Nonequilibrium Fe–Cr Alloys Produced by Vapor Quenching

By Kenji Sumiyama*, Norikazu Ohshima** and Yoji Nakamura*

X-ray diffraction, magnetization and the Mössbauer effect have been measured for Fe_{1-x}Cr_x alloys produced by a typical vapor quenching method of sputtering. The single bcc phase appears for 0<x<0.4 and 0.65<X<1.0. For 0.45<x<0.55, on the other hand, the σ phase appears on a part of the substrate far from Ar plasma, while the A15 and σ mixed phase appears on the other part of the substrate near Ar plasma. The bcc phase, the σ phase and the A15 phase are ferromagnetic at low temperatures. The difference in local atomic configurations of the σ phase and the A15 phase is reflected in the Mössbauer spectra of Fe_{1-x}Cr_x alloys in the paramagnetic state.

(Received May 13, 1987)

Keywords: iron-chromium alloys, vapor quenched alloy, nonequilibrium phase, magnetic properties, Mössbauer effect

I. Introduction

Vapor quenching techniques such as sputter-deposition and thermal evaporation are very useful to produce a wide variety of nonequilibrium alloys, in contrast to their limited production by liquid quenching(1)(2). In sputter-deposited Fe alloys, a primary bcc solid solution of the α Fe-type has been extended in the Fe-rich region. Moreover, in sputter-deposited Fe alloys with early transition metal elements, such as Ti, V and Mo(3)-(5), an amorphous phase has been obtained for the alloy concentrations corresponding to the topologically close packed (TCP) phases in their equilibrium phase diagrams(6)(7).

The equilibrium Fe_{1-x}Cr_x alloys have the single bcc phase in the whole concentration range above 1100 K, while the σ phase for 0.42<x<0.52 and the single bcc phases on both the Fe-rich and Cr-rich sides between 800 and 1100 K(8). Below 800 K, the single bcc phases are restricted to very narrow ranges of both ultimate concentrations(9), although pure Fe and pure Cr have the same bcc structure in this temperature range. In the Fe–Cr alloys produced by several vapor deposition methods, the Fe-rich bcc (α) phase has been obtained by sputter-deposition(9), the σ phase by thermal evaporation(10), while the A15 phase has been obtained by evaporating Fe and Cr in a high Ar gas atmosphere of about 2.7 kPa (20 Torr) and condensing them onto the inner wall of a vacuum chamber(11).

Here, the σ and A15 phases are classified as TCP structure, because their large crystalline unit cells contain few tens of atoms on several lattice sites and have a high degree of close-packed planar stacking(12). These TCP phases appear in many alloys, which have a proper value of electron atom ratio and whose constituent elements have an appropriate atomic size ratio(13).

This paper deals with the experimental results of X-ray diffraction, magnetization and Mössbauer effect measurements on sputter-deposited Fe_{1-x}Cr_x alloys. We discuss how nonequilibrium phases extend in these alloys and also their characteristics of the magnetic properties and the Mössbauer spectra.

II. Experimental Procedures

Using a conventional rf sputtering method under an Ar gas pressure, P_{Ar}, of 0.53 Pa (4 mTorr), we prepared a few μm thick films of Fe_{1-x}Cr_x alloys (x=0−1.0) on water-cooled...
polyimide film substrates. The substrate temperature was kept at about 350 K. Some Fe–Cr alloys were sputter-deposited under $P_{Ar} = 0.53$ Pa (4 mTorr) on liquid nitrogen-cooled substrates whose temperatures were kept at about 100 K. They were also sputter-deposited on water-cooled substrates under $P_{Ar} = 13$ Pa (10 mTorr). Chemical compositions of sputter-deposited alloys were determined by electron probe microanalysis and partly by fluorescence X-ray analysis. X-ray diffraction measurements were done at 290 K using a graphite monochromator. X-ray diffraction patterns of these alloys are roughly the same to those of the alloys deposited on the water-cooled substrates under $P_{Ar} = 0.53$ Pa (4 mTorr). The chemical composition was homogeneous on the whole area of deposited alloy films, while the thickness of deposited alloys on a part of the substrate far from Ar plasma was thinner than that on the other part of the substrate near Ar plasma and X-ray diffraction patterns were different for the specimens deposited on the different positions of the substrate.

The magnetization was measured at 4.2 and 290 K in magnetic fields up to 1.03 MA/m (13 kOe) by a torsion balance magnetometer. Since the magnetization of deposited alloys on a part of the substrate far from Ar plasma was almost the same as that deposited on the other part of the substrate near Ar plasma, we mainly measured magnetizations of $Fe_{1-x}Cr_x$ alloys deposited on a part of the substrate far from Ar plasma. Mössbauer spectra were observed at 4.2 and 290 K by a constant acceleration type spectrometer using a $^{57}$Co source doped in copper, where the velocity scale was calibrated relatively to $\alpha$-Fe at room temperature. In the Mössbauer spectra we detected a difference between the deposited alloys on the parts of the substrate far from and near Ar plasma.

### III. Results

Figures 1 and 2 show the X-ray diffraction patterns of $Fe_{1-x}Cr_x$ alloys sputter-deposited on the substrate far from Ar plasma for $0.3 < x < 0.7$ and (b) those for $0.4 < x < 0.55$ in an expanded scale.

![Figure 1](image)

Fig. 1 (a) X-ray diffraction patterns of the $Fe_{1-x}Cr_x$ alloys sputter-deposited on the substrate far from Ar plasma for $0.3 < x < 0.7$ and (b) those for $0.4 < x < 0.55$ in an expanded scale.

The diffraction linewidth of $Fe_{1-x}Cr_x$ alloys deposited on the substrate far from Ar plasma is very broad, probably due to Ar contamination, lattice defects and strain in sputter-deposited alloys as well as their small grain sizes\(^{(15)}\). Provided that the line broadening is mainly ascribed to small grain sizes of sputter-deposited alloys, the

---

\(^{15}\)V. Results

Figures 1 and 2 show the X-ray diffraction patterns of $Fe_{1-x}Cr_x$ alloys sputter-deposited on water cooled substrates far from Ar plasma and near Ar plasma. Due to a preferred orientation of grain growth in sputter-deposited alloys, the intensities of low Miller index planes parallel to the film plane are strong, while those of high index diffraction lines are very weak. Therefore, we estimated crystal structures of the present sputter-deposited alloys by comparing the reported results of Fe–Cr alloys produced with several methods\(^{(8)-(11)}\). The bcc phase appears for $x < 0.4$ and $x > 0.65$. For $0.45 < x < 0.6$, on the other hand, the $\sigma$ phase is obtained on the substrate far from Ar plasma, while the $A15$ phase appears together with the $\sigma$ phase on the substrate near Ar plasma. The diffraction linewidth of $Fe_{1-x}Cr_x$ alloys deposited on the substrate far from Ar plasma is very broad, probably due to Ar contamination, lattice defects and strain in sputter-deposited alloys as well as their small grain sizes\(^{(15)}\). Provided that the line broadening is mainly ascribed to small grain sizes of sputter-deposited alloys, the
average grain size is about 15 nm. On the contrary, the diffraction linewidth of Fe\(_{1-x}\)Cr\(_x\) alloys deposited on the substrate near Ar plasma is rather narrow. The difference in the X-ray diffraction patterns of these Fe-Cr alloys is probably ascribed to the thickness of specimens and the effect of annealing, i.e., the Fe-Cr alloy film deposited on the substrate near Ar plasma is thicker than the Fe-Cr alloy film deposited on the substrate far from Ar plasma and the alloy deposited on the substrates near Ar plasma was annealed by plasma radiations so that lattice defects were removed.

The lattice constants of vapor quenched Fe\(_{1-x}\)Cr\(_x\) alloys estimated from X-ray diffraction measurements are shown in Fig. 3. With the increase in \(x\), the lattice constant monotonically increases for both the Fe-rich and Cr-rich bcc alloys. The lattice constants in the sputtered bcc alloys are almost independent of the position on the substrate and they are about 0.3% larger than those of the solid quenched alloys\(^{14}\). This lattice expansion may be due to a loosely packed structure produced by an incorporation of Ar atoms in the sputtered alloys and interstitial atoms caused by a peening effect\(^{15}\). The lattice constants of the \(\sigma\) phase and the \(\gamma\) phase roughly agree with the reported values\(^{16}\): \(a=0.882\) and \(c=0.442\) nm for the \(\sigma\) phase and \(a=0.457\) nm for the \(\gamma\) phase in the sputter-deposited Fe-Cr alloys.

The spontaneous magnetization was ob-
obtained by linearly extrapolating a magnetization curve at high fields to zero field. Figure 4 shows the magnetic moments, $\mu$, of sputter-deposited Fe$_{1-x}$Cr$_x$ alloys together with the results of bulk Fe$_{1-x}$Cr$_x$ alloys$^{17(18)}$. With the increase in $x$, the magnetic moment at 4.2 K of sputter-deposited bcc alloys decreases in accordance with the concentration dependence of the bulk bcc alloys, following the Slater-Pauling curve. However, it deviates downwards from the Slater-Pauling curve for 0.4 < $x$ < 0.6. This deviation corresponds to the appearance of the $\sigma$ phase, i.e., the $\sigma$ phase is also ferromagnetic at low temperature and its magnetic moment is very small$^{18}$. The magnetization of sputter-deposited alloys recovers to that of bulk bcc alloys for $x$ > 0.6, where the bcc peak reappears, and shows a maximum around $x$ = 0.65.

Figure 5(a) and (b) show the Mössbauer spectra at 4.2 K of Fe$_{1-x}$Cr$_x$ alloys deposited on substrates far from and near Ar plasma, respectively. A ferromagnetic sextet is observed for $x$ < 0.4 and $x$ > 0.65, where a line broadening is due to a distribution of the hyperfine field. A central spectrum superposes on the ferromagnetic sextet and becomes prominent for 0.4 < $x$ < 0.6, where both the $\sigma$ phase and the A15 phases are detected by X-ray diffraction measurements. The line broadening of the central line is attributable to distributions of hyperfine field and electric field gradient caused by a random atomic arrangement in the neighboring configuration of $^{57}$Fe atoms$^{19}$.

From the distribution analysis of the hyperfine field in the Mössbauer spectrum$^{(3)-(5)}$, we obtained the average hyperfine field, $H_{hf}$, of vapor quenched Fe$_{1-x}$Cr$_x$ alloys as shown in Fig. 6. With increasing $x$, $H_{hf}$ gradually decreases in the single bcc phase regions of 0 < $x$ < 0.35 and $x$ > 0.6. These results agree with those of the bulk bcc alloys$^{20(21)}$ and consistent with the concentration dependence of magnetization shown in Fig. 4. The concentration dependence of $H_{hf}$ and $\mu$ in the bcc Fe-Cr alloys has been interpreted by the effect of local environment on the magnetic moment of Fe atoms: the local Fe moment decreases with the increase in the number of Cr atoms on the nearest neighbor atomic sites$^{21}$. Moreover, in the $\sigma$ phase and the $\sigma$ and A15 mixed phase regions with 0.35 < $x$ < 0.6, $H_{hf}$ of vapor

![Mössbauer spectra at 4.2 K of Fe$_{1-x}$Cr$_x$ alloys, (a) sputter-deposited on the substrate far from Ar plasma and (b) sputter-deposited on the substrate near Ar plasma.](image-url)
Nonequilibrium Fe–Cr Alloys Produced by Vapor Quenching

quenched alloys is very small, being in agreement with the result of the bulk σ phase alloy. This result suggests that the Fe atoms carry rather small magnetic moments in these phases. A modified Pauling valence gives very small magnetic moments of Fe atoms in TCP phases. Especially, the magnetic moments of Fe atoms, whose coordination number CN = 12, may be very small or nearly zero. In this context, the σ phase and the A15 phase of Fe–Cr alloys are probably weak ferromagnets.

The Mössbauer spectra at 290 K of Fe$_{1-x}$Cr$_x$ alloys deposited on substrates far from and near Ar plasma for 0.45 $<$ x $<$ 0.65 are shown in Figs. 7(a) and (b). Since these alloys are paramagnetic at 290 K, the broad resonance lines are ascribed to distributions of quadrupole splitting, QS, and isomer shift, IS. Each spectrum was fitted to the superposition of sets of two Lorentzians with different QS, leading to a distribution of QS. Here, the halfwidth of the Lorentzian was assumed to be 0.25 mm/s. Since the doublet structure is asymmetric, we assumed a linear relation between IS and QS to get the best fitting. As shown in Figs. 8(a) and (b), the distribution curves cover the velocity range between 0 and 1.0 mm/s. In the Fe$_{1-x}$Cr$_x$ alloys deposited on the substrate far from Ar plasma, where the σ phase is predominant, they show a very broad distribution without any characteristic structure. On the other hand, the distribution curve has two peaks in the Fe$_{1-x}$Cr$_x$ alloys.

Fig. 6 Concentration dependence of the average hyperfine field, $H_{hf}$, for Fe$_{1-x}$Cr$_x$ alloys. ● and ○: the results at 4.2 and 290 K for the alloys sputter-deposited on the substrate far from Ar plasma. ■ and □: the results at 4.2 and 290 K for the alloys deposited on the substrate near Ar plasma. ▲ and Δ: the results at 4.2 and 290 K for the bulk bcc alloys. ▼: the result at 4.2 K for the σ phase alloy.

Fig. 7 Mössbauer spectra at 290 K of the vapor quenched Fe$_{1-x}$Cr$_x$ alloys with 0.45 $<$ x $<$ 0.65. (a) the results for the alloys sputter-deposited on the substrate far from Ar plasma and (b) the results for the alloys sputter-deposited on the substrate near Ar plasma.

Fig. 8 Distribution of quadrupole splitting, QS, of the Fe$_{1-x}$Cr$_x$ alloys, (a) sputter-deposited on the substrate far from Ar plasma and (b) sputter-deposited on the substrate near Ar plasma.
deposited on the substrates near Ar plasma, where the A15 and σ phases coexist. Since the σ phase has five different atomic sites with different coordination numbers while the A15 phase has only two different atomic sites, we expect five different QS values for the σ phase and two different QS values for the A15 phase. However, lattice defects introduced during sputter-deposition process give rise to a wide variety of the number, spacing and angular distributions of near neighbors around Fe atoms, yielding a distribution of QS in the present Fe-Cr alloys. In this context, QS of the σ phase distributes more widely than QS of the A15 phase, as shown in Fig. 8. The average values of the isomer shift, IS, were -0.12 and -0.15 mm/s for the σ phase and the A15 and σ mixed phase alloys. The negative value of IS is probably ascribed to an increase in the density of s-electrons at Fe nuclei by the addition of Cr atoms whose electronegativity is lower than that of Fe atoms(3)-(5).

### IV. Discussion

Figure 9 shows the nonequilibrium phase diagrams of vapor quenched Fe$_{1-x}$Cr$_x$ alloys determined with X-ray diffraction measurements together with the reported phase diagrams(6)(11)(14). In the vapor quenched alloys, the single bcc phase is obtained for $x<0.4$ and for $x>0.65$, respectively, in contrast to the very narrow stable bcc fields at 290 K in the equilibrium phase diagram. For $0.45<x<0.6$, on the other hand, the σ phase is obtained on the substrate far from Ar plasma, while the A15 and σ mixed phase is obtained on the substrate near Ar plasma. These phase changes reflect in the magnetic and Mössbauer measurements being consistent with the results of X-ray diffraction measurements. A considerable number of alloys forming an amorphous phase have TCP phases in their equilibrium phase diagrams, i.e., for Fe-V alloys, the σ phase appears in the equilibrium state and the amorphous phase in the vapor quenched state(4). However we could not obtain any amorphous phase in the vapor quenched Fe-Cr alloys. Since it has been empirically proposed that the atomic size ratio of the components should be larger than 1.1 for amorphous phase formation(1), the size difference between Fe and Cr is too small to give an amorphous Fe–Cr alloy: Goldschmidt’s radii of Fe and Cr are 0.126 and 0.127 nm(23).

The phase boundaries shown in Fig. 9(a) and (b) are roughly the same to those of Fe$_{1-x}$Cr$_x$ alloys sputter-deposited on liquid-nitrogen cooled substrates and those of Fe$_{1-x}$Cr$_x$ alloys sputter-deposited under $P_{Ar} = 13$ Pa (10 mTorr). The A15 phase has been obtained in the Cr-rich Fe–Cr fine particles by evaporating Fe–Cr alloys in a very high Ar gas atmosphere(11). In this context, we expect the effect of Ar atoms on the A15 phase formation is the
sputter-deposition process. However, we observed no distinct correlation between the Ar gas pressure and the formation of the A15 phase, while the Ar gas pressure shows a strong effect on the morphology of sputter-deposited alloys\(^9\).

It has been proposed that the presence of oxygen impurities plays an important role for the stability of TCP phases\(^{(12)}\): (1) in bulk Fe–Cr alloys, the surface oxidization induces the formation of the \(\sigma\) phase together with an enrichment of Cr concentration at the surface\(^{(24)}\) and (2) in vapor quenched Nb–Ge alloys, the A15 phase is stabilized by a small amount of oxygen during the deposition process\(^{(25)}\). Since Fe–Cr alloys are chemically very active in dissolving oxygen during the sputtering process, oxygen impurities may play a role of catalyst for the formation of the \(\sigma\) phase and the A15 phase.

In intertransition metal alloys with early and late transition metal elements, d-electron bonding gives rise to a large cohesive energy\(^{13,26}\). However, the energy differences between conceivable phases are rather small. In these alloys, preparation methods and conditions take part in the phase stability. Therefore, several nonequilibrium phases can be realized by vapor quenching, because metals and alloys are energized and quenched in this process and, moreover, the surface diffusion of deposited atoms is suppressed enough to inhibit the nucleation of the equilibrium phase on the substrate, (Ostwald step rule)\(^{(27)}\). The present results of vapor quenched Fe–Cr alloys may give a typical example indicating this rule.

**Acknowledgments**

The authors wish to thank Mr. M. Satoh for his assistance in the experiments, Mr. R. Jehara for his technical support and Mr. T. Unesaki for making EPMA (Hitachi, X-650). This work was supported partially by a Grant-in-Aid for Scientific Research given by the Ministry of Education, Science and Culture, Japan (Grant No. 60850132 and Grant No. 61550532).

**REFERENCES**

(1) S. Mader: J. Vac. Sci. Tech., 2 (1965), 35.
(2) K. Sumiyama: Bull. Japan Inst. Metals, 25 (1986), 615.
(3) K. Sumiyama, H. Ezawa and Y. Nakamura: Phys. Status Solidi, (a) 93 (1986), 81.
(4) N. Kataoka, K. Sumiyama and Y. Nakamura: Trans. Japan Inst. Metals, 27 (1986), 823.
(5) K. Sumiyama, H. Ezawa and Y. Nakamura: J. Phys. Chem. Solids, 48 (1987), 255.
(6) D. Turnbull: Metall. Trans., 12A (1981), 695.
(7) R. Wang: Nature, 278 (1979), 700.
(8) R. P. Elliott: Constitution of Binary Alloys, First Suppl., McGraw-Hill, New York, (1965), p. 345.
(9) K. Saiki, K. Saito, K. Onishi, T. Numata, S. Inokuchi and Y. Sakurai: IEEE. Trans. Magnetics, MAG-21 (1985), 1471.
(10) H. J. Schüller and P. Schwaab: Z. Metalluk., 51 (1960), 81.
(11) N. Yukawa, M. Hida, T. Imura, M. Kawamura and Y. Mizuno: Metall. Trans., 3 (1972), 887.
(12) M. V. Nevitt: Intermetallic Compounds ed. by J. H. Westbrook, John-Wiley & Sons. Inc., New York, (1967), p. 217.
(13) R. E. Watson and L. H. Bennett: Acta Metall., 32 (1984), 477.
(14) W. B. Pearson: A Handbook of Lattice Spacings and Structures of Metals and Alloys, Pergamon Press, New York, (1958), p. 332.
(15) K. Sumiyama and Y. Nakamura: Trans. Japan Inst. Metals, 23 (1982), 108.
(16) A. Kimbara: Sputtering Phenomena, Tokyo University Press, Tokyo, (1984), p. 194.
(17) A. T. Aldred: Phys. Rev., B14 (1976), 219.
(18) N. Mōri and T. Mitsui: J. Phys. Soc. Japan, 26 (1969), 1087.
(19) Y. Sumitomo, T. Moriya, H. Ino and F. E. Fujita: J. Phys. Soc. Japan, 35 (1973), 461.
(20) L. H. Schwartz and D. Chandra: Phys. Status Solidi, (b) 45 (1970), 201.
(21) M. Shiga and Y. Nakamura: J. Phys. Soc. Japan, 49 (1980), 528.
(22) V. N. Bykov and I. I. Rudnev: Fiz. Metal. Metallov.-ed., 31 (1971), 1322.
(23) L. S. Darken and R. W. Gurry: Physical Chemistry of Metals, McGraw-Hill, New York, (1953), p. 50.
(24) R. Frattini, G. Longworth, P. Matteazzi, G. Principi and A. Tiziani: Scripta Met., 15 (1981), 873.
(25) A. B. Hallak, R. H. Hammond, T. H. Geballe and R. Zubeck: IEEE Trans. Mag., MAG-13 (1977), 311.
(26) D. G. Pettifor: Phys. Rev. Lett., 42 (1979), 846.
(27) P. H. Shingu and K. Ishihara: Bull. Japan Inst. Metals, 25 (1986), 16.