—Communication—

Effects of Hydroxycarboxylic Acids on the Electrodeposition of Fe-C Alloys

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1 INTRODUCTION

Electrodeposited Fe films have been used for various engineering applications such as glass molds, record stampers, electroforming and repairing worn parts¹⁾ as well as soldering iron tips. Although the wear resistance is required in most of these applications, the commercially electrodeposited Fe films exhibit fairly low hardness ranging from Hv 150 to Hv 500¹⁾.

Recently, Izaki et al.²⁾ reported that Fe-1.0wt% C alloy films with hardness above Hv 800 are electrodeposited from FeSO₄ solutions containing a small amount of citric acid and L-ascorbic acid. They³⁾ also found that the Fe-C alloy electrodeposits have a body centered tetragonal martensite type structure. The Fe-C alloy deposits are probably useful as an alternative to the Fe electrodeposits in engineering applications because of their high hardness.

To determine the optimum operating conditions of the Fe-C alloy plating baths for commercial use, it is important to know the essential bath constituent to obtain hard Fe-C alloy deposits. Our preliminary study has shown that Fe-C alloys are also deposited from the baths without L-ascorbic acid⁴⁾ although bath stability became insufficient due to FeOOH precipitation³⁾. The aim of this work was to elucidate whether carbon codeposits with Fe from the baths containing various organic acids. We have

measured the current efficiency and carbon content in deposits, examined the appearance and surface morphology of deposits and discussed the structure of deposits based on the powder X-ray diffraction measurements. Organic acids used in this work were hydroxycarboxylic acids having both -OH groups and -COOH groups, namely glycolic acid [CH₂(OH)COOH], L-lactic acid [CH₃CH(OH)COOH], L-malic acid [COOH·CH₂·CH(OH)·COOH], L-tartaric acid [COOH·CH(OH)·C(OH)H·COOH] and citric acid [CH₂COOH·C(OH)(COOH)·CH₂COOH].

2 EXPERIMENTAL

The plating baths were prepared from reagent grade chemicals and deionized distilled water and contained 0.14 mol/dm³ FeSO₄ and 5.4×10⁻³ mol/dm³ one of the hydroxycarboxylic acids; these concentrations are the same as those of the bath proposed by Izaki et al.²⁾ The pH of the baths was not adjusted and was ranging from 2.6 to 3.0. Hydroxycarboxylic acids were entirely dissolved in the bath. The substrate was a 20mm×20mm×0.1mm Cu sheet except the X-ray diffraction study where a stainless steel sheet was used. The anode was a large area mild steel sheet. Electrodeposition was carried out galvanostatically at 10 mA/cm² for 1000 C in an electrolyte having a volume of 0.5 dm³ unless otherwise noted. Bath temperature was 50°C. Bath agitation decreases current efficiency because of the enhancement of proton reduction reaction occurring more noble potential than Fe deposition⁵⁾. Therefore, the bath was not agitated.

Current efficiency was evaluated from the weight of the deposits obtained at a given amount of charge assuming that only Fe was deposited from Fe²⁺; this assumption is valid because of the low carbon content in deposits.

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Table 1 Current Efficiency(η), Carbon Content in Deposits(w_{carbon}) and Appearance of Deposits at 10 mA/cm²

Additive	η (%)	w_{carbon} (wt%)	Color and appearance
glycolic acid	93	0.0	grayish, dull
L-lactic acid	79	0.0	grayish, dull
L-malic acid	90	0.6	black, bright
L-tartaric acid	108*	0.5**	burnt(black precipitate)
citric acid	83	1.0	black, bright

* including the weight of black precipitates.

** determined after removing black precipitates

Carbon content in deposits was determined using a carbon analyzer EMIA-1110 (Horiba, Ltd.), measuring the amount of CO₂ evolved by high frequency induction heating of samples in an O₂ atmosphere. As to the deposits from the bath containing L-tartaric acid, black precipitates on the deposits described later were mechanically removed before carbon analysis.

Surface morphology of deposits was examined using a JSM T-100 (JEOL Co.) scanning electron microscope (SEM).

X-ray diffraction measurements of powdered deposits were made using an MXP18 X-ray diffraction system (MAC Science Co.) and monochromated CuK α at 50kV and 200mA.

3 RESULTS AND DISCUSSION

Table 1 shows current efficiency (η), carbon content in deposits (w_{carbon}) and appearance of deposits from the baths containing various hydroxycarboxylic acids at 10 mA/cm². Current efficiency was about 80% or higher for all the baths. Carbon content and appearance of the deposits were, however, changed with hydroxycarboxylic acid added in the bath.

Carbon was not actually codeposited and bright deposits were not obtained from the baths containing monocarboxylic acids, namely glycolic acid and L-lactic acid. On the other hand, carbon was codeposited from the baths containing polycarboxylic acids, namely L-malic

acid, L-tartaric acid and citric acid. The Fe-C alloy deposits obtained from the baths containing L-malic acid or citric acid showed bright appearance and black color, while the appearance of the Fe deposits from the baths containing monocarboxylic acid was dull and the color was grayish. In contrast, burnt deposits were obtained from the baths containing L-tartaric acid although carbon was codeposited.

Figure 1 shows SEM photographs of the surface of the deposits from the baths containing glycolic acid(A), citric acid(B) and tartaric acid(C). The surface of the Fe deposit from the bath with glycolic acid showed angular grains whereas that of the Fe-C alloy deposit from the bath with citric acid was smooth. The Fe deposits from the bath containing L-lactic acid and the Fe-C alloy deposits from the bath containing L-malic acid exhibited similar surface morphology to Fig. 1(A) and (B), respectively.

However, cracks and coarse precipitates were observed on the Fe-C alloy deposits from the baths containing L-tartaric acid. These precipitates were observed on the deposits obtained at 5 mA/cm² or higher and caused the burnt appearance. These precipitates are probably certain ferrous or ferric oxides containing large amount of L-tartaric acid or its degradation products because carbon content determined without removing the precipitate (2.7wt%) was significantly higher than that shown in Table 1.

Fig.1 SEM photographs of the surface of the deposits from the baths containing glycolic acid (A), citric acid (B) and L-tartaric acid (C).

Similar "black oxides" were also precipitated on the Fe-C alloy deposits from the baths containing L-malic acid or citric acid at higher current densities. The critical current density where the "black oxides" begin to precipitate was 33 mA/cm^2 for the bath with L-malic acid and 39 mA/cm^2 for those with citric acid. Moreover, the black color of the smooth Fe-C alloy deposits at lower current densities was due to a surface film on the deposits because the color was changed with polishing to grayish. Thus, the "black oxides" formed the thin and dense film at low current densities but exhibited irregularly grown precipitates at higher current densities. These "black oxide" may also contain the added hydroxycarboxylic acid or its degradation products.

In contrast, the "black oxide" films were not formed on the deposits and carbon was not codeposited from the baths containing monocarboxylic acids. Therefore, Fe-C alloys are probably deposited through the "black oxide" films formed on the cathode. Figure 2 shows the powder X-ray diffraction patterns of the Fe deposit from the bath containing glycolic acid(A) and the Fe-C alloy deposit from the bath containing citric acid(B). All the diffraction peaks were apparently assigned to α -Fe. However, the full width at half maxima (FWHM) of the (110) and (200) diffraction peaks were increased with the codeposition of carbon. Moreover, a shoulder was observed at the peak corresponding to the (211) diffraction of α -Fe in the Fe-C alloy deposits from the bath with citric acid.

Fig.2 Powder X-ray diffraction patterns of the Fe deposit from the bath containing glycolic acid(A) and the Fe-C alloy deposit from the bath containing citric acid(B).

It is well known that the Fe-C martensite has a body centered tetragonal structure and is an interstitial solid solution with carbon atoms on the octahedral sites. The lattice constants of the Fe-C martensite are close to α -Fe (a body centered cubic structure) but that of the c axial and the axial ratio (c/a) of the martensite slightly increases with increasing its carbon content⁶⁾. Therefore, the lattice spacing of the (hkl) plane of the martensite slightly differs from that of the (hkl) plane. This leads to the splitting of a diffraction peak into two peaks; for example, the (211) peak splits into the (112) peak appearing at lower diffraction angle (2θ) and the (211) peak at higher 2θ . The increase in the FWHM of the (110) and (200) peaks and the shoulder observed at the so-called (211) peak of the Fe-C deposits are attributed to the peak splitting due to the tetragonal martensite type structure as with the discussion by Izaki et al.³⁾.

In conclusion, Fe-C alloys were electro-deposited with high current efficiency from the baths containing one of hydroxy-polycarboxylic acids, namely L-malic acid, L-tartaric acid and citric acid without the addition of L-ascorbic acid. The Fe-C alloy deposits obtained at relatively low current density showed smooth surface, black color and a tetragonal martensite type structure.

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