Deformation Behaviors around/at the Interface between Zn-electrodeposition and Fe-substrate

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In order to examine the deformation behaviors at/around the interface between η-Zn electrodeposited layer and α-Fe substrate with Burgers orientation relationship, (110) Fe//(0001)Zn and [111] Fe//[1120]Zn, slip systems operated at/around the interface have been analyzed using X-ray back-reflection Laue method, optical microscope and stereographic analyses. The Zn-electrodeposited specimen was deformed at room temperature under a tensile strain rate of 2.8×10⁻⁴/². Under low tensile strains below 10 %, slip systems having large Schmid factor operate in Fe-substrate. In Zn-layer, slip systems having smaller Schmid factor operate to relax the tensile strain at the interface due to deformation in Fe-substrate, suggesting the constraint due to the cohesion at the Zn/Fe interface. As increasing the tensile strain, the slip systems forming corrugated configuration operate in Fe-substrate and their shear strains at the interface are difficult to be relaxed smoothly by deformation of Zn-layer. As increasing tensile strain, twinning occurs in Zn-layer and the slip system with low critical resolved shear stress operates in the twinned region. The decohesion of Zn-layer from Fe-substrate is induced as increasing the twinned region in Zn-layer.

KEY WORDS: Zn/Fe; electrodeposition; interface structure; coherency; slip behavior; twinning; Schmid factor; interface adhesion.

1. Introduction

Zinc-electrodeposited layer on Fe-base materials greatly improves the corrosion resistance of the Fe-base materials and has contributed to the development of practical materials. The cohesion between Zn-layer and Fe-base material is then important controlling factor to manufacture car-body and so on.

Systematic studies on the cohesion at the interface between Zn-layer and Fe-substrate have been required, because deformation behaviors by dislocation motions and twinnings under the constraint due to epitaxy at Zn/Fe interface are complicated. However, decohesion at the interface is inevitable under heavy deformation, and it has been then studied in terms of interface structure and deformation behaviors.

In the present investigation, large-grained α-Fe (bcc structure) substrate and hetero-epitaxially grown η-Zn (hcp structure) electrodeposition are used to clarify the deformation behaviors at/around the interface. Interface structure is crystallographically analyzed, and slip- and twinning-systems could be also deduced in both Fe-substrate and Zn-layer. It is discussed about deformation behaviors at/around interface under the constraint by the epitaxial growth of Zn-layer on Fe-substrate, and its effects on the cohesion of the interface.

2. Experimental Procedure

Commercial Al-killed 0.04 % C steel sheet 2 mm thick was cold rolled 50 % and shaped for tensile test as shown in Fig. 1. The specimen was recrystallized by annealing at 800°C for 24 h, and elongated 2 %, followed by annealing at 880°C for 72 h to get grains of 5 mm in average size. Chemical polishing was performed in a solution of 100 mL HOCOCOOH · 2H2O-saturated distilled water and 30–50 mL H2O2 at 40–50°C. Zinc was electrodeposited for 1.2 ks on one side of the specimen after the chemical polishing. The Zn-electrodeposited specimen was deformed for 1.2 ks on one side of the specimen after the chemical polishing, using the electrolyte of 360 g ZnSO4·7H2O, 30 g NH4Cl, and 15 g CH3COONa in 1 L distilled water under the conditions of 100 mL HOCOCOOH·2H2O-saturated distilled water and 30–50 mL H2O2 at 40–50°C. Zinc was electrodeposited for 1.2 ks on one side of the specimen after the chemical polishing, using the electrolyte of 360 g ZnSO4·7H2O, 30 g NH4Cl, and 15 g CH3COONa in 1 L distilled water under the conditions of 100 mL HOCOCOOH·2H2O-saturated distilled water and 30–50 mL H2O2 at 40–50°C. Thickness of Zn-layer was about 30 μm. Final chemical polishing of specimen surfaces was performed to observe slip bands clearly with optical microscope.

The electrodeposited specimen for tensile test was de-
formed at room temperature under a strain rate of $2.8 \times 10^{-3}$/s. Microstructures such as slip band and twin on surfaces of Fe-substrate and Zn-layer were observed by an optical microscope.

In order to identify slip system operated under tensile test, the crystallographic information about specimen is obtained by back-Laue X-ray diffraction method. White X-ray generated from W target irradiated with 35 keV and 30 mA electrons was utilized for the crystallographic analysis.

3. Experimental Results
3.1. Microstructure Evolutions due to Deformation

Figure 2 shows optical micrographs taken from both sides of specimen before tensile test. Figures 2(a) and 2(b) show surfaces of Fe-substrate and electrodeposited Zn-layer, respectively. Figure 3 shows the stereographic projection obtained by analyzing the back-Laue X-ray diffraction taken from both Fe-substrate and Zn-layer. In spite of the deviation of specimen surface from (110)$_{Fe}$, the Burgers orientation relationship, (110)$_{Fe}$//(0001)$_{Zn}$ and [111]$_{Fe}$//[1120]$_{Zn}$ is maintained. It suggests that the surface of Fe-substrate consists of fine (110)-terraces and steps to keep the epitaxy between Fe-substrate and Zn-layer, resulting in the Burgers orientation relationship.

Figure 4 shows optical micrographs taken from just opposite area on surfaces of specimen with 6% tensile strain. Slip bands form along ‘slip band 1’ and/or ‘slip band 2’ on (a) Fe-substrate and (b) Zn-layer. The direction of slip band in Fe-substrate is not parallel to that in Zn-layer. In specimen with 10% tensile strain, two directional slip bands and two directional twins form in Fe-substrate and Zn-layer, respectively, as shown in Fig. 5. In Fig. 5(b), slip bands are...
scarcely observed because of twins being focused in the micrograph, but exist along the two directions as shown in Fig. 4(b).

In Table 1, values of Schmid factor are listed for the slip and twinning systems in Fe-substrate and Zn-electrodeposition. According to the analyses based on both the calculated results in Table 1 and the trace analyses in Fig. 6, slip systems of (101)/[111] and (112)/[111] could be operated in Fe-substrate. Because, the slip systems have large Schmid factors, and crystallographic directions normal to the slip band are nearly parallel to the slip planes of (101) and (112) as indicated with rigid line in Fig. 6. The slip planes largely inclines to the specimen surface as shown in Fig. 6, resulting in clear slip band formation on specimen surface. In Zn-layer, both of (112)/[1123] and (1122)/[1123] slip systems and both of (121)/[1213] and (0110)/[2110] slip systems could operate in the slip bands 1 and 2 in Fig. 4, respectively. These slip systems could be suggested to operate, because the slip planes are nearly parallel to the slip directions in Fe-substrate as shown in Fig. 6 and Fig. 7. In Fe-substrate, the systems having relatively large Schmid factor operate, but in Zn-layer, the operated systems have relatively low values of Schmid factor. It suggests that deformation of Zn-layer is restricted by the deformation behavior of Fe-substrate. The slip system on basal plane, (0001)/[1120], might be also operative, because of small critical resolved shear stress on the basal plane. The basal plane is, however, nearly parallel to the specimen surface, resulting in the difficulty of formation of slip band.

In the case of 10% tensile strain, slip systems of both

Table 1. Schmid factors for slip and twinning systems in both Fe-substrate and Zn-electrodeposition.

| Slip system in Fe | Schmid factor | Slip system in Fe | Schmid factor |
|-------------------|---------------|-------------------|---------------|
| (101)/[111]       | 0.427         | (011)/[111]       | 0.214         |
| (211)/[111]       | 0.427         | (011)/[111]       | 0.116         |
| (011)/[121]       | 0.351         | (121)/[111]       | 0.116         |
| (121)/[111]       | 0.358         | (101)/[111]       | 0.114         |
| (110)/[111]       | 0.317         | (121)/[111]       | 0.083         |
| (112)/[111]       | 0.310         | (211)/[111]       | 0.068         |
| (101)/[111]       | 0.278         | (110)/[111]       | 0.066         |
| (112)/[111]       | 0.278         | (112)/[111]       | 0.035         |
| (121)/[111]       | 0.271         | (211)/[111]       | 0.033         |
| (110)/[111]       | 0.240         | (011)/[111]       | 0.031         |

| Slip system in Zn | Schmid factor |
|-------------------|---------------|
| (1010)/[1210]     | 0.497         |
| (1122)/[1123]     | 0.392         |
| (1100)/[1120]     | 0.294         |
| (1212)/[1213]     | 0.236         |
| (1212)/[1213]     | 0.207         |
| (0110)/[2110]     | 0.203         |
| (0001)/[2110]     | 0.030         |
| (0001)/[2110]     | 0.039         |
| (2112)/[2113]     | 0.022         |

| Twinning system in Zn | Schmid factor |
|-----------------------|---------------|
| (0112)/[0111]        | 0.483         |
| (0112)/[0111]        | 0.468         |
| (1012)/[101]         | 0.218         |
| (1012)/[101]         | 0.211         |
| (1012)/[101]         | 0.045         |
| (1012)/[101]         | 0.043         |

Fig. 6. Stereographic projection for Fe-substrate showing the directions (rigid lines), denoted by 1 and 2, normal to traces of slip bands 1 (Figs. 4(a) and 5(a)) and 2 (Fig. 5(a)), respectively. The operating systems are (101)[111] and (121)[111], indicated by ● (slip plane) and ■ (slip direction), in the slip band 1. In the slip band 2, the slip system of (011)[111], indicated by ● (slip plane) and ■ (slip direction), is operating. The center of stereographic projection is the direction normal to specimen surface. T is the tensile direction.

Fig. 7. Stereographic projection for Zn-deposited layer showing the directions (rigid lines), denoted by S1 and S2, normal to traces of slip bands 1 and 2 (Fig. 4(b)), respectively. The operating systems are (1122) [1123] and (1122) [1123] in the slip band 1, and (1122) [1123] and (0110) [2110] slip systems could operate in the slip bands 1 and 2, respectively. The operating systems are (0112)/[0111] and (1122)/[1123] slip systems and both of (121)/[1213] and (0110)/[2110] slip systems could operate in the slip bands 1 and 2 in Fig. 4, respectively, respectively. These slip systems could be suggested to operate, because the slip planes are nearly parallel to the slip directions in Fe-substrate as shown in Fig. 6 and Fig. 7. In Fe-substrate, the systems having relatively large Schmid factor operate, but in Zn-layer, the operated systems have relatively low values of Schmid factor. It suggests that deformation of Zn-layer is restricted by the deformation behavior of Fe-substrate. The slip system on basal plane, (0001)/[1120], might be also operative, because of small critical resolved shear stress on the basal plane. The basal plane is, however, nearly parallel to the specimen surface, resulting in the difficulty of formation of slip band.
(011)/[111] and (011¯)/[111] could operate, corresponding to the slip band 2 in Fe-substrate as shown in Fig. 5. In Zn-layer, twinning systems of (0112)/[0111] and (0112)/[0111] operate for the two directional twins, 1 and 2, as shown in Fig. 5(b). These systems are indicated on the stereographic projection in Fig. 7. The slip planes operating in both Fe and Zn are not parallel among them, resulting in the concentration of stress at/around the Zn/Fe interface, inducing the twinning. Increasing in the tensile strain up to 25%, amount of twins increased remarkably, and slip bands newly formed inside twin as shown in Fig. 8. Stereographic projection for the slip systems in (0112) twin was drawn in Fig. 9. It could be deduced that the slip system on basal plane operated in the twinned region, resulting in formation of slip bands clearly.

4. Discussion

4.1. Interface Structure

The back-Laue X-ray diffraction indicates that Burgers orientation relationship is maintained between Fe-substrate and Zn-deposition, and the Zn/Fe interface is inclined about 10° from (110)Fe. However, the interface would have both (110)Fe-terraces and two-directional (111)Fe steps under the growth of Zn-layer with the Burgers orientation relationship. Because, the invariant line exists along [223]Fe//[341]Zn under the interface being {110}Fe//[0001]Zn as shown in Fig. 10. In this case, the coherency at the interface is fairly maintained, resulting in good cohesion even under tensile strain of 25%.

4.2. Early Stages of Deformation

Below about 10% tensile strain, the slip systems having large Schmid factors, 0.427 ((101)/[111]) and 0.338 ((121)/[111]), operate in Fe-substrate. In Zn-layer, the slip systems having relatively small Schmid factors, 0.236 ((1212)/[1213]) and 0.203 ((0110)/[2110]), are operating except those having large Schmid factors, 0.392 ((1122)/[1123]) and 0.349 ((1122)/[1123])). It is reasonable that the slip system having large Schmid factor operate at first in Fe-substrate. However, the slip systems in Zn-layer having low Schmid factors, 0.236 and 0.203, operate probably by the constraint due to coherency of the Zn/Fe interface. The deformation of Zn-layer is, therefore, controlled by that of Fe-substrate. The slip direction, [111]Fe, is nearly parallel to the slip plane, (0110)Fe, and the slip direction, [111]Fe, is nearly parallel to the slip plane, (1212)Fe. The two slip di-
rections in Fe-substrate, [111] and [111], are nearly parallel to the slip planes of the slip systems in Zn-layer having small Schmid factors. In this case, however, the slip planes in Fe-substrate, (101) and (121), are away from parallelism for the slip planes in Zn-layer. It should be suggested that the shear strain in Fe-substrate is partly relaxed by the deformation of Zn-layer, but dislocations could not glide through the Zn/Fe-interface, resulting in stress concentration at the interface due to the accumulation of dislocations at/around the interface.

4.3. Deformation under Higher Tensile Strain

Under more than about 10% tensile strain, the slip band 2 in Fig. 5(a) remarkably formed in Fe-substrate, and twinning occurs in Zn-layer. The twinning is induced mainly near Zn/Fe interface, because stress would concentrate due to pile-up of dislocations at the interface. As a qualitative evidence, in Zn-layer twins could be observed in nearer region from Zn/Fe interface, and deformed region by dislocation motion exists above the twinned region, that is, near surface as shown in Fig. 11. The micrograph of Fig. 11 is taken from the same specimen as used for Fig. 5, chemically polished locally after 10% tensile deformation, and from the region slightly away from the remarkable twinned region.

As increasing tensile strain, multiplication and pile-up of dislocations at the interface due to the differences of slip-planes and -directions between Zn-layer and Fe-substrate induce stress concentration at the interface, resulting in twinning besides dislocation motion in Zn-layer. The twinning would contribute the relaxation of stress concentration at the interface, but the lattice displacement due to the twinning would enhance the decohesion between Zn-layer and Fe-substrate.

5. Conclusions

The deformation processes of Zn-electrodeposited Fe have been investigated mainly by means of metallographic observations and crystallographic analyses, and the following results have been obtained.

(1) Below about 10% tensile strain, the slip systems having larger Schmid factor operate in Fe-substrate. However, the deformation process of Zn-layer is controlled by that of Fe-substrate. The shear strain in Fe-substrate could be relaxed by the operation of slip systems in Zn-layer, whose slip planes are nearly parallel to slip directions in Fe-substrate. However, the slip systems in Zn-layer have relatively small Schmid factors.

(2) Above about 10% tensile strain, twinning would occur in Zn-layer near the Zn/Fe interface by the stress concentration due to pile-up of dislocations in Fe-substrate at the interface. In order to relax the stress concentration, slip systems would operate also inside/around the twinned region. The twinning near the interface may induce decohesion of Zn-layer from Fe-substrate.

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