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Sol-gel protective coatings for metals

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32 SOL-GEL PROTECTIVE COATINGS FOR METALS

32.1 Introduction

32.2 Corrosion Concepts

Corrosion is a phenomenon that occurs spontaneously in the majority of metals and alloys as a result of their interaction with their environment, which makes them tend towards a situation of stable balance. According to the definition given by the European Corrosion Federation (1974), corrosion is the attack on a metal caused by its reaction to the environment, with the consequent degradation of its properties (Uhlig 1985; Andrade 1991). This environment could either be an electrolyte, which is when the process is called *electrochemical corrosion*, or another high-temperature atmosphere, when it is called, *oxidation*, *dry corrosion* or *high-temperature corrosion*.

High-temperature or dry corrosion is of great technological importance, even though it is not as common as electrochemical corrosion. This degradation process is the result of the direct reaction between the atoms of the metal surface and aggressive gas at high temperatures. It takes place in accordance with thermodynamics –the tendency to form the combined species- and because of the kinetics of the reactions that intervene at high temperatures. In principle, regardless of the atmosphere in which we find ourselves, high-temperature corrosion problems usually start when the materials are working in a temperature range of between 30-40% of their fusion temperature. This implies that, for aluminium and its alloys, this process will start at relatively low temperatures, around 200°C; in carbon steels at temperatures below 425°C and, in stainless steels in a somewhat wider range between 425 and 800°C.

The composition of the gas surrounding the metal conditions the type of reaction that will take place on the metal surface: oxidation (O_2), sulfidation (SO_2), cementation (CO_2/CO), hydrogen (decarburisation) or the formation of volatile haloids.

In the process of oxidation, first, the oxidants are adsorbed on the metal surface, forming a metal-oxygen bond. As there is chemical affinity between the metal and the oxidant, the chemically adsorbed coat changes to the state of an oxide coat. Figure 32.1 shows schematically what the ionic and electronic transfer would be like during the process of the oxidation of iron. At a first stage, Fe^{2+} ions would be formed and electrons released. These move through the layer of oxide from the metal/oxide interface towards

the outside, the oxide/atmosphere interface. The oxygen that reaches the most external interface reacts with the electrons and is incorporated into the oxide. Thus, a concentration gradient of Fe^{2+} and O^- ions is created in the oxide which activates their exit and entry, respectively, causing the layer of oxide to grow.

(insert Figure 32.1)

Thus, to adequately protect metals against this degradation process, the protective coatings employed must prevent the ionic diffusion of both the aggressive gas and the metal ions and electronic conduction.

Electrochemical corrosion is more common because of the larger volume of material exposed to the atmosphere and to room temperature.

The basic fundamentals of this type of corrosion are established on the basis of the concept of the electrochemical cell. Generally speaking, metal materials are heterogeneous. Their constituents (precipitates, phases, intermetallic, different orientation of the grains, tensions, grain boundaries, etc.) have a different electrochemical nature, which leads to the appearance of noble areas (cathodes), together with less noble areas (anodes). These cause the formation of micro-cells when they come into contact with an aqueous medium. When the phenomenon of corrosion occurs, the electrodes that act as anodes dissolve, releasing metal ions into the solution, while at the same time the oxidant is reduced in the cathodes. Thus, the corrosion process is constituted by two partial semi-reactions:

a) Oxidation reaction

(for instance: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$; $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$; $\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$)

where the electrons are produced. These are transported through the inside of the metal to the cathode, where they are consumed in the reduction reaction.

b) Reduction reaction.

Depending on the medium, this cathode reaction may be of the following types:

- aereated acid media : $\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$
- deaereated acid media: $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$
- aereated neutral or alkaline media: $\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$
- deaereated neutral or alkaline media: $2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$

although a reduction reaction of the metal itself or, even, deposit reactions are also possible.

There is wide variety of protection methods, which try to attack the corrosion problems from different fronts: by modifying the medium in an attempt to reduce its aggressiveness, by seeking a suitable design for the material according to the aggressive working conditions, by acting on the metal taking it to areas of passivity, or by using protective coatings which isolate the metal material from the aggressive medium in which it performs its work.

Protective coatings can be of different types and may be layers deposited on the metal surface or superficial modifications induced on the most external layers of the metal material. Table 32.1 shows a wide variety of coatings used to protect different metal substrates.

[\(insert Table 32.1\)](#)

32.3 Protective Coatings

The techniques for modifying the surface make it possible to alter the structure or composition of a substrate or generate a new material on it in order to obtain coatings. These can be deposited with a view to improving the metal substrate or providing it one or several properties such as its capacity to act as a barrier, improve resistance to wear, scratching, impact, etc. Undoubtedly one of the most important uses of coatings is their capacity to enhance resistance to corrosion, by depositing barriers that isolate the metal surface from the aggressive medium surrounding it.

Thanks to the development of new deposition and analysis techniques, the development and synthesis of coatings has boomed in recent years, making it possible to obtain a wide variety of coatings with very different properties and compositions. This means that versatility is the fundamental characteristic of this area of research. Table 32.2 shows some of the methods that can currently be used to obtain protective coatings.

[\(insert Table 32.2\)](#)

All of these methods also lead to a wide variety of compositions, so that coatings can be classified roughly into: metal, polymers and ceramic or vitreous.

32.3.1 Metal Coatings

In general, *metal coatings* consist of the generation on a metal substrate of another metal or alloy with improved properties with respect to the base. They may be obtained through traditional techniques, such as dipping or electrodepositing, or by more sophisticated techniques such as laser or thermal spray which today are already implanted at the industrial level. On many occasions, the use of metallic coatings instead of polymer coatings is considered, because the preparation of thicker layers is easier, the adherence is greater and because of properties such as good wetability, ease of application and resistance to corrosion (Palma 1998; Marder 2000).

32.3.2 Polymer Coatings

Paints are the *polymer coatings* that for years have been most used to cover all types of surfaces. Notable amongst their many applications is their role as a protective coating against corrosion, accompanied by their decorative function (Pérez 1999; Hunter 1998).

The majority of paints are formed by three basic components: a liquid phase, a polymer matrix and a set of particles (pigments, extenders or spreaders) (Feliú 1991; Uhlig 1985). Drying of the film is produced by the polymerisation of the organic species, which may be autoxidators, condensers or additives. Other types of polymer coatings are varnishes and lacquers (Hunter 1998; Uhlig 1985).

Although these coatings are generally deposited in the form of multi-layers to optimise their protective properties, these are lost over time as a result of ageing (Murray 1997). This process starts with the diffusion of the ionic species present in the aggressive medium through the micro-pores of the polymer system. Initially, although the species reach the substrate, the corrosion started in these areas is still negligible. However, with time, the diffusion of water molecules increases and the adherence in the metal/coating interface diminishes. The area affected becomes larger and blisters start to appear in the coating. In time, these blisters burst due to osmotic pressure and to the pressure exercised by the corrosion products accumulated on the inside, leading to the delamination of the coating.

Thus, the porosity and permeability of a coating will be two very important characteristics which will condition the long-term protection capacity of a coating.

All of this knowledge acquired from paints is an excellent basis for understanding and explaining the degradation processes of a sol-gel coating.

32.3.3 Ceramic and glass coatings

Ceramic and glass coatings make it possible to combine the properties of mechanical resistance of the base metal with the chemical inertia of ceramic materials. Ceramic oxides have unusual properties, such as a high resistance to wear, low chemical activity, high electric and thermal resistance, resistance to scratching, etc., which make them ideal for acting as good coatings, offering excellent resistance to corrosion and oxidation (Taylor 1982).

There is a wide variety of ceramic materials, ranging from oxides (Al_2O_3 , TiO_2 , ZrO_2 , $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), carbides (SiC , TiC , BC), nitrides (Si_3N_4 , BN , AlN), borides (TiB_2 , YB_6) to combinations of the same.

The basic properties that determine the protective behaviour of this type of coatings are the difference in expansion coefficient between the substrate and the coating, the type of mechanical and/or chemical bond and the surface tension between the two (Fisher 1986). Amongst the ceramic and vitreous coatings, enamels merit a special mention, because their vitreous nature is responsible for properties such as low chemical inertia, great hardness, shine and thermal stability, which make them suitable for being used as a protection system in high temperatures and in extremely aggressive environments (Conde 2000; 2002). Ceramic coatings, both oxide and non-oxide, and in particular, the so-called *hard-coatings* are also of great interest.

32.3.4 Coating by Sol-Gel Process

The development of the science and technology of sol-gel processes has had a strong technological impact on research into coatings, since ceramic and vitreous materials can be obtained from colloid suspensions, or through low temperature hydrolysis and polymerisation of organic-metal compounds.

Although functional materials with tailored properties (controlled porosity, reflectivity, hardness, etc.) can be obtained through this synthesis process, one of the most interesting applications is its capacity to produce coatings or layers. In fact, the first patent related to the sol-gel process focused on obtaining SiO_2 and TiO_2 coatings (Geffchen 1939).

Through the sol-gel route it is possible to synthesize and deposit coatings of various compositions and specific properties on such different substrates as glasses, ceramics, metals and even plastics.

There is a wide variety of methods for depositing sol-gel coatings: dipping, spinning, spray, floating and, more recently, electrophoretic deposition (EPD). In comparison with other methods of obtaining coatings such as PVD or CVD (Barrow 1996), they are

characterized by being purely mechanical processes, which do not require much equipment, and can be applied on substrates with large complex shapes, without having to previously heat the substrate.

Of all the methods of deposition, dip-coating is the most frequently used to study the structure of the coating and its influence on the properties of the same. This process consists of the immersion of the substrate into the sol, allowing perfect coverage of the piece. The coated sample is then extracted at a controlled rate in a steady state. The substrate attracts the sol in a uniform film. Fast drying produced by contact with the atmosphere induces the film to gel. Glass-like films are further sintered in an appropriate atmosphere between 350-600°C while hybrid polymer coatings are cured normally below 200°C.

Another method being intensively investigated is electrophoretic deposition (EPD). EPD is a versatile technique for manufacturing either self-supported deposits or thin or thick coatings on conductive and insulating electrodes. EPD is a combination of two processes, electrophoresis and deposition. Electrophoresis involves the movement of charged particles in a stable suspension under an electric field. The deposition is the result of the impact of these particles against the electrode of the opposite sign. This process makes it possible to obtain homogeneous coatings with a controlled thickness, usually denser than those obtained by dipping.

Before going on to discuss some of the most important results as regards sol-gel coatings, some of the techniques used for studying the processes of high-temperature corrosion and of corrosion in electrolyte media are described.

32.4 Experimental Techniques and Tests for Studying Metal Corrosion

32.4.1 High Temperature Gaseous Environment Testing . Oxidation and Nitridation Tests

The most common experiments for the evaluation and selection of corrosion-resistant materials focus on the variation of the mass according to the length of exposure to the aggressive atmosphere, which is determined through the equation:

$$Mass\ change = \frac{W_f - W_o}{A} \quad \text{where } \begin{array}{l} W_f \text{ is the final weight (g)} \\ W_o \text{ is the original weight (g)} \\ A \text{ is the original area, } m^2 \end{array} \quad (32.2)$$

The plus or minus sign would indicate the gain or loss of mass produced in each case. In other cases, resistance is evaluated according to the loss of metal material which will be determined according to the ASTM G 54 standard through the equation:

$$Metal \cdot loss = \frac{T_o - T_m}{2} \quad \text{where } T_o \text{ is the original thickness or diameter (mm)} \\ T_m \text{ is the final thickness or diameter (mm)} \quad (32.3)$$

In this type of phenomenon there are two parameters controlling the process: one which is thermodynamic, the Gibbs energy, and a second which is kinetic. The first, taking oxidation as an example, is the driver that controls the oxygen-metal reaction. It is a parameter that depends on temperature. Thermodynamically, the oxide will form when the pressure of oxygen from the atmosphere is higher than the pressure of dissociation of the oxide in equilibrium with the metal. Once the probability of an oxide being formed exists, the kinetics of the process will vary depending on the controlling stage in each case.

There are different ways of determining the rate of oxide formation. The simplest system consists of the representation of the variation of the mass by surface unit with the length of exposure to the gas. If the increase in the oxide is linear, the controlling stage of the oxidation process is the oxygen-metal reaction. In this situation, the corrosion products formed, that is, the resulting oxides tend to be porous, non-adherent and non-protective. In a parabolic increase, diffusion through the oxide is the process controlling the increase in the coating. In this case, the rate is inversely proportional to the exposure time of the material, so that over very long periods of time it increases very slowly. Lastly, a parilinear increase occurs when coats break and the speed of the so-far controlling stage increases.

The experiments used to determine resistance to corrosion at high temperatures will differ depending on the aggressive gas that acts on the metal. There are general behaviour patterns which make it possible to evaluate the character of the attack. Thus, the study of the change in the mass with the exposure time, or the analysis of the transversal cut in the samples studied will reveal the rate of the corrosion process at high temperatures and determine the profundity of the attack.

The standard test for evaluating the resistance of materials to oxidation is based in the ASTM G 54. This test enables to study the initial mechanisms in the formation of the oxide layers when exposure periods are below 100 h. However, in order to evaluate the resistance of a material to oxidation, longer periods, between 500 h and 1000 h are necessary.

Another method used for evaluating the resistance to oxidation of steels is Cu K_a X-ray diffraction with a glancing angle technique. This method aims to determine the area (A) of

peaks at $2\theta = 35.5$ ($\text{Fe}_3\text{O}_4 + \alpha\text{-Fe}_2\text{O}_3$) and $2\theta = 44.6$ ($\alpha\text{-Fe}$) for uncoated (R_u) and coated (R_c) samples. The ratio R_u/R_c determines the degree of oxidation, which is expressed as the protection factor (PF) (Gugliemi 1992).

$$PF = \frac{\frac{A_{recubierto}(\text{Fe}_3\text{O}_4 + \alpha \text{Fe}_2\text{O}_3)}{A_{recubierto}(\alpha \text{Fe})}}{\frac{A_{acero}(\text{Fe}_3\text{O}_4 + \alpha \text{Fe}_2\text{O}_3)}{A_{acero}(\alpha \text{Fe})}} \quad (32.4)$$

More specific experiments are used to determine the resistance to the sulfidation of the materials employed in the petrochemical industry or in turbine components, which use oxidising/reducing gas mixtures in order to reproduce the different work cycles where the material will be found.

In the carburisation process, changes occur in the mechanical and chemical properties of the material. In general, the standard test ASTM G 79 is used to determine the profile of C concentration in the affected area. This analysis, together with the study of the change in hardness according to the ASTM E10 standard, will indicate the profundity of the area affected by carburisation.

Lastly, there is no normalized laboratory test for halogen corrosion as such, although there is an evaluation protocol. This was described by Brown (Brown 1947) for the case of atmospheres enriched in Cl, while the method of study was described by Tyreman (Tyreman 1983) for the case of F.

Other tests are used to evaluate corrosion from nitridation by anhydrous ammonium (Sanctis 1995), by treating the samples at different temperature for different lengths of time. The extent of corrosion is determined gravimetrically and by metallographic microscopy, and the corrosion rate can be determined by kinetic tests.

23.4.2 Methods for Evaluating Resistance to Electrochemical Corrosion

There is a wide range of tests for studying the degradation of a material as a result of electrochemical corrosion. These tests are divided into two large groups: electrochemical techniques and non-electrochemical tests. Within these two broad categories, the results obtained from each of them may be quantitative or qualitative.

32.4.2.1 Non-electrochemical tests

Since the performance of a material depends on its working conditions, undoubtedly the best way of determining resistance to metal corrosion is by exposing the material to the real conditions in which it will be offering its services. In this respect, atmospheric exposure experiments constitute the most reliable method of study for characterizing the behaviour of a material with regard to corrosion. Given the wide variety of atmospheres that have with different degrees of aggressiveness perfectly characterized through the ISO/TC 1546 standard, these experiments may be carried out in different atmospheres, ranging from non-aggressive atmospheres, such as a rural environment, to moderately aggressive atmospheres, such as marine environments, to more aggressive atmospheres such as industrial environments.

The major drawback of these tests are the long periods of time required to obtain results. For this reason, the alternative resides in accelerated laboratory experiments, in order to optimise the period of time in which corrosion takes place, by speeding up the degradation of the material, eliminating the stages when there is no attack or this occurs slowly, with the corresponding reduction in the time necessary to obtain results.

These tests are conducted in closed cabinets with controlled atmospheres, so that it is possible to change the factors that influence the corrosion phenomenon, with a view to ensuring an increase in its kinetics, without there being any change in the corrosion mechanism. Although these experiments are generally designed to produce similar results to those obtained in natural conditions, they do not always fully coincide. However, accelerated experiments are normally used in the comparative evaluation of materials and in their quality controls.

There is a wide variety of these experiments, which can range from the simplest, conducted in cabinets with a constant temperature and humidity, to other more sophisticated ones which involve the incorporation of factors that speed up corrosion, such as: UV radiation, temperature cycles, wetting and drying, aerosol spraying, incorporation of salts, changes in pH, etc. Thus, the appropriate selection of the accelerated experiment and of the environmental conditions imposed in the cabinet makes it possible to develop the corrosion process that one wishes to study. Table 32.3 shows a set of normalized experiments that give a correlation between the results obtained in real atmospheres and in the laboratory for different materials (Haynes 1995).

(insert Table 32.3)

Notable amongst all the accelerated experiments is the ASTM B117 salt spray fog test, because of its widespread use. This experiment makes it possible to conduct cycles of humidification with NaCl saline solutions of concentrations between 3.5 y 20%, followed by

drying periods of different lengths. Depending on the material to be studied, there are variations with specific purposes that are perfectly normalized (Haynes 1995) (Table 32.4).

(insert Table 32.4)

Once the atmospheric or accelerated test has been completed, the results obtained will be evaluated; to do this, certain guidelines are used so that the damage produced by corrosion is correctly evaluated. The ASTM G1 and ASTM G 33 standards define the general rules for evaluating corrosion and provide the necessary information for establishing the degree of damage produced by looking at the samples. Other standards such as the ASTM D1654 are specific for painted samples.

After the visual inspection of the damage produced by corrosion conducted in accordance with the mentioned standards, other more destructive techniques are used, with a view to quantifying the damage. In the case of uniform corrosion, the loss of mass is measured. If the attack is local, metallographic analysis of the areas affected is used. Similarly, problems produced by dealloying, exfoliation or cracking can be determined using optical and scanning electronic microscopy (Dean 1990).

On other occasions, the existence of a localized attack by pitting or an intergranular attack can be identified by carrying out tensile tests and determining the reduction in the tensile strength or in the elongation.

32.4.2.2 *Electrochemical techniques*

The electrochemical nature of corrosion and the quantitative relation between the electric current that goes through the electrode and the amount of material dissolved mean that electrochemical techniques are ideal for studying this phenomenon.

These techniques have the advantage of making it possible to separate the coupled elements by determining the reactions controlling each of the stages of the process. They also provide information on the reaction mechanism governing the electrochemical interface.

A wide variety of electrochemical techniques have been developed over the years and have gradually contributed more and more information. Table 32.5 shows some of these techniques together with the type of information each of them provides. The majority of these techniques involve the controlled interference of the potential or of the current, and measuring the value the other variable acquires as a result of the said interaction imposed on the system. In general, all of these techniques can be divided into two large groups: steady state techniques and non-steady state techniques.

(insert Table 32.5)

Steady state techniques aim to determine the rate of corrosion of the system from the i vs E curves (current against potential) obtained by application of direct current signals. By means of these techniques it is possible to determine the speed of the slowest reaction which turns out to be the stage that controls the corrosion process. However, on many occasions, this information is insufficient to characterise the system, so it is necessary to use non-steady state techniques to detect the coupled phenomena that take place in the corrosion process.

These **non-steady state techniques** are based on the application of a perturbation to a system in equilibrium or in a steady state, and on the later study of the relaxation of the system. As the different elementary processes which intervene in the corrosion phenomenon have different relaxation constants, a low amplitude signal with a wide range of frequencies is used as perturbing signal, which makes it possible to induce a linear response from the system. The response of the system will be the sum of the contributions of each elementary process, as each of them relaxes exponentially over time with a characteristic time constant.

The most commonly-used steady state techniques are potentiodynamic tests to determine the corrosion rate in systems that experience a uniform corrosion process. This type of attack can also be studied by measuring resistance to polarisation. Cyclical polarisation curves are also used to study localized corrosion and potentiokinetic reactivation is the most suitable study technique for evaluating intergranular corrosion produced by a sensitisation phenomenon following ASTM G108 standard test.

Amongst the non-steady techniques are the electrochemical impedance spectroscopy (EIS) and the techniques which work by applying a potential step or current and analysing the response of the system after its relaxation.

All of them have been very successfully used in the past few years in a wide variety of systems: metals, alloys, coatings, etc., and despite their strong diffusion in the study and characterization of the performance of coatings (Murray 1997), it is only recently that they have started to be used to evaluate the protective properties of coatings obtained through sol-gel route.

Potentiodynamic tests

As was mentioned earlier, metal corrosion is an electrochemical process comprising oxidation and reduction reactions different from the medium in which the process takes place. It requires anodes and cathodes in electrical contact, as well as an ionic conduction path through an electrolyte. The electron flow between the anodic and cathodic areas quantifies the

rates of the oxidation and reduction reactions and the conversion of the reaction rate from current to mass loss is in accordance with Faraday's law.

The typical electrochemical cell used to perform electrochemical tests is described in Figure 32.2. This cell consists of three electrodes; the reference electrode (REF), usually a saturated calomel electrode (SCE), the counter-electrode (CE) which is a metal piece nobler than the sample (usually a Pt wire) and the working electrode (WE), which is the material to be analysed.

(insert Figure 32.2)

The anodic reaction occurring in anodes (WE):

removes the metal atom by oxidizing its ion. In this reaction, the number of electrons produced is equal to the valence of the metal. All the electrons generated by the anodic reactions are consumed by corresponding reduction reactions in cathodic areas. In equilibrium conditions, the metal is corroded to a characteristic potential, depending on its nature and the medium. This potential is denoted by corrosion potential E_{corr} .

In the equilibrium, in the absence of any type of external influence, and considering the electro-neutrality principle, the current density of the anodic (i_a) and cathodic (i_c) reactions are equal between them and equal to the corrosion current density (i_{corr}).

$$i_a = i_c = i_{\text{corr}} \quad (32.6)$$

This parameter can serve to measure the rate of corrosion, considering that in the equilibrium the speed of net transformation is nil or, what amounts to the same, the rates of corrosion, oxidation and reduction are the same:

$$v_{\text{ox}} = v_{\text{red}} \quad (32.7)$$

Through Faraday's law, which establishes the relationship between the density of the current in the electrochemical process and the speed of the process, it is possible to calculate the corrosion rate:

$$v = \frac{iA}{nF} = \frac{i_{\text{oxidation}}A}{nF} \quad (32.8)$$

where A is the atom mass, n is the number of electrons interchanged in the reaction and F is the Faraday constant, 96,500 coulombs per mol of electrons.

According to this, it would be possible to measure the corrosion rate by measuring the intensity of oxidation or reduction, but it is not possible to do it directly, since in the equilibrium what is measured is the density of the net current, which is the sum of the two and is equal to zero.

One way of studying the system is to break the equilibrium, perturbing the system by imposing a potential different from that of corrosion. In these conditions, there is a change in the potential of the electrode and the electrode is said to have been polarized. The density of the net current is no longer zero and is given by the sum of the anodic and cathodic process:

$$i_{net} = i_a + i_c \quad (32.9)$$

The density of the net current is related to the potential applied through Butler-Volmer's kinetic law (Bockris 1980).

$$i_{net} = i_{corr} \left[\exp\left(\frac{\alpha nF}{RT} \eta\right) - \exp\left(\frac{-(1-\alpha)nF}{RT} \eta\right) \right] \quad (32.10)$$

where α is the transfer coefficient and η is the over-potential which corresponds to the difference in potential between the equilibrium potential and the potential applied, (E-E_{corr}).

If E-E_{corr} is a large positive voltage, the previous reaction can be simplified:

$$i_{net} = i_{corr} \exp[\alpha_a F(E - E_{corr} / RT)] \quad (32.11)$$

Similarly, when E-E_{redox} is a high negative value the expression can be reduced to:

$$i_{net} = i_{corr} \exp[-\alpha_c F(E - E_{corr} / RT)] \quad (32.12)$$

The polarisation curves (i/E) correspond to the graphic representation of this expression (Sastri 1998). Analysis of these curves provides basic information on corrosion phenomena, which are very useful for studying sensitivity to corrosion from pitting, by determining the breakage potential, also known as *pitting nucleation potential* E_p and *repassivation potential*, E_{pr}.

Figure 32.3 shows a typical polarisation curve, where the different parameters that can be found are indicated. Two zones can be distinguished on the curve: the cathode region and the

anode region; the intersection of the two branches defines the corrosion potential (E_{corr}) and the cut through the x axis gives the value for the corrosion current density (i_{corr}). Three intervals of potential can be distinguished on the anode stretch: zone ① corresponds to the $E_{\text{corr}} - E_{\text{pp}}$ stretch, denominated active zone; zone ② corresponds to the $E_{\text{pp}} - E_{\text{t/p}}$ stretch, where the metal is immune to the corrosion and zone ③ where the corrosion takes place. The passive stretch ② corresponds to potentials at which solid products of metal corrosion are stable and protect the metal.

(insert Figure 32.3)

In this type of curve, the current density is seen to diminish as the potential applied increases until it reaches the *corrosion potential* E_{corr} . The increasing of the potential in the noble direction from E_{corr} produces an increase in the current density until it reaches the *primary passivation potential* (E_{pp}). From here on, the current density begins to decrease, this range being known as *active-passive transition*. Above this potential, the current density drops to a very low value, i_{pas} , (the *passive current density*) and remains at a low value over a wide range of potentials. The potential range over which the current density remains constant is defined as the *passive potential range*, and it is this range which defines passivity for a given metal/environment combination. The corrosion rate in this range is very low.

On continuing to increase the applied potential, another potential will be reached at which the current again begins to increase. This potential is known as the *pitting potential*, E_{p} .

From potentiodynamic curves obtained with a Potentiostat/Galvanostat it is possible to determine the passive current density and the length of the passive stage which is defined by the difference between the E_{corr} and E_{pp} . E_{corr} is a thermodynamic parameter which indicates the tendency for an electrochemical reaction to occur spontaneously. In this sense, it supplies an idea about the tendency of the material to corrode. If the corrosion potential of the coated steel is greater than that of the same steel uncoated, the coating induces a more “noble” behaviour of the material and, thus, a lesser tendency to be corroded. Moreover, the passivity current density values (i_{pas}) give an idea of the rate of corrosion. In this way, lower values than those measured in naked steels indicate a more protective behaviour or, in other words, a slower rate of corrosion. The change in the corrosion and pitting potential is another of the parameters to take into account in considering the behaviour of the coatings: the greater the change, the better the coating will be.

Linear (resistance) polarisation

In the realization of a polarisation curve, the work electrode reaches high potential values causing a strong irreversible dissolution of the material. Thus, when attempts are made to evaluate the change in the corrosion rate over time of a metal under a uniform corrosion process, under control for activation, another type of non-destructive experiment is employed, namely the measurement of *resistance to polarisation*. This is also a steady state technique and it is based on the application of a low amplitude signal of direct current around the corrosion potential, ensuring that the material continues in a situation of equilibrium.

This technique is based on the theoretical and practical demonstration that at a potential very close to E_{corr} ($\eta \rightarrow 0$), the slope of the potential/applied current curve is approximately linear and inversely proportional to the corrosion rate (Stern 1957). Under this condition, and considering the Tafel slope, the equation 10 is transformed to:

$$i_{\text{corr}} = \frac{\beta_a \beta_c}{2,303(\beta_{a+} + \beta_c)} \left(\frac{di_{\text{net}}}{d\eta} \right)_{\eta \rightarrow 0} = B \left[\frac{di_{\text{net}}}{d\eta} \right] \quad (32.13)$$

where β_a y β_b are the anodic and cathodic Tafel slopes, respectively and B is related to the system's Tafel constants and may vary within relatively narrow limits:

$$B = \frac{\beta_a \beta_c}{2,303(\beta_a + \beta_c)} \quad (32.14)$$

By determining $\frac{d\eta}{di_{\text{net}}} = \frac{\Delta E}{\Delta I}$, which corresponds to the slope on the curve, i_{corr} may be calculated. The slope has resistance dimensions and is known by the name of *polarisation resistance* (R_p). The simplified expression of i_{corr} is given by:

$$i_{\text{corr}} = \frac{B}{R_p} \quad (32.15)$$

Measurement of corrosion rate by Tafel

Another method used to determine the corrosion rate as well as polarisation resistance is the extrapolation method. This method consists of the exploration of the linear segments of potential-current density curves. In this case, the metal is initially made to act as a cathode. The cathodic potential-current density curve is measured by applying a potential range, defined by the variation between the E_{corr} and some potential active to E_{corr} , for example E_c , Figure 32.4. The cathodic current density approaches zero in the E_{corr} . Increasing the applied potential in the noble direction, the metal behaves as an anode, and the other part of the curve can be obtained.

(insert Figure 32.4)

In theory, the cathodic and anodic potential-current density variations should be linear and should cut a point defined by $E_{\text{corr}}/i_{\text{corr}}$. However, the curves deviate from linearity on approaching E_{corr} . This deviation is a consequence of the development of anodic and cathodic sites in the metal. However, the curves present linear segments, defined as Tafel regions. Extrapolating these, it is possible to obtain the E_{corr} and the i_{corr} .

The corrosion rate can be calculated from i_{corr} by applying the relationship:

$$R_{\text{mpy}} = 0.13 i_{\text{corr}} \frac{e}{\rho} \quad (32.16)$$

where the R_{mpy} is the corrosion rate (mils/year), e the equivalent weight of metal and ρ the density of the metal.

AC tests: Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) was revealed as one of the most useful and reliable techniques for investigating coating degradation (Hirayama 1991; Hack 1991). For this reason, it has been widely used for the characterization of a wide variety of protective systems (McCluney 1992; Xiao 1994). This technique is especially interesting because of its sensitiveness to changes in the resistance-capacitive nature of coatings as well as the interface coating/substrate. Through these techniques it is possible to monitor the polarisation resistance of the corroding interface. In this respect, EIS offers several advantages over DC techniques. The main one is that the resistance related to the corrosion rate can be separated from high DC resistance of the dielectric coating. The reason for this lies in the capability of EIS to discriminate between properties of the coating because of its ionic and/or electronic conductivity and its capacitive nature resulting from its dielectric constant, area and thickness.

Besides, it is a non-destructive and particularly sensitive method for detecting small changes in the system promoted by water uptake, presence of pinholes, cracks or other defects which lead to the onset of the coating failure.

These tests are also carried out using a three-electrode cell according to the ASTM G3-89 standard. The system is perturbed by a sinusoidal voltage of small amplitude to keep the equilibrium conditions. The response of the system is a current signal with the same frequency but different phase and amplitude. The ratio between voltage and the current for a AC current is the impedance of the system which is a complex magnitude. Corrosion studies use an extended bandwidth of frequencies to obtain information on the different mechanisms

taking place on the electrode/electrolyte interface. If $V = V_o \sin(\omega t)$ is a perturbation signal applied to the system, and $I = I \sin(\omega t + \theta)$ the response of the system, the electrochemical impedance $Z(\omega)$, is the frequency-dependent factor that acts as a transfer function by establishing a relationship between the excitation voltage signal and the current response of the system

$$Z(\omega) = V(\omega)/i(\omega) \quad (32.17)$$

$Z(\omega)$ is a complex magnitude with real and imaginary components whose values are frequency-dependent.

$$Z(\omega) = Z'(\omega) + j Z''(\omega) \quad (32.18)$$

Where: $Z'(\omega) = |Z(\omega)|\cos(\theta)$ is the real component of impedance,
 $Z''(\omega) = |Z(\omega)|\sin(\theta)$, the imaginary component of impedance,
 $|Z(\omega)| = (Z'(\omega)^2 + Z''(\omega)^2)^{1/2}$, the impedance magnitude, and
 $\theta = \tan^{-1}(Z''(\omega)/Z'(\omega))$

Impedance is a fundamental characteristic of the electrochemical system it describes. This magnitude can be plotted by Nyquist or Bode plots, Figure 32.5. The latter clearly reveals the frequency dependence of impedance.

(insert Figure 32.5)

According to Randles (Randles 1947), any electrochemical cell can be described by an equivalent electric circuit comprising resistors and capacitors connected either in series or in parallel. This electric circuit makes it possible to correlate the impedance process with the chemical process that has occurred on the surface. For simple corroding metal the electrical equivalent circuit is very simple, Figure 32.6, where, R_s is the solution resistance, R_t represents polarisation resistance and C_d , is the double layer capacitance. In this case, Nyquist and Bode plots depict only a time constant. However, in most real systems the plots represent deviations from this response leading to a more difficult interpretation of the impedance spectra.

(insert Figure 32.6)

The ageing process of a coating is a typical case which shows how complex the interpretation of impedance results can be. Despite this, the impedance technique has been used for years with increasing success. A common model for simulating the behaviour of a coating is described in Figure 32.7. In this case, R_{po} , is the coating defect resistance, R_t is the charge transfer resistance at the metal interface where the water has penetrated, C is the

coating capacitance and, C_{dl} is the double layer capacitance of the bare metal surface.

(insert Figure 32.7)

By monitoring the evolution of these parameters, it is possible to obtain important information about the damaging process. For instance, from the variation of the coating capacitance it is possible to calculate the water uptake in an organic coating by means of the expression:

$$volume\% H_2O = \frac{100 \log \left(\frac{C_t}{C_o} \right)}{\log 79} \quad (32.19)$$

where: C_t = coating capacitance after some exposure time and,
 C_o = coating capacitance at time zero when the exposure begins

The coating resistance can be also monitored as a function of exposure time. Large decreases signify permeation of ionic species through the coating or the presence of defects in the coating. The breakpoint frequency is a useful method for estimating the area fraction of physical defects in an organic coating (Haruyama 1980; Scully 1989; Kending 1990; Hack 1991). The following expression describes the relationship between the high-frequency breakpoint and the defect area:

$$f_{bpt} = \frac{1}{2\pi\epsilon\epsilon_o\rho} \left(\frac{A_d}{A} \right) \quad (32.20)$$

where: A_d = defect area,

A = total area

ϵ = dielectric constant for the film

ϵ_o = the dielectric permittivity of a vacuum ($8.854 \cdot 10^{-12}$ F/m)

ρ = the resistance of the coating at the defect

This equation provides a rough measure of the estimated change in the defect area provided that decreases in ρ with electrolyte uptake are offset by increases in ϵ with water ingress. Under such circumstances, the ratio A_d/A remains constant. In this case, increases in f_{bpt} occur mainly as a result of the increases in the defective area. However, circumstances may exist where small increases in ϵ and very large decrease in ρ occur, so that f_{bpt} does not relate linearly to the defect area. Moreover, naked metal under delaminated coating regions may not be detected in all circumstances.

32.5. Sol- Gel Protective Coatings

It is common knowledge that metals have many applications, thanks to their excellent

mechanical properties and good resistance to corrosion. However, they have a disadvantage in that in certain working conditions they may be prone to corrosion. Depending on the metal and the environment in which it is used, the attack could be homogeneous, affecting the entire surface equally, uniform corrosion, or it could occur in certain areas of the metal surface, giving rise to localized corrosion. The latter type of attack occurs more frequently in passive materials and is due to the existence of aggressive agents in the environment which cause local deterioration of the protective oxide film. A typical example of this sensitivity to localized attack are stainless steels and aluminium alloys in the presence of halides.

The use of protective coatings permits the deposition of a barrier coat that insulates the metal from the aggressive medium. This will imply that, in many cases, the field of applications of metals and alloys appreciated for their mechanical, physical or chemical features and which, however, have moderate resistance to corrosion in demanding environments, can be extended.

In this respect, ceramic coatings and, in particular, sol-gel technology makes it possible to enhance the chemical and mechanical properties, such as resistance to corrosion and oxidation, to scratching and wear, due to its greater tenacity and lesser sensitivity to chemical attack.

One case of particular chemical importance is constituted by the metal structures used in the aerospace industry, made of aluminium and its alloys, which should ensure 40-year protection of the metal substrate.

The literature on the behaviour of coatings produced by sol-gel and deposited on metals in the face of corrosion and oxidation gives results that are very often contradictory.

An extensive bibliographical review has enabled us to classify these studies according to the metal substrate used. The majority of studies were on the protection of stainless steels AISI 304, 310, 430, 316L (Shane 1990; Sanctis 1990, Atik 1992; Damborenea 1995; Gallardo 2000), followed by aluminium and its alloys (Kato 1993 Hirai 1998; Voevodin. 2001a, 2001b, 2001c; Conde 2002, 2003) and, to a lesser extent, studies on carbon steels (Giampaolo 1997; Fallet 2001), copper (Innocenzi 1992; Boysen 1999), nickel, etc.

Considering the nature of the coatings, they can be divided into two large groups:

1. *Inorganic coatings*: notable amongst these are the coatings of SiO_2 , ZrO_2 , B_2O_3 , SiO_2 - B_2O_3 , SiO_2 - ZrO_2 , SiO_2 - TiO_2 , ZrO_2 - Y_2O_3 , ZrO_2 - CeO_2 , etc., obtained on the basis of the reactions of hydrolysis and polycondensation of metal alcoxides.

2. *Organic-inorganic hybrid coatings*, obtained from the incorporation of organic groups in the inorganic network in order to obtain thicker, more flexible coats. These coatings can go

from having low content of residual organic material, deriving from the use of alkylalcoxides as precursors, to being fundamentally organic. The organic content and, thus, the consolidation temperature used can be distinguished between:

2.a) *Hybrid coatings of SiO₂, SiO₂/ZrO₂ and ZrO₂* mainly, sintered at temperatures between 400-500°C.

2.b) Coatings of SiO₂ with high organic content, cured at temperatures of below 200°C, which henceforth are called *polymer hybrid coatings*.

Tables 32.6, 32.7 and 32.8 show the main works published on protective coatings on different metal substrates, distinguishing between the type of substrate, the nature and type of coating, and the experiments conducted for inorganic, hybrid and polymer coatings, respectively.

[\(insert Tables 32.6, 32.7 and 32.8\)](#)

32.5.1 Inorganic Coatings on Different Substrates

The first works on inorganic coatings were published from 1990 (Sanctis 1990, 1995) and mainly focused on studying the resistance of metal substrates to oxidation and nitridation at high temperatures. In the first study the authors evaluated the static oxidation resistance in air of several stainless steels (AISI 304, 316 and 310) coated with a silica film of 400 nm over a period of 24 h at temperatures slightly lower than the maximum temperature recommended for the different steels (650 and 950°C). The results show that the weight change of coated steel is lower by more than one order of magnitude than in the case of the uncoated steel (Table 32.9). The appearance of coated surfaces remains unchanged, whereas uncoated substrates are strongly affected. This result indicates that the silica coatings act as an effective protection of metal substrates, notably increasing their resistance to oxidation.

[\(insert Table 32.9\)](#)

Later (Sanctis 1995) they evaluated the behaviour of these same coatings with respect to nitridation in an anhydrous ammonia atmosphere in a temperature range between 400 and 600°C. The results showed a substantial increase in resistance to nitridation of the coated steels in comparison with the uncoated substrates. The measurement of corrosion rates in samples treated for 20 h at temperatures between 400 and 600 °C show that the uncoated 304 and 316 samples underwent significant attack at 400°C, Figure 32.8. In contrast, SiO₂ coated steels did not show appreciable corrosion and the protective behaviour subsists up to 600°C, even as the ammonia is almost wholly dissociated.

(insert Figure 32.8)

The oxidation resistance in dry atmosphere of SiO_2 , TiO_2 , B_2O_3 y $\text{SiO}_2\text{-B}_2\text{O}_3$ coatings on mild steel, Ni, Fe, Al and Cu was further studied (Guglielmi 1992; Innocenzi 1992; Maliavski 1995) They evaluated the resistance to oxidation of the coated samples by measuring the weight gain (mg/cm^2) and using X-ray diffraction analysis. The protective action of the coatings was noticeable although they observed that in the case of $\text{SiO}_2\text{-B}_2\text{O}_3$ coatings onto Ni the improvement is greater than when SiO_2 coating is used. They considered that boron oxide probably has the effect of reducing the intrinsic stresses in the sol-gel films and therefore may reduce the presence of micro-cracks, increasing the protective behaviour.

The results obtained by the static oxidation test were compared with the XRD analysis and similar results were observed. They prepared $\text{B}_2\text{O}_3\text{-SiO}_2$ coatings on mild steel by mixing tetraethoxysilane and triethylborate and evaluated the protection factor (PF) through XRD. The results obtained indicated that the coated steel gave better protection against oxidation, with a PF value of 78% as against the 4% for uncoated steel.

Other studies on resistance to oxidation are those on ZrO_2 and $\text{ZrO}_2\text{-Y}_2\text{O}_3$ coatings (Izumi 1989; Miyazawa 1995), on $\text{CeO}_2\text{-TiO}_2$ coatings (Nazeri 1997; Trzaskoma-Paulette 1997), on Al_2O_3 coatings (Özer 1999) and on silica films through salt fog tests (Kato 1992;1993). Kato found that the corrosion resistance depended on the structure of the SiO_2 coating and is enhanced by repeating the coating cycle and the temperature of the heat treatment. In general, the protective behaviour against oxidation increases with the presence of a coating which act as a barrier hindering the ionic transport.

This ability of inorganic coatings is applied for the protection of solar mirrors. Silver and aluminium first surface mirrors for solar collectors are protected from oxidation up to 350°C with thin dense inorganic SiO_2 coatings (Guglielmi 1993) maintaining the solar reflectance of the protected mirrors above 90% after 10 years (Morales 1995; 1997; 1999).

However, it was soon observed that the sintering temperatures employed could have harmful effects on the substrate and cause the sensitization of the austenitic steels, which induces the precipitation of chromium carbides on the boundary of the grain. These micro-structural changes increase the sensitivity to intergranular attack, with the corresponding loss of their properties. In order to determine the influence of the sintering treatment on the metal substrate, sensitization experiments were conducted by measuring polarisation in mixtures of $0.5 \text{ M H}_2\text{SO}_4 + 0.01 \text{ M KSCN}$ on steels treated at maximum temperatures of 500°C for 1 hour (Damborenea 1995). The test is based on the EPR method (electrolytic potentiodynamic polarisation) and it consists of polarizing from the corrosion potential (E_{corr}) in an anodic

direction until the passivation region is reached. At this point, the potential is swept back towards corrosion potential. According to this method, the quotient of the current density at which activation and reactivation occur, shows the degree of sensitivity of the material. This is minimal at a quotient lower than 0.01 and appreciable for quotients of 0.1-1. Materials with intermediate values are moderately susceptible to intergranular attack (Damborenea 1989). The sensitization measurement performed on AISI 304 indicates that no sign of possible reactivation of the material was observed at temperatures below of 500°C (Figure 32.9). This behaviour reveals that the treatment does not sensitize the base metal to possible attacks from intergranular corrosion.

(insert Figure 32.9)

Al₂O₃ coatings were also studied (Biswas 1997) by plotting potentiodynamic polarisation curves for uncoated 316 steel subjected to heat treatment at 450°C, 600°C and 800°C (Figure 32.10). The results show that increasing the temperature of the heat treatment produced decreasing values of E_{corr} and higher i_{cor} , indicating the sensitization from the precipitation of carbides at the grain boundaries. This same effect was confirmed on coatings of TiO₂-CeO₂ (Nazeri 1997).

(insert Figure 32.10)

Damborenea (Damborenea 1995) also studied the behaviour of coated steels in aqueous media (NaCl 0,6 M and HCl 2 M) through voltametry experiments. It is observed that the values for the corrosion potential measured as a function of time range between 220 mV and 140 mV in the case of coated steels, and between -200 mV a -50 mV on uncoated steel. However, the kinetic measurements using complex impedance and polarisation resistance showed that the resistance to corrosion diminished notably over time, with the R_p values reaching the same levels as those of naked steel after 24 hours (Figure 32.11). This downturn revealed the presence of defects or pores in the coating, which permitted the movement of ions and, consequently, the contact of the environment with the metal substrate.

(insert Figure 32.11)

Impedance measurements were carried out on the naked steel and on those coated with one and two layers of SiO₂, immersed in HCl. After three hours of testing, the impedance measurement indicated that the coating was not a pure insulator but rather porous, permitting the ionic movement of the species in the electrolyte towards the surface of the steel substrates.

Another explanation for this behaviour must be based on the appearance of defects in the films during the sintering process. It is, thus, the first work to describe the measurement of the corrosion kinetics of coatings produced through sol-gel.

Aegerter and his group investigated resistance to oxidation and corrosion in aqueous media through weight loss and potentiostatic polarisation measurements on AISI 316L stainless steel (Atik 1992). The bulk of the work conducted by this group focuses on studying the resistance to corrosion of ZrO_2 coatings, although they have also worked with TiO_2 - SiO_2 (Atik 1994 b; Neto 1994) and Al_2O_3 - SiO_2 (Atik 1994 a; 1995 b) coatings. All the coatings were treated at temperatures of around 800°C . The electrochemical results showed the reduction in resistance to corrosion and the increase in sensitivity to intergranular attack deriving from the presence of cracks in the coating - which gave the medium access to the metal substrate -, and due to the sensitization of the steel induced by the high sintering temperatures employed.

The corrosion resistance studies of ZrO_2 coatings onto 316L in 15% H_2SO_4 and 3% NaCl (Atik. 1995 a;1996) through anodic polarisation measurements showed the coated steel has a lower i_{pass} and a higher corrosion potential (E_{corr}) value as compared to as-received steel. According to these authors, the high E_{corr} values indicate good behaviour against corrosion. However, this thermodynamic parameter should be evaluated with caution as it does not permit the characterization of the system's corrosion phenomena (Krivian 1991). Its variations are determined by different factors, such as the nature of the metal, the medium or the electronic reactions that take place, the presence of defects in the coating or, simply, by the use of high sweep speeds (1 mV/s), which prevent the system from reaching stabilization between one measurement and the next. A decisive parameter when it comes to studying the protective nature of a coating and which was not considered in any of the studies conducted by this group is the length of the passive potential range. The longer this range, the greater the resistance to corrosion. The potentiodynamic curves measured in aqueous 3% NaCl solution for uncoated steel compared with steel coated with ZrO_2 , 75 SiO_2 -25 Al_2O_3 and 70 SiO_2 -30 TiO_2 show a smaller passive range for all the coated substrates than for the uncoated steel, indicating the activation of the substrate with respect to the uncoated one and not protection of the metal.

Moreover, neither can the reduction in the density of current observed in the experiments made in H_2SO_4 be considered as decisive in determining the increase in resistance to corrosion, since it could be associated with the passivation of the metal in the said medium. This passivation phenomenon was studied by Di Maggio (Di Maggio 1997 a; 1997 b) through

complex impedance measures on coatings of $\text{ZrO}_2\text{-CeO}_2$ in H_2SO_4 (Figure 32.12), where the passivation of the steel was observed, despite it being coated. This can only be explained if the coating has defects or pores that allow the medium to penetrate and put it in contact with the steel, masking the protective effect. To prevent the passivation of the metal and check whether or not the coating has fissures, which determine its protection, more aggressive media that do not mask performance must be used.

(insert figure 32.12)

Studies on resistance to corrosion have also been published where electrochemical measures are used on SiO_2 coatings (Vasconcelos 2000; Simoes 2000) and on ZrO_2 coatings (Quinson 1996). The analysis of the behaviour of these coatings in NaCl reveals the presence of porosity within the coatings, which allows chloride ions to diffuse up to the coating-steel interface. Quinson through impedance diagrams on zirconia coatings aged in aerated NaCl solution for 2 hours, 10 days and 30 days showed that the capacitance increase and the resistance decreases strongly with the time, observing the same effect as Damborenea (Damborenea 1995) for SiO_2 coatings. When the medium used was H_2SO_4 a decrease in the i_{corr} is observed, but, as was mentioned earlier, this reduction is associated with the passivation of the steel and, thus, to the presence of cracks in the coating.

Guglielmi (Guglielmi 1997) published an entire review on inorganic coatings, which includes the studies conducted until that time and where the problems of this type of coating are detected. In general, it can be considered that the coating behaviour is conditioned by thickness (Kato 1992; Izumi 1989), although other parameters also have an influence such as the medium of attack, the sintering temperature and the conditions for processing the coating.

An important conclusion is the power of protection of these coatings against oxidation or nitridation in anhydrous media, but also the sensitivity to corrosion in electrolytic media caused by the presence of micro-cracks or defects in the coating.

32.5.2 Inorganic-Organic Hybrid Coatings on Different Substrates

Organic-inorganic coatings can be classified according to the organic quantity present and, thus, to the sintering or curing temperature, as:

Hybrid coatings. Low organic content and $T \sim 400 - 500^\circ\text{C}$

Polymer hybrid coatings. High organic content and $T < 300^\circ\text{C}$

32.5.2.1 Hybrid coatings on metal substrates

Izumi (Izumi 1993) studied the resistance to corrosion of aluminised steel coated with hybrid layers of silica (70 nm), obtained through the hydrolysis of different alkylalcoxides ($R'(Si(OR)_3)$), heat-treated at 400°C for 1 min. The resistance to corrosion of the coated aluminised steel was evaluated by a humidity cabinet test against the evolution of the change loss. The L-value (JIS Z8729) was measured with a colour analyser. The colour of the uncoated aluminised steel went dark due to oxidation of the surface, whereas the coated steel showed good resistance to corrosion. They also observed that this effect changes with the ageing time, being more effective for aged solutions.

In addition, Mennig (Mennig 1998) compiled the work of different authors where the behaviour with respect to corrosion of polished and rough AISI 304, covered with inorganic layers of $B_2O_3-SiO_2$ and $MgO-SiO_2$ and hybrid layers of MTES with silica particles treated at different temperatures is compared through tests of static oxidation, X-ray diffraction analysis, electrochemical measurement and salt spray corrosion test (ASTM B117). The results of the static oxidation tests show that the thick silica coating on polished steel produced the highest protection factor (PF) against oxidation at 800°C. The analysis of resistance to oxidation in dry atmospheres and the electrochemical measures in NaCl show that the hybrid coats of MTES with colloidal particles reduce the penetration of O_2 to a greater extent than the inorganic coats and present better electrochemical behaviour. This difference may be associated with the variation in thickness, since the hybrid films have $\sim 2 \mu m$ as against the 600 or 400 nm of the inorganic coats and with the absence of micro-fissures or defects, reduced by the more ductile nature of the hybrid coating. Electrochemical measurements in NaCl (0.6 M) confirms the very good results for SiO_2 coatings, remaining passive after 200 h of electrochemical attack. In addition, they observe that resistance to corrosion is lower in the case of rough substrates than the polished ones; this is associated with the appearance of defects because the layers are not thick enough to entirely cover the roughness of the steel.

Within this group of authors, notable work was done on coatings on AISI 316L steel, coated with layers of SiO_2 obtained through the hydrolysis and polycondensation of TEOS/MTES in an acid medium (Galliano 1998). Figure 32.13 shows the impedance diagrams for an inorganic coating compared with a hybrid coating after 200 h of electrochemical attack in a physiological solution. For hybrid coatings, impedance values are higher than those of inorganic films, revealing better corrosion behaviour and a notable improvement with respect to the metal substrate.

(insert Figure 32.13)

Moreover, the results of complex impedance and voltametries for coatings obtained from TEOS/MTES sols and TEOS/MTES suspensions with window-glass and bioactive glass powders (Gallardo 2000; 2001; 2003) showed a very large increase in resistance of the metal to corrosion, which is influenced by the sintering temperature or, what amounts to the same, by the final amount of organic material in the coatings. For a hybrid SiO₂ film treated at 400°C for 30 minutes, resistance to corrosion is strongly enhanced, reducing the current density by almost two orders of magnitude and increasing the length of the passive stage from 0.6V to 1.1V. EIS measurements through the $Z_{f \rightarrow 10\text{mHz}}$ parameter (Figure 32.14), show that the higher the sintering temperature, the lower the organic content, leading to a worsening of the protective properties (Gallardo 2003).

(insert Figure 32.14)

Impedance values for samples treated at 400°C are one order of magnitude higher than those of films sintered at 550°C. This could be explained in terms of the higher content of CH₃ groups in the films sintered at lower temperatures, deriving in higher hydrophobicity that delays the access of the electrolyte inside the defects and also reduces micro-crack density. The presence of glass powder improves the resistance to abrasion, maintaining a long passive stage after one month of immersion (Figure 32.15). On the other hand, the presence of bioactive powder in the coatings induces, in contact with the physiological solution, the formation of hydroxiapatite, but slightly reduces resistance to corrosion. The use of a first hybrid coating of SiO₂, plus a top coat with bioactive glass powder enhances both properties since it notably improves the resistance of this type of coating and acts by heightening its bioactive role, permitting the formation of osseous tissue with high vascularity in in-vivo experiments (Gallardo 2000; 2001).

(insert Figures 32.15)

Recently, electrophoretic deposition (EPD) has been used to produce hybrid SiO₂ coatings from particulate basic sols and suspensions. This method makes it possible to obtain thick coatings without cracks with excellent resistance to corrosion. The particulate sols and suspension include dense particles produced during the synthesis in basic conditions or colloidal particles which are added to the sol (Schmidt 2000; Mennig 1992). These particles

can migrate under an electric field and deposit, forming the coating. SiO₂ coatings onto AISI 304 were prepared by EPD and dipping (Castro 2002; 2003) using a particulate sol prepared by mixing MTES and TEOS with NaOH, following the process described by Jonschker (Jonschker 1998). In order to check the protection supplied by these coatings, potentiodynamic tests and polarisation resistance were performed on coated and uncoated polished stainless steel. Figure 32.16 shows the polarisation curve measured in a 3.65 wt% NaCl medium for two coatings with a thickness of 2,8 µm obtained by dipping and by EPD process compared with the uncoated steel. The corrosion current density of the EPD coating was reduced by four orders of magnitude, from 10⁻⁷ A/cm² for the uncoated steel to 10⁻¹¹ A/cm², whereas the i_{pass} is only reduced by three orders of magnitude for the dipping coating. In all the samples measured the registered current density was in the nearness of the detection limit of the equipment (10⁻¹² A/cm²). This indicates that the thick glass-like coatings produced by EPD are efficient barriers against electrolytic corrosion and the density of these coating appears as higher than coatings produced by dipping. Moreover, EPD makes it possible to produce much thicker coatings, improving the protective behaviour.

(insert Figure 32.16)

On the other hand, the excellent behaviour of these coatings has been confirmed by measurement of polarisation resistance (PR) in NaCl and 1N HCl. Figure 32.17 shows the PR of the EPD coated of 7 µm and uncoated steel in 1 N HCl. The PR of the uncoated steel fell to 10³ Ω/cm² in less than an hour, indicating the very rapid degradation of the substrates. On the contrary, the PR of the EPD coated steel remained above 10¹² Ω/cm² for 100 h in contact with the medium. After this time, the PR slowly decreased until it reached the PR of the uncoated steel after 1000 h.

(insert Figure 32.17)

A bigger problem is the deposition of hybrid coatings on carbon steels. In this case, SiO₂-Na₂O (Conde submitted) obtained from basic catalysis were worked with. The results were not good, even after the steel had been subjected to different superficial passivation treatments, such as phosphating, chromating, etc. Only in the case of a galvanized and galvanized steel were satisfactory results obtained, with a decrease in corrosion rate of two orders of magnitude, although these improvements depend on the correct choice of the sintering treatment applied to the coating.

Potentiodynamic studies carried out on coated galvanized specimens showed strong

changes in the system's response compared with the uncoated material. Corrosion rate estimated from Tafel slopes reveals a decrease of two orders of magnitude for optimal sintering conditions. These results represent a notable improvement in corrosion behaviour compared to other protection systems, surpassing by as much as one order of magnitude the results recently published relating to the use of rare earth-based environmentally-friendly corrosion inhibitors (Arenas 2001). However, for the coated galvanised samples, the behaviour strongly depends on the sintering procedure, Figure 32.18. Furthermore, sol-gel coating does not always yield improvements in corrosion behaviour. The figure shows that the optimum treatment is carried out at 400°C for 10 minutes for which the reduction in the limit current density of almost 2 orders of magnitude is achieved, $i_L=10^{-7}$ A/cm².

(insert Figure 32.18)

From these results, it is possible to conclude that hybrid coatings can protect metal substrates from electrochemical corrosion, qualitatively better than inorganic coatings. The incorporation of organic groups make it possible to increase ductility and thickness, reducing defects and the appearance of micro-cracks and enhancing behaviour towards electrolytic corrosion.

32.5.2.2 Polymer hybrid coatings

One of the fields of increasing development within polymer hybrid coatings focuses on the replacement of the chromate coatings used in the transport industry, especially in aeronautics (Twite 1998; Khobaib 2001; Osborne 2001 a), due to the environmental risk associated with the use of Cr⁶⁺ and the total ban on it as from 2007. Such use requires that the new coating present an. excellent adhesion to the metal and the primer, and a corrosion protection performance comparable to chromates.

The current protection systems used in the aircraft industry are based on the three-coat system, consisting of the surface being pre-treated with chromates, followed by a layer of epoxy-polyamide primer with the incorporation of anti-corrosion pigments, strontium chromate, and finally the top coat based on a system of two components: an epoxy paint or resin cross-linked through the addition of curing agents, such as amines or polyamides. In these systems, the protection function is largely based on the pre-treatment with chromates and on the pigments added to the primer (SrCrO₄).

Generally, the first undercoat is deposited either through anodes, by applying an electric current, or chemically through the reaction of a tri- or sex-valent chromium salt with the

surface. Its main function is to provide good resistance to corrosion, while also improving surface adherence. The top coat should have minimum durability of 8 years. It is deposited by means of the electrostatic assisted spray coating method and its main function is to ensure the durability of the full protection system. It should also have other additional properties such as good resistance to UV radiation and stains and it should be easy to eliminate to facilitate possible repairs to the aircraft (Bierwagen 2001).

The use of chromates, both as additives, in anodising processes, and in conversion coatings, has amply proved its success. However, the environmental risks associated with the use of Cr^{6+} ions has led to it being totally banned as from 2007. For this reason, a great deal of research currently focuses on the replacement of these coatings with others that have similar properties but avoid the toxic risk. One of the solutions proposed is replacement with hybrid coatings produced through sol-gel (Du 2001).

Osborne (Osborne 2001 b) has conducted neutral salt fog tests (ASTM B117), electrochemical impedance spectroscopy (EIS), and electrochemical noise method on SiO_2 - ZrO_2 coatings obtained from a dilute aqueous zirconium and functionalized silicom alkoxide solution on naked aluminium AA2024-T3 and AA7075-T6. The experiments showed that the coatings obtained fail to meet the protection requirements of the demanding aircraft industry and indicated that, so far, some minimum amount of chromate in the coating system is essential for acceptable corrosion performance.

Another line of research that is arousing great interest in this area of research is the incorporation of corrosion inhibitors capable of playing an active role in protecting against corrosion similar to that of Cr^{6+} . Thus, studies are to be found that incorporate a wide variety of compounds such as cerium acetate, cerium oxalate, calcium borate, potassium metavanadate and cerium vanadate.

Voevodin (Voevodin 2001 a; 2001 b; 2001 c) worked on hybrid coatings of ZrO_2 -GPTMS (glycidoxypyriltrimethoxy silane) with and without corrosion inhibitors ($\text{Ce}(\text{NO}_3)_3$, Na_2MoO_4 , and NaVO_3) on A2024-T3 aluminium. Electrochemical measurements for uncoated Al 2024-T3, aluminium coated with chromate conversion coating (Alodine 1200) and with a ZrO_2 -GPTMS coated, Figure 32.19, show that the coated Alodine 1200 had a corrosion potential of -620 mV and presents a small passive region (30 mV) while the ZrO_2 -GPTMS coating has a corrosion potential of -550 mV and exhibited a reduction of four orders of magnitude in corrosion current density (a reduction of two orders in comparison to Alodine 1200), describing a longer passive region about 500mV approximately.

(insert Figure 32.19)

The addition of inhibitors to sol-gel coatings, such as a chromate inhibitor ($\text{Na}_2\text{Cr}_2\text{O}_7$), show comparable results in current density and similar to the sol-gel coatings doped with $\text{Ce}(\text{NO}_3)_3$. However, doped Na_2MoO_4 and NaVO_3 sol-gel coatings exhibit poor passive response and the effects of delamination could be observed by the naked eye, indicating poor adhesion to the substrate. Then, as result of the potentiodynamic screening tests, it was found that the choice of inhibitor is very important since, while the zirconia/epoxy sol-gel and Zr-epoxysol-gel with $\text{Ce}(\text{NO}_3)_3$ performed well and provided corrosion protection of Al 2024-T3, the other classes of inhibitors incorporated offered little protection and massive delamination.

Subsequent EIS tests performed on Alodine 1200 and ZrO_2 -GPTMS coatings exposed in a ProhesionTM Cabinet (ASTM G85.A5) showed no visual signs of corrosion on the coatings after exposure for up to 3600 h, ensuring protection against more severe testing conditions.

On the other hand, the corrosion behaviour of aluminium coated with a sol-gel conversion coating containing SiO_2 and ZrO_2 was studied by EIS (Yang 2001). This coating inhibits the dissolution on the aluminium surface and the impedance modulus increases steadily during the first four weeks of immersion, respect to the uncoated aluminium where the modulus initially increased and then decreased. This indicates that the sol-gel coating stabilized the protecting layer on the aluminium surface.

Du (Du 2001) studied different polymer hybrid coatings cured at 120 °C or below, incorporating some corrosion inhibitors. The best results in salt fog were obtained for coatings with potassium metavanadate inhibitor. However, no electrochemical data were presented.

On the basis of these results, replacing the chromate coatings with polymer hybrid coatings could be considered, but the factors that would limit this application have to be taken into account. Amongst these are the low curing temperature, no more than 150°C, which gives coatings that are not very dense and have low resistance to scratching, so that a small defect would soon lead to the degradation of the coating. This was verified by Khobaib (Khobaib 2001) by means of complex impedance measurements on SiO_2 coatings, prepared from a commercial sol (Aeroglaze 110) and compared with chromate coatings. In spite of their promising protective performance, these coatings have the additional drawback of their low resistance to ultraviolet radiation, a characteristic required of coatings likely to be used in the aircraft industry.

Sugama (Sugama 1991 a; 1992b) studied the resistance to corrosion of the Al-2024-T3 coated with N-(3-(triethoxysilyl)propyl)-4, 5-dihydroimidazole, TSPI sols, with a metal

alcoxide, $M(OC_3H_7)_n$ where $M = Zr, Ti, Al$, with $n = 3$ or 4 and treated at a maximum temperature of $350^\circ C$. The coatings with high ratios of $TSPI/M(OC_3H_7)_n$ (50/50) present lower resistance to corrosion, caused by the degradation of the organic due to the high curing temperatures. On the other hand, the addition of a cross-linking agent, germanium (IV)-ethoxide ($Ge(OC_2H_5)_4$) (Sugama 1992) produces a decrease in the i_{corr} values, which is proportional at $TSPI/Ge(OC_2H_5)_4$ ratio. However the cracks observed in the photographs for all coatings do not tally with the good corrosion results described.

In the bibliography there are other works that study the protective nature of polymer hybrid coatings on other aluminium alloys (Chen 1998) and on stainless steels (Schmidt 1990; Wen 1996). Messaddeq (Messaddeq 1999) studied the properties of AISI 316L stainless steel, coated with hybrid coatings prepared from polymethyl-methacrylate (PMMA) and a zirconia alcoxide, treated at $200^\circ C$. Its performance is analyzed according to different parameters, such as composition, number of coats, etc. The potentiodynamic measurement was carried out in deaerated H_2SO_4 aqueous solution. The results showed that the ZO_2 -PMMA coated samples had a passivation current about one order of magnitude lower than uncoated stainless steel and is invariant with the PMMA concentration. However, this decrease is not the result of the barrier effect introduced by the coating, but is due to the passivation of the substrate in the said medium.

Chou (Chou 2001) studied the protection provided by coatings prepared from TEOS- γ -MPS (3-methacryloxypropyltrimethoxysilane) sols on AISI 304 stainless steel, electro-polished and exposed to nitric acid. The coatings were cured at $300^\circ C$ for 30 min. Electrochemical analyses were performed in an aqueous saturated sodium chloride solution, and the results showed that the coated steel presented a passivation region with a rather low passivation current density of $3.5 \cdot 10^{-8} A/cm^2$, which implied that the sol-gel coatings indeed provided a physical barrier. However, the efficiency of the protection decreases with the ageing of the sol, Figure 32.20. This effect could be produced by a further condensation reaction and, consequently, the formation of a stronger network which could resist the capillary force and prevent the formation of a dense sol-gel coating. Another explanation is that the increasing of viscosity by ageing generates a higher density of defects in the coatings.

(insert Figure 32.20)

In his extense review of both inorganic and inorganic-organic coatings deposited on stainless steel and aluminium, Metroke (Metroke 2001) concludes that sol-gel coatings are good candidates for protective coatings. Similarly to Guglielmi, he affirms that inorganic

coatings inhibit the oxidation of the metal substrates, creating a chemically inert barrier to the diffusion of the species. However, he opts for polymer hybrid coatings to replace chromate coatings, perhaps a rather hasty judgement considering the limitations of these coatings.

More recently, Conde (Conde 2002; 2003) found that the corrosion resistance of Al3005 and Al5555 was improved when the aluminium alloys were coated with hybrid polymeric sols prepared by mixing GPTS(3-glicidoxiporpiltrimetosisilane) with a MTES and TEOS. The i_{pass} is reduced by three orders of magnitude with respect to the uncoated aluminium. Particulate coatings were also obtained by the addition of two types of commercial particles. Potentiodynamic curves revealed that the particulate coatings notably improve the behaviour towards corrosion, decreasing the i_{pass} by three orders of magnitude with respect to the uncoated aluminium, as can be seen in Figure 32.21. Similar results were obtained by Voevodin (2001 a; b; c) for 2024-T3 aluminium alloys but in these last works both, the length of the passive stage and the pitting resistance were lower than those reported by Conde. Moreover, the impedance values reached at lower frequencies (about $10^8 \Omega \cdot \text{cm}^2$) tally with the values reported by Khobaib (2001) although over longer times a slight decrease of the impedance modulus was observed as consequence of the water intake experienced by some of the particulate coatings.

(insert Figure 32.21)

On the other hand, EIS measurements showed that the addition of particles to epoxysilane coatings remarkably improves the final properties, since the value of the impedance at low frequencies rises by one order of magnitude and the porosity decreases in comparison with a similar coatings with no particles (Figure 32.22).

(insert Figure 32.22)

Therefore, this work reveals that, apart from the ability of the impedance technique to distinguish the mechanism which controls the corrosion process in each case, it distinguishes between particulate and non-particulate coatings. The technique is also sensitive enough to notice the differences in the hydrophobic nature of the coatings, depending on the type of particles added to the sol, even though the general shape of the plots do not change.

3.6. Conclusions

From its significant success in the research conducted in previous decades and its many

potential practical applications, it may be assumed that the prospect for sol-gel is quite promising as a method of protecting against corrosion. Some particularly good examples have been obtained in the protection with glass-like hybrid coatings sintered below 500°C and using alternative coating deposition techniques like EPD.

The adequate performance of these films requires, however, to take into account different parameters, including the composition, sol processing conditions, deposition methods, thermal treatments and final structure. Similar compositions obtained by different processing routes usually lead to different behaviour in service. Therefore, for designing a coating to fulfil a specific requirement, it is essential to consider the type of substrate and its properties, and the precise role it must accomplish.

Special attention must be paid to solving specific problems in sol-gel processing or coating/metal systems. A clear example are the aluminium alloys used in the aircraft industry which, together with the low curing temperatures needed to avoid the loss of mechanical properties, demands high protection from potential substitutes for the current protection systems. Alternatively, new sol-gel deposition methods should be developed so that the coating process can be implemented on an industrial scale.

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