Electrochemical Behavior of a Chromated 55mass%Al–Zn Coated Steel Sheet before and after a Heat Treatment

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The final production step of a hot-dip 55mass%Zn–Al coating normally consists in the passivation of the coating. The passivation is important to protect the material against corrosion during transport and storage. A common passivation agent used is the chromic acid leading to a complex chromate film which contains Cr(III) and Cr(VI) compounds. Two main reasons have been proposed to explain protection of a hot-dip galvanized zinc coating by the passivation treatment. The first reason would be that the Cr(III) compounds form a barrier that isolates the zinc layer from the environment. The second reason would be related to the Cr(VI) compounds. These compounds would be able to form a film, by incorporating water molecules, spreading over the areas not covered by the Cr(III) compounds. Therefore the effect of Cr(III) and Cr(VI) would complement one another. The presence of Cr(VI) compounds and their importance on the corrosion resistance has been proposed in several papers.

It has been suggested that one can significantly improve the ductility of 55mass%Al–Zn coatings by an annealing heat-treatment. However a possible inconvenient of these treatments is that they might decrease the protecting effect of the passivation. This would make the heat-treated material more susceptible to corrosion during transportation and storage.

Electrochemical techniques are a convenient way to study the effect of the chromate layer on the dissolution of the substrate. These techniques have the advantages of a comparatively simple and inexpensive experimental apparatus and easy specimen preparation. In addition, relatively "large" areas, of the order of 10 cm², can be analyzed.

In recent works a direct current (DC) anodic voltammetric technique was applied to the qualitative characterization of the phases present in galvannealed coatings and to investigate the relationship between the dissolution behavior and the microstructure of the 55mass%Al–Zn coating that changes as a consequence of the heat treatment. These works demonstrated that the voltammetric technique produced results which were consistent with microstructural characterization by SEM. In other words, the voltammograms were sensitive to the microstructural changes produced by the heat treatment in these coatings.

In this work the electrochemical behavior of hot-dip 55mass%Al–Zn coated steel sheets with and without the chromating treatment before and after an annealing heat-treatment is studied by means of a DC anodic voltammetric technique. The aim of the present work is to investigate the effect of the chromating treatment on the dissolution behavior of the 55mass%Al–Zn coating that changes as a consequence of the heat treatment.

Commercial 55mass%Al–Zn coated steel sheets with and without the final surface chromating treatment were used. The samples had a nominal total coating weight (computing the coating weight on both sides) of 160 g/m². The substrate chemical analysis was (in mass%): C - 0.063; Mn - 0.23; P - 0.008; S - 0.0046; Si - 0.037; N - 0.0085; Al - 0.037; Fe - balance. The coating had a nominal composition of 55mass%Al–43.5mass%Zn–1.5mass%Si. Two heat treatment temperatures: 200 and 360°C were used following the recommended practice for improving coating ductility.

The specimens were held at the annealing temperature for 16 h (57 600 s) under a protecting nitrogen atmosphere and slowly cooled, 0.02°C/s, in the furnace.

The voltammetric dissolution of the coated samples was carried out in two electrolytes: an aqueous solution containing 0.25 mol l⁻¹ of H₂SO₄ and a phthalate-buffered solution with pH = 5.3. The area of the sample was equal to 9.08 cm², limited by an O-ring in the polarization cell. The counter electrode was a platinum wire and the reference electrode was the Normal Calomel Electrode (NCE). A scan rate of 0.001 V s⁻¹ from an initial potential of −1 V until a final potential of +1 V was used for the voltammetric dissolution and curves of current density against potential, voltammograms, were obtained.

In order to determine the electrochemical behavior of the main components of the 55mass%Al–Zn coated steel sheet a preliminary study of electrodes of pure zinc, pure aluminum and the steel substrate in these electrolytes was carried out. From the polarization curves obtained for Zn and Al in 0.25 mol l⁻¹ of H₂SO₄, for potentials between −1.050 V and −0.525 V one can expect to be able to dissolve the 55mass%Al–Zn coating without dissolution of the steel substrate. In the phthalate-buffered solution for potentials more anodic than −1.100 V only Zn will dissolve as Al is passivated.

The microstructure of both heat treated and non-heat treated material was described in a previous work, see Figs. 1 and 3 of Ref. 10. In the as received condition the material consisted of Al rich dendrites surrounded by interdendritic Zn rich regions (see Fig. 1a of Ref. 10). After the heat treatment, (see Fig. 1b of Ref. 10)), the original dendritic structure could still be perceived but now one could see a copious precipitation within the formerly precipitation free Al dendrites.

The voltammograms, obtained by a DC anodic voltammetric technique, are shown in Figs. 1–3 for the as received and heat treated at 200 and 360°C, respectively. As said above, the heat treatments have a significant effect on the microstructure. This results in different electrochemical behavior and consequently different voltammograms. This can be clearly seen comparing, for example, Figs. 1a, 2a and 3a, which correspond to the non-chromated samples. The peak related to Zn dissolution significantly decreases.
as the temperature of the heat treatment increases. This reduction is a consequence of the decrease in the amount of interdendritic Zn as a consequence of the homogenization during the heat treatment. A more detailed discussion of the relationship of the Zn dissolution with the voltammograms can be found elsewhere.\textsuperscript{10}

In view of this when one compares a chromated as received specimen with a heat treated one, two effects are being observed together: the effect of the microstructural change and the effect of the heat treatment on the chromate layer itself. This work is mainly concerned with the latter effect so that one must compare the behavior of chromated and non-chromated samples subjected to the same heat treatment.

In the as received condition, Fig. 1, one can see a remarkable effect of the chromate layer on the dissolution processes of the coating. The as received non-chromated samples present voltammograms that exhibit a well-defined Zn peak in both electrolytes, Figs. 1a and 1c. On the other hand in the voltammograms of the heat-treated chromated samples, Figs. 1b and d, the current density is small in the more aggressive H\textsubscript{2}SO\textsubscript{4} electrolyte, Fig. 1b, and virtually nil in the less aggressive phthalate-buffered, Fig. 1d.

The effect of heat treating at 200°C can be seen in Fig. 2. One can see that even after the heat treatment the chromating still affects the voltammograms. In the H\textsubscript{2}SO\textsubscript{4} electrolyte, Figs. 2a and 2b, a Zn peak can be seen in both the chromated and non-chromated sample. However the current density of the Zn peak of the chromated sample is about half that of the non-chromated sample and the current does not rise sharply towards higher voltages as in the voltammogram of the non-chromated sample. This difference is more pronounced in the phthalate-buffered electrolyte, Figs. 2c and 2d, the Zn peak is significantly smaller in the chromated sample.

The effect of heat treating at 360°C can be seen in Fig. 3. One can see that although the chromating still affects the voltammograms its passivating effect is smaller than in the samples treated at 200°C. In the H\textsubscript{2}SO\textsubscript{4} electrolyte, Figs. 3a and 3b, the Zn peak and the rise in current density as the voltage increases in the non-chromated and chromated sample are similar with only perhaps a small effect of the chromating. In the phthalate-buffered electrolyte, Figs. 3c and d, there is still some effect but the voltammograms are more similar than those for the samples treated at 200°C.

The comparison of voltammograms presented above showed that the chromate layer partially “survives” the heat treatment. This results in current densities in the voltammograms of the chromated samples smaller than those of non-
chromated samples even after heat treatment. However this residual passivation decreases as the heat treating temperature increases and it is comparatively small after heat treating at 360°C. One can interpret these results taking into account that the observed current is mainly due to the dissolution of the interdendritic Zn (see Fig. 3 of Ref. 10)). In the chromated samples without heat treatment it is likely that the chromate layer effectively protects most of the exposed interdendritic Zn. As a consequence, dissolution will proceed slowly starting from the top surface on the few unprotected spots of interdendritic Zn. So that the small dissolving Zn area leads to a small anodic current. After heat treatment the results suggest that some of the chromate layer coverage is lost and more interdendritic Zn areas can be preferentially dissolved. Still it appears that after the 200°C heat treatment not all the interdendritc areas are without coverage so that the chromated samples still have lower dissolution currents compared with the non-chromated sample. As the heat treatment temperature is increased to 360°C more coverage is lost and the chromated sample dissolution current approaches that of the non-chromated sample.

One might attempt to explain the behavior described above with the idea that hydrated Cr(VI) compounds are an important component of the protecting film. During heat treatment it might happen that these Cr(VI) compounds are dehydrated2) and therefore lose their ability to cover the surface in the regions where Cr(III) compounds are absent. In this way the higher heat treating temperatures and longer times would result in less coverage by the Cr(VI) compounds. Some residual passivation could still remain due to the Cr(III) compounds.

In summary, the voltammetric technique employed here was able to show that the heat treatment significantly decreases the ability of the chromate layer to passivate the coating but even at samples heat treated at high temperatures some residual passivation can still remain.

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