Electrodeposited Fe-Co films Prepared from a Citric-acid-based Plating Bath

T. Yanai, H. Uto, T. Shimokawa, M. Nakano, and H. Fukunaga

Graduate School of Engineering, Nagasaki University, Nagasaki 852-8521, Japan

K. Suzuki

Department of Material Engineering, Monash University, Melbourne 3800, Australia

Electrodeposited Fe-Co films are commonly prepared in a boric-acid-based bath. In this research, we applied citric acid instead of boric acid for the plating of Fe-Co films because boron in the waste bath is restricted by environmental-protection regulations in Japan. We evaluated the effect of citric acid on the magnetic and structural properties of the films. The saturation magnetization of the Fe-Co films slightly increased while the Fe content in the Fe-Co films decreased with increasing citric acid concentration. The lowest coercivity value of 240 A/m was obtained at a citric acid concentration of 100 g/L. The plating bath with this citric acid concentration enabled us to obtain Fe-Co films with high saturation magnetizations and smooth surface morphologies.

PACS numbers: 75.50.S, 75.50.Bb, 75.70.-I

Keywords: Soft magnetic properties, Fe-Co Film, Electrodeposition, Citric acid

Email: t-yanai@nagasaki-u.ac.jp

Fax: +81-95-819-2554

I. INTRODUCTION

Fe-Co based alloys are well–known as high saturation magnetization materials, and their advantage of the high magnetization is particularly useful in magnetic storage devices. Typically, mass-productive Fe-Co films in electric devices prefer chemical processes such as electrodeposition methods to physical processes such as sputtering methods because the chemical processes have high economic viability and simplicity of fabrication equipment. Although many electrodeposited Fe-Co base films with good soft magnetic properties have been reported [1-4], boron, which is restricted by environmental-protection regulations in Japan, was included in the plating bath as boric acid. Doi and Mizumoto reported that a citric-acid-based bath was one of the hopeful candidates for the plating of Ni films and that the electroplating from the citric-acid-based bath was effective to obtain Ni films with texture-free fine crystalline structures [5, 6]. Fine crystal structures are effective in reducing the coercivity because the strong exchange coupling among crystal grains may suppress the effective magnetic anisotropy [7-10]. Therefore, Fe-Co films prepared in a citric-acid-based plating bath are expected to exhibit good soft magnetic properties. In this research, we prepared Fe-Co films from a citric-acid-based plating bath, and we evaluated the effects of citric acid on the magnetic and the structural properties of the films.

II. EXPERIMENTAL PROCEDURES

1. Preparation of Electrodeposited Fe-Co Films

We carried out electroplating to obtain the Fe-Co films by using direct current in the galvanostatic mode. The contents of the electrolyte in the plating bath are shown in Table 1. The content of citric acid was varied from 0 to 160 g/L. We also show the electroplating conditions in Table 2. The pH in the bath was not adjusted, and its value depended on the content of citric acid. The values of pH were 2.5 for 0 g/L and 1.8 for 160 g/L of citric acid, respectively. Five-hundred-μm-thick and 5-mm-wide Fe and Cu plates were used as the anode and the cathode, respectively. The distance

between the electrodes was fixed at 50 mm, and Fe-Co films were deposited on the Cu plate from 50 mL of the plating bath. The current density and the deposition time were controlled by using a computer-aided dc current source. Consequently, we obtained 75-mm^2 Fe-Co films by plating.

2. Measurements

The thicknesses and the dc-hysteresis loops of the electrodeposited Fe-Co films were measured with a micrometer (Mitutoyo CPM15-25MJ) and a B-H tracer (Riken Denshi BHS-40) operated at a field sweep rate of 50 mHz, respectively. A maximum excitation field of approximately 4 kA/m was used for the B-H measurements, and the coercivity was determined from the loop. The saturation magnetization for the Fe-Co films was measured at an excitation field of approximately 1.2 MA/m by using a vibrating sample magnetometer (VSM). The surface morphology and the compositions of the films were analyzed by means of spell out SEM-EDX (SEM-EDX, Hitachi High-technologies S-3000). All measurements were carried out for the Fe-Co films in an as-deposited state.

3. RESULTS AND DISCUSSION

Figure 1 shows the film's thickness and the coercivity for the electrodeposited Fe-Co films as functions of the deposition time. The film thickness increases proportionately with the deposition time. The deposition rate, which was calculated from the slope of the linear fitting line, had a relatively high value of 48 μm/h. The coercivity drastically decreases with increasing deposition time from 1 to 10 min. This result indicates that the boundary states, such as the lattice mismatch and the roughness of the substrate, affect the soft magnetic properties of the films. From these results, we found that at least a 10-minute deposition time was needed to obtain good soft magnetic properties.

Figure 2 shows the saturation magnetization and the Fe content of the Fe-Co films as functions of the citric acid content in the plating bath. The deposition time was set at 30 min. The Fe content

decreases with increasing citric-acid content, and the saturation magnetization slightly increases with increasing citric acid content. Figure 3 shows the coercivity of the Fe-Co films as a function of the citric-acid content in the plating bath. The inset indicates the B-H loop of the Fe-Co films prepared at a citric-acid concentration of 100 g/L. The lowest coercivity value is obtained at around 100 g/L of citric acid, and the value was lower than those for previously reported films prepared from boric-acid-based bath [1-4].

Figure 4 shows surface morphologies of the films prepared with various citric-acid contents of 40, 100 and 160 g/L. As shown in Fig.4, the surfaces of the films prepared at low acid concentrations were rough. At higher acid concentrations, many cracks were observed and this result implies the existence of high stress in the electrodeposits. On the other hand, the surface of the film obtained at a citric-acid content of 100 g/L appears smooth. Thus, the result that the coercivity shows a low value at around this citric-acid content could be explained by a low inner stress in the films and a good film quality. From the above-mentioned results, we conclude that the citric-acid-based bath is applicable as a plating bath for obtaining Fe-Co films with good soft magnetic properties.

4. CONCLUSION

We have investigated the structural and magnetic properties of electrodeposited Fe-Co films prepared from a citric acid based bath. The obtained results are summarized as follows:

(1) Fe-Co films with low coercivity could be obtained for thicknesses above 10 μm.

(2) The deposition rate of the Fe-Co films for a citric-acid-based bath shows a relatively high value of 48 μm/h.

(3) The Fe content was reduced by increasing the content of citric acid from approximately 54 to 48 at.%

(4) Fe-Co films with low coercivity values of less than 300 A/m were obtained around a citric acid concentration of approximately 100 g/L.

REFERENCES

[1] J. S. Santos, R. Matos, F. Trivinho-Strixino, and E. C. Pereira, Electrochim. Acta **53**, 644 (2007).

[2] C. Qianga, J. Xua, S. Xiaoa, Y. Jiao, Z. Zhanga, Y. Liua, L. Tiana, and Z. Zhoua, Appl. Surf. Sci. **257**, 1371 (2010).

[3] H. Kockar, M. Alper, T. Sahin, and O. Karaagac, J. Magn. Magn. Mater. **322**, 1095 (2010).

[4] S. H. The, and I. I. Yaacob, IEEE Trans. Magn. **47**, 4398 (2011).

[5] T. Doi and K. Mizumoto, Metal Finishing **102**, 26 (2004).

[6] T. Doi and K. Mizumoto, Metal Finishing **102**, 104 (2004).

[7] Y. Yoshizawa, S. Oguma, and K. Yamauchi, J. Appl. Phys. **64**, 6044 (1988).

[8] K. Suzuki, A. Makino, N. Kataoka, A. Inoue, and T. Masumoto, Mater. Trans., JIM **32**, 93 (1991).

[9] M. A. Willard, M. Q. Huang, D. E. Laughlin, M. E. McHenry, J. O. Cross, V. G. Harris, and C. Franchetti, J. Appl. Phys. **85**, 4421 (1999).

[10] G. Herzer, IEEE Trans. Magn. **26**, 1397 (1990).

Table 1. Contents of the electrolyte in the plating bath.

Components	Concentration
$FeSO_4 \cdot 7H_2O$	100 g/L
$CoSO_4 \cdot 7H_2O$	100 g/L
NaCl	50 g/L
Citric acid ($C_6H_8O_7 \cdot H_2O$)	0-160 g/L

Table 2. Electroplating conditions for the Fe-Co film.

Condition	Value
pH(Not adjusted)	1.8 - 2.5
Bath temperature	50 °C
Current density	2.0 mA/mm^2
Deposition time	1- 50 min

Figure Captions.

Fig. 1. Thickness and coercivity of the Fe-Co films as functions of deposition time.

Fig. 2. Saturation magnetization and Fe content of the Fe-Co films as functions of the content of citric acid.

Fig. 3. Coercivity of the Fe-Co films as a function of the content of citric acid. The inset indicates the B-H loop of the Fe-Co films prepared at a citric-acid concentration of 100 g/L.

Fig. 4. Surface morphologies of the films prepared with various contents of citric acid.

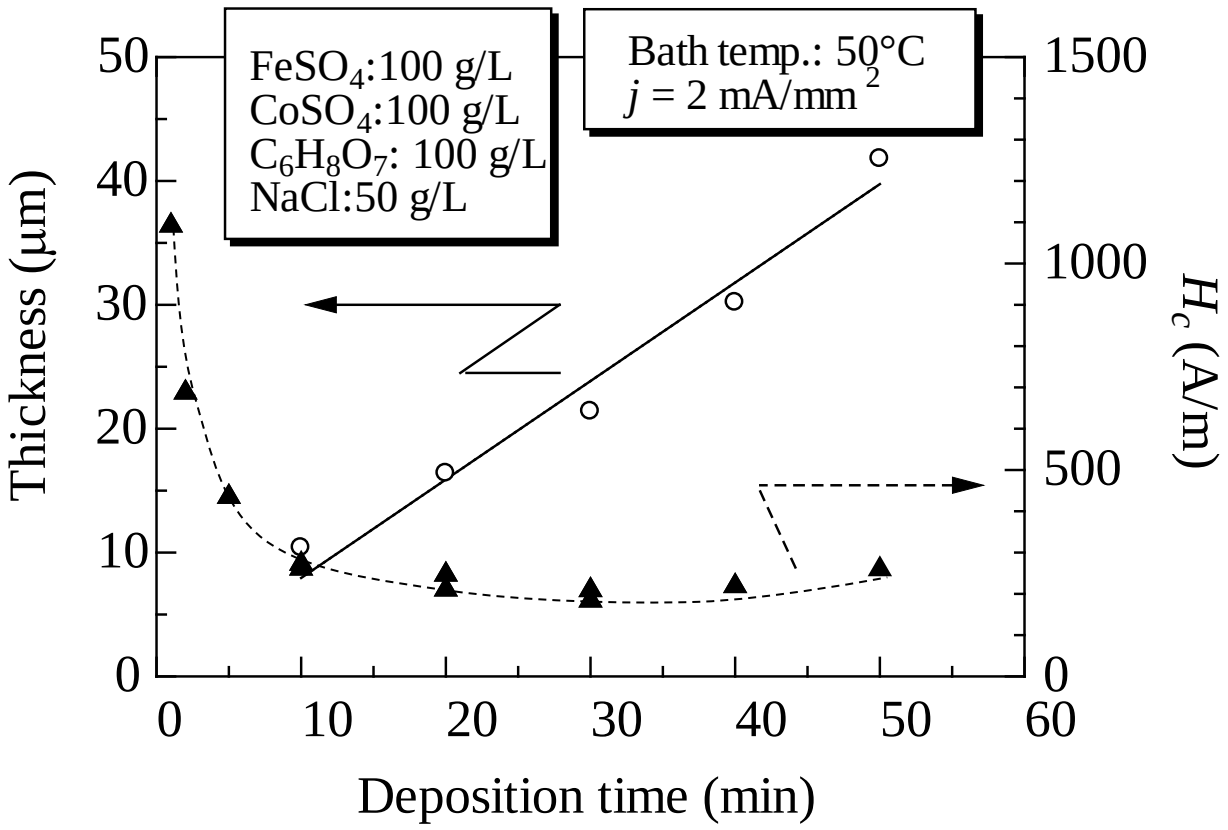
FeSO4:100 g/L
CoSO4:100 g/L
C6H8O7: 100 g/L
NaCl:50 g/L
Bath temp.: 50°C
j = 2 mA/mm 2
Thickness (μm)
Hc (A/m)
Deposition time (min)
0
10
20
30
40
50
60
500
1000
1500

Fig.1

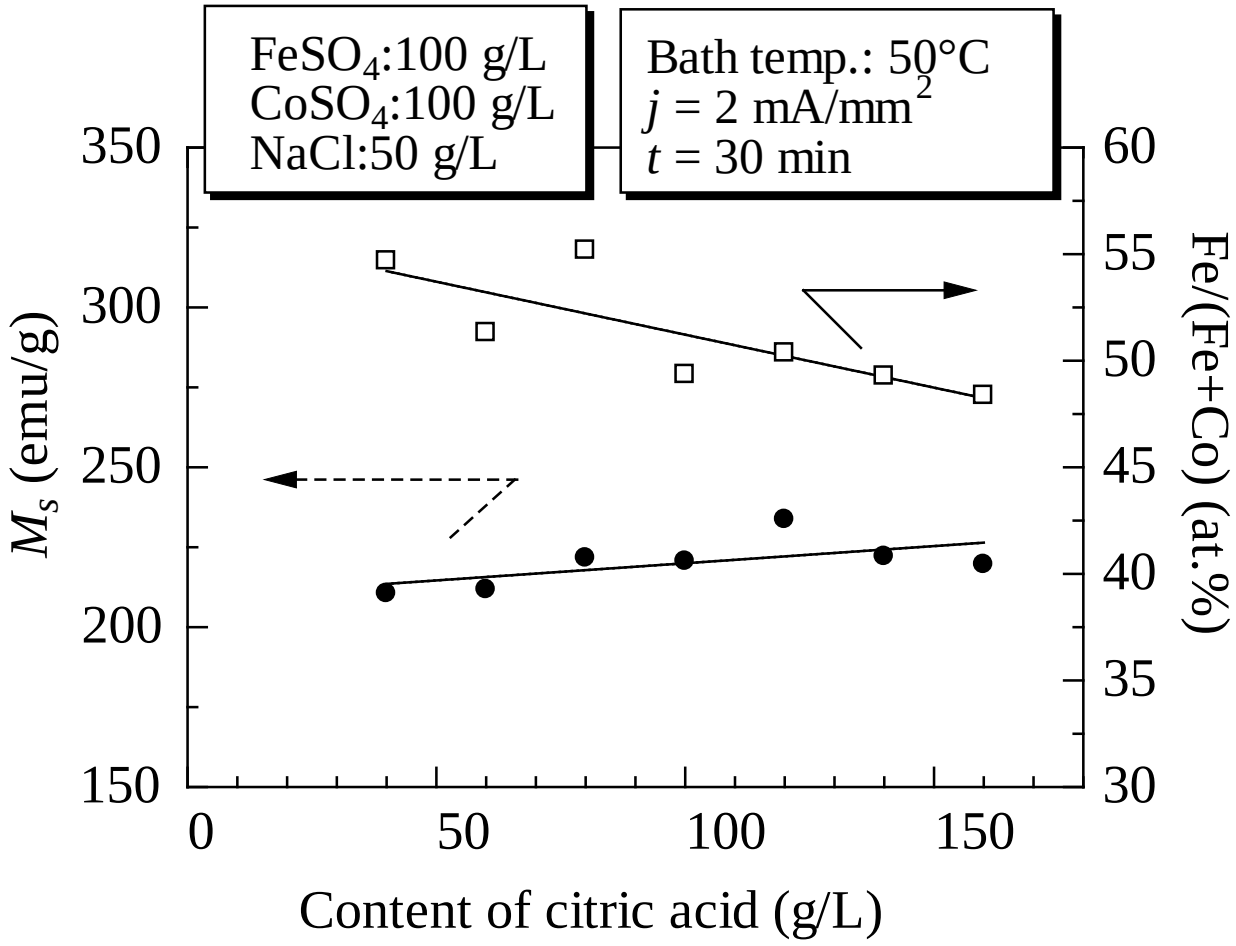
FeSO4:100 g/L
CoSO4:100 g/L
NaCl:50 g/L
Bath temp.: 50°C
j = 2 mA/mm2
t = 30 min
Ms (emu/g)
Fe/(Fe+Co) (at.%)
Content of citric acid (g/L)
350
300
250
200
150
60
55
50
45
40
35
30
0
50
100
150

Fig.2

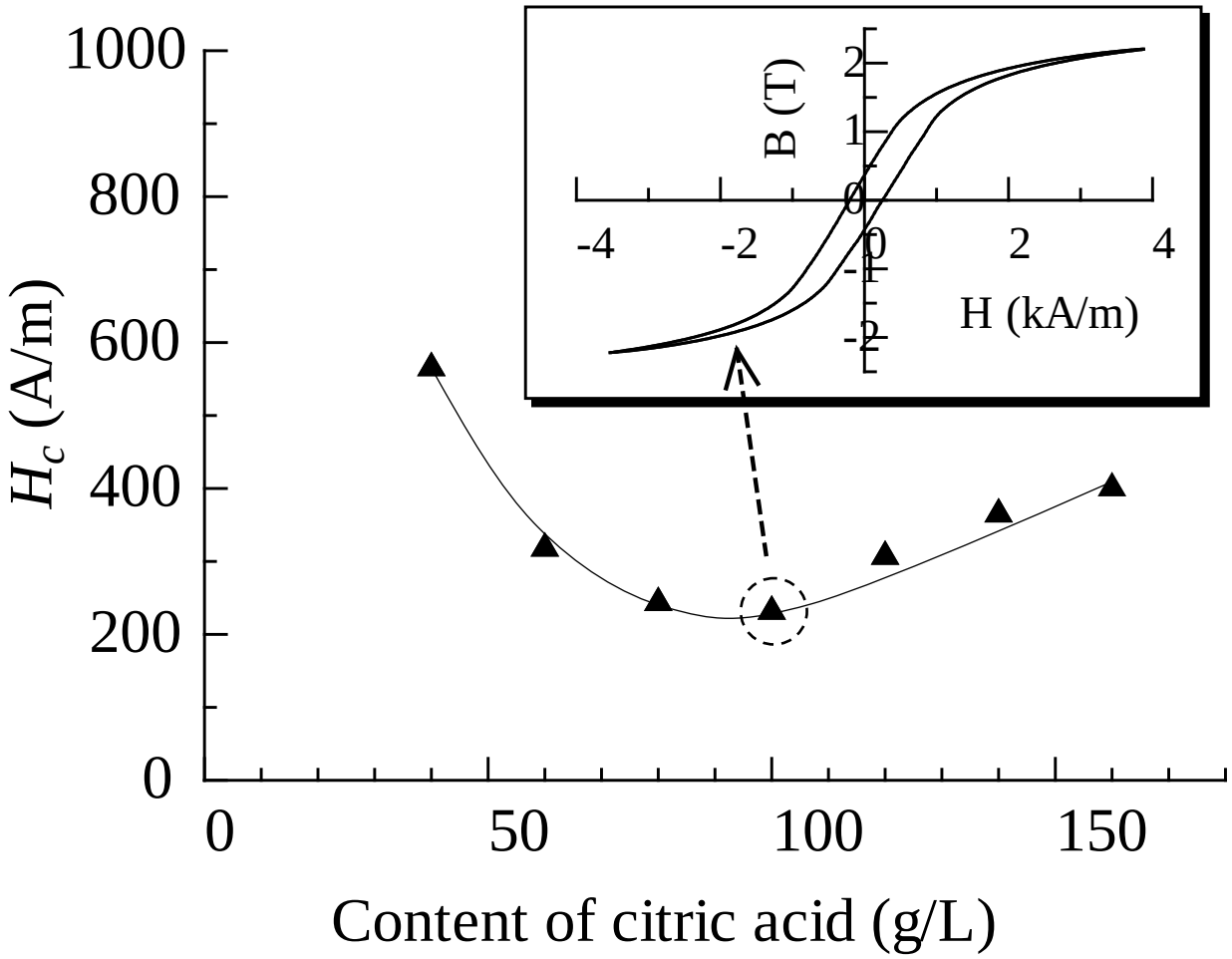
1000
800
600
400
200
0
H_c (A/m)
0
50
100
150
Content of citric acid (g/L)
B (T)
2
1
0
-1
-2
-4
-2
0
2
4
H (kA/m)

Fig.3

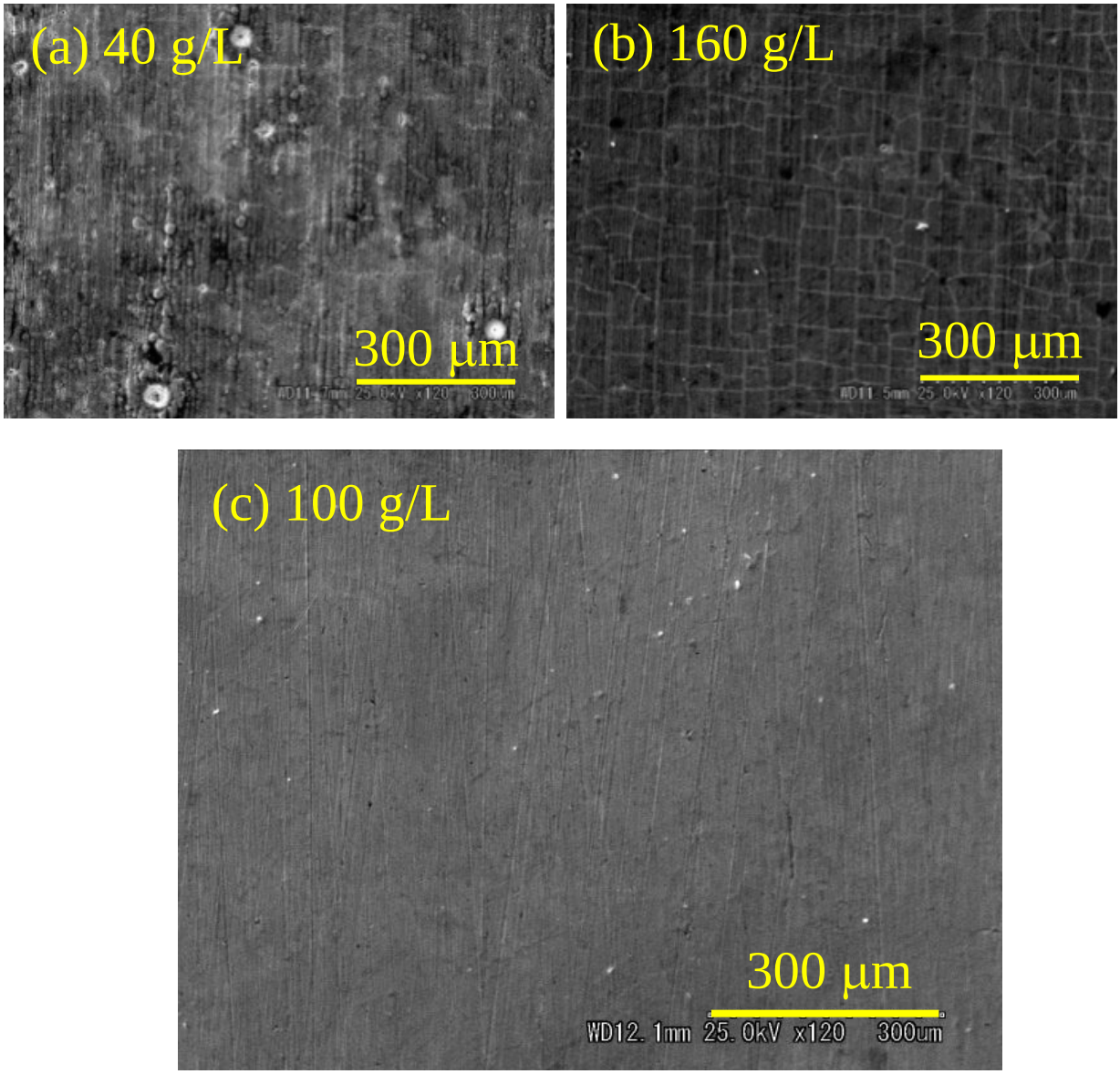
(a) 40 g/L
300 μm
(b) 160 g/L
300 μm
(c) 100 g/L
300 μm
WD12.1mm 25.0kV x120 300um

Fig.4