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THE INFLUENCE OF DICHROMATE AND CERIUM PASSIVATION TREATMENTS ON THE DISSOLUTION OF Sn/Zn COATINGS

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Abstract—The electrochemical behaviour of an 80Sn–20Zn electro-deposited alloy following passivation in a dichromate solution and a cerium-containing solution, was studied. It was found that both the dichromate and cerium passivation procedures lead to an increase in the corrosion protection afforded by the 80Sn–20Zn electro-deposit. This was attributed to a reduction in the rate of the zinc dissolution reaction from the electro-deposit which in turn extended the cathodic protection periods of the deposit. Passivation of the electro-deposited alloy in the cerium-containing solution lead to the precipitation of cerium oxides/hydroxides in a non-uniform manner over the surface. This precipitated film of cerium had the appearance of a cracked-mud layer. Nevertheless, the additional corrosion protection afforded by the cerium passivation treatment was equivalent to that provided by the dichromate passivation treatment. © 1997 Elsevier Science Ltd

Keywords: A. 80Sn–20Zn alloy, B. cerium, C. dichromate, C. corrosion protection.

INTRODUCTION

It is well know that tin and zinc combine to provide an attractive combination of barrier and cathodic protection when applied as alloy coatings to iron-based materials.[1–3] The life time of these coatings can be further lengthened on passivating the coatings in chromium-containing solutions.[4,5] However, this traditional method of surface modification involves the use of hexavalent chromium, a substance which is now recognized as both highly toxic and carcinogenic. The search for more environmentally acceptable alternatives has lead to the identification of rare-earth metal species as possible replacements for the well-know chromium inhibitor.[6–18]

The methods by which cerium has been incorporated into, or deposited on to, surfaces range from ion implantation,[17] immersion of the electrodes in cerium-containing solutions,[8,13,18] to the electro-deposition of cerium from solution.[14,15] Corrosion inhibition by cerium is generally associated with a reduction in the rate of the cathodic reduction reactions, which in turn, has been attributed to the formation and precipitation of cerium oxides, or hydroxides, over the cathodic sites, giving rise to a blocking effect.[8–17] This has been shown clearly for copper-containing aluminium alloys where cerium-rich insoluble films have been identified at copper precipitates, these films precipitating from solution because of the local increase in alkalinity at the copper cathodic sites.[11–13,15,16]

In this work, the electrochemical behaviour of an 80Sn–20Zn alloy coating following various post treatments involving chromium and cerium was studied in an effort to examine the additional level of corrosion protection afforded by the cerium treatments and to compare these with that provided by the chromium treatments.

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EXPERIMENTAL METHOD

Tin–zinc alloy deposits, with the composition 80Sn–20Zn, were electro-deposited on to mild steel plate cathodes from a stannate–cyanide bath, operated at 60°C. Plating was carried out for a 10 min period, this produced an 8–10 µm deposit. Then the plated cathodes were removed, rinsed in distilled water and dried. Alloy-coated steel plate samples were cut into suitable working electrodes, 4 × 4 cm, and then, were mounted in a beeswax–colophony resin so as to expose a circular working electrode surface, 1 cm^2 in area.

Treatment of the alloy electrodes in the dichromate-containing solution involved polarizing the electrodes at a cathodic current density of 30 mA/cm^{-2} for 30 s in a 0.1 mol dm^{-3} $Na_2Cr_2O_7$ solution at a pH of 4. The cerium passivation treatments were carried out by polarizing the electrodes at a cathodic current density of 30 mA/cm^{-2} for 30 s in a 0.1 mol dm^{-3} $Ce(NO_3)_3$ solution.

Potentiodynamic polarization measurements were carried out using an EG&G 263 potentiostat controlled by the Model 342 corrosion-measurement-software package. The alloy electrodes were pre-polarized at -1.6 V (SCE) in the cell electrolyte for a 1 min period to ensure a reproducible surface from test to test. Then, the applied potential was scanned in the anodic direction at a rate of 1 mV s^{-1}. Electrochemical impedance measurements were made using a Capcis–March Model CV2001 frequency response analyser in conjunction with a Capcis–March interface at various applied potentials in the frequency range 10^4–10^{-2} Hz.

The electrochemical cell consisted of a Pyrex glass cell, graphite auxiliary electrodes and a saturated calomel reference electrode. All solutions were prepared from AnalaR grade reagents and de-ionised water. The pH of the aqueous test solutions was adjusted to the desired values by the addition of NaOH or HCl.

Suitable surface areas of the specimens were examined using a Hitachi scanning electron microscope operated in a secondary-electron imaging mode, with accelerating voltages of 20 kV. Elemental compositions of surface regions were analysed using the Link 1000 EDAX unit (energy dispersive X-ray analyses) coupled to the SEM.

EXPERIMENTAL RESULTS

Typical potentiodynamic polarization curves recorded in a neutral 0.5 mol dm^{-3} NaCl solution for 80Sn–20Zn electro-deposits untreated and post-treated in cerium and dichromate passivation solutions are shown in Fig. 1. It can be seen from a comparison of these three plots that the anodic dissolution behaviour of the electro-deposit is modified considerably following the passivation treatments. The anodic maximum observed in the potential region from -750 to -980 mV(SCE) which is consistent with the active dissolution of zinc from the electro-deposit is not evident following the cerium or dichromate passivation treatments. Rather a much slower increase in the anodic current is observed with increasing applied potentials. Also, the pseudo-repassivation region which is evident for the untreated electrodes is not seen for the passivated electrodes. Although the cathodic polarization behaviour seems to be little influenced by the cerium passivation treatment a decrease in the cathodic current by one order of magnitude is evident following the dichromate passivation treatment.

The influence of the cerium and dichromate passivation treatments on the individual components of the electro-deposit can be seen from the data presented in Fig. 2. In Fig. 2(a)

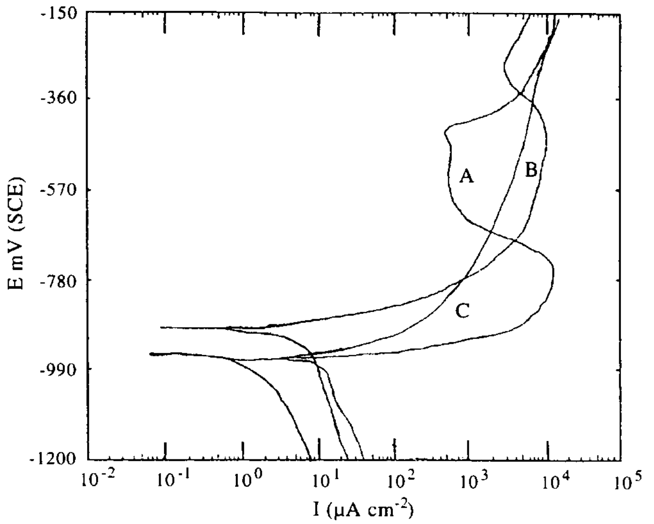

Fig. 1. Polarization data recorded in a neutral 0.5 mol dm^{-3} NaCl solution for an 80Sn–20Zn electro-deposited alloy, (A) untreated (B) treated in cerium and (C) treated in dichromate solutions.

the potentiodynamic polarization behaviour of pure zinc untreated and treated by passivation in dichromate and cerium passivation solutions is shown, while similar data obtained for pure tin are presented in Fig. 2(b). Both the dichromate and cerium passivation treatments seem to have a significant passivation effect on the electrochemical behaviour of pure zinc. The corrosion potentials are displaced in the electronegative direction, a reduction in the cathodic current density is observed, a clear passive region is evident and higher breakdown potentials are seen following both the dichromate or the cerium passivation treatments. However, both treatments appear to give rise to an activating effect when applied to pure tin. This can be seen from the higher passive current densities recorded for pure tin following either the cerium or dichromate passivation treatments. The dichromate passivation treatments seem to give rise to an ennoblement in the breakdown potential, but have no effect on the cathodic polarization behaviour, whereas the cerium passivation treatments have little effect on the breakdown potential or the cathodic polarization behaviour of pure tin.

The open circuit potentials as a function of the immersion period in a neutral 0.5 mol dm^{-3} NaCl solution for 80Sn–20Zn electro-deposits untreated and post-treated in cerium and dichromate passivation solutions are shown in Fig. 3. The gradual potential ennoblement observed in all three cases may be attributed to the preferential dissolution, or leaching, of zinc from the alloy coating. However, it is clearly seen that the rate of this potential ennoblement is reduced following the cerium passivation treatment and to a lesser extent the dichromate passivation treatment. This seems to suggest that the cerium passivation treatments, in particular, inhibit the rate of the zinc dissolution reaction.

A similar conclusion may be drawn from the polarization resistances shown, as a function of the immersion period in a neutral 0.5 mol dm^{-3} NaCl solution for the untreated, cerium-treated and chromium-treated electro-deposits, in Fig. 4. These polarization resistances were calculated from impedance data measured at the corrosion

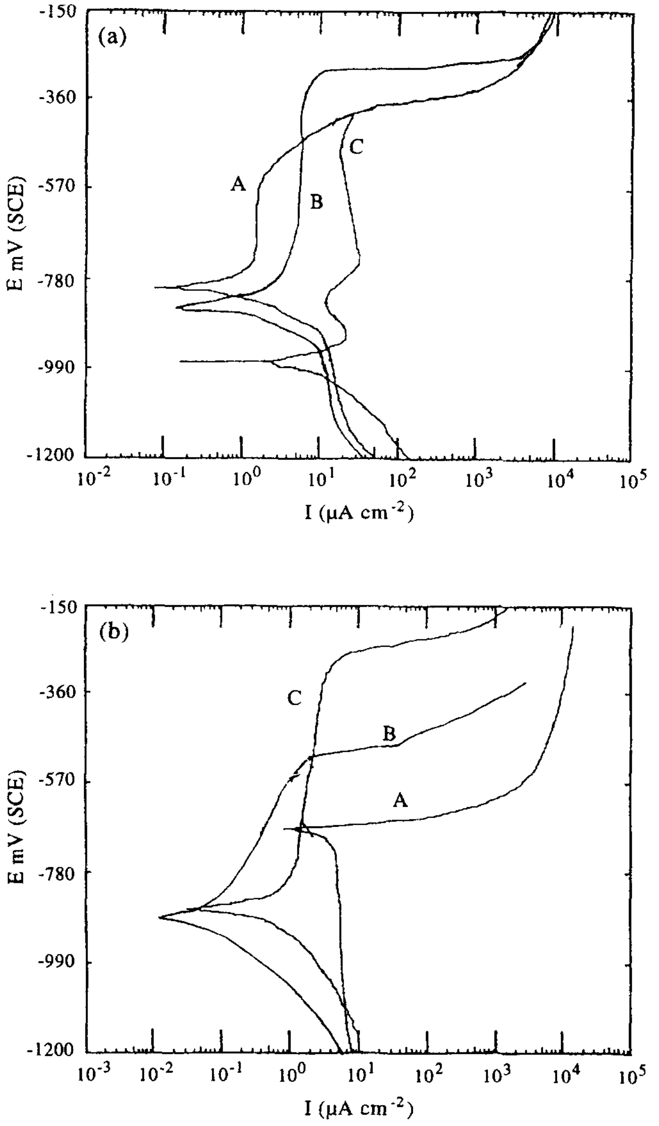

Fig. 2. (a) Polarization data recorded in a neutral 0.5 mol dm^{-3} NaCl solution for pure Sn, (A) untreated, (B) treated in dichromate and (C) treated in cerium solutions; (b) Polarization data recorded in a neutral 0.5 mol dm^{-3} NaCl solution for pure Zn, (A) untreated, (B) treated in dichromate and (C) treated in cerium solutions.

potential of the electro-deposits as a function of the immersion period. A significant increase in the polarization resistance can be seen for the untreated electrode during the early stages of immersion. This seems to be associated with the build-up of zinc corrosion products on the alloy surface which give rise to an apparent passivation effect, the accumulation of corrosion products being the result of relatively intense dissolution of zinc from the alloy electro-deposit. However, this phenomenon is not seen for the cerium- or chromium-treated

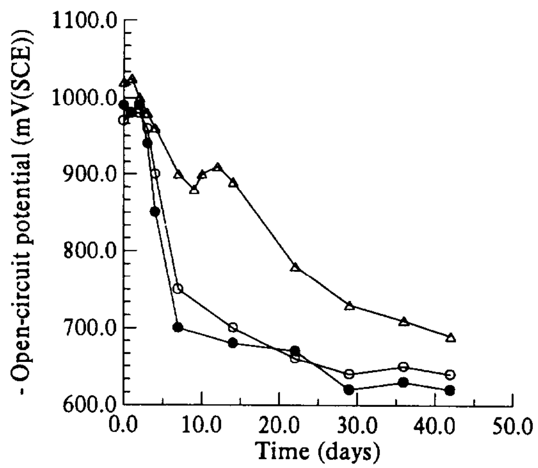

Fig. 3. Open-circuit potential recorded in a neutral 0.5 mol dm^{-3} NaCl solution for an 80Sn–20Zn electro-deposited alloy, ● untreated ○ treated in dichromate and △ treated in cerium solutions.

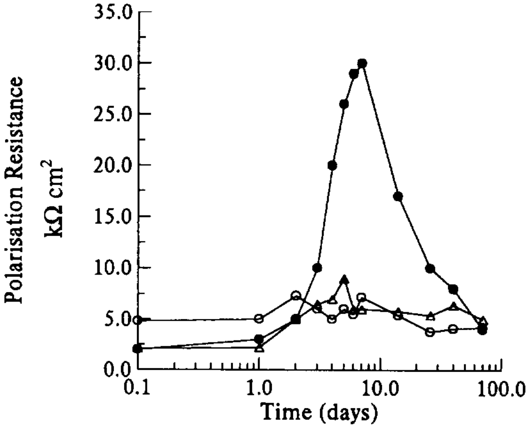

Fig. 4. Polarization resistance as a function of the immersion period in a neutral 0.5 mol dm^{-3} NaCl solution for an 80Sn–20Zn electro-deposited alloy, ● untreated ○ treated in dichromate and △ treated in cerium solutions.

electro-deposits. Instead, the polarization resistances, which are initially somewhat higher, remain essentially constant during the early stages of immersion and then exhibit a gradual decrease indicative of an increase in the rate of dissolution.

The ability of these untreated and treated electro-deposits to protect the underlying steel substrate from corrosion can be seen from the weight-loss data presented in Fig. 5. Here, the % mass loss of the untreated, cerium-treated and chromium-treated electro-deposits as a function of the immersion period in a neutral 0.5 mol dm^{-3} NaCl solution are shown; the % mass loss being calculated for coupons having the same dimensions and shape. The untreated electro-deposit provides considerable protection to the steel substrate, however an even lower rate of mass loss can be observed following the chromium and cerium

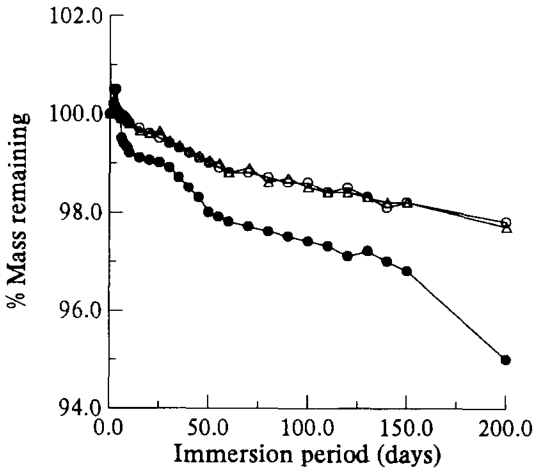

Fig. 5. Weight-loss measurements as a function of the immersion period in a neutral 0.5 mol dm^{-3} NaCl solution for an 80Sn–20Zn electro-deposited alloy, ● untreated ○ treated in dichromate and △ treated in cerium solutions.

passivation treatments. The % mass losses calculated for the untreated electro-deposit, the chromium-treated electro-deposit and the cerium-treated electro-deposit averaged over a 200 day period were 0.030, 0.011 and 0.010 per day, respectively.

A further comparison of the corrosion protection capabilities of the untreated, cerium-treated and chromium-treated electro-deposits can be seen from the visual examination data presented in Table 1. Here, the percentage red rust coverage of the surface over a 30 day immersion period in a neutral 0.5 mol dm^{-3} NaCl solution is shown where the entries A indicate no iron corrosion, B less than 2% coverage, C between 2 and 5% coverage and D greater than 5% coverage with iron corrosion products. Again, it can be seen that the chromium and cerium passivation treatments offer extended corrosion protection to the base material and that the cerium passivation treatments appear to be as superior as the well-known chromium passivation treatments.

In Fig. 6(a) a micrograph of the surface of an electro-deposit treated using the cerium passivation treatment is shown. This cracked-mud appearance was only observed following

Table 1. Visual examination data of the untreated, chromium-treated and cerium-treated electro-deposits where the entries A B C and D refer to no iron corrosion, less than 2% coverage, between 2 and 5% coverage and greater than 5% coverage with iron corrosion products, respectively

Immersion period/days	Untreated deposit	Chromium-treated deposit	Cerium-treated deposit
1	A	A	A
3	A	A	A
5	A	A	A
10	B	A	B
14	B	B	B
19	C	B	B
29	D	B	B

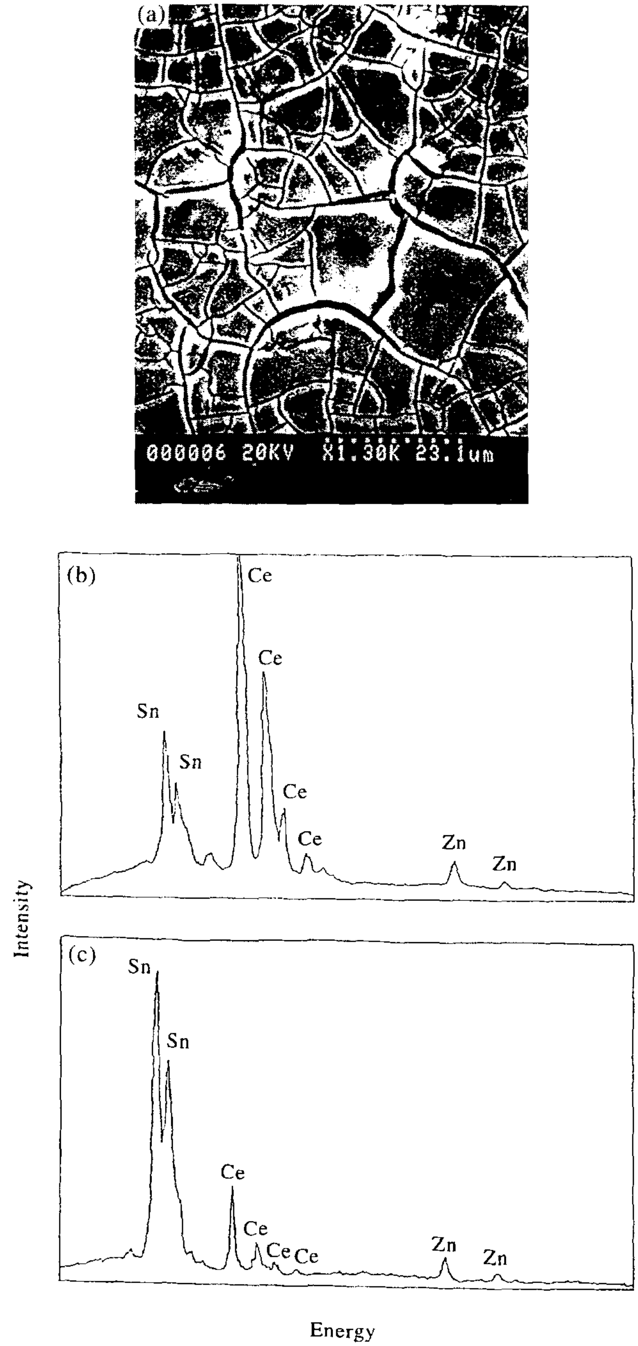

Fig. 6. (a) SEM micrograph of an 80Sn–20Zn electro-deposit post-treated in a cerium solution; (b) EDAX analysis of the large precipitate-like layers in (a); (c) EDAX analysis of the grooves between the precipitates in (a).

the cerium-passivation treatment, the surfaces of the chromium-treated electro-deposits appeared similar to that of the untreated electro-deposits. The accompanying EDAX profiles for the large precipitate-like layers and the grooved regions between the precipitates in this micrograph are shown in Fig. 6(b) and (c), respectively. A significant cerium signal is evident for the precipitated regions. The slightly reduced cerium signal observed on analysing the grooved regions indicates considerable variation in the concentration of cerium over the electro-deposit surface.

Alternative post-treatment procedures, which involved polarising the electrodes between -1600 and $-1200\,\mathrm{mV}$ (SCE) at a scan rate of $1\,\mathrm{mV\,s^{-1}}$ in $0.1\,\mathrm{mol\,dm^{-3}}$ $Na_2Cr_2O_7$ or in $0.1\,\mathrm{mol\,dm^{-3}}$ $Ce(NO_3)_3$ solutions, gave similar results to those reported in Figs 1–5. However, less variations in the concentration of cerium over the electro-deposit surface were observed for this latter treatment, and the high level of cracking evident in Fig. 6(a) was not observed. Nevertheless, no difference in the corrosion protection afforded by the cerium coatings, applied using both procedures, was evident.

DISCUSSION

The results presented in this communication show clearly that the corrosion protection capabilities of an 80Sn–20Zn coating can be increased considerably by applying either a chromium or cerium passivation treatment. This is evident from a lower rate of mass loss, Fig. 5, the delayed appearance of iron corrosion products, Table 1, and a slower rate of dissolution of zinc from the alloy coating, Figs 1, 3 and 4 for the cerium or chromium-treated electro-deposits. Furthermore, it is seen that the cerium passivation treatments appear to be as superior as the well-known chromium treatments in increasing the corrosion resistance of the alloy electro-deposits. The appearance of iron corrosion products is delayed to essentially the same extent, Table 1, and the rate of mass loss is reduced by essentially the same factor, Fig. 5, following both treatments.

The onset of substrate corrosion seems to be connected with the dissolution of zinc from the alloy coating which results in the formation of a porous tin-enriched coating, through which substrate corrosion initiates. Both passivation treatments seem to enhance the corrosion protection afforded by the electro-deposit by reducing the rate at which zinc is dissolved from the alloy coating. This is seen from Fig. 1 where the anodic maxima associated with the dissolution of zinc from the alloy coating is reduced considerably on treating the electrodes in either the chromium or cerium passivation treatments. The adoption of more electronegative open-circuit potentials for longer periods of time by the treated electro-deposits, Fig. 3, is consistent with the retention of greater amounts of zinc in the alloy coating. Furthermore, the polarization resistances calculated for the treated alloys remain essentially constant during the early stages of immersion, but a significant increase in the polarization resistance occurs for the untreated electrodes. This apparent increase in the corrosion resistance of the untreated electro-deposit seems to be associated with rapid dissolution of zinc from the alloy coating and the formation and precipitation of zinc corrosion products on the surface leading to a short-lived passivation effect. The fact that this phenomenon is not seen with the treated electro-deposits suggests a much slower controlled dissolution of zinc from the alloy electro-deposit. The data presented on the polarization behaviour of pure tin and zinc following the cerium and chromium passivation treatments, Fig. 2, show that these treatments lead to a reduction in the activity of zinc, but an increase in the activity of tin. In Fig. 2(a) a clear passive region is seen for the cerium-treated zinc electrode, and to a lesser extent the chromium-treated electrode. These observations further indicate that the beneficial effects of the passivation treatments are connected with a slower rate of dissolution of zinc from the alloy coating, and in turn, a longer period of cathodic protection of the underlying steel substrate.

The manner in which cerium and chromium interact with the electro-deposit surface to enhance the corrosion protection capability seem to be somewhat different. Chromium seems to be incorporated in a more or less uniform manner, in relatively low concentrations, over the entire surface. It is generally accepted that the formation of the chromium-enriched coating involves a dissolution-precipitation mechanism [4,19] whereby the dissolution of zinc favours the reduction of the hexavalent chromium species to the trivalent chromium species which then is precipitated as a Cr(III) oxide/hydroxide to form a mixed chromium-metal oxide. It has also been proposed that some of the hexavalent chromium species are trapped in the mixed oxide film to enhance further the corrosion protective properties of the coating. In this study passivation of the alloy system at a cathodic current density in the dichromate-containing solutions should facilitate a similar process, namely the reduction of Cr(VI) to Cr(III) in this deep cathodic region and the precipitation of chromium hydroxides. The increase in the alkalinity at the electrode surface because of the enhanced reduction of dissolved oxygen at these cathodic potentials will increase the rate of precipitation of the chromium oxides/hydroxides.

On the other hand cerium appears to be deposited in an non-uniform manner in relatively large concentrations over the electro-deposit surface, Fig. 6. These observations are consistent with the precipitation of insoluble cerium oxides/hydroxides at regions where cathodic reactions give rise to a local increase in the pH of the solution adjacent to the electrode surface. These alkaline conditions result in the localised precipitation of hydrated cerium oxide. It is apparent from Fig. 6 that the film which develops on the metal surface contains regions of large particles or precipitates. The presence of these precipitates is an indication that, despite the fact that a complete surface coverage occurs, anodic and cathodic processes continue through sub-microscopic defects in the film.

The initial generation of the alkaline regions adjacent to the electrode surface may involve the cathodic reduction of dissolved oxygen to produce hydroxyl ions as proposed by Hinton,[8]

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

or the cathodic reduction of dissolved oxygen via a two-electron transfer process to produce hydrogen peroxide.[15,16]

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$$

It has been proposed [15,16] that cerium(III) is oxidised in hydrogen peroxide-containing solutions to cerium(IV) by the formation of $Ce(OH)_2{}^{2+}$ either by

$$4Ce^{3+} + O_2 + 2H_2O + 4OH^- \rightarrow 4Ce(OH)_2^{2+}$$

or

$$2Ce^{3+} + H_2O_2 + 2OH^- \rightarrow 2Ce(OH)_2^{2+}$$

Finally, the solution species precipitate as ceria in the presence of a local pH rise due to cathodic oxygen reduction,

$$Ce(OH)_2^{2+} + 2OH^- \rightarrow CeO_2 + 2H_2O$$

It is not clear whether the cerium resides in the trivalent or tetravalent state on the electro-deposit surfaces, but it is seen that a relatively high concentration of cerium oxides/hydroxides are detected, Fig. 6.

CONCLUSIONS

Passivation of an 80Sn–20Zn electro-deposited alloy in a dichromate solution and a cerium-containing solution lead to similar increases in the corrosion protection afforded by the electro-deposit. Although the cerium oxide/hydroxide film formed as a result of the passivation treatment was non-uniform and had the appearance of a cracked-mud covering, it provided additional corrosion protection equivalent to that of chromium. The enhanced corrosion protection provided by both treatments was attributed to a reduction in the rate of the zinc dissolution reaction from the electro-deposit which in turn extended the cathodic protection periods of the deposit.

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