Composition and behaviour of cerium films on galvanised steel

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Abstract

The composition and corrosion performance of galvanised steel treated by immersion in cerium nitrate solution was investigated by electrochemical techniques and surface analysis. The surface film consists of a mixture of Ce(III) and Ce(IV) compounds, being very rich in Ce(III) in the first instants of the deposition process and becoming gradually enriched in the more oxidised form, Ce(IV). The presence of this film on the surface hinders the corrosion reaction by reducing the rate of both the cathodic and the anodic reactions. The film becomes thicker but more uneven when the time of film growth increases, with the development of defects in the film, which in contact with electrolyte behaves anodic with respect to the covered areas of the surface. These thicker films have revealed lower resistance to corrosion initiation. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chromates have been widely applied as corrosion inhibitors in aqueous media. Surface pre-treatments based on the use of chromates have been successfully applied on a large number of metal and alloys. The success of these pre-treatments is mainly due to their high protection efficiency/cost ratio. However, hexavalent chromium presents very high toxicity and its use has been leading to legislation that will soon prohibit these pre-treatments. Therefore, new alternative and more environmentally friendly surface pre-treatments need to be developed. Recent efforts have been focussed on the use of rare earth salts as corrosion inhibitors. Among these, cerium has risen as a possible alternative. The first studies on this field are those of Hinton [1–3], who found that cerium was effective in reducing the corrosion rate of aluminium alloys by inhibiting the cathodic reactions. These preliminary studies using cerium salts, namely CeCl₃, as corrosion inhibitors for aluminium alloys have shown that the inhibition mechanism is associated with a reduction in the rate of aluminium alloy corrosion. These studies have shown that the inhibition mechanism is associated with a reduction in the rate of aluminium alloy corrosion. These studies have shown that the inhibition mechanism is associated with a reduction in the rate of aluminium alloy corrosion. These studies have shown that the inhibition mechanism is associated with a reduction in the rate of aluminium alloy corrosion. These studies have shown that the inhibition mechanism is associated with a reduction in the rate of aluminium alloy corrosion. These studies have shown that the inhibition mechanism is associated with a reduction in the rate of aluminium alloy corrosion. These studies have shown that the inhibition mechanism is associated with a reduction in the rate of aluminium alloy corrosion.
2. Experimental

2.1. Materials

In order to produce a cerium surface film, cleaned and degreased hot-dip galvanised (HDG) steel substrates were immersed in cerium nitrate solutions (0.01 M) at ambient temperature. Although long immersion times are not realistic in an industrial perspective, it was decided to test a wide range of immersion times, in order to follow the Ce deposition process. Therefore, immersion times between 10 s and 24 h were tested. After immersion, the samples were oven-dried at 150 °C (50 s). For the samples pre-treated during 10 s and 24 h of immersion, wet adhesion was tested, by using samples coated with a polyester–melamine primer.

2.2. Analytical experiments

AES and XPS analysis were performed using a VG Scientific Microlab 310F. XPS experiments were performed using a non-monochromatic Mg anode (Kα = 1253.7 eV). Auger depth profiles and Auger imaging (SAM) were obtained using a 10 keV primary electron beam rastered over a ×2000-magnified area.

2.3. Electrochemical experiments

The surface potential distribution was investigated on an area of 9 mm², using an SKP from UBM. The corrosion behaviour of the pre-treated samples was studied during immersion in a 0.3% NaCl solution, using a three-electrode arrangement. EIS measurements were made using a 1255 Solartron Frequency Response Analyser and a 1286 Solartron Electrochemical Interface. Potentiodynamic polarisation was made using an Eco Chemie Autolab Potentiostat. The scanning rate was 1 mV/s in the cathodic or anodic direction, depending on the branch under study.

Samples previously treated in cerium nitrate were coated with a polyester primer and tested under immersion in a 5% NaCl solution. The corrosion process was evaluated by electrochemical impedance using a Gamry Instrument constituted by an ECM8 Multiplexer, a FAS1 Femtostat and a PC4 controlled board.

3. Results

The evolution of the open circuit potential during immersion in cerium nitrate solution revealed an initial decay, probably due to dissolution of zinc oxides on the surface.

![Fig. 1: Evolution of the open circuit potential obtained on a sample immersed in 0.01 M Ce(NO₃)₃.](image1)

![Fig. 2: Auger depth profiles obtained on samples treated with 0.01 M Ce(NO₃)₃ during different times.](image2)
followed by a gradual shift in the cathodic direction and finally a stabilisation after approximately 15 min of immersion (Fig. 1). The potential shift in the cathodic direction is probably caused by the development of a cerium layer on the surface, and suggests some polarisation of the anodic reaction.

Auger depth profiles obtained on the samples treated during 10 s, 30 min and 24 h (Fig. 2) distinctly revealed the presence of a layer of cerium deposited on the zinc surface since the first instants of immersion. The thickness of the film increases with increasing time of immersion, although most of the final thickness was developed in the first 30 min, in agreement with the potential evolution. Assuming an identical etching rate for all the samples, then approximately half of the final film thickness had been attained after the first 30 min. The cerium-to-oxygen ratio also increased with the time of immersion, suggesting an evolution in the composition of the film.

The elemental distribution on the surface was determined by scanning Auger microscopy (SAM) (Fig. 3). In these maps the lighter areas correspond to a high content of the element under study, whereas the darker areas correspond to depletion of that element. For the samples treated during 10 s the SAM maps (Fig. 3a) revealed a reasonably uniform distribution of cerium and oxygen on the surface, with a very weak signal from zinc. For longer immersion times, however, the surface became heterogeneous (Fig. 3b and c, with an increasing number of zinc-rich spots. AES spectra obtained at these spots (Fig. 4) revealed a strong signal from zinc and a very weak signal from cerium. The number of these zinc-rich spots increased with the immersion time. Their size was variable, but roughly in the range 5–10 μm.

Identification of the species formed on the surface was made by XPS (Fig. 5). After 10 s, the shape of the spectra

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**Fig. 3.** SAM obtained on samples treated during different immersion times in 0.01 M Ce(NO$_3$)$_3$.

**Fig. 4.** AES spectra obtained on a sample treated during 30 min P1 on the spot; P2 outside the spot.

**Fig. 5.** XPS spectra obtained after different treatment times in Ce(NO$_3$)$_3$: (A) 10 s; (B) 30 min; (C) 24 h.
revealed the presence of Ce(III) species, probably Ce(OH)₃. For longer immersion times, the development of a satellite at ~916.0 eV, characteristic of the presence of Ce(IV) [11], suggests the formation of CeO₂. The film can thus be described as a mixture of Ce(III) and Ce(IV) compounds, with a predominance of Ce(III) in the first instants of immersion followed by an enrichment in Ce(IV). For the samples treated during 24 h, XPS analysis also revealed the presence of zinc oxides and/or hydroxides and zinc carbonates on the surface, resulting from the development of the zinc-rich spots mentioned above.

The distribution of the surface potential was investigated using the SKP technique. Fig. 6a shows a potential map obtained on a zinc sample in which a part of it was treated with cerium nitrate during 10 s and another part was kept without treatment. A potential difference up to 350 mV was detected between the Ce-treated areas and the untreated areas, the anodic potentials being detected at the untreated areas. The same effect observed on a sample treated during 24 h (Fig. 6b), which was the one that revealed the largest number of zinc rich features observed during SAM analysis. The potential map revealed localised potential gradients larger than 400 mV on the surface. The anodic areas (depressed areas in the picture) are probably related with the presence of the zinc oxides/hydroxides spots observed by AES and XPS, whereas the cathodic areas (plateaux) are associated with the presence of the cerium film. These results are in good agreement with SAM, suggesting that when the film thickens and becomes more uneven, large potential gradients are generated on the surface. Given the spatial resolution of the SKP technique, only the larger zinc spots can be detected, but it can be assumed that the behaviour is the same for the smaller ones. The presence of these potential gradients may accelerate the corrosion process when the samples are exposed to an aggressive environment.

The corrosion behaviour of the samples treated during different immersion times in cerium nitrate was studied by EIS, under exposure to 0.3% NaCl solution. Fig. 7 depicts the impedance spectra obtained on samples treated during 10 s and 24 h, during immersion in NaCl. After 1 h of exposure to NaCl (Fig. 7a) the samples treated during 10 s (those with the thinner films) revealed the highest impedance values. This suggests that the presence of the zinc-rich spots mentioned before may facilitate the initiation of the corrosion process. Thus, the thick, but uneven films formed by 24 h immersion did not achieve the protection afforded by
The thinner and uniform films formed on the samples treated during 10 s. After 6 h of immersion (Fig. 7b), the impedance of the sample treated during 10 s had decreased to about half of its initial value, approaching that of the sample treated during 24 h. The samples treated for 24 h thus seem to be less protective in a first stage, but to be more stable during immersion in NaCl. This is possibly because the corrosion process occurs mainly in the defective areas of the film, where the zinc is exposed.

The electrochemical behaviour of samples with different treatment times in Ce(NO₃)₃ during exposure to 0.3% NaCl was also studied by potentiodynamic polarisation. It was observed that the cerium layer decreased the rate of both the anodic and the cathodic reactions (Fig. 8). The treatment time affected the anodic response of the system (Fig. 8A). Samples treated during 10 s and 30 min showed higher corrosion potentials and lower corrosion currents than the untreated HDG steel samples. The samples treated during 24 h revealed the lowest corrosion potential, whereas the corrosion current similar to the one measured on the untreated HDG steel. The surface film formed on the samples treated during 10 s and 30 min slightly decreased the anodic currents. Thus, the anodic dissolution of zinc seems to be decreased in the presence of the thinner, but more homogeneous films. In the cathodic branch, both the reduction of oxygen and the reduction of zinc oxides [8,12] may occur. The presence of the cerium film also decreased the rate of the cathodic reactions. The treatment time also exerts a strong influence on the cathodic response of the system (Fig. 8B). The sample treated during 10 s revealed
the lowest cathodic current. Samples treated during 30 min revealed cathodic currents slightly lower than HDG steel and the behaviour of the sample treated during 24 h was very close to that of untreated HDG.

Since the sample treated during 10 s revealed the best corrosion resistance, its behaviour was compared with that of a substrate pre-treated with Cr (Fig. 9). Relative to the untreated HDG substrate, the treatments with Ce-10 s and Cr resulted in a decrease of the cathodic currents, the lowest values being obtained with the Cr treatment. The corrosion current and corrosion potential were very similar for these two samples. Thus, the presence of a uniform Ce(III)-rich film seems to lead to increased cathodic protection. On the other hand, the anodic response shows that Cr seems to be more effective than Ce in constraining the anodic reactions. Cr and Ce revealed anodic currents lower than those of untreated HDG. These results suggest that for HDG substrates, Ce exerts its influence mainly in the cathodic reactions, whereas Cr affects more significantly the anodic processes.

Following the results obtained above, pre-treated samples were coated with a primer. After 1 day of immersion in 5% NaCl, the sample with the thinner film (Fig. 10a) clearly revealed a capacitive response over the frequency range under study, which can be correlated with the coating capacitance. At high frequencies the response was capacitive, however, at low frequencies the resistance of the coating was observed, with a value of ~1 MΩ·cm². A time constant developing at low frequencies reveals some corrosion activity. After 1 week of immersion, the shape of the spectra was identical for both samples (Fig. 10b). At this stage, the coating resistance is determined at the high frequencies, and it was approximately 5 × 10⁴ Ω·cm² in the sample treated during 10 s, in comparison with a value of ~2 × 10³ Ω·cm² in the other sample. Also the charge transfer resistance was higher in the sample with the 10 s treatment, although its exact value cannot be observed in the spectrum. The EIS results obtained on the coated samples has shown that the corrosion initiation was delayed in the presence of the uniform Ce(III)-rich film. The presence of the spots observed on the films formed during longer immersion times seems to help to decrease the corrosion resistance, in accordance with the previous electrochemical results obtained on the uncoated samples.
4. Discussion

Cerium is known to act as a cathodic inhibitor for aluminium, zinc and steel in solutions of sodium and cerium chlorides [3]. Further to this inhibiting effect, it has been shown that the deposition of a film of cerium oxides and/or hydroxides can be beneficial as a pre-treatment. The mechanism widely accepted for the formation of cerium films is strictly correlated with the cathodic process occurring in the surface. Thus, the production of alkaline conditions in the cathodic areas due to oxygen reduction leads to precipitation of cerium oxides and/or hydroxides. These compounds block the cathodic sites, leading to a decrease of the corrosion rate [13]. This effect has been shown for copper-containing aluminium alloys [4,14,15], where a cerium-rich film was detected over the copper precipitates as a consequence of the increased cathodic activity at these sites.

In this work, the nature of the surface film was associated with the presence of cerium oxides and hydroxides, namely, Ce(OH)₃ and CeO₂, its amount depending on the treatment time. Film thickening and development of more heterogeneous films where anodic sites were identified, seems to be closely associated with the formation of CeO₂. This result suggests that a number of defects need to develop in order to support the film thickening. In that case some non-covered zinc zones must be observed on the surface. This behaviour was confirmed for the thicker films formed by immersion. The non-uniformity of the film is correlated with the presence of some anodic sites. These results are in accordance with Hinton et al. [2,16], who have pointed out the need for the existence of anodic sites to promote further growth of the film.

In another work, Geary and Breslin [17] observed the presence of a non-uniform cerium film, however, protective, on the surface of Sn/Zn alloy coatings. The non-uniformity of the film was attributed to the fact that anodic and cathodic processes continue through sub-microscopic defects in the film. The electrochemical results correlate well with the analytical data; the formation of a uniform film hinders the initiation of the corrosion process (as shown by EIS) and significantly reduces the rate of the cathodic reactions (as shown by polarisation). On the other hand, the presence of defects in the film, irrespective of its thickness, decreases the resistance against corrosion initiation.

Therefore, the presence of anodic sites on the film facilitates the initiation of the corrosion process upon immersion in sodium chloride solution. In this situation, the covered areas may still remain protected, but the presence of defects is determinant in the initiation of the corrosion process. Thus, the treatment time seems to play a determinant role on the characteristics of the surface film. Short treatment times have resulted in a surface with better resistance to chloride-induced corrosion.

Polarisation data provided evidence that the cerium pre-treatment reduces the corrosion rate, by hindering the rates of both the anodic (zinc dissolution) and the cathodic (oxygen reduction) reactions. The inhibition of the anodic reaction was also observed by Lu and Ives [6,18].
The deposition of cerium nitrate results in a surface film, whose thickness increases with the treatment time. The presence of the Ce film constrains the cathodic reduction of oxygen and the anodic dissolution of zinc resulting in a decrease of the corrosion rate.

Short treatment times result in uniform surface films mainly composed by Ce(III) species, which are more resistant to the initiation of the corrosion process both for uncoated and coated substrates.

For long immersion times, the film becomes uneven and is mainly composed by Ce(IV) oxides. The heterogeneity of the surface results in areas where the zinc is exposed and that work as anodic sites. A solid-state mechanism for the oxidation of the Ce(III) to Ce(IV) is proposed.

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