

Evolution of zinc morphology during continuous electrodeposition

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Abstract: The morphology evolution of zinc continuous electrodeposits with nano-sized crystals on the ferrite substrate has been studied by in-situ scanning tunnel spectroscopy (STM). It is found that the morphology of zinc electrodeposits varies from initial granules with a size of about 30 nm to layered platelets with increasing deposition time. Meanwhile, the crystal structure of the zinc electrodeposits is identified to be hexagonal η -phase by X-ray diffraction. The orientation relationship between zinc crystals and the substrate surface can be interpreted in terms of the misfit and the atomic correspondence of the interphase boundary between the η -phase deposits and α -Fe substrate.

Key words: Zn electrodeposit; crystal morphology; epitaxial growth; orientation relationship; scanning tunnel spectroscopy

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Electrodeposited zinc and zinc alloys have been widely used for corrosion resistant coatings of steel plates. Thick deposits of zinc electrodeposit, zinc-nickel alloy codeposit and hot dip galvanizing have recently been used to the steel sheets for automobiles [1]. A basic understanding of crystal growth of the deposits certainly promotes the development of zinc and new type of zinc alloy electrodeposits.

By using transmission electron microscopy (TEM) and scanning electron microscopy (SEM), Kondo *et al.* [2] reported the morphology and microstructure of zinc-iron and zinc-nickel electrodeposits containing η/γ -binary phases. The deposits consist of triangular-pyramidal shaped crystals that form the apexes of hexagonal columnar crystals. These crystals are made up by side-by-side stacking of similar sized hexagonal-shaped plates that are thin in the direction of c -axis [3,4]. Furthermore, the refinement mechanism of these hexagonal columnar crystals of zinc-nickel electrodeposits with cadmium as additive has been explained by the nucleation site on the $(0001)_\eta$. The dendrite evolution of the hexagonal columnar crystals in zinc-nickel electrodeposits with copper as additive has also been explained by the nucleation site on the $(0001)_\eta$ [5]. Park *et al.* [6] observed a fish-scale-like morphology with atomic force microscopy (AFM) at the initial stage of zinc-iron electrodeposition. Kamei *et al.* [7] have discussed the epitaxial growth of zinc and Omori *et al.* [8,9] further have reported the role of anion on the epit-

axial growth of zinc electrodeposition.

The objective of this paper is to examine the morphology evolution of zinc continuous electrodeposit with nano-sized crystals on ferrite substrate by STM. The crystal structure of the zinc electrodeposit is determined by X-ray diffraction method and the orientation relationship between the zinc electrodeposit and ferrite substrate will be discussed by considering the misfit and the atomic correspondence between the two phases.

1 Experimental procedures

The bath composition was: ZnSO_4 , 0.1 mol/L; Na_2SO_4 , 0.05 mol/L, and the condition of electrodeposition is: current density, 6 kA/m²; pH, 2.0; temperature, 338 K. The electrochemical cell used in this study was schematically shown in **figure 1**. The system with three electrodes was used for in-situ STM which can make continuous measurement of electrodeposits poss-

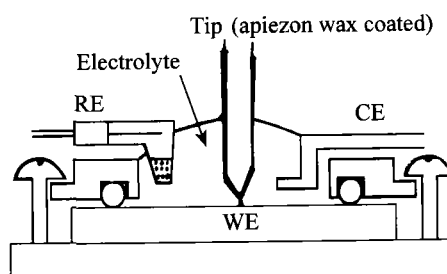


Figure 1 Schematic drawing of the electrochemical cell.

ible. The reference electrode (RE) was silver-silver chloride (Ag/AgCl) in dehydrated NaCl-KCl-LiCl (molar fraction 10%-38%-52%) eutectic. The counter electrode (CE) was made of Pt wire with a diameter of 0.2 mm. The working electrode (WE), *i.e.*, the substrate, was made of pure single crystal ferrite with the surface parallel to (110) plane. The WE was a thin plate in shape with sizes of 1 mm in thickness, 5 mm in width, and 50 mm in length. The substrate was obtained from a commercially cold-rolled 1 mm thick low carbon steel sheet by strain annealing at 1 123 K for 2 h in an encapsulated and evacuated silica tube after receiving a pre-strain up to 1% by an Instron type tensile machine at room temperature. The substrate was chemically polished, degreased in acetone with ultrasonic cleaning, rinsed in deionized water, and finally dried in air at room temperature prior to electrodeposition. The electrolyte was agitated with a magnetic stirrer.

The morphology of deposits was examined by in-situ STM. A Pt-Ir wire with the diameter of 0.3 mm was used as the probe. The bias voltages of the STM probe and the substrate were controlled at -0.2 V and 1.08 V respectively, and the tunnel current was kept at 4 nA during STM observation. The crystal structure of the zinc electrodeposits were determined by X-ray diffraction method.

2 Results and discussion

Figure 2 shows the STM image of the surface for substrate which had undergone strain annealing at 1 123 K for 2 h and has a (110) surface plane. It is clear that the trace formed during cold-rolling is still observed even after strain annealing and chemical polishing. Previously, the important effect of substrate surface on the morphology of electrodeposits was reported by Ohtsubo *et al.* [9]. **Figure 3** shows the images of zinc continuous electrodeposits at different deposition times. **Figure 3(a)** is the initial deposit after 9 min deposition. It is clear that about 30 nm granular crystals are observed to uniformly cover the substrate surface. **Figure 3 (b)** shows the electrodeposit in the case of 45 min deposition. It can be seen that no significant change is found in the morphology except the growth in grain size. After 62 min deposition, the morphology of zinc deposits as shown in **figure 4** is quite different from those in **figure 3(a)** and **(b)**. The epitaxial growth of thin layered platelet crystals along a specific orientation is featured. In order to confirm the formation of the platelet crystals, the tilting experiment was done. **Figure 5** shows the STM image after the specimen was tilted about 20° . It is clear that the deposits show a shape of platelet crystals and the angle between the two

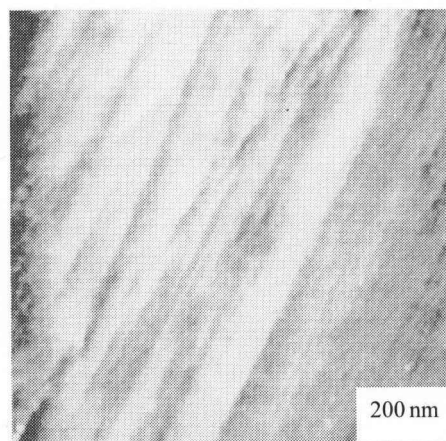


Figure 2 STM micrograph of the substrate surface.

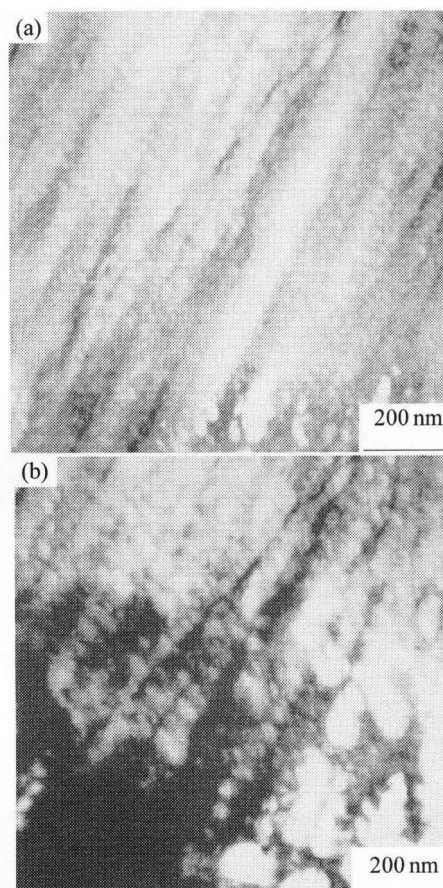


Figure 3 The zinc morphology after 9 min (a), 45 min (b).

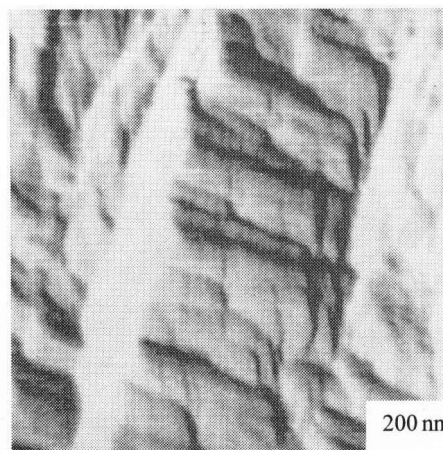


Figure 4 The zinc morphology after 62 min.

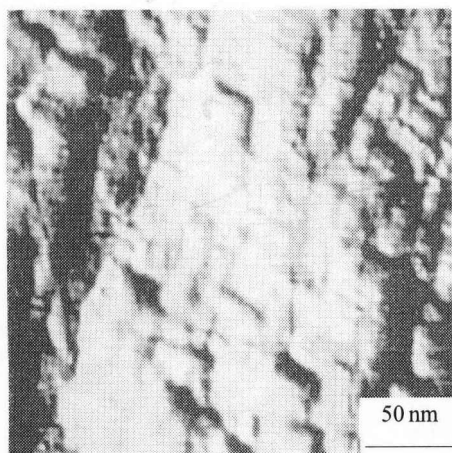


Figure 5 The zinc morphology after stopping electrodeposition by titling the specimen about 20° from {110}_α plane.

neighboring edge surfaces perpendicular to platelet is measured to be 120°.

To identify the crystal structure, the X-ray diffraction method was employed. Figure 6 is the X-ray diffraction file for the electrodeposit after 62 min deposition. The analyzed result indicates that the zinc deposits are of hexagonal η-phase and the {0001}_η reflection shows the strongest intensity. The orientation relationship between the deposits and the substrate surface can be described as:

$$(110)_\alpha // (0001)_\eta$$

$$[\bar{1}11]_\alpha // [\bar{2}110]_\eta$$

where the subscript α denotes the α-Fe substrate and η denotes the η-zinc deposit. It is interesting to note that the (110)_α plane which is the close-packed plane in the bcc structure and is previously existing after chemical polishing process is parallel to the (0001)_η basal plane, which is the growth direction along the c-axis of η-zinc. This is the Burgers orientation relation, which is well-

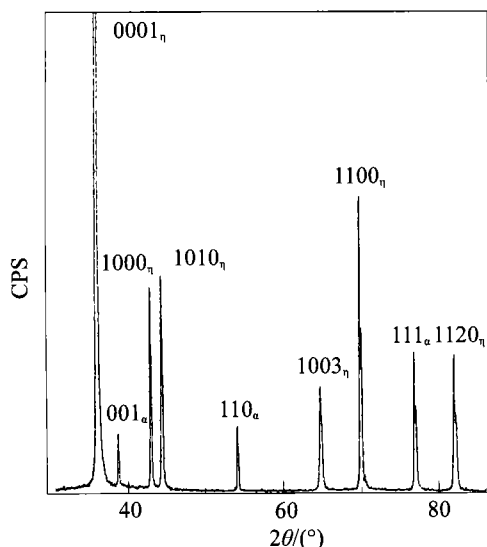


Figure 6 X-ray diffraction-pattern after 62min electrodeposition.

known between bcc and hcp phases orientation relationship. Such an orientation relationship between (0001)_η and the substrate surface has been previously determined by Kamei and Ohmori [7] by using the stereographic crystallographic analysis of η-zinc deposits.

As the specific Burger's orientation relationship is concerned, it can be explained by considering the following two factors. The one is the parallelism between the close-packed planes in the both phases, i.e., (110)_α//(0001)_η, the atomic arrangements on these planes being quite similar as shown in figure 7 [7]. A particularly good fit between both configurations along the $[\bar{1}11]_\alpha$ and $[\bar{2}110]_\eta$ is clearly seen. It is also important to consider that the lattice parameters of α-Fe along $[\bar{1}11]$ direction and η-Zn along $[\bar{2}110]$ direction have almost the same value. The lattice parameters of α-Fe and η-Zn are $a_\alpha = 0.2866$ nm and $a_\eta = 0.2665$ nm, $c_\eta = 0.4947$ nm, respectively. The misfit between $[\bar{1}11]_\alpha / [\bar{2}110]_\eta$ is 6.5% which is smaller than that between $[001]_\alpha / [1010]_\eta$, along which the misfit is 8.1%. The value of the misfit between α-Fe and η-Zn takes a minimum in the <111> direction of the α-Fe. Therefore, it must be natural to form a parallel orientation relation of $[\bar{1}11]_\alpha // [\bar{2}110]_\eta$. The second factor is the nucleation sites of η-zinc crystals at the substrate surface. It has been well established that the close-packed planes such as {110}_α are often those with lowest surface energy and that etching of a steel often produces the surface comprising the planes parallel to {110}_α [9]. In this case, the η-zinc crystals will preferentially nucleate on them with the orientation relationship of $(110)_\alpha // (0001)_\eta$.

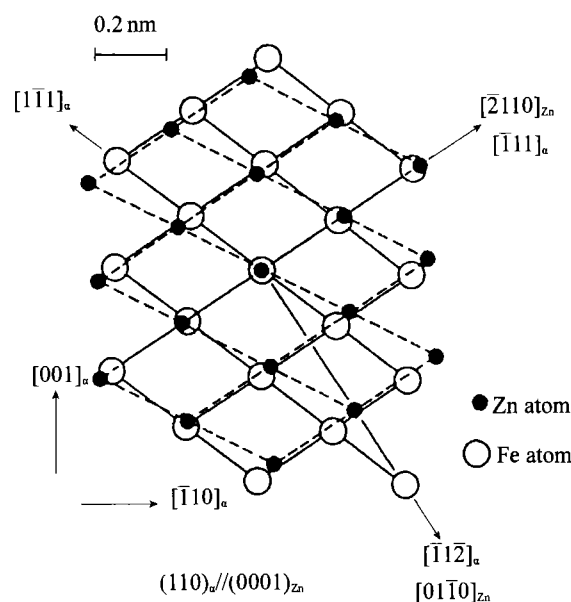


Figure 7 Lattice matching on the (110)_α//(0001)_η phase between zinc deposits and the substrate.

3 Conclusions

(1) The morphology of zinc electrodeposits is found to vary during continuous electrodeposition process. In the initial stage of 9 min deposition, the deposits show a granular shape with a size of about 30 nm which uniformly cover the substrate surface. In the case of 45 min deposition, the morphology shows no significant difference except a growth in grain size. After 62 min deposition, the zinc deposits show a epitaxial growth along a specific orientation and exhibit a layered platelet shape.

(2) The orientation relationship between η -Zn deposits and α -Fe substrate is found to be $(110)_\eta // (0001)_\alpha$ and $[\bar{1}11]_\eta // [\bar{2}110]_\alpha$. The orientation relationship between the two phases and the specific growth orientation of Zn deposits can be interpreted in terms of the misfit and the atomic correspondence of the interphase boundary between the η -phase deposits and α -Fe substrate.

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