

Effect of Carbon Content on Structural and Mechanical Properties of Fe-Co-C Alloy Electrodeposited from Aqueous Solutions

Norikazu Miyamoto, Shinsuke Sakamoto, Hiroto Tamura, Masao Matsuoka,^{*,z} and Jun Tamaki^{*}

Department of Applied Chemistry, Faculty of Science and Engineering, Ritsumeikan University, Nojihigashi, Kusatsu, Shiga 535-8577, Japan

Fe-Co-C alloy coatings were electrodeposited from a sulfate solution containing citric acid and L-ascorbic acid as additives. Crystal structure and mechanical property of the coatings were examined by using X-ray diffraction (XRD) and Vickers hardness tester. The atomic ratio of Fe/Co in Fe-Co-C alloy coatings is essentially the same as that in carbon-free Fe-Co alloy coatings. However, the crystal structure of Fe-Co-C alloy is quite different from that of Fe-Co alloy. In the case of Fe-Co-C alloys, coatings with 30.0 to 83.8 mass % Co, an intermediate phase was detected. XRD analysis indicated that the phase had the same crystal structure as the cubic cobalt phase that was produced by the evaporation of Co on cold substrate under He atmosphere. However, the cubic structure changes to a tetragonal system by the incorporation of carbon. This intermediate phase is quite unstable and then then structure of of carbon. The maximum hardness of ca. Hv 800 was obtained for the Fe-10.9 mass % Co-1.1 mass % C alloy. The improvement in hardness of Fe-Co-C alloy coatings is discussed in detail from the viewpoint of alloy composition and crystal structure.

© 2005 The Electrochemical Society. [DOI: 10.1149/1.1931468] All rights reserved.

Manuscript submitted September 20, 2004; revised manuscript received February 7, 2005. Available electronically June 7, 2005.

As-deposited Fe-C alloy coatings prepared by cathodic deposition from iron(II) salts solution containing citric acid at 323 K showed the Vickers hardness of Hv 800, and it increased to the maximum value of Hv 1150 by annealing at 623 K.¹ This value is larger than twice the industrial iron electrodeposits and comparable to those of the carbonized steels or nitriding steels. Therefore, Fe-C alloy is a promising material as an alternative to hard chromium electrodeposits or heat-treated nickel-phosphorus coatings. For the practical use of Fe-C alloy,² it is necessary to improve the mechanical properties such as hardness and wear resistance, etc.

A few attempts have been made to improve the mechanical properties of Fe-C alloy coatings by introducing a third element. For example, ternary Fe-C-B alloy coatings had excellent wear resistance.³ In addition, Fe-C-P alloy coatings had excellent hardness and wear resistance, due to the formation of solid solution in which carbon and phosphorous were supersaturated.⁴ In both cases, the third elements (B and P) effectively reduced the oxygen content in the alloys, which significantly improved wear resistance of the coatings.

An addition of cobalt as the third element to Fe-C alloy coatings is of interest to improve mechanical properties of Fe-C alloy coatings. In addition, the electrodeposited Fe-Co alloy (90 atom % Co) is an attractive material because of the high saturation magnetization (1.9 T) as reported by Liao.⁵ Although the mechanical properties are an important factor in engineering the soft magnetic thin coatings, there are few reports on the mechanical properties of Fe-Co alloy coatings. Klingenmaier pointed out that the Fe-6 wt % Co alloy electrodeposited from a chloride solution yielded low stress and the Vickers hardness number of Hv 640.⁶

In this study, the ternary Fe-Co-C alloys were systematically investigated to improve the mechanical properties as a function of Co content. The Fe-Co-C alloy coatings were electrodeposited galvanostatically, and the effect of alloy composition on the crystal structure and mechanical properties of Fe-C alloy coatings were discussed based on the fundamental data derived from X-ray diffraction (XRD) and the measurements of Vickers hardness.

Experimental

Fe-Co-C alloy coatings were prepared at 323 K from an aqueous solution consisting of $0.14\ mol\ dm^{-3}\ (FeSO_4\cdot 7H_2O$

+ CoSO_4·6H_2O), $~6.2\times10^{-3}\ mol\ dm^{-3}$ citric acid, and 17 $\times 10^{-3}$ mol dm⁻³ L-ascorbic acid. Carbon-free Fe-Co alloy coatings were prepared from the corresponding electrolyte free from organic acid. All the solutions were prepared with deionized water and special grade chemicals. The solution was adjusted to pH 2.7 by using sulfuric acid. Stainless steel (SUS304) or brass sheets used as cathodes for electrodeposition were degreased in an electrolyte consisting of 1.1 mol dm^{-3} KOH and 0.10 mol dm^{-3} K₄P₂O₇, and rinsed with deionized water prior to each run. Two rectangular steel sheets (7.0 \times 15.0 cm, JIS SPCC) were used as active anode. Electrodeposition was carried out galvanostatically at 30 mA cm⁻² under the unstirred condition. The thickness of the alloy coatings was controlled to be ca. 20 µm. The carbon and oxygen contents of the coating were determined using a carbon-sulfur analyzer (Horiba EMIA-920V) and oxygen analyzer (LECO TC-436AR), respectively. The iron and cobalt contents of the coating were determined by atomic absorption spectrophotometry (Hitachi Z-8200). Scanning electron microscope (SEM, Hitachi S-2460) was used for observation of surface morphology. X-ray diffraction was carried out using Cu Ka radiation (RIGAKU RINT2000; 40 kV, 20 mA). The diffraction angles were calibrated with reference to pure Si diffraction lines. The deconvolution of diffraction peaks was done with the least-square fitting technique based on a pseudo-Voight formula by using the computer programs supplied by Toraya.⁷ X-ray photoelectron spectroscopy (Ulvac-Phi ESCA-5700MC) was performed by using Mg K α radiation under vacuum of ca. 10⁻⁹ Torr. Binding energy was calibrated with reference to the O 1s peak of iron oxide. Hardness measurements were carried out using a Vickers hardness tester (Akashi MS-55) under the load of 0.098 N.

Results and Discussion

Chemical composition of Fe-Co-C coatings.—Cobalt, iron, carbon, and oxygen contents of Fe-Co and Fe-Co-C alloy coatings are shown in Fig. 1a and b, as a function of Co^{2+} concentration. Cobalt content of Fe-Co alloy coatings linearly increased and iron content linearly decreased with an increase in Co^{2+} concentration. ⁸⁻¹⁰ The behavior of so-called anomalous codeposition, which was frequently observed for electrodeposition of the iron-group binary alloy system, ¹¹ was not detected in this study. The Co/Fe ratio in Fe-Co-C coatings was essentially the same as in carbon-free Fe-Co alloy coatings. Carbon content of Fe-Co-C alloy coatings was ca. 1.1 mass % and this value was kept constant in the range from 0 to 60 mol % Co^{2+} ; however, it decreased abruptly with a further

^{*} Electrochemical Society Active Member.

^z E-mail: matsuoka@se.ritsumei.ac.jp



Figure 1. (a) Composition of Fe-Co alloy coatings as a function of Co^{2+} concentration. Open triangle: Fe; open square: Co; open diamond: O. (b) Composition of Fe-Co-C alloy coatings as a function of Co^{2+} concentration. Filled triangle: Fe; filled square: Co; filled diamond: O; filled circle: C.

increase in Co^{2+} concentration. The oxygen content of Fe-Co-C coatings was remarkably higher than that of Fe-Co coatings as a whole. The relationship between carbon and oxygen contents of Fe-Co and Fe-Co-C alloy coatings is shown in Fig. 2. It was disclosed that the oxygen content increased in proportion to the carbon content. The same tendency was also detected for the martensitic Fe-C and Fe-P-C coatings.^{4,12} Consequently, an increase in oxygen content with carbon content is exclusively attributable to inclusion of a reaction intermediate derived from organic acid. The signifi-



Figure 2. Relationship between C and O contents in Fe-Co and Fe-Co-C alloy coatings. Filled circle: Fe-Co-C; open circle: Fe-Co.



Figure 3. Powder XRD patterns of Fe-Co alloy coatings as a function of Co content. (a) Fe; (b) Fe-18.8% Co; (c) Fe-38.5% Co; (d) Fe-57.8% Co; (e) Fe-79.4% Co; (f) Fe-91.6% Co. Filled circle: bcc-Fe; filled square: hcp-Co.

cance of the oxide layer formed on the coating surface has been pointed out by Izaki³ and Fujiwara.¹² Judging from the low oxygen content for the coatings deposited from organic acid-free electrolyte, it is concluded that oxygen uptake through oxide layer is quite small.

Crystal structure of Fe-Co and Fe-Co-C coatings.— The powder XRD spectra of carbon-free Fe-Co alloy with different compositions are shown in Fig. 3. The diffraction profiles from (a) to (d) indicate that the carbon-free Fe-Co alloys take a single phase with a body-centered cubic (bcc) structure when the Co content is less than 60 mass %. However, the other phases assigned to hexagonal closepacked (hcp)-Co and bcc-Fe are detected for the Fe-Co alloys with further increase in Co content [profiles (e) and (f)]. The results are in fairly good agreement with the previous report.⁸⁻¹⁰

The powder X-ray diffraction spectra of Fe-Co-C alloy (0 to 18.6 mass % Co) are shown in Fig. 4. All diffraction lines are assigned to a bcc structure with the lattice constant of a = 0.28655 nm. The diffraction peaks were shifted to the higher angle direction with an increase in Co content. Such changes are attributable to solid solution formation of cobalt and iron atoms. However, a discernible shoulder was detected at the higher angle to the side of the {211} line, which could be divided into (112) and (211) lines. The deconvolution results of {211} diffraction lines are shown in Fig. 4 as the insertion. In the case of {200} diffraction



Figure 4. Powder XRD patterns of Fe-Co-C alloy coatings and an insertion showing deconvolution profiles of $\{211\}$ diffraction line. (a) Fe-1.1% C; (b) Fe-10.9% Co-1.2% C; (c) Fe-18.6% Co-1.1% C.



Figure 5. XRD patterns of as-prepared Fe-Co-C alloy coatings with different Co contents. (d) Fe-30.0% Co-1.1% C; (e) Fe-39.1% Co-1.2% C; (f) Fe-48.1% Co-1.2% C; (g) Fe-57.3% Co-1.2% C; (h) Fe-64.9% Co-1.0% C; (i) Fe-74.2% Co-0.8% C; (j) Fe-83.8% Co-0.5% C; (k) Fe-88.5% Co-0.05% C. Filled circle: bcc-Fe; filled square: hcp-Co; filled star: intermediate; filled triangle: unknown phase.

lines, the shoulder was detected at the lower angle to the side of the $\{200\}$ line, which could be deconvoluted into (002) and (200) lines. The shoulders detected in $\{200\}$ and $\{211\}$ lines are caused by the solute carbon atoms occupying the interstitial site. As reported by Izaki *et al.*¹ the interstitial carbon atoms in Fe-C alloy occupied (0, 0, 1/2) and (1/2, 1/2, 0) sites and the *c*-axial and the axial ratio *c/a* increased in proportion to the carbon content. The observed peak splits indicate that all the Fe-Co-C alloys take a martensitic single phase with a body-centered tetragonal structure.

The XRD spectra of as-prepared and pulverized Fe-Co-C alloy (30.0 to 83.8 mass % Co), are shown in Fig. 5 and 6, respectively. In the case of as-prepared Fe-Co-C alloy coatings (30.0 to 83.8 mass % Co), the diffraction peaks located at 39°, 49°, 76°, and 85° could not be assigned to any phase of hcp-Co, face-centered cubic (fcc)-Co, or bcc-Fe. In this paper, this unknown phase is referred to as the intermediate phase. The powder XRD spectra indicate that main peaks are assigned to the hcp-Co or bcc-Fe phase. The intensity of the hcp-Co peak increased and that of the bcc-Fe decreased with an increase in cobalt content. Consequently, the crystal structure of an intermediate phase is transformed to the mixture of hcp-Co and



Figure 6. Powder XRD patterns of Fe-Co-C alloy coatings with different Co contents. (d) Fe-30.0% Co-1.1% C; (e) Fe-39.1% Co-1.2% C; (f) Fe-48.1% Co-1.2% C; (g) Fe-57.3% Co-1.2% C; (h) Fe-64.9% Co-1.0% C; (i) Fe-74.2% Co-0.8% C; (j) Fe-83.8% Co-0.5% C. Filled circle: bcc-Fe; filled square: hcp-Co; filled star: intermediate; filled triangle: unknown phase.

Table I. Crystallographic parameters of intermediate phase with a composition of Fe-57.3% Co-1.2% C alloy. The observed intermediate phase had a = 0.4567 nm as cubic system and the reported intermediate phase of cubic system had a = 0.460 nm.¹³

No.	$d_{\rm obs}/{\rm nm}$	$d_{\rm cal}/{\rm nm}$	Difference/nm	h, k, l
1	0.2292	0.2284	0.0008	2, 0, 0
2	0.1867	0.1865	0.0003	2, 1, 1
3	0.1260	0.1267	-0.0007	3, 2, 0
4	0.1144	0.1142	0.0002	4, 0, 0

bcc-Fe by the pulverization. The intermediate phase would be induced by solute carbon, because such a phase could not be detected in carbon-free Fe-Co alloy. Further details of the intermediate phase will be discussed in the following section.

Although SEM images are not shown here, the surface morphologies of Fe-Co-C alloy coatings were smoother than those of Fe-Co alloy, regardless of cobalt content. However, few cracks were detected for the Fe-Co-C alloy with 64.9-83.8 mass % Co. In the case of the Fe-Co-C coating (>89.3 mass % Co), the needle-shaped crystal growth characterizing hexagonal structure was detected.

Identification of the intermediate phase.—An attempt was made to identify the intermediate phase from the XRD spectra of as-prepared Fe-Co-C coatings. The calculated and observed crystallographic parameters of typical intermediate phase (Fe-57.3 mass % Co-1.2 mass % C alloy) are shown in Table I. All the peaks are assigned to a cubic cobalt phase with a lattice constant of 0.460 nm, which has the same structure as detected for the cobalt evaporated on a cold substrate under He atmosphere.¹³ All the peaks observed at 39, 49, 75, and 85° are assigned to the index of {200}, {211}, {320}, and {400}, respectively. This intermediate phase was exclusively detected for Fe-Co-C coatings with the cobalt content of 30.0-83.8 mass %.

As shown in Fig. 5, a discernible shoulder can be seen at a lower angle to the side of the $\{320\}$ line and at higher angle to the side of the $\{400\}$ line, respectively. The $\{320\}$ and $\{400\}$ lines were deconvoluted by the same manner as described in the previous section. The deconvolution result is shown in Fig. 5 as the insertion. Such a deconvolution result indicates that the crystal structure of intermediate phase belongs to a tetragonal system. This situation is quite similar to that of a martensitic single phase being detected for the Fe-Co-C alloys (<18.6 mass %). In this case, the interstitial carbon atom also plays an important role in the formation of the tetragonal phase.

For the alloys with the composition of 30.0-57.3 mass % Co, the intensity of $\{200\}$ and $\{400\}$ lines was larger than that of $\{211\}$ and



Figure 7. Lattice constants as a function of Co content in Fe-Co-C alloy coatings. Filled circle: *a*-axial length; filled square: *c*-axial length.





{320}, but the reverse was true for the alloys containing 64.9-83.8 mass % Co. This fact suggests that the orientation of the intermediate phase changes as a function of cobalt content.

The small peaks originated from an unknown phase unassigned to the intermediate, and the other phases were detected for the alloys with higher Co content as shown in Fig. 5 and 6. However, it was impossible to identify the unknown phase because of its weak diffraction intensity.

Lattice parameters of Fe-Co-C alloy coatings.— The effect of cobalt content on lattice parameters of Fe-Co-C alloy coatings is shown in Fig. 7. The lattice constants a and c increased abruptly at ca. 20-30 mass % Co accompanying the changes in crystal structure. The lattice parameters a and c decreased with increasing Co content both in the martensitic and intermediate regions. The decrease in lattice constants in the martensitic and intermediate region is explained by the formation of Fe-Co solid solution as observed for the Fe-Co alloy with bcc structure.⁸

Chemical state of elements in the alloys.—Figure 8 shows the typical photoelecton spectra being measured to figure out the chemical states of each element in Fe-Co-C coatings with different cobalt contents. The O 1s peak at 530 eV is ascribed to Fe-O and Co-O bond as detected for Fe₂O₃ and Fe₃O₄,^{1,3,4} Co₂O₃, and Co₃O₄,¹⁴ Although the alloys contained ca. 5 mass % O, and O 1s peak of iron or cobalt oxides was detected, no diffraction lines corresponding to oxides were detected in the XRD profile shown in Fig. 4. Therefore, iron oxides are supposed to be in an amorphous state. The Co 2p peaks located at 778 and 794 eV are assigned to Co $2p^{3/2}$ and Co $2p^{1/2}$ in the metallic state, respectively.¹⁵ The Fe 2p peaks located at 707 and 720 eV are assigned to Fe $2p^{3/2}$ and Fe $2p^{1/2}$ in the metallic state, respectively.¹⁵ The Fe 2p peaks located at 283 eV and shoulder peak at 286 eV was detected. The peak around 286 eV is assigned to the oil contamination from the apparatus.¹ The binding energy of Co-C bond is unknown; however, it is estimated to be 283 eV, judging from the binding energy reported for Cr-C,¹⁶ Ni-C,¹⁶ and Fe-C. ^{13,4} Consequently, the C 1s peak around 283 eV is ascribed to Fe-C and Co-C

bonds. The chemical states of corresponding elements for the martensitic and intermediate phases resemble each other, independent of cobalt content. In addition, the chemical states of corresponding elements for the Fe-Co-C alloy coatings are essentially identical to those for Co-free Fe-C alloy coatings except for cobalt.¹

Effect of cobalt and carbon contents on mechanical properties of Fe-Co-C alloy coatings.—The hardness of Fe-Co and Fe-Co-C alloy coatings as a function of Co content is shown in Fig 9. The hardness of Co-free Fe-C alloy coating was found to be ca. Hv 700. The hardness of martensitic Fe-Co-C alloy coatings was remarkably greater than that of Fe-Co alloys. Such a hardening was dependent on the amount of interstitial carbon atoms as reported for Fe-C alloys.¹ Maximum hardness of ca. Hv 800 was obtained for Fe-10.9 mass % Co-1.1mass % C alloy coating. The higher hardness would be ascribed to the lattice strain produced during the formation of carbon-supersaturated solid solution.

Although carbon content was kept constant at ca. 1.1 mass % for



Figure 9. Vickers hardness number of Fe-Co and Fe-Co-C alloy coatings as a function of Co content. Filled circle : Fe-Co-C alloy; filled square : Fe-Co.

the alloys with a composition of 0 to 64.9 mass % Co, the hardness of intermediate phase (30.0-83.8 mass % Co) was smaller than that of Fe-Co-C alloys with a composition of 0-18.6 mass % Co. This result indicates that the lattice strain produced in the intermediate phase is not as excessive as that in a martensitic phase, despite the constancy of carbon content. Fe-Co-C alloy coatings gave the higher hardness, compared to binary Fe-Co alloy coatings. Supersaturated carbon is found to be effective to improve the mechanical property of Fe-Co alloy coating.

Conclusions

The structural and mechanical properties of Fe-Co-C alloy coatings, which were galvanostatically electrodeposited from a sulfate solution containing citric acid, were investigated. The carbon content of Fe-Co-C alloy coatings was found to be 0.06-1.1 mass % and arbitrary Fe/Co ratio could be obtained by adjusting the ionic ratio of Fe²⁺/Co²⁺. Although the Fe/Co ratio of Fe-Co-C alloy coatings is identical to that of Fe-Co alloy coatings, crystal structure is remarkably influenced by carbon content. XRD analysis indicated that Fe-Co-C alloy coatings (0 to 18.6 mass % Co) were a martensitic single phase. An intermediate phase was detected in the region of 30.0-83.8 mass % Co. The detailed analysis of intermediate phase disclosed that the phase had a tetragonal structure that was the same as the cobalt phase produced on cold substrate under He atmosphere by evaporation. No intermediate phase was detected for carbon-free Fe-Co alloy coatings. As the intermediate phase is thermodynamically unstable, it transforms to the mixture of bcc-Fe and hcp-Co phases by pulverization. The maximum hardness of ca. Hv 800 was obtained for the Fe-10.6 mass % Co-1.1 mass % C alloy coating. Accordingly, the hardness of Fe-C coating was improved by alloying with cobalt. In addition, codeposition of carbon is significantly effective for improving mechanical property of Fe-Co alloy coating, especially in the martensitic region. It is concluded that supersaturated interstitial carbon and substitutional cobalt synergistically play an important role to give rise to the maximum hardness.

Acknowledgments

The authors thank Dr. Masanobu Izaki of Osaka Municipal Technical Research Institute for his kind assistance and helpful discussion on XPS measurements

Ritsumeikan University assisted in meeting the publication costs of this article.

References

- 1. M. Izaki and T. Omi, Metall. Mater. Trans. A, 27A, 483 (1996).
- Technical Catalogue "Carboplus, ®" Fuso Chemical Co. Ltd, Osaka, Japan (1994). M. Izaki, N. Miyamoto, A. Nakae, T. Hasegawa, S. Watase, M. Chigane, Y. Fuji-3.
- wara, M. Ishikawa, and H. Enomoto, J. Electrochem. Soc., 149, C370 (2002). N. Miyamoto, K. Yoshida, M. Matsuoka, and J. Tamaki, J. Electrochem. Soc., 151, 4. C645 (2004).
- S. H. Liao, IEEE Trans. Magn., 23, 2981 (1987).
- O. J. Kllingenmaier, U.S. Pat. 4,388,379 (1983).
- H. Toraya, J. Appl. Crystallogr., 19, 440 (1986).
- E. Jartych, J. K. Zurawicz, and M. Budzyynski, J. Phys.: Condens. Matter, 5, 927 8. (1993)
- N. Fukumuro, M. Chikazawa, and T. Watanabe, J. Surf. Finish. Soc. Jpn., 50, 448 9. (1999)
- E. M. Kakuno, C. H. Mosca, I. Mazzaro, N. Mattoso, W. H. Schreiner, and M. A. B. Gomes, *J. Electrochem. Soc.*, **144**, 322 (1997).
 K. Y. Sasaki and J. T. Talbot, *J. Electrochem. Soc.*, **142**, 775 (1995).
- 12. Y. Fujiwara, T. Nagayama, A. Nakae, M. Izaki, H. Enomoto, and E. Yamauchi,
- J. Electrochem. Soc., 143, 2584 (1996). 13. P. Villars and L. D. Calvert, Pearson's Handbook of Crystallographic Data for Intermetallic Phases, Vol. 2, p. 1736, American Society for Metals, Metals Park, OH (1985).
- J. Chastain, Handbook of X-Ray Photoelectron Spectroscopy, p. 231, Perkin-Elmer Corporation, Eden Prairie, MN (1992).
- 15. J. Chastain, Handbook of X-Ray Photoelectron Spectroscopy, p. 219, Perkin-Elmer Corporation, Eden Prairie, MN (1992).
- 16. J. Chastain, Handbook of X-Ray Photoelectron Spectroscopy, p. 216, Perkin-Elmer Corporation, Eden Prairie, MN (1992).