Development of Fe–P–C–Cu Immiscible Amorphous Alloys with Liquid Phase Separation

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The rapid solidification microstructure and magnetic properties of melt-spun ribbons in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ (at%) alloys were investigated, focusing on the occurrence of liquid-phase separation and simultaneous amorphous-phase formation. The $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ alloys were designed as a combination of Fe–P–C alloy with high glass-forming ability and Cu. Amorphous-phase formation was observed in the melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys. For the melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10$) alloy, a composite of Fe–P–C amorphous matrix and FCC–Cu globules was obtained, whereas in the melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 20$) alloy, multistep liquid-phase separation resulted in a particular solidification microstructure.

KEY WORDS: alloy design; amorphous alloys; metallic glass; rapid solidification; electron microscopy; microstructure; magnetic property.

1. Introduction

Liquid-phase-separation-type (LPS-type) amorphous alloys, in which both LPS and amorphous-phase formation were realized, demonstrated the supercooling of the separated liquids to the liquid-to-glass transition temperature (glass transition temperature) without the crystallization of the liquids, resulting in a particular solidification microstructure that simultaneously included LPS and amorphous-phase formation. LPS behavior with a large amount of supercooling and/or multistep LPS leads to the formation of a solidification microstructure that cannot be achieved through conventional solidification processes in metals. In the case in which a large volume fraction ratio exists in the two liquid phases formed by LPS and a large amount of supercooling of the separated liquids is realized, a nano-emulsion-like structure, in which fine globules from the minor separated liquid are embedded in the matrix from the major separated liquid, is formed. Among the number of immiscible alloys with LPS reported to date, Fe–Cu and Co–Cu alloy systems have been extensively studied both experimentally and theoretically. The Fe–Cu alloy system shows a flat liquidus

line in the thermal-equilibrium phase diagram and does not exhibit a liquid miscibility gap.¹⁾ The existence of a metastable liquid miscibility gap was found experimentally by Nakagawa in an Fe–Cu alloy system.²⁾ The development of LPS-type amorphous alloys was achieved in 2005 and 2006 in Fe–Cu-based alloys of Fe–Cu–Si–B,³⁾ Fe–Cu–Zr–B,⁴⁾ and Fe–Cu–Ni–Si–Sn–B–Y.⁵⁾ To date, a number of LPS-type amorphous alloys were developed in Fe–Cu based alloys of Fe–Cu–Si–B,^{3,6,8)} Fe–Cu–Zr–B,^{4,6,7,9–11)} Fe–Cu–Ni–Si–Sn–B–Y,⁵⁾ Fe–Cu–Nb–B,¹²⁾ Fe–Cu–Ni–P–Si–B,^{13–15)} Fe–Cu–Si–B–Al–Ni–Y,^{16,17)} Fe–Cu–Si–B–Nb,¹⁸⁾ Fe–Cu–Co–Si–B,¹⁹⁾ Fe–Cu–Ni–P,²⁰⁾ and Fe–Cu–Ag–La.^{21–24)} Most of the above-described alloy systems were not developed on Fe–P–C amorphous alloys, whereas the Fe–P–C alloy system was well known as an Fe-based amorphous alloy system.^{25–33)} In this study, Fe–Cu-based LPS-type amorphous alloys based on Fe–P–C amorphous alloys were designed and developed, and the solidification microstructure and magnetic properties of Fe–Cu–P–C alloys were investigated. Notably, the present study did not focus on spinodal-type phase separation or Cu-rich cluster formation in Fe-based amorphous alloys with small amounts of elemental Cu but rather the behavior of LPS in Fe-based amorphous alloys with large amounts of Cu of over 10 at%.

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2. Materials and Methods

(Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x ($x = 10, 20$) (at%) was investigated in the present study, and the alloy design of the (Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x is explained in detail in Section 3. The pre-alloy ingots of Fe–P–C alloy with the nominal alloy composition of Fe₇₅P_{12.5}C_{12.5} [at%] were fabricated from the mixture of electrolytic Fe rumps (Toho Zinc Co. Ltd, Japan, Purity = 3 N), Fe–P pre-alloy ingots (Osaka Alloying Works, Co. Ltd, Japan, 2 N), and artificial graphite (Marutoyo Co., Ltd., Japan) by induction melting with a silica-based crucible under Ar flow and vacuum suction casting using a silica tube. The casting equipment for the fabrication of Fe–P–C pre-alloy ingots was explained in detail in other studies.^{34,35} The melt-spun ribbons were prepared from the mixture of Fe–P–C pre-alloy ingots and Cu wire cuts (Mitsuba Chemical Co., Ltd., Japan, 4 N) by single-roller melt-spinning methods. In the melt-spinning process, the thermal melt of Fe–P–C–Cu alloy was obtained by high-frequency induction heating in a quartz nozzle; then, the thermal melt was ejected onto a Cu roll, which had a circumferential velocity of 42 ms^{−1}. **Table 1** shows the nominal alloy composition (Nom.) and chemical alloy composition (Chem.) evaluated by inductively coupled plasma atomic emission spectroscopy and the infrared absorption method after combustion in the rapidly solidified melt-spun ribbons of the (Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x ($x = 10, 20$) alloys. There is a significant difference in the P composition between the Nom. and Chem., which can be explained by the loss of elemental P during the melting process because of the high vapor pressure of elemental P. The formation of an amorphous phase in the melt-spun ribbons was evaluated by X-ray diffraction (XRD), thermal analysis was performed using differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). DSC was performed at a heating rate of 40 Ks^{−1} under an Ar flow. TEM and scanning TEM (STEM) samples were prepared by an ion-milling method. Microstructures of some alloys were observed by scanning electron microscopy (SEM), TEM, and STEM. The magnetic properties of the samples were measured in the vibrating sample magnetometer mode of the Physical

Properties Measurement System at 300 K. The heat of mixing of an i–j binary alloy (ΔH_{i-j}) was used for the design of the alloy, and the value of ΔH_{i-j} was obtained from the literature.³⁶ The predicted phase diagram based on ab initio calculations was obtained using the Materials Project.^{37,38} The thermal-equilibrium phase diagrams related to the Fe–P–C–Cu alloy system were obtained from AtomWork.^{39,40} The thermodynamic calculations were performed using FactSage (version 7.3)⁴¹ and the SGTE2017 database,⁴² in which all the binary pairs of Fe–Cu, Fe–P, Fe–C, Cu–P, Cu–C, and C–P in the Fe–P–Cu–C alloy system were assessed in SGTE2017.

3. Alloy Design

The mixing enthalpy of the i–j atom pair (ΔH_{i-j}) was an important indicator for the design of LPS-type amorphous alloys. From the perspective of LPS and the formation of an amorphous phase, a basic concept of alloy design is the conflict in characteristics based on the mixing enthalpy. In a binary i–j alloy system, the positive value of the mixing enthalpy of the i–j atom pair (ΔH_{i-j}) is favorable for LPS,^{43–45} whereas the large negative value of ΔH_{i-j} is favorable for amorphous-phase formation.⁴⁶ We suggested the concept for the alloy design of an LPS-type amorphous alloy in a previous paper.¹² This was accomplished with the following two concepts: (1) alloy prediction based on a combination map of mixing enthalpy (ΔH_{i-j}) [kJ/mol] for the binary atomic pairs of the constituent elements and a predicted quaternary phase diagram based on ab initio calculations for forecasting the intermetallic compound formation and (2) thermodynamic calculation for predicting the LPS and the chemical composition of the separated liquids. The alloy design technique was determined to be effective for the design of not only Fe–Cu-based LPS-type amorphous alloys but also other alloys including Fe–Ag-based LPS-type amorphous alloys of Fe–Ag–Si–B,⁴⁷ Co–Cu-based LPS-type amorphous alloys of Co–Cu–Zr–B⁴⁸ and Co–Cu–Zr–Ti–B,⁴⁹ Al–Pb-based LPS-type amorphous alloys of Al–Pb–Co–La,⁵⁰ and high-entropy Co–Cr–Mo–Fe–Mn–W–Ag alloys with LPS behavior.⁵¹ In the present study, the possibility of simultaneous amorphous-phase formation and LPS in the Fe–P–C–Cu alloy system, combining the Fe–P–C alloy system with high glass-forming ability (GFA) and Cu was discussed.

Figure 1 shows the prediction for LPS-type amorphous alloys in the Fe–P–C–Cu alloy system by the alloy design method suggested in the literature.¹² In the ΔH_{i-j} [kJ/mol] matrix (Fig. 1(a)), Cu–Fe pairs showed large positive values (+13), corresponding to the flat liquidus in the Fe–Cu thermal-equilibrium phase diagram.⁵² The ΔH_{i-j} in the Fe–P (−39.5) and Fe–C (−50) pairs showed large negative values. These corresponded to the existence of Fe–P compounds⁵³ in the thermal equilibrium phase diagram and the formation of Fe₃C (cementite) in the Fe–C alloys. The negative atomic pairs of Fe–P (−39.5), Fe–C (−50), and P–C (−4.5) indicate a high GFA in the Fe–P–C alloy system. The value of ΔH_{i-j} in Cu–P (−17.5) was large negative, and this corresponded to the existence of Cu–P compounds⁵⁴ in the thermal equilibrium phase diagram. The value of ΔH_{i-j} in Cu–C (−33) was large negative, similar to that in Cu–P.

Table 1. Nominal alloy composition (Nom.) and chemical alloy composition (Chem.) evaluated by inductively coupled plasma atomic emission spectroscopy and the infrared absorption method after combustion in high-frequency induction furnace in the rapidly solidified melt-spun ribbons of the (Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x ($x = 10, 20$) alloys. The composition was expressed by the atomic percent [at%]: (a) $x = 10$, (b) $x = 20$.

(a) $x = 10$				
	Fe	P	C	Cu
Nom.	67.50	11.25	11.25	10.00
Chem.	73.15	7.06	10.61	9.18
(b) $x = 20$				
	Fe	P	C	Cu
Nom.	60.00	10.00	10.00	20.00
Chem.	65.00	6.30	9.45	19.24

(a) Heat of mixing, ΔH_{i-j} [kJ/mol]

	Fe	P	C	Cu
Fe		-39.5	-50	+13
P			-4.5	-17.5
C				-33
Cu				

(b) Predicted phase diagram

Fig. 1. Prediction method for the possibility of simultaneous amorphous-phase formation and liquid-phase separation in Fe–P–C–Cu alloy system: (a) predicted Fe–P–C–Cu quaternary phase diagram by ab initio calculations, (b) combination map of ΔH_{i-j} [kJ/mol] of binary atomic pairs of constituent elements in quaternary Fe–P–C–Cu alloys. (Online version in color.)

The occurrence of LPS from the single-liquid phase to the separated liquid condition, composed of Fe–P–C-rich and Cu-rich liquids, was not predicted only by the ΔH_{i-j} matrix (Fig. 1(a)). Figure 1(b) shows the predicted Fe–P–C–Cu phase diagram shown in the ground state at 0 K. Focusing on the relationship between Fe–P–C and Cu in Fig. 1(b), the following tendencies can be observed. (1) There are no intermetallic compounds in the binary Fe–Cu or C–Cu alloy systems, ternary Fe–Cu–C alloy system, or quaternary Fe–P–C–Cu alloy system. (2) Only binary Cu–P compounds were seen in the binary Cu–P alloy system. The ΔH_{i-j} matrix and predicted phase diagram in the Fe–P–C–Cu alloy system (Fig. 1(a)) indicated the possibility of a separation of the liquid phase to Fe–P–C-rich and Cu-rich liquid when the formation of Cu–P was suppressed during the cooling of the thermal melt. The LPS tendency in Fe–P–C–Cu alloy system was discussed in more detail by the thermodynamic calculation as denoted in the latter part.

(a) Free energy

(b) Predicted liquid miscibility gap

Fig. 2. Thermodynamic calculation of the Gibbs free energy of liquid phase and calculated phase diagram focusing on the liquid-phase separation in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 0\text{--}100$) alloys: (a) Gibbs free energy of the single liquid (broken lines) and the mixture of the separated liquids (solid lines) and (b) the calculated phase diagram focusing on the liquid-phase separation (the inset is the magnified image at the Fe–P–C-rich side). (Online version in color.)

The alloy composition of quaternary Fe–P–C–Cu alloys was determined by the following procedure with the discussion about the LPS tendency. (1) The alloy composition with the highest GFA in ternary Fe–P–C alloy,⁵⁵⁾ $\text{Fe}_{75}\text{P}_{12.5}\text{C}_{12.5}$ [at%] was selected in this study. (2) The free energy of the liquid phase in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ alloys, which was a combination of $\text{Fe}_{75}\text{P}_{12.5}\text{C}_{12.5}$ and Cu, was evaluated by thermodynamic calculation using FactSage ver. 7.3 and SGTE2017. The alloy compositions that contained the possibility of LPS was selected. The thermodynamic calculations are shown in Fig. 2. Figure 2(a) shows the temperature dependence of the Gibbs free energy curves of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ alloys. The Gibbs free energy of

the single-liquid phase (indicated by the black broken line) was higher than that of the two-liquid state (indicated by the red solid line) at 1 000, 1 500, and 2 000 K, with a wide x range in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ alloys. This indicates the occurrence of LPS in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ alloys at temperatures at and below 2 000 K when the crystallization of the thermal melt is suppressed. The liquid miscibility gap in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ alloys constructed by the Gibbs free energy is shown in Fig. 2(b). The mixture of the separated Fe–P–C-rich and Cu-rich liquids was more stable than that of the single-liquid state with a wide x range in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ alloys. **Table 2** shows the composition of the separated Fe-rich liquids evaluated by the thermodynamic calculations. The atomic composition ratio of Fe/P/C in the Fe-rich liquid phase was roughly similar to 75/12.5/12.5 in $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ at $x = 10$ (Table 2(a)) and $x = 20$ (Table 2(b)) regardless the temperature (Fe/P/C = 75/12/13 at 1 500 K in $x = 10$ alloy, Fe/P/C = 76/11/13 at 1 000 K in $x = 10$ alloy, Fe/P/C = 75/12/13 at 2 000 K in $x = 20$ alloy, Fe/P/C = 76/11/13 at 1 500 K in $x = 20$ alloy, Fe/P/C = 77/10/13 at 1 000 K in $x = 20$ alloy, respectively), where $\text{Fe}_{75}\text{P}_{12.5}\text{C}_{12.5}$ was reported to show the highest GFA in ternary Fe–P–C alloys.⁵⁵⁾ The solubility of Cu in Fe-rich liquid drastically decreased with a decrease in temperature. This indicates that the high GFA of the separated Fe-rich liquid phase was formed through the LPS behavior. Based on the above-described prediction and calculation results, $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys, namely, $\text{Fe}_{67.5}\text{P}_{11.25}\text{C}_{11.25}\text{Cu}_{10}$ ($x = 10$) and $\text{Fe}_{60}\text{P}_{10}\text{C}_{10}\text{Cu}_{20}$ ($x = 20$) (at%) alloys, were prepared. The thermodynamic calculation implies the high LPS tendency in Fe–P–C–Cu alloys (Fig. 2), while the ΔH_{i-j} matrix (Fig. 1(a)) and the predicted ground states (Fig. 1(b)) implies the difficulty in LPS via Cu–P intermetallic compounds formation. The difference may be low melting temperature of Cu–P intermetallic compound: for example, the congruent melting temperature of Cu_3P is 1297 K at SGTE2017, and temperature is lower than the liquid miscibility gap temperature in $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys.

Table 2. Thermodynamic calculation results of the atomic composition of the separated Fe-rich liquids in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys. The composition was expressed by the atomic percent [at%]: (a) $x = 10$, (b) $x = 20$.

(a) $x = 10$				
Temp [K]	Fe	P	C	Cu
1500	71.60	11.27	12.01	5.12
1000	75.34	11.27	12.58	0.82

(b) $x = 20$				
Temp [K]	Fe	P	C	Cu
2000	64.52	10.03	11.06	14.39
1500	72.59	10.08	12.36	4.98
1000	76.42	10.01	12.78	0.79

4. Results and Discussion

Figure 3 shows the outer appearance of the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys. The continuous ribbon formation was observed in the melt-spun ribbon of Fe–P–C–Cu alloys, regardless of alloy composition. The $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10$) alloy exhibits a metallic silver color (Fig. 3(a)), whereas the melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 20$) alloy (Figs. 3(b1), 3(b2)) show a coppery with metallic luster color, which was also reported in Co–Cu–Si–B alloys^{56,57)} wherein the formation of a macroscopically phase-separated dual-layer structure, including a Cu-based

Fig. 3. Outer appearance of the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys. The inset shows the magnified images for (a) $x = 10$, (b1, b2) $x = 20$. Figure 3(b2) is the magnified image of melt-spun ribbons including free surface side (Free surface) and wheel-contacted side (wheel-contacted). (Online version in color.)

alloy layer on the free surface side and a Co-based amorphous alloy layer, was established. The coppery color was observed on the free surface side, while the metallic silver color was detected in the Co–Cu–Si–B alloy.^{56,57)} Figure 3(b2) shows the magnified image of the melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 20$) alloy. The smooth surface, typical of melt-spun amorphous ribbons, was observed on the free surface side, whereas the rough surface was noticed on the wheel-contacted side, which was due to gas entrainment during the melt-spinning process. Although the coppery color was observed on both the free surface and wheel-contacted sides of the melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 20$) alloy (Fig. 3(b2)), the surface roughness posed a difficulty toward presenting detailed discussions on the color of the melt-spun ribbons. The color difference between the free surface and wheel-contacted sides, which was similar to the case of Co–Cu–Si–B alloys,^{56,57)} was unobservable in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 20$) alloy. This result shows that the Fe–P–C–Cu alloys possessed high ribbon-forming ability, and the color of the melt-spun ribbons was dependent on the alloy composition.

Figure 4 shows the XRD patterns of the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys. No difference in XRD patterns was found between the free-surface side (Free) and wheel-contacted side (Wheel), regardless of alloy composition. This result indicates that the formation of a macroscopically phase-separated dual-layer structure, reported in the melt-spun ribbon of LPS-type amorphous alloys of Fe–Ag–Si–B⁴⁹⁾ and Co–Cu–Si–B,^{56,57)} was not observed in Fe–P–C–Cu alloys. Sharp diffraction peaks (black open circle, ○) overlapping the broad peak were observed in the $x = 10$ and $x = 20$ alloys. Sharp diffraction peaks could be indexed as FCC–Cu. These results indicate that an amorphous phase

was formed in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys, regardless of alloy composition, and a composite of an amorphous phase and FCC–Cu crystalline phases was formed in the $x = 10$ and $x = 20$ alloys.

To clarify the formation of an amorphous phase in the Fe–P–C–Cu alloys, DSC analysis and TEM observation of the melt-spun ribbons were performed. **Figure 5** shows the DSC curves of the melt-spun ribbons in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys. The $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys showed a sharp exothermic peak, independent of alloy composition. The onset temperature of the exothermic peak was 736 K for the $x = 10$ alloy and 735 K for the $x = 20$ alloy at a heating rate of 0.67 K s^{-1} . The heat release by exothermic reaction was 105.1 J g^{-1} for the $x = 10$ alloy and 65.2 J g^{-1} for the $x = 20$ alloy. The morphology of the exothermic peak and the onset temperature for the $x = 10$ alloy were similar to those for the $x = 20$ alloy, whereas the amount of heat released for the exothermic peak decreased with increasing Cu concentration in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys. The crystallization temperature (T_x) in the Fe–P–C amorphous alloys was reported as follows: $T_x = 693 \text{ K}$ evaluated by thermal analysis with a heating rate exceeding 1.67 K s^{-1} for $\text{Fe}_{83.1}\text{P}_{9.8}\text{C}_{7.1}$ alloy,²⁵⁾ $T_x = 690 \text{ K}$ evaluated by DSC with a heating rate of 0.33 K s^{-1} for $\text{Fe}_{75}\text{P}_{15}\text{C}_9$ alloy,³⁰⁾ $T_x = 693 \text{ K}$ evaluated by DSC with a heating rate of 0.033 K s^{-1} for $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy,³¹⁾ $T_x = 703 \text{ K}$ evaluated by DSC with a heating rate of 0.05 K s^{-1} for $\text{Fe}_{80}\text{P}_{15}\text{C}_5$ alloy,³³⁾ $T_x = 784 \text{ K}$ evaluated by DSC with a heating rate of 0.17 K s^{-1} for $\text{Fe}_{83}\text{P}_{13}\text{C}_7$ ($\text{Fe}_{78.5}\text{P}_{13.25}\text{C}_{7.25}\text{Ti}_{0.55}\text{Cr}_{0.45}$ with trace elements of Mo and Al) alloy,⁵⁸⁾ $T_x = 713\text{--}723 \text{ K}$ evaluated by DSC with a heating rate of 0.33 K s^{-1} for $\text{Fe}_{83}\text{P}_{10}\text{C}_7$, $\text{Fe}_{80}\text{P}_{15}\text{C}_5$, and $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloys,⁵⁹⁾ respectively. The similarity in the onset temperature of the exothermic peak in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys (Fig. 5) and the T_x reported in the above-described studies

Fig. 4. XRD patterns of the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys. The indices Wheel and Free refer to the wheel-contacted side and free-surface side, respectively. (Online version in color.)

Fig. 5. DSC curves of the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys. (Online version in color.)

Fig. 6. TEM-BF images and corresponding SAD patterns of the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys: (a1) (a2) $x = 10$, (b1) (b2) (b3) $x = 20$.

and the similarity in the morphology of the exothermic peak of the DSC curve in Fig. 5 and that of the DSC curve in the above-described studies indicate that the exothermic peak in DSC curves (Fig. 5) corresponded to the crystallization of an amorphous phase.

Figure 6 shows the TEM-BF images and corresponding selected area electron diffraction (SAD) patterns of the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys. In the bright field (BF) image of the $x = 10$ alloy (Fig. 6(a1)), the crystalline globules with diameters of 10–100 nm were embedded in the featureless contrast matrix. Amorphous-phase formation at $x = 10$ alloy was confirmed by the featureless contrast region in the TEM-BF images (Figs. 6(a1)) and the halo rings in the SAD pattern (Fig. 6(a2)). The discontinuous Debye rings in Fig. 6(a2) can be indexed as FCC–Cu phase. In the $x = 20$ alloy, two different microstructures indicated by index A (Figs. 6(b1), 6(b2)) and index B (Fig. 6(b3)) were observed. In the TEM-BF image of region A in the $x = 20$ alloy (Fig. 6(b1)), the composite structure of the crystalline globules and amorphous matrix was observed. In the corresponding SAD pattern (Fig. 6(b2)), discontinuous Debye rings corresponding to the FCC–Cu phase and broad halo rings corresponding to an amorphous phase were observed. The microstructure in region A of the $x = 20$ alloy (Fig. 6(b1)) was similar to that of the $x = 10$ alloy (Fig. 6(a1)). Figure 6(b3) shows the TEM-BF images focusing on region B, where the featureless contrast phases with ellipsoidal morphology were embedded in the white contrast matrix. The broad peaks in the XRD patterns (Fig. 4), exothermic peak in DSC curves (Fig. 5), and featureless contrast in the TEM-BF image (Figs. 6(a1), 6(b1)) and halo rings in the SAD patterns (Figs. 6(a2), 6(b2)) indicated the formation of an amorphous phase in the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys.

To investigate the solidification microstructure in the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$

Fig. 7. STEM-BF image and elemental mapping of Fe, P, and Cu of the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10$) alloy.

($x = 10, 20$) LPS-type amorphous alloys in more detail, STEM observations were performed focusing on the elemental distribution of elemental Fe, P, and Cu. **Figure 7** shows the STEM-BF image and elemental mapping of Fe, P, and Cu of the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10$) alloy. The STEM-BF image (Fig. 7, left and upper side) shows a similar structure as that shown in the TEM-BF image (Fig. 6(a1)). The results of elemental mapping show the following features: (1) elemental Cu is concentrated in the spherical crystalline phases embedded in the amorphous matrix, (2) solubility of Fe and P in the spherical Cu crystalline phases is much lower than that in the amorphous matrix, (3) elemental Fe and P are concentrated in the amorphous matrix, while the solubility of Cu in the Fe–P-rich amorphous matrix is significantly small. The XRD analysis (Fig. 4), DSC mea-

surements (Fig. 5), and TEM (Fig. 6) and STEM (Fig. 7) observations indicate the formation of a composite structure with FCC–Cu nanocrystalline globules and Fe–P–C amorphous matrix in the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10$) alloy. The particular solidification microstructure in the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10$) alloy was explained by the LPS as the following. (1) LPS occurred during the cooling of the thermal melt, resulting in the formation of major Fe–P–C-rich liquid and minor Cu-rich liquid. This assumption was supported by the thermodynamic calculation results (Fig. 2, Table 2). (2) Major Fe–P–C-rich liquid was frozen at the glass transition temperature, resulting in a Fe–P–C amorphous matrix. (3) Minor Cu-rich liquid droplets dispersed in the Fe–P–C matrix crystallized, resulting in the formation of FCC–Cu nanocrystalline globules.

Figure 8 shows the STEM-HAADF image and elemental

(a) low magnification image

(b1) magnified image, region A

(b2) magnified image, region B

Fig. 8. STEM-HAADF image and elemental mapping of Fe, P, and Cu of the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 20$) alloy: (a) low magnification image, (b1) elemental mapping focusing on region A, (b2) elemental mapping focusing on region B. (Online version in color.)

(a) $x = 10$

(b) $x = 20$

Fig. 9. Magnetic properties of the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys: (a) $x = 10$, (b) $x = 20$. (Online version in color.)

mapping of Fe, P, and Cu of the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 20$) alloy, focused on the differences in regions A and B in the TEM-BF image (Fig. 6(b3)). In region A (Figs. 8(a), 8(b1)), elemental Cu was enriched in the globules embedded in the Fe–P-rich matrix, indicating that the characteristics of the elemental distribution in region A in the $x = 20$ alloy were similar to those in the $x = 10$ alloy. In region B (Figs. 8(a), 8(b2)), the Fe–P-rich phase with ellipsoidal morphology was embedded in the Cu-rich matrix. The LPS temperature of the $x = 20$ alloy was higher than that of the $x = 10$ alloy in the calculated phase diagram focused on the liquid miscibility gap (Fig. 2). The solidification microstructure in $x = 20$ alloy can be explained by the multistep LPS during cooling without any discrepancy: (1) the LPS occurred during the

cooling of the thermal melt, resulting in the formation of a Fe–P–C-rich liquid with Cu and Cu-rich liquid with Fe, P, and C; (2) subsequent LPS in the Fe–P–C-rich liquid with Cu occurred, resulting in the formation of region A; (3) subsequent LPS in the Cu-rich liquid with Fe, P, and C occurred, resulting in the formation of region B.

Figure 9 shows the magnetic properties of the rapidly solidified melt-spun ribbons of the $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10, 20$) alloys. The magnetization-magnetic-field (M-H) loops and the magnified image displayed in the inset show that the rapidly solidified melt-spun ribbons has typical ferromagnetism. The coercive force (H_c) was 1.6×10^3 A/m for the $x = 10$ alloy and 1.9×10^3 A/m for the $x = 20$ alloy. The value of H_c of the Fe–P–C and Fe–P–C related amorphous alloys was reported as the following: $H_c = 9.5$ A/m for the

X in Fe-X-based or Co-X-based alloys		Cu	Ag
Structures			
(1) Macroscopically separated ribbons			Fe-P-C-Ag
(2) Macroscopically phase separated structure			Fe-Si-B-Ag
(3) Macro- and nano- phase separated structure		Fe-Cu-Si-B-Nb Fe-Cu-Co-Si-B Co-Cu-Si-B	
(4) Macro- and nano- phase separated structure		<u>Fe-P-C-Cu</u> (high Cu) Fe-Cu-Ni-Si-Sn-B-Y Fe-Cu-Ni-P-Si-B Fe-Cu-Si-B-Al-Ni-Y	
(5) Nano-scale phase separated structure		<u>Fe-P-C-Cu</u> (low Cu) Fe-Cu-Si-B Fe-Cu-Zr-B Fe-Cu-Nb-B Fe-Cu-Ni-P-Si-B Co-Cu-Zr-B Co-Cu-Zr-Ti-B	

Fig. 10. Taxonomy of the microstructure in melt-spun ribbons of the Fe–Cu-, Fe–Ag-, and Co–Cu- based immiscible amorphous alloys with liquid phase separation. In the alloy systems, the underlined alloys of Fe–P–C–Cu (low Cu) and Fe–P–C–Cu (high Cu) mean $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 10$) and $(\text{Fe}_{0.75}\text{P}_{0.125}\text{C}_{0.125})_{100-x}\text{Cu}_x$ ($x = 20$), respectively.

Fe₈₀P₁₃C₇ alloy,⁶⁰⁾ $H_c = 80$ A/m for the Fe₇₃P₁₁C₅Al₅Ga₂B₄ alloy,⁶¹⁾ and $H_c = 2.9$ A/m for the Fe₈₀P₉C₉B₂ alloy.⁶²⁾ The H_c values in the (Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x ($x = 10, 20$) alloys were at least one order of magnitude higher than those in the Fe–P–C and Fe–P–C-related amorphous alloys developed to date. The dispersion of the FCC–Cu nanocrystalline globules in the Fe–P–C amorphous matrix led to the increase in H_c in the (Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x ($x = 10, 20$) alloys.

The characteristics of the microstructure of the Fe–P–C–Cu immiscible amorphous alloys with LPS were discussed based on the taxonomy of the microstructures of Fe- and Co-based immiscible alloys with LPS. The result is presented in Fig. 10. Notably, the microstructure of Fe- and Co-based immiscible amorphous alloys was strongly dependent on the liquid ejection temperature,^{15–18)} as well as other processes, such as the rotating-water-atomization process,³⁾ double-chamber-crucible-type melt-spinning process,²⁰⁾ and arc-melt-type melt-extraction method.⁶³⁾ Figure 10 does not present the fine but, rather, the rough classification of the microstructure of melt-spun ribbons. The formation of macroscopically phase-separated ribbons (1) was reported in Fe–P–C-based Fe–P–C–Ag alloys. The macroscopic phase-separated structures among types (2), (3), and (4), as well as the differences in the constituent phase and color between the free surface and wheel-contacted sides or those between the outer and inner regions of the melt-spun ribbons were observed in cases (2) and (3), while such differences were undetected in case (4). Macroscopically phase-separated structures with Ag-based crystalline phase layers and Fe-based Fe–Si–B amorphous phase layers (2) were reported in Fe–Si–B–Ag alloys,⁴⁷⁾ whereas these structures with Cu-based alloy layers and Fe-based amorphous phase layers, including the Cu-based alloy dispersed phase (3), were reported in Fe–Si–Nb–B–Cu¹⁸⁾ and Fe–Co–Si–B–Cu¹⁹⁾ alloys. Furthermore, macroscopically phase-separated structures with Cu-based alloy phase layers and Co-based amorphous phase layers, including the Cu-based alloy dispersed phase (3), were reported in Co–Si–B–Cu alloys.^{56,57)} The above-mentioned structures of the immiscible amorphous alloys formed via LPS (1, 2, and 3) were not observed in the Fe–P–C–Cu alloys in this study, while the structure composed of an Fe-based amorphous region with a Cu-rich alloy dispersed phase, as well as a Cu-rich alloy region with an Fe-based alloy dispersed phase (4) was obtained in the Fe–Ni–Si–B–Y–Cu–Sn,⁵⁾ Fe–Ni–P–Si–B–Cu,^{13–15)} Fe–Cu–Si–B–Al–Ni–Y,^{16,17)} and (Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x ($x = 20$) (Fe–P–C–Cu (high Cu)) alloys. Nano Cu crystalline globule dispersed Fe-based amorphous alloy melt-spun ribbons (5) were obtained in quaternary (Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x ($x = 10$) (Fe–P–C–Cu (low Cu)) alloys, wherein the characteristic of the microstructure of the melt-spun ribbons was similar to that in the quaternary Fe–Cu–Zr–B of Fe₆₀Cu₁₀Zr₁₀B₂₀,^{4,10,11)} Fe₅₀Cu₂₀Zr₁₀B₂₀,^{4,10,11)} Fe–Cu–Si–B of Fe_{52.5}Si₇B_{10.5}Cu₃₀,⁶⁾ Fe–Cu–Nb–B of Fe₆₀Nb₈B₁₂Cu₂₀,¹²⁾ alloys. Moreover, nano Cu crystalline globule dispersed Co-based amorphous alloy melt-spun ribbons (5) were also reported in Co–Cu-based Co–Cu–Zr–B⁴⁸⁾ and Co–Cu–Zr–Ti–B⁴⁹⁾ alloys. The severe phase-separated structure categorized by types (1), (2), and (3) was not observed in (Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x ($x = 10, 20$) alloys. The microstructure of the immiscible amorphous alloys with LPS was strongly dependent on the alloy system,

and the characteristics of the Fe–P–C-based Fe–P–C–Cu immiscible amorphous alloy with LPS, including the Cu composition dependence, were clarified herein.

5. Conclusions

Fe–Cu-based LPS-type amorphous alloys based on Fe–P–C alloys, with high GFA were developed. The microstructure and magnetic properties of the melt-spun ribbons in the (Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x alloys were investigated. The obtained results and conclusions are summarized as follows.

(1) Amorphous-phase formation was detected in the (Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x ($x = 10, 20$) alloys.

(2) Spherical FCC–Cu nanocrystals on the order of 10–100 nm were dispersed in a Fe–P–C amorphous matrix in the rapidly solidified melt-spun ribbons of the (Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x ($x = 10$) alloy.

(3) Multistep LPS in (Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x ($x = 20$) resulted in the particular solidification microstructure composed with the “FCC–Cu globules dispersed in Fe–P–C amorphous matrix” and “Fe–P-based phases with ellipsoidal morphology dispersed in Cu-rich matrix.”

(4) Rapidly solidified melt-spun ribbons of the (Fe_{0.75}P_{0.125}C_{0.125})_{100-x}Cu_x ($x = 10, 20$) alloys showed typical ferromagnetism.

(5) Alloy design using the mixing enthalpy map, predicted phase diagrams constructed by the Materials Project, and thermodynamic calculation using FactSage and SGTE database was effective in obtaining Fe–Cu–P–C LPS-type amorphous alloys.

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