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Corrosion of steel alloys with ferrite coating

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Abstract

The corrosion protection offered by coatings of hexagonal Sr ferrites on steel samples in the presence of chloride was evaluated by electrochemical techniques. Different samples were prepared using Nd-Co doped and un-doped strontium hexaferrite coatings, and tested in sodium chloride (NaCl) solutions during 45 days. Time variation of the corrosion potential and polarization resistance measurements were carried out for each of the tested steel samples at different immersion times. All the samples were characterized by scanning electronic microscopy and energy dispersive X-ray analysis (SEM/EDX).

All the tested ferrite coatings offered good protection and corrosion resistance, which increased as the samples remained immersed in the chloride solution. When a concentrated NaCl solution was employed as corrosive agent, the coatings continued offering protection and the currents increased one order of magnitude, while remaining constant with the variation of the immersion time. The samples coated with doped ferrite showed the highest resistance to the aggressive environment, with low corrosion rates even after 48 hours of immersion in NaCl 0.5 M.

Keywords: Corrosion; Steel; Strontium Hexaferrite; Lineal Polarization; SEM-EDX.

1. Introduction

One of the most widely used methods for protection against metallic corrosion is the application of organic polymeric coatings, often described as paintings. Among the main organic coatings that improve the corrosion resistance of steel are paintings with an epoxy resin, in which inorganic particles or passivating compounds may be incorporated, in order to delay the corrosion phenomenon. The resin exerts a barrier effect, separating the metal

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from the corrosive aqueous medium. However, the barrier properties are often insufficient, since aggressive ions can penetrate through the pores of the coating, initiating the corrosive process. The incorporation of inorganic substances has an inhibitory effect, limiting anodic, cathodic or both reactions. In the case of iron, the inhibition is produced by the formation of iron compounds at the anode or the creation of insoluble compounds at the cathode. Inorganic inhibitory pigments include zinc or strontium chromate, zinc or lead tetraoxochromate, and zinc phosphates (Bard et al., 2003). While chromates are one of the most efficient substances in protecting against corrosion, in recent decades they had to be replaced with compounds which are more environment-friendly (WTO Committee, 1998).

Strontium hexaferrite ($\text{SrFe}_{11}\text{O}_{19}$) is an inorganic mixed oxide with ferrimagnetic characteristics and various applications as permanent magnets, magnetic recording, microwave absorber, etc. (Lechevallier et al., 2007). In previous works, we have reported an improvement in the magnetic properties of this material by the inclusion of Nd and Co in their structure (Jacobo et al., 2010), (Herme et al., 2012). One of the applications of these ceramic materials (currently under study), is their use as electromagnetic radiation absorbers, for which they are included in a polymer matrix (epoxy resin). In order to explore the potential applications of a painting with these particles, the study of resistance to corrosion of this material was carried out.

2. Experimental techniques

Two different samples of strontium hexaferrite were prepared. One of them, called M0, with an iron deficient theoretical formulation ($\text{SrFe}_{11}\text{O}_{19}$), and the other one, called M20, was doped with 20% Co^{2+} and Nd^{3+} , with nominal composition $\text{Sr}_{0.8}\text{Fe}_{10.8}\text{Co}_{0.2}\text{Nd}_{0.2}\text{O}_{19}$. The samples were prepared by the gel combustion technique (Jacobo et al., 2010). Stoichiometric amounts of the reactants $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$, SrCO_3 , $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4 \text{H}_2\text{O}$, and Nd_2O_3 were weighed and dissolved in HNO_3 . Then, the mixtures were neutralized with concentrated ammonia and the resulting precipitates were re-dissolved in a solution of citric acid, $\text{HOC}(\text{CH}_2\text{CO}_2\text{H})_2\text{CO}_2\text{H}$, until the relation citrate:nitrate was 1:1. The pH value of these citrate complexed solutions was adjusted to 8 and then they were slowly evaporated. The citrate solutions became into gels and then combustion started spontaneously. The resulting ashes were grinded and calcined at $1100 \text{ }^\circ\text{C}$ for 2 hours. Finally, the ferrite powders were meshed to obtain a particle mean size smaller or equal to $200 \text{ }\mu\text{m}$.

Samples powders (M0 and M20) were dispersed into an epoxy resin of high viscosity by sonication at room temperature, during 30 minutes before the addition of a hardener, with a final mass percentage hexaferrite:epoxy resin:hardener of 40:35:25. After that, coverings of the two different paintings obtained with the hexaferrite particles were applied on rectangular steel plates of $4.0 \text{ cm} \times 3.6 \text{ cm} \times 1.6 \text{ mm}$. These coats of paint were dried at room temperature for 5 days, which is the recommended time by the supplier for the resin to get its final hardness. Control samples were prepared in a similar way, but using the epoxy resin without including ferrite particles (samples named B). All the plates were made of cold-cast steel of total hardness quality, whose surface was free of imperfections, with the following composition (in mass): carbon 0.13%, manganese 0.60%, phosphorus 0.03%, sulphur 0.035%, and aluminum 0.01% (minimum). The painted faces of the plates were put in contact with aqueous solutions of NaCl 0.3% (0.05 M) or 3.0% (0.5 M), during 45 days at room temperature, leaving no air between the solution and the exposed surfaces. The NaCl solutions were replaced every 48 hours in order to maintain a constant composition. Once the exposures were finished, the plates were rinsed with distilled water and dried. In each plate, the exposed zone was a circle of a 3.2 cm diameter. Other coated plates, without exposure with the NaCl solutions, were left as controls.

The different plates were named after its coating, using the following nomenclature:

Nomenclature

B	epoxy resin only
M0	undoped ferrite in resin
M20	Nd-Co doped ferrite in resin

Control samples (not exposed to NaCl):

B control

M0 control

M20 control

Samples exposed to NaCl 0.3% (0.05 M) for 45 days:

B-0.3%

M0-0.3%

M20-0.3%

Samples exposed to NaCl 3% (0.5 M) for 45 days:

B-3%

M0-3%

M20-3%

In order to evaluate the corrosion resistance of the different coatings, electrochemical determinations were carried out on all the samples, at two different concentrations of NaCl solutions (0.1 M and 0.5 M), after being immersed for 1 h, 24 h and 48 h in the corresponding solution. Measurements of the corrosion potential (for one hour) and polarization resistance (with a scan rate of 0.2 mV/s) were carried out. These experiments allowed obtaining the corrosion rate for different times, and thus evaluating the effect of the chloride ion concentration and immersion time in the coating performance.

The measurements were carried out with a potentiostat from EG&G Princeton Applied Research, model Parstat 2273. The Flat electrochemical cell, model K0235, consistent in a glass cylinder horizontally placed between two plates at each end, was used. At one end, the work electrode is placed, setting an area of 1 cm² in contact with the NaCl solution, while the plate at the other end contained a platinum counter electrode. A saturated calomel electrode (0.242 V vs SHE) was used as reference.

A scanning electron microscope Sigma Zeiss with an Oxford X-ray detector was used to study the morphology and composition of the corrosion products.

3. Results and discussion

3.1. Structural characteristics of the used ferrite powders

Figure 1 shows the powders used in the preparation of paintings. The micrographs were taken with different magnification, as they show different characteristics.

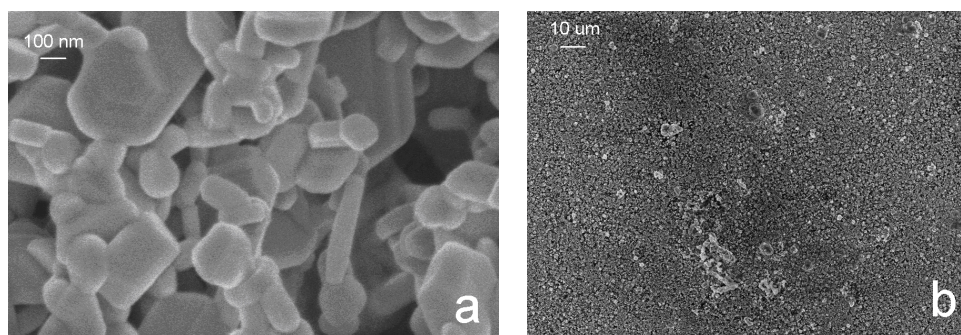


Figure 1. Images of: (a) M0 particles; (b) M0 particles dispersed in epoxy resin (40% mass).

The strontium hexaferrite particles, SrFe₁₁O₁₉ (Fig. 1a), are hexagonal platelets, showing the characteristic shape of hexaferrite crystals, with sizes between 100 and 150 nm. The obtained paint (Fig. 1b) shows a homogeneous distribution inside the composite material.

The used hexaferrites are hard ferrimagnetic materials, whose main magnetic characteristics are listed in Table 1. The addition of Nd and Co (sample M20) increases the coercivity (H_C) 12% and diminishes the saturation magnetization (M_S) 5%. In addition, the crystallite size (obtained from X-ray diffraction, using Scherrer's formula) is slightly reduced. These ferrites are useful for a variety of electronic applications (Bercoff et al., 2009), (Herme et al., 2010), (Rezlescu et al., 2008).

Table 1. Characteristics of strontium hexaferrite powders.

Sample	M_S [emu/g]	H_C [kOe]	Crystallite size [nm]
M0 ($\text{SrFe}_{11}\text{O}_{19}$)	97	4.9	120
M20 ($\text{Sr}_{0.8}\text{Fe}_{10.8}\text{Co}_{0.2}\text{Nd}_{0.2}\text{O}_{19}$)	92	5.5	90

3.2. Electrochemical evaluation of the corrosion rate

Polarization resistance or the lineal polarization technique (LPR) is an electrochemical method that allows to determine the instantaneous speed of corrosion, applying a voltage signal to the work electrode, very close to the corrosion potential value. Since the difference between the applied voltage and the potential of corrosion is very small, the tested surface is not affected by the measurement, and this technique can be considered as non-destructive. From the slope of the plot of potential *versus* current, the polarization resistance (R_p) can be measured. R_p is inversely proportional to the corrosion current (i_c), according to the Butler-Volmer equation:

$$R_p = \frac{B}{i_c} \quad (1)$$

where B is a proportionality constant, that can be calculated from the two Tafel constants (β_a and β_c).

The corrosion rate, expressed in units of $\text{mg} / (\text{dm}^2 \text{ day})$ (mdd) can be calculated from the i_c values.

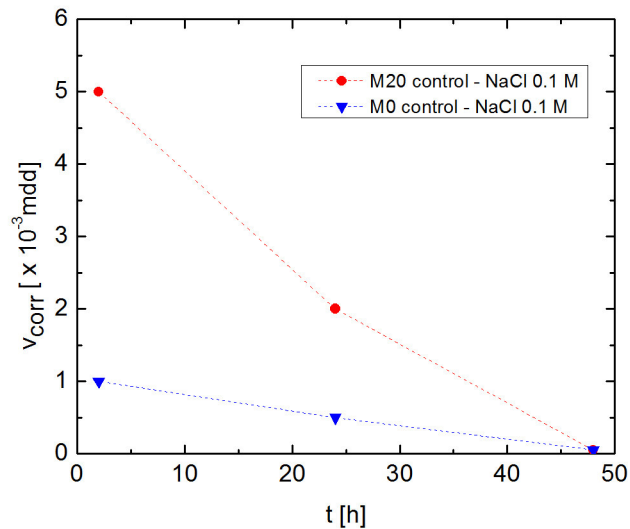


Figure 2. Corrosion rate *versus* time for control samples M0 control and M20 control in NaCl 0.1 M.

Figure 2 shows the variation of the corrosion rate in mdd ($\text{mg}/\text{dm}^2 \text{ day}$) *versus* time, for samples M0 control and M20 control in NaCl 0.1 M. For the un-doped ferrite coating (M0) a progressive decrease of the corrosion rate can be observed for the longest immersion times, whereas for the doped ferrite coating (M20) there is a dramatic reduction every 24 hours. The corrosion rate of both coatings reaches similar values, tending to zero, at 48 h of

immersion time ($i_c \approx 7 \times 10^{-7}$ A/cm² and $R_p \approx 30,000$ k Ω). The values of corrosion current and corrosion rate obtained in both solutions clearly show the protection that the coatings have provided, offering resistance to the presence of chloride in the solution.

The measurements of the variation of corrosion potential with time confirm these results, showing a trend to more “noble” values, with an important change in the corrosion potential at 48 hours. On the contrary, the sample covered only with resin (B) presents constant protection with the immersion time, but smaller than those offered by the M20 or M0 coatings ($i_c \approx 10^{-6}$ A/cm²).

Figure 3 shows the variation with time of the corrosion rate, in mdd (mg/dm² day), for samples M0-3% and M0-0.3%, which were previously exposed for 45 days in 3% and 0.3% NaCl corrosive solutions, respectively. The measurements were performed in NaCl 0.1 M and 0.5 M solutions. In samples M0-3% and M0-0.3%, the corrosion rate values are one order of magnitude higher than the ones obtained for sample M0 control (Fig. 2). This can be related to the loss of protective power of the coating after its prolonged exposure to the chloride solution. It is also observed that the corrosion rate values of sample M0-0.3% are smaller than the corresponding to M0-3%, since the previous corrosion exposure would reduce the passive effect of the coating, because of the higher chloride concentration in the corrosive solution. When the samples were measured in NaCl 0.1 M, the coatings continued offering protection. It was also observed that, for all samples, the corrosion rate diminished with longer immersion times. The same trend was observed for the samples with doped ferrite coatings (M20), with even smaller corrosion rate values, becoming negligible for sample M20-0.3%. The same behavior was observed for the paintings measured in NaCl 0.5 M solution, with higher corrosion rates. Also in this solution, the doped ferrite coating showed better resistance to environmental aggression.

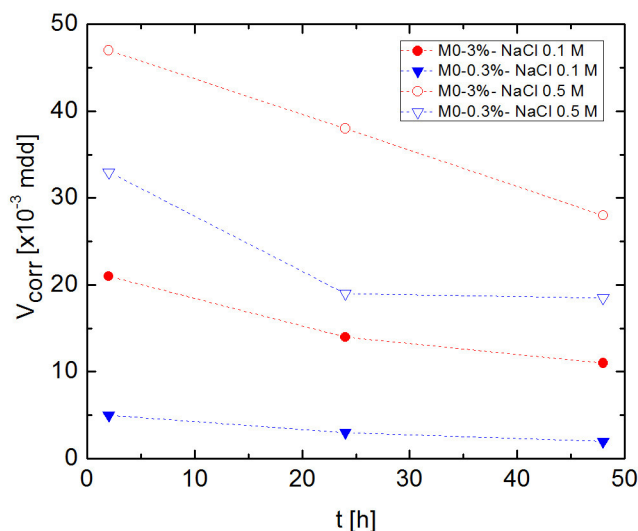


Figure 3. Corrosion rate versus time for samples M0-0.3% and M0-3% in NaCl 0.1 M and 0.5 M.

3.3. Morphology of the paintings during the corrosion tests

Figure 4 shows the SEM micrographs of two different coatings (B-0.3% and M0-0.3%), exposed to the corrosive solution of NaCl 0.3% for 45 days (see Section 2).

A very uniform crystalline structure can be observed in Figure 4(a), with the epoxy resin scaly-shaped particles regularly arranged. In Figure 4(b), the resin particles are mixed with platelet-shaped particles of hexaferrite, forming a more compact layer of painting. The observed hexagonal platelets match the Sr hexaferrite particles (see Figure 1(a)).

This crystalline film is also observed in the samples that were exposed to a higher concentration of saline solution (NaCl 3%), but in this case, this layer became more agglomerated, forming bunches of crystals. EDX analyses

confirm the nominal composition of each sample before the corrosion experiments. These compositions were slightly modified after the tests because of the percentage increase of oxygen, while the metallic ions proportions remained constant. These results suggest the presence of hydroxides and/or oxides within the area of NaCl solution exposure, which would form a passive layer on the steel surface. This can be observed in both ferrite samples, M0 and M20.

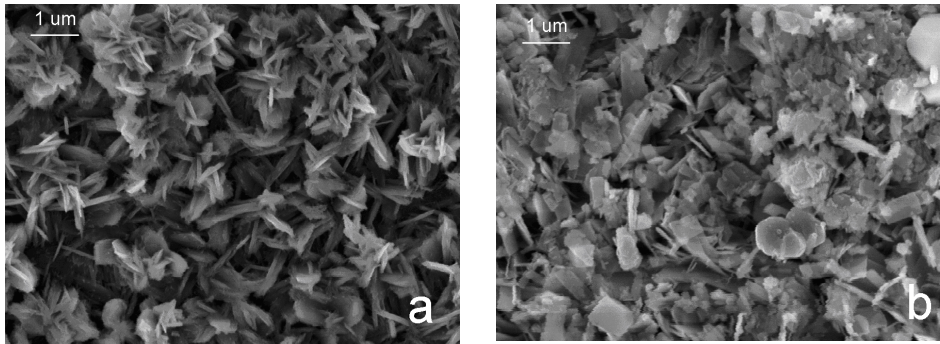


Figure 4. Images of coatings: (a) B-0.3%; (b) M0-0.3%.

The SEM/EDX analyses confirm the results obtained from electrochemical measurements, indicating that these paintings are appropriate to cover steel external surfaces and protect them from corrosion.

4. Conclusions

Strontium hexaferrite acts inside the painting like an inhibiting additive against corrosion, increasing the barrier effect of the epoxy resin coating. From SEM/EDX observations it could be inferred that this effect would occur due to the formation of a passive shell of insoluble oxides. The presence of iron and strontium ions, characterized by the poor solubility of their hydroxides and/or oxides, also suggests this mechanism. In the case of sample M20, substitution with Nd and Co would induce the formation of compounds with higher density, which may produce a continuous passive shell over the steel surface to be protected.

The results of electrochemical measurements reinforce this hypothesis, since the addition of strontium hexaferrite raises the protection against corrosion of the steel when comparing with a simple epoxy resin coating. This increase is even greater in the case of the paint with Nd-Co doped ferrite. These hexaferrite-modified paints can be applied to external surfaces obtaining—in addition of radiation shielding—a good protection from corrosion.

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