Nonequilibrium Crystalline and Amorphous Fe–Cu–Ag Ternary Alloys Produced by Vapor Quenching

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Fe$_{1-y}$(Cu$_{1-x}$Ag$_x$)$_y$ alloys sputter-deposited on liquid nitrogen-cooled substrates have been investigated by X-ray diffraction and differential scanning calorimetry. Although this ternary alloy system is typically immiscible in the equilibrium state, a single bcc phase is formed at the Fe-rich corner and a single fcc phase at the Cu- and Ag-rich corners, while an amorphous phase is formed in the central concentration region. The formation of the single bcc and fcc phases is consistent with the results of the vapor quenched binary Fe–Cu, Fe–Ag and Cu–Ag alloys. However, the formation of the single amorphous phase is a new aspect for the vapor quenched ternary Fe–Cu–Ag alloys. The crystallization temperature of amorphous alloys is about 400 K, being insensitive to the alloy concentration.

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I. Introduction

In vapor quenching techniques such as sputter-deposition and thermal evaporation, a high energy vapor solution is condensed onto a cold substrate, leading to several nonequilibrium alloy phases\(^{(1)(2)}\). The following characteristics have been reported for Fe-based binary alloys sputter-deposited on water cooled substrates\(^{(3)}\).

1. Single phase regions of primary solid solutions are greatly extended beyond their narrow concentration regions in the equilibrium phase diagrams.

2. An amorphous phase has been produced in the alloy systems which form topologically close-packed intermetallic compounds in their equilibrium phase diagrams.

Fe forms no solid solution with Cu and Ag at room temperature, and Fe and Ag are immiscible in each other even in the liquid state above 2000 K\(^{(4)}\). The Cu–Ag alloy system is also of two phase separation type\(^{(5)}\). In binary Fe–Cu, Fe–Ag and Cu–Ag alloys sputter-deposited on water-cooled substrates, however, we have obtained wide single phase regions of bcc and fcc\(^{(5)(6)}\).

As the substrate temperature goes down, the surface diffusion of arriving atoms is more reduced on the substrate and nonequilibrium phases can be more easily produced. For thin Cu–Ag alloy films, an amorphous phase has been thermally evaporated on liquid nitrogen cooled substrates\(^{(7)(8)}\), where the amorphous phase is not clear because of the experimental limitation of thin film specimens. Moreover, an amorphous-like phase has been reported for Fe–Ag alloys sputter-deposited on liquid nitrogen cooled substrates\(^{(9)(10)}\), but it has not been clearly defined as an amorphous phase.

On the other hand, by using an rf sputtering apparatus and a liquid-nitrogen cooled substrate, we have obtained no clearly amorphous phase in binary Fe–Cu, Fe–Ag and Cu–Ag alloys\(^{(11)(12)}\), i.e., wider single phase regions of primary solid solutions in Fe–Cu, Fe–Ag and Cu–Ag alloys. Since the ternary alloy may give a variety of nonequilibrium phases, we prepared Fe$_{1-y}$(Cu$_{1-x}$Ag$_x$)$_y$ alloys on liquid nitrogen cooled substrates\(^{(13)}\).
II. Experimental Procedures

Composite type targets were prepared from 99.9% pure Fe, Cu and Ag plates: Fe and Cu square plates of $5 \times 5 \times 1$ mm$^3$ were placed on a Ag disc plate of 80 mm in diameter and 5 mm in thickness. Here, the alloy composition was adjusted by the numbers of Fe and Cu plates. About 2 $\mu$m thick alloy films were deposited onto a polyimide film substrate by a conventional rf sputtering method. The operation parameters are listed in Table 1. Since the substrate was indirectly cooled by liquid nitrogen, the substrate temperature was about 100 K during the sputtering process. The chemical compositions of sputter-deposited alloy films were determined mainly by electron probe microanalysis (EPMA). They were partly measured by an induction coupled plasma (ICP) method and Auger electron spectroscopy (AES). These results were almost consistent with each other. However, a surface segregation was detected by AES measurements on the free side and substrate side layers of about 100 nm thickness in some alloy films. This was indirectly confirmed by EPMA measurements by changing the acceleration voltage of incident electrons. This may mainly be ascribed to oxidation of the film surface and to reactions in boundary layers between the alloy film and the substrate.

In order to know the concentration dependence of physical properties of Fe$_{1-y}$(Cu$_{1-x}$Ag$_x$)$_y$ alloys we tried to keep the value of x or y constant. We could obtain Fe$_{1-y}$(Cu$_{1-x}$Ag$_x$)$_y$ alloys with $y=0.65$ and 0.85 within the experimental error of 1.5%, but we could not obtain those with a constant x value. By using Fe-$K \alpha$ radiations and a graphite monochromator, X-ray diffraction patterns were observed at 290 K. Differential scanning calorimetry (DSC) was done for some deposited films in an Ar atmosphere with a heating rate of about 0.3 K/s in order to detect an exothermic peak.

III. Experimental Results

Figure 1 shows X-ray diffraction patterns of Fe$_{1-y}$(Cu$_{1-x}$Ag$_x$)$_y$ alloys, where the concentration ratio of Ag to Cu is chosen to be around $x=0.4$. The bcc peaks are observed for $y<0.4$, the fcc peaks for $y>0.7$ and both the bcc and fcc peaks for $0.4<y<0.5$, while a halo pattern is observed for $0.5<y<0.65$. In Fig.2, X-ray diffraction patterns of Fe$_{0.35}$(Cu$_{1-x}$Ag$_x$)$_{0.65}$ alloys show the fcc peaks for both $x<0.45$ and $x>0.8$, while a halo pattern for $0.45<x<0.7$. As shown in Fig.3, X-ray diffraction patterns of Fe$_{0.15}$(Cu$_{1-x}$Ag$_x$)$_{0.85}$ alloys show the fcc peaks for both $x<0.4$ and $x>0.55$, while the fcc peaks and a halo pattern for $0.4<x<0.55$. In Fig. 4, X-ray diffraction patterns of Cu$_{1-x}$Ag$_x$ alloys have only fcc peaks for all of x. Moreover, in Figs. 1, 2, 3 and 4, broad tails are observed around Bragg peaks for $x=0.5$ and $y>0.4$.

From these X-ray diffraction measurements, the lattice constants of fcc Fe$_{1-y}$(Cu$_{1-x}$Ag$_x$)$_y$:

| Background pressure | $<80 \mu Pa$ (0.6 \text{ Torr}) |
|---------------------|----------------------------------|
| Ar gas pressure     | 0.53 Pa (4 \text{ mTorr})       |
| Substrate temperature | 100 K                         |
| Input power         | 150 W                           |
| Deposition rate     | 0.08 nm/s                       |

Table 1 Sputtering parameters.
alloys with \( y = 0.65, 0.85 \) and 1.0 are estimated as shown in Fig. 5. The lattice constant monotonically increases with the increase in \( x \).

Since X-ray diffraction measurements are not enough to distinguish an amorphous alloy from a crystalline alloy composed of very small crystallites, DSC measurements were made for some alloy specimens. \( \text{Fe}_{1-y}(\text{Cu}_{1-x}\text{Ag}_x)y \) alloys with \( x \approx 0.4 \) shows a sharp exothermic peak for \( y > 0.4 \) as shown in Fig. 6, while \( \text{Fe}_{0.35}(\text{Cu}_{1-x}\text{Ag}_x)0.65 \) alloys show a sharp exothermic peak only for \( x = 0.5 \) and no sharp
peak for both \(x<0.3\) and \(x>0.75\), as shown in Fig. 7. After the observation of this sharp exothermic peak in the DSC trace for an Fe\(_{0.48}\)(Cu\(_{0.5}Ag\(_{0.5}\))\(_{0.6}\) alloy, we cooled down the specimen to room temperature and measured X-ray diffraction pattern, which gave weak Bragg peaks as shown Fig. 8(b), being different from that of the as-sputtered alloy shown in Fig. 8(a). Therefore, the sharp exothermic peak is ascribed to the crystallization of an amorphous phase. The crystallization temperature, \(T_x\), was determined as the starting temperature of this exothermic effect. For Fe\(_{1-y}\)(Cu\(_{1-x}Ag\(_x\))\(_y\) alloys containing the amorphous phase, \(T_x\) is about 400 K and almost independent of the alloy composition. Non-equilibrium crystalline phases decompose rather gradually, giving no sharp exothermic peak below 600 K, while their phase decomposition is enhanced above 700 K\(^{14,15}\) (see Fig. 8(c)).

IV. Discussion

Figure 9 shows the ternary nonequilibrium
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Phase diagram of Fe$_{1-y}$(Cu$_{1-x}$Ag$_x$)$_y$ alloys determined by X-ray diffraction and DSC measurements. The single phase region of bcc appears in the Fe-rich corner and that of fcc in the Cu- and Ag-rich corners, while the single amorphous phase region in the central concentration region of the triangle. The hatched region indicates the concentration range where we observed a sharp exothermic peak in the DSC trace.

In a vapor quenching process, depression of surface diffusion of adatoms gives rise to a nonequilibrium phase on a low temperature substrate. The possibility of obtaining non-equilibrium phases has been discussed based on the free energy versus composition diagram, while no ternary equilibrium phase diagram has been obtained for the Fe–Cu–Ag alloy system. However, since Cu and Ag are miscible in each other in the liquid state, we can draw schematically the free energy versus composition diagram of pseudobinary Fe$_{1-y}$(Cu$_{1-c}$Ag$_c$)$_y$ alloys for a given value of $x=c$ as shown in Fig. 10. If the nucleation and growth of equilibrium phases are prohibited in this pseudobinary alloys$^{16}$, the single bcc phase is obtained for Fe-rich alloys and the single fcc phase for Cu$_{1-c}$Ag$_c$-rich alloys. In the central concentration range, on the other hand, the amorphous phase is expected, because the atomic arrangement of an amorphous alloy has been often thought to be similar to that of a supercooled liquid alloy and an amorphous phase has been often produced around the eutectic composition of liquid quenched alloys$^{17}$.

The heat of formation of binary alloys has been empirically discussed in terms of the work function, $\phi^*$, and the electron density at the Wigner-Seitz cell boundary, $n_{WS}^{18}$. $\phi^*$ is the electronegativity parameter and a larger difference in $\phi^*$ between constituent elements, $\Delta \phi^*$, gives a more negative formation enthalpy, while a larger difference in $n_{WS}$, $\Delta n_{WS}$, gives a more positive formation enthalpy. Since $\Delta \phi^*$ is very small and $\Delta n_{WS}$ is large for Fe–Cu, Fe–Ag and Cu–Ag alloys, no wide range solution is expected in the equilibrium states. The wide range of solid solutions of

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**Fig. 9** Nonequilibrium phase diagram of ternary Fe$_{1-y}$(Cu$_{1-x}$Ag$_x$)$_y$ sputter-deposited on liquid nitrogen cooled substrates. The results of X-ray diffraction measurements are shown as follows: ◆: the single bcc phase, ○: the single fcc phase, Δ: the single amorphous phase, •: the bcc and fcc mixed phase, Θ: the bcc and amorphous mixed phase, ◼: the fcc and amorphous mixed phase and H: the bcc, fcc and amorphous mixed phase. The hatched region indicates the concentration region where the amorphous phase coexists, as confirmed by an exothermic peak in the DSC trace.

**Fig. 10** Schematic free energy versus concentration diagram of Fe$_{1-y}$(Cu$_{1-c}$Ag$_c$)$_y$ alloys.
vapor quenched Fe\textsubscript{1-y}(Cu\textsubscript{1-x}Ag\textsubscript{x})\textsubscript{y} alloys indicates that a random ternary mixture is favorable at finite temperatures. This suggests that a high temperature phase characterized by a large entropy and a random atomic configuration has a low free energy\textsuperscript{(2)}. Moreover, on the assumption that an amorphous phase is a supercooled liquid, the formation enthalpy of a liquid alloy, $\Delta H_L$, is an appropriate measure for the forming ability of an amorphous phase: an amorphous phase is probably obtained easily for a large negative value of $\Delta H_L$, while it is difficult for a large positive value of $\Delta H_L$. By using the values of $\phi^*$ and $n_{WS}$\textsuperscript{(19)}, the values of $\Delta H_L$ are estimated as +64, +94 and +4 kJ/mol for equiatomic Fe–Cu, Fe–Ag and Cu–Ag alloys, respectively. In this context, the Cu–Ag alloy system is the most favorable for the amorphous phase formation. However, in the present results, the single amorphous phase region is obtained around the central concentration region of the ternary phase diagram of Fe\textsubscript{1-y}(Cu\textsubscript{1-x}Ag\textsubscript{x})\textsubscript{y} alloys.

It has been proposed that the size difference of constituent atoms is a decisive factor in the formation of primary solid solutions in equilibrium alloys: the equilibrium solid solutions may not be obtained if the atomic sizes of the solvent and solute differ by more than 15\%\textsuperscript{(20)}. This empirical rule is consistent with the immiscibility in the equilibrium Fe–Ag and Cu–Ag alloys, but conflicts with the very narrow solubility in the equilibrium Fe–Cu alloy, where Goldschmidt’s radii of Fe, Cu and Ag are 0.126, 0.127 and 0.147 nm\textsuperscript{(21)}. In vapor quenched alloy films prepared on liquid nitrogen cooled substrates, amorphous phases have been obtained for the alloys in which the atomic size ratio of the constituent elements is larger than 10\%\textsuperscript{(1)}. Although this condition is satisfied in Fe–Ag and Cu–Ag alloys, no clear amorphous Fe–Ag alloy could be obtained even on a liquid nitrogen cooled substrate\textsuperscript{(10)}, while an amorphous phase has been reported in Cu–Ag thin films produced by thermal evaporation onto liquid nitrogen cooled substrates\textsuperscript{(8)} and the amorphous and fcc mixed phase is formed in the Cu\textsubscript{0.55}Ag\textsubscript{0.45} alloy sputter-deposited on a liquid nitrogen cooled substrate. On the contrary, the amorphous alloy is obtained for ternary Fe–Cu–Ag alloys, in which the size mismatch condition is almost the same as those of Fe–Ag and Cu–Ag alloys.

In the nonequilibrium phase diagram of Fe–Cu–Ag alloys, the single amorphous phase region is too narrow to discuss the concentration dependence of crystallization temperature, $T_x$, whereas the thermal stability of amorphous alloys may be strongly related with nucleation and growth kinetics of competing crystalline phases at the phase boundary and two phase regions\textsuperscript{(22)}. However, on the assumption that the crystallization process of amorphous alloys is of diffusion-control type, its activation energy turns to be proportional to the formation enthalpy of a monovacancy having the size equal to that of a smaller atom, $\Delta H_h$\textsuperscript{(23)(24)}. $\Delta H_h$ is estimated to be about 118, 103 and 88 kJ/mole for equiatomic Fe–Cu, Fe–Ag and Cu–Ag alloys, respectively, indicating that the thermal stability of amorphous Cu–Ag alloys is improved by an addition of Fe.

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