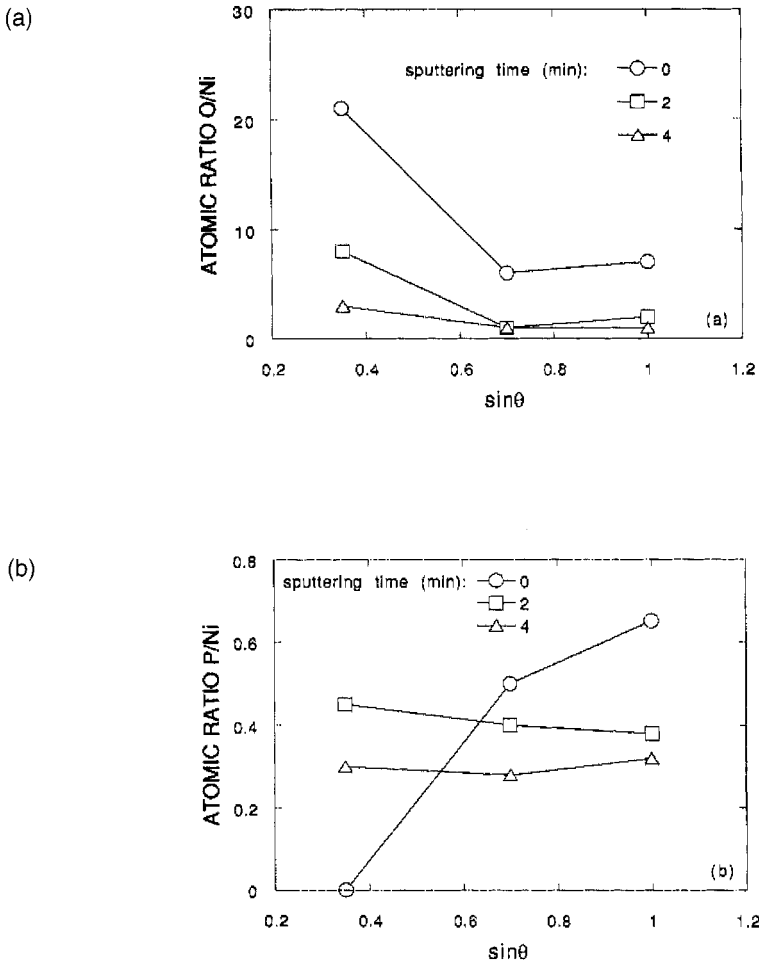


Fig. 8 O/Ni (a) and P/Ni (b) atomic ratio as a function of $\sin \theta$ across the corrosion layer on the Ni-P coatings deposited from the SGMP bath without stabilisers.

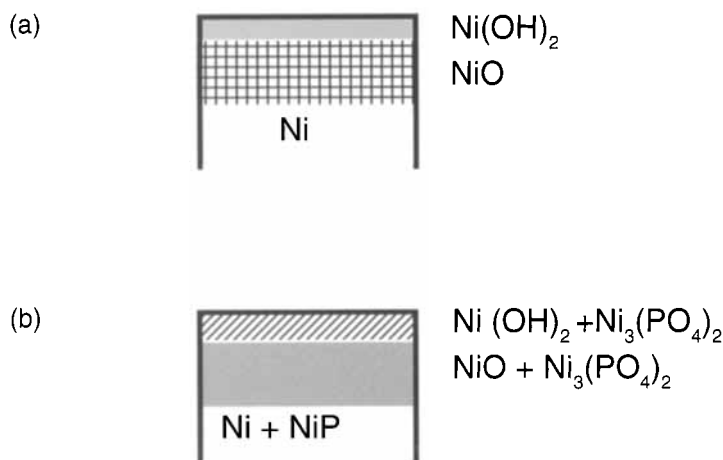


Fig. 9 Composition of the corrosion products layer on (a) the e.p. Ni coating; and (b) the electroless Ni-P coatings.

Apart from minor differences concerning the thickness of the two layers and the distribution of its constituents, there are no substantial differences between the films formed on the coatings deposited from the same type of bath (with or without stabilisers) as shown by the diagrams in Fig. 10, related to the SAL coatings, at a sputtering time of 0 min (a) and with an incidence angle of 45° (b).

Hence, both electroplated Ni and electroless Ni-P coatings are covered by a film produced by corrosion processes.

At the open circuit potential the electroplated Ni shows a lower corrosion rate due to its higher nobility. Nevertheless, a high P content can improve the corrosion resistance of the Ni-P alloys perhaps by inhibiting the cathodic reaction [7]. At more positive potentials the formation of phosphate anions in the corrosion film enhances its protectiveness by effectively hindering the penetration of Cl^- ions which, consequently, leads to a low pit initiation rate [8].

4. Conclusions

- Bi and Te can be successfully used as stabilisers of electroless Ni plating baths to replace Pb and/or Cd. In a concentration range from 2 to 8 ppm they also behave as brightening agents and morphology refiners.
- The addition of these stabilisers improves the efficiency of the deposition baths but worsens the throwing power and causes some lowering of P content in the deposited Ni-P alloys.

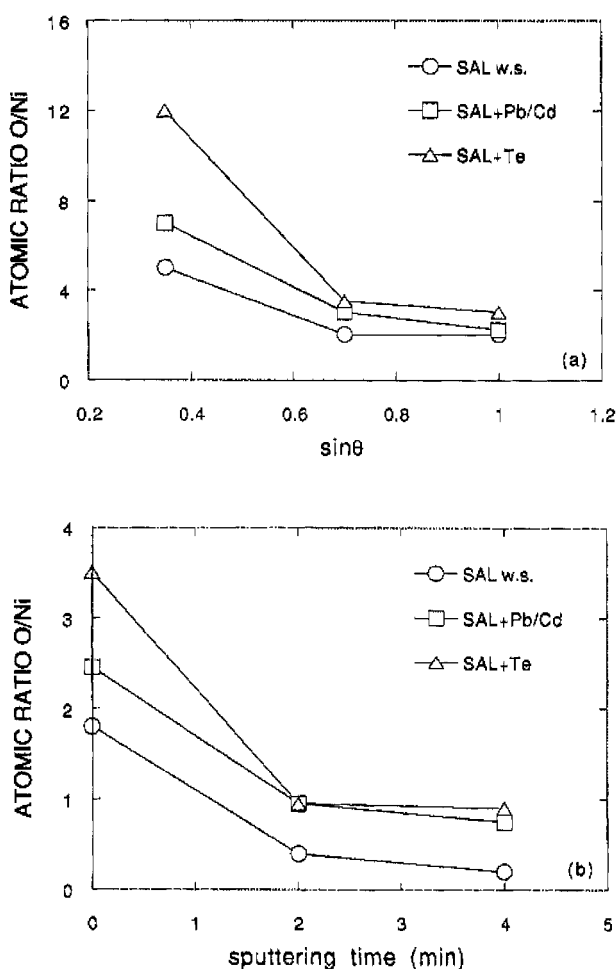


Fig. 10 O/Ni atomic ratio as a function of (a) $\sin \theta$ and (b) the sputtering time across the corrosion product layer on the SAL series Ni-P coatings.

- The electroless Ni coatings tested in the present work are less corrosion resistant to an aerated 3.5 % NaCl solution than a Ni coating electroplated from a sulfamate bath but they are more efficiently passivated at more positive potentials as a result of the precipitation of Ni phosphates in the corrosion produced film.
- The corrosion resistance of the Ni-P coating is somewhat impaired by the addition of stabilisers to the deposition bath, but their refining effect on the coating texture can be beneficial to the protectiveness of the coating by making it less sensitive to localised corrosion processes such as 'tunnelling' or internodular cracking.

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Interaction of Tin Plate Cans with Packaged Food Products

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ABSTRACT

The interaction of stewed foods with tin cans produced from (Euronorm) E5,6/5,6 quality tin plate internally lacquered (two coats) was studied. Filled cans were stored for 24 months at room temperature with inspections of the condition of the product and of the coating immediately after production, after 1 month and then after successive 3-month intervals. Measurements were made of pH, NaCl content and of metal ions in the stew as well as changes in colour, smell, taste and consistency. The condition of the lacquer was also examined. Pronounced corrosion of the lacquer layer and development of metallic taste occurred between the 21st and 24th months. This was accompanied by diffusion of Fe and Sn ions into the stew although there was insignificant increase in the contents of Zn, Pb, Cd and As.

1. Introduction

Tin can packaging satisfies all the requirements for the stability of heat treated foodstuffs providing air-tightness is complete. The main problem during storage is to prevent chemical reaction between content and packaging material. For that reason, the basis steel plate in the case of food packaging is ennobled with a tin layer, the thickness of which depends on the kind of product which is packed and the time of storage. When the foodstuffs are more chemically aggressive, a reaction between the tin plate and the contents can start. These reactions have two results:

- adverse quality changes (taste, odour, colour etc.) resulting from migration of metal ions from the packaging material to the contents, and
- corrosion of the packaging itself, which, in extreme cases, can lead to a formation of a hole, and consequent loss of airtightness.

The application of protective lacquers to the surface of tinned plate, to prevent the material-content interaction, has proved to provide the most effective protection from corrosion in the fruit and vegetable processing industry [1-3].

Heavy metals can originate both from the raw material and from the packaging. The heavy metals content of the raw material is an indicator of environment pollution and can even increase during processing, while the presence of heavy metals which enter the content packed in metal containers points to a product-packaging interaction [2-4].

Due to their acidic nature, pasteurised stews belong to the group of products

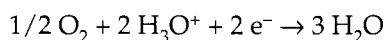
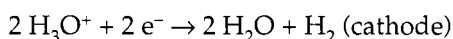
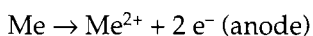
which are considered as aggressive to metal packaging, since they accelerate electrochemical processes responsible for the corrosion of metal packaging and the electromigration of metals into the contents [5, 6].

2. Corrosion Processes

Corrosion starts at the contact surface of two phases and is a chemical oxidation process, in which exchange of electrons occurs in the presence of electrolytes. When food is packed in metal packages, electrochemical corrosion takes place, and the packed food acts as the electrolyte [7].

During electrochemical corrosion the metal ions that are produced (by loss of electrons from metal atoms) in the electrolyte (food) change the nature of some of the food components (vitamins, coloured matter, fats, etc.) [1,2,5,7].

The basis layer (steel) of the metal packaging is also oxidised. H_3O^+ ion, as well as oxygen are the oxidising agents especially in acid media, such as food of low pH values [7, 8].



The tendency of metals to release or accept electrons differs, depending on the metal and can represent the measure of their reactivity [9].

The factors affecting the corrosion can be connected both with the nature of the material and external factors, as well as with the structure and state of the metal surface and any stress in the metal [2,7–9].

The external factors affecting the corrosion rate are: the nature of the electrolyte, temperature, pressure and movement of electrolyte (the can contents in the present case). Contents with lower pH values favour the corrosion of metals like Fe, Mn and Mg. Tin (Sn) is reactive both in acid and basic solutions, and resistant in neutral electrolytes. Oxygen significantly accelerates the corrosion e.g. it activates the corrosive reactions [7–9].

Intensive corrosion may be prevented by coating the cans with appropriate lacquers. However, the lacquer layer cannot completely cover the metal surface and 'primary microporosity' invisible to the naked eye is formed.

Two types of corrosion can be distinguished in lacquered cans (schematically presented in Figs 1a and 1b):

- when tin is more electronegative than iron in the can contents, surface degradation of the tin layer takes place in the pores of the lacquer (Fig. 1a);
- when iron is more electronegative than tin in the can contents, iron dissolves faster than tin causing formation of pits below the lacquer pore (Fig. 1b) [7].

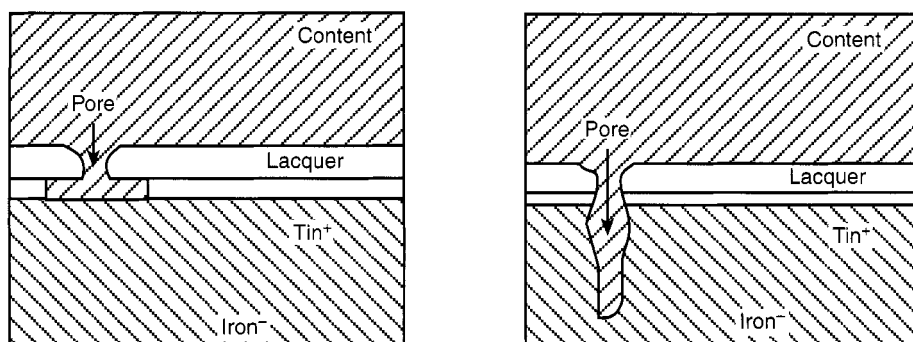


Fig. 1 Electrochemical corrosion.

During storage, these pores become visible and the pits can cause perforation of the can. Furthermore, a metallic taste to the content can be detected and the colour of the contents may become darker or lighter, depending on the composition [1–3,5,7].

3. Materials and Methods

Cans were made of white tin consisting of a low-carbon thin rolled steel base, protected from both sides with tin layer, applied electrolytically, of E 5.6/5.6 quality (5.6 gm⁻² Sn according to the Euronorm for white tin) [10]. The analysis of the steel base, according to the producer's specification is given in Table 1.

The thickness of the the tin layer was measured by the electrolysis method using a Stanomatic Sumetal Sn/Cr 6101 H electronic tinplate coating analyser, according to Euronorm 145-78. A constant current, *ca.* 90 mA, is supplied between the anode (sample) and the cathode part of the electrolytic cell, containing HCl as the electrolyte. During tin electrolysis the cell potential changes. The current gradually strips the coating until the iron base (Fe) is free of tin. The amount of tin in the applied layer can then be determined from the potential change curve, using a computerised program [11].

The adhesion of the lacquer layer amount in the can samples was determined gravimetrically, measuring the sample (tin plates of defined dimensions) before and

Table 1. Composition of steel base (%)

Sample	C	Mn	Si	P	S	Al	Cu	Cr
1	0.060	0.170	0.010	0.009	0.011	0.059	0.002	0.009
2	0.060	0.150	0	0.007	0.010	0.058	0.002	0.010
3	0.060	0.160	0.010	0.007	0.012	0.037	0.009	0.017

after removing the lacquer by appropriate solvent (H_2SO_4). The results are expressed in gm^{-2} [12, 13].

The adhesion of the lacquer layer was determined by the JUS H.C8.059 net test method [14], by net trial. In this, a net is formed on the lacquer layer using an appropriate tool and a number of $\approx 1 \text{ mm}^2$ squares is formed. An adhesive tape is stuck on the formed net and abruptly pulled. Less than 5% of lacquer layer should adhere to the tape [12, 13].

The porosity of the lacquer layer was investigated with CuSO_4 solution. The principle of the procedure is the reaction of the solution with Sn from places not covered with lacquer. A filter paper soaked with CuSO_4 solution is placed on the lacquer surface. The noncovered places can be recognised after a 5 min reaction as tiny dots or spots [12].

The thermochemical resistance of a lacquer layer to three test solution (A, B and C) used to simulate certain types of packaged food was conducted by pasteurisation or sterilisation of lacquered samples in the solutions.

- Test solution A consists of: 3.0% NaCl, 3.0% CH_3COOH and 1.0% of edible oil.
- Test solution B consists of: 65% of saccharose and 1% of tartaric acid.
- Test solution C consists of: 2% NaCl, 0.02% NaNO_2 and 0.4% of a polyphosphate preparation.

The results are descriptive. No observable colour, taste and smell changes of the test solutions are allowed and no separation of lacquer from the white tin base [12].

The stews investigated in this work were prepared from a mixture of vegetables by normal industrial processes [15].

The dry matter, acidity, pH-value and NaCl-content were determined in the stews by standard laboratory methods [16].

The packaged product samples were opened and the content and changes of cans were investigated immediately after the production, and later after 1, 3, 6, 9, 12, 15, 18, 21 and 24 months of storage.

After the determination of initial quality, any changes of the inside surface of the can, i.e. — corrosion — as the consequence of the aggressivity of the stews during the storage were followed visually [2, 3, 17].

The interaction between the packaged stew and the cans was followed by the change of sensory characteristics of the content (colour, taste, odour and consistency) and by following the content of metal ions (Sn, Fe, Zn, Pb, As and Cd) in the contents [1, 18–20].

The sensory evaluation of the content was conducted using a point-system, on the basis of data obtained from a descriptive evaluation of certain quality criteria (colour, smell, taste and consistency). The descriptive marks were transformed to numerical values and statistically processed. The maximal mark for certain characteristics is 4–6 points and the possible highest mark for the total quality is 20 points [18].

Sn, Fe and Zn were determined by atomic-absorption spectrophotometry, As by

photometrical analysis with ammonium–heptamolybdate and the content of Pb and Cd by potentiometric stripping analysis [2,3,12,19,20].

4. Results

4.1. Quality Investigation of the Content

The stew was produced by the usual procedure. Changes in the chemical composition of the stew during storage are given in Table 2. On the basis of the measured values it can be concluded that there were no significant changes of quality of the packaged stew. The dry matter was in the range from 6,8 to 7,4%, acidity 0.37–0.50%, and pH value from 4.2–4.4. The salt content was up to 1.26%. The slight variation of results is caused by the initial composition of the product.

4.2. Initial Quality of Cans

The amount of tin layer on the outside and inside surface of white tin samples was measured and the results were computer processed and presented in Figs 2 and 3.

At the initial phase of the measurement, the tin layer is stripped. When the tin layer is completely stripped (point 1), the current continues and the alloy layer is

Table 2. Change of chemical composition of stew

Storage time (months)	Dry matter (%)	Acidity (citric acid %)	pH	NaCl (%)
Start	6.8	0.70	4.3	1.15
1	6.6	0.41	4.2	1.10
2	6.9	0.35	4.3	1.02
6	7.1	0.38	4.3	1.09
9	7.2	0.38	4.2	1.12
12	6.9	0.39	4.4	1.05
15	7.2	0.42	4.4	1.20
18	7.4	0.45	4.2	1.26
21	7.2	0.48	4.3	1.25
24	7.2	0.50	4.3	1.10

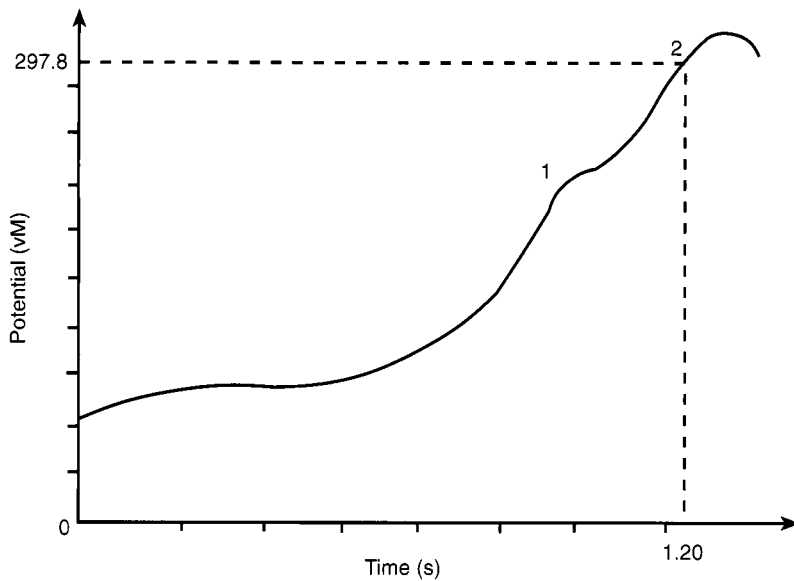


Fig. 2 Measurement of applied tin layer on the outside surface of white tin sample.

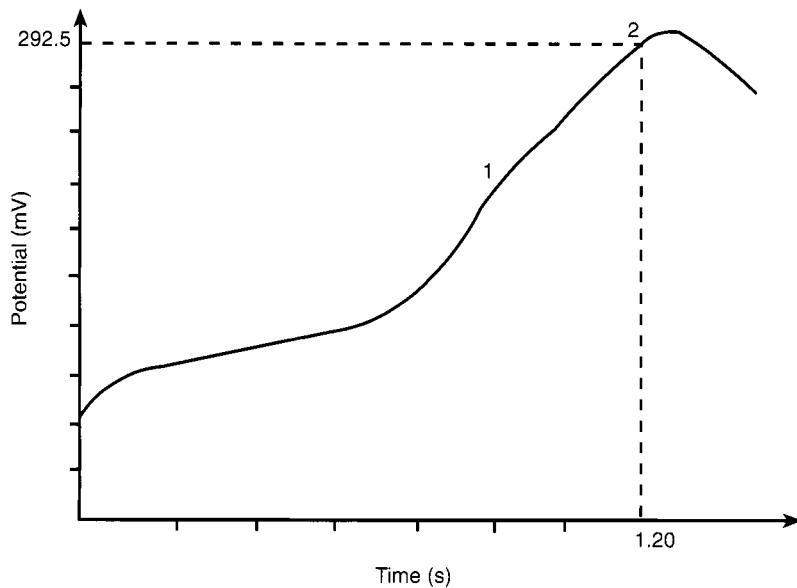


Fig. 3 Measurement of applied tin layer on the inside surface of white tin sample.

then stripped. When the measurement finally reaches the Fe layer (steel base) (point 2), the measurement is automatically stopped. As each of those layers is stripped, a typical potential is developed across the cell.

The tin amount was determined on the basis of the measured dissolving potential of white tin and alloy layers (point 2 in the diagram). The measured potential values are computer processed and the white tin quality, according to Euronorm, is obtained.

The applied tin layer on both sides of the investigated white tin sample was 5.6 gm^{-2} , i.e. the quality of white tin, according to Euronorm, is E5.6/5.6.

The internal lacquer layer of the body of the can was $10.6\text{--}11.6 \text{ gm}^{-2}$, and that on the covers, i.e. the ends of the can, was $10.8\text{--}11.0 \text{ gm}^{-2}$. No increased lacquer porosity was estimated. The adhesivity and thermochemical stability (resistance) of the lacquer were also good.

4.3. Sensory Changes of the Stew

The results obtained are presented in Table 3.

The changes in colour and smell of the product occurred gradually during the storage, whereas the change of taste was more pronounced.

After 18 months of storage, a metallic taste was detected in the investigated samples, as well as the first signs of corrosion at the inside lacquer layer. The pores in the lacquer layer became extended and visible, especially at points where the white tin was deformed, by bending. This can be explained by the mechanical extension of the lacquer layer.

More pronounced porosity, found near the top of the can, points to pronounced corrosion processes brought about by the oxygen in the space above the can contents [3,7–9].

Table 3. Sensory evaluation of stored stew

Storage (months)	Colour (1–5)	Smell (1–4)	Taste (1–5)	Consistency (1–6)	Total (max. 20)
Start	4.0	3.5	4.0	4.3	15.8
1	4.0	3.5	4.0	4.2	15.7
3	3.8	3.3	4.2	4.5	15.8
6	3.5	3.5	4.0	4.5	15.5
9	3.5	3.5	3.8	4.3	15.1
12	3.5	3.2	3.7	4.5	14.9
15	3.5	3.3	3.5	4.4	14.7
18	3.5	3.2	3.2	4.2	14.3
21	3.1	3.2	3.2	4.2	13.6
24	3.0	3.2	2.5	4.2	13.6

4.4. Metal Content Change of the Stew

The results of metal content changes of the packaged stew are given in Table 4. After 21 months of storage expansion of the initial micropores was observed, resulting from corrosion affecting the inner lacquer layer. This was the consequence of increased diffusion of Fe and Sn ions to the content, as proved by the metallic taste of the stew. The increase of Zn and Pb content was insignificant and there was effectively no change in the Cd and As contents. The content of metals that was found was in the range of permitted values for canned fruit and vegetable [19].

5. Conclusion

The quality of packaged stew in tin cans after 24 months storage, satisfies the legislative rules though a trend for the content of Fe ions to increase was noted after 21 months of storage, as well as a visible corrosion and metallic taste of the packaged product. After further storage, the corrosion processes may become more pronounced leading to a quality change of the product.

Table 4. Chemical analysis of metals in stored canned stew

Time of storage (months)	Metal content in mg kg ⁻¹ sample					
	Sn	Fe	Zn	Pb	As	Cd
Start	3.10	2.90	0.89	0.18	0.15	0.033
1	3.90	2.50	0.84	0.27	0.18	0.038
3	5.20	3.20	0.96	0.36	0.15	0.038
6	6.80	4.00	1.10	0.42	0.17	0.032
9	9.90	5.10	1.20	0.42	0.25	0.032
12	12.50	6.20	1.10	0.39	0.22	0.033
15	13.50	6.30	1.10	0.34	0.10	0.036
18	13.70	8.60	1.20	0.36	0.17	0.032
21	19.70	8.90	1.30	0.33	0.20	0.038
24	24.80	16.30	1.40	0.36	0.22	0.037

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Effect of the Microstructure of Aluminised Steel on its Corrosion Resistance in 3.5% NaCl Solution

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ABSTRACT

Studies were made of the effects of various intermetallic (Fe–Al, Ni–Al, Cu–Al) phases in the aluminium matrix on the corrosion resistance of aluminised carbon steel in NaCl solutions.

Intermetallic phases were characterised by X-Ray microdiffractometry. Surface quantitative analysis (XPS) was also used to assess the surface composition of specimens before exposure.

Electrochemical (polarisation and electrode impedance measurements) as well as free corrosion tests were carried out in aqueous aerated solutions at pH 6.5 and with dissolved oxygen content of 6.5 ppm. The exposure times ranged from 2 to 360 hours. Passive films formed on metallic surfaces were characterised using the XPS technique. The corrosion morphology was assessed by optical microscopy.

It was found that: (1) intermetallic phases in the aluminium matrix enhance both general and localised corrosion processes, and (2) intermetallic phases (mainly copper) hinder the film self-repairing property, thus preventing the formation of a homogeneous passive film and thereby stimulating localised corrosion.

1. Introduction

Hot dip aluminising is widely used to protect carbon steel against atmospheric corrosion because of the barrier effect of the aluminium passive layer which is practically impermeable to, and insoluble in, the most common oxidising media. Hence, the protective effect of aluminium is linked to its oxidation film composition rather than to its sacrificial power, since the free corrosion potential of aluminium is only slightly lower than that of carbon steel [1]. Therefore, aluminium has a limited ability to cathodically protect steel, since its preferential corrosion is self-limiting [2].

The protective power of the corrosion layer is dependent on its composition as well as its homogeneity, which is mainly controlled by the presence of intermetallic phases of some elements, such as Ni, Fe, Si, Cu, etc., in the metallic matrix.

Fe–Al intermetallic compounds may be formed during aluminising process as a result of Fe and Al interdiffusion at steel–aluminium interface to form intermetallic compounds (FeAl_2 , Fe_2Al_3 , FeAl_3 , FeAl) [3] or solid solutions that are able to migrate in the aluminium matrix up to the aluminium surface. Other intermetallic phases (Al_2Cu [4], NiAl [5], Ni_3Al [6–8]) could also be formed during aluminisation of various multilayer systems such as steel–copper or steel–copper–nickel. Their presence can significantly affect the corrosion behaviour of aluminium coatings because they can

form islands at the metallic surface which can then act as cathodic sites[9–11]. At the same time, the nearby matrix will undergo anodic dissolution with subsequent onset of pitting corrosion and rupture of the passive film formed on the metallic surface.

The aim of the present work was to study the influence of the metallic substrate (steel, multilayer steel/copper, steel/nickel, steel copper nickel) on: (a) the corrosion resistance of the aluminium coating both to general and localised corrosion, and (b) the chemical composition, morphology and protective power of the corrosion film that is formed on the aluminium surface.

2. Materials and Methods

Cylinders cut from tubes of composite multilayer materials (carbon steel–Al; carbon steel–Cu–Al; carbon steel–Ni–Al; carbon steel–Cu–Ni–Al) respectively labelled A, B, C, D, were tested. The various substrates (carbon steel or multilayer materials such as carbon steel–Cu, etc.) were protected by hot dip aluminising in a bath of fused aluminium in a reducing atmosphere. The aluminium layer thickness ranged from 150 μm (B and D specimens) to 100 μm (A and C specimens).

The specimens were microscopically examined, after polishing with alumina 0.5 μm and metallographic etching with Keller's reagent [12]. A heterogeneous micro structure was observed (580 $\times$ with optical microscope) (Fig. 1) at the steel–aluminium interface in all specimens and some intermetallic phases were identified (Table 1) [13] by X-Ray microdiffractometry (Rigaku DC-1Max, Cu K α radiation, microfocus).

In the aluminium layer some intermetallic phases were also microscopically observed, but, because of their very small size, they could not be identified. However, their presence is consistent with the diffusion of Fe, Cu and Ni from the inner layers up to the aluminium surface, as shown by XPS quantitative (Table 2) and qualitative surface analyses (Table 3) (VG — Escalab 210 photoelectron-spectrometer, Mg K

Table 1. X-Ray diffractometric identification of different intermetallic phases. (ASTM card numbers.) [13]

Sample	Intermetallic compounds
A	Al_5Fe_2 (29–43); $\text{Al}_{13}\text{Fe}_4$ (29–42)
B	Al_5Fe_2 (29–43); Fe_3Al (6–0695); Al_2Cu (25–12); AlCu_3 (28–5)
C	$\text{Al}_{13}\text{Fe}_4$ (38–1147); $\text{Al}_{75}\text{Ni}_{10}\text{Fe}_{15}$ (42–1042); AlNi_3 (21–8)
D	$\text{Al}_{13}\text{Fe}_4$ (38–1147); AlCu (26–16A); Cu_9Al_4 (24–3); AlCu_3 (28–5); AlNi_3 (21–8); Al_3Ni_2 (14–648)

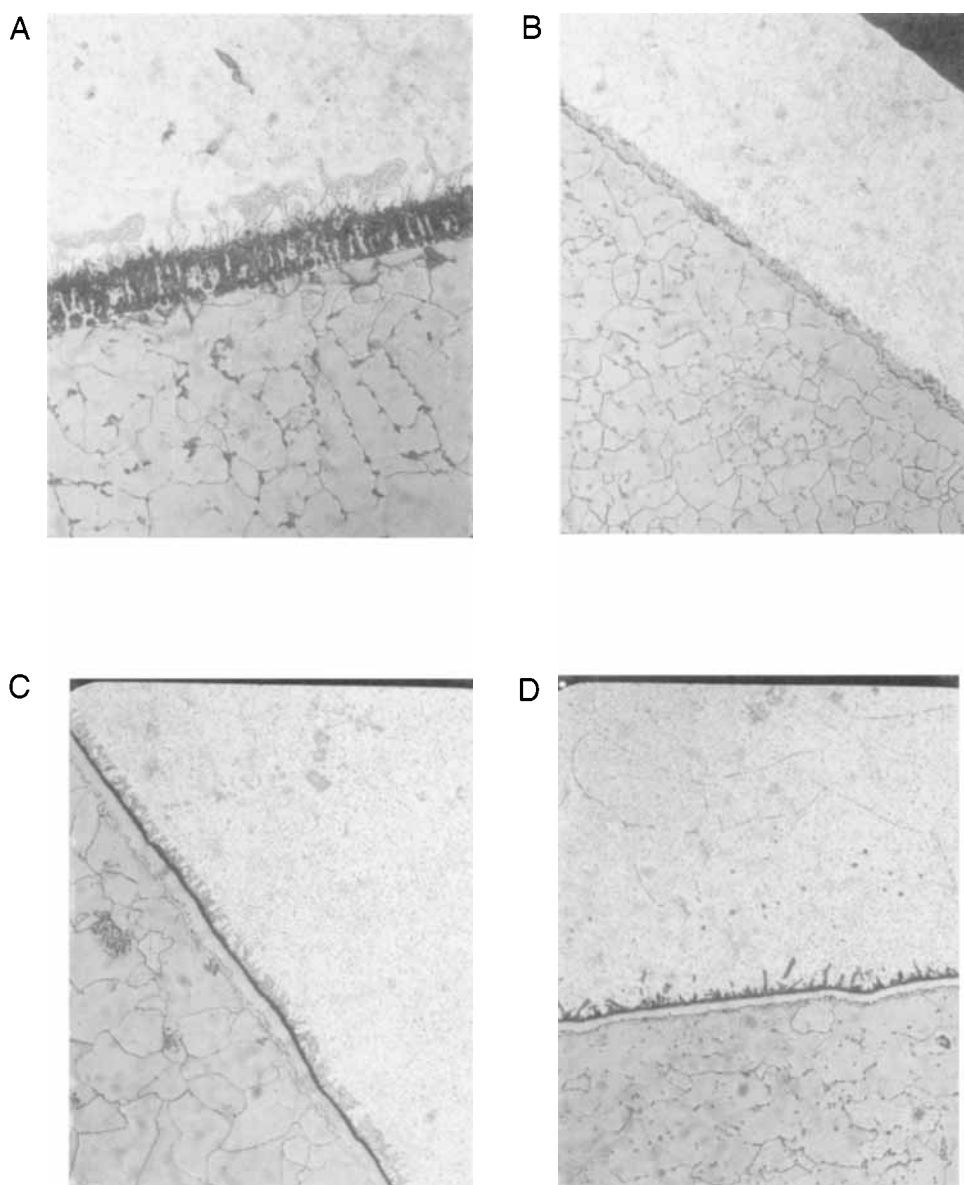


Fig. 1 Microscopical examination (580 $\times$) of uncorroded surfaces of A, B, C, D specimens, after Keller's etch.

radiation, 1253 eV). XPS analysis reveals that both aluminium, which is the main component in the surface layer, and iron are present in the metallic and in oxide form, whereas Cu and Ni are mainly in the metallic form.

The experiments were carried out at 25°C in 3.5% NaCl quiescent aqueous solution at pH 6.5 with a dissolved oxygen content of 6.5 ppm.

Table 2. Al, Fe, Cu, Ni at.% on different specimen surfaces, before (b) and after (a) 360 h exposure in NaCl solution

Sample		Al	Fe	Cu	Ni
A	(b)	98.7	1.2	0.0	0.0
	(a)	96.9	2.8	0.1	0.0
B	(b)	97.8	0.9	1.3	0.0
	(a)	96.5	1.5	1.9	0.0
C	(b)	99.0	0.2	0.1	0.6
	(a)	95.5	4.3	0.0	0.1
D	(b)	98.6	0.4	0.8	0.2
	(a)	98.0	1.4	0.4	0.2

Potentiodynamic polarisation tests were carried out with a scanning rate of $50 \mu\text{Vs}^{-1}$ on specimens previously held for 2h in the corrosive solution during which time the corrosion current density, corresponding to average corrosion rate, was measured. Breakdown potential (E_p) and repair potential (E_{pp}) of the film were also measured. Starting from the free corrosion potential (E_{fc}), the working electrode potential was increased until the E_c potential (indicated by the strong increase in the

Table 3. Qualitative analysis of the aluminium layer of different specimens before (b) and after (a) the corrosive attack. The corresponding Binding Energy (BE, eV) values are shown.

Sample		Element speciation
A	(b)	Al ^o (72.9), Al ₂ O ₃ (74.3), Fe ₂ O ₃ (711.6), Fe ^o (706.7)
	(a)	AlO(OH)(74.2), Al(OH) ₃ (73.9), Al ₂ Cu(933.9), FeO(OH)(710.8), Fe ₂ O ₃ (711.6)
B	(b)	Al ^o (72.9), Al ₂ Cu(933.9, 71.8), Al ₂ O ₃ (74.3), Fe ₂ O ₃ (711.6)
	(a)	AlO(OH)(74.2), Al(OH) ₃ (73.9), Al ₂ Cu(933.9) FeO(OH)(710.8), Fe ₂ O ₃ (711.6)
C	(b)	Al ^o (72.9), Al ₂ O ₃ (74.3), Fe ^o (706.7), NiO (854.1)
	(a)	AlO(OH)(74.2), Al(OH) ₃ (73.9), FeO(OH)(710.8), Fe ₂ O ₃ (711.6), Ni(OH) ₂ (857.4)
D	(b)	Al ^o (72.9), Al ₂ O ₃ (74.3), Fe ₂ O ₃ (711.6), Cu ₂ O(933.4), Al ₂ Cu(933.9)
	(a)	AlO(OH)(74.2), Al(OH) ₃ (73.9), FeO(OH)(710.8), Al ₂ Cu(933.9), Ni ^o (852.5)

anodic current) was reached. As soon as E_p was established the working electrode potential was lowered until the backward anodic curve crossed the forward curve: this value was considered as E_{pp} .

Electrode impedance measurements were also carried out by perturbing the equilibrium potential of the specimens, previously held for 2 and 120 h in NaCl solution, with 10 mV a.c. with a frequency decreasing from 65 kHz to 10 mHz. EIS spectra were recorded as Nyquist plots which were deconvoluted with the Solartron Shlumberger Z-view program.

Free corrosion experiments were carried out for periods ranging from 120 to 360 h. The weight loss of corroded specimens was assessed with atomic absorption spectrophotometry by adding to the amount of aluminium soluble corrosion products the amount of aluminium solid corrosion products adhering to the metallic surface. The latter were dissolved by a selective acidic solution (HF-HNO_3) [14]. The corrosion layer composition was characterised by XPS spectroscopy and X-Ray diffractometry (Cu K_α radiation).

Microscopical examinations of corroded specimens were also carried out to assess the onset of localised corrosion.

3. Results and Discussion

3.1. Electrochemical Tests

Potentiodynamic polarisation curves (Fig. 2 and Table 4) show that the steel-Cu-Al multilayer (specimens B) has the highest corrosion current density value (i_{corr}) (Table 4) thus suggesting a stimulating effect of Cu on the corrosion of aluminised steel.

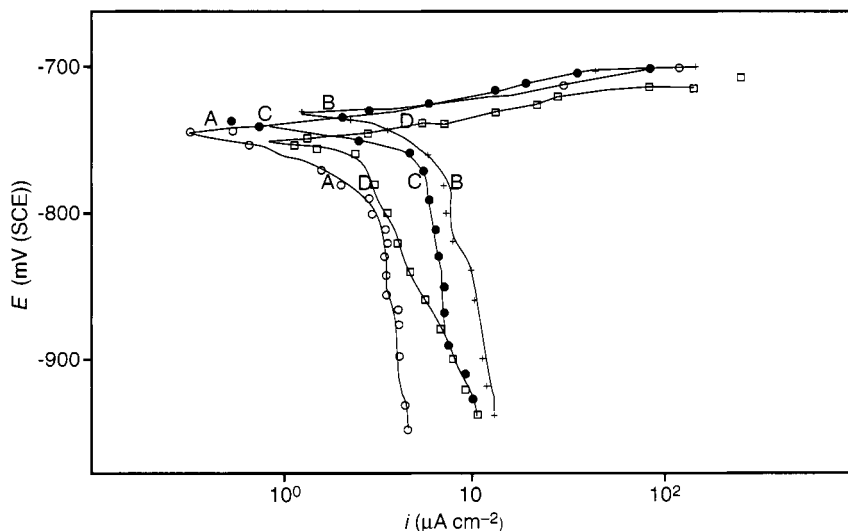


Fig. 2 Potentiodynamic polarisation curves of A, B, C and D specimens after 2 h pre-immersion time in NaCl solution.

Table 4. Polarisation curves of A, B, C and D specimens, after 2 h exposure time in NaCl solution. Mean values from three measurements

Sample	β_a (mV/dec)	β_c (mV/dec)	E_{corr} (mV, SCE)	i_{corr} $\mu\text{A}.\text{cm}^{-2}$
A	9	-29	-739	0.739
B	37	-77	-759	1.120
C	20	-17	-741	0.859
D	27	-23	-743	0.702

Pitting corrosion susceptibility measurements (Table 5) show that all specimens undergo pitting corrosion, since they exhibit a very small passivity domain ($E_p - E_{fc}$), significantly lower than that of pure Al (≈ 300 mV) under the same experimental conditions [15]. This is consistent with the presence of intermetallic phases on the metallic surface (see Table 1), which are cathodic to the matrix and form microgalvanic cells whose electromotive force (emf) depends on the nature of the intermetallic compounds. Thus, these can act as weaker or stronger pitting stimulators. The Al_2Cu intermetallic phase shows a very high emf against the Al matrix (200mV [16]) which remains unchanged when aluminium undergoes dissolution; similar emf values are shown by some intermetallic Al–Ni compounds, such as AlNi_3 ; this may be associated with the negative perfect passivity domain ($E_{pp} - E_{fc}$) value of B and C specimens which suggests a strong matrix attack hindering the self-repairing property of the passive film. This hypothesis is supported by literature data [17] in which Al–Ni or Al–Cu were found to be efficient cathodes which enhanced and accelerated preferential anodic corrosion paths leading to a directional attack of the matrix.

Table 5. Free corrosion potential E_{fc} , film breakdown potential E_p , pitting protection potential E_{pp} of A, B, C, and D specimens after 2 h exposure time in NaCl solution. Mean values of three measurements

Sample	E_{fc} (mV, SCE)	E_p (mV, SCE)	E_{pp} (mV, SCE)
A	-745	-700	-740
B	-750	-722	-758
C	-734	-705	-744
D	-757	-720	-738

Conversely, other intermetallic phases containing Fe, such as Fe–Ni–Al [18] or Al–Fe particles [19], are not such efficient cathodes and do not affect the localised corrosion attack in such a significant manner e.g. the Al_3Fe emf value is similar to that of the Al matrix. In the first steps of the corrosion, the Al_3Fe phase does not show cathodic behaviour relative to the aluminium matrix since it undergoes selective Al dissolution. As the corrosion progresses, the Al_3Fe surface crystals become richer in Fe. The Fe on oxidation, forms a protective layer of Fe_3O_4 which passivates the crystals leading to a rapid shift in E_{fc} to a more positive, stable value cathodic to aluminium so that localised corrosion can then take place. The higher pitting resistance of specimens A may be the result of the presence of an Al–Fe intermetallic phase. The greater pitting resistance of D specimens, where a higher Fe intermetallic phase concentration was found on the surface, may also be due to a thicker aluminium layer.

Impedance measurements, carried out on specimens previously held 2 and 120 h in NaCl solutions confirm the potentiodynamic polarisation test results. Impedance spectra were recorded as Nyquist diagrams and deconvoluted using a rough model (Fig. 3) in which the total impedance (Z_{tot}) was simply written as the sum of the impedance of both interfaces (Z_{mo} and Z_f) and the impedance of the oxide film itself (Z_{os}) [20]:

$$Z_{tot} = Z_{mo} + Z_f + Z_{os} \quad (1)$$

Roughly speaking, the impedance of the metal–oxide interface Z_{mo} can be represented by a simple parallel circuit consisting of charge transfer resistances ($R_{mo'}$) due to electron and aluminium cation transfer resistance contributions, and of an interfacial double layer capacitance C_{dlmo} . The impedance of the oxide–solution interface Z_{os} can be considered as a simple parallel circuit of a charge transfer resistance ($R_{os'}$ due to Al and O redox reactions) and a double layer capacitance C_{dlos} , while the film impedance Z_f can be described as the transport of vacancies in parallel with electron and hole resistance. According to some authors [21], this impedance linked to the transport of oxygen and aluminium ion vacancies across the film can be considered as a Warburg impedance. Good agreement was found between EIS spectra obtained with experimental results and EIS spectra simulated according to the model in Fig. 3.

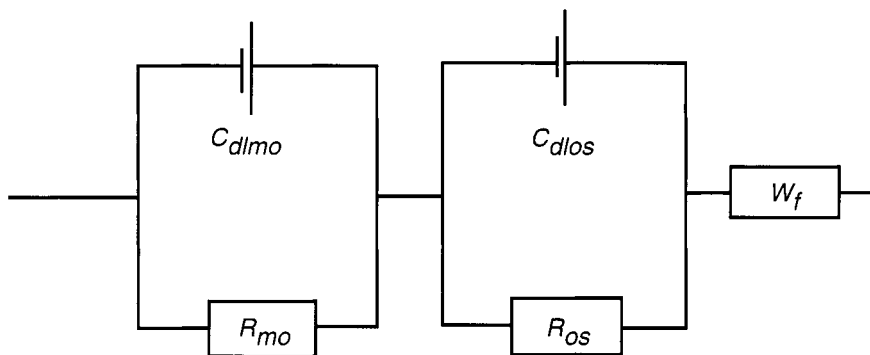


Fig. 3 Electrical circuit model used to deconvolute impedance spectra.

The electrochemical parameters obtained with a curve simulation programme are shown in Table 6. This Table shows that the charge transfer resistance at the oxide-solution interface as well as the Warburg film impedance of all specimens decrease with increasing exposure time. This may be consistent with the decrease in passive film protective power arising from changes in its composition or morphology which, in turn, can be linked to the increases in the number and sizes of defects.

Specimens B, with coarse Cu–Al intermetallic phases, had the lowest charge transfer resistance as well as the highest capacitance at the metal–oxide interface over the whole exposure time range: this is consistent with specimens B having the lowest corrosion resistance, as indicated by the polarisation tests (Table 5).

Specimens A, with Fe–Al intermetallic phases, exhibit the highest film impedance and hence the greatest passivating power (Fig. 4). This leads to a decrease in average corrosion rate and to an increase (ennoblement) in breakdown film potential as shown in the potentiodynamic polarisation results (Tables 4, 5). Literature data [19] showing Fe–Al particles to be weakly cathodic to the aluminium matrix suggest a more homogeneous dissolution with the subsequent formation of a more compact, less defective passive film, at least in the first steps of corrosive attack. Conversely, for longer exposure times, Al–Fe intermetallic phases become richer in Fe and hence more cathodic to the aluminium matrix: this is in agreement with the marked decrease in R_{os} and the Warburg film impedance W_f .

For shorter exposure times, the transfer charge resistance at oxide–solution interface and Warburg film impedance values of specimens D (Fig. 7) are higher than those of B (Fig. 5) and C (Fig. 6) specimens (with Cu–Al or Ni–Al intermetallic cathodic phases). This can be ascribed to the dominating presence of Fe–Al intermetallic phases which, for short exposure times, do not stimulate the aluminium matrix dissolution.

Table 6. *Electrochemical parameters from impedance spectra of specimens exposed in NaCl solution*

Sample	Pre-exp. time (h)	R_{mo} ($k\Omega cm^2$)	C_{dlmo} ($\mu F cm^{-2}$)	R_{os} ($k\Omega cm^2$)	C_{dlos} ($\mu F cm^{-2}$)	W_f ($k\Omega cm^2$)
A	2	3.5	80	45	5.0	30
	120	3.5	40	15	1.0	1
B	2	3.2	150	12	10.0	12
	120	2.0	29	9	80.0	0
C	2	3.5	80	19	7.0	12
	120	3.5	40	15	2.5	3
D	2	3.5	80	44	5.5	14
	120	3.5	40	10	0.9	1

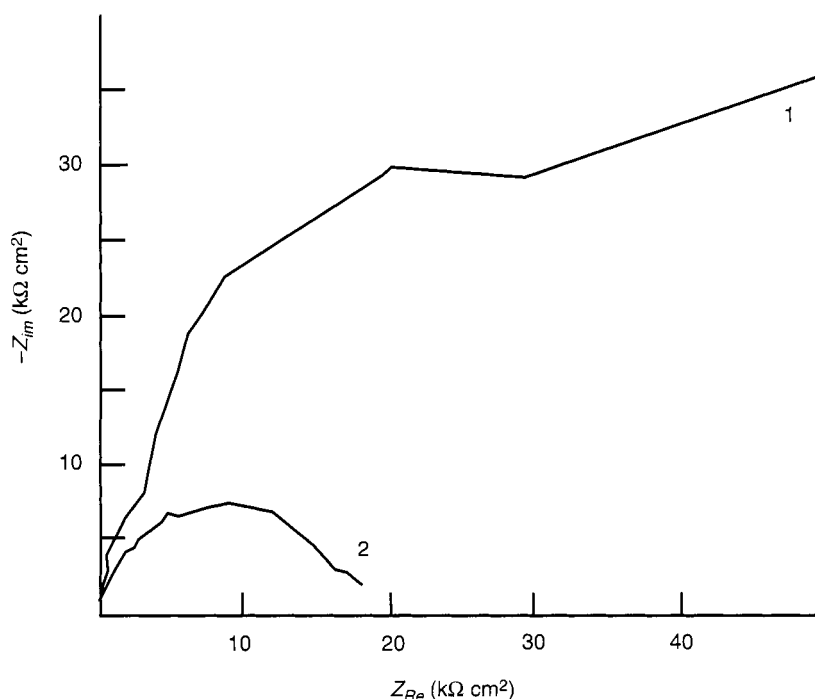


Fig. 4 Nyquist diagrams of A specimens after 2 h (1) and 120 h (2) exposure time in NaCl solution.

3.2. Free Corrosion Tests

With weight loss tests (Fig. 8) it was possible to discriminate between the influences of different intermetallic phases on the aluminium layer dissolution. Figure 8 shows that specimens A and C, in which only an insignificant copper atomic percentage was found at the surface, have the lowest average corrosion rate. Conversely, specimens B, where coarse intermetallic Al-Cu phases, strongly cathodic to aluminium matrix were found at the surface, have the highest corrosion rate. The highest corrosion rate of specimens B is likely to be due to a higher copper surface content as well as to the copper phase size which hinders the self-passivating effect of the aluminium oxide film, as confirmed by the absence of a perfect passivity domain $E_{pp}-E_{fc}$, shown by Table 5.

The total weight loss WL of all specimens vs time t follows an exponential relationship. This is consistent with a complex dissolution process in which a homogeneous aluminium matrix dissolution (governed by a parabolic WL vs t law [22] with rate decreasing with time), has a localised dissolution process (due to Al-intermetallic phase microgalvanic cells) superimposed. Hence, since WL vs t follows an exponential law, the dissolution rate increases with increasing exposure time. This confirms the impedance test results showing that the passive films of all specimens decrease in protective power with increasing exposure time.

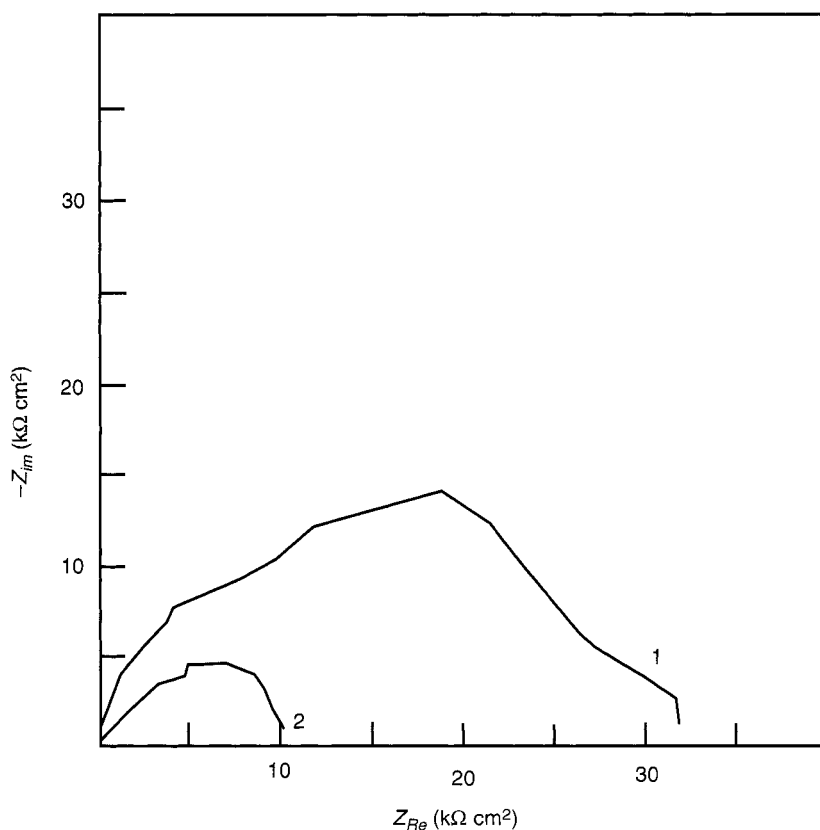


Fig. 5 Nyquist diagrams of B specimens after 2 h (1) and 120 h (2) exposure time in NaCl solution.

3.3. Surface Analysis

XPS analysis (Tables 2 and 3) carried out on specimens before and after exposure (360 h) in NaCl solutions shows:

- aluminium compounds to be the main component of all surface films: 'dry' aluminium oxides are formed on uncorroded specimens while aluminium oxyhydroxides (bayerite and bohemite) are formed on corroded specimens (Tables 2 and 3);
- a higher iron compound concentration on corroded specimens: this is consistent with preferential dissolution of aluminium in Al-Fe intermetallic phases and with their enrichment in Fe, in agreement with literature data [19];
- a small decrease in copper compound concentration on corroded specimens: this may be consistent with their undermining of the metallic matrix, anodic to copper intermetallic phases. Hence the aluminium phase is preferentially

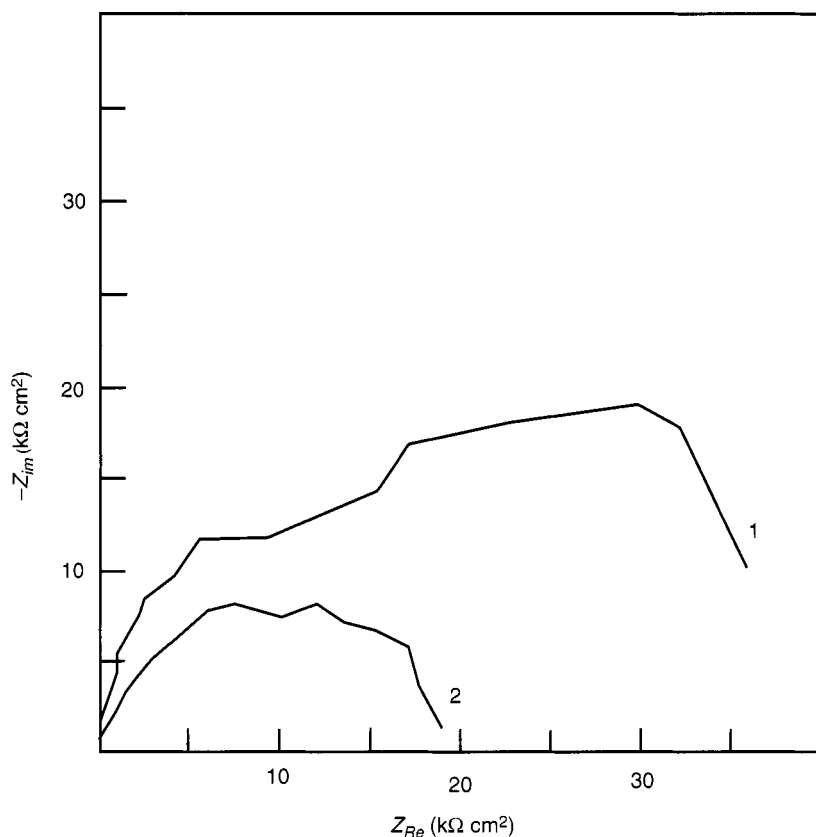


Fig. 6 Nyquist diagrams of C specimens after 2 h (1) and 120 h (2) exposure time in NaCl solution.

dissolved during the corrosive attack, while Cu–Al phases remain unchanged in composition, as shown by XPS (Table 3) and X-ray diffractometric analyses.

Surface analysis shows that the same compounds ('dry' oxides on uncorroded, 'wet' oxides on corroded specimens) are formed on the surface layers of all specimens. The different passivating power of passive films, suggested by their different Warburg impedances, must be ascribed to the presence of intermetallic phases, different in composition or in size, which leads to a non-homogeneous, defective passive film in which its self-repairing property can be hindered.

3.4. Microscopical Examination

Microscopical examinations show that on the surface of specimens B with the coarse Cu–Al intermetallic phases that are highly cathodic to matrix, deeper and more numerous pits are formed. Conversely, on specimens A with Fe–Al intermetallic phases that are slightly cathodic to the matrix, few and only superficial pits are formed.

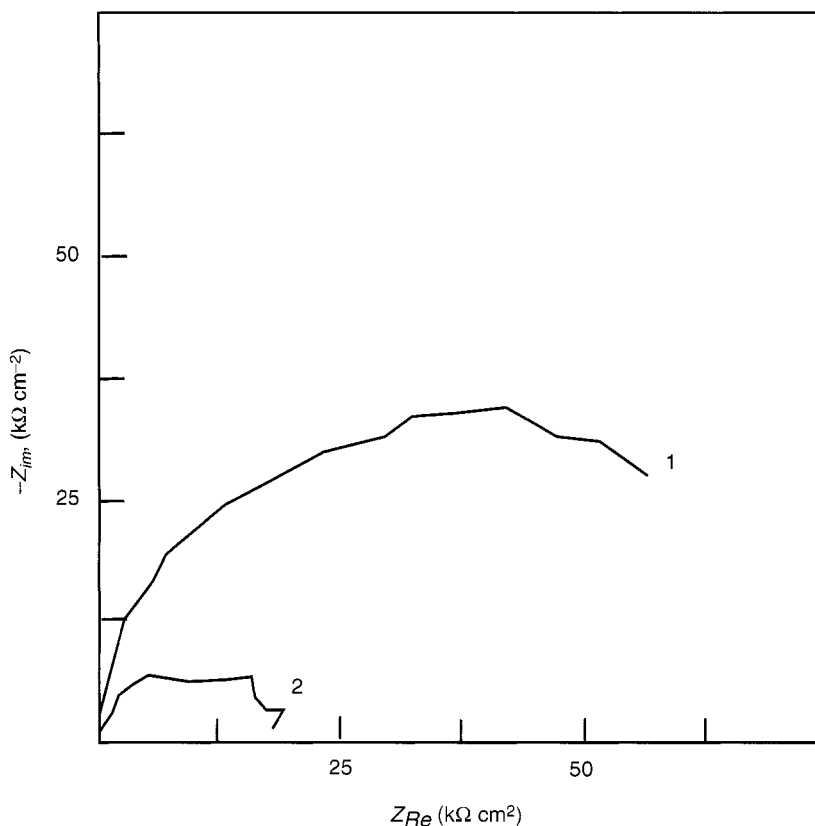


Fig. 7 Nyquist diagrams of D specimens after 2 h (1) and 120 h (2) exposure time in NaCl solution.

4. Conclusions

In aluminised carbon steel, and aluminised multilayer material (carbon steel–Cu–Al, carbon steel–Ni–Al and carbon steel–Cu–Ni–Al) the presence of intermetallic phases in the aluminium matrix enhances both general and localised corrosion processes.

Intermetallic phases (mainly of copper) hinder the film self-repairing property, thus preventing the formation of a homogeneous passive film and thereby stimulating localised corrosion.

5. Acknowledgement

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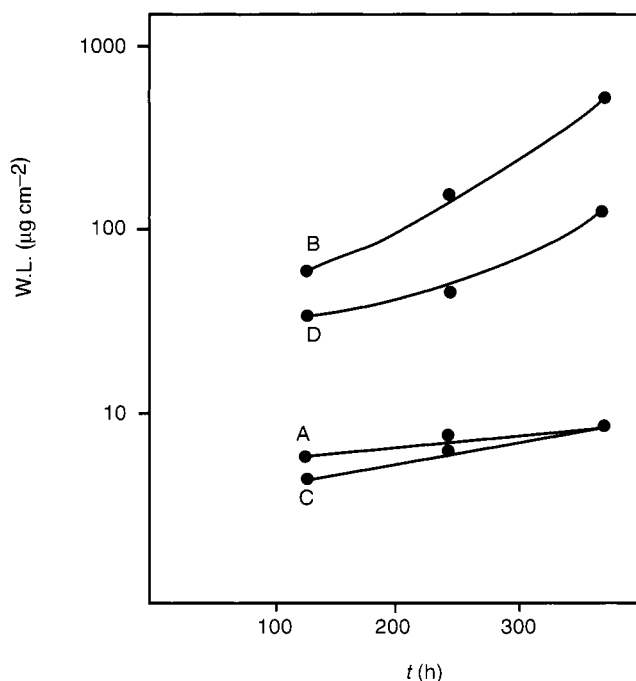


Fig. 8 Weight loss vs exposure time of A, B, C and D specimens in NaCl solutions.

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Contribution to the Study of the Mechanism of Corrosion of Nanocrystalline Nickel Coatings Obtained by Ball Milling

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ABSTRACT

The electrochemical behaviour in various electrolytes of nanocrystalline Ni coatings obtained by ball milling was investigated by potentiodynamic test methods and compared with that of polycrystalline Ni. The results are discussed and the passivation mechanism is proposed.

Nanocrystalline materials are polycrystalline materials with grain sizes of up to about 100 nm. Because of the extremely small dimensions, a large fraction of the atoms in these materials is located at the grain boundaries, and this confers special attributes.

1. Introduction

Nanocrystalline materials have received much attention as a result of their unique physical, chemical and mechanical properties. However, little work has been performed to establish the corrosion behaviour of these materials. Rofagha *et al.* [1, 2] studied nanocrystalline Ni and Ni-P produced by an electrodeposition technique. The observed behaviour was considered to be consistent with substantial contributions to the bulk electrochemical behaviour from the intercrystalline regions (i.e. grain boundaries and triple junctions) of these materials.

Inturi and Szklarska-Smialowska [3] have observed improved localised corrosion resistance in HCl for sputter deposited nanocrystalline type 304 stainless steel in comparison with conventional material, they attributed this to the fine grain size and homogeneity of the nanocrystalline materials.

Thorpe, Ramaswami and Aust [4] studied the corrosion behaviour of nanocrystalline $\text{Fe}_{32}\text{Ni}_{36}\text{Cr}_{14}\text{P}_{12}\text{B}_6$ alloy obtained by crystallisation of the melt-spun amorphous ribbon. They determined that the corrosion resistance was significantly greater than that of its amorphous counterpart. The authors attributed this improved corrosion resistance to the observed greater Cr enrichment of the electrochemical surface film via rapid interphase boundary diffusion [4].

Schneider *et al.* [5] observed that in the nanocrystalline state in strongly acidic solution FeCr as well as FeAl had a lower corrosion resistance than in the polycrystalline state. The authors explained this by the high defect density (density of the grain boundaries).

The objective of this study was to assess the corrosion behaviour of ball-milled nanocrystalline Ni coatings in 0.1M H₂SO₄ and 0.1M Na₂SO₄ media, and to contribute to the understanding of the corrosion mechanism.

2. Experimental Procedure

Nanocrystalline Ni coatings (ncNi) were produced by ball-milling: 10 g of Ni were introduced into a cylindrical tempered steel container (vial) of capacity 45 mL. Each container was loaded with five quenched steel (type 100 C6) balls (dia. 1.5 cm, mass 14 g). The containers were sealed with a Teflon O-ring and the milling conducted in stationary air without exchange with the laboratory atmosphere. The milling was carried out using the so-called G5 specially designed planetary high energy machine which allows independent choice of the shock frequency and shock energy [6, 7]. The effective conditions during the mechanical alloying were the following: $\Omega = 268$ r.p.m., $\omega = 500$ r.p.m. where Ω is the rotation speed of the disc on which the containers are fixed and ω the rotation speed of the containers.

The related shock energy (E), frequency (ν) and injected mechanical power (P) are equal to (according to [8]) :

$$E = 0.0978 \text{ J/hit}, n = 61.5 \text{ Hz}, P = 0.60 \text{ W/powder g}$$

The duration of the process was equal to 12 and 24 h. Such a short duration was chosen to avoid excessive contamination from the friction and the impacts between the balls and the walls of the vials but this milling duration is long enough to obtain a nanocrystalline Ni structure as was shown by X-ray diffraction investigations (Fig. 1).

The nanocrystalline nickel covered balls (dia. 1.5 cm) were mounted in epoxy resin to leave a surface area of 0.196 cm² exposed to the test solution. The electrical contact with each sample was assured by a small diameter copper wire. 'Conventional' nickel specimens (pcNi) were prepared from a polycrystalline nickel rod (99.99%) of dia. 1.3 cm obtained from commercial sources (Goodfellows).

All corrosion specimens (pc and ncNi) were mechanically polished to 6 μm on SiC paper and diamond paste and then cleaned in ultrasonic bath, and finally rinsed with alcohol.

Corrosion testing was conducted in 0.1M H₂SO₄ and 0.1M Na₂SO₄ media using a PGP 201 potentiostat connected to a computer and a printer, a standard corrosion cell (300 mL) with three electrodes. The circular conventional nickel electrode and the auxiliary platinum electrode had the same area, 1.32 cm² and were fixed vertically, face to face. The reference electrode was a saturated calomel electrode (SCE) near the surface of the metallic sample. All corrosion tests were carried out at a temperature of 298 K.

On immersion in the test solution, specimens were cathodically charged for 600 s at a potential of -800 mV in order to reduce existing surface films [9].

Potentiodynamic anodic polarisation tests were conducted using a potential scan rate of 50 mV/min. For each curve, the reproducibility was checked.

Scanning electron micrographs (Figs 2, 3) show a typical surface morphology of coatings obtained by ball milling.

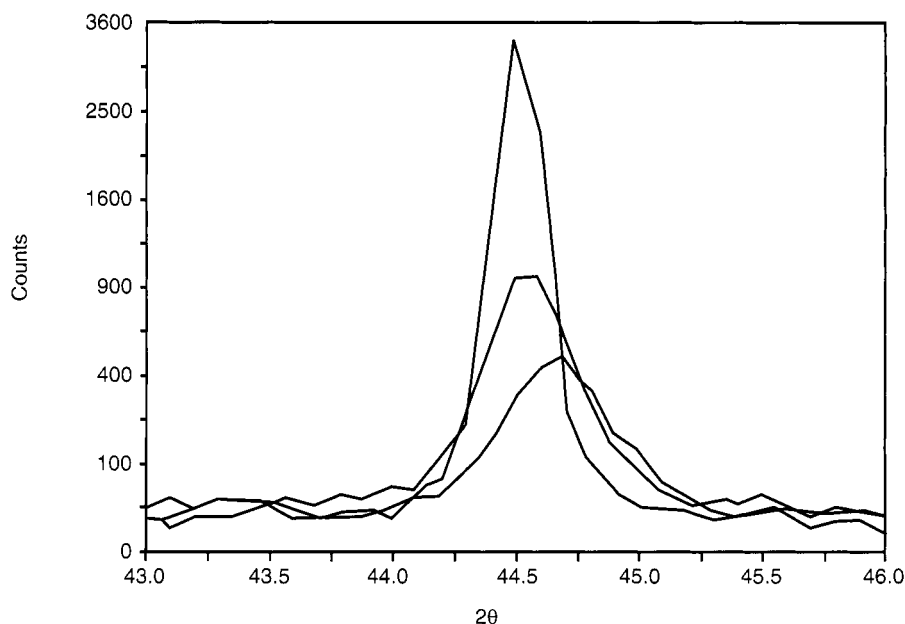


Fig. 1 X-ray [111] diffraction peaks of Ni corresponding to: (a) initial state; (b) milling duration = 12 h $\rightarrow$ crystallite thickness based on the FWHM: 52.3 nm; (c) milling duration = 24 h $\rightarrow$ crystallite thickness based on the FWHM: 35.6 nm (FWHM: Full Width at Maximum Height).

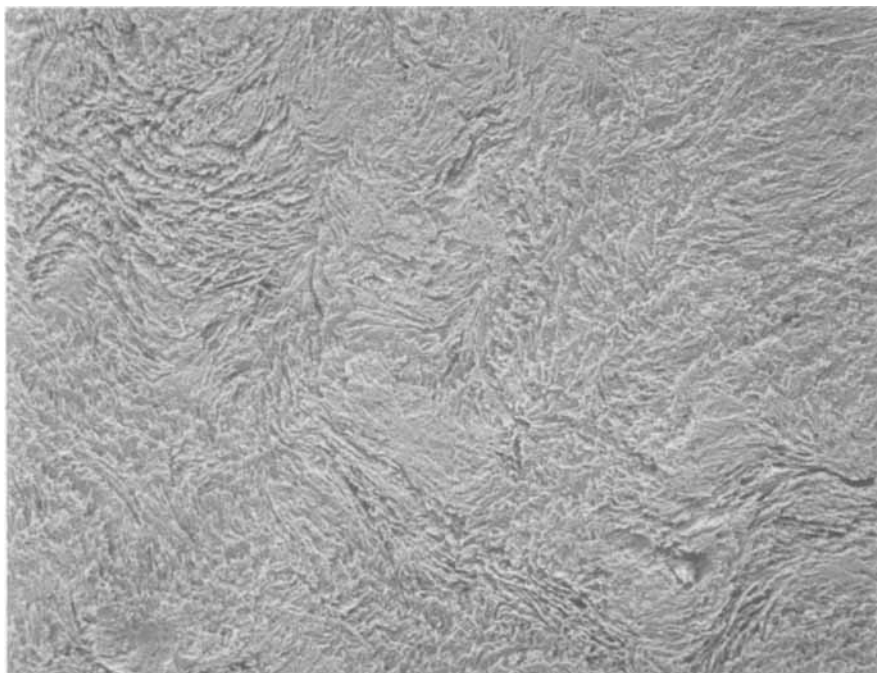


Fig. 2 SEM micrograph of nc-Ni coating (12 h). Secondary electron image mode. Magnification $\times 200$.

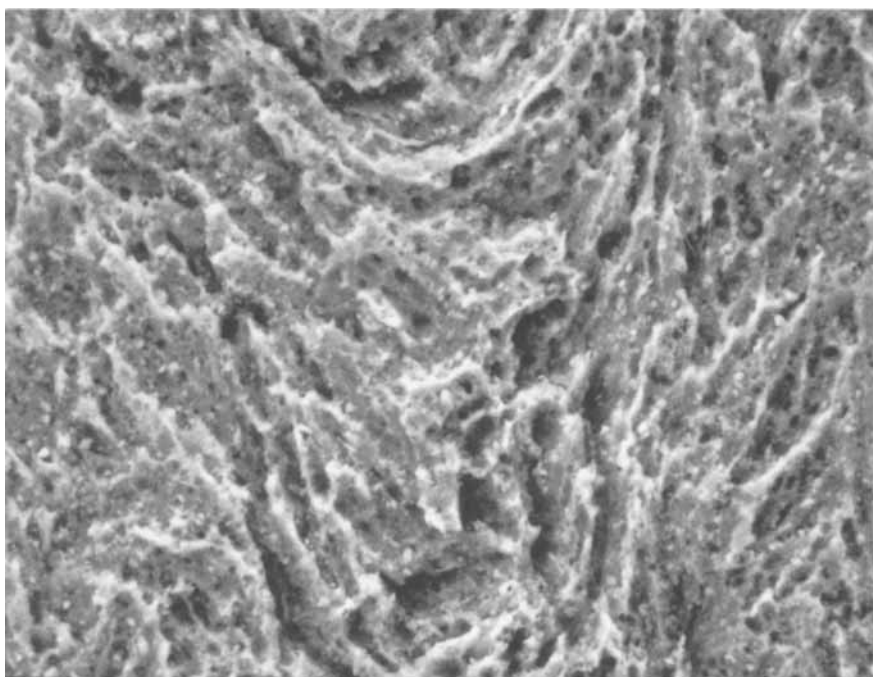


Fig. 3 SEM micrograph of nc-Ni coating 5 (12 h). Secondary electron image mode. Magnification $\times 1600$.

3. Results and Discussion

Figure 4 shows the current–density potential measurements of pc-Ni and nc-Ni in weekly acid solution ($0.1\text{M Na}_2\text{SO}_4$; $\text{pH} = 6$). There is a notable difference in the apparent free corrosion potential of these materials. The E_{corr} of the ball milling nc-Ni is more anodic than for the pc-Ni. No passive domain could be observed for any of the materials.

On comparing the polarisation curves for the two nanocrystalline materials and the polycrystalline material, it can be seen that the pc-Ni specimen exhibits lower dissolution rates. This may be due to the grain boundary and triple junction content of the specimens. Intercrystalline constituents, grain boundaries and triple junctions are considered to be distinct defects which provide active dissolution sites [2].

Figure 5 shows the potentiodynamic anodic polarisation behaviour observed for all specimens in 0.1M sulphuric acid media. They are, to a first approximation, comparable to those obtained by other authors [10–13] on mostly polycrystalline samples, and exhibit a passivation peak, related to the formation of the protective oxide layer NiO. The mechanism of formation of such a layer has been discussed in detail elsewhere [14].

The E_{corr} of the ball-milled nc-Ni coatings is found to be more anodic than for the conventional Ni. This is in agreement with Rofagha *et al.* [1] who reported that the nanocrystalline material showing E_{corr} values approximately 200 mV more anodic

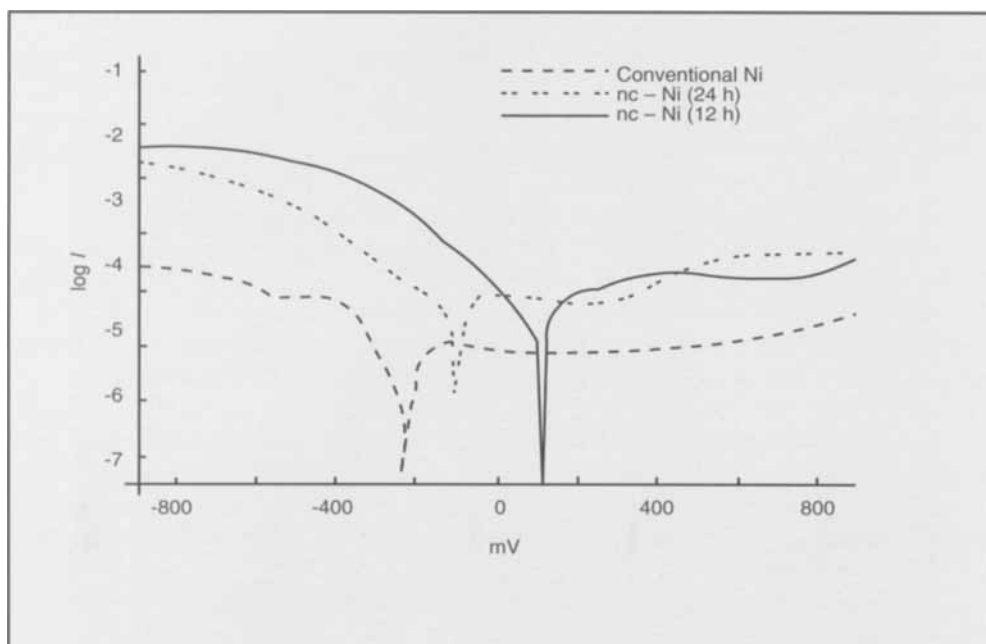


Fig. 4 Polarisation curves for pc-Ni and nc-Ni in 0.1M Na₂SO₄.

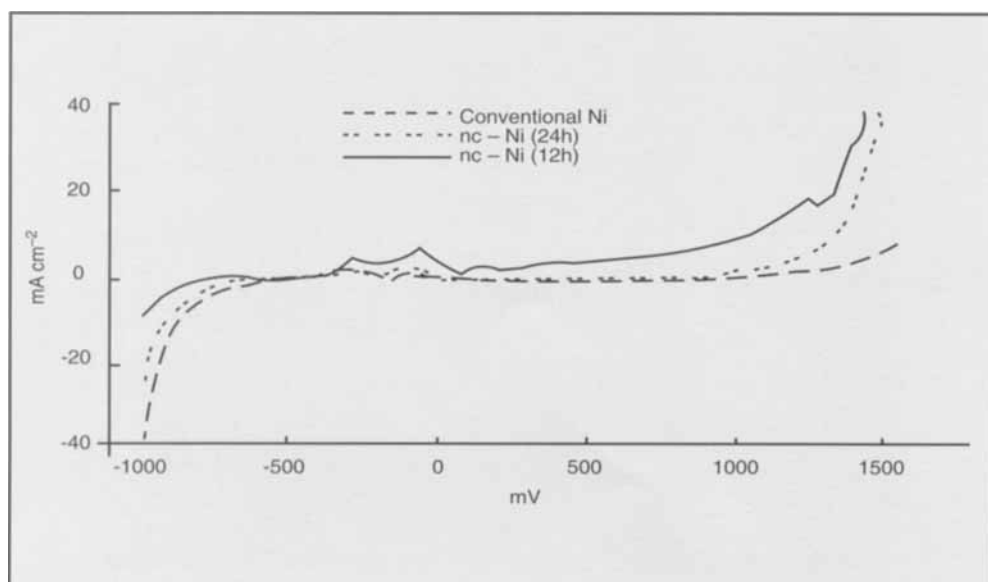


Fig. 5 Polarisation curves for pc-Ni and nc-Ni in 0.1M H₂SO₄.

(positive) than those displayed by conventional Ni. The authors explain that the positive shift in E_{corr} may be due to the catalysis of the hydrogen reduction process by the substantial quantity of crystalline defects (e.g. grain boundaries) at the nanocrystalline electrode surface [1]. The high volume fraction of grain boundaries and triple junctions on the nc specimens resulted in enhanced dissociative adsorption of oxygen and hydroxyl species from solution [15]. The origin of this phenomena was the introduction of high energy during the ball milling preparation process.

As shown in Fig. 5, it is evident that the corrosion resistance parameters (peak active current density, minimum passive current density, width of passivation domain) of ball milled nc-Ni were higher than those of the conventional Ni. The nanocrystalline structure increased the peak active current density I_a , minimum passive current density I_p and transpassive current density I_{tr} . This may be due to defects in the interfaces of nc-Ni (e.g. free volumes and microvoids) (Fig. 6). Consequently, the true surface area considered is higher than the real surface area. Investigations carried out by scanning electron microscopy (Fig. 7) show a very rough morphology of a nanocrystalline Ni coating after potentiodynamic polarisation. It seems that the corrosion attack is aimed at the contact boundaries between the crystallite agglomerates.

From the obtained results, it can be seen that the microstructure of the material has a strong effect on electrochemical behaviour.

It is difficult to explain the significant corrosion resistance of the nc-Ni. Nevertheless, the following mechanism is suggested. A specific difference between the nanocrystalline materials and the usual crystalline materials is that in the former

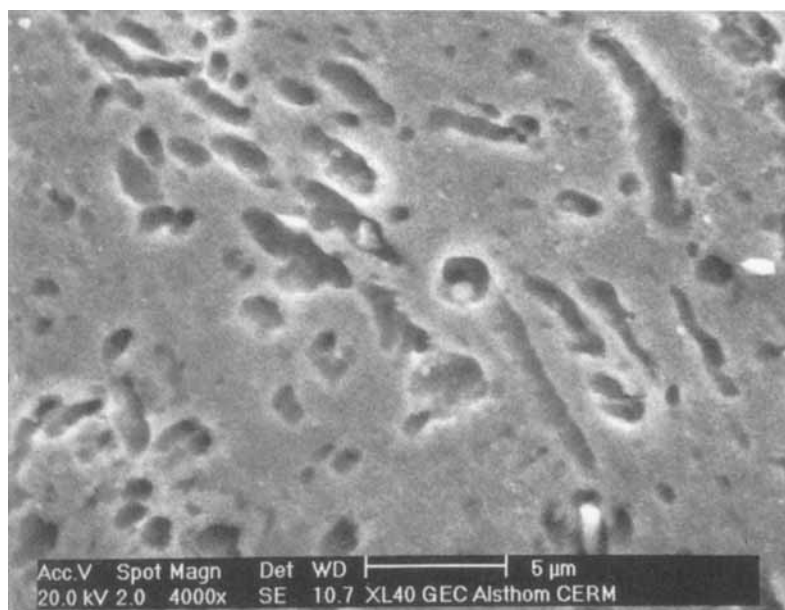


Fig. 6 Microvoids and porosities observed on the polished surface of the as-milled powder. Secondary electron image mode — scanning electronic microscopy micrograph.

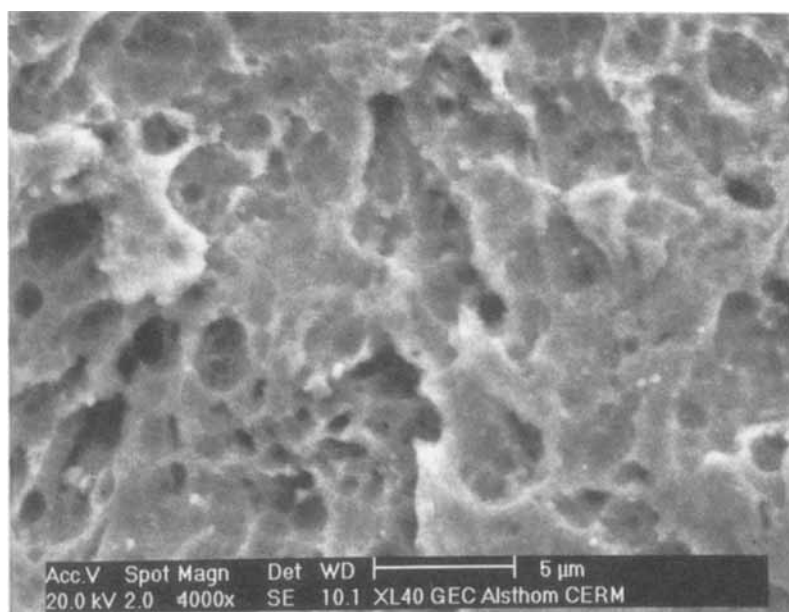


Fig. 7 SEM micrograph of nc-Ni coating after potentiodynamic polarisation. Secondary electron image mode.

the interfaces have become an important structural component in addition to the crystallites. Correspondingly, many physical and mechanical properties of nanocrystalline materials, which are highly sensitive to their microstructural character, have resulted in some anomalous phenomena [16]. For example, fast diffusion behaviour has been reported [17]. In our case, the enhancement of corrosion resistance can be attributed to the larger fraction of the interphase boundaries and the fast diffusion character of the nanocrystalline materials. This is in agreement with the work of Splinter *et al.* [15] that characterised by XPS the corrosion films formed on nanocrystalline Ni-P alloys in sulphuric acid. They explained that the high volume fraction of grains boundaries and triple junctions on the nc specimens resulted in enhanced dissociative adsorption of oxygen and hydroxyl species from solution.

Meanwhile, because of the fast diffusion effect, a large amount of Ni will accumulate on the surface of the samples to form a continuous NiO film (Fig. 8) [5, 16].

4. Conclusion

Nanocrystalline Ni coatings obtained by ball-milling exhibit a better corrosion performance than conventional Ni. They are promising for the development of protective wear and corrosion resistant materials.

However, the nature of the differences of the corrosion behaviour with different microstructures requires further theoretical and experimental studies.

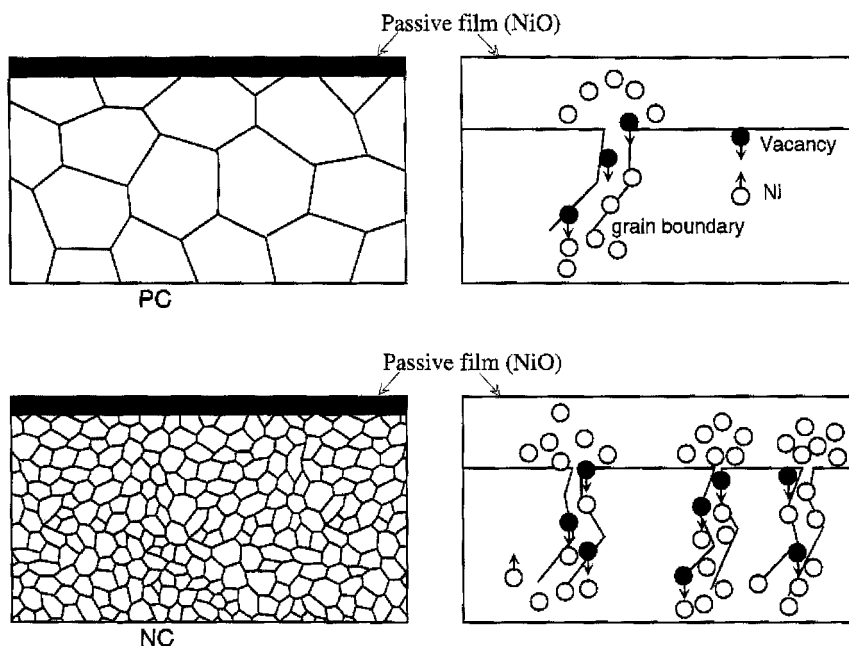


Fig. 8 Proposed passivation mechanism of nc-Ni and pc-Ni [18].

5. Acknowledgements

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Part 4

Ceramic Coatings

Rates and Mechanisms of Combined Erosion and Corrosion of Ceramic–Metallic Coatings/Surfaces

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ABSTRACT

In the investigation of different carbide–metal HVOF (High Velocity Oxygen Fuel) thermal spray coatings and monolithic cemented carbides exposed to silica sand slurries, the various contributions to erosion–corrosion weight losses have been determined: corrosion (electrochemical weight loss), pure erosion and synergy effects. The effects of metal matrix composition, the electrochemical characteristics and the mechanisms of deterioration are discussed. A duplex stainless steel was used as a reference material.

1. Introduction

Combined sand erosion and corrosion is a problem in various industrial environments, e.g. in oil and gas production, process industries and hydro power plants. To improve the performance of components under erosive and more or less corrosive conditions, a large number of coatings and monolithic materials have been investigated in several projects at SINTEF Corrosion and Surface Technology. In particular, erosion and corrosion of carbide-metal composites have been measured and analysed.

When a material is exposed to erosive and corrosive conditions the total mass loss rate T may be expressed by

$$T = E + C + S_{EC} + S_{CE}$$

where E is the pure erosion rate, i.e. mass loss rate when corrosion is eliminated, C is the corrosion rate in the absence of sand erosion, S_{EC} and S_{CE} are both synergy effects of erosion and corrosion: S_{EC} is the increase in erosion rate due to corrosion and S_{CE} is the increase in corrosion rate due to erosion.

In many cases reported in the literature surface materials for combined erosive and corrosive conditions have been evaluated on the basis of separate erosion and corrosion studies, with the consequence that the synergistic effects are left out of the evaluation. Since one or both of these effects are frequently large the conclusions may be quite wrong. The S_{CE} contribution is particularly high for normally passive materials, since the sand erosion destroys the passive oxide layer (C is very low for these materials). S_{EC} is most pronounced for ceramic–metallic materials in which the metal phase has inferior corrosion resistance. This may be the case even if the

measured corrosion rate under erosive conditions makes up a small percentage of the total mass loss rate.

Studies of the relative importance of corrosion in sand erosion–corrosion systems have earlier been carried out on carbon and stainless steels [1–11] and on ceramic-metallic coatings [6–11]. Quantitative determination of erosion, corrosion and synergistic contributions are described in a few of these publications [1,2,6–11]. Monolithic ceramic-metallic materials exposed to sand erosion and corrosion conditions have been studied to a less extent by weight loss measurements [12].

Particularly high erosion corrosion rates and synergistic effects may occur when materials exposed to erosive and corrosive conditions are in galvanic contact with a corrosion resistant material not exposed to the erosive conditions. This may be the case in various applications, e.g. in the offshore industry, where an increased use of stainless steels is taking place. Therefore, the galvanic effects need to be studied more closely in combined erosion and corrosion experiments.

In the present work, some results are presented to illustrate the various contributions to the materials loss of a few selected thermal spray [TS] coatings and monolithic cermets, the extent of synergism, galvanic effects and the mechanisms of deterioration of cermets under erosive–corrosive conditions.

In most cases in the present work, corrosion rates have been measured under sand erosion conditions, i.e. the corrosion rate measured is $C_E = C + S_{CE}$. The quantities T , E and S_{EC} defined above have also been determined.

2. Experimental

2.1. Methods and Equipment

Most of the erosion corrosion experiments were carried out with equipment developed and described in former work [6,7] (see Fig. 1). In this, six cylindrical specimens were fixed to a rotating disk. The specimens were electrically insulated from the disk and from each other, with a conductor leading from each specimen to external instruments so that various electrochemical characteristics could be determined separately for each specimen. The disk was rotated in a slurry of silica sand of different concentrations.

Total mass loss rates T were determined by weighing the specimens before and after the experiments. Corrosion rates, C_E , were measured electrochemically during the exposure. Erosion rates, E , on the same specimens were determined from weight loss in separate experiments where corrosion was eliminated by cathodic protection.

The surface topography of some of the test specimens was studied by scanning electron microscopy [SEM].

2.2. Materials

The coatings and monolithic materials dealt with in this publication are listed in Table 1.

The three coatings were selected because they are frequently used and have quite different behaviours. The stainless steel was used as a reference. The two cermets are presented for comparison with the coatings because they show a similar

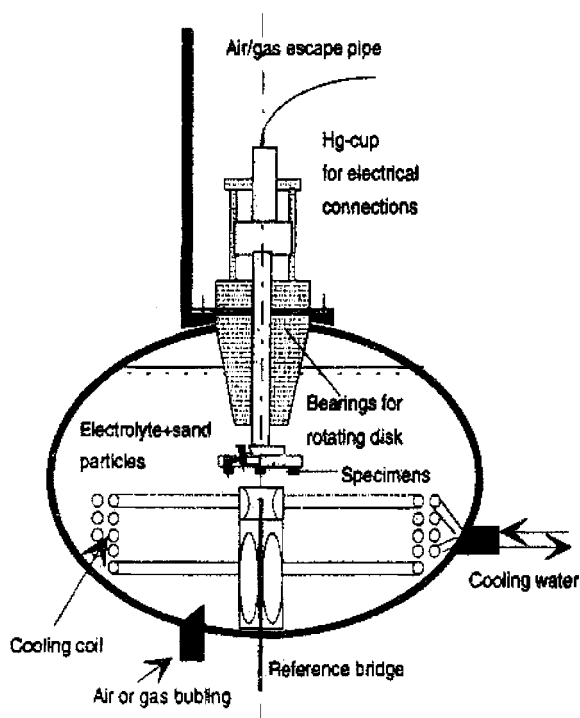


Fig. 1 Test equipment for sand erosion and corrosion studies.

Table 1.

Materials	Composition	Density gcm ⁻³
Coating 1	83 WC 17Co	13.7
Coating 2	86 WC 10Co4Cr	13.8
Coating 3	80 CrC20NiCr	6.8
Duplex stainless steel		
UNS S31803	22Cr5.5Ni3Mo bal Fe	7.8
Cermet 1	95 WC 5Co	15
Cermet 2	94.9 WC, 5.1 CoNiCrMo	15

dependence of erosion–corrosion on composition as the coatings. One of the cermets, Cermet 1, has a composition close to 94WC6Co which has been frequently used for choke valves in service while the other, Cermet 2, seems to represent a considerable improvement in many erosive–corrosive environments.

2.3. Environments

The coatings and duplex stainless steel specimens were exposed in synthetic sea water of 20°C with 2.5, 0.25 or 0 wt % silica sand of average grain size 230 μm . The liquid was usually saturated with air, in a few cases with CO_2 . Some tests were carried out with air saturated tap water slurries.

The monolithic cermets were exposed in a simulated oil well formation water at 54°C, saturated with CO_2 and with the same sand contents as given above.

3. Results and Discussion

3.1. Total Material Loss and the Contributions of Erosion, Corrosion and Synergy Effect

Results for the three coatings in as-sprayed condition and the duplex stainless steel are summarised in Table 2. The corrosion contributions were determined by LPR (Linear Polarisation Resistance) measurements at different times during the test period combined with determination of polarisation curves at the end of the exposure. Total weight loss (under free corrosion) and erosion contribution (under cathodic protection) were determined by weighing.

It is seen from the Table that the smallest weight loss is obtained with Coating 3 followed by Coating 2 at a sand concentration of 2.5% and stainless steel at 0.25% sand. Coating 1, with pure Co-binder gives the highest weight loss in both cases.

Table 2. Total material loss rate and the relative contribution of erosion, corrosion and synergy effects. Electrolyte: Synthetic sea water; air saturated; Velocity: 14.3 ms^{-1} ; Temperature: 20.0°C

Material Coating	Sand conc.	Total material loss mm/y	Erosion E		Corrosion C_E		Synergy effect S_{EC}	
			mm/y	%	mm/y	%	mm/y	%
Coating 1 83WC 17Co	0.25	5.292	0.836	16	1.905	36	2.551	48
	2.5	10.928	3.604	33	2.513	23	4.811	44
Coating 2 86WC 10Co 4Cr	0.25	1.225	0.831	66	0.201	16	0.223	18
	2.5	4.157	2.983	72	0.166	4	1.008	24
Coating 3 80CrC 20[CrNi]	0.25	0.855	0.888	104	0.051	6	-0.084	-10
	2.5	3.453	3.387	98	0.138	4	-0.072	-2
UNS S31803 22Cr 5Ni 3Mo BalFe	0.25	0.658	0.625	95	0.059	9	-0.026	-4
	2.5	8.611	8.455	98	0.172	2	-0.016	0

It is interesting to note that the weight loss due to pure erosion is quite similar in the three coatings. It is reported in the literature [13] that chromium may have a strong positive effect on the erosion resistance when alloyed with Co in such coatings. This is not in agreement with the small differences in pure erosion between Coatings 1 and 2.

With regard to corrosion, however, there is a great difference. Coating 1, with a pure Co-matrix, corrodes much more than the other materials, and this high corrosion rate leads to a strong synergy effect with this coating, as seen in the right hand column. Some synergy effect is also indicated for Coating 2, while it is not significant for Coating 3, which has the most corrosion resistant metal phase (NiCr) of the three coatings.

It should also be noticed that the corrosion percentages for Coating 1 (36 and 23%) are higher than the % of metal content (17%) in the coating. The result has some connection with the short exposure time (3 h) in the actual tests. In other tests with long exposure times [8,10] the steady state corrosion percentage was approximately 17 % in many cases, indicating that all the metal lost was removed by corrosion. At higher velocities the corrosion proportions were a few % lower due to a relatively higher effect of erosion.

The present results show that the high material loss rate of Coating 1 is caused by the inferior corrosion resistance of the Co-matrix. The effect is particularly large in aerated sea water (in this case, synthetic sea water). It is shown in Fig. 2 that synthetic

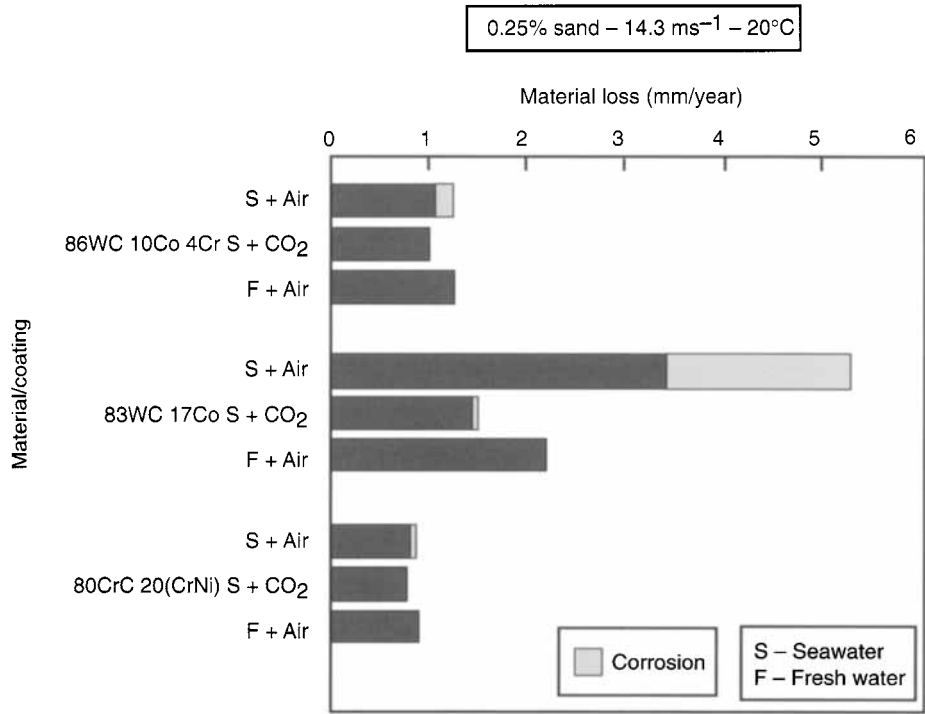


Fig. 2 Material loss rates of the three coatings exposed to different environments containing 0.25% sand particles.

sea water saturated with CO_2 as well as aerated tap water is considerably less aggressive to this coating. Coatings 2 and 3 are however better in this case also.

The qualities of the investigated coatings are not particularly good. Recent experiments have shown that it is possible to improve significantly the TS-coatings. The present results are however reasonably representative with regard to the relative importance of erosion, corrosion and synergy effects, and to the relative difference between the coatings.

An example of the contributions of erosion, corrosion and synergism to material loss on the two monolithic cemented carbides is shown in Fig. 3. A very large synergy effect is demonstrated for the material with pure Co-binder also in this case.

3.2. Electrochemical Characteristics

Polarisation curves for the Coatings 1 and 2 and the duplex stainless steel in a slurry with 0.25 % sand are shown in Fig. 4. The position of the curves for Coating 1 to the right in the diagram reflects the high corrosion rates of this coating.

Corresponding curves without sand in the water are given in Fig. 5. The positions of the curves for the coatings are not changed very much from Fig. 4, indicating that both coatings will corrode much as in cases with high flow rates of sea water without sand. The anodic curve of stainless steel in Fig. 5 is quite different from that in Fig. 4, showing a higher corrosion potential and very low corrosion rate in the case of flowing water without sand.

The polarisation curves may be used for judging the risk and extent of galvanic corrosion. If one of the coatings is surrounded by uncoated duplex stainless steel, and both the coating and the stainless steel are exposed to sand erosion in synthetic sea water, there will not be any noticeable galvanic corrosion, because the free corrosion potential of the stainless steel is approximately equal to or more negative than that of the two coatings (Fig. 4).

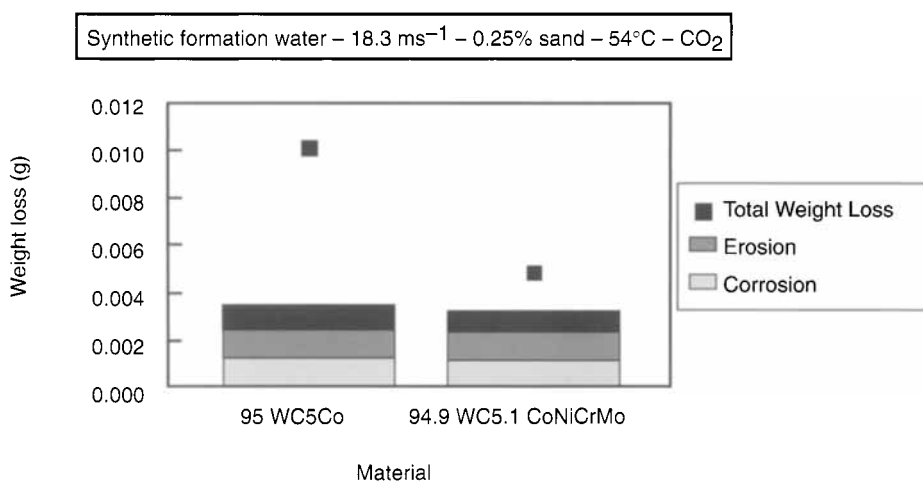


Fig. 3 Total weight loss and weight loss contributions due to pure erosion and electrochemically measured corrosion of materials 95WC5Co and 94.9WC5.1CoNiCrMo. Average of two specimens of each material.

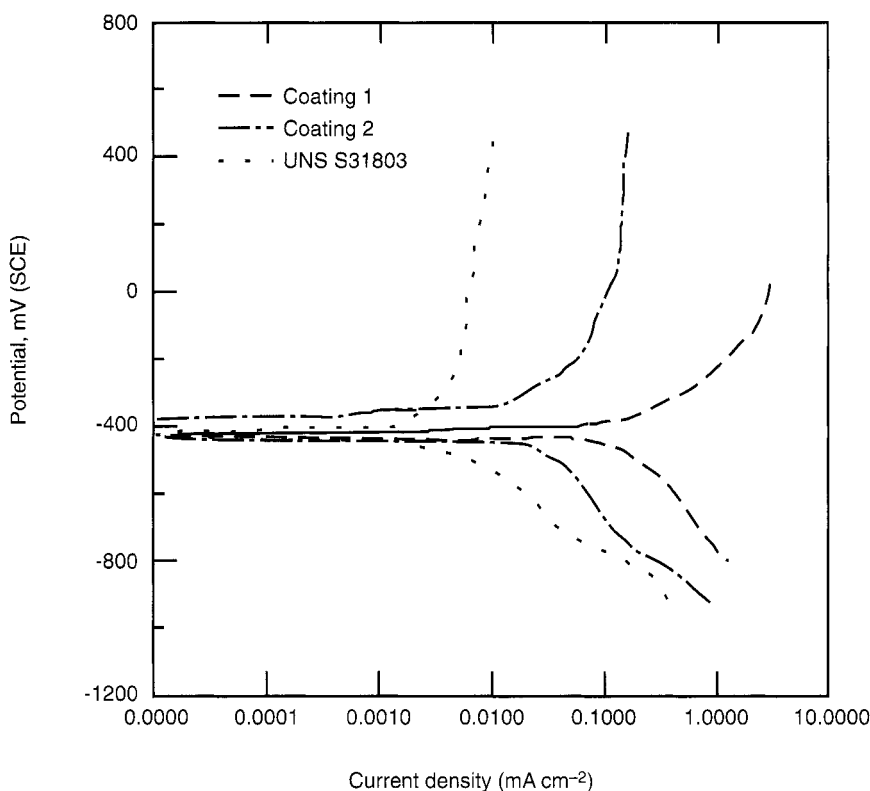


Fig. 4 Polarisation curves of Coatings 1 and 2 and duplex stainless steel UNS S31803 in air saturated synthetic sea water with 0.25% sand at a peripheral velocity of 14.3 ms^{-1} .

If there is no sand in the synthetic sea water, the corrosion potential of the duplex steel is about 400 mV higher than that of the coatings (Fig. 5). The cathodic efficiency on the stainless steel in this case is low. However, considering Coating 2 as an example, an evaluation of the polarisation curves indicates that there will be a noticeable and increasing rate of galvanic corrosion at increasing area ratio duplex steel/coating above 10:1. A similar result is obtained if sand particles attack the coatings but not the duplex steel. The reason is the very limited effect of sand on the polarisation curves of the coatings (compare Figs 4 and 5).

The conditions described above may or may not change if the synthetic sea water is replaced by natural sea water. The result depends on the conditions for developing biological slime layers on the stainless steel surface. If the flow velocity is moderate or low and there is no sand erosion of the stainless steel surface biofilms may develop and lead to a strong increase in the cathodic efficiency [14]. The cathodic current density on stainless steel will be of the order of 0.01 mA cm^{-2} or higher at a potential as high as +200 mV SCE. If the area ratio is unfavourable, then high rates of galvanic corrosion may be expected on the cermet coatings, with or without sand erosion of the coatings. The potential of the coatings may in extreme cases be lifted several hundred mV. It is seen from the polarisation curves in Figs 4 and 5 that the corrosion current densities on Coating 1 may be extremely high. Coating 2 is better, but even

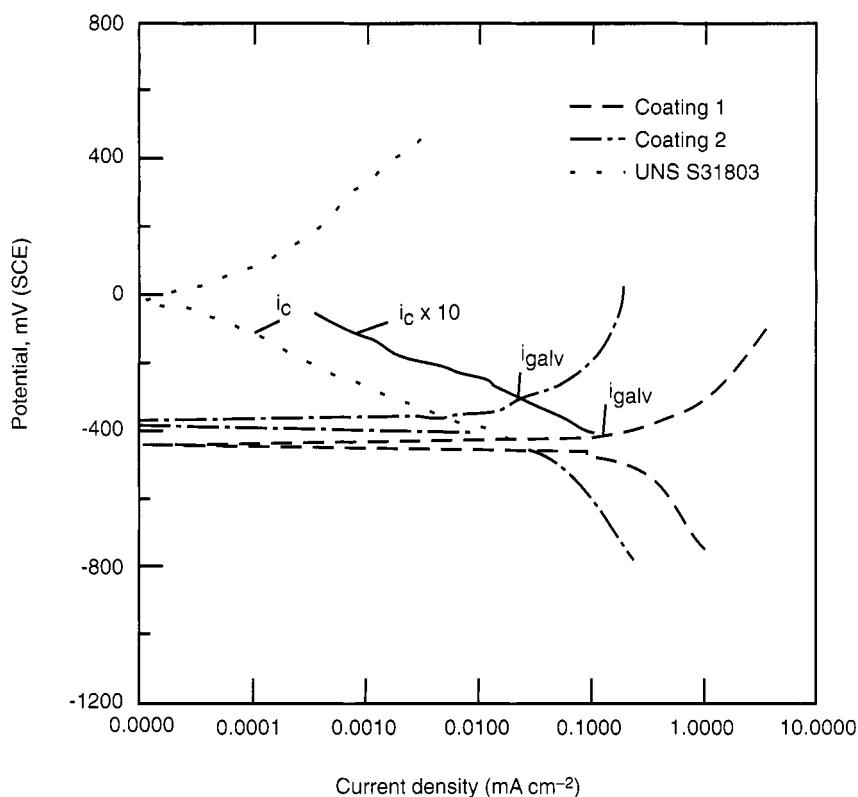


Fig. 5 As Fig. 4, but without sand. Constructed curve indicating galvanic corrosion current density at an area ratio of 10:1 between stainless steel and coating surface.

in this case the galvanic corrosion rate may be very high. The average corrosion current density over the entire coating surface area may be $0.1\text{--}0.2\text{ mA cm}^{-2}$ at $0\text{--}200\text{ mV}$. Taking into consideration that the metal content in the coating is only 14%, the corrosion rate of the matrix may be of the order of 5 mm/year or higher.

If the flow rate is high or the stainless steel surface is exposed to eroding particles, or the sea water is chlorinated [14] there will be no basis for biofilms to develop on the surface and the electrochemical conditions at the actual potentials will be similar to that described for synthetic sea water.

In water saturated with CO_2 the possibilities of galvanic corrosion on coatings surrounded by stainless steel is more limited than in chlorinated or synthetic sea water [15].

The above discussion indicates that under certain conditions, particularly with unfavourable area ratios and non-erosive conditions on adjacent stainless steels, it is important that the metal matrix of the coating should have a corrosion resistance at the same level as the stainless steel itself.

3.3. Microstructure and the Mechanism of Combined Erosion and Corrosion

Cross section SEM images of a coating with composition similar to Coating 1 (mainly

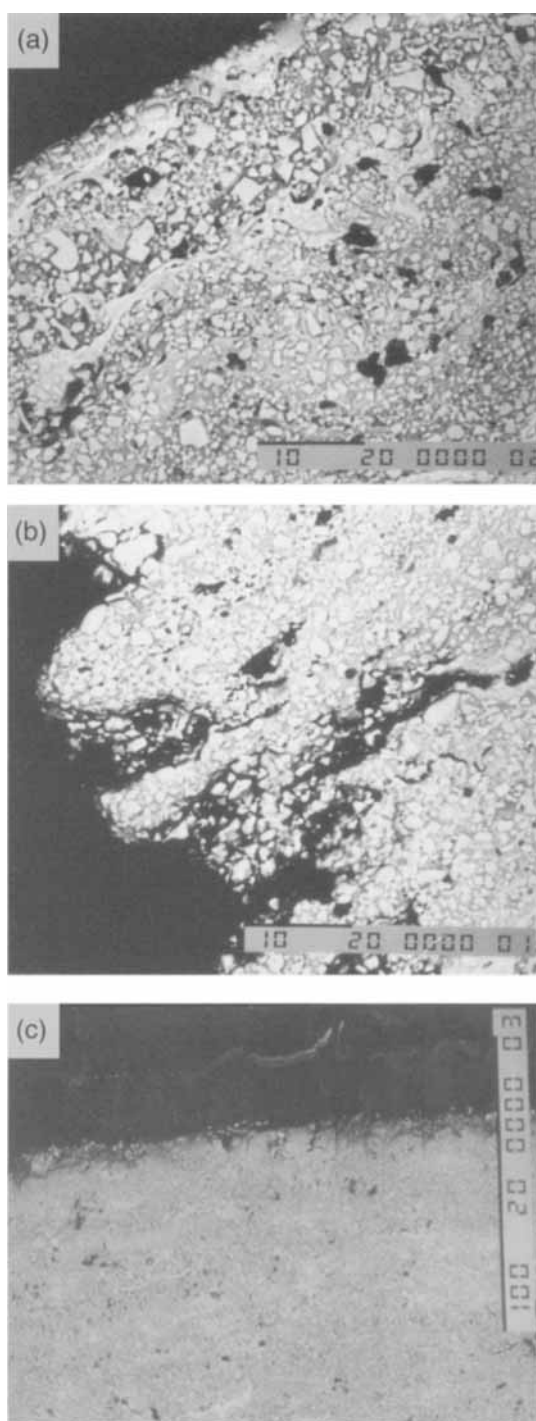


Fig. 6 SEM images of cross section showing surface profile of Coating 1 in (a) unexposed ground condition, and (b) and (c) in eroded-corroded condition.

Co in the matrix) are shown in Fig. 6 both in unexposed condition (a) and in the eroded–corroded condition (b and c). Figure 6(b) shows significant local attack, with the metal matrix partly removed to a considerable depth, leaving a very porous structure of carbide particles. This picture explains that the corrosion contribution to the weight loss after relatively short exposure time (e.g. 36%, see Table 2) is higher than the original metal content of the composite (e.g. 17%). After a long exposure time, however, a stationary state may be reached, where the corrosion contribution is approximately as large as the metal content. This has been demonstrated in several experiments. The marked corrosion attack between the carbide particles also explains the strong synergy effect, i.e. the increase in erosion rate due to corrosion (S_{EC}). Thus, carbide particles are easier to remove by the erosive forces after the actual corrosion.

The reported attack on the matrix of Co has been described as wear by Karimi *et al.* [13]. They interpret the positive effect of Cr as the result of improved binding between matrix and carbide. The present results indicate however that the attack is the result of corrosion and the effect of Cr is mainly to improve corrosion resistance (see Table 2).

Figure 7 (a and b) show corresponding SEM images for a coating with CoCr matrix (composition similar to Coating 2). In this case only small pits, with depths similar to the carbide particle diameters, can be seen on the eroded–corroded surface. The unexposed state (a) and the eroded–corroded state (b) can be illustrated as in Fig. 8. This case is typical when the metal matrix has only a moderate corrosion resistance and the composite is exposed to relatively low-erosive conditions. The corrosion properties are much better than for a pure cobalt matrix, but still the metal matrix is mainly removed by corrosion, as also indicated for Coating 2, 0.25% sand in Table 2. The table shows a corrosion contribution of 16%, while the nominal metal content of the coating is 14%. Therefore, the carbide particles are undermined more or less by corrosion also in this case, which explains the synergy effect given in Table 2. The extent of this is however less than for Coating 1.

The low direct effect of erosion on the metal matrix is easy to understand when the sand particle size is taken into consideration. The sand particles are two orders of magnitude larger than the carbide particles. Therefore the metal matrix is to a high extent shielded from erosion by the carbide particles. This also means that sand particles have relatively little effect on the electrochemical conditions on the metal surface between the carbide particles. This is demonstrated by the polarisation curves for the two coatings in Figs 4 and 5. There is only a small difference between the curves for 0.25% and 0% sand. The curves for the stainless steel show an extreme contrast to the coating curves. With sand in the water, the passivity of the steel is destroyed, and this is strongly reflected in the polarisation curves.

Considering the figures of Coating 3 in Table 2, the NiCr metal matrix seems to be considerably more corrosion resistant than the CoCr matrix in Coating 2. This gives little tendency for undermining the carbide particles and therefore no significant synergism of erosion and corrosion for Coating 3.

Regarding the monolithic WC-materials represented in Fig. 3, the least resistant of these responds to erosion and corrosion in the same way as Coating 1, while the most resistant material behaves more like Coating 2.

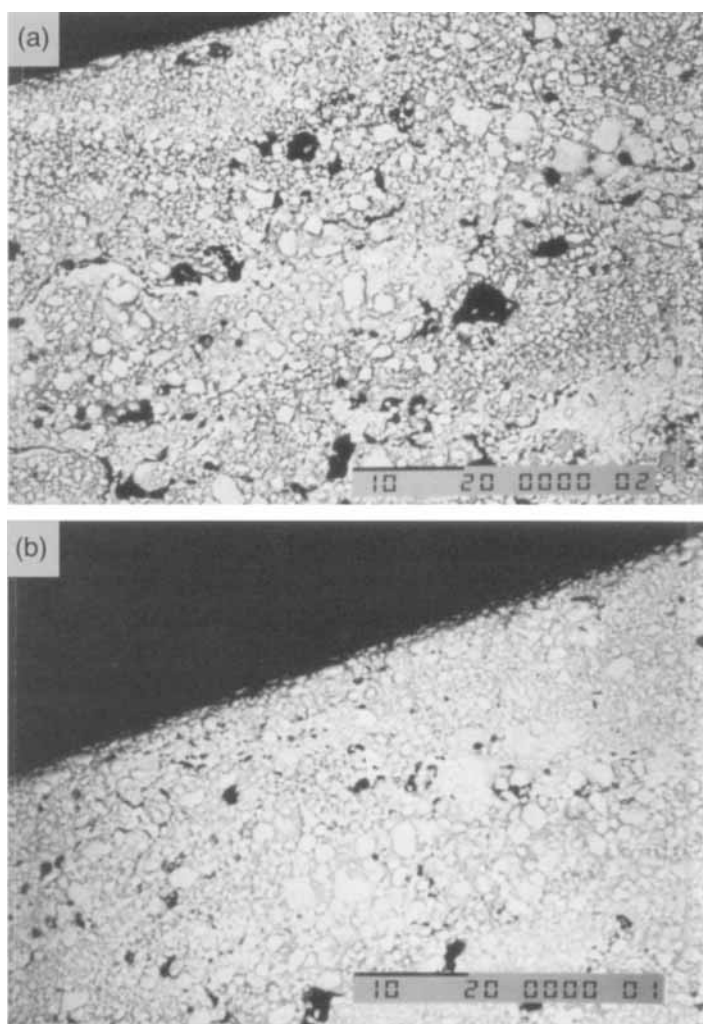


Fig. 7 As in Fig. 6 for Coating 2. (a) Unexposed and (b) eroded–corroded.

4. Conclusions

Erosion–corrosion in aerated silica sand slurries has been studied on three HVOF thermal spray coatings: 83WC17Co (Coating 1), 86WC10Co4Cr (Coating 2) and 80CrC20NiCr (Coating 3) and compared with the behaviour of a duplex stainless steel.

The weight loss due to pure erosion was similar for the three coatings but the corrosion contribution and the synergistic weight loss decreased in the following order: Coating 1-2-3 (no significant synergism for Coating 3). The main effect of Cr added to Co-matrix was to improve the corrosion resistance.

Under relatively low-erosive conditions all the metal lost from Coatings 1 and 2 was removed by corrosion. Under steady state conditions the corrosion contribution

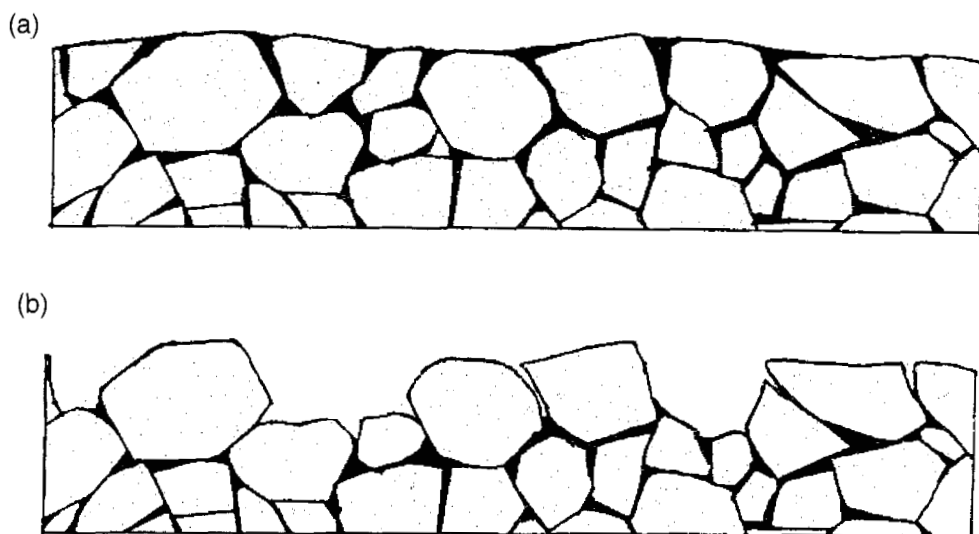


Fig. 8 Schematic view of cemented carbide (a) before testing and (b) after exposure under corrosive and low-erosive conditions.

approached the nominal metal content of these two coatings. In short duration tests the percentage of weight loss due to corrosion of Coating 1 was higher than the nominal metal content. The reason for this is that local corrosion extended many carbide particle diameters into the coating. The corrosion attack of the metal matrix for the Coatings 1 and 2 undermined the carbide particles and this explains the synergistic effect S_{EC} .

When a carbide–metal coating is in galvanic contact with a stainless steel, high rates of galvanic corrosion may occur under certain conditions, i.e. unfavourable area ratios and non erosive conditions on the stainless steel surface. There is a decreasing tendency to galvanic corrosion in the following order of environments: air saturated natural sea water — air saturated synthetic or chlorinated sea water — synthetic sea water or oil well formation water saturated with CO_2 . Under unfavourable conditions the metal matrix of the coating should have a corrosion resistance approaching that of the stainless steel.

Sand particles in the water have only a small effect on the electrochemical conditions and the corrosion rate of Coatings 1 and 2, in strong contrast to the effects on stainless steel surfaces.

The effects of matrix composition and the mechanisms of deterioration of monolithic cermets is similar to that described for the carbide–metal coatings.

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Electrochemical Behaviour of (Ti,Cr) N Coatings Obtained by Reactive Sputtering

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ABSTRACT

Titanium nitride is a compound that finds wide use because of its interesting mechanical and optical properties as well as its very good corrosion resistance.

The aim of this work is the study of the corrosion resistance properties, in acidic and neutral solution, of some (Ti,Cr) N_x films deposited by reactive cathodic sputtering. Chromium was chosen because of its aptitude to produce passive oxide layers with excellent protective properties and is used in the production of stainless steels.

Coating films were deposited on an inert glass substrate and on an AISI 304 stainless steel under optimised sputtering conditions.

Chromium appears to be beneficial as far as the corrosion resistance of titanium nitride is concerned, in particular when the chromium content is more than 14%.

Nitride coatings are also able to improve the corrosion resistance of AISI 304 stainless steel in sulfuric acid solutions more than in hydrochloric acid.

The preparation of bilayer coatings allows a further increase of the protection properties of these nitrides to be achieved and, in particular, in the resistance to localised attack.

1. Introduction

Titanium nitride is a compound that finds wide use because of its interesting mechanical and optical properties as well as its very good corrosion resistance. A large number of papers have been devoted to this subject for example [1–5]. Some reports are concerned with the properties of nitrides containing two different metals such as (Ti,Al) N_x , (Ti,Cr) N_x , (Ti,Zr) N_x and (Ti,Nb) N_x . Thus, Andrievski *et al.* [6] have studied the structure and microhardness of these films, produced by the arc deposition method, as opposed to magnetron sputtered coatings. Penttinen *et al.* [7], comparing the corrosion resistance of TiN and (Ti,Al)N coatings deposited onto stainless steel (AISI 316), have shown that the best corrosion resistance was obtained when there was a thin chromium-rich layer at the substrate–coating interface. Jenh *et al.* [8] have studied (Ti,Cr) N_x films reactively deposited on stainless steel (AISI 304) but only in a neutral pH solution or in a weakly acidic solution (Na_2SO_4 and NaCl). These authors have shown that corrosion behaviour is improved by the addition of chromium, i.e. compared with the TiN coating. Wirz *et al.* have studied the properties of films prepared by thermal coevaporation of Cr and Ti in nitrogen and this study indicates that the chemical resistance and electrical conductivity of TiN films can be improved by chromium addition without degradation of tribological performances [9].

The aim of the present work is the study of the corrosion resistance properties, in acidic and neutral solution, of some (Ti,Cr) N_x films deposited by reactive cathodic sputtering. Chromium was chosen because of its ability to produce passive oxide layers with excellent protective properties as is well known in the case of stainless steels. Hence, to evaluate the effectiveness of the produced coatings the intrinsic electrochemical properties of the deposit need to be known, i.e. without any galvanic coupling with a metal substrate. Consequently, in the first part of this work the coating films were deposited on an inert glass substrate. In order to obtain a bimetallic nitride with the best corrosion behaviour, the study was conducted with different (Ti,Cr) N_x compounds that were obtained by changing the nitrogen pressure in the deposition chamber and the amount of chromium.

In the second part of the experimental work the nitride films were deposited as protective coatings on an AISI 304 stainless steel under optimised sputtering conditions.

2. Experimental

2.1. Film Preparation

To produce bimetallic compounds, a circular target was divided in two halves (one titanium and one chromium). A moving mask, left at a floating potential, allowed part of the target to be hidden so as to expose different surface ratios of the two metals. The coatings deposited on glass had a thickness of about 150 nm, whereas those obtained on stainless steel had a thickness in the range of 600–800 nm. The different films obtained on glass were produced under the experimental conditions shown in Table 1, whereas those obtained on stainless steel were obtained using a nitrogen partial pressure of 4.5×10^{-5} torr and a chromium percentage area in the cathode of 28. Finally bilayer coatings were produced with a deposition of a first layer, 200 nm thick, of titanium.

2.2. Microstructural Characterisation

To determine the Ti/Cr ratio in the various coatings, the samples were dissolved in an HCl-HNO₃ mixture and the concentration of the elements was determined by Direct Current Plasma (DCP) analysis using an ARL[®] plasma spectrophotometer.

The X-ray diffraction (XRD) tests were carried out using a SIEMENS D5000 diffractometer. The measurements were obtained using the Cu K α wavelength with an incidence angle of 0.5°. DIFFRACT AT software was used to characterise the crystallised phases existing in the various samples.

2.3. Electrochemical Experiments

Electrochemical experiments were conducted in aerated 0.5M H₂SO₄, 0.1M HCl and 0.1M NaCl solutions. The potentials were recorded with respect to a saturated sulfate electrode (SSE) in sulfuric acid solutions and with respect to calomel electrode (SCE) in chloride containing solutions; a gold sheet was used as the counter electrode. In

Table 1. Coatings deposited on glass

Dissolution time*	% Cr [†]	% Cr**	p_{N_2} (torr)	X-ray results
13 min	8	14	4×10^{-5}	TiN pattern
8 min	3	14	6×10^{-5}	TiN overstoichiometric
30 min	24	28	4.5×10^{-5}	traces of crystallised TiN
14 min	25	28	6.7×10^{-5}	crystallised TiN
5 h	51	55	5.4×10^{-5}	diffraction peaks between the diffraction pattern of TiN and CrN
40 min	46	55	8.2×10^{-5}	microcrystallised CrN

* Dissolution time in HCl-HNO₃ mixture.

† Data obtained by DCP analysis after coating dissolution in HCl-HNO₃ mixture.

** Chromium percentage area of the cathode.

the acid solutions, polarisation curves were obtained at a 0.5 mV s^{-1} scanning rate starting from a cathodic potential; curves obtained in the NaCl solution were obtained at 0.2 or 0.01 mV s^{-1} .

After one hour of immersion at the free corrosion potential, electrochemical impedance spectroscopy (EIS) measurements were carried out in the $100 \text{ kHz} - 10 \text{ mHz}$ frequency range using a 10 mV sinusoidal signal.

The impedance diagrams were interpreted on the basis of equivalent electrical circuits using Boukamp software [10] for the fitting of the experimental data.

3. Results and Discussion

3.1. XRD Characterisation

The diffraction peaks of the sample obtained using the titanium cathode correspond to the TiN phase; a small shift of the peaks towards the lower angles indicates that the coating is slightly nitrogen overstoichiometric. None of the diffraction patterns relating to the bimetallic nitrides correspond to the Cr₂N phase. The experimental peaks of bimetallic nitrides are situated between the typical diffraction angles of the f.c.c. structure of TiN and CrN [11].

It is important to point out that, using a high nitrogen pressure, in the bimetallic nitrides with the highest chromium amount (55% Cr) only the CrN phase can be detected by X-ray diffraction. Moreover, the higher the chromium percentage in the coating, the more the film microstructure becomes poorly crystallised.

From the last column of Table 1 it is possible to see that when the chromium content is higher than 14% the samples obtained under high nitrogen pressure show

a better crystallised structure with respect to the samples obtained under low nitrogen pressure.

In the case of coatings obtained on AISI 304 stainless steel ($p_{N_2} = 4.5 \times 10^{-5}$ torr, %Cr = 28) the diffraction patterns indicate the presence of a microcrystalline TiN structure.

3.2. Electrochemical Tests on Glass

The results of both d.c. and a.c. electrochemical tests obtained in sulphuric acid solution are shown in Table 2. The electrochemical impedance data were interpreted using a simplified R [RQ] equivalent electrical circuit. Figs 1 and 2 are representative of these results.

As shown by the very high values of the measured resistance component (in the order of $M\Omega \text{ cm}^2$) the electrochemical behaviour of the coating in the potential range of E_{corr} is mainly capacitive.

Moreover, the measured values of Rt independently of the testing solution (hydrochloric or sulfuric acid) indicate that the corrosion resistance in free immersion increases as the chromium content in the film increases. When the chromium content in the film is more than 14%, it is possible to observe in the polarisation curves, obtained both in hydrochloric or sulfuric acid, a transpassivation phenomenon which occurs around 900 mV (SCE) in HCl and around 500 mV (SSE) in H_2SO_4 solution. As proposed by Armstrong [12] in such a situation chromium can pass into the solution as chromate. On the contrary, the polarisation curves of samples having a chromium amount less than 14% appear to be very similar to that of TiN only coating.

In the potential range between E_{corr} and the transpassivation potential all the samples containing chromium show anodic currents, which are systematically lower than that of TiN samples; moreover, these anodic currents, appear to be lower as the

Table 2. Electrochemical parameters of various coatings deposited on glass

Samples Cr%, p_{N_2}	$E (i = 0)$ mV (SSE)	E_{corr} mV (SSE)	i_{corr} $\mu A \text{ cm}^{-2}$	Q $\mu F \text{ cm}^{-2}$	n (CPE factor)	Rt $\Omega \text{ cm}^2$
TiN 0%, 6×10^{-5}	-212	-171	0.19	85	0.93	0.57×10^6
(Ti. Cr)N 14%, 4×10^{-5}	-284	-218	0.09	92.5	0.93	0.91×10^6
(Ti. Cr)N 14%, 6×10^{-5}	-206	-146	0.11	74.4	0.95	1.15×10^6
(Ti. Cr)N 28%, 4.5×10^{-5}	-332	-243	0.02	66.3	0.93	$>> 1 \times 10^9$
(Ti. Cr)N 28%, 6.8×10^{-5}	-420	-265	0.02	78	0.93	$> 6 \times 10^6$
(Ti. Cr)N 55%, 5.4×10^{-5}	-316	-211	0.03	71	0.92	$>> 1 \times 10^9$
(Ti. Cr)N 55%, 8.2×10^{-5}	-282	-223	0.015	65.6	0.91	$> 6 \times 10^6$

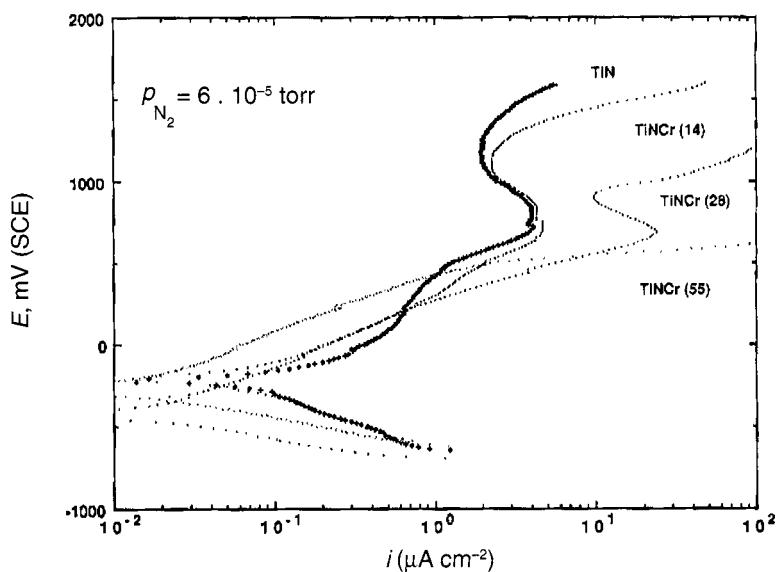


Fig. 1 Polarisation curves of nitride coatings deposited on glass obtained in a sulfuric acid solution.

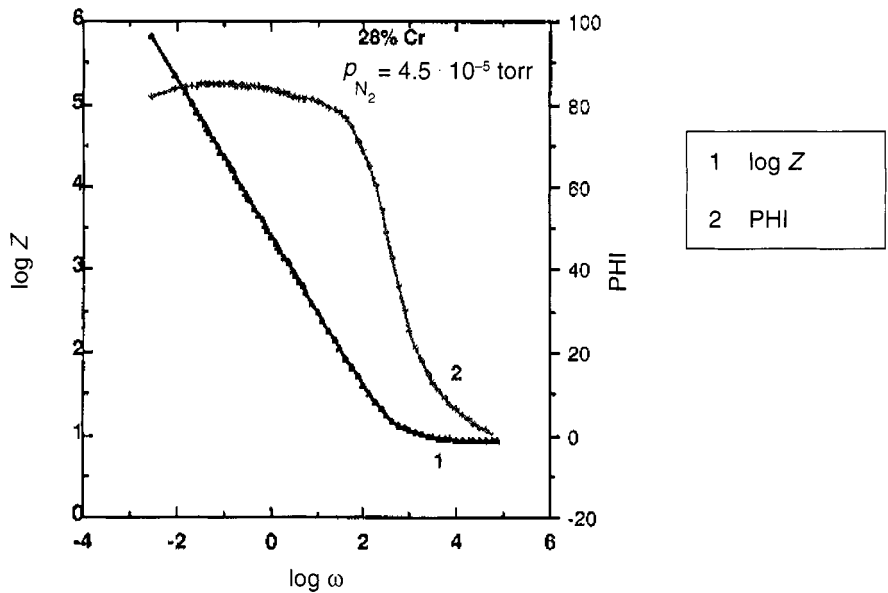


Fig. 2 Impedance diagram of a nitride coating obtained in a sulfuric acid solution.

chromium content increases in the film. When the potential passes above the transpassivation potential, the samples having 28% or 55% chromium show a remarkable increase of the anodic current.

The results obtained using d.c. and a.c. electrochemical methods are in agreement and indicate that the presence of chromium increase the corrosion resistance of the processed films. On the other hand, changes in the nitrogen partial pressure do not seem to be able to modify noticeably the polarisation curves.

Hence, this study carried out on inert substrate has shown that bimetallic nitrides can be proposed for producing protective coatings which can be more effective than traditional TiN coatings.

3.3. Electrochemical Tests on AISI 304

In Table 3 are shown the results of polarisation curves and electrochemical impedance tests conducted using nitride coatings on stainless steel substrates. The behaviour of coated samples appears to be better than that of the substrate material in both the environments used. Moreover, in the less aggressive sulfuric acid solution it is possible to point to a better performance of the bimetallic nitride with respect to the titanium nitride. These considerations are suggested by the values of the corrosion current as extrapolated from the polarisation curves and from the values of Rt obtained by a suitable fitting of the impedance data as proposed before.

The good behaviour of the coated samples was further improved by using bilayer coatings consisting of a first layer of titanium (*ca.* 200 nm) followed by the titanium nitride or bimetallic nitride layer.

In order to obtain detailed information concerning the resistance to localised attack, all the differently coated samples were submitted to a polarisation test in a 0.1M NaCl solution using a 0.2 mVs⁻¹ potential scan rate.

Apart from the TiN sample, the presence of the nitride coating greatly improved the behaviour of the metal substrate raising the breakdown potential to the higher

Table 3. *electrochemical parameters of samples deposited on AISI 304 stainless steel*

Samples Cr %; p_{N_2}	Solution	$E(i = 0)$ mV	E_{corr} mV	i_{corr} $\mu A\ cm^{-2}$	Rt $\Omega\ cm^2$	Q $\mu F\ cm^{-2}$	n
304 L	HCl	-336 (SCE)	-385	15	811	186.5	0.9
(Ti. Cr)N/304L 28%; 4.5×10^{-5}	HCl	-301 (SCE)	-336	4	9594	62.5	0.96
TiN/304L	H ₂ SO ₄	-265 (SSE)	-279	0.1	130 000	90	0.92
304 L	H ₂ SO ₄	-447 (SSE)	-395	0.80	108 000	83.5	0.88
(Ti. Cr)N/304L 28%; 4.5×10^{-5}	H ₂ SO ₄	-2 (SSE)	127	0.05	174 000	38.4	0.94

values shown in Fig. 3. In the same Figure it is possible to observe the better behaviour of the nitride coatings containing chromium which appear to be able to enlarge the passive potential range. The presence of the titanium underlayer further increases the resistance to localised attack of the metal substrate as shown by the very high values of the breakdown potential. The effect of the titanium underlayer can be explained by considering that such a layer can favour the growth of a less defective nitride coating. These results were also confirmed by polarisation curves obtained using a very low potential scan rate (0.01 mV s^{-1}).

4. Conclusions

The study of $(\text{Ti}, \text{Cr})\text{N}_x$ films containing different amounts of chromium deposited by reactive cathodic sputtering on a glass substrate allowed the intrinsic electrochemical properties of such nitride layers to be determined.

The X-ray diffraction characterisation of the bimetallic nitrides showed the presence of an f.c.c. structure with diffraction peaks situated between those of the TiN and CrN phases. As the amount of chromium increased these peaks shifted towards the CrN peaks and a more and more microcrystalline structure appeared, this also being favoured by the increase in the nitrogen partial pressure.

Chromium appears to be beneficial as far as the corrosion resistance of titanium nitride is concerned and, in particular, when the chromium content is more than 14%.

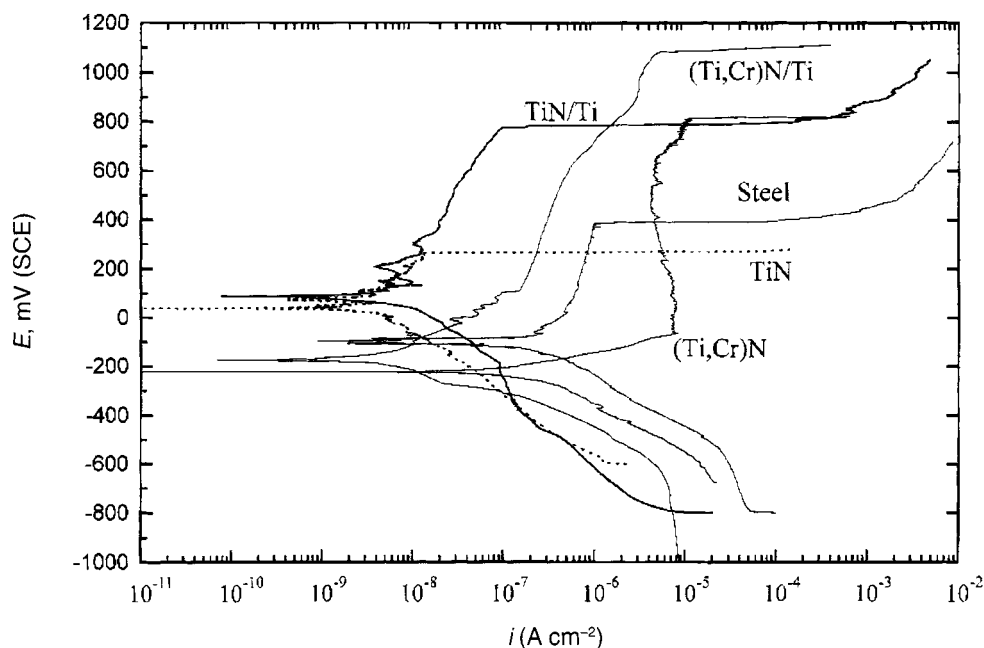


Fig. 3 Polarisation curves of nitride coatings deposited on AISI 304 stainless steel obtained in a sodium chloride solution.

Nitride coatings are also able to improve the corrosion resistance of AISI 304 stainless steel in sulfuric acid solutions more than in hydrochloric acid.

The preparation of bilayer coatings allowed a further increase of the protection properties of these nitrides to be obtained particularly in respect to localised attack.

5. Acknowledgement

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Formation of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ Double Oxide Thin Films and Evaluation of their Corrosion Resistance

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ABSTRACT

In order to obtain double oxide films with corrosion resistance against both HCl and NaOH solutions, $\text{Al}_2\text{O}_3\text{-ZrO}_2$ films were formed on Pt, Si and Al substrates by low pressure MOCVD techniques using $\text{Al}(\text{O-}i\text{-C}_3\text{H}_7)_2$ and $\text{Zr}(\text{O-}i\text{-C}_3\text{H}_7)_2$ as source gases and O_2 as reaction gas. The films obtained were composed of double oxide with uniform in-depth composition. The changes in the corrosion resistance of the films were investigated as a function of film composition. The corrosion resistance of the films in 1M HCl and 1.0M NaOH increased with increasing cationic fraction of Zr, X_{Zr} , in the films. The films with X_{Zr} values larger than 0.62 hardly dissolved in both solutions. The double oxide coatings with such X_{Zr} values showed good protection of an Al substrate in 1.0M HCl. The coatings, however, showed poor protection in 1.0M NaOH. The two layer coating of the double oxide film gave relatively good protection in the NaOH solution.

1. Introduction

Artificial passivation films, which reproduce the composition and thickness of real passive films on corrosion-resistant alloys, are useful experimental materials for studying the corrosion and electrochemical nature of passive films which cannot be separated from alloy matrices. For example, passive films on stainless steels have been simulated by $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-NiO}$ films [1-3] and corrosion resistances of these films have been examined as a function of composition.

It is of importance to examine the corrosion characteristics of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ double oxide films because these films are presumed to have high corrosion resistance against both acid and alkali solutions. Al_2O_3 [4] and ZrO_2 [5] films formed by metallorganic chemical vapor deposition (MOCVD) using aluminum-tri-*isopropoxide* ($\text{Al}(\text{O-}i\text{-C}_3\text{H}_7)_3$) and zirconium-tetra-*isopropoxide* ($\text{Zr}(\text{O-}i\text{-C}_3\text{H}_7)_4$) as precursors have been reported to have good corrosion resistance in HCl and NaOH solutions, respectively. If $\text{Al}_2\text{O}_3\text{-ZrO}_2$ double oxide films can be obtained, they would be expected to provide superior protective coatings which could be used over a wide pH range.

An $\text{Al}_2\text{O}_3\text{-ZrO}_2$ double oxide film is also interesting from a scientific point of view because it simulates an imaginary homogeneous passive film on an Al-Zr alloy. Since Al-Zr bulk alloys usually have heterogeneous multiphase structures it is difficult to

obtain homogeneous passive films and to elucidate the nature of the passive film as a function of composition. It may be possible to achieve this by using the double oxide film.

The purpose of the present investigation is to synthesise such double oxide films by the MOCVD technique and to examine the corrosion characteristics as a function of film composition in both acid and alkali solutions. The protective capacity of these films as a coating on an Al substrate was also examined in these solutions.

2. Experimental

2.1. Synthesis of Al_2O_3 – ZrO_2 Double Oxide Films

Al_2O_3 – ZrO_2 films were synthesised by MOCVD technique. $\text{Al}(\text{O}-i\text{-C}_3\text{H}_7)_3$ (99.999 mass%, High-Purity Chemicals Laboratory) and $\text{Zr}(\text{O}-i\text{-C}_3\text{H}_7)_4$ (98 mass%, High-Purity Chemicals Laboratory) were used as vapor sources and heated at 373 K and 433 K respectively. N_2 (99.999 vol%) was used as a carrier gas. The total flow rate of carrier gases for each vapor source was kept constant at a value of $6.7 \times 10^{-6} \text{ m}^3\text{s}^{-1}$. O_2 (>99.99 vol%) was used as a reaction gas and mixed with the source gases just before the introduction into a CVD cell. The flow rate of O_2 was kept constant at a value of $5.0 \times 10^{-6} \text{ m}^3\text{s}^{-1}$. The formation of double oxides films was carried out at a substrate temperature of 623 K.

A polycrystalline Pt plate and a single crystal Si (100) plate (each $25 \times 15 \times 0.5$ mm) were used as substrates. The surface of the Pt plate was finished with 1 μm -diamond paste and degreased ultrasonically in acetone. Surface oxide films on the Si (100) were removed by dipping in 2 mass% HF at 298K just before the experiment. KBr disks were used as substrates for films to be examined by transmission electron microscopy and electron diffraction. Al plates ($25 \times 15 \times 1$ mm) were used as the substrate for coatings of the double oxide films. The Al plates were chemically polished in a H_3PO_4 – HNO_3 solution (H_3PO_4 : HNO_3 : H_2O = 60:30:10 in vol.%).

Figure 1 shows schematically the MOCVD system. Each source was heated in an evaporator kept at a constant temperature. Source gases, which were carried by the carrier gas, were mixed with O_2 in a pipeline and then introduced into a CVD cell. The total pressure of the CVD cell was kept at 2.0 kPa. The substrate was attached to a holder with a heater. A cover with three small slits was set on the substrate to obtain homogeneous gas flow. The composition of the films was controlled by the flow rate of the carrier gas. The thickness of the films was adjusted to *ca.* 90 nm by controlling the deposition time.

2.2. Ellipsometry

The thickness and optical constants of the films were determined by ellipsometry. Figure 2 shows the rotating analyser type automatic ellipsometer that was used. This ellipsometer had the conventional polariser-compensator-specimen-analyser configuration. Monochromatic light of wavelength 546.1 nm was used for the measurements with an angle of incidence of 60° . The polariser was fixed at an angle of 45° . The analyser was rotated at an angular velocity of 360°s^{-1} . The intensity of

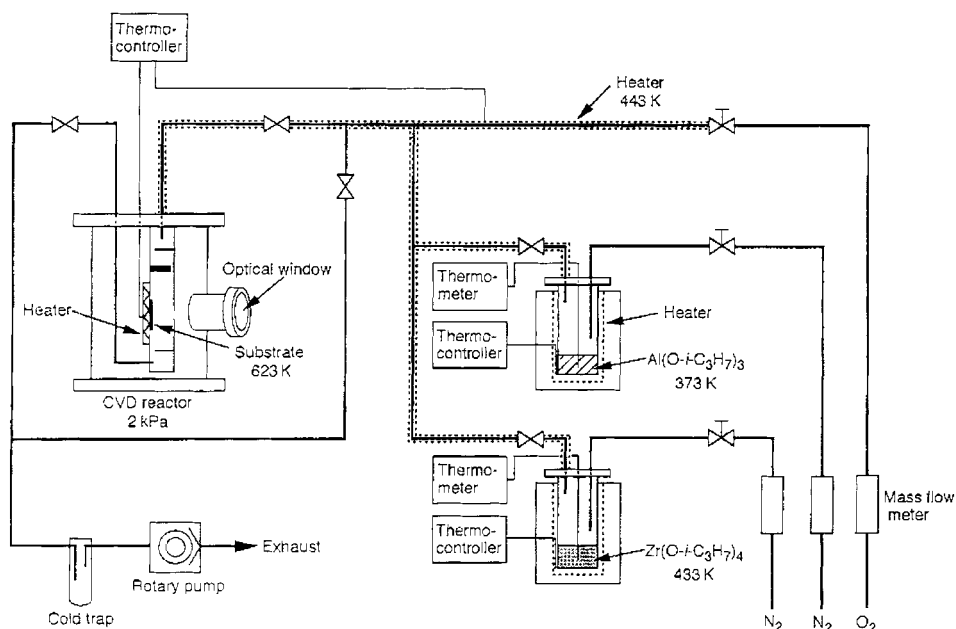


Fig. 1 Apparatus for MOCVD.

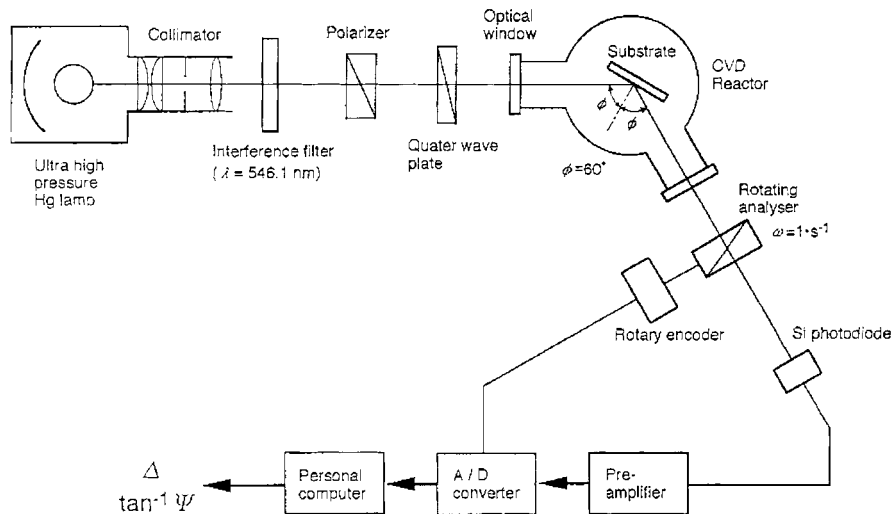


Fig. 2 Optical configuration of ellipsometer.

light through the analyser was measured by a photodiode and recorded with a computer as a function of rotation angle.

The quantity measured by an ellipsometer is the ratio ρ of the complex-amplitude reflection coefficient R_p and R_s for the p - and s -polarisation, respectively, given by the equation [6]:

$$\rho = R_p \cdot R_s^{-1} = \tan \Psi \exp(i\Delta) \quad (1)$$

where Δ is the relative phase retardation and Ψ is the arc tangent of the relative amplitude reduction. The thickness and optical constants of deposited films were determined using theoretical Δ vs Ψ curves which fit the experimental ellipsometric data (Δ, Ψ) with minimal error. Theoretical Δ vs Ψ curves were calculated using Drude's exact optical equations developed from eqn (1).

2.3. ICPS Analysis

The chemical composition of the double oxide films was determined by chemical analysis: films were dissolved in 10 mL of 98 mass% H_2SO_4 at 473 K and the solution was diluted to 2.5 mL by adding distilled water. This diluted solution was analysed by inductively coupled plasma-emission spectroscopy (ICPS), which gave the content of Al and Zr in the films, W_{Al} and W_{Zr} . The cationic mass fractions of Al and Zr, X_{Al} and X_{Zr} , of the films were calculated from W_{Al} and W_{Zr} , for example, $X_{\text{Zr}} = W_{\text{Zr}} / (W_{\text{Al}} + W_{\text{Zr}})^{-1}$; $X_{\text{Al}} + X_{\text{Zr}} = 1$.

2.4. AES Analysis

In-depth composition profiles of Al_2O_3 – ZrO_2 films were obtained by Auger electron spectroscopy (AES) in combination with Ar ion sputtering. The Si (100) was used as substrates for double oxide films of *ca.* 70 nm thickness. The measurement of the spectra was carried out under a pressure of 4×10^{-7} Pa. The applied voltage for the acceleration of primary electrons was 3 keV and the current was 0.5 μA .

2.5. TEM Observation

Micro- and crystal structures were examined by transmission electron microscopy (TEM) and electron diffraction (ED), respectively. Double oxide films of *ca.* 150 nm thickness were deposited on KBr discs and then the discs were dissolved in distilled water to separate the films. The separated films were picked up on a Cu grid (180 mesh) for subsequent observation.

2.6. Corrosion Test

The corrosion resistance of Al_2O_3 – ZrO_2 films was tested in 1.0M HCl and 1.0M NaOH at 298 K. The films formed on Pt substrates were used for this test. The thickness of the films was adjusted to *ca.* 90 nm. The decrease in film thickness was measured by ellipsometry after the corrosion test in each solution. The corrosion behaviour of Al specimens coated with the double oxide films was also examined in 1.0M HCl and 1.0M NaOH at 298 K. The specimen was mounted in a plastic holder and sealed by a Viton O-ring except for an exposed area of $7.85 \times 10^{-6} \text{m}^2$. The mass loss of the specimen with time was measured in each solution.

3. Results

3.1. Film Formation Process

Figure 3 shows experimental and calculated $\Delta\text{-}\Psi$ loci in the formation process of films with various X_{Zr} values. Good agreement can be seen between the experimental and the calculated locus. With increasing X_{Zr} values, the real part of the optical constant N_2 increases. The imaginary part of N_2 , however, remains at zero, which means that every film formed was transparent. The thickness of films can be checked by monitoring such a $\Delta\text{-}\Psi$ locus.

3.2. In-depth Composition Profile

Figure 4 shows an AES composition profile for a film with $X_{\text{Zr}} = 0.15$, which was formed at 623 K. The ratio of Zr to Al was approximately constant except for the interface region between the film and the substrate. The same composition profiles were obtained for other films of different X_{Zr} values. Therefore, the composition of the films formed by the MOCVD process was thought to be homogeneous.

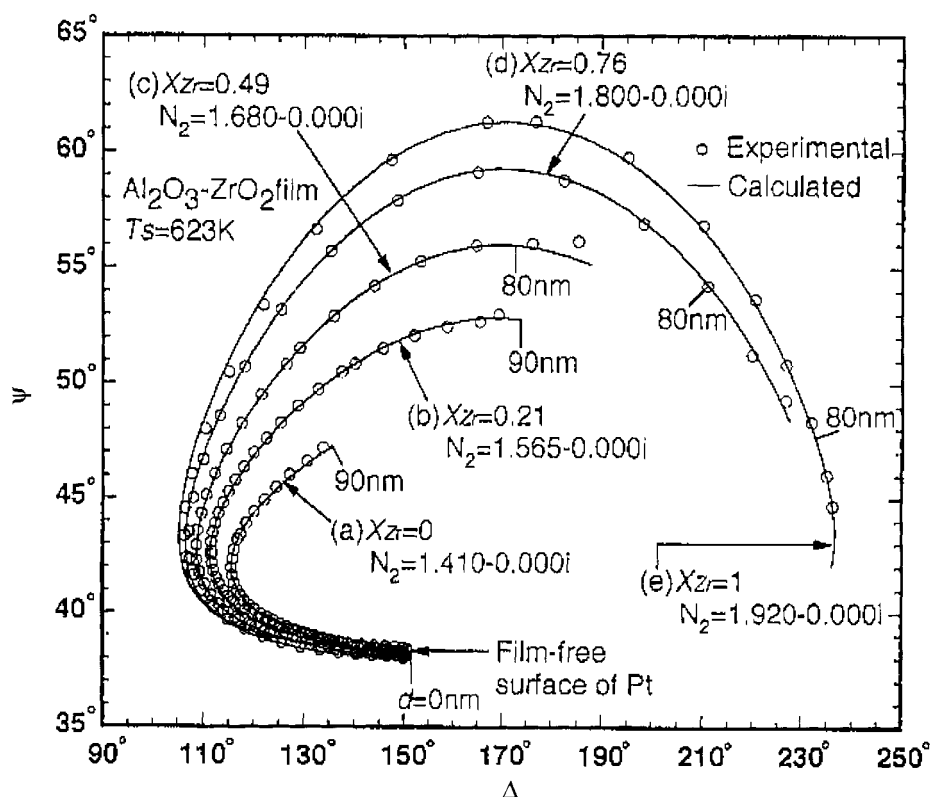


Fig. 3 $\Delta\text{-}\Psi$ loci for film formation.

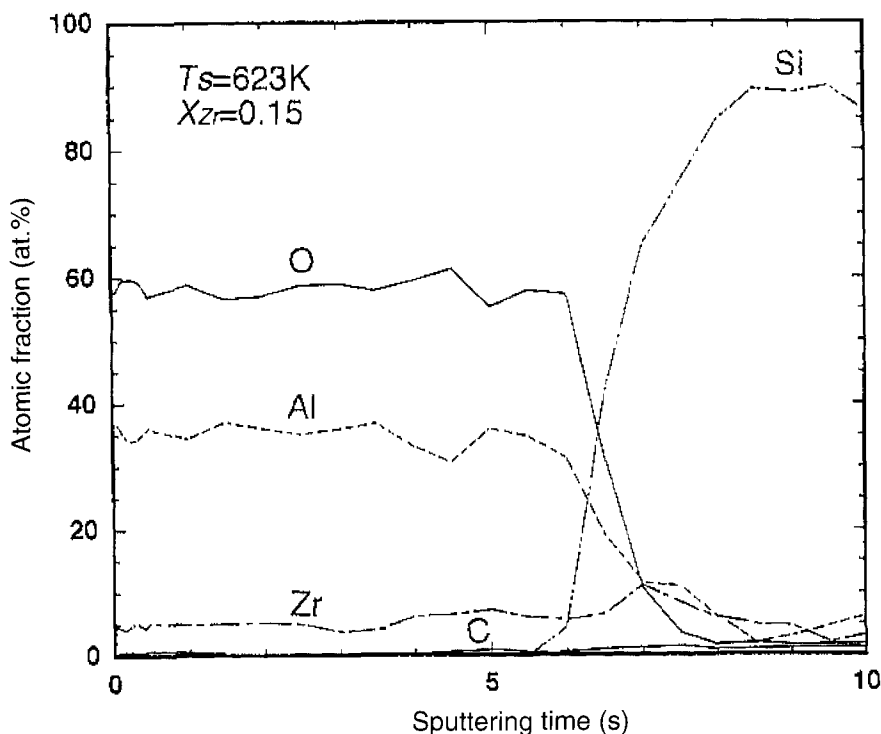


Fig. 4 AES depth profile of a double oxide film with $X_{Zr} = 0.15$.

3.3. Micro- and Crystal Structure

Figure 5 shows transmission electron micrographs and electron diffraction patterns for double oxide films of different X_{Zr} values, which were formed at 623 K.

The ZrO_2 film ($X_{Zr} = 1$) has fine crystal grains. However, the films of $X_{Zr} = 0.74$, 0.29, and Al_2O_3 ($X_{Zr} = 0$) have no crystal grains and show a homogeneous structure. The ZrO_2 film shows a tetragonal structure instead of a monoclinic structure and is stable at a low temperature. The tetragonal structure in ZrO_2 films has also been reported by other researchers [7]. Diffraction rings showing the crystalline structure disappeared on double oxide films of X_{Zr} values less than 0.85. That is, the double oxide film of $X_{Zr} = 0 - 0.85$ were all amorphous and homogeneous. The amorphous structure of Al_2O_3 films formed at temperatures lower than 800 K by using $Al(O-i-C_3H_7)_3$ has been reported already [4].

3.4. Corrosion Resistance in HCl Solution

Figure 6 shows changes in ellipsometric parameters, Δ and Ψ , with time for a double oxide film of $X_{Zr} = 0.09$ in 1.0M HCl. Theoretical Δ - Ψ curves for films with different optical constants, $N_2 = n - ki$, which show changes in Δ and Ψ with the change in film thickness, are also given in Fig. 6. The experimental Δ - Ψ locus moves from a theoretical curve for a high optical constant, $N_2 = 1.600 - 0.000i$, to that for a low optical

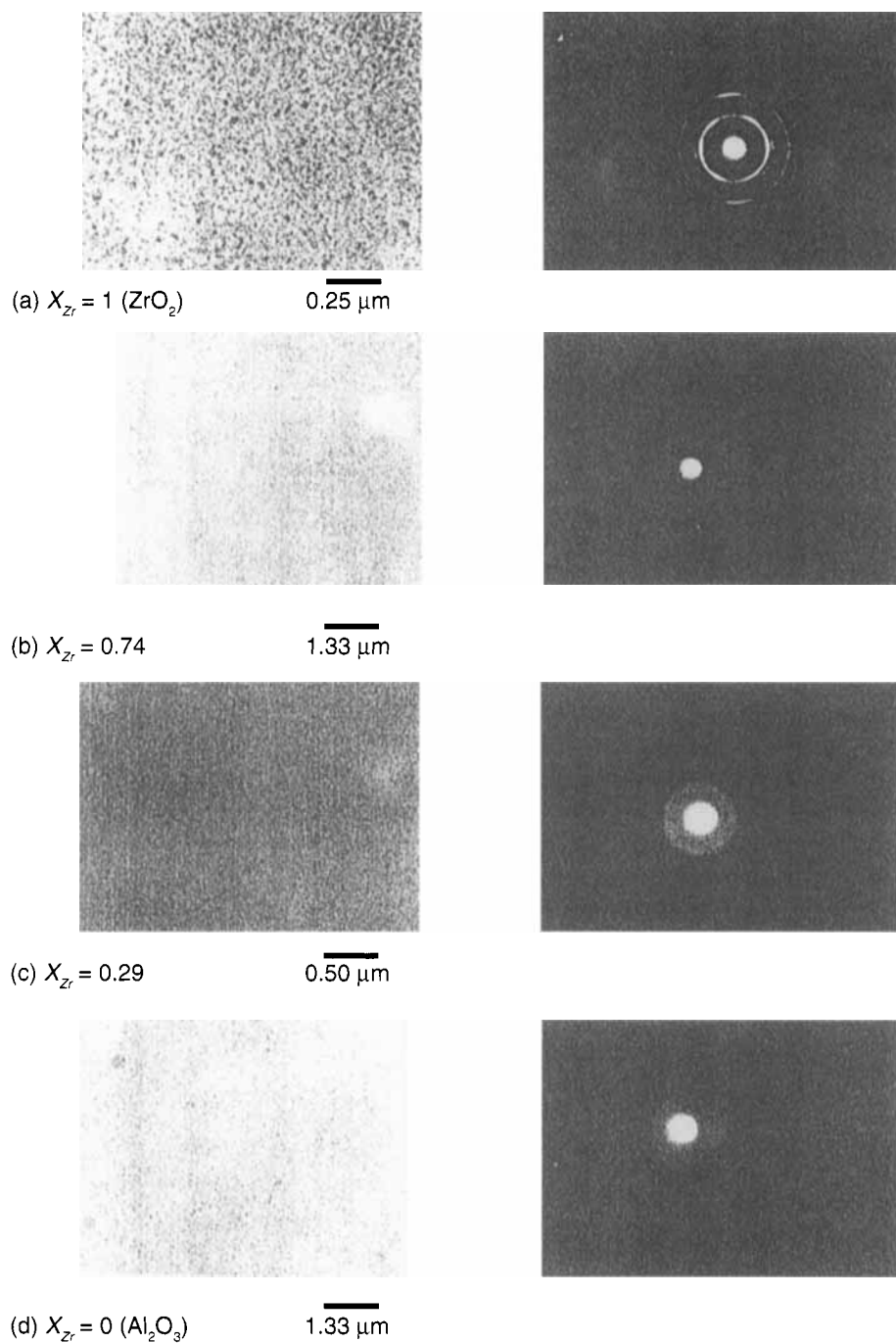


Fig. 5 Transmission electron micrographs (left) and electron diffraction patterns (right) for films of $X_{\text{Zr}} = 1.0$ (ZrO_2)(a), 0.74 (b), 0.29 (c), and 0.0 (Al_2O_3)(d).

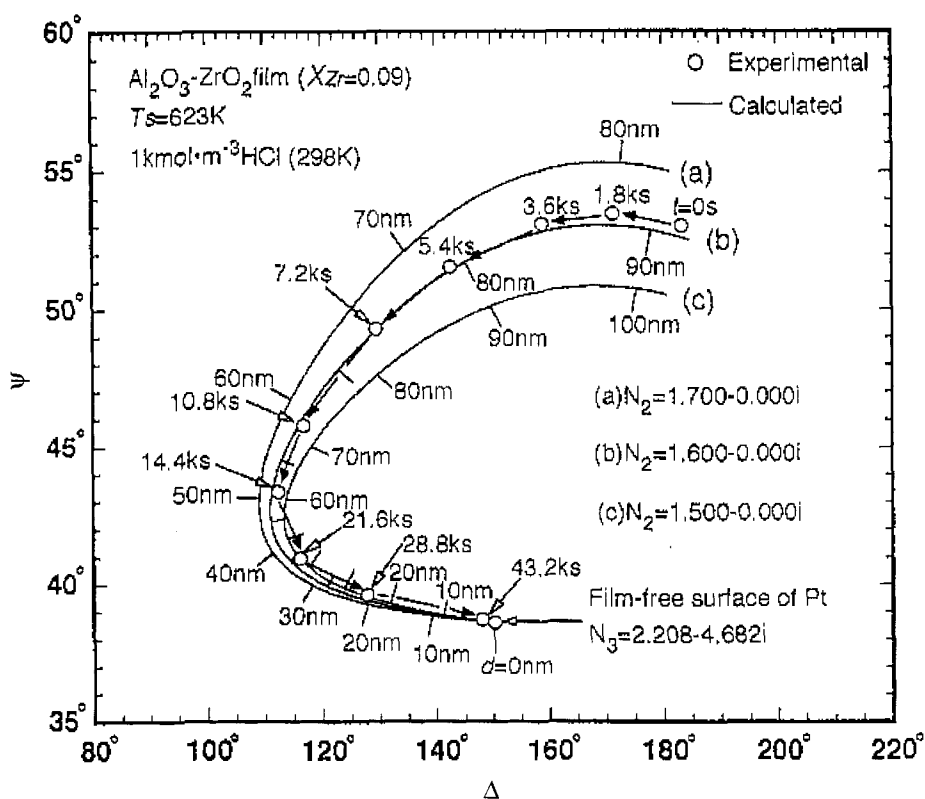


Fig. 6 Experimental Δ - Ψ locus for dissolution of double oxide film of $X_{\text{Zr}} = 0.09$ in 1.0M HCl and theoretical Δ - Ψ curves for films with optical constants of $N_2 = 1.700 - 0.000i$, $N_2 = 1.600 - 0.000i$, and $N_2 = 1.500 - 0.000i$.

constant, $N_2 = 1.500 - 0.000i$, with increasing time, t . This decrease in the optical constant may be due to an increase in the surface roughness of the film with the progress of dissolution. In this case, the theoretical curve for the optical constant of $N_2 = 1.600 - 0.000i$, was selected as approximately the best fit curve through the whole test duration. The film thickness at a given time was determined by drawing a perpendicular to the theoretical curve from the experimental curve.

The decrease in the film thickness as a function of time for double oxide films of $X_{\text{Zr}} = 0-0.47$ is shown in Fig. 7. Every film dissolved linearly with time. The dissolution rate of films, that is, the rate of decrease of film thickness, $-\Delta d \cdot \Delta t^{-1}$, can be determined by the gradient of the Δd vs Δt curves.

The rates of decrease of film thickness thus obtained are given in Fig. 8 as a function of X_{Zr} . The rate of decrease of film thickness in 1.0M HCl decreases with increasing X_{Zr} value and reaches an analytical limit, $2.8 \times 10^{-6} \text{ nm s}^{-1}$, at $X_{\text{Zr}} = 0.47$. The double oxide films with X_{Zr} values larger than 0.47 have good corrosion resistance in 1.0M HCl.

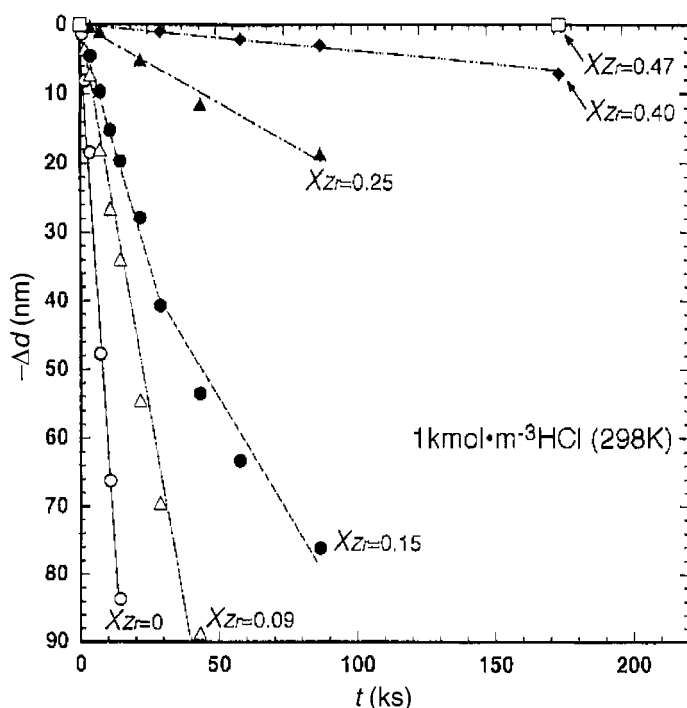


Fig. 7 Decrease in rate of film thickness, $-\Delta d \cdot \Delta t^{-1}$, as a function of time, t , for double oxide films in 1.0M HCl at 298 K.

3.5. Corrosion Resistance in NaOH Solution

Figure 9 shows changes in ellipsometric parameters, Δ and Ψ , with time for a double oxide film of $X_{\text{Zr}} = 0.23$ in 1.0M NaOH at 298 K. Theoretical Δ - Ψ curves for films with optical constants of $N_2 = 1.740 - 0.000i$, $N_2 = 1.650 - 0.000i$, and $N_2 = 1.500 - 0.000i$ are also given in Fig. 9. The experimental Δ - Ψ locus moves from the curve of $N_2 = 1.650 - 0.000i$ to the curve of $N_2 = 1.500 - 0.000i$ with the progress of dissolution. In the determination of film thickness, however, the curve of $N_2 = 1.650 - 0.000i$ was used as a curve which approximates most experimental plots.

The decrease in the film thickness as a function of time for double oxide films of $X_{\text{Zr}} = 0 - 0.63$ is shown in Fig. 10. Every film dissolves linearly at least in the early stage of dissolution. However, in the case of double oxide films of $X_{\text{Zr}} = 0.23-0.47$, the rate of decrease of film thickness becomes smaller in the later stage of dissolution. This suggests that the selective dissolution of the Al_2O_3 component and the enrichment of the ZrO_2 component proceed on the surface of the double oxide films. Therefore, the rate of decrease of film thickness, $-\Delta d \cdot \Delta t^{-1}$, was determined by the gradient of Δd vs Δt curves in the early stage of dissolution.

The rates of decrease of film thickness obtained are given in Fig. 11 as a function of X_{Zr} . The rate of decrease of film thickness becomes smaller with increasing X_{Zr} value and reaches the analytical limit, $2.8 \times 10^{-6} \text{ nms}^{-1}$, at $X_{\text{Zr}} = 0.62$. Taking into account the result in 1.0M HCl, the double oxide films with X_{Zr} values larger than

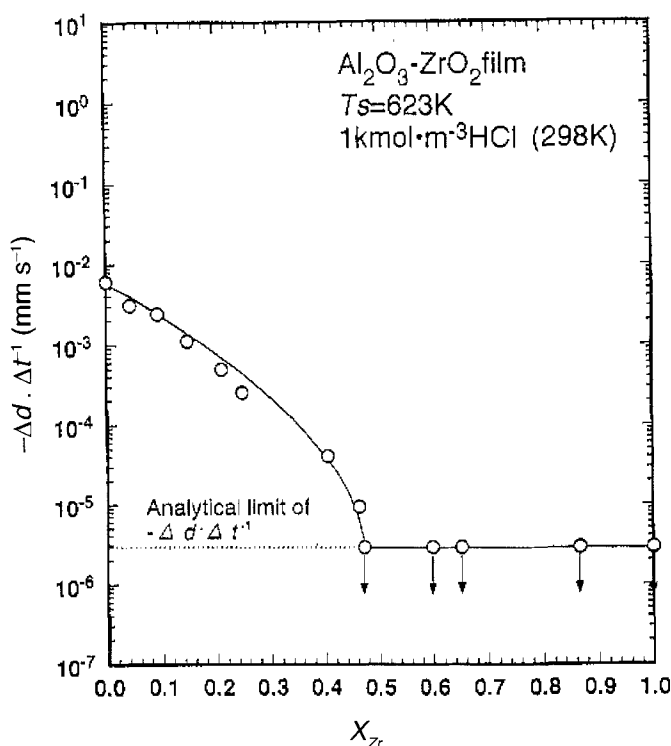


Fig. 8 Decrease in rate of film thickness, $-\Delta d \cdot \Delta t^{-1}$, as a function of cationic fraction of Zr, X_{Zr} , for double oxide films in 1.0M HCl at 298 K.

0.62 are seen to have superior corrosion resistance in both the acid and the alkali solutions.

3.6. Corrosion Protection by Double Oxide Film Coating

Figure 12 compares the change in mass loss with time for Al specimens coated with the double films in 1.0M HCl at 298 K. Double oxide films with X_{Zr} values of *ca.* 0.85 and thickness of 200 nm and 1 μm were used for the coating. The dissolution rate of bare Al is also shown in Fig. 12.

It can be seen that the 200 nm thickness coating suppresses the dissolution of the specimen up to 7.2×10^5 s. The 1 μm thickness coating, however, shows no protection because of numerous microcracks in the coating. Microcracks occur in the coating with thickness larger than 450 nm.

The change in the mass loss with time in 1.0M NaOH is shown in Fig. 13. Double oxide films of $X_{Zr} = 0.64$ –0.85 and thickness $d = 200$ –450 nm were used for the coating. Two layer coatings of Al₂O₃-ZrO₂ ($X_{Zr} = 0.67$, $d = 300$ nm)/Al₂O₃ ($d = 100$ nm) and Al₂O₃-ZrO₂ ($X_{Zr} = 0.56$, $d = 200$ nm)/Al₂O₃-ZrO₂ ($X_{Zr} = 0.67$, $d = 200$ nm) were also tested.

The double oxide film coating with $X_{Zr} = 0.85$ and $d = 200$ nm, which showed good protection against 1.0M HCl, could not suppress the corrosion and the mass

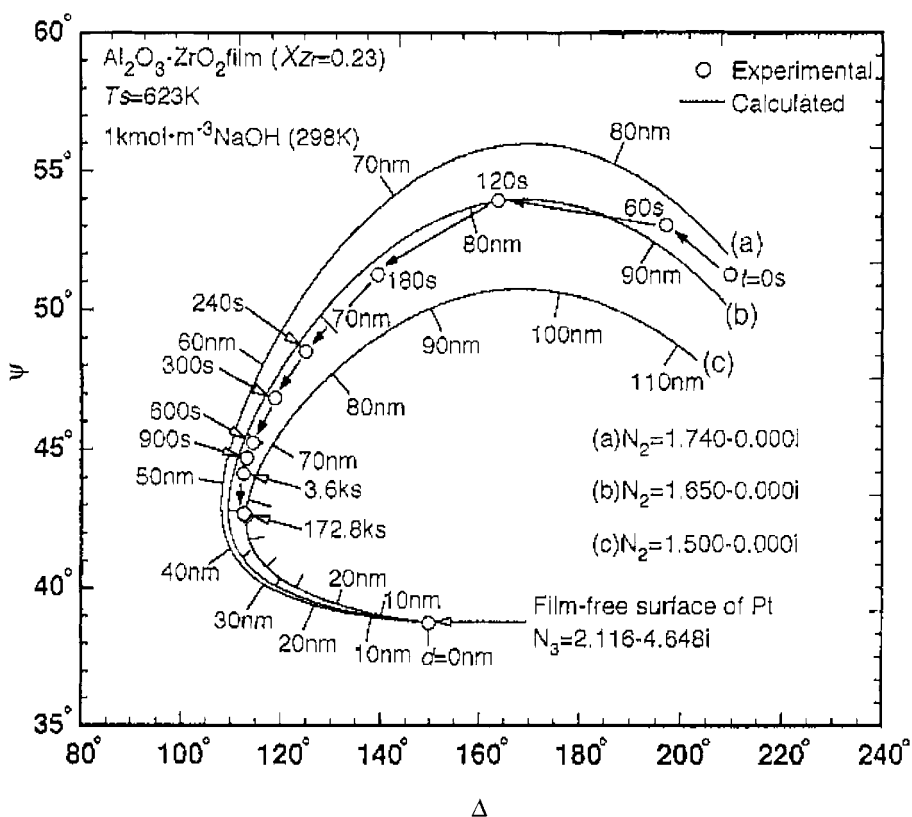


Fig. 9 Experimental Δ - Ψ locus for dissolution of double oxide film of $X_{\text{Zr}} = 0.23$ in 1.0 mol L^{-1} NaOH and theoretical Δ - Ψ curves for films with optical constants of $N_2 = 1.740 - 0.000i$, $N_2 = 1.650 - 0.000i$, and $N_2 = 1.500 - 0.000i$.

loss increased in 1.0M NaOH after 7.2 ks . The 450 nm thickness coating also showed no good results in this solution. Two layer coatings, especially the $\text{Al}_2\text{O}_3\text{-ZrO}_2/\text{Al}_2\text{O}_3\text{-ZrO}_2$ coating, gave relatively good results. This is probably the result of the upper layer providing a covering effect which conceals defects in the lower layer.

4. Conclusions

1. $\text{Al}_2\text{O}_3\text{-ZrO}_2$ double oxide films were formed by MOCVD using $\text{Al(O-}i\text{-C}_3\text{H}_7)_3$ and $\text{Zr(O-}i\text{-C}_3\text{H}_7)_4$ as source gases.
2. The double oxide films, with formed at 623 K and X_{Zr} values between 0 and 0.85 , showed homogeneous amorphous structures.
3. The double oxide films X_{Zr} values larger than 0.62 , which were formed at 623 K , exhibited high corrosion resistance in both 1.0M HCl and 1.0M NaOH.

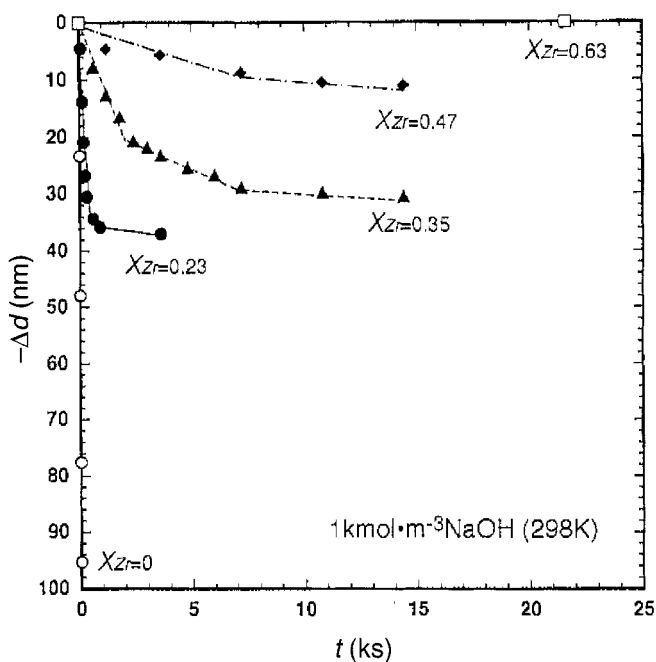


Fig. 10 Decrease in film thickness, $-\Delta d$, as a function of time, t , for double oxide films in 1.0M NaOH at 298 K .

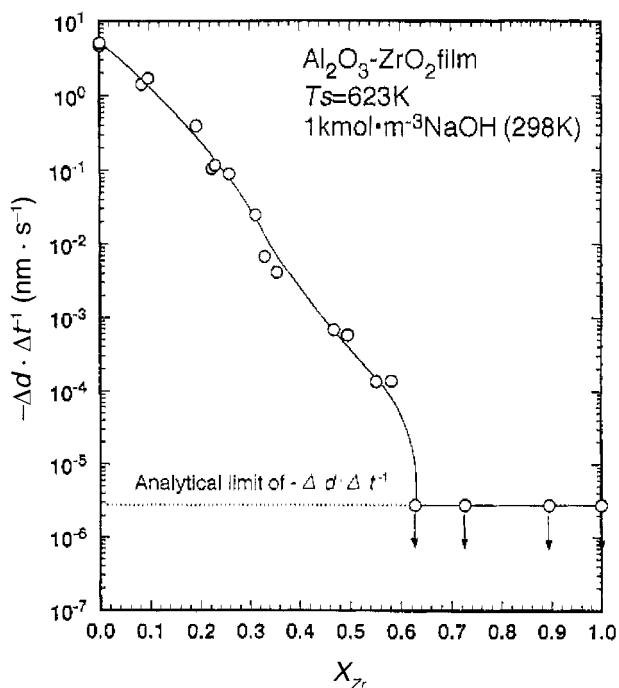


Fig. 11 Decrease rate of film thickness, $-\Delta \cdot \Delta t^{-1}$, as a function of cationic fraction of Zr, X_{Zr} , for double oxide films in 1.0M NaOH at 298 K .

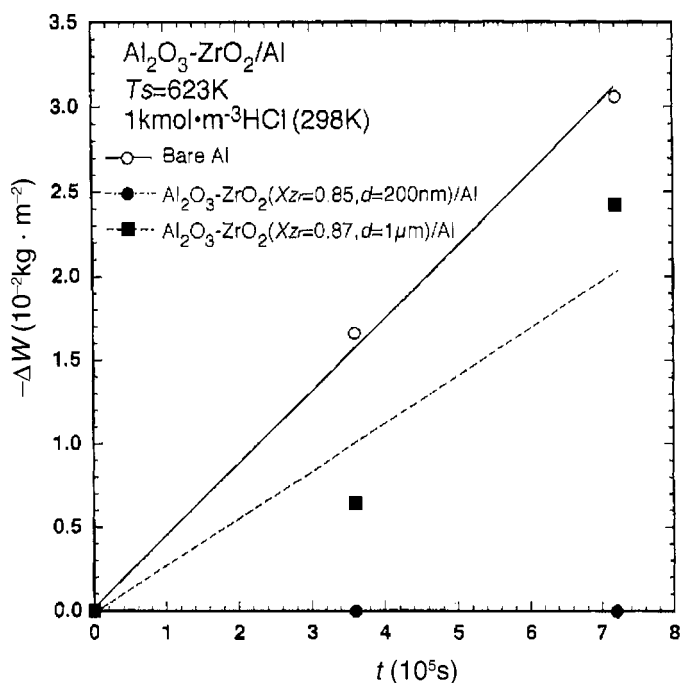


Fig. 12 Mass loss, $-\Delta W$, as a function of time, t , for Al specimens coated with double oxide films in 1.0M HCl at 298 K.

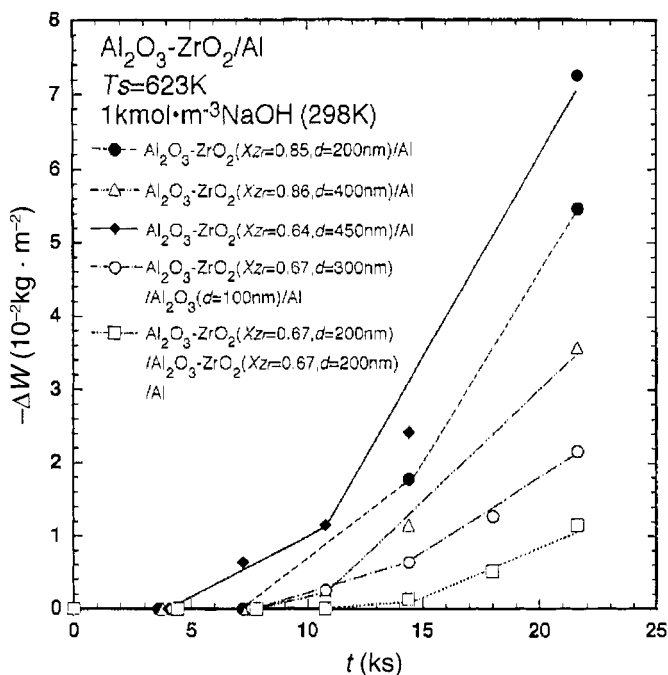


Fig. 13 Mass loss, $-\Delta W$, as a function of time, t , for Al specimens coated with double oxide films in 1.0M NaOH at 298 K.

4. The double oxide film coating with an X_{Zr} value of 0.85 and 200 nm thickness showed good protection of Al substrate in 1.0M HCl. However, it provided hardly any protection in 1.0M NaOH. Two layer coatings of double oxide films, in which the X_{Zr} value and thickness of each layer are 0.67 and 200 nm, respectively, gave relatively good protection in 1.0M NaOH.

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New Surface Layer Systems for the Improvement of the Corrosion Resistance of Implants

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ABSTRACT

The effect of vapour deposited TiNbN and/or of electrodeposited calcium phosphate coatings on the anodic dissolution of polished and roughened X5CrNi18.10 stainless steel specimens in 0.9% NaCl solution was investigated. Both coatings provide an increase in the pitting corrosion resistance. The results were compared with those of similarly prepared and coated TiAl6V4 specimens.

1. Introduction

In orthopaedic surgery and particularly in total hip replacement metals are the most favoured materials because of their good mechanical stability. On the other hand, metals corrode in contact with aggressive body fluids or tissues [1,2]. An effective protection of metallic implants against corrosion should improve both their biostability and also their biocompatibility.

The aim of this work was to investigate the effect of vapour and/or electrodeposited layers on the anodic metal dissolution of X5CrNi18.10 stainless steel and TiAl6V4 in a neutral physiological NaCl solution.

2. Experimental

X5CrNi18.10 stainless steel specimens, 0.8 mm thick and TiAl6V4 discs, 3 mm thick, with an exposed area of 300 mm² were used.

The ceramic coatings were deposited by cathodic arc (TiNbN — on stainless steel) and hollow cathode arc (TiN — on the TiAl6V4 alloy) techniques. The calcium phosphate coatings were produced by electrodeposition from solutions containing calcium and phosphate ions.

The electrochemical behaviour and the structure of the coated stainless steel and Ti-alloy specimens were evaluated with potentiodynamic techniques and electrochemical impedance spectroscopy (EIS). The results and discussions of the impedance spectroscopy will be presented in a later paper. Here we discuss only the results of potentiodynamic measuring. For this method we used an AUTOLAB-System (ECO Chemie, NL). As a measure of corrosion resistance (or corrosion

protection) we used the value of current density at +300 mV vs open circuit voltage (O.C.V.). The measuring point for comparison of current densities is shown in Fig. 1. The i/E curve has been smoothed previously in the +300 mV region. The parameters of the potentiodynamic polarisation (Pol.) were:

Pol. speed:	1 mVs ⁻¹
Pol. range:	-100 mV to +1000 mV (vs O.C.V.)
Electrolyte:	0.9 g NaCl-sol. (neutral physiol. NaCl-sol.)
Ref. electrode:	Ag/AgCl (SSE)
Temp.:	21°C

The morphology and the composition of the coatings were examined by means of a scanning electron microscope (SEM) with an energy dispersive spectroscopy (EDS). We examined the samples before and after the electrochemical investigation.

3. Results

The electrodeposited calcium phosphate coatings consist of separate 10–25 μm long, plate-like crystals. The free volume or the porosity of these coatings reaches values of 80%. Compared to monolithic plasma-sprayed coatings (Fig. 2), this porous structure allows excellent fixation in the surrounding biological matrix and in case of bone implants a direct mineralisation of the osteoblasts on the surface of the implant (Figs 2–4).

The influence of these electrodeposited calcium phosphate coatings on the corrosion resistance of stainless steel and Ti-alloy implant materials was investigated by means of current density–potential-curves. For this, the current density values at 300 mV above the corrosion potential were compared (Fig. 1).

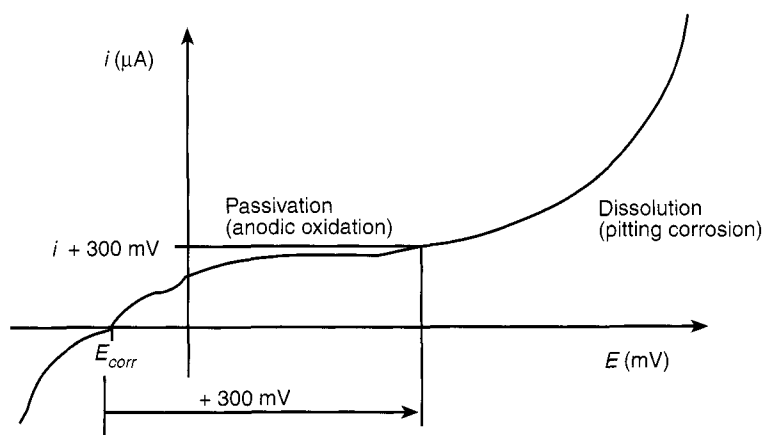


Fig. 1 Schematic current density–potential-curve of the investigated electrodes. The measuring point for comparison of current densities is shown. The i/E -curve has been smoothed in the region of +300 mV.

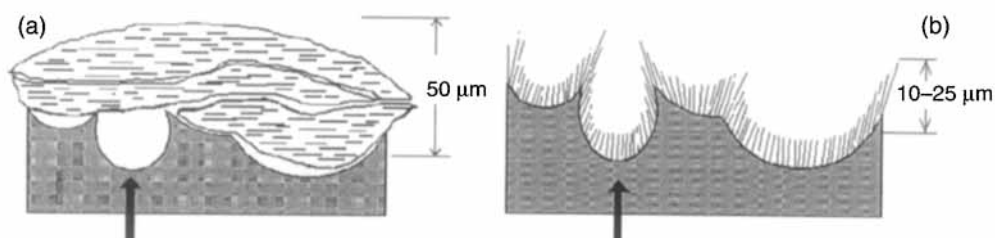


Fig. 2 Comparison between two methods of calcium phosphate deposition of porous implant surfaces; (a) a plasma-spray deposited surface; (b) an electrochemically deposited surface with improved cell adhesion and ingrowth.

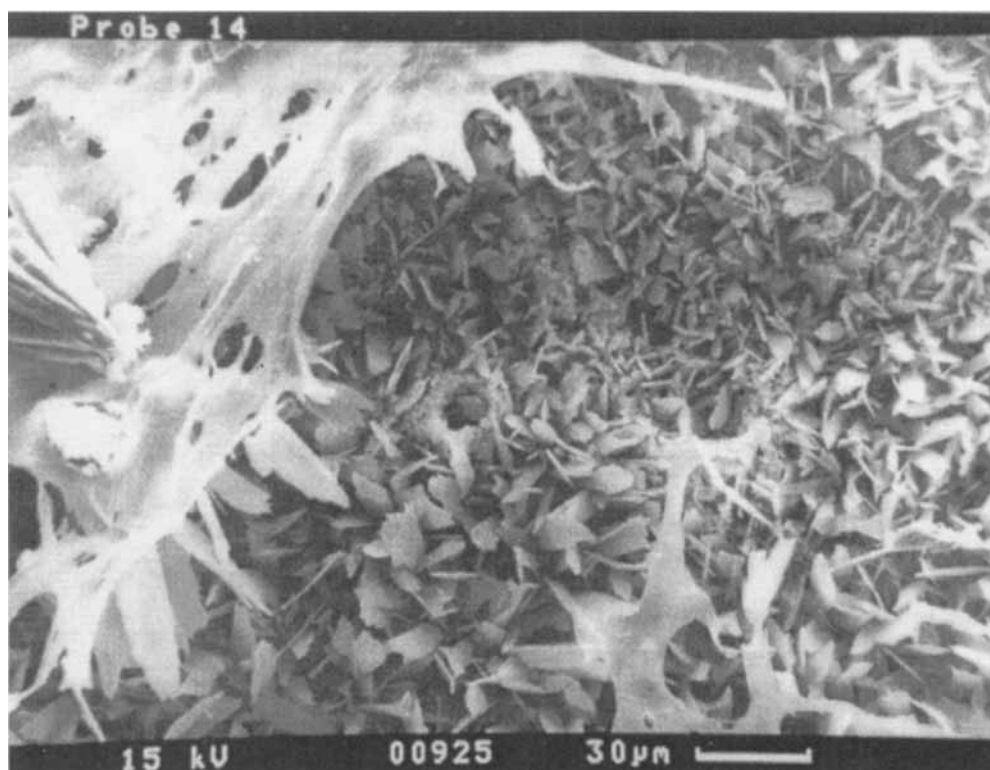


Fig. 3 Osteoblastic cells on calcium phosphate/TiN coated TiAl6V4 specimens.

From Fig. 5 it is seen that the corrosion resistance of calcium phosphate coated stainless steel at first increases with the duration of coating. After 3 min a significantly higher anodic dissolution current can be observed. With further deposition this current slowly decreases.

Figure 6 shows the situation for TiNbN-coated stainless steel. The high current density in comparison with uncoated stainless steel (Fig. 5) is a sign of pitting

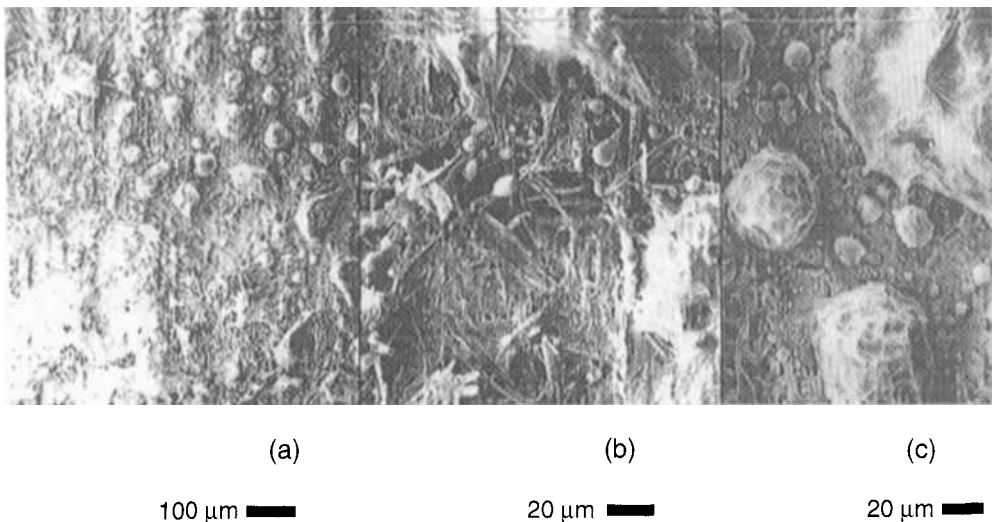


Fig. 4 Osteoblast-like cells on coated stainless steel specimen: (a) total print; (b) calcium phosphate/TiNbN coated region (magnified upper left corner of picture (a)); (c) TiNbN coated region (magnified upper right corner of picture (a)).

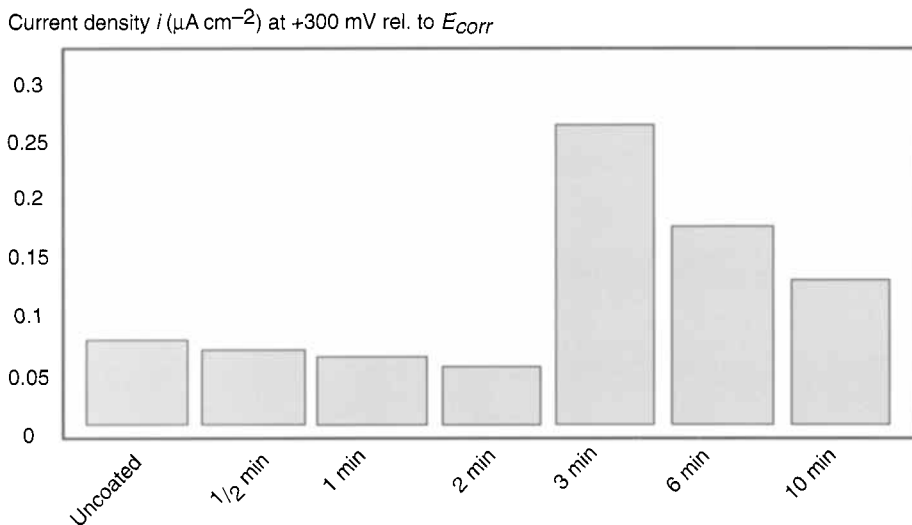


Fig. 5 The influence of electrodeposited calcium phosphate coating time on anodic metal dissolution. Substrate: X5CrNi18.10 (1.4301 or 316L); polished ($< 1 \mu\text{m}$).

corrosion (Fig. 1). An additional calcium phosphate coating clearly improves the corrosion resistance.

Polished stainless steel compared with the Ti-alloy shows good protection against corrosion (Fig. 7) although the stainless steel has a higher anodic metal dissolution if

Current density i ($\mu\text{A cm}^{-2}$) at +300 mV rel. to E_{corr}

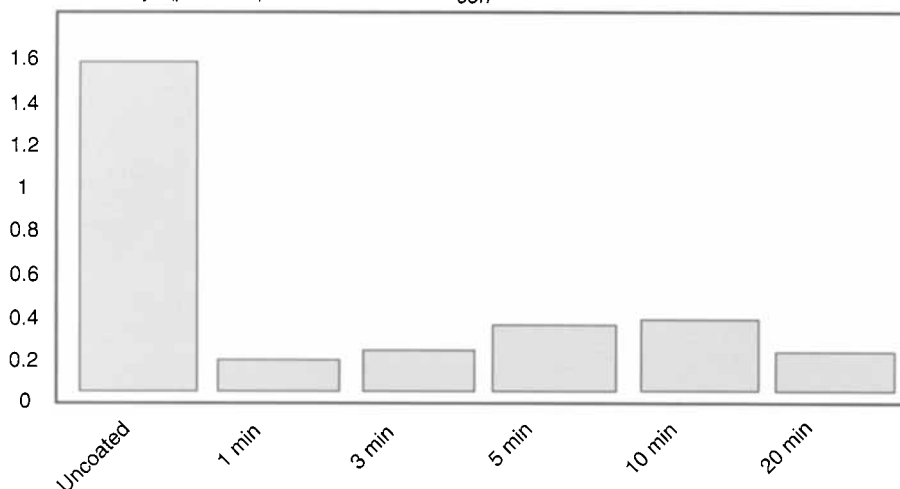


Fig. 6 The influence of electrodeposited calcium phosphate coating time on anodic metal dissolution. Substrate: TiNbN ($4 \mu\text{m}$) on X5CrNi18.10; polished ($< 1 \mu\text{m}$).

Current density i ($\mu\text{A cm}^{-2}$) at +300 mV rel. to E_{corr}

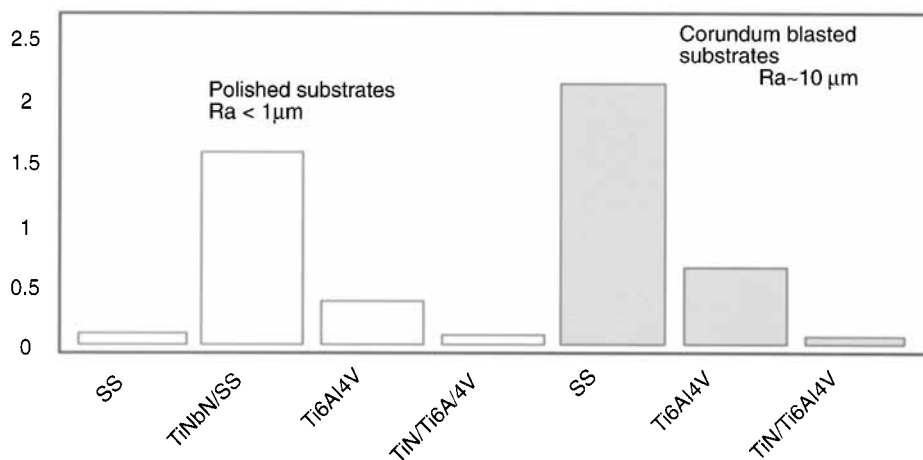


Fig. 7 The influence of surface preparation on anodic metal dissolution. Substrates: X5CrNi18.10 (SS) and TiAl6V4; polished ($< 1 \mu\text{m}$) or corundum blasted.

the specimens are corundum blasted. A TiN coating on polished and roughened Ti-alloys improves the corrosion protection, whereas a TiNbN coating on stainless steel favours pitting corrosion.

An additional calcium phosphate coating (Figs 8 and 9) generally improved the passivation.

Current density i ($\mu\text{A cm}^{-2}$) at +300 mV rel. to E_{corr}

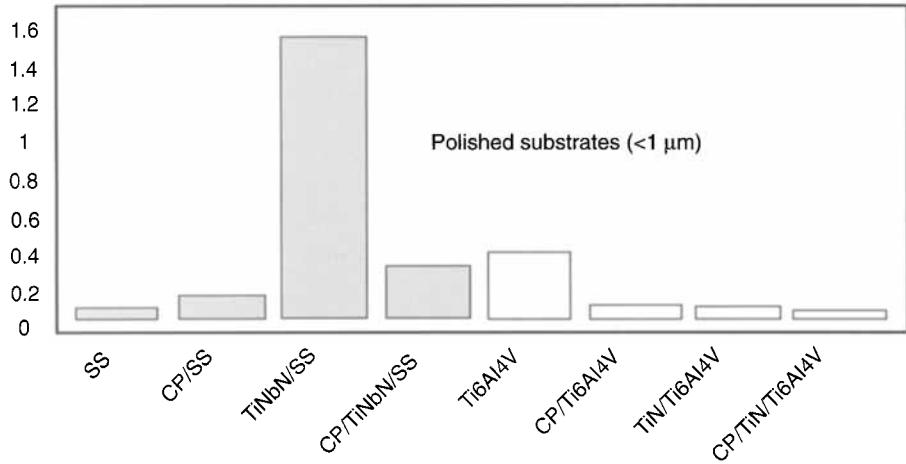


Fig. 8 The influence of surface preparation and electrodeposited calcium phosphate (CP) coating (10 min) on anodic metal dissolution. Substrates: X5CrNi18.10 (SS) and TiAl6V4; polished ($< 1 \mu\text{m}$).

Current density i ($\mu\text{A cm}^{-2}$) at +300 mV rel. to E_{corr}

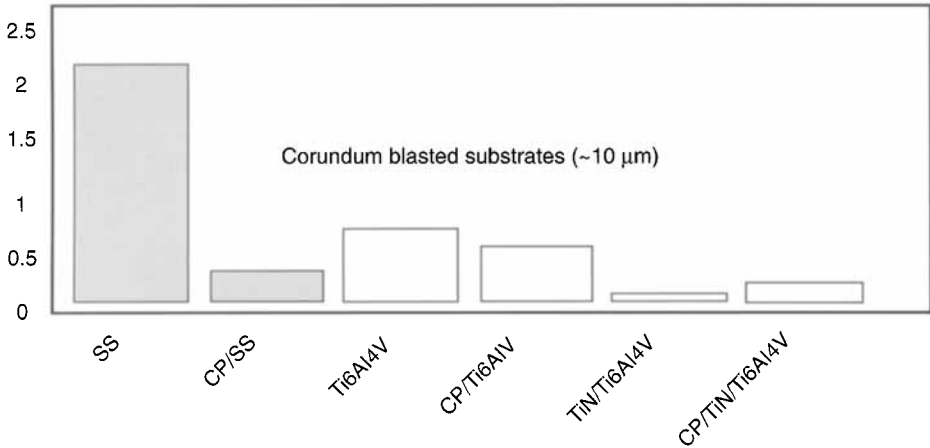


Fig. 9 The influence of surface preparation and electrodeposited calcium phosphate (CP) coating (10 min) on anodic metal dissolution. Substrates: X5CrNi18.10 (SS) and TiAl6V4; corundum blasted (ca. $10 \mu\text{m}$).

4. Discussion

The electrodeposition of calcium phosphate can be used to provide additional corrosion protection. Regions on the surface with weak passivation (pinholes) favour pitting corrosion but they are also the first sites for electrodeposition (Fig. 6). With

such deposition the corrosion protection can be remarkably improved.

The quality of this additional passivation depends on good adhesion of the growing calcium phosphate crystals to the substrates. To eliminate crystals with poor adhesion to the substrate calcium phosphate was deposited under the action of ultrasonic fields. With increasing length of the calcium phosphate crystals their vibration amplitude increases and finally weakly bonded crystals are removed from the substrate. At first, a higher corrosion rate was observed at these areas but as the electrocrystallisation proceeded they again became coated with calcium phosphate and were passivated. Consequently, the current density finally decreased as the thickness of the calcium phosphate coating increased (Figs 5 and 6).

In the case of ceramic (TiNbN) sublayers (Fig. 6) the calcium phosphate coating clearly decreased the anodic dissolution with only slight dependence on the coating time. One reason for this behaviour could be, that at the beginning of the crystal growth (of the calcium phosphate coating) the pinholes in the ceramic layer are filled and their removal by ultrasonic vibration will not occur. A more probable reason is, that the crystals break at the surface of the TiNbN. The 'roots' of these crystals remaining in the ceramic layer improve the corrosion resistance of the coated specimens.

In Figs 7–9, polished and corundum blasted substrates are compared. It is seen that there is a good agreement between polished, but TiNbN coated, and corundum blasted stainless steel specimens. In both cases the calcium phosphate coating closes the microporous surface structure, stops the pitting corrosion and thereby improves the passivation.

For the Ti-alloy a TiN coating shows the best corrosion protection for roughened samples. An additional calcium phosphate coating has no clear influence on the corrosion. A single calcium phosphate coating on Ti-alloy improves the passivation similarly to the case of corundum blasted or TiNbN coated stainless steel specimens.

5. Summary

It has been shown, that single or combined Ti(Nb)N and electrodeposited calcium phosphate coatings can improve the corrosion resistance of stainless steel and Ti-alloy implant materials. In particular, the enhancement of passivation against pitting corrosion provided by electrochemically deposited calcium phosphate creates the possibility of implants with improved bio-compatibility. More specific investigations are now in preparation.

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Characterisation and Behaviour of Various Ceramic Coatings in Seawater. Influence of the Surface Preparation on the Adhesion and Corrosion Control

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ABSTRACT

The object of this study was to determine the influence of the substrate preparation on the adhesion and corrosion resistance of various ceramic coatings used in seawater.

The adhesion properties of the various coatings were characterised using a four-point bend test or a pull-out test, and the corrosion performance of the coatings was evaluated by electrochemical measurements and exposure tests.

It was shown that substrate sandblasting was without effect both on adhesion and corrosion control. The presence of a sub-layer is not necessary to obtain good adhesion of the three kinds of ceramic coating studied here. The sub-layer/substrate interface is weaker than the ceramic/sub-layer or ceramic/substrate interface. Thus, the risk of decohesion of the multilayer coatings is higher than that of a single ceramic coating. The severity of cracking under mechanical stress depends on the thickness ratio of the ceramic and the sub-layer, and on the nature of this sub-layer.

The electrochemical measurements have confirmed that all the ceramic coatings are porous. For both oxide ceramic coatings, the presence of a sub-layer has a beneficial effect on corrosion control but for the carbide coating it is not possible to conclude whether the presence of a sub-layer is beneficial.

1. Introduction

Ceramic coatings used for their wear or erosion resistance in systems operating in seawater should generally also ensure protection of the substrate against corrosion [1–6]. However, it is known that these coatings are often porous and do not always offer good corrosion resistance because seawater penetrates through the network of pores down to the metallic substrate [1,3–6].

One method for improving the corrosion resistance of the coated part for a ceramic coating, is to deposit one (or several) intermediate layer(s) between the ceramic and the substrate [3,4]. These sub-layers may also improve the adhesion of the coating to the substrate [3,4,7].

The aim of the present study was to determine the influence of the substrate

preparation on the adhesion and corrosion resistance of various commercial ceramic coatings. The surface of the substrate may or not be sandblasted. Single or multi layer coatings were obtained by thermal spraying on martensitic stainless steel.

2. Materials and Microstructures

2.1. Materials and Surface Treatments

The substrate was a quenched and tempered martensitic stainless steel X6 Cr16 Ni5 Mo1.

One or several surface treatments were applied to the substrate before applying the ceramic coating. These included surface modification by sandblasting and/or thermal spraying of a corrosion resistant sub-layer. Two such sub-layers were used:

- Ni80 Cr20
- Ni Cr21 Mo9 Nb4 (625-type alloy).

Three ceramic coatings deposited by thermal spray were characterised:

- Cr_2O_3
- 80% Cr_2O_3 + 20% Al_2O_3
- 25%WC + (W,Cr) carbides + 5%Ni

After coating, the surfaces were machined and polished to a roughness level of $\text{Ra} \leq 0.1 \mu\text{m}$.

2.2. Characterisation

2.2.1. Microstructural examination

Microstructures were examined before and after mechanical and corrosion tests, both on the surface and on polished sections. The thicknesses of the ceramic and sub-layer coatings were measured on optical or secondary electron micrographs of polished sections.

The ceramic thickness/total thickness ratio was calculated.

Porosity was measured by image analysis (using secondary electron micrographs) inside ceramic coatings and at the interfaces. Intrinsic porosity was quantified on at least three images (magnification $\times 2000$) for each coating. Linear porosity at the metal/ceramic interface was measured (magnification $\times 1000$), on a 5 mm length (linear porosity = length of inclusions+pores/total length).

2.2.2. X-Ray analysis

Ceramic coatings were analysed by X-ray diffractometry using a cobalt anticathode.

2.2.3. Hardness

The Vickers hardness of HV 0,1 was measured on sections at 10, 20, 40, 60 and 80 μm from the surface of the ceramic coating, and three series of measurements were carried out on each sample.

2.3. Results

Microstructural examinations and X-ray analysis showed that there was no effect of the sub-layer on the appearance and the composition of the ceramic coating. The measurements which were carried out during the microstructural examination of the various samples with different surface preparations are summarised in Table 1.

The Cr_2O_3 coating showed a uniform microcracked surface. Its porosity varied

Table 1. Thickness and porosity of the different coatings (#: not measured)

Ceramic coating	Sand blasting	Sub-layer type	Thickness			Inclusions + Porosities at the interface (length %)	Intrinsic ceramic porosity (vol.%)
			Ceramic (μm)	Total (Ceramic + sub-layer) (μm)	Ceramic Total		
Cr_2O_3	YES	—	100	100	1	26	5.5
			100	100	1		
	YES	Ni-Cr	250	450	0.55	20	2.4
			180	490	0.37		
	YES	625	250	480	0.52	10	3.1
			240	540	0.44		
Cr_2O_3 + Al_2O_3	YES	—	120	120	1	5	0.3
			100	100	1		
	YES	Ni-Cr	350	460	0.76	15	#
			190	410	0.46		
	NO	Ni-Cr	430	480	0.89	0	#
	YES	625	350	600	0.58	10	#
			140	460	0.30		
	NO	625	40	490	0.08	0	#
WC + (W, Cr) C+Ni	NO	—	150	150	1	<1	4.5
			100	100	1		
	YES	Ni-Cr	270	380	0.71	1	#
			150	380	0.39		
	YES	625	420	550	0.76	3	#
			160	430	0.37		

between 3 and 5 vol.% and its hardness between 1600 and 1700 HV0.1. The X-ray analysis of the ceramic coating showed only the presence of the Cr_2O_3 phase, with the same structure as the powder used for the thermal spray. The substrate/coating or substrate/sub-layer interfaces showed numerous alumina particles (Fig. 1) which were not removed after sandblasting. This phenomenon explains the high value of the linear porosity at the interface. The ceramic layer thickness varied between 100 and 250 μm , and the Ceramic thickness/Total thickness ratio varied between 0.37 and 0.55.

The 80% Cr_2O_3 + 20% Al_2O_3 ceramic coating had a stratified structure of Cr_2O_3 and Al_2O_3 phases (Fig. 2). The X-ray analysis showed that some Cr_2O_3 did transform during spraying into Cr_3O_4 and pure chromium. The porosity measured by image analysis was low (*ca.* 0.3 vol.%), but the coating was microcracked. The hardness varied between 1200 and 1500 HV0.1. As for the chromium oxide coating, the substrate/coating or substrate/sub-layer interfaces showed numerous alumina particles which were not removed after sand blasting. The ceramic layer thickness varied between 100 and 350 μm , and the Ceramic thickness/Total thickness ratio between 0.37 and 0.76 for the coatings produced after sandblasting. The thickness of the ceramic and sub-layers coatings, sprayed onto non-sandblasted substrates, were not so well controlled because the Ceramic thickness/Total thickness ratio for these samples was either too small (0.08) or too large (0.89).

The coating of the W and Cr carbides + Ni mixture showed a more complex

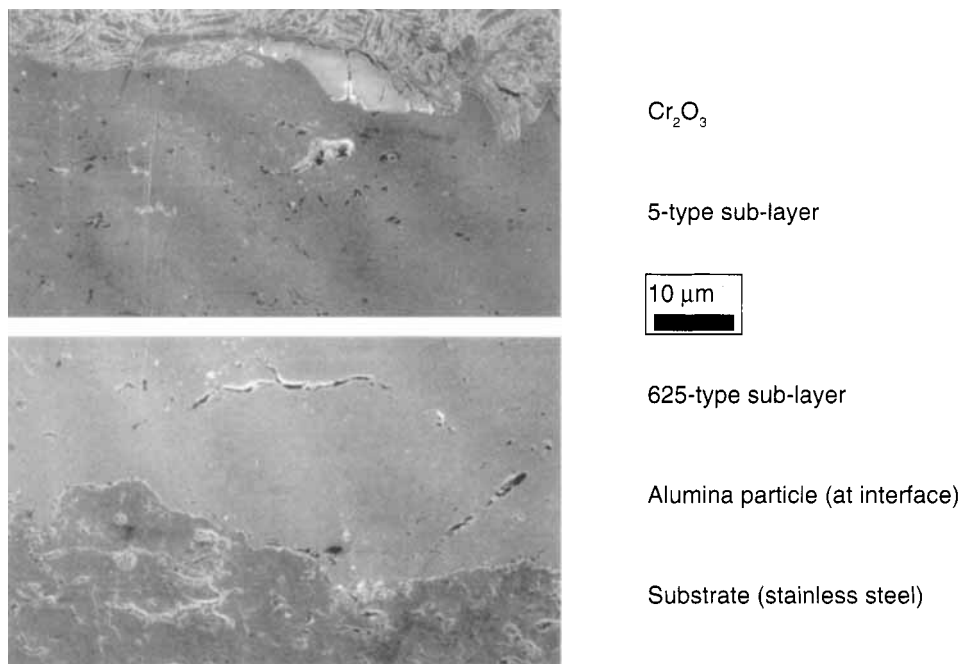


Fig. 1 Secondary electron micrographs of Cr_2O_3 ceramic coating with a 625-type sub-layer: views of the ceramic/sub-layer and sub-layer/substrate interfaces.

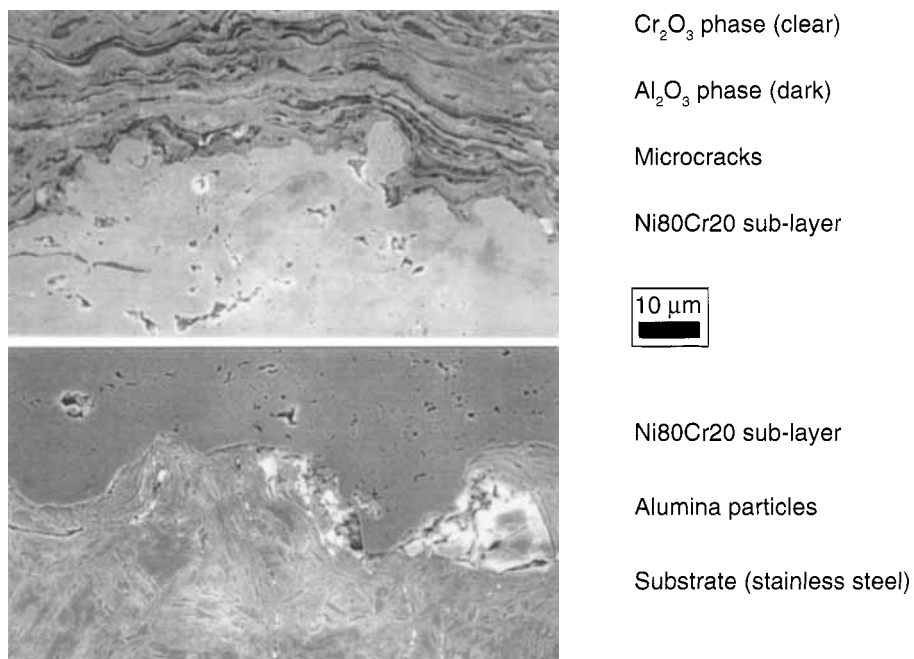


Fig. 2 Secondary Electron Micrographs of Cr₂O₃ + Al₂O₃ ceramic coating with a Ni80Cr20 sub-layer: views of the ceramic/sub-layer and sub-layer/substrate interfaces.

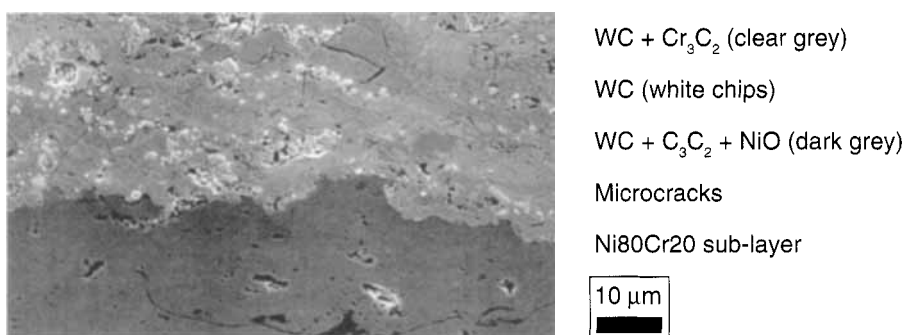


Fig. 3 Secondary Electron Micrographs of the WC+(W,Cr)C+Ni ceramic coating with a Ni80Cr20 sub-layer: view of the ceramic/sub-layer interface.

microstructure (Fig. 3). It contained pure W, WC, WC + Cr₃C₂ carbides and also NiO. The ceramic layer thickness varied between 100 and 420 µm, and the Ceramic thickness/Total thickness ratio between 0.39 and 0.76. The porosity of the ceramic layer varied between 4 and 5 vol.%, but this coating was also microcracked. Its hardness varied between 1100 and 1500 HV0.1.

3. Coatings Adhesion

3.1. Characterisation

3.1.1. Bend test

The samples $60 \times 25 \times 3$ mm were submitted to a four-point bend test (central rolls being applied on the coating-free side of the sample). The test was carried out on a traction-compression INSTRON machine. Two samples were characterised for each type of single or multilayer coating (ceramic or ceramic + sub-layer coatings). The maximum displacement was 3 mm, at a rate of 0.002 or 0.1 mm.s⁻¹.

3.1.2. Pull out test

The coating was sprayed on a cylindrical substrate of 20 mm dia. A cylindrical arm of the same diameter was glued to this coating, and a traction load progressively applied perpendicularly to the coating surface. The load was applied using an INSTRON traction machine at a rate of 0.5 mm/min. In the case of full adhesive fracture (at the coating/substrate interface), the load applied for rupture quantifies the adhesion of the coating. In the case of a cohesive fracture it quantifies the internal cohesion of the coating where the fracture occurs.

3.2. Results

For the four-point bend test, the recording of the tests shows load gaps coupled with a decrease in the stiffness of the samples due to the progressive damage of the layers by transverse cracking and sometimes by spalling of the coating. The number of these gaps, and the number of transverse cracks onto the surface of the samples was counted. These qualitative or quantitative values were supplemented with microstructural examinations of polished sections of the samples (samples were embedded before cutting).

The obtained results are summarised in Table 2.

3.3. Discussion: Influence of the Surface Treatment on the Adhesion

3.3.1. Sand blasting

Sand blasting of the substrate was carried out to improve the adhesion. In fact, for the three types of ceramic coating, for the same thickness (*ca.* 100 μ m) and without a sub-layer, with or without sandblasting, no decohesion was noticed at the ceramic/substrate interface after the four-point bend test (Fig. 4) or after the pull-out test. The presence of numerous alumina particles at the interface due to sandblasting did not weaken the interface.

For samples with a sub-layer, the influence of sandblasting was masked by other parameters, particularly by the Ceramic thickness/Total thickness ratio: these values were too low or too high for the non-sandblasted specimens.

Table 2. Results of the adhesion tests. th = thickness; # = not measured; -, -- and --- = cracks at the interface; ++ = no cracks; coh. = cohesive

Ceramic coating	4-Point bend test					Pull-out test		
	Sand blasting	Sub layer type	$\frac{th_{ceramic}}{th_{total}}$ (2 samples)	Number of cracks on the surface (2 samples)	Sublayer /steel interface	Ceramic /sub-layer interface	Location of the fracture	Rupture strength (MPa)
Cr ₂ O ₃	YES	NO	1–1	Many fine cracks		++	Glue	>48
	YES	Ni-Cr	0.55–0.37	28–31	–	++	Glue + 5% coh.	>75
	YES	625	0.52–0.44	9–9	–	++	Glue + 3% coh.	>50
Cr ₂ O ₃ + Al ₂ O ₃	YES	NO	1–1	Many fine cracks		++	Glue	>50
	YES	Ni-Cr	0.76–0.46	Many fine cracks	---	--	Glue + 2% coh.	60
	NO	Ni-Cr	0.89	1–1	---	++	#	#
	YES	625	0.58–0.30	8–8	--	++	Glue	>76
	NO	625	0.08	1–1	---	++	#	#
WC+ (W,Cr)C +Ni	NO	NO	1–1	Many fine cracks		++	Glue + 50% coh.	About 55
	YES	Ni-Cr	0.71–0.39	38–38	–	++	Glue + 10% to 20% coh.	About 52
	YES	625	0.76–0.37	13–13	--	–	Glue	>37

3.3.2. Sub-layers

Without a sub-layer, the three ceramic coatings showed good adhesion characteristics: no decohesion at the ceramic/substrate interface was noticed after the four-point bend tests or after the pull-out test.

After the four-point bend test the cracks in all the coatings were very fine but did not have the same appearance (Fig. 4). The particular features were for Cr₂O₃: fine cracks perpendicular to the interface and regularly spaced in the coating ; for Cr₂O₃ + Al₂O₃: similar fine cracks perpendicular to the interface and regularly spaced were observed as in the pure Cr₂O₃ coating, but here fragments flew out during the test. (probably due to a decohesion between the Cr₂O₃ rich and the Al₂O₃ rich layers inside the ceramic coating); for WC+(W,Cr)C+Ni the cracks were very fine and formed a network in the ceramic layer.

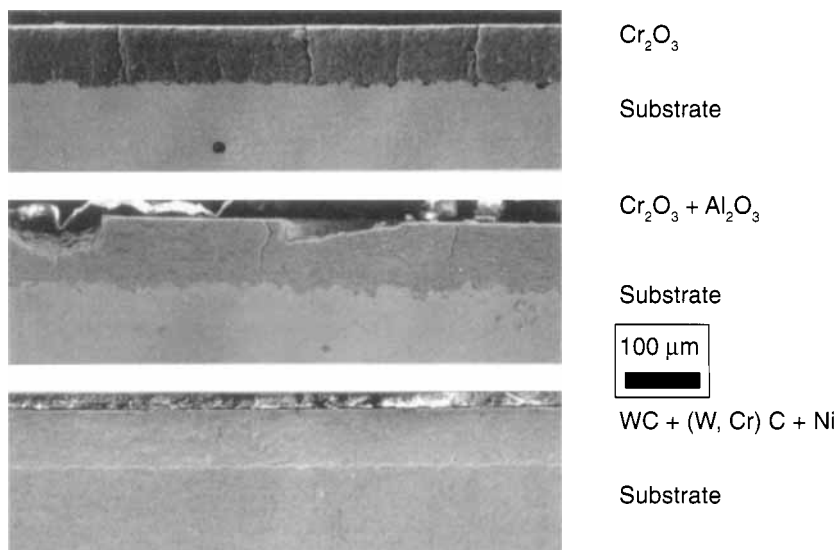


Fig. 4 Secondary electron micrographs of the three ceramic coatings after the 4-point bend test.

Whichever the ceramic coating, the same phenomenon was noticed with a sub-layer during the four-point bend test, that is, cracks perpendicular to the interfaces with some propagated along the interfaces. The sub-layer/substrate interface was always the weakest.

The resistance to cracking and interfacial decohesion correlates with the Ceramic thickness/Total thickness ratio.

Thus, if the thickness ratio is too large or too small, the fracture is quick and complete. For medium values of this thickness ratio (in this study, between about 0.30 and 0.76), the cracking of the coating is dependent on the type of sub-layer. Thus, in the case of a 625-type sub-layer, steps can be seen on the traction curves (Fig. 5). The cracks go through the ceramic and the sub-layer, and there is a quasi-continuous fracture at the sub-layer/substrate interface (Fig. 6), whereas in the case of a Ni–Cr sub-layer, only a change in the slope is visible (Fig. 5). The cracks also pass through the two layers, but there is no decohesion at the sub-layer/substrate interface (Fig. 6).

The results obtained with the pull-out test showed the good adhesion of the single or multilayer coatings to the substrate. The results show also that the rupture strength is independent of both the presence and type of the sub-layers.

The presence of a sub-layer is not necessary to obtain a good adhesion for the three kinds of ceramic coatings studied here.

As the sub-layer/substrate interface is weaker than the ceramic/sub-layer or ceramic/substrate interface, the risk of decohesion of the multilayer coatings is higher than that of a single ceramic coating. The severity of cracking under mechanical stress depends on the Ceramic thickness/Total thickness ratio and on the nature of the sub-layer.

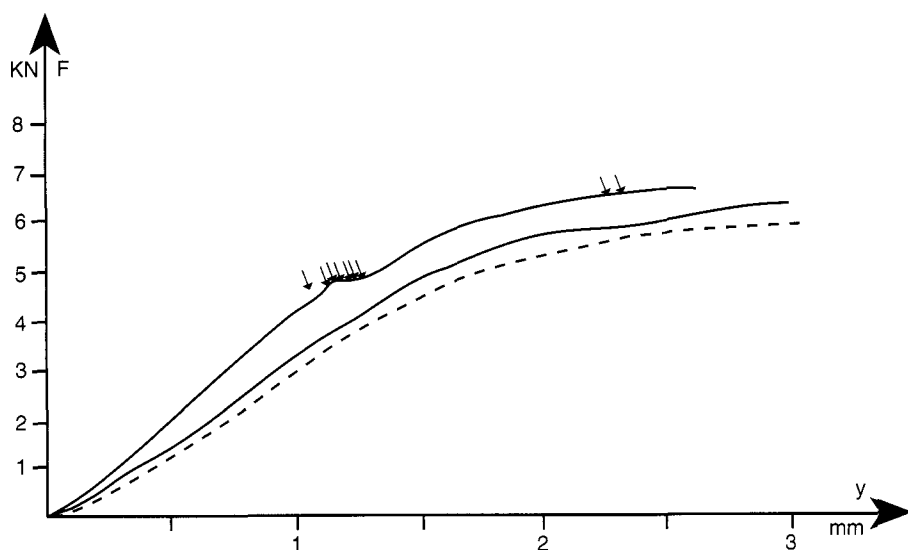


Fig. 5 Applied stress vs displacement curves during bending test.

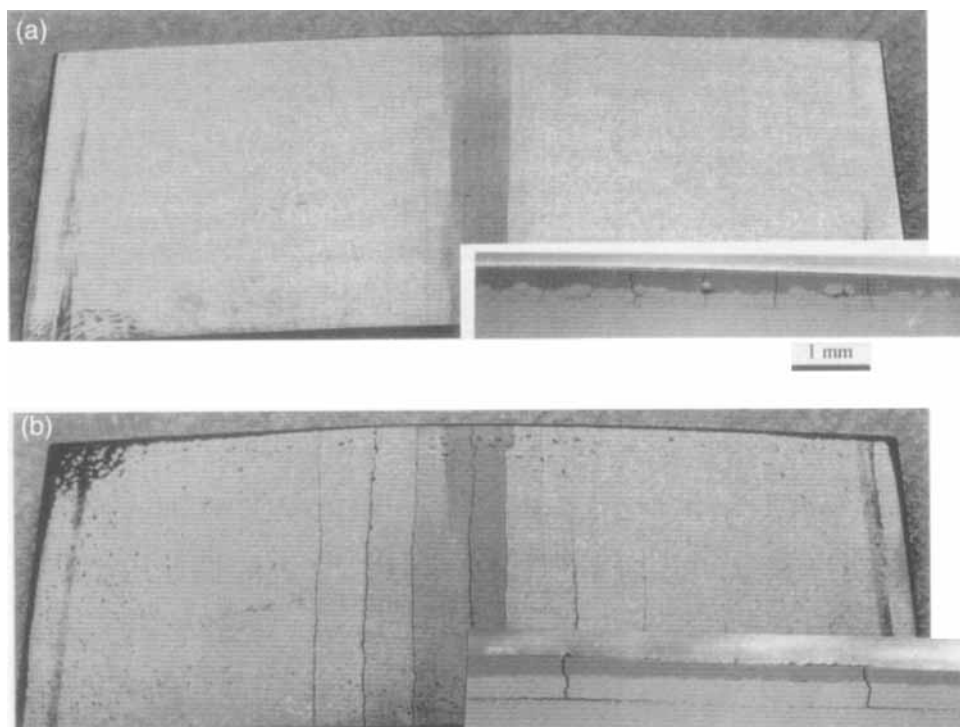


Fig. 6 Macroviews and secondary electron micrographs of the samples with Ni80Cr20 or 625-type sub-layer, after 4-point bend test. (a) Ceramic coating (Cr_2O_3) on a Ni80Cr20 sub-layer; (b) ceramic coating (Cr_2O_3) on a 625-type sub-layer.

4. Corrosion Behaviour

4.1. Characterisation

4.1.1. Electrochemical study

Free potential and potentiodynamic polarisation measurements were performed in naturally aerated synthetic seawater ($30 \text{ gL}^{-1} \text{ NaCl}$, pH8). The samples were embedded in resin so that only ceramic coated surfaces were exposed to the electrolyte. These samples were fixed to a rotating electrode (1000 rev/min). The reference electrode was a Saturated Calomel Electrode (SCE).

The free potential was measured for 8 h after immersion of the sample.

To plot the current density vs potential curves, the sample was polarised at -1200 mV during 10 min and then the scanning of potential was conducted at 1 mV s^{-1} .

4.1.2. Salt spray test

This test was carried out according to NF X 41 002 [9] (salt solution of 5% NaCl), at a temperature of 35°C and with a total exposure of $5 \times 8 \text{ h}$ (40 h). The samples were designed to reproduce the geometry of existing mechanical parts (Fig. 7). The coating was sprayed in a groove. The samples were inclined at 45° in the exposure chamber. Two samples were examined for each type of surface preparation.

4.1.3. Immersion

The samples, with the same geometry as those used for the salt spray tests, were immersed in a container containing natural seawater, at *ca.* 50 cm from the surface. The seawater was changed daily. The temperature of the seawater was maintained between 18 and 20°C .

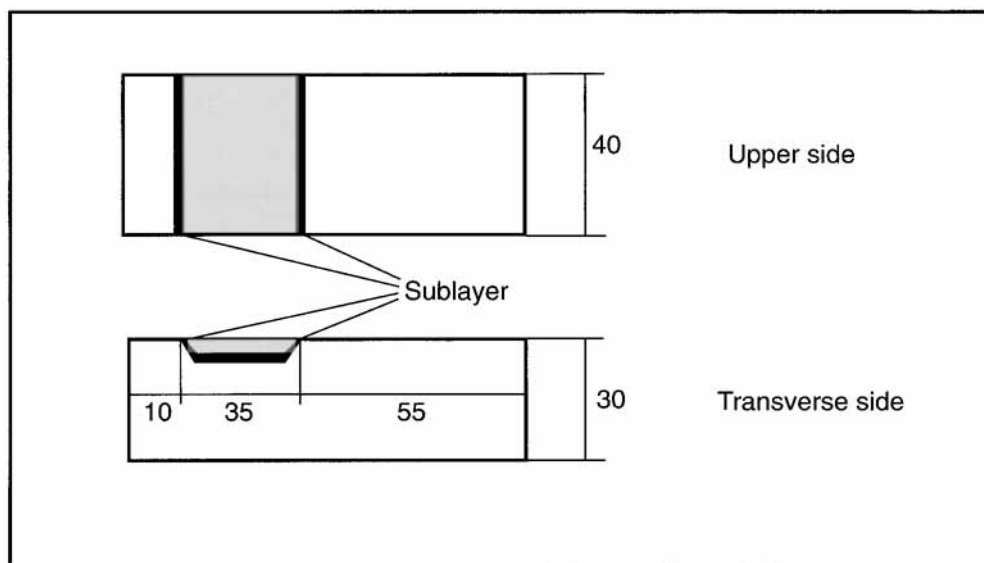


Fig. 7 Design of samples used for salt spray and immersion testing.

4.2. Results

4.2.1. Electrochemical study

Measurement of the free potential. The measurement of the free potential value for the various coatings is summarised in Table 3.

A difference of behaviour was noticed between the oxide and the carbide ceramic coatings. For the two kinds of oxide ceramic coatings without a sub-layer the free potential decreased (became more negative) with time. When a sub-layer was present under the ceramic, the free potential always increased with time. The obtained values tended to be more negative (less noble) for the samples with Ni80Cr20 than for the 625-type alloy sub-layer. For the carbide ceramic coating, the free potential always increased after 8 h, even without a sub-layer. In contrast to the results obtained with oxide coatings, the values obtained in this case with a sub-layer were more negative than without a sub-layer.

All these results show that the free potential of the samples depends mainly on the presence and the type of sub-layer which protects the steel substrate in the case of oxide coatings, and they confirm that the ceramic coatings are porous and that the electrolyte penetrates down to the ceramic/metal interface.

4.2.2. Potentiodynamic polarisation measurements

Typical current density vs potential curves are presented in Figs 8–10. The obtained values of corrosion current are always higher without a sub-layer. The highest corrosion current is obtained with the carbide coating. The corrosion current is the same for the two oxide coatings, although they have neither the same porosity nor the same microstructure. The corrosion current is nevertheless slightly lower for the

Table 3. Free potential with or without a sub-layer. Each value is the mean of two samples

Ceramic coating	Sand blasting	Sub-layer	Initial potential ($t = 0$) mV (SCE)	Final potential ($t = 8$ h) mV (SCE)
Cr ₂ O ₃	YES	–	–169	–215
	YES	Ni–Cr	–135	–82
	YES	625	–118	–45
Cr ₂ O ₃ + Al ₂ O ₃	YES	–	–183	–203
	YES	Ni–Cr	–128	–93
	YES	625	–117	–55
WC + (W, Cr) C+Ni	NO	–	–148	–80
	YES	Ni–Cr	–138	–96
	YES	625	–143	–109

less porous coating ($\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3$). In all cases, the shape of curves is the same for Ni80Cr20 and 625 type sub-layers.

The shape of the curves changes with the nature of the ceramic coating. For the Cr_2O_3 coating, an activity peak and a pitting potential appear when there is a sub-layer under the ceramic. For the $\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3$ coating this peak and a pitting potential do not appear. For WC + (W,Cr) C + Ni, one activity peak appears before passivation. The pitting potential is slightly less electronegative with a sub-layer.

In similar testing conditions [8], an activity peak was also observed for a $\text{Cr}_3\text{C}_2 + \text{Ni,Cr}$ coating without a sub-layer. This peak was due to the dissolution of the nickel binder of the ceramic coating. The same phenomenon can be observed for the WC + (W,Cr) C + Ni coating in the present study.

The record of the values of the potential for which the current density tends to zero (Fig. 11) shows that the samples coated with oxide and those coated with carbides had different behaviours:

- For the samples coated with oxide ceramics (Cr_2O_3 or $\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3$) the presence of a sub-layer gives less electronegative values (more noble materials). The values obtained for Ni80Cr20 and 625 alloy sub-layers are very close.
- For the WC + (W,Cr) C + Ni carbide ceramic coating, the values obtained are very close to those obtained in similar conditions for $\text{Cr}_3\text{C}_2 + \text{Ni,Cr}$ coatings without a sub-layer [8]. The presence of a sub-layer tends to decrease the potential values (the materials become less noble).

4.2.3. Salt spray results

For all single or multilayer coatings, the corrosion, when present, appeared as pitting of the ceramic/metal interfaces at the surface or on the edge of the samples (see geometry of the samples Fig. 7, and typical damage on Fig. 12) and at the sub-layer/metal interface.

One exception was obtained with the $\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3$ coating on a Ni80Cr20 sublayer: some corrosion products were observed over the whole surface. But in this case, it was noted that the ceramic layer was more microcracked before testing than in the case of the other samples.

The behaviour of all the ceramic coatings without a sub-layer was generally good. No effect of the sub-layer nature on the corrosion resistance was observed; similar results being obtained with the Ni80Cr20 and 625 type sub-layers.

4.2.4. Immersion results

The type of damage was the same as for salt spray testing, i.e. pitting at the interfaces exposed at the surface or at the edge of the samples.

The $\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3$ coating (the least porous of the three coatings) with or without sub-layer showed the best resistance to corrosion, i.e. having the smallest number of pits and crevices, and the smallest quantity of corrosion products.

The WC + (W,Cr) C + Ni coating with or without a sub-layer showed slightly more pits and corrosion products. The worst results were obtained with the Cr_2O_3 coating.

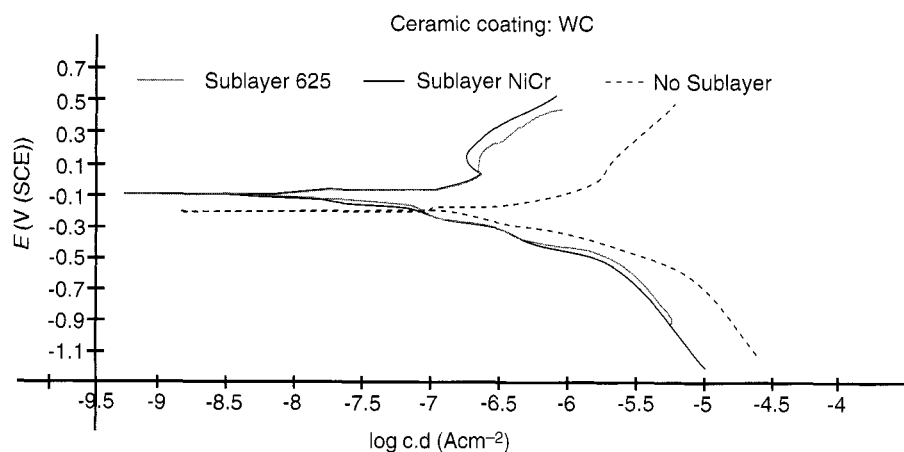


Fig. 8 Potentiodynamic polarisation curves of Cr_2O_3 coating with and without a sub-layer.

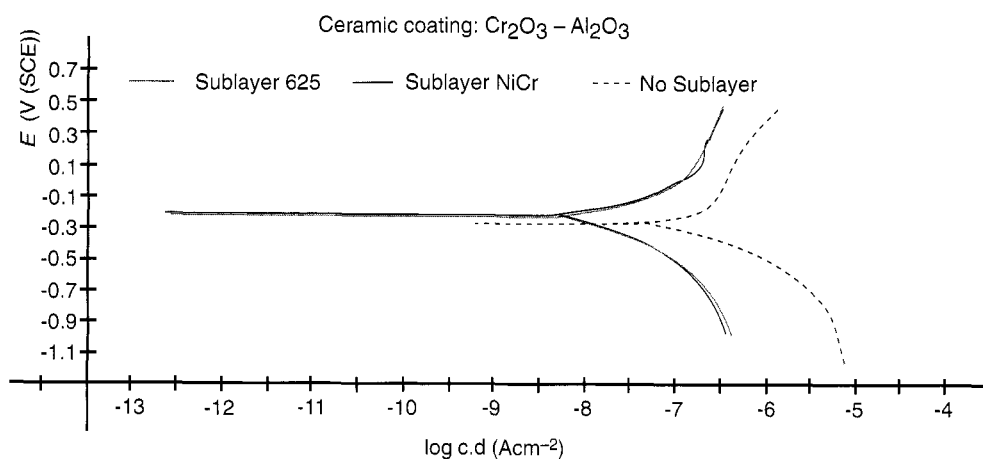


Fig. 9 Potentiodynamic polarisation curves of Cr_2O_3 coating with and without a sub-layer.

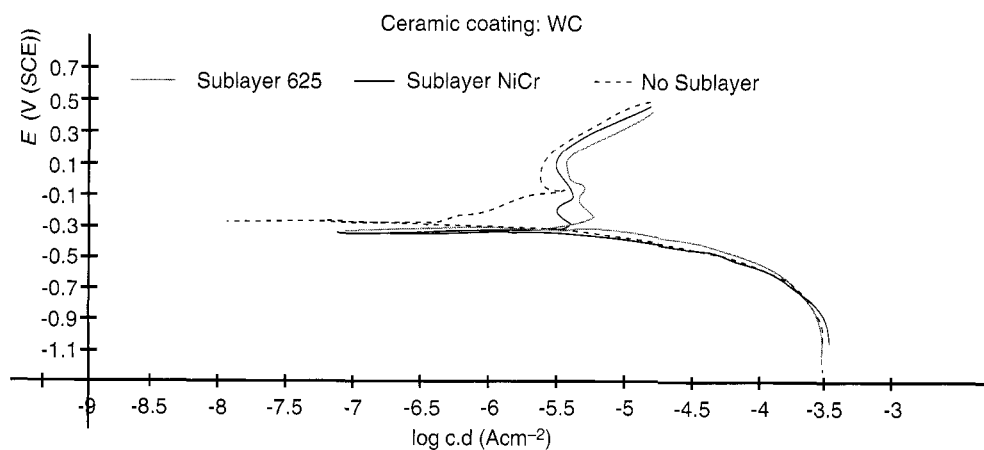


Fig. 10 Potentiodynamic polarisation curves of Cr_2O_3 coating with and without a sub-layer.

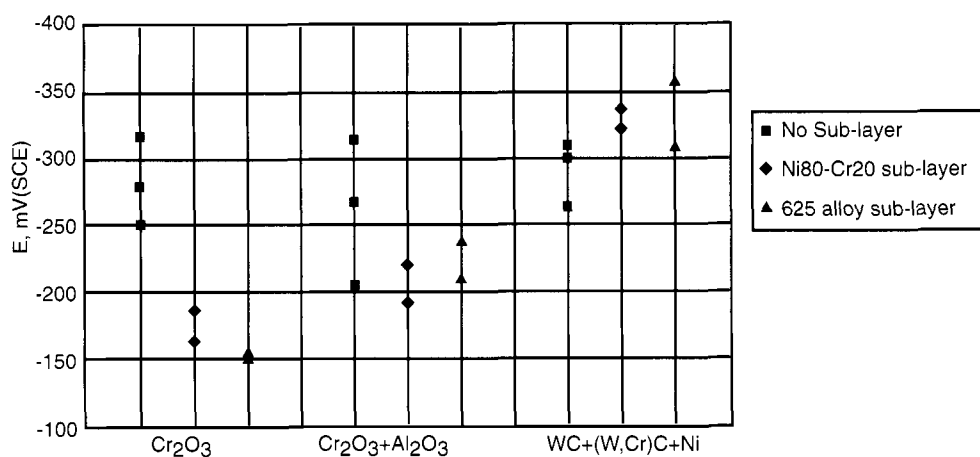


Fig. 11 Results of the potentiodynamic study: values of E at $(i = 0)$ for the different single or multilayer coatings.

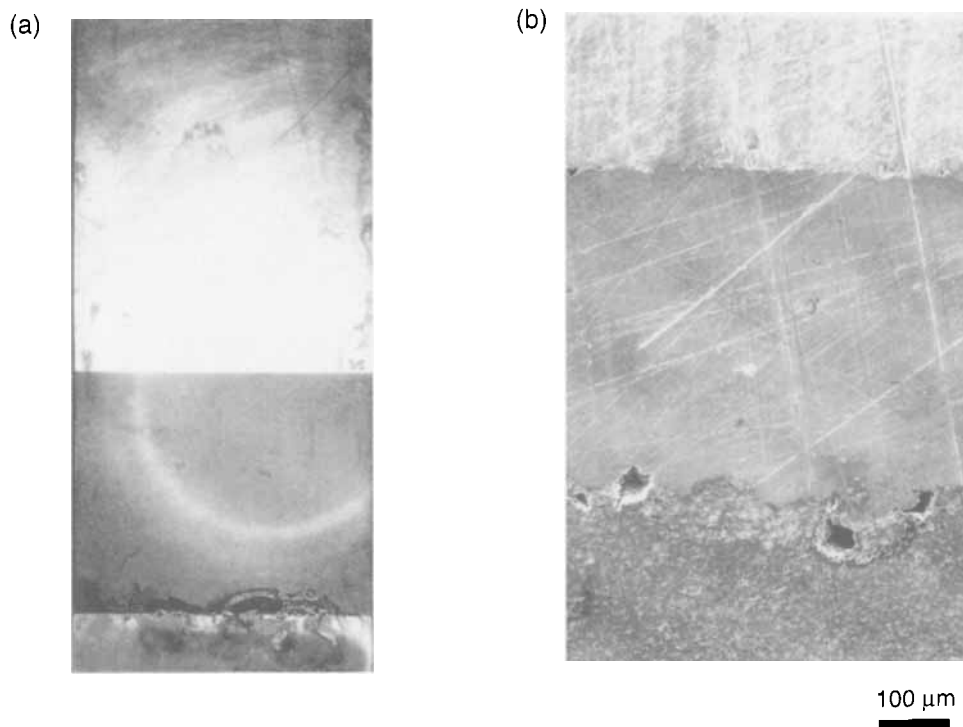


Fig. 12 Typical damage of a sample (Cr_2O_3 coating on a Ni80Cr20 sublayer) after salt spray testing. (a) Macroview; (b) SEM image after cleaning.

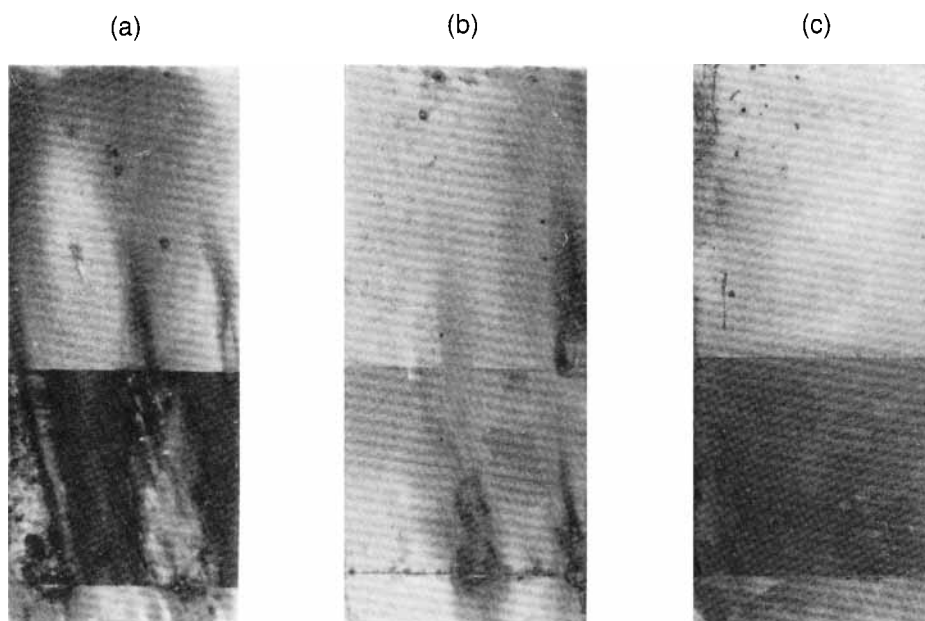


Fig. 13 Typical damage of samples after seawater immersion testing. (a) Cr_2O_3 without a sub-layer; (b) WC + (W,Cr)C + Ni with a Ni80Cr20 sub-layer; and (c) WC + (W,Cr)C + Ni with a 625-type sub-layer.

4.3. Influence of the Substrate Surface Treatment on Corrosion

4.3.1. Sandblasting

Sandblasting the substrate was observed to have no influence on the potentiodynamic polarisation curves of the ceramic coatings.

4.3.2. Sub-layers

The electrochemical study is well adapted to show the effect of the type of sub-layer on the corrosion resistance. It is more sensitive than the exposure tests, because in the exposure test the geometry of the end edge of the ceramic coating is the main parameter governing the formation of pitting and crevices at the interfaces. Such a preferential attack at the edge between the ceramic coating and the adjacent uncoated surface has already been observed by the authors after seawater exposure [9].

For all the ceramic coatings the effects on corrosion resistance of Ni80Cr20 and NiCr21Mo9 Nb4 (625 type) sub-layers are the same; the two sub-layers have the same effects on potential, corrosion current, and resistance to corrosion during salt spray and immersion testing.

For the oxide ceramic coatings, the presence of a sub-layer has a positive effect on corrosion control as shown by the increase of the corrosion potential and the lowering of the corrosion current: the electrolyte goes through the porosity to the ceramic/sub-layer interface which is less active than the ceramic/substrate interface. The same protective effect has been reported by other authors using a titanium sub-layer

under a titanium nitride coating [3], and also with NiCr and NiCrAlY sub-layers under Cr_2O_3 , ZrO_2 and Al_2O_3 coatings [4].

For the carbide ceramic coating, the presence of a sub-layer did not have the same effect. In this case, the potential was more electronegative in the presence of a sub-layer and there was no decrease of the corrosion current. Nevertheless, a larger passivation plateau appears on all the potentiodynamic polarisation curves, and the pitting potential is thus higher.

In addition, the ceramic coating itself is sensitive to corrosion: a dissolution of the nickel binder may occur, as shown by the activity peak on the potentiostatic polarisation curves.

It is not easy to conclude whether the presence of a sub-layer is, or is not, an advantage in this case.

5. Concluding Remarks

The object of this study was to determine the influence of the substrate preparation on the adhesion and corrosion resistance of various ceramic coatings.

The four-point bend test has been useful for obtaining a good comparison of the adhesion properties of the various coatings.

Electrochemical measurements have provided a quick method for evaluating the corrosion performance of the coatings but the interpretation of the various phenomena was difficult because of the complex microstructure of the coatings (volume and shape of porosities, phases, etc...).

Correlation of electrochemical results and exposure tests was not possible due to the shape of the specimens exposed to the seawater. Thus, it could not identify the 'intrinsic' corrosion resistance of the single or multilayer coatings since the particularly weakest corrosion points occurred at the interfaces exposed to the seawater. Nevertheless, it showed that the geometry of the part and the limits of the coating in contact with the seawater are very important parameters: even with a very good coating, corrosion damage may rapidly appear if interfaces are exposed to the seawater.

The substrate sandblasting was without effect both on adhesion and corrosion control. It would be better to avoid this step during the spraying process.

The presence of a sub-layer is not necessary to obtain good adhesion of the three kinds of ceramic coating studied here. The sub-layer/substrate interface is weaker than the ceramic/sub-layer or ceramic/substrate interface. Thus, the risk of decohesion of the multilayer coatings is higher than that of a single ceramic coating. The severity of cracking under mechanical stress depends on the thickness ratio of the ceramic and the sub-layer, and on the nature of this sub-layer: the Ni80Cr20 sub-layer gives a finer and more progressive cracking than the NiCr21Mo9Nb4 sub-layer when the coating is subject to mechanical stresses.

The electrochemical measurements have confirmed that all the ceramic coatings are porous. The Ni80Cr20 and NiCr21Mo9Nb4 sub-layers behaved similarly with respect to corrosion control, although a small advantage was noticed for the NiCr21Mo9Nb4 sub-layer.

For both oxide ceramic coatings, the presence of a sub-layer has a beneficial effect

on corrosion control but for the carbide coating it is not possible to conclude whether the presence of a sub-layer is beneficial.

6. Acknowledgements

Microstructural characterisation and four point bending tests were carried out at the CESMAN of DCN Indret. The authors wish to thanks all the staff and particularly J. M. Corrieu for his contribution. The pull-out tests were conducted by the ENSAM Paris (Prof. Le Brun).

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Cementitious Coatings: An Approach to Environmentally Friendly Corrosion Protection?

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ABSTRACT

Cementitious mortar coats have been successfully employed for corrosion protection of steel reinforcements in the course of concrete rehabilitation. The use of such coats for other corrosion protection applications would offer several advantages, such as good protective properties and insensitivity to rusty substrates. Because of the extremely low content of volatile organic compounds (VOC) they would also be environmentally friendly. However, there are some reservations concerning carbonation and also the rapid evaporation of the mixing water during the application since the latter will affect the setting process. Finally, the application of the coating is likely to cause difficulties.

An investigation was conducted to examine the behaviour of epoxy modified (ECC) and polymer modified (PCC) type mortars with and without top coats, both on blast cleaned and on manually cleaned steel substrates. As expected, the application of the mortars posed serious problems. Apart from this, the results were very encouraging. It was of interest that the results of accelerated tests as well as of natural weathering ranked mortar coats without an additional top coat as among the best. It is worth noting, that even after 8 years of natural weathering the alkalinity and, as a result of this, the passivity of the steel, had been maintained.

1. Introduction

By tradition and long experience concrete has come to be accepted as a durable construction material. Due to its inherently high alkalinity it affords outstanding corrosion protection to steel reinforcement embedded in it. However, as unpleasant experiences have taught, environmental influences can often threaten this useful characteristic. For example, chloride ions, penetrating into the concrete, can initiate pitting corrosion, and atmospheric CO₂ can lower the pH value by carbonation of the cementitious matrix and thereby promote corrosion of poorly covered rebars.

In view of the enormous economical significance, the development of sophisticated methods like electrochemical realkalisation [1] or electrochemical removal of chlorides [2] for repairing damaged concrete buildings is not surprising. In numerous cases, however, concrete repair is a much simpler procedure, encompassing, among others, the following steps: (a) uncovering of the corroding rebars, (b) derusting them or, at least, removing loose rust layers, and (c), application of a corrosion protective coat, which nowadays is most frequently some kind of polymer modified cementitious mortar.

The following question then arises: Why should such mortar coats not be used for other corrosion applications? These would offer several advantages as follows:

- The good corrosion protective properties of cementitious materials are well established.
- An extremely low VOC content would render such materials environmentally friendly.
- They should also be more tolerant than the more commonly used organic coatings to rusty steel substrates.

But there would also be some reservations:

- Thin and extended mortar layers are likely to suffer early carbonation. This problem could be overcome by the use of top coats, which, consequently, were originally considered to be essential.
- Rapid evaporation of the mixing water could create defects such as shrinkage cracks. Top coats could also prevent this. However, would it always be possible in practice to apply the top coat sufficiently quickly?
- Another reservation concerns the applicability. If it is not intended to develop new materials, difficulties would be very likely to arise where application is to relatively smooth and extended steel surfaces for which the existing mixes were not designed.

An investigation was therefore set up to study these problems.

2. Experimental

Two different types of polymer modified cementitious mortars were selected as base coats, both with and without corrosion inhibitive agent. Table 1 shows some characteristics. The abbreviations 'PCC' and 'ECC' are technical terms in mortar technology. 'PCC' refers to 'polymer modified' in general, and 'ECC' stands for 'epoxy modified' in particular. Within this paper, the extensions 'm' and 'o' were introduced in order to distinguish between mortars with and without corrosion inhibitive agent, respectively. A combination of sodium nitrite, organic acids and aliphatic amines was used as the corrosion inhibitor.

Originally, these mortars were designed for concrete repair applications. In order to enhance the contrast, they were green-coloured. Although irrelevant within this study, the green colour shade nevertheless rendered efflorescences far more visible than would have been the case with the grey colour of conventional mortars.

The top coats according to Table 2 were standard organic coatings. (Further top coats were examined in an additional test series. One of these tests was set up to assess possible effects of the time interval, i.e. 3 h to 7 days, between the application

Table 1. Cementitious mortar base coats

Type of mortar	Modifying resin	Corrosion inhibitor	Maximum grain size (mm)	Water/cement ratio
ECCm	Epoxy resin	Present	0.25	<0.5
ECCo	Epoxy resin	Absent	0.25	<0.5
PCCm	Acrylic resin	Present	0.25	<0.5
PCCm	Acrylic resin	Absent	0.25	<0.5

of base and top coat. No detrimental effects could be detected. However, this problem has not yet been definitively settled, because the result was obtained only in laboratory applications. (In field applications, e.g. as influenced by direct sunlight, the result could be quite different.)

Prior to coating, steel panels were prepared by blast cleaning to Sa 3 according to DIN 55 928 and by manual wire-brushing to approximately C St 1 according to SIS 05 5900.

The application of the mortars posed problems, as expected. Application by brush or roller was quite unsatisfactory. Only air spraying turned out to be possible and this required the grouts to be diluted with 1% of water in excess of the recommended water/cement ratio. Even then the spraying output remained rather poor, just sufficient for laboratory work, but by no means acceptable for field applications.

Each material was applied as a single and as a double layer coat. The layer thicknesses of the cementitious base coats were 0.5 and 1 mm, respectively. (0.5 mm was twice the maximum grain size; less is not advisable.) The build of the top coats ranged approximately from 50 to 150 μm , depending on the individual specifications. After coating all test panels were deliberately damaged by grinding the edges to the bare metal.

The use of mortars for the original area of application, i.e., for coating reinforcing bars, is already well established and so only the behaviour of the individual coating systems in natural environmental conditions needed to be examined. The Kesternich

Table 2. Organic top coats

No.	Type of top coat
0	No top coat
1	Epoxy resin, waterborne
2	Acrylic dispersion
3	Modified epoxy resin, solvent based

test (condensation water test with SO₂ DIN 50 018) was initially intended as the only accelerated test. However, after 8 weeks of testing no signs of deterioration were visible. So the test was stopped and the same specimens were then subjected to the (continuous) condensation water test as for DIN 50 017 for another 10 weeks. In addition to accelerated testing, outdoor exposure for 8 years was conducted.

Both accelerated and outdoor testing conditions caused undercutting and/or delamination at the originally polished edge. During accelerated testing, but curiously not during natural weathering, blisters were also formed. These occurred between top and base coat as well as between base coat and substrate. Pull-off tests for adhesion were also conducted, but did not provide any further information.

3. Results of Accelerated Testing

Regardless of the presence or absence of a top coat, all samples exhibited strong efflorescences and/or blushing, which rendered the visual appearance rather poor. Except with ECCm, all uncoated mortars on blast cleaned substrates showed some rust spots ($\leq$ Ri 1, ISO 4628/3), which, however, were not considered to be serious. (This point will be referred to later.) In the following description of results, these rust spots as well as efflorescences are left out of further consideration.

Figures 1 and 2 represent the behaviour of the mortar base coats after accelerated testing, both on blast cleaned and manually cleaned substrates. The relative performance was derived by subtracting points from 10, according to the degree of blistering and delamination.

The result is remarkably clear. The different coating systems either passed the test without, or with only minor, damage, or they failed completely.

ECCo performed best. All other mortars suffered at least one breakdown. In particular, the materials containing corrosion inhibitors turned out to be vulnerable to the conditions of testing, owing to a tendency of the inhibitive agent to support

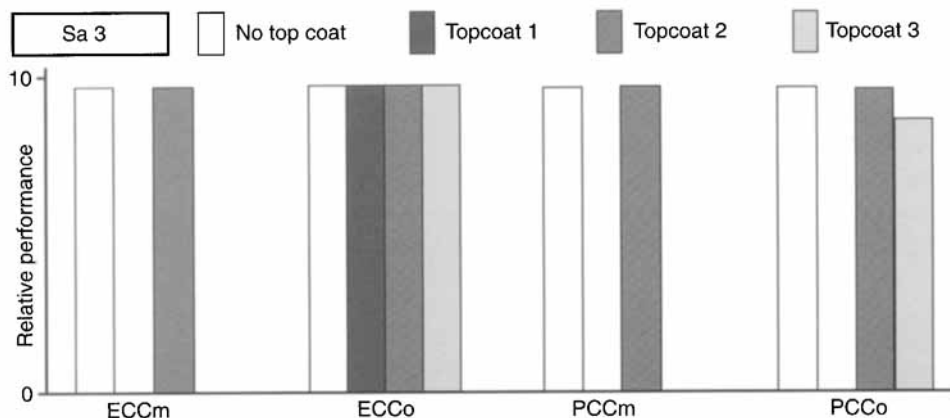


Fig. 1 Accelerated testing, performance of the mortar base coats. Surface preparation: Blast cleaning.

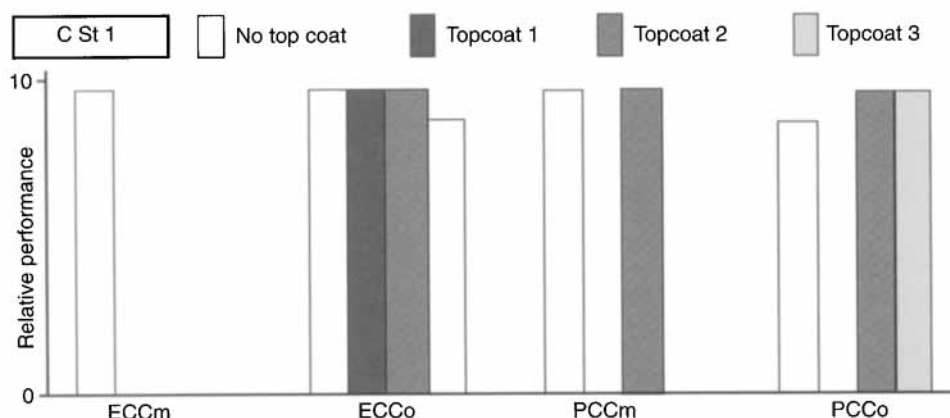


Fig. 2 Accelerated testing, performance of the mortar base coats. Surface preparation: Manual derusting.

blistering. On the other hand, no significant difference between substrate types could be detected.

Adhesion tests also confirmed this. With regard to the breaking strength, exactly half of all coating systems did better on Sa 3 substrate, and with the other half the opposite happened. Concerning the exposed substrate area, the relation was slightly in favour of the St 1 substrate, but the effect was too small to be statistically significant.

However, there is another point of view. Figures 3 and 4 show exactly the same test results, but in a different representation, emphasising the performance of the individual top coats (including no top coat at all) rather than the behaviour of the mortar base coats.

It can clearly be recognised, that not only ECCo, but all uncoated mortars behaved very well on both substrate types, regardless of the presence of corrosion inhibitor. This led to the conclusion, that it was mainly the top coats that were responsible for the failures, though the inhibitor may also have made some contribution.

This observation is particularly valid for the waterborne epoxy topcoat (1), which in the majority of cases yielded disastrous results. The solvent based epoxy top coat (3) was also not the very best, whereas the acrylic top coat (2) exhibited a fairly good performance.

4. Results of Natural Weathering

The test specimens were inspected in a non-destructive manner after 14 months and after 3 years. Delamination at the edge was the main effect encountered, and this, for some samples, was typically linked to the top coat (1), and amounted to a dramatic 20–30% of the whole area. These panels were eliminated at an early stage while the rest remained under test.

After 8 years of exterior exposure the remaining test specimens were subjected to a destructive, final examination. As with accelerated testing, the uncoated mortars on blast cleaned substrates showed some rust spots, except in the case of ECCm.

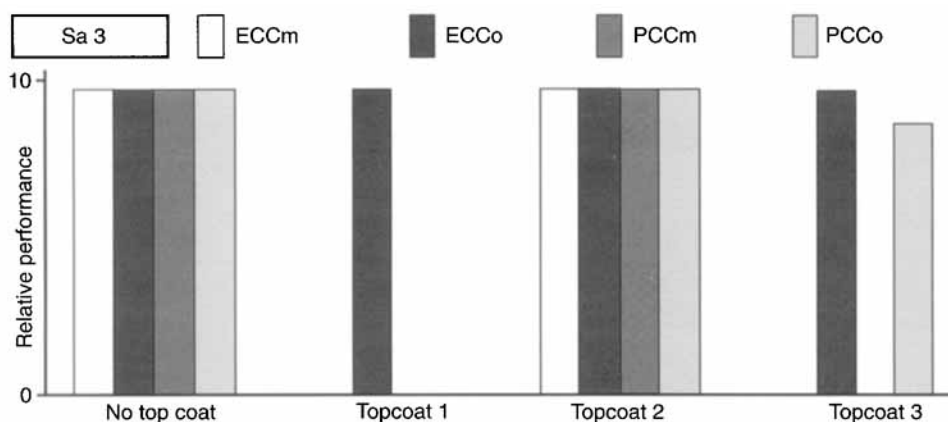


Fig. 3 Accelerated testing, performance of the top coats. Surface preparation: Blast cleaning.

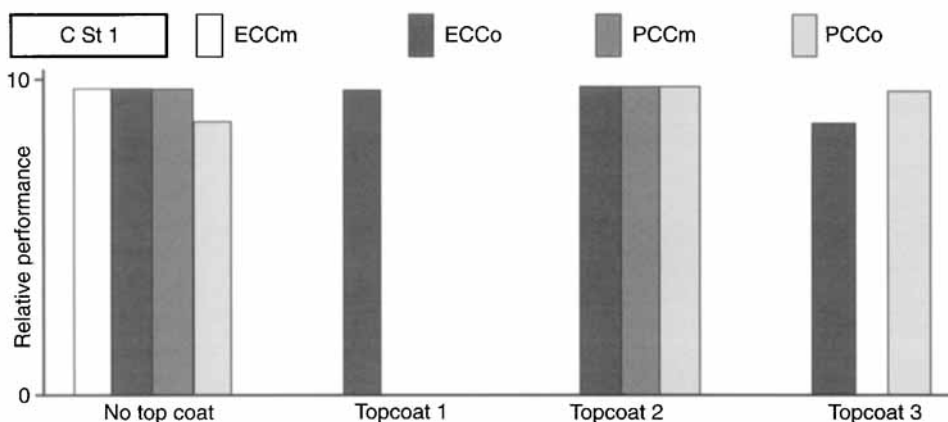


Fig. 4 Accelerated testing, performance of the top coats. Surface preparation: Manual derusting.

These spots were already present during the first examination, and subsequently no further propagation took place.

It was therefore assumed, that the rust spots were already formed during or soon after the application. It is well known, that freshly mixed cement paste can be rather corrosive, because the pH value has not yet reached its final level, and soluble sulphate and chloride ions are still present [3]. During the setting process both conditions improve, thus stopping the early rust formation. This would also explain, why no such rust spots appeared on St 1 substrates, where the rust layer acted as a protective barrier. Some deterioration affecting the visual appearance was also observable, e.g. chalking of the epoxy based top coats. This, however, is not discussed further here.

All in all, the result of outdoor exposure is rather similar to the outcome of accelerated testing, though sometimes the differences among the individual materials are less pronounced.

Figures 5 and 6 describe the conditions of the mortar base coats after 8 years of

natural weathering. As has already been mentioned, blistering was unimportant. Therefore, the 10 minus % of delamination per unit area was chosen as the rating number. However, this gives a rather magnified view of the degradation. As an example, PCCo without top coat on manually cleaned substrate looks rather poor (Fig. 6), and yet, 3% of delamination at the originally polished edge after 8 years of natural weathering is not serious.

The outstanding performance of ECCo remained unchallenged. However, ECCm, though not superior, outperformed both PCCs, which was not the case after accelerated testing. There is also an indication that manually cleaned steel substrates are more critical, because the majority of failures was linked to this type of substrate. Adhesion tests reveals a similar tendency.

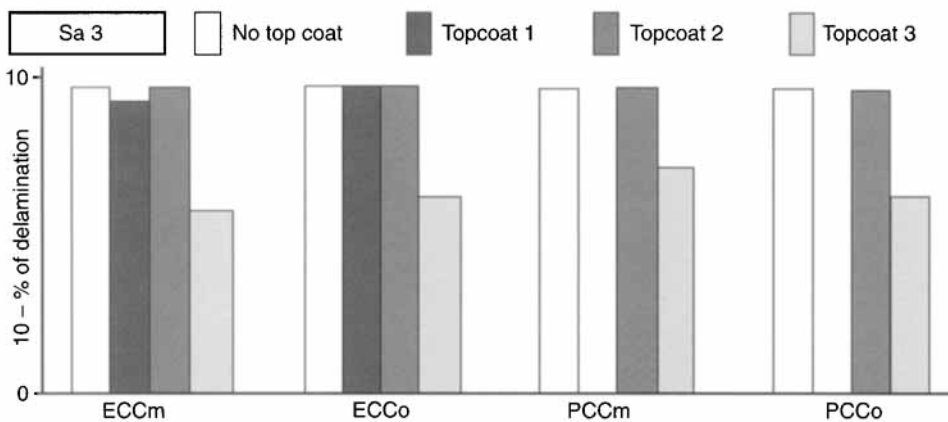


Fig. 5 Natural weathering, performance of the mortar base coats. Surface preparation: Blast cleaning.

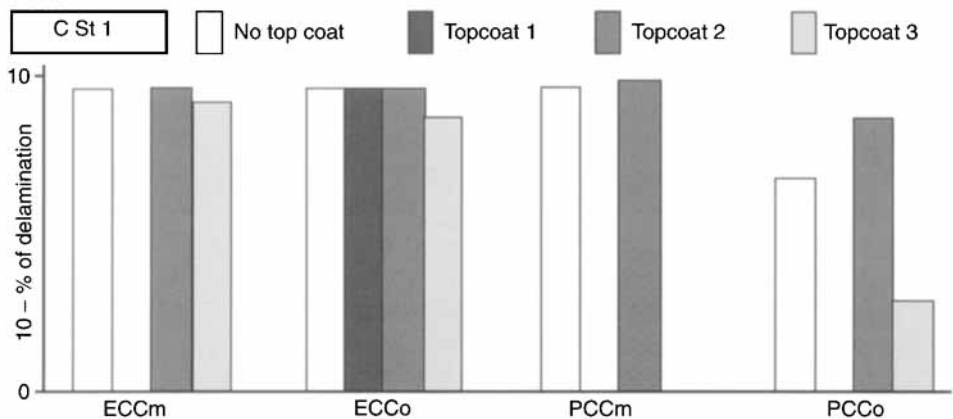


Fig. 6 Natural weathering, performance of the mortar base coats. Surface preparation: Manual derusting.

The conditions of the top coats can be seen on Fig. 7 and 8. Once more, all uncoated mortars behaved very well. The performance order of the top coats also remained unaltered, but the acrylic top coat (2) performed well without any reservations, and better than in accelerated testing.

By bending the panels, small strips of the coats were splintered off, enabling a partial inspection of the steel surface to be made. As an example, the left hand part of Plate 1 shows the ECCm mortar without top coat. No traces of rust are visible inside both strips, neither on the steel surface nor at the edges.

However, the positive reaction of the well known alkalinity test with phenolphthalein was completely unexpected (Plate 1, right hand.) It was difficult to believe that such a thin and unprotected mortar layer should be able to retain its alkalinity during 8 years of natural weathering. But all other test samples exhibited the same behaviour, regardless of whether a top coat was present or whether the substrate was blast cleaned or manually cleaned.

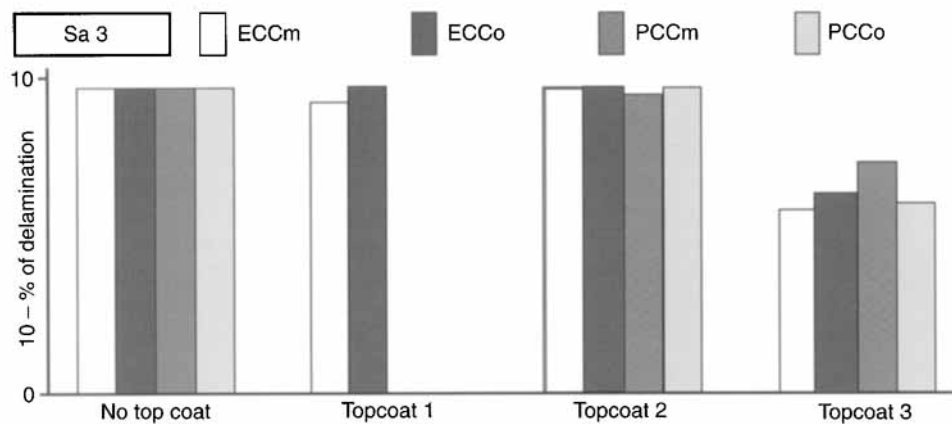


Fig. 7 Natural weathering, performance of the top coats. Surface preparation: Blast cleaning.

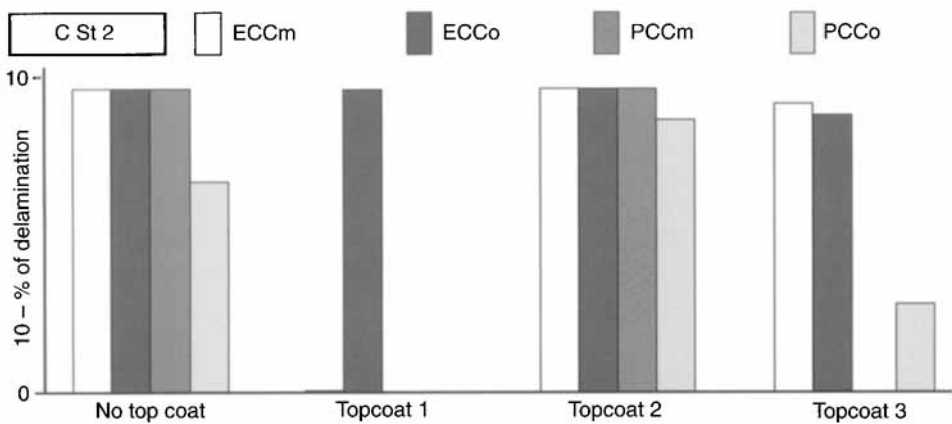


Fig. 8 Natural weathering, performance of the top coats. Surface preparation: Manual derusting.

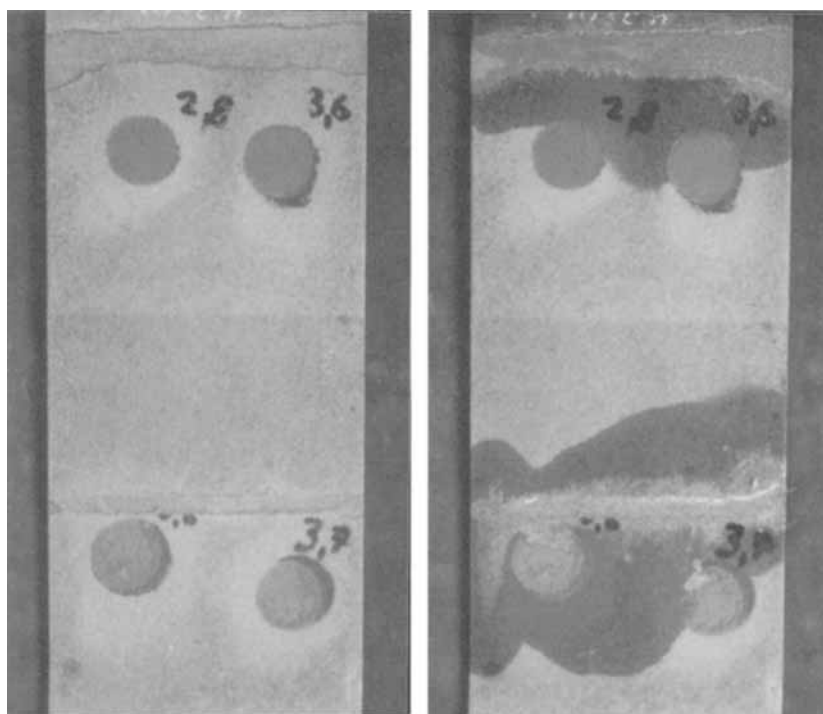


Plate 1. ECCm without topcoat on blast cleaned substrate. Left: Prior to the alkalinity test. Right: Positive reaction of the alkalinity test.

In addition, potential measurements clearly revealed that the steel was still passive. Table 3 gives the potential of the test samples without top coat. The more positive potentials related to the St 1 substrate and may be due to the presence of soluble iron salts in the rust layer.

The preservation of the passivity was definitely the most striking result of this investigation!

5. Conclusions

Polymer modified cementitious mortars in particular of the (epoxy) ECC type, used as conventional corrosion protective materials, proved to be very promising. Applied to blast cleaned as well as to manually cleaned steel surfaces, they exhibited excellent resistance to natural weathering. Top coats are not mandatory, and may be even detrimental. Nevertheless, if desired, top coating will be possible, provided that only thoroughly selected materials are used.

There are also disadvantages. For instance, the aesthetic appearance is rather unfavourable. The main drawback, however, is the poor applicability. Air spraying is only acceptable for laboratory work, but not for field applications. Sometimes mortar spraying, known under the trade term 'Shotcrete' or 'Gunité', may be feasible. But for a general solution of this problem further development efforts are needed.

Table 3. Potentials, mV (SHE)

Type of mortar	C St 1	Sa 3
ECCm	+115	+10
ECCo	+140	+45
PCCm	+90	+10
PCCo	+210	+35

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List of Abbreviations

Abbreviations used both in the text and in the index.

AES	Auger Electron Spectroscopy	PCC	Polymer modified mortar
CPE	Constant Phase Element	PVC	Polyvinyl Chloride (also)
		PVC	Pigment Volume Concentration
DCP	Direct Current Plasma	SAL	Sulfate–Acetate–Lactic Acid (bath)
DSC	Differential Scanning Calorimetry	SE	Spectroscopic ellipsometry
ECC	Epoxy modified mortar	SEM	Scanning Electron Microscopy
EDXA	Energy Dispersive X-ray Analysis	SGMP	Sulfate–Glycine–Malic acid–Na propionate (bath)
EIS	Electrochemical Impedance Spectroscopy		
ENM	Electrochemical Noise method	TEOS	Tetra Ethyl Ortho Silicate
EPMA	Electron Probe Microanalysis	TEM	Transmission Electron Microscopy
		TOF SIMS	Time Of Flight Secondary Ion Mass Spectroscopy
GA	Galvanneal		
		UPD	Under Potential Deposition
HD	Hot Dipped		
h.e.r.	Hydrogen evolution reaction	VOC	Volatile Organic Compounds
HVOF	High Velocity Oxygen Fuel		
		XRD	X-Ray Diffraction
ICP	Inductively Coupled Plasma Spectroscopy	XPS	X-ray Photoelectron Spectroscopy
MIO	Micaceous Iron Oxide	ZREP	Zinc Rich Epoxy Paint
MOCVD	Metallorganic Chemical Vapour Deposition	ZRP	Zinc Rich Paint

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