Journal of University of Science and Technology Beijing
Volume 11, Number 6, December 2004, Page 529

Materials

Effect of current density on the morphology of Zn electrodeposits

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(Received 2003-11-21)

Abstract: The effect of current density on the morphology of Zn electrodeposits prepared by a flow-channel cell was investigated by scanning electron microscopy (SEM). It was found that the morphology of Zn electrodeposits evolves from thin-layered hexagonal η-phase crystals to pyramidal η-phase particles with increasing the current density. The morphological evolution at various flow rates was also examined and the results show that the morphological evolution at a lower flow rate is more remarkable than that at a higher flow rate with increasing the current density. To reveal the mechanism of the morphological evolution in detail, the atomic configuration on both $(0001)_\eta$ and $\{1\bar{1}00\}_\eta$ planes under different current densities was investigated, it was noted that a specify current density could provide a good condition for the layered epitaxial growth of hexagonal η-phase.

Key words: Zn electrodeposit; current density; flow rate; morphological evolution

[This work was financially supported by the collaboration program between Nippon Steel Corporation and University of Science and Technology Beijing and the National Natural Science Foundation of China (No.571014569).]

1 Introduction

Steel sheets electroplated with zinc or zinc alloys are widely used for automotive body panels due to their superior corrosion resistance, even with a light coating mass compared with other types of coated products [1]. In continuous steel strip electroplating, zinc or zinc alloys are normally electrodeposited from either sulfate- or chloride-based electrolytes with simple chemical formulations by applying high current densities at a high flow rate [2].

The study of elctrodeposition can be classified into two different types, *i.e.* electrochemical and crystallographic approaches. In electrochemical studies, the reaction paths, the rate controlling processes and the nucleation and growth theory of deposits have been the major subjects of the researches [3, 4]. The crystallographic features, on the other hand, are also of interest because the morphology of deposits varies with the depositing condition remarkably. For example, it has been reported that the growth of zinc crystals largely depends on the surface condition of the ferrite substrates [5-7]. Ohtsubo *et al.* [8] have found that the morphology of zinc crystals depends on the composition of the bath. Thus, a basic understanding of crystal growth of the deposits would certainly accelerate the developments of zinc and new types of zinc alloy electrodeposits. Therefore, a further detailed study on the crystallographic features is still necessary to reveal the mechanism of their formation.

In the present work, the morphology of zinc electrodeposits from chloride bath was observed, focusing mainly on the effect of current density on the morphology of zinc electrodeposits during electroplating. The objective of this paper is to reveal the mechanism of the morphological evolution as a function of current density.

2 Experimental procedure

In continuous steel-strip plating, the steel strip of the cathode moves relative to the electrolyte with the superposition of injected flow. Such a flow pattern may be characterized as a modified Couette-flow between two parallel electrodes, and the experiments can be conducted in laboratory using a rectangular type of flow-channel cell. In this study, a flow-channel cell that can simulate the flow pattern to the continuous steel strip plating was used and its schematic diagram is shown in **figure 1**. The apparatus was mainly composed of a plating cell, an electrolyte reservoir, a circulation pump and connecting pipes. The electrolyte

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was supplied to the plating cell with the parallel-positioned cathode and anode from the reservoir *via* the pump at a controlled flow rate. To ensure a uniform flow transition from the circular pipe to the rectangular cell, lower and upper transition tubes, with gradual changes in cross-sectional shape, were inserted. Low-carbon steel panels, with a thickness of 0.6 mm, were used as cathode specimens, and a zinc plate was used as an anode. The effective area of the cathode or anode was 50 mm×100 mm, and the distance between the electrodes was 12 mm. The electrical charge was monitored to be constant (6000 C/dm^2) by the coulometer.

The electrolyte was prepared from simple salts such as zinc chloride and potassium chloride. The Zn^{2+} concentration used in this study was 1000 mol/m^3. The bath temperature was 323 K. The pH value was controlled to 3.0 using dilute hydrochloric acid. The flow rate was kept at 1.0 and 2.0 m/s, respectively. The current density was monitored in the range of 50-200 A/dm^2. Its effect on the morphology of zinc deposits was examined by scanning electron microscope (SEM), Hitachi S-520. The steel substrates were polished, degreased in acetone with ultrasonic cleaning, rinsed in deionized water and finally dried in air at room temperature prior to electrodeposition. The deposited specimens were quickly rinsed by spraying with water and were stripped in dilute hydrochloric acid.

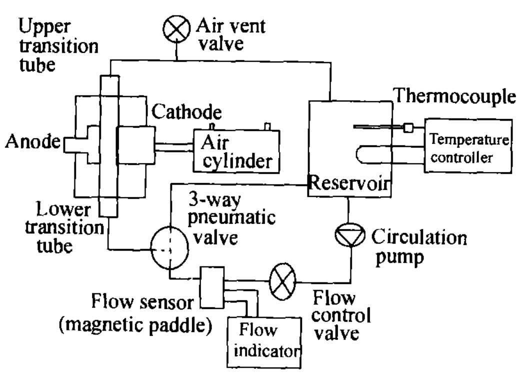

Figure 1 Schematic diagram of the adopted flow-channel cell apparatus.

3 Results and discussion

Figures 2(a)-(c) are the SEM images of Zn deposits formed under the current densities of 50, 100 and 200 A/dm^2, respectively, showing the effect of current density on the morphology of Zn deposits at a flow rate of 1.0 m/s. Figure 2(a) shows that the morphology of zinc deposits appears thin-layered hexagonal η-phase crystals under a lower current density, *i.e.* 50 A/dm^2. When the current density is monitored to 100 A/dm^2, the morphology of zinc deposits changes remarkably, and thin layered hexagonal η-phase crystals are mostly covered by thick angular-shaped crystals as presented in figure 2(b). This type of morphology is referred to as 'pyramidal' shape hereafter. Further increasing the current density up to 200 A/dm^2, the pyramidal-shape crystals can be observed and the thin-layered hexagonal η-phase crystals disappear (figure 2(c)). Meanwhile, the electrodeposit formed at a flow rate of 2.0 m/s was also examined for various current densities. **Figures** 3(a)-(c) show the SEM images of Zn deposits formed at current densities of 50, 100 and 200 A/dm^2, respectively. It can be seen that the morphological change is not so remarkable in the current density range of 50-100 A/dm^2 at a higher flow rate, *i.e.* 2.0 m/s, as shown in figures 3(a) and 3(b). The morphological evolution of zinc deposits in figures 3(a) and (b) is similar to that in figure 2(a). When the current density is increased up to 200 A/dm^2, the thick pyramidal-shape crystals can be observed and the thin-layered hexagonal crystals are gradually covered as shown in figure 3(c). It can be considered that the pyramidal η-crystals begin to deposit on the substrate after it is completely covered by layered hexagonal η-phase crystals by comparing the observations mentioned so far. That is, the morphology of η-Zn deposits varies from thin layered hexagonal plates to pyramidal-shape crystals with increasing the current density. Ohmori *et al.* [9] also found a similar variation phenomenon of zinc deposits with increasing the current density. The morphological variation of η-phase crystals with increasing the current density can be shown schematically in **figure 4** [9].

As the mechanism of the morphological change is concerned, it can be explained by considering the effect of current density on the crystal structure. It is reported that the ratio of η-phase lattice parameters (*c*/*a*) decreases with increasing the current density during electrodeposition [8]. This suggests that the atomic configurations of some other η-phase planes are quite close to $(0001)_\eta$ plane of the initially formed plates [6] and that the new η-phase crystals grow with keeping parallelism among these planes. Thus, the atomic configuration of various planes in an η-phase lattice was examined and the minimum misfit plane to $(0001)_\eta$ plane was confirmed to be $\{1\bar{1}00\}_\eta$ as reported previously [6, 7]. To further reveal the effect of current density in detail, the atomic configuration was compared on both $(0001)_\eta$ plane and $\{1\bar{1}00\}_\eta$ plane under different current densities, *i.e.* 2, 15 and 30 A/dm^2. **Figure 5** shows the result. It is interesting to note that the best fitness between these two planes can be obtained under a specific current density, *i.e.* 15A/dm^2, as shown in figure 5(b). That is, a specific current density can provide a good condition for the layered epitaxial growth of hexagonal η-phase (see figures 2(a) and 3(a)). Ohmori *et al.* [9] indicated that the dimensional difference between $<1\bar{1}00>_{\eta 1}$ direction on $(0001)_{\eta 1}$ plane of an η-phase plate formed directly on the substrate surface and $<0001>_{\eta 2}$ direction on $\{0\bar{0}11\}_{\eta 2}$ plane parallel to the above $(0001)_{\eta 1}$ increases with increasing the current density. The crystals of initially formed plates are referred to as η_1 and the crystals of lately formed plates are referred to as η_2. It is, therefore, likely that under a specific current density, η-phase crystals formed at different periods with different orientations can precipitate on $(0001)_{\eta 1}$ plane. This would result in the collapse of the layered epitaxial growth and the formation of pyramidal η-phase crystals. The present observations are agreeable with the investigation of Ohmori *et al.* [9]. The mechanism of the morphological change can be explained in terms of the atomic configurations on both $(0001)_\eta$ and $\{1\bar{1}00\}_\eta$ planes.

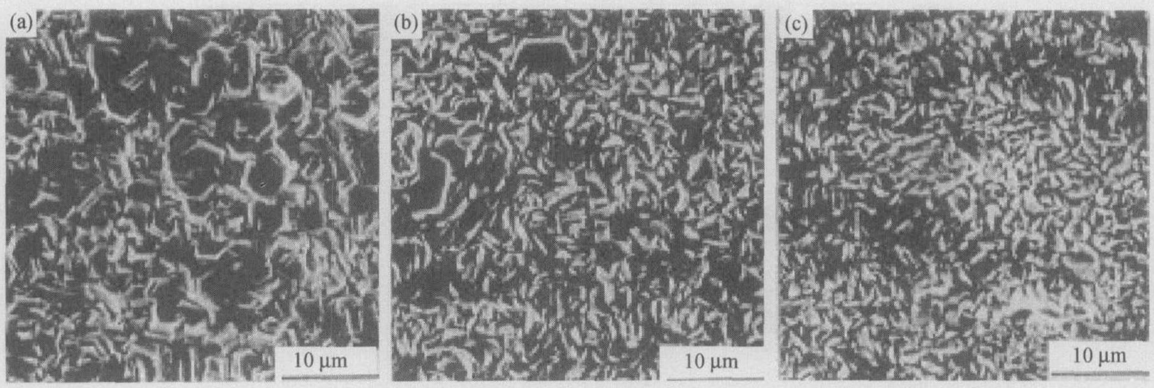

Figure 2 Morphological evolution of zinc electrodeposits with increasing the current density at a flow rate of 1.0 m/s, the corresponding current density is (a) 50, (b) 100 and (c) 200 A/dm^2, respectively.

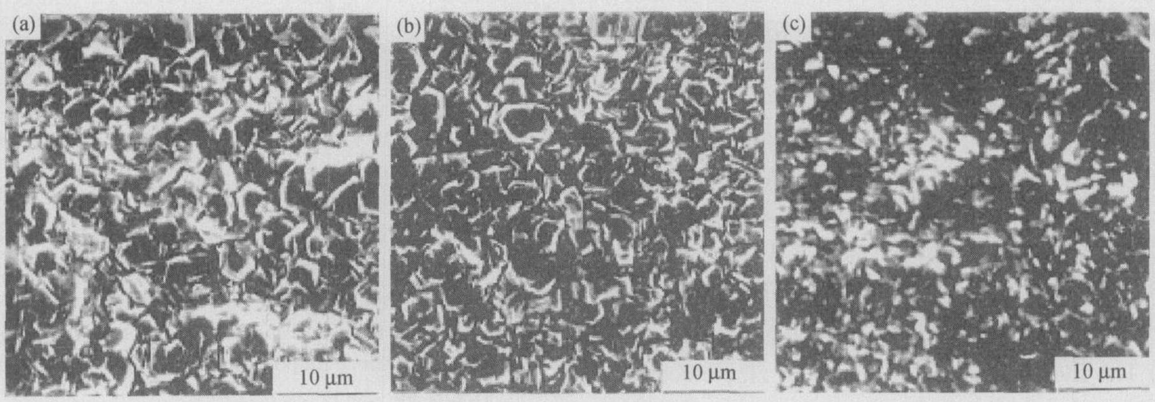

Figure 3 Morphological evolution of zinc electrodeposits with increasing the current density at a flow rate of 2.0 m/s, the corresponding current density is (a) 50, (b) 100 and (c) 200 A/dm^2, respectively.

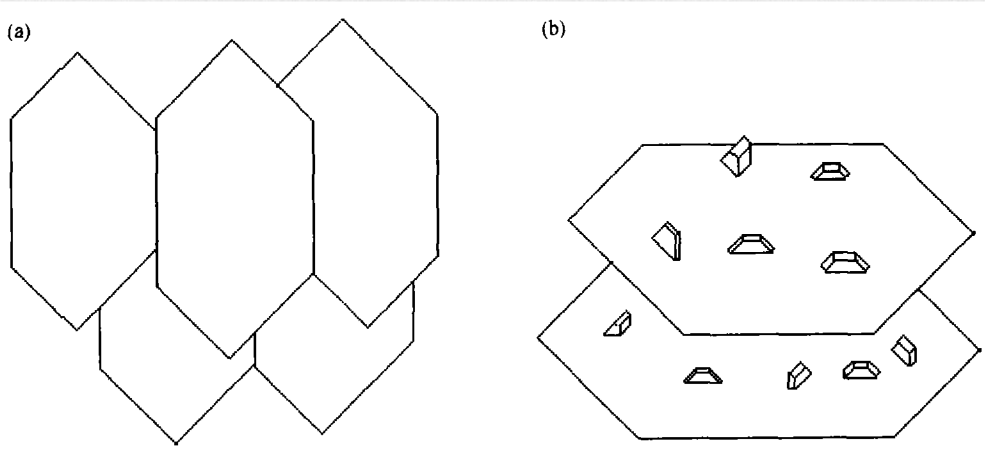

Figure 4 Schematic illustration of the morphological evolution of η-phase crystals with increasing the current density: (a) hexagonal plates; (b) nucleation of pyramidal crystals on hexagonal plates.

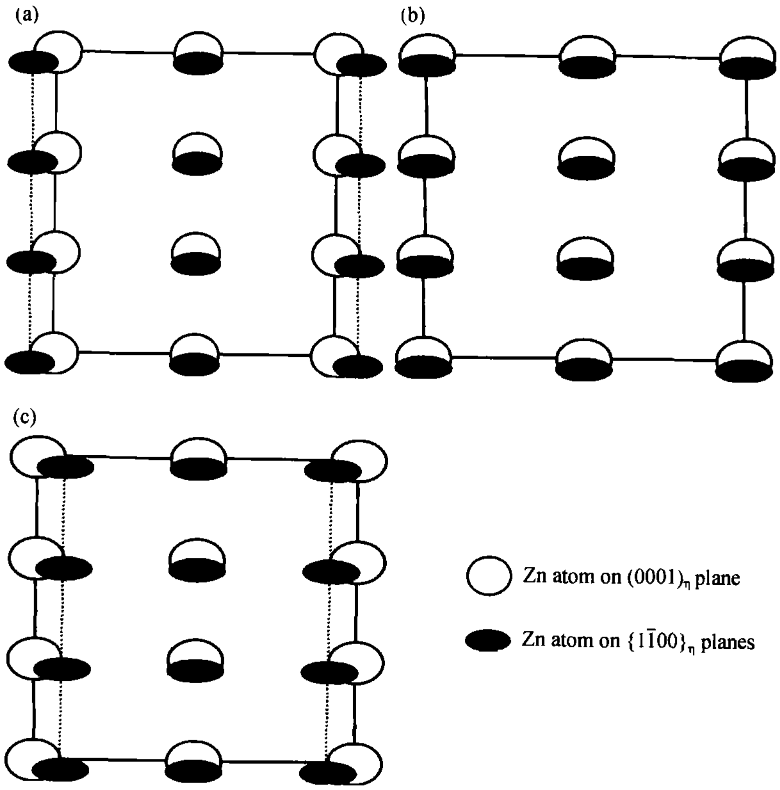

Figure 5 Superposition of atomic configurations on both $(0001)_\eta$ plane and $\{1\bar{1}00\}_\eta$ plane under different current densities: (a) 2A/dm^{-2}, c/a=1.86; (b) 15 A/dm^{-2}, c/a=1.70; (c) 30 A/dm^{-2}, c/a=1.63 [9].

4 Conclusions

(1) The effect of current density on the morphology of zinc deposits is significant. SEM observations show that the morphology of zinc electrodeposits changes from thin-layered hexagonal η-phase crystals to pyramidal η-phase particles with increasing the current density.

(2) The morphological evolution of zinc electrodeposits at a lower flow rate, *i.e.* 1.0 m/s, is more remarkable than that at a higher flow rate, *i.e.* 2.0 m/s, with increasing the current density.

(3) The atomic configuration on both $(0001)_\eta$ and $\{1\bar{1}00\}_\eta$ planes was investigated under different current densities. It is interesting to note that the best fitness between these two planes can be obtained under a specific current density, *i.e.* 15 A/dm^2. That is, a specific current density can provide a good condition for the layered epitaxial growth of hexagonal η-phase. The mechanism of the morphological evolution can be explained in term of the atomic configurations on both $(0001)_\eta$ and $\{1\bar{1}00\}_\eta$ planes.

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