Relationship between the Crystallographic Structure of Electrodeposited Fe–Zn Alloy Film and Its Thermal Equilibrium Diagram

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The microstructures and morphologies of Fe–Zn alloys electrodeposited at different chloride bath compositions have been studied in detail by using TEM, SEM, XRD, and compared to those appearing in the Fe–Zn thermal equilibrium phase diagram. The results indicate that the α , Γ , Γ_1 and η phases appear in the Fe–Zn electrodeposits, whereas δ and ζ phases which appear in the thermal equilibrium phase diagram do not appear. The surface appearance and microstructure of the intermetallic phases in Fe–Zn alloy electrodeposits depend on the Zn content in the Fe–Zn alloy deposit. It was also found that there is an orientation relationship among the Γ , Γ_1 and η phases when these three phases appear simultaneously.

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1. Introduction

It is well known that all physical characteristics of electrodeposits depend on their structures. Accordingly, desired physical properties of an electrodeposit can be obtained if its structure can be controlled properly. Up to now a lot of research works have been done in order to understand the structure, governing mechanisms of electrodeposits.^{1–16)} There are many deposition parameters such as bath composition, current density, pH value during electrodeposition, if one of the parameters is varied for some reason, the other parameters will usually change. Furthermore, the experiments done before are difficult to reproduce now because of various impurities in electrodeposits, so it is still impossible to form a complete electrodeposition theory that can be accepted widely. On the other hand, there is a theory in electrochemistry which states that the structure of an electrodeposit is dependent on the deposition over-potential, that is, the grain size of an electrodeposit is refined at high over-potential, and vice versa.^{6,10)} But this theory can't be used to explain all the experimental results in practice since it is not in accordance with some experimental results.

The authors have been engaged in studying structures and morphologies of various pure metal electrodeposits, and comparing structures of a variety of alloy electrodeposits with their structures appeared in equilibrium phase diagrams,^{17–25)} and believe that the structure of an electrodeposit should be studied by (1) structure of metallurgy, (2) grain size, (3) surface morphology, (4) orientation, (5) internal stress and (6) other factors respectively, not by over-potential. Although there is a close relationship among the above the six factors, there exists an independent factor which can be used to control the structure of an electrodeposit.

The structure of an alloy electrodeposit is not always in accordance with that in the corresponding alloy equilibrium phase diagram, but there exists a close relationship between these structures. There are researches on the structures of electrodeposits metallurgically, but many of them are not so complete because of some reasons such as poor research equipments or too much narrow research ranges. The authors,

therefore, have restudied the structures of various alloy electrodeposits, and made comparisons with the same alloy in the equilibrium phase diagram.^{17–59)}

According to the many experimental results^{17–22)} the authors have got, it is believable that an electrodeposit can be studied completely by metallurgical way. But there are still some questions to be solved, for instance, there exist some phases in some electrodeposits that do not exist in equilibrium phase diagram, and also some x-ray diffraction lines which can not be found in the JCPDS card. Up to now, there are no reports on thermodynamically meta-stable phases obtained from electrodeposits. In fact, meta-stable crystals^{28,29,31,36–38,53–66)} and amorphous materials^{18,22,40)} can be obtained by not only electrodeposition, but also quenching method, and metal with relatively high melting point prefers to form metastable phase, while other metal with low melting point tends to form stable phases which are the exactly same with the standard equilibrium phase diagram.

This paper is one of the authors' recent series research results, the investigation of metallurgical structures of the Fe–Zn binary alloy electrodeposits.

2. Experimental Procedures

The solution used for Fe–Zn electrodeposition is $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, ZnCl_2 , and 20 g/L NaCl as a supporting electrolyte. pH is adjusted at 1.5 by adding hydrochloric acid. The substrate used is high purity (99.999%) polycrystalline copper plate, and a platinum plate is selected as anodic material. The copper plate is electrochemically polished, rinsed by distilled water, and dried by nitrogen gas before the deposition. The distance between the anode and cathode is 50 mm, and the area ratio of the two electrodes is 1 to 1. The bath composition is composed of x mol/L $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $1 - x$ mol/L ZnCl_2 . The solution is stirred magnetically. All the deposition procedures were carried out at 24°C, with current density of 750 A/m² for 100 Coulomb. To prevent the bath from ferrous oxidation, all the experiments are carried out immediately after solutions used are built up.

The microstructure of Fe–Zn alloy deposit is determined

by XRD method (model RIGAKU RAD-1C) with Cu-K α radiation, 35 kV and 20 mA. Orientation index is calculated by Wilson's formula.⁶⁷⁾ TEM method is also used to determine the microstructures of Fe-Zn alloy deposits with TEM model JEM2000FX to confirm the XRD results. Surface morphologies of the electrodeposited Fe-Zn alloys at different zinc content are observed by scanning electron microscopy (model JEOL-JSM-6100), the samples are set at 45° tilt in order to get better observation results. The zinc contents in the deposits are analyzed by EDS (JED-2001). Current efficiency is calculated by weighing samples before and after the electrodeposition.

3. Results and Discussion

3.1 Zinc content in deposit and zinc concentration in bath

The relationship between zinc content in the Fe-Zn deposit and zinc concentration in the bath is shown in Fig. 1. The zinc content in the deposit increases sharply with increasing the zinc concentration in the bath, and the zinc content is 99 at% in the deposit when the bath zinc molar ratio is over 70%. Since Fe-Zn deposition is the process of an anomalous codeposition of the binary deposition,¹⁷⁻²⁰⁾ it is also found in this research that the zinc content in the deposits is always higher than $Zn^{2+}/(Zn^{2+} + Fe^{2+})$ in the baths. Generally, this can be explained by hydroxide suppression mechanism.⁶⁸⁻⁷¹⁾ Zn(OH)₂ forms at cathode neighborhood region corresponding to the current density region for anomalous co-deposition that Zn(OH)₂ film inhibits the electrodeposition of noble iron.

From Fig. 2 it can be seen that the current efficiency always keeps near to 95% when current density applied is 750 A/m² at pH1.5 and 26°C, and Zn²⁺ concentration in the bath seems to have no obvious effect on the current efficiency. It can be calculated that the deposition rate reaches 0.1 nm/s from the data of the current density and current efficiency.

3.2 X-ray diffraction study

3.2.1 Relation between the film structure and its thermal equilibrium diagram

X-ray diffraction studies were carried out to analyze various Fe-Zn alloy deposits at different zinc content. According to the diffraction results shown in Fig. 3, in the range of 0–25 at% Zn in the deposit, only α -Fe phase (Fe: bcc) can be found, and the Γ phase (Fe₄Zn₉: cubic) appears when the zinc content in the deposit increases to 30.5 at% Zn. When the zinc content reaches 38.7 at%, Γ_1 phase (FeZn₄: cubic) appears as a third phase while α -Fe phase lines gradually weakens, and completely disappears when the zinc content in the deposit reaches up to 71.9 at%. The η (Zn: hcp) phase in the Fe-Zn deposit appears when the zinc content exceeds 74.8 at%. When the zinc content exceeds 94.9 at%, there only η phase exists.

The relationship between the phases and the zinc content in the Fe-Zn deposits can be displayed in Figs. 4(b) and (c). The δ and ζ phases, which exist in the Fe-Zn alloy phase diagram, do not appear in the electrodeposits (Fig. 4(a)).⁷²⁾

Adaniya *et al.*⁷¹⁾ obtained α , Γ , δ and η phases from a sulfate Fe-Zn bath at 40°C, pH3.0 with 5000 A/m², but Kondo⁷³⁾ found α , Γ (bcc), Γ_1 (fcc) and η (hcp) phases from a sulfate

Fig. 1 Relationship between bath composition and zinc content in electroplated film.

Fig. 2 Current efficiency for Zn-Fe alloy electroplating in the baths of various compositions.

Fe-Zn bath at 50°C, pH1.5 with 800 A/m², which is similar as our results.

3.2.2 Crystal orientation and lattice constant

From the XRD results (Fig. 3), the variations of the orientation index (Fig. 5(a)) and the lattice constant of α -Fe (Fig. 5(b)) were calculated based on the diffraction line (110) plane. It was found that with the increase of zinc content in the deposit, the orientation index of (211) plane decreases quickly and loses orientation, and (110) plane takes a dominant role in the crystal orientation although it doesn't show so much strong at first. Consequently, the Fe-Zn deposits will keep (110) orientation no matter how the zinc content increases in the research range. The results also show that the lattice constant of the α -phase containing zinc calculated from (110), (211) and (002) planes is always larger than that of pure iron (0.2866 nm, in the dotted line). This can be probably attributed to hydrogen or some precipitates like ferrous hydroxide existed in the deposits. The results also imply that the increase of lattice constant may results in the formation of a meta-stable α -Fe(Zn) phase when the zinc is supersaturated.

The lattice constant of Γ phase is calculated with diffrac-

Fig. 3 XRD patterns of Fe–Zn electroplated films of various compositions.

Fig. 4 Relationship between phases and zinc content in Fe–Zn alloy film.
 (a) equilibrium phase diagram, (b) phases appeared in electroplated Fe–Zn film, (c) phase diagram of electroplated film.

tion line of (321)(37.4°), and the trend of lattice constant of Γ phase along with the increase of zinc content in the deposits is shown in Fig. 6(a). It was found that the lattice constant of Γ phase is almost the same as the Γ phase (0.895 nm at 69.2%Zn containing intermetallic compound) in JCPDS card, and generally it increases with increasing zinc content in the deposits. In a similar way, the lattice constant of Γ_1 phase is calculated with diffraction line of (733)(41.1°), (880)(58.0°) and (1171)(68.0°) respectively. The trend of lattice constant

of Γ phase along with the increase of zinc content in the deposits is shown in Fig. 6(b). The lattice constant of Γ_1 phase has its minimum value when the zinc content is about 70 at%, but it is in accord with the JCPDS' s standard value (1.798 nm, in the dotted line) in the all range. It is still not clear why all the lattice constants calculated from (880) plane is always above 1.815 nm.

The tendency of the lattice constants, c/a ratio and the orientation index of η phase with zinc content in the deposit are shown in Fig. 7. It can be found that the lattice constants in a -axis and in c -axis (Figs. 7(a), (b)) are larger than that of standard η phase in JCPDS card (0.2665 nm, 0.4947 nm, in the dotted line), and the c/a ratio is always smaller than that of standard η phase in JCPDS card (1.856, in the dotted line). This means that the hcp structure of η -Zn(Fe) turns a little flat than that of pure zinc. Generally it is impossible that iron atoms are dissolved in zinc at ordinary temperature, but iron may be supersaturated in zinc by electrodepositing. It is not enough by using super-saturation theory to explain the change in the lattice constants and c/a ratio in the Fe–Zn deposits, hydrogen and some precipitates existing in the deposits may be considered.

The (103) plane in η phase always has a strong orientation index although it takes a secondary position in orientation when the zinc content is below 80 at% (Fig. 7(d)). The (102) plane and (112) planes also shows orientation especially at the low zinc range. The (002) plane almost shows no preferred orientation in the all zinc range.

3.3 TEM observations

TEM observations were also carried out in order to confirm the results obtained from XRD. Figure 8 shows TEM micrographs of the deposited Fe–Zn alloys at different zinc contents with bright field images and electron diffraction patterns. Figure 8(a) indicates that like pure iron deposit, there only exists bcc structure when zinc content is below about 35.3 at%. By analyzing the Γ XRD patterns, the deposit can be affirmed as single phase with poly crystal. In Fig. 8(b),

Fig. 5 Relationship between zinc content and orientation indices of α -Fe phase (a), and zinc content and lattice constants of α -Fe phase (b). (Dotted line shows a standard lattice constant value of α phase).

Fig. 6 Lattice constant of Γ phase (a) and Γ_1 phase (b) at different zinc content. (dotted line refers to the standard lattice constant of Γ phase and Γ_1 phase).

there appears a new phase and it can be affirmed as Γ phase when the zinc content is below about 43.9 at%Zn. It is also found that the grain size of the deposit is very fine within 0–43.9 at%Zn range, only about 15–30 nm by TEM image.

Figure 8(c) shows the bright field image and diffraction pattern of the Fe–Zn deposit in the range of 43.9–61.2 at% Zn in the deposit. It is found that Γ and Γ_1 appear in the deposit, and its quantity increases with the increase of the zinc content while a pattern gradually becomes weak. There only exist Γ_1 and Γ exist in the deposit when the zinc content reaches up to 61.2 at%.

When the zinc content in the deposit reaches 74.8 at%, a three phases region forms, i.e., besides Γ_1 and Γ phases, η phase also appears (Fig. 8(d)). When the zinc content exceeds 94.9 at%, (Fig. 8(e)), it can be found by analyzing electron diffraction pattern shown in Fig. 9 that the orientation relationship among Γ_1 phase, Γ phase and η phase can be expressed as follows (the arrowheads show the zone axis directions of these phases):

$$(\bar{1}\bar{2}1)\Gamma \parallel (11\bar{1})\Gamma_1 \parallel (0\bar{1}11)\eta$$

$$\langle 012 \rangle \Gamma \parallel \langle 011 \rangle \Gamma_1 \parallel \langle \bar{7}253 \rangle \eta$$

It is found that the grain sizes of α phase and η phase are only 15–20 nm, but the grain size Γ of and Γ_1 phases can reach 50–80 nm. Γ_1 phase disappears when zinc content increases further, only η phase, expressed in hcp structure, exists in the deposit (Fig. 8(f)), its TEM result is the exactly same with that of pure zinc deposit. It can be found that TEM results are in accordance with the XRD results (Fig. 3).

3.4 Surface morphology

From the SEM micrographs of Fe–Zn deposits at different zinc contents shown in Figs. 10(a)–(f), it can be seen that the appearance of pure iron deposit is full of tiny corrosion pits and cracks (a). Iron electrodeposited at room temperature always has a lot of micro cracks when the current density exceeds 500 A/m². These micro cracks are networks of cracks visible with the aid of magnification, and they form during deposition when the tensile stress strength exceeds the coherent strength of iron deposit. As the deposition develops, the tensile stress increases until micro cracking occurs, this will

Fig. 7 Effects of Zn content in η phase on the lattice constant in a-axis (a), the lattice constant in c-axis (b), the c/a ratio (c), and on the orientation of η phase (d).

relieve the stress in the iron deposit. The micro cracks remain visible until the zinc content exceeds 43.9 at%, this can probably be attributed to the great internal stress in the deposit; The nodular-like morphology appears when the zinc content in the deposit increases to 35.3 at% (b). When the zinc content in the deposit increases up to 43.9 at%, the nodular become refined gradually (c), and the nodular number increases with increasing zinc content, corresponding to the appearance of Γ_1 phase. The main appearance characteristic of Γ_1 phase is cauliflower-like deposit (d), this crack-free and bright grey deposit appears when zinc content in the deposit reaches up to 74.8 at%; The surface morphology turns gradually to thin stacked deposit when the zinc content reaches 94.9 at%, just when Γ_1 and Γ phase disappear (e). When Zn content in the deposit increases above to 94.9 at%, the surface morphology gradually turns to typical hexagonal-like deposit of pure zinc deposited from the chloride bath (f).

4. Conclusions

By using XRD, TEM, EDS and SEM methods, the microstructure of Fe-Zn alloy electrodeposited with different zinc content from the chloride bath are examined, and the results are as follows:

(1) There appear Γ_1 , Γ and η phases in sequence in the

Fe-Zn deposit by increasing zinc concentration in the bath. There are no δ and ζ phases in the deposits, which generally exist in the Fe-Zn alloy equilibrium phase diagram. The meta-stable α -Fe(Zn) phase forms when the zinc is supersaturated.

(2) It is found out that the orientation relationship between Γ_1 , Γ phase, and η phase is as follows:

$$(1\bar{2}1)\Gamma \parallel (11\bar{1})\Gamma_1 \parallel (0\bar{1}11)\eta$$

$$\langle 012 \rangle \Gamma \parallel \langle 011 \rangle \Gamma_1 \parallel \langle \bar{7}253 \rangle \eta$$

(3) According to XRD results, it is found that in α phase, (110) plane always plays a dominant role in orientation index although (211) plane shows the strongest orientation when the zinc content is extremely low. In η phase, (103) and (102) planes play a dominant role in orientation index, although (112) also shows the strongest orientation when the zinc content in the deposit is below 80 at%.

(4) The changes in surface morphologies of the Fe-Zn alloy deposited from the chloride bath with different zinc content have been revealed. There are a lot of microcracks in the Fe-Zn alloy when α phase takes dominant role in the Fe-Zn alloy. The main morphology characteristic of the Γ_1 phase is a cauliflower-like deposit. The η phase appears in hexagonal morphology.

Fig. 8 TEM images of electroplated Fe-Zn alloy films of various compositions.

Fig. 9 Electron diffraction pattern of Fe-Zn alloy composed of Γ + Γ_1 , and η phases (a) and key diagram of it (b).

Fig. 10 SEM micrographs of the deposited Fe-Zn alloy at different zinc content.

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