Electrochemical Method to Characterize the Chromate Layer on a Zinc Coated Steel Sheet

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1. Introduction

Passivation of the surface is normally the final production step of a zinc coated steel sheet. The passivation layer is important to avoid corrosion during handling, transportation and storage. A commonly used passivation agent is the chromic acid leading to a complex chromate film, which contains Cr(III) and Cr(VI) compounds.1) The protection of a hot-dip galvanized zinc coating by the passivation treatment2) is thought to occur owing to two main reasons. The first reason is that Cr(III) compounds form a barrier that isolates the zinc layer from the environment. The second reason is related to Cr(VI) compounds. These compounds are able to form a film, incorporating water molecules, and spreading over the areas not covered by 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.3–5)

Chemical methods, for example, atomic absorption, are most commonly used to characterize the chromium layer. Those methods do not analyze Cr directly on the surface. They first need the Cr to be extracted by an acid solution and the analysis of this solution is performed. The disadvantage of those methods is that they are only able to determine the total Cr content. They cannot distinguish between Cr(III) and Cr(VI). A well-known chemical method using diphenyl carbazide can be employed to determine the amount of Cr(VI). Unfortunately results obtained by this method are difficult to reproduce when applied to zinc coated steel sheets.

The total Cr content is important but the specific knowledge of the individual contents of Cr(III) and Cr(VI) adds the possibility of fundamental understanding of the protection mechanisms afforded by the passivation layer. Nevertheless, in view of the experimental difficulties, one often avoids the determination of these quantities and empirically correlates the specimen performance with the composition of the chromatizing baths and the processing conditions. Therefore, it would be of great interest to have a technique that could reliably determine the amounts of Cr(III) and Cr(VI) directly from the passivation layer.

Electrochemical techniques are a convenient way to study the passivation layer. These techniques have the advantages of a comparatively simple and inexpensive experimental apparatus and easy specimen preparation.6) In addition, relatively “large” areas, of the order of 10 cm², can be analyzed.

In this work an electrochemical method employing a DC anodic voltammetric technique is developed. This method allows the determination of Cr(III) within the passivation layer. The basis of our technique is the anodic charge of oxidation of Cr(III) to Cr(VI) during anodic voltammetry. Total Cr content can be obtained from chemical analysis. Thus, combining these results one obtains the passivation layer Cr(III) and Cr(VI) contents.

2. Experimental Methods and Materials

Commercial hot-dip galvanized steel sheets with and without the final surface chromatization treatment were used. The chromatized steel sheets came from two different batches labeled “A” and “B” obtained under different processing conditions. Samples from batches “A” and “B” were analyzed by a chemical method and by an electrochemical method that are described below. In addition, samples from batches “A” and “B” underwent salt spray test following the ASTM B-117 standard. We investigated the electrochemical behavior of pure Zn and pure Cr performing anodic voltammetries in different solutions. In this way, the most effective electrolyte could be found.

For the chemical analysis of the total Cr content on the Zn coated sheets the chromium film was dissolved from an area of 25.88 cm² using a HCl 1 : 1 solution containing a steel corrosion inhibitor: hexamethylene-tetramine. The resulting solution was diluted up to 100 mL and analyzed in a Spectroflame (Spectro Analytical Instruments) spectrophotometer. Synthetic Merck standards were used to determine the chromium calibration curve.

The voltammetric analysis of the coated samples were carried out in four buffered aqueous electrolytes containing 0.1 M of H₃BO₃ with increasing additions of 0.1 M of NaOH to attain solutions with pHs of 8, 9, 10 and 11. These pHs were chosen based on the Pourbaix diagrams to find out the ranges in which Zn is passivated and Cr dissolves in the transpassivation region. 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).

3. Results and Discussion

First, anodic voltammetry was performed on pure Zn and Cr electrodes and non-chromatized Zn coated steel sheet using a scanning rate of 10 mV/s. The electrochemical behavior of Zn and Cr was established for four pHs: 8, 9, 10 and 11. Figure 1 depicts the voltammograms of pure Cr and Zn using a solution with pH equal to 10. Figure 1 shows that Cr began its oxidation process around 0.5 V and around 1 V the transpassivation of Cr could be visually confirmed by the appearance of the characteristic strong orange color of the Cr(VI) on the surface of the electrode. No evolution of oxygen (bubbles) was observed. It is worthy of note that the Pourbaix diagrams depict spontaneous reac-
tions at the electrode surface in water. However, in this work, as said above, we are using a water solution of borates. These borate anions may change the potentials relative to those shown in the Pourbaix diagrams. Figure 1 also shows that Zn was passivated over the whole scanning range: from $-0.5$ to $+1.5$ V. No oxygen evolution was observed on the surface of the Zn electrodes. The small current observed is a consequence of the passivation process that probably generated a Zn oxide layer that insulated the Zn from the solution. The Zn passivation current density increased significantly for pH above 11 and had a minimum value for pH equal to 9. Consequently, solutions with pH above 11 are not indicated for voltammetry because a high passivation current could contribute to the oxidation current of the chromate layer on Zn. As a result, solutions with pH between 8 and 10 remained as candidates. The solutions with pH 9 and 10 were chosen. These pH values were confirmed to be the optimum values by performing a similar study on a non-chromatized Zn coated steel sheet. For pH 8 and 11 solutions in non-chromatized Zn coated steel sheet the passivation becomes unstable. Figure 2 shows voltammograms of a non-chromatized Zn coated steel sheet in the solutions with pH 9 and 10. Figure 2 confirms the passivation of Zn up to approximately $+1.5$ V.

After the choice of pH 9 and 10 solutions it was necessary to establish the best scanning rate to characterize the chromate layer on Zn coated steels sheets. Scanning rates between 1 and 20 mV/s were employed. It was found that the total apparent charge related to the oxidation of Cr(III) increased with decreasing scanning rate but tended to remain constant for scanning rates approaching 20 mV/s. The Cr oxidation current is naturally a result of the oxidation of Cr(III) to Cr(VI). This increase in the current for a decreasing scanning rate was attributed to the contribution of the Zn passivation current. For that reason, a scanning rate of 20 mV/s was found to be the best choice to minimize the interference of the Zn passivation current. Moreover, the solution with pH equal to 10 was considered to be better than that with pH equal to 9. The reason for this is that a comparison of the two suggested that at pH 9, for a scanning rate equal to 20 mV/s, not all Cr was oxidized. This was reconfirmed by studying the Cr film dissolution by means of consecutive anodic scanning. It was found that after two consecutive voltammograms a characteristic Cr(III) peak was still present in the third scanning in a pH equal to 9 solution.

As a result of what was described above, we chose a buffered aqueous electrolyte containing $\text{H}_3\text{BO}_3$ and NaOH with pH equal to 10 and a scanning rate of 20 mV/s as the optimum pH and scanning rate for the electrochemical method, respectively. Using these conditions, a typical voltammogram of a chromatized Zn coated steel sheet is shown in Fig. 3. No oxygen evolution was observed in this case. It is worthy of note that the values at which the Cr(III)$\rightarrow$Cr(VI)$+3e^-$ took place is somewhat higher than the values found in Fig. 1 for pure Cr. This occurs because Fig. 3 shows Cr(III) being oxidized from within a Zn oxide matrix, which will require an overpotential. In the potential range in which the reaction Cr(III)$\rightarrow$Cr(VI)$+3e^-$ took place, the total current is constituted both by the contribution of the Cr(III)$\rightarrow$Cr(VI)$+3e^-$ reaction and the contribution of the Zn passivation. The baselines of Fig. 2 and Fig. 3 are not equal because the chromate layer present in specimens studied for Fig. 3 covers part of the surface. During voltammetry of Zn with chromate layer, the area of the sample that is not covered by chromate will contribute to the baseline current, but, because part of the surface is covered by the
chromate layer, the passivation current in Fig. 3 will be smaller than that of Fig. 2. This is clear from a comparison of Fig. 2 (at pH 10) and Fig. 3 (at pH 10). Moreover, as Cr(III) is oxidized to Cr(VI), ‘fresh’ Zn areas will be exposed and then passivated. It is precisely the passivation currents from those ‘freshly’ exposed areas that contribute to the increase in the baseline during the Cr(III)→Cr(VI) reaction (the peak in Fig. 3), relative to the baseline observed at smaller voltages, before the beginning of the Cr(III)→Cr(VI) reaction. However, although Cr(VI) is soluble in the aqueous solution not all Cr(VI) will leave the surface into the solution. Even at the end of the process when all Cr(III) is oxidized to Cr(VI), we still observed an orange color (characteristic of Cr(VI)) at the surface indicating that not all Cr(VI) went into the aqueous solution. It is also worthy of note that Fig. 3 is a typical voltammogram, an illustration of the behavior of a single specimen with a chromate layer. The baseline in Fig. 3 may vary from specimen to specimen because of two factors: a) different relationships of Cr(III)/Cr(VI) may be present; b) different amounts of Cr(VI) may dissolve and thus different ‘fresh’ Zn areas might be exposed. This latter factor (b) is difficult to control.

The contribution of the Zn passivation current can be subtracted by choosing as the baseline the dashed line shown in Fig. 3. The amount of Cr(III) can be obtained from the area, above the dashed baseline, marked in Fig. 3. The total charge is the marked area divided by the scanning rate. Notice that this area is the integral of the current as a function of scanning voltage. The possibility of subtracting the Zn passivation current from the total current to obtain solely the current of the reaction Cr(III)→Cr(VI)+3e in the way we did highlights the advantage of the voltammetric method over the galvanostatic method. In this latter method this separation of the Zn and Cr oxidation processes would not have been possible. In Fig. 2, at the end of the scanning range, there might have been oxygen evolution in addition to Zn passivation. We did not visually observe this oxygen evolution in the experiment of Fig. 2 perhaps because the current was small. Nevertheless, we believe that the subtraction of the baseline, as explained above, also subtracts any parallel processes occurring together with Zn passivation.

In order to illustrate the usefulness of the method some experiments were performed in two commercial chromatized hot-dip galvanized steel sheets. The results are given in Table 1. From Table 1 one can see that chemical analysis gave a total Cr content of 12.7 mg/m² for batch A and 12.1 mg/m² for batch B. Thus, total Cr content was similar for both batches and, based exclusively on this result, one might expect both batches to have similar performance. However, salt spray tests revealed that some white corrosion could be detected in batch A in spite its slightly higher total Cr content. This different behavior can be understood when the Cr(III) contents of each batch determined by the electrochemical method developed here are compared. One notices from Table 1 that Cr(III) content for batch A is significantly higher than for batch B. Hence, the difference in corrosion behavior between batch A and B can be attributed to different proportions of Cr(III)/Cr(VI) on the chromate layer of each batch. A detailed correlation between these quantities and corrosion behavior is beyond the scope of the present paper but the electrochemical technique developed here can be a useful tool for such a study.

4. Conclusions

In conclusion, an electrochemical method has been developed that allows the determination of the Cr(III) content directly from the chromate layer on a zinc coating surface. The method was illustrated by applying it to samples with similar total Cr contents but that exhibited different response to the salt spray test. It was shown that each sample had a different Cr(III) content that might explain the observed difference in corrosion behavior. Finally, it is worthy of note, that we applied this method to a Zn coated steel sheet, which was chromatized with a traditional Cr(VI) solution. In view of Cr(VI) undesirable environmental effect, a recent trend has been to develop chromatizing solutions based on Cr(III) in which the concentration of Cr(VI) is as low as possible. Our method is in principle also applicable to passivation layers generated by these new solutions. Indeed, our method can be helpful in the very development and improvement of these new passivation processes.

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