DEVELOPMENT OF AN ANTI-CORROSIVE COATING BASED ON A CERAMIC NANOPIGMENT

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Abstract
Corrosion is the physicochemical interaction between a metal and its environment which results in changes in the properties of the metal. Corrosion protection requires the use of corrosion inhibitor coatings that protect the underlying metal. These coatings can be of different nature, from organic or hybrid to totally inorganic. In this study, a Fe-Cr ceramic nanopigment was synthesized by sol-gel method and applied over SAE 1015 carbon steel specimens by thermodiffusion.

The characterisation of the pigment was carried out by X-ray diffraction (XRD), scanning electron microscope (SEM), wavelength-dispersive X-ray fluorescence (WD-XRF), and oxygen elemental analysis by thermal decomposition and IR detection.

The Fe-Cr pigment was applied over the cited carbon steel and subjected to various real corrosive environments: a chloride-rich atmosphere, a marine atmosphere, and an atmosphere exempt of specific contaminants. The test specimens were exposed for 9 months to study the long-term corrosion resistance and understand the deterioration mechanism.

The inhibition power achieved was determined by XRD, SEM-EDS, and weight difference. The analyses undertaken permitted the evaluation of the changes generated in the steel and the coated steel, studying the appearance of rust phases, and/or disappearance of the original phases, the changes in the surface morphology, and quantifying the corrosion grade.

Keywords: Corrosion inhibitor; inorganic coating; ceramic nanopigment; XRD; SEM-EDS
Introduction

Corrosion occurs due to the physicochemical interaction between a metal and the environment which results in changes in the properties of the metal and which may lead to a decrease in the functionality of the metal, the environment, or the technical system of which these form a part [1, 2]. Corrosion generates a considerable amount of economical loses, the global annual cost of corrosion being estimated around 4.2% of the gross national products (approximately $100 billion in USA and around $200 billion in Europe) [3, 4].

Corrosion protection requires the use of anticorrosion pigments or corrosion inhibitors that protect the underlying metal. For many years, the most effective corrosion protection systems were based on the use of chromates. However, the current legislation imposed by REACH prohibits the use of Cr(VI) in almost all sectors except the aerospace industry. Thus, there is a need for more advanced coatings for conventional applications and there is also a need to answer requirements of several new Hi-Tech applications [2].

Inorganic pigments such as Cr$_{1.3}$Fe$_{0.7}$O$_3$ nanopigment have been investigated due to their chemical stability such as resistance to chemical attacks by acids and alkalis, excellent hardness and high temperature stability [8, 9].

In this study, a Fe-Cr ceramic nanopigment was synthesized to be used as corrosion inhibitor. The characterisation was carried out by X-ray diffraction (XRD) (to identify the crystalline phases), scanning electron microscope (SEM) (to investigate the morphology and size of the particles), wavelength-dispersive X-ray fluorescence (WD-XRF) (to determine the chemical composition), and oxygen elemental analysis by thermal decomposition and infrared (IR) detection (to analyze the oxygen content and calculate the exact stoichiometry of the pigment).

The real effectiveness of the coating developed was studied by applying it over a carbon steel specimen and subjecting it to various corrosive environments: a chloride-rich atmosphere, a marine atmosphere, and an atmosphere exempt of specific contaminants (atmospheric pressure – 100 kPa, relative humidity – 64%), which were selected considering the different classifications of corrosive atmospheres [7, 18, 19]. Test specimens were exposed to these real environment conditions for long periods of time, evaluating the corrosion resistance in real conditions overtime (after 3 and 9 months of exposure).

Many studies have investigated the corrosion applying XRD and SEM [20, 21], which information obtained is quite enriching from a corrosion mechanism point of view. However, these techniques do not permit its quantification. Other studies have calculated the corrosion rate, which can be established either by mass loss or mass gain [20, 22-24].

In the present study, the inhibition power achieved with the inorganic coating was assessed by applying XRD and SEM-EDS to better understand the corrosion mechanisms; and calculating the difference of weight of the test specimens (as a quantitative measurement) at different exposure times.

Experimental

Synthesis and characterisation of the Fe-Cr ceramic nanopigment

Cr$_{1.3}$Fe$_{0.7}$O$_3$ ceramic nanopigment was prepared using sol-gel method. For that, stearic acid was melted in an oven at a temperature of 73°C. Then, Fe(NO$_3$)$_3$·9H$_2$O and (NH$_4$)$_2$Cr$_2$O$_7$ were added in stoichiometric proportion to a mixture of water and nitric acid (1:1 %v/v). The aqueous solution was added into the melted stearic acid and heated in an oven at 90°C for 48 hours until a homogeneous light brown sol was obtained. The sol was cooled down to room temperature and dried in an oven for 12 hours [8, 9].
Identification of crystalline phases was carried out with a BRUKER model D8 Advance XRD instrument, using ICCD (International Center for Diffraction Data) cards for pure crystalline phases. The morphology and size of the nanoparticles was studied using a FEI model FEG-SEM Quanta 200 field-emission environmental scanning electron microscope equipped with an energy dispersive X-ray microanalysis [Si(Li) EDAX Genesis 7000 SUTW (super ultrathin window)].

Chemical characterisation was carried out using a PANalytical model AXIOS WD-XRF spectrometer with a Rh tube, 4 kW power, and three detectors: flow, scintillation, and sealed, using the analysis program based on fundamental parameters UNIQUANT provided by PANalytical to determine all the impurities, and Fe and Cr were quantified preparing calibration curves with certified reference materials which correction factors, slope, and ordinate at the origin were obtained by regression, using PANalytical’s SuperQ software.

The determination of the oxygen content was performed by thermal decomposition in an electrode furnace using helium as a carrier and infrared (IR) detection, using a LECO model TC-436 elemental analyser, which value permitted the calculation of the exact stoichiometry of the pigment.

Application of the coating over the substrate

30-mm diameter test specimens were prepared from SAE 1015 carbon steel (referenced in accordance with the American Iron and Steel Institute -AISI-), which present the following chemical composition: 0.7% Mn, and 0.04% C, Fe being the major constituent.

The ceramic nanopigment was applied by thermodiffusion treatment at 900ºC for 4 h. During this heating process, atoms of Fe of the nanopigment diffused into the vacancies the carbon steel created during its solidifications, at high temperatures [8].

Corrosion evaluation

Coated and non-coated test specimens were subjected to the following corrosive environments to study the real inhibitor effect:

- **Chloride-rich atmosphere**: generated inside a fume hood with a device containing HCl which is continuously boiling, chloride-rich vapours being generated.

- **Marine atmosphere**: coastal area in the Mediterranean east coast of Spain.

- **Atmosphere exempt of specific contaminants**: sea level area, 20 km far from the sea, with 100 kPa atmospheric pressure and 64% relative humidity.

Test specimens were placed in the selected corrosive environments for 9 months to induce corrosion. This exposure time was much longer than those stated in the different test standards consulted and enough to result in some real conclusions.

The corrosion mechanism was evaluated using XRD, SEM-EDS, and weight difference (as a quantitative measure) at different times of exposure: before the experiment, after 3-month exposure, and after 9-month exposure. Weight difference was evaluated using a Mettler-Toledo model XA105 balance with a sensibility of 0.01 mg, the weight difference being calculated as follows:

\[ \Delta P = \frac{P_1 - P_0}{S} \]  

where \( P_0 \) is the initial weight of the test specimen (mg), \( P_1 \) is the test specimen weight after a certain time of exposure (mg), and \( S \) is the test specimen area (dm²).
**Results**

**Ceramic nanopigment characterisation**

Figure 1 shows the XRD pattern obtained, being indexed as solid solution of Cr/Fe (SS) [26]. There were no peaks that could be attributed to the prior reagents. Besides, the sharp peaks in the XRD pattern showed that Fe-Cr nanopigment had been intensely crystallized.

![Figure 1 XRD pattern for Fe-Cr ceramic nanopigment](image)

Consequently, the synthesized pigment not only did it present the desired crystalline structure but also the appropriate average particle size distribution.

![Figure 2 SEM micrograph for Fe-Cr ceramic nanopigment](image)

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Table 1 shows the results obtained for the chemical analysis.
Table 1 Chemical characterisation of the Fe-Cr nanopigment synthesized

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (%)</th>
<th>Stoichiometry</th>
</tr>
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<tbody>
<tr>
<td>Fe</td>
<td>26.3</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>43.9</td>
<td>Cr&lt;sub&gt;1.3&lt;/sub&gt;Fe&lt;sub&gt;0.65&lt;/sub&gt;O&lt;sub&gt;3.05&lt;/sub&gt;</td>
</tr>
<tr>
<td>O</td>
<td>31.9</td>
<td></td>
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</table>

The nanopigment synthesized presented almost the theoretical stoichiometry, which confirmed that the synthesis process had been correctly undertaken.

Corrosion evaluation

Table 2 shows the crystalline phases identified for the uncoated and coated test specimens before being subjected to the experiment and after three and nine months of exposure to the three corrosive environments studied.

Table 2 Crystalline phases identified in the uncoated and coated test specimens subjected to the different corrosive conditions

<table>
<thead>
<tr>
<th>Chloride-rich</th>
<th></th>
<th></th>
<th>Marine</th>
<th></th>
<th></th>
<th>No specific contaminants</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>Uncoated</td>
<td>Coated</td>
<td>Uncoated</td>
<td>Coated</td>
<td>Uncoated</td>
<td>Coated</td>
<td>Uncoated</td>
<td>Coated</td>
</tr>
<tr>
<td>corrosion</td>
<td>Fe=Iron (Fe)</td>
<td>SS=Solid solution Fe/Cr</td>
<td>Fe=Iron (Fe)</td>
<td>SS=Solid solution Fe/Cr</td>
<td>Fe=Iron (Fe)</td>
<td>SS=Solid solution Fe/Cr</td>
<td>Fe=Iron (Fe)</td>
<td>SS=Solid solution Fe/Cr</td>
</tr>
<tr>
<td>3-month</td>
<td>Fe=Iron (Fe)</td>
<td>Akaganeite (Fe&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sub&gt;0.25&lt;/sub&gt;O&lt;sub&gt;3.75&lt;/sub&gt;(OH)&lt;sub&gt;4.25&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;0.2&lt;/sub&gt;)</td>
<td>Fe=Iron (Fe)</td>
<td>Magnetite (Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;)</td>
<td>Fe=Iron (Fe)</td>
<td>SS=Solid solution Fe/Cr</td>
<td>Fe=Iron (Fe)</td>
<td>SS=Solid solution Fe/Cr</td>
</tr>
<tr>
<td>exposure</td>
<td>Ak=Akaganeite (Fe&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sub&gt;0.25&lt;/sub&gt;O&lt;sub&gt;3.75&lt;/sub&gt;(OH)&lt;sub&gt;4.25&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;0.2&lt;/sub&gt;)</td>
<td>SS=Solid solution Fe/Cr</td>
<td>Ak=Akaganeite (Fe&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sub&gt;0.25&lt;/sub&gt;O&lt;sub&gt;3.75&lt;/sub&gt;(OH)&lt;sub&gt;4.25&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;0.2&lt;/sub&gt;)</td>
<td>SS=Solid solution Fe/Cr</td>
<td>Ak=Akaganeite (Fe&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sub&gt;0.25&lt;/sub&gt;O&lt;sub&gt;3.75&lt;/sub&gt;(OH)&lt;sub&gt;4.25&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;0.2&lt;/sub&gt;)</td>
<td>SS=Solid solution Fe/Cr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9-month</td>
<td>Fe=Iron (Fe)</td>
<td>Akaganeite (Fe&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sub&gt;0.25&lt;/sub&gt;O&lt;sub&gt;3.75&lt;/sub&gt;(OH)&lt;sub&gt;4.25&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;0.2&lt;/sub&gt;)</td>
<td>Fe=Iron (Fe)</td>
<td>Goethite (α-FeOOH)</td>
<td>Fe=Iron (Fe)</td>
<td>SS=Solid solution Fe/Cr</td>
<td>Fe=Iron (Fe)</td>
<td>SS=Solid solution Fe/Cr</td>
</tr>
<tr>
<td>exposure</td>
<td>Ak=Akaganeite (Fe&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sub&gt;0.25&lt;/sub&gt;O&lt;sub&gt;3.75&lt;/sub&gt;(OH)&lt;sub&gt;4.25&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;0.2&lt;/sub&gt;)</td>
<td>SS=Solid solution Fe/Cr</td>
<td>Lep=Lepidocrocite (γ-FeOOH)</td>
<td>SS=Solid solution Fe/Cr</td>
<td>Lep=Lepidocrocite (γ-FeOOH)</td>
<td>SS=Solid solution Fe/Cr</td>
<td></td>
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</table>

The DRX pattern obtained for SAE 1015 carbon steel was indexed as iron (Fe), as expected as iron is its major component, not showing any other crystalline phase, while the coated steel was indexed as solid solution (SS), showing the same XRD pattern as the synthesized pigment.

Regarding the uncoated tests specimens, to be noted was the appearance of rust phases overtime and the diminution of the peak intensity of the iron (crystalline phase present in the uncoated test specimen before experimentation), which indicated a loss in crystallinity. The one subjected to the chloride-rich environment showed the appearance of a new crystalline phase of Akaganeite (Fe<sub>4</sub>Cl<sub>0.25</sub>O<sub>3.75</sub>(OH)<sub>4.25</sub>(H<sub>2</sub>O)<sub>0.2</sub>), probably due to an interaction between the chloride and moisture present in the atmosphere with the test surface. These results were in accordance with the ones obtained by De la Fuente et al. where the characterisation of the rust surface formed on mild steel in an environment rich in chloride was studied [27]. The uncoated test specimen subjected to the marine atmosphere showed a completely disappearance of crystallinity after 9 months of exposure, the only structures identified being the oxyhydroxides goethite (α-FeOOH) and lepidocrocite (γ-FeOOH), although present in the
specimen as minorities. In the first stages of corrosion appearance, iron from the substrate reacted with the oxygen of the environment to form the ferrous-ferrie oxide magnetite ($\text{Fe}_3\text{O}_4$). Overtime, the oxides evolved to oxyhydroxides, also stated by De la Fuente [27]. Besides, the presence of sylvine ((Na, K)Cl) could be attributed to dust deposition in the surface specimen. Finally, the one subjected to the atmosphere exempt of specific contaminants showed a lower loss of crystallinity, as this atmosphere was less corrosive than the previous ones, Akaganeite appearing after 9 months of exposure, present in the sample as a minority.

Comparing these results with the ones obtained for the coated specimen, it was clearly shown that neither structures due to the oxidation of the steel were formed nor loss of crystallinity was observed after 9 months of exposure, not revealing any evidence of corrosion after 9 months of exposure to the different corrosive environments.

Figures 3 to 5 show the results of the EDX analyses of the top surface of either the uncoated carbon steel test specimens and the coated ones, together with the SEM-micrographs, subjected to the three corrosive environments studied after 9 months of exposure.

**Figure 3 EDX analyses and SEM micrographs of the test specimens (uncoated and coated) subjected to a chloride-rich atmosphere**

**Figure 4 EDX analyses and SEM micrographs of the test specimens (uncoated and coated) subjected to a marine atmosphere**
Figure 5 EDX analyses and SEM micrographs of the test specimens (uncoated and coated) subjected to an atmosphere exempt of specific contaminants

SEM image of SAE 1015 carbon steel before exposure showed a homogeneous surface whose EDX analysis revealed the only presence of iron. After 9 months of exposure, uncoated specimens subjected to the three environments underwent an oxidation process which can be confirmed by the appearance of a high intensity peak of oxygen and the diminution of the intensity peak of iron in their EDX analyses, being more pronounced in the specimen exposed to the marine atmosphere. Apart from this, a little peak of chloride also appeared, being higher in the specimen subjected to the chloride atmosphere, as expected. The appearance of Si and Al in the specimens submitted to the marine atmosphere and the one with no specific contaminants could be attributed to the presence of environmental dust. Comparing SEM images of the corroded specimens, the ones subjected to the chloride-rich and marine atmospheres showed a heterogeneous surface, while SEM image of the one exposed to the atmosphere with no specific contaminants showed zones that had suffered from corrosion while other parts were not corroded.

On the other hand, EDX analysis of the coated specimen before corrosion showed the elements present in the nanopigment composition. In the subsequent EDX, after 9 months of exposure, no significant peak intensity variations were observed for these elements. In the test specimen exposed to a chloride-rich atmosphere, a peak of chloride can be detected, although SEM images showed that chloride particles were deposited on the surface, not damaging it. No signs of corrosion could be observed in any of the coated test specimens.

Measurements of weight difference were used to quantify the grade of corrosion. The variation of weight obtained from Eq. (1) is plotted in figure 6 for both the uncoated and coated test specimens subjected to the three corrosive environments selected for this study.
Figure 6 Weight differences for SAE 1015 carbon steel uncoated and coated in chloride-rich atmosphere

The results showed a gain of mass in the uncoated test specimens which increased overtime. This gain of mass was attributed to the appearance of rust phases, such as Akaganeite, magnetite, goethite, and lepidocrocite, identified in the DRX analyses, whose molecular mass is much higher than the one of iron (major component in carbon steel). Comparing the results, it can be seen that test specimens subjected to a marine atmosphere underwent a much higher gain of weight than the ones subjected to the other corrosive environments. When the steel has no protection, the higher the aggressiveness of the corrosive atmosphere the higher the gain of weight. However, coated specimens did not show any significant weight difference even after 9 months of exposure irrespective of the environment, which is an indicative of the suitability of the ceramic nanopigment coating in all the studied conditions.

Conclusions

1. Fe-Cr ceramic nanopigment coating showed excellent performance and effectiveness in all the corrosive environments studied and presents the advantage of being able to be used in processes which involve high temperatures.

2. The oxygen determination provides valuable information in those chemical compounds that do not have a concrete stoichiometry. Together with the analysis by WD-XRF, it allows the calculation of the exact molecular formula.

3. The use of techniques such as XRD, SEM-EDX permits the assessment of the changes generated in the steel due to corrosion (appearance of new phases and disappearance of the original phases and changes in the morphology of the surface) and the corrosion grade quantification is determined by the determination of the difference of weight.

4. Each environment caused the formation of different rust phases (Akaganeite ($\text{Fe}_4\text{Cl}_{0,25}\text{O}_{3,75}(\text{OH})_{4,25}(\text{H}_2\text{O})_{0,2}$), goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), and/or
magnetite ($\text{Fe}_3\text{O}_4$)) in the same steel, which could result in different corrosion behaviour. Taking this into consideration, it is important to test the materials in real use conditions, as the standardized methodologies based on accelerated tests can lead to no translatable results.

5. Marine atmosphere, as expected, was the most corrosive environment (higher presence of rust phases in the uncoated steel and much higher variation of weight than the other environments studied) because of the additive effects of humidity and the presence of chloride.

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