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EFFECTS OF A SMALL ADDITION OF MN ON MODIFYING THE COATING THICKNESS, STRUCTURE AND CORROSION RESISTANCE OF HOT-DIP GALVANIZED COATINGS

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Abstract

Alloying elements in the galvanic coatings can have significant influence in improving the structure and performance of the coatings. The present work addressed this aspect. Steel substrate was galvanized in molten zinc containing 0.01, 0.05 and 0.1 wt. % Mn. The coatings were studied with optical microscopy, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Corrosion behavior was analyzed by Tafel extrapolation test. From experimental results, it was found that thickness of Γ, δ and ζ layers would be decreased by increasing the Mn content of the zinc bath and conversely, thickness of η layer was increased. In addition the morphological study shows that Mn refines the feathery structure of the coatings. Furthermore, corrosion resistance of hot-dip galvanized coatings would be increased by increasing the Mn content of the zinc bath.

Key words: Alloying elements, Hot-dip galvanized coatings, Coatings thickness, Intermetallic layers, Corrosion resistance

Introduction

The usage of zinc coatings for the corrosion protection of ferrous substrates is very widespread. The protective action of these coatings results from the fact that zinc reacts with atmospheric constituents such as O_2, H_2O and CO_2 forming a dense and adherent film which is highly insoluble in water and forms a barrier that isolates zinc from the aggressive environment. Furthermore, zinc is anodic to iron and steel and as a result, in the case of galvanic corrosion, zinc becomes the anode while the ferrous substrate becomes the cathode and does not corrode [1].

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Minor addition of alloying elements may change the structure and properties of the coatings. Aluminum is added to the bath in order to prevent the formation of thick and very brittle Fe-Zn intermetallic layers that affect the further material forming process. With Al a very thin ternary Fe-Al-Zn phase is formed which acts as a diffusion barrier retarding the formation of Fe-Zn intermetallic compounds [2]. Ni has been reported to have significant role in the improvement of the process. A nickel-rich barrier layer was identified as the cause for substantial improvement of the coating performance [3]. Bismuth addition in the zinc bath is mainly accumulated in the upper parts of the coatings in the form of inclusions. These inclusions could accelerate the corrosion of the coatings because bismuth is cathodic to zinc but the addition of bismuth in molten zinc reduces the thickness of the galvanized coatings and improves the formability of the coatings [4]. It has been reported [5] that Mn at a concentration 0.5 wt.% can significantly decrease the reactivity of Si. The effect of Mn addition on the coating thickness was found to depend on the type of steel substrate. For the galvanized steels containing 0.02 wt. % Si, the effect of Mn on the coating thickness can be neglected, while for the galvanized steels containing 0.2 wt. % Si, Mn addition decreases the coating thickness by about 30 % compared with the commercially-pure Zn coating. Boshkov. [6] Reported that an 11 wt. % Zn-Mn alloy produced by electrodeposition shows increased corrosion resistance and protective ability. The high corrosion resistance is due to the rapid formation of $Zn_5(OH)_8Cl_2 \cdot H_2O$ (ZHC) on the Zn-Mn alloy. Boshkov proposed that dissolution of Mn causes a slight increase of the pH of the medium up to a value, which favours the formation of ZHC.

The aim of this study is to assess the effects of Mn addition in the zinc bath on the structure of zinc hot-dip galvanized coatings. The preliminary results of this study indicate that there is an opportunity for the prediction of the performances of galvanized coatings such as their formation and corrosion resistance.

Experimental procedure

All the tests were carried out three times with commercially available JIS G3302 hot-dip galvanized steels and the average of results were considered as the final report. In this study, manganese content of the zinc bath was changed from 0.01 wt. % to 0.1 wt. %.

Cross-sections of the coatings were studied using scanning electron microscopy (SEM) and optical microscopy. The chemical composition of the coatings was analyzed by energy dispersive spectroscopy (EDS). The size of spangles was determined using line intercept method. In this method, several lines (10 cm in length) were drawn on different regions of the specimen surface and the intersected spangles were counted. Then the length of every line was divided by the number of intersected spangles (by the line) and the average result was considered as the spangle size.

Tafel polarization tests were conducted in 3.5% NaCl solution at room temperature using a standard corrosion cell kit with the working electrode, two graphite center electrodes and an AgCl reference electrode. Potentiodynamic scanning was performed by stepping the potential at a scan rate of 1 mVs^{-1} from -250 to 250.

Results and discussion

Fig. 1 shows a typical cross-section of the zinc coated sample containing 0.1 wt. % Mn; four distinct coating layers of hot-dip galvanized steel containing different amount of Fe can be identified in this micrograph. It can be seen from Fig. 1, that Mn has no any effect on the number of the Zn-Fe intermetallic layers. The chemical composition of these layers is given in Table 1. EDS analysis of coating layers indicated that coating consisted of four layers**:** γ, δ, ζ and η. It was observed that increasing the Mn content of the zinc bath was to produce a uniform and compact coating.

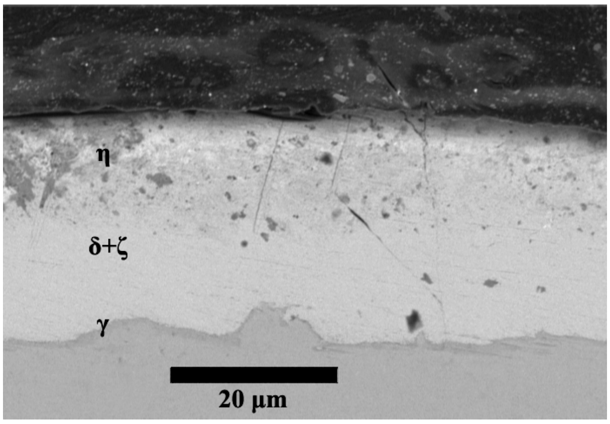

Fig. 1. SEM micrograph of the cross-section of a coating formed in a bath containing 0.1 wt.% Mn.

Table 1. Results of EDS of the phase composition the coating in Fig. 1.

Phase	Zn (wt.%)	Fe (wt.%)
γ	21.3	78.7
δ	94.92	5.08
ζ	95.31	4.69
η	99.9	0.1

Comparison between the intermetallic layers thickness as a function of content of Mn is illustrated in Fig. 2.

From Fig. 2 it is evident that by increasing the Mn content of zinc bath, thickness of γ, δ and ζ layers decrease and, conversely, thickness of η layer increases. In addition, by increasing the Mn content of zinc bath, total thickness of coating was decreased. To explain the phenomenon it could be assumed (although no data is available in the case of Mn) that Mn prevented diffusion of zinc and iron by the reduction of diffusion rate which decreases thickness of coatings. It is clear that Mn has significant effect on the layer growth and coating thickness at a concentration 0.1 wt.%.

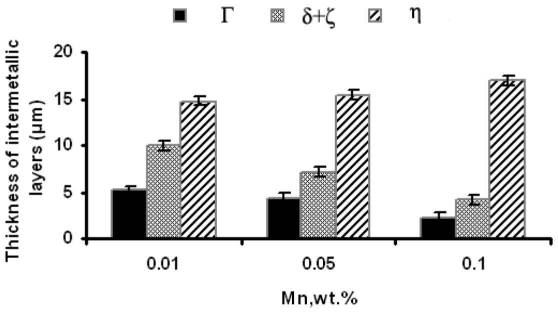

Fig. 2. Thickness of each identified zone in the coating for different content of Mn.

Tafel polarization curves of samples with different content of Mn are shown in Fig. 3.

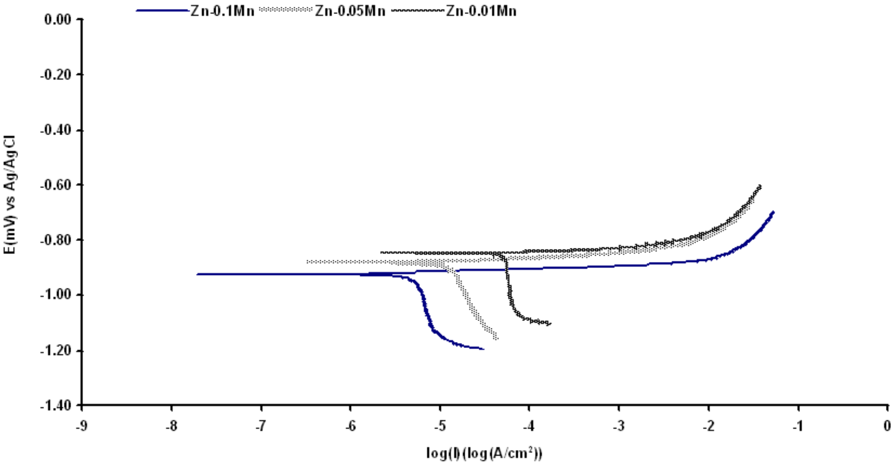

Fig. 3. Tafel polarization curves of samples with different content of Mn.

From Fig. 3 it is evident that increasing the Mn content of zinc bath would result in shifting the Tafel polarization curves towards the left. Consequently, corrosion current density is decreased by increasing the Mn content of zinc bath. Thickness of the hot-dip galvanized coatings has an important role in the case of corrosion resistance and formability. As the coating thickness increases; the corrosion resistance and formability of hot-dip galvanized coatings decreases. Increasing the thickness of coatings results in the weakening of (00.2) basal texture component and strengthening of (20.1) high angle pyramidal and (10.1) prism texture components. Coatings with strong (00.2) texture component and weak (20.1) and (10.1) texture component have higher corrosion resistance and better formability than the coatings with weak (00.2) texture component and strong (20.1) and (10.0) texture components. [7, 8].

Fig. 4 shows the appearance of feathery structure of coatings.

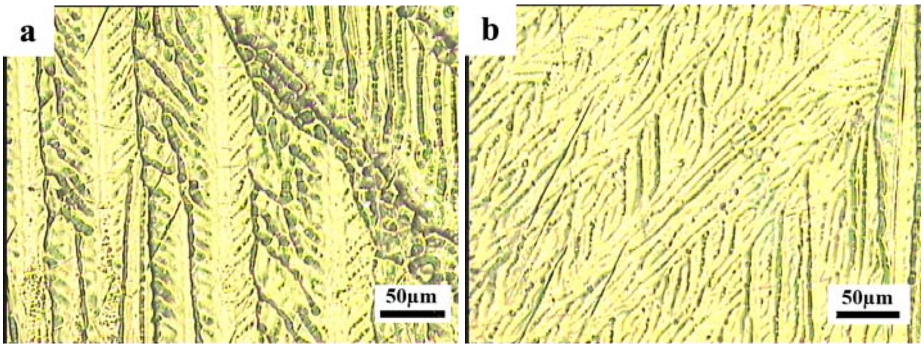

Fig. 4. Optical micrograph of feathery structure of the coatings containing0.01 wt.% Mn (a), 0.1 wt.% Mn (b).

Different solidification morphologies were observed on the surface of coatings, i.e. coarse and fine feathery structure. This result implies that increased addition of Mn refines the structure of coating.

Fig 5 shows the surface of hot-dip galvanized coating which is covered with spangles. The size of crystallites in galvanized coatings is an aesthetic feature, known as a spangle. By varying the number of particles added for heterogeneous nucleation and the rate of cooling in a hot-dip process, the size of spangle can be adjusted from an apparently uniform surface (crystallites too small to be seen with the naked eye) to grains several centimeters wide.

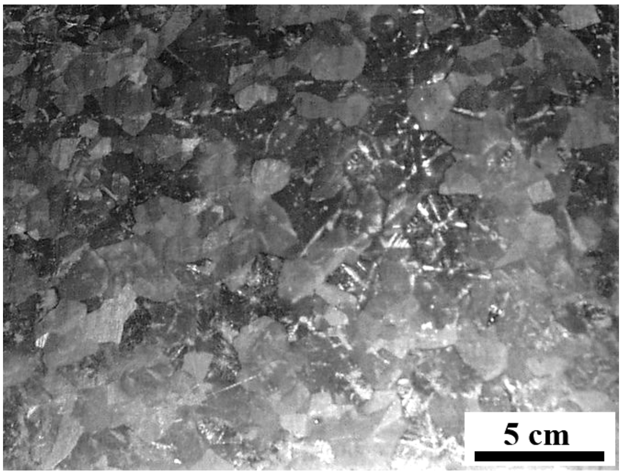

Fig. 5. Optical micrograph of hot-dip galvanized surface.

In Fig. 6 decreasing in the spangle size due to increasing the Mn content of the zinc bath can be observed.

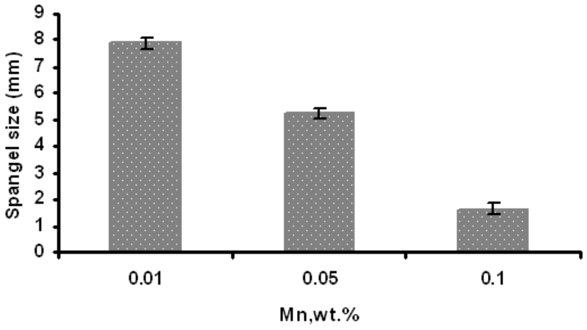

Fig. 6. Effects of Mn content of zinc bath on spangle size of coatings.

The spangle size is related to the surface tension of the alloying elements addition, the size decreasing as the melt vapor surface tension of the alloying elements increases. In addition, it is proposed that spangle form dendritically from a nucleus in the melt. Alloy addition with low interfacial energies and very limited solid solubility are highly concentrated ahead of the dendrite tip. This decreases the tip radius and increases the dendrite velocity, producing large spangles [9]. According to the Zn-Mn phase diagram, in the Zn-rich corner, this system has a eutectic composition at about 1.2 wt. % Mn. Mn has relatively high solubility (about 0.5 wt. %) in Zn at the eutectic temperature (419°C). However, at 200°C the solubility of Mn in Zn drops to 0.02 wt. % [10].

In the hot-dip galvanized coatings with large spangle most surface areas have been covered with dull spangle, whereas coatings with small spangles have shown bright surface. The surface of bright spangles was parallel to the (00·1) plane and was crystallographically more homogeneous than that of dull spangles whose surface was mostly parallel to the (10·1) plane. This seems responsible for higher corrosion resistance of bright spangles than any other spangles [11-12].

Conclusions

From the above investigation, it could be deduced that:

Mn addition affects the coating thickness and decreased it at a concentration 0.1 wt.%. The addition of Mn in molten zinc reduced the thickness of γ, δ and ζ intermetallic layers. This reduction would be beneficial for coatings corrosion resistance. Although it is necessary to go deeper into the study of the process mechanism, as well as to confirm the tendencies observed in the present work, it is possible to conclude that Mn addition to the galvanized bath will be an effective method for avoiding the coarsening of coatings structure. In addition, increasing the Mn content in the zinc bath would result in increased corrosion resistance of hot-dip galvanized coatings.

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