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The effect of electrochemical adsorbates on texture and morphology development during zinc and zinc–cobalt electrodepositions

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Abstract

Electrochemical impedance spectroscopy (EIS) investigation of zinc electrodeposition at 10 mA cm^{-2} indicated the possibility of hydrogen adsorption during deposition process. This causes low angle pyramidal $\{1 1.5\}$ and $\{1 0.3\}$ texture component via lateral bunching and results the morphology of ridges type. Conversely, at the same current density used in zinc–cobalt deposition the hydrogen adsorption is less pronounced due to adsorption of cobalt and/or cobalt-contained species during the growth stage. This leads to a strong inhibition resulted in a different type of growth, called "Field-Oriented Texture". This kind of growth promoted columnar grain growth results in a large number of elongated crystals almost normal to the substrate surface followed by some blocky crystals on top of them. This develops prism planes as a major texture component besides some basal and low angle pyramidal planes.

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1. Introduction

During the electrodeposition of some metals and alloys near redox potential, the surface could be covered by adsorbed species such as hydrogen and alloy element-contained species. The adsorbed hydrogen atoms, which are capable of continually regenerating on the surface, can lead to relaxation during the zinc electrodeposition at low overpotentials [1]. Thus, the mechanism of electrodeposition can be strongly affected by the adsorbates [1,2].

In zinc electrodeposition, adsorbed hydrogen ZnH_{ad}^+ can act as an interface inhibitor preventing direct incorporation of adions (adatoms) into the microsteps. This increases two-dimensional nucleation frequency [1,2] thereby encouraging the lateral bunching growth of zinc [3]. Multiplication of the microsteps to macrosteps is the so-called "bunching". Fisher has described bunching growth mechanism of microsteps, which are regenerated by two-dimensional nucleation. It is mentioned that the process of coalescence of microsteps to form macrosteps is ener-

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0013-4686/\$ - see front matter © 2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2008.01.085 getically favorable, because the edge energy per atom is always higher than the surface energy [4,5]. According to Fisher, the bunching is possible by the presence of blocking adsorbates [3].

In zinc-alloy electrodeposition, some electrochemical species rather than hydrogen would form and adsorb onto the substrate surface [6]. In zinc–cobalt electrodeposition, reduction of cobalt (or cobalt-contained species) and its adsorption is expected to occur strongly at the early stage as well as during the deposition at low overpotentials [7]. This adsorption can affect the zinc deposition mechanism and stimulate the hydrogen evolution strongly [7]. In contrary to zinc electrodeposition, it is reported that in the presence of cobalt ions, the mechanism of hydrogen evolution involves a diffusion-controlled process [7]. In addition, a strong inhibition for hydrogen evolution due to the coverage of adsorbed cobalt and/or cobalt-contained species can be achieved.

The aim of this work is to study the intermediate adsorption and its consequence inhibition effect on texture formation in zinc and zinc–cobalt electrodeposition. For this purpose, electrochemical impedance spectroscopy (EIS) and orientation distribution function (ODF) methods were used to find the possibility of adsorption and to evaluate the texture components of coatings, respectively.

2. Experimental procedure

Substrates were prepared from a commercial cold rolled low carbon steel sheet with a thickness of 1 mm. Specimens were sealed in a stainless steel foil sack and annealed at 880 °C for 3 h. Specimens were then mechanically polished using 600-grit abrasive SiC paper and subsequently electropolished in a solution of 95 vol% acetic acid and 5 vol% perchloric acid for 2.5–3 min. After electropolishing, the specimens were washed with distilled water and soaked in 10% sulfuric acid solution for 20 s. Specimens were then washed again with distilled water and immediately placed in the electroplating bath.

The bath compositions used were $ZnSO_4 \cdot 7H_2O$ (620 g l⁻¹) plus Na₂SO₄ (75 g l⁻¹) for zinc deposition and ZnSO₄ · 7H₂O (620 g l⁻¹) and CoSO₄ · 7H₂O (125 g l⁻¹) plus Na₂SO₄ (75 g l⁻¹) for zinc–cobalt deposition. The pH of the baths was adjusted to 2 using dilute sulfuric acid solution. Deposition was conducted in a standard corrosion cell, with two graphite counter electrodes and a saturated calomel reference electrode (SCE), at a current of 10 mA cm⁻². The reference electrode was placed close to the cathode surface via a luggin capillary, filled with bath solution. The temperature of the cell was kept at 25 ± 2 °C. The current density of 10 mA cm⁻² was found suitable for both zinc and zinc–cobalt electrodeposition, as it provides a large amount of surface coverage by adsorbates.

An EG&G computer controlled potentiostat/galvanostat model 263A was used to maintain the current density at 10 mA cm^{-2} . In order to produce a constant coating thickness of 5 µm, the plating time was set to 1100 s. An EG&G AC responser (model 1025) was coupled with potentiostat/galvanostat to read AC impedance resistance. AC impedance measurements were taken using a conventional cell with a platinum counter electrode and a SCE as the reference electrode, with a similar arrangement as in the standard corrosion cell.

Philips XL30 scanning electron microscope was used to observe the morphology of the deposits. A Siemens D500 diffractometer was used to determine substrate and coating texture. The diffractometer was operated using Cu K α at an accelerating voltage of 40 kV and a current of 40 mA. For the coatings, three pole figures were measured for the planes of $\{0 0.2\}, \{1 0.0\}$ and $\{1 0.1\}$ using the reflection technique in five deg polar and angular intervals. The ODFs were then calculated using "TexTools" software.

3. Results and discussion

Fig. 1 shows cross section of the ODF of steel substrate sheet at $\varphi_2 = 45^\circ$. The main texture component is the so-called γ fiber [9] that is characterized by $\langle 1 \ 1 \ 1 \rangle$ directions parallel to normal of the steel sheet. According to Fig. 1, a strong $\{1 \ 1 \ 1 \} \langle 1 \ 1 \ 0 \rangle$ and $\{1 \ 1 \ 1 \} \langle 1 \ 1 \ 2 \rangle$ orientations can be considered for the steel substrate grains.

Fig. 2 shows cross sections of the ODF of electrodeposited zinc at $\varphi_2 = 30^\circ$ and 55°. These cross sections were selected because they can reveal all the texture components sufficiently. A sharp non-fiber texture component, which involves pyramidal $\{1 \ 1.5\}$ $\langle \bar{3} \ \bar{3} \ 1 \rangle$ and pyramidal $\{1 \ 0.3\}$ $\langle \bar{3} \ \bar{2} \ 1 \rangle$ component is evi-

Max. Intensity =5.8 4.8 3.9 2.9 2.0 $\phi_1 = 0^{\circ}, 90^{\circ}$ $\Phi = 0^{\circ}, 90^{\circ}$

Fig. 1. Cross section of the ODF of steel substrate sheet at $\varphi_2 = 45^\circ$.

dent from this figure using the location map depicted in Fig. 3. The pyramidal texture component is essentially produced due to epitaxial growth of zinc on steel substrate grains [8–10]. It is believed to be strongly under the influence of γ fiber texture intensity of steel substrate [11]. Epitaxial growth of zinc can be developed by constructing the Burger's orientation relationship between the {00.2} planes of zinc crystallites and {110} terraces of the surface of steel substrate created by electropolishing [12,13]. In this way, zinc atoms are incorporated one after another into microsteps or kinks of substrate surface [8–10].

Fig. 4 shows the morphology of zinc deposited at 10 mA cm^{-2} . The coating consists of thin-layered hexagonal plates aligned in a specific way on each grain of substrate. This would make a specific kind of morphology called "ridges morphology" which is an evidence for epitaxial growth [8,9,11].

Fig. 5 shows the Nyquist plot of zinc deposition. This AC impedance reading was performed at -1.05 V. This potential



Fig. 2. Cross sections of the ODF of electrodeposited zinc at $\varphi_2 = 30^\circ$ and 55° .



Fig. 3. location map of some texture components in ODF of hexagonal lattice at $\varphi_2 = 30^\circ$ and 55° .

corresponds to the current density of 10 mA cm^{-2} and is read directly from cathodic scan curve obtained for zinc deposition in Fig. 6. The AC impedance data shows one capacitive loop at high frequencies and two possible inductive loops at low frequencies. The high frequency capacitive loop corresponds to the impedance created by double-layer capacitance in parallel



Fig. 4. Morphology of the zinc deposited at 10 mA cm^{-2} .



Fig. 5. Nyquist plots of zinc deposition at -1.05 V.

with the charge-transfer resistance [1,2]. The two low-frequency inductive loops correspond to the relaxation of both the coverage of Zn_{ad}^+ and ZnH^+_{ad} in order of decreasing frequencies [1,2]. As it was mentioned by Ichino et al. [2], adsorbed hydrogen covers the entire surface of zinc growing deposit near the zinc redox potential [2].

The adsorbed hydrogen ZnH+ad could be considered as a blocking adsorbate with an interfacial inhibition behavior [2] which is commonly necessary for bunching growth [8]. The bunching only comes about by the fact that younger microsteps overtake the older ones during the growth and then all microsteps coalesce to form the macrosteps. For this purpose, the older steps in their lateral growth must be hindered more than the younger ones [3]. This succeeds by the time dependency of inhibitor adsorption [3]. It seems that ZnH+ad poses all the mentioned requirements to act as an effective interface inhibitor needed for the bunching growth. Finally, the lateral aggregation of the created macrosteps occurs and results in ridges morphology as seen in Fig. 4. This kind of growth has also been discussed previously by Itoh et al. [4] and is expected to occur only on surfaces that are electrolytically polished which comprise microsteps [12,13]. In this way, a fully epitaxial growth of zinc onto the electropolished steel substrate can be obtained [8-10]. Eventually, It can be con-



Fig. 6. Cathodic scan curves for zinc and zinc–cobalt, scan rate = 40 mV s^{-1} .



Fig. 7. Schematic representation of lateral growth of zinc on steel substrate surface.

sidered that the steel substrate microsteps has been transformed to the zinc deposit macrosteps through bunching and resulted low angle pyramidal texture components such as $(1\ 1.5)$ and $(1\ 0.3)$, as seen from the ODF results in Fig. 2. Development of the low angle pyramidal planes could be assumed schematically as it is drawn in Fig. 7.

Fig. 8 shows the cross sections of the ODF of electrodeposited zinc–cobalt. It is noted that the maximum intensity of the planes is much lower than that of zinc (Fig. 2). Non-fiber prism {11.0} (01.6) orientation is taken to be account as the major texture component besides the basal {00.2} and some low angle pyramidal {11.5} $\langle \bar{3} \bar{3} . 1 \rangle$ and {10.3} $\langle \bar{3} \bar{2} . 1 \rangle$ orientations.

The AC impedance data for zinc–cobalt deposited at -1.08 V corresponding to 10 mA cm^{-2} is seen in Fig. 9. It shows one capacitive loop at high frequencies, an inductive loop followed by a capacitive loop at low frequencies. This feature predicts a different electrochemical behavior for zinc–cobalt deposition



Fig. 8. Cross sections of the ODF of electrodeposited zinc–cobalt at $\varphi_2 = 30^{\circ}$ and 55° .



Fig. 9. Nyquist plots of zinc-cobalt deposition at -1.08 V.

with respect to the zinc deposition. The high frequency capacitive loop, similar to that observed for zinc, corresponds to impedance created by the double-layer capacitance in parallel with the charge-transfer resistance. The inductive loop appeared at low frequencies corresponds again to relaxation of Zn⁺_{ad} coverage [1,2]. The surprising capacitive loop observed at low frequencies on the Nyquist plot may reflect the relaxation of cobalt and/or cobalt-contained species onto the entire growing surface of deposit. Similar results have also been reported by previous works on zinc-nickel deposition [14] and zinc deposition from baths with small amount of lead [2]. The absence of any inductive loop at low frequencies on the spectrum reflects the inhibited adsorption of hydrogen ZnH⁺ad during the coating growth. As it was seen, hydrogen adsorption was the predominant adsorbate in zinc deposition (Fig. 5). This could be related to the high tendency for coverage of the growing surface by cobalt and/or cobalt-contained species which markedly reduce the hydrogen adsorption.

Fig. 10 shows morphology of the zinc–cobalt deposited at 10 mA cm^{-2} . The morphology consists of η -phase crystallites with cobalt percentage of about 1.4 wt% determined by EDAX analysis. This kind of morphology differs from the zinc morphology (Fig. 4), because a large number of elongated crystals are grown normal to the substrate without merging, as it is shown in Fig. 11 with more details. This observation indicates that the



Fig. 10. Morphology of the zinc–cobalt deposited at 10 mA cm^{-2} .



Fig. 11. Morphology of the zinc–cobalt deposited at $10 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ at higher magnification.



Fig. 12. Schematic representation of perpendicular growth of zinc-cobalt on steel substrate surface.

growth mode described in zinc deposition, i.e. lateral bunching growth, is not valid for zinc-cobalt electrodeposition.

By adsorption of cobalt and/or cobalt-contained species, another interfacial inhibition is created with fairly strong inhibitive effect. Therefore, a high degree of two-dimensional nucleation could occur. This phenomenon prevents lateral bunching growth which naturally needs a small degree of inhibition to slow down the growth rate of two-dimensional nucleation dependant microsteps [3,15]. In this way, a different type of growth called "Field-Oriented Texture" can be created [3,15]. This kind of growth is based on a high frequency of twodimensional nucleation and eventually creates a crystallographic structure which comprises of numerous crystal fibers which are grown almost normal to the substrate surface [3,15]. Each fiber crystal is composed of many macrosteps that are piled upon another one but cannot merge with each other [3]. Therefore, a large number of elongated crystals perpendicular to the substrate is expected to form. The prism texture component in the coating is developed by this kind of growth as a manner described schematically in Fig. 12. As it was mentioned, the presence of cobalt and/or cobalt-contained species inhibits the lateral growth mode and encourages the perpendicular mode of growth.

As it can be seen from Fig. 10, some blocky crystals are also found on top of the coating, which seems to have no contact with the steel substrate surface. This indicates that perpendicular growth supported by the steel substrate is degraded by increasing the deposit thickness. It seems that random three-dimensional nucleation has developed these blocky crystals on top of the prismatic crystallites. The low intensity basal and pyramidal texture components represented in the corresponding ODF (Fig. 7) can be related to the presence of these blocks.

4. Conclusion

- Hydrogen adsorption during zinc electrodeposition process develops non-fiber low angle pyramidal {11.5} and {10.3} texture through lateral bunching growth. This develops ridges morphology in the deposit.
- 2. Strong inhibition resulted by the adsorption of cobalt and/or cobalt-contained species is responsible for the high frequency of two-dimensional nucleation which results "Field-Oriented Texture" type of growth in Zn–Co electrodeposition. A special kind of morphology consisted of numerous fibers appeared as a large number of elongated crystals normal to the substrate is resulted. This develops non-fiber {11.0} prism as the major texture component in the coating.

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