Microstructure and Magnetic Properties of Cu–Ag–La–Fe Immiscible Alloys with an Amorphous Phase^{*1}

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The solidification microstructure and magnetic properties of rapidly solidified melt-spun ribbons in Cu_{43.2}Ag_{32.0}La_{4.8}Fe₂₀ (at%) alloy, which was designed as the combination of the Cu–Ag-based Cu₅₄Ag₄₀La₆ alloy with high glass-forming ability and Fe, was investigated. The composite of an amorphous matrix and dispersed crystalline phases were obtained in the melt-spun ribbons. The spherical BCC-Fe nanocrystals, which were surrounded by Cu-rich crystalline phases, were embedded in a Cu–Ag–La-based amorphous matrix. The particular solidification structure in melt-spun ribbons can be explained by liquid-phase separation to form major Cu–Ag–La-rich and minor Fe-rich liquids, an amorphous phase formation in major Cu–Ag–La-rich liquid, and the crystallization of the separated Fe-rich liquid globules during the cooling of the thermal melt. The melt-spun ribbon shows typical ferromagnetic magnetic properties caused by the 10 nm-ordered spherical BCC-Fe nanocrystals. [doi:10.2320/matertrans.Y-M2019803]

(Received December 25, 2018; Accepted January 15, 2019; Published March 1, 2019)

Keywords: amorphous alloy, rapid solidification, electron microscopy, microstructure, magnetic property

1. Introduction

Liquid-phase-separation-type amorphous alloys, in which both liquid-phase separation and amorphous-phase formation were realized, showed 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 with liquid-phase separation and an amorphous-phase formation. The liquid-phase-separation behavior with a large amount of supercooling and/or multistep liquid-phase separation leads to the formation of a solidification microstructure that cannot be achieved through conventional solidification processes in metals. In the case where a large volume fraction ratio exists in two liquid phases formed by liquid-phase separation and a large amount of supercooling of the separated liquids is realized, a nano emulsion-like structure, in which the fine globules from the minor separated liquid are embedded in the matrix from the major separated liquid, is formed. Among a number of immiscible alloys with liquid-phase separation

reported to date, the Fe–Cu alloy system has been extensively studied experimentally and theoretically. The Fe–Cu alloy system shows a flat liquidus line in the thermal-equilibrium phase diagram,¹⁾ and does not show a liquid miscibility gap. When the liquid phase is supercooled, it shows a metastable liquid miscibility gap.²⁾ The development of liquid-separation-type amorphous alloys was achieved in 2005 and 2006 in Fe–Cu-based alloys.^{3–5)} Fe–Cu-based liquid-separation-type amorphous alloys were summarized in the literature.⁶⁾ The Fe–Ag alloy system exhibits a clear liquid miscibility gap in the equilibrium phase diagram, and the Ag solid solubility in the Fe crystal and the Fe solid solubility in the Ag crystal are extremely small.⁷⁾ A liquid-phase-separation-type amorphous alloy can also be obtained in the Fe–Ag alloy system.^{8–10)} The microstructures of Fe–Cu-based and Fe–Ag-based liquid-phase-separation-type amorphous alloys developed to date were classified into the following two types: (1) the composite of minor Cu-based fine crystalline globules and Fe-based amorphous matrix and (2) the composite of minor Ag-based crystalline phase and Fe-based amorphous matrix with a macroscopically phase-separated structure. Cu-rich and Ag-rich liquid-phase-separation-type amorphous alloys have not been reported. Cu-rich Cu–Fe-based and Ag-rich Ag–Fe-based liquid-phase-separation-type amorphous alloys were significantly interesting, because of the microstructure and magnetic properties: the alloys show a particular microstructure composed of nanoscale spherical BCC-Fe nanocrystals and a nonmagnetic Cu-based and/or Ag-based amorphous matrix. The nanoscale BCC-Fe globules may show specific magnetic properties due to the nano-scale size effect, such as superparamagnetics.

In this study, Cu–Ag-rich liquid-phase-separation-type amorphous alloys with nanoscale spherical BCC-Fe nano-

^{*1}This Paper was Originally Published in Japanese in J. Jpn. Soc. Powder Powder Metallurgy **65** (2017) 45–51. To explain more precisely the background, the purpose of the study, experimental procedures, and results, some parts of the contents were slightly revised. Reference 10) was added as the reference for the Fe–Ag-based liquid-phase-separation-type amorphous alloys. References 11–13) were added to explain the liquid-phase-separation behavior in the Fe–Cu-based alloy system in more detail. Reference 14) was added to explain the relationship between an amorphous-phase formation and the mixing enthalpy of constituent elements in more detail. Reference 27) was added to explain the cooling rate during the arc-melting process in more detail. References 31–33) were added as references for the Co–Cu-based liquid-phase-separation-type amorphous alloys.

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Fig. 1 Prediction method for Cu–Ag–La–Fe alloys, showing the possibility of amorphous-phase formation and liquid-phase separation simultaneously: (a) combination map of $\Delta H_{i,j}$ of binary atomic pairs of constituent elements in quaternary Cu–Ag–La–Fe alloys and (b) predicted Cu–Ag–La–Fe quaternary phase diagram by *ab initio* calculations.

crystals were designed and developed, and the solidification microstructure and magnetic properties of Cu–Ag–La–Fe alloys were investigated.

2. Alloy Design

From the viewpoint of liquid-phase separation and formation of an amorphous phase, a basic concept of alloy design is the conflicting 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 ($\Delta H_{i,j}$) is favorable for the liquid-phase separation,^{11–13)} whereas the large negative value of $\Delta H_{i,j}$ is favorable for an amorphous-phase formation.¹⁴⁾ A new concept for the alloy design of liquid-phase-separation-type amorphous alloys was previously suggested.¹⁵⁾ This was accomplished with the following two concepts: (1) alloy prediction based on a combination map of mixing enthalpy ($\Delta H_{i,j}$) for binary atomic pairs of the constituent elements and a predicted quaternary phase diagram based on *ab initio* calculations for predicting the intermetallic compound formation and (2) thermodynamic calculation for predicting the liquid-phase separation and the chemical composition of the separated liquids.

Figure 1 shows the prediction results for liquid-phase-separation-type amorphous alloy formation in the Cu–Ag–La–Fe alloy system combining the Cu–Ag–La alloy system with high glass-forming ability (GFA)¹⁶⁾ and Fe. The Cu–Ag–La–Fe alloy system was designed based on (1) liquid-phase separation to form the Cu–Ag–Fe-rich liquid and Fe-rich liquid and (2) an amorphous-phase formation in the separated Cu–Ag–La-based liquid. In this study, the heat of mixing in i – j binary alloy ($\Delta H_{i,j}$) was taken from the literature,¹⁷⁾ and the predicted phase diagram based on the *ab initio* calculation was obtained using the Materials Project.^{18,19)} The thermal-equilibrium phase diagrams related to the Cu–Ag–La–Fe alloy system were obtained from AtomWork.^{20,21)} In the enthalpy map (Fig. 1(a)), Cu–Fe and Ag–Fe pairs showed large positive values, corresponding to the flat liquidus in the Fe–Cu thermal-equilibrium phase diagram²⁾ and liquid miscibility gap in the Fe–Ag thermal-equilibrium phase diagram.⁷⁾ The heat of mixing in the Fe–La pair shows a small positive value. The Fe–La thermal-equilibrium phase diagram was not perfectly assessed, and the possibility of the existence of a liquid miscibility gap was

reported.^{23,24)} Based on the Fe–La thermal equilibrium phase diagram, the solubilities of La in the Fe phase and that of Fe in the La phase were extremely small. In contrast, the heat of mixing in Cu–La and Ag–La pairs showed large negative values, and these corresponded to the existence of Cu–La- and Ag–La-based intermetallic compounds in thermal-equilibrium phase diagrams.^{24,25)} The heat of mixing in the Ag–Cu pair shows small negative values. The thermal-equilibrium Ag–Cu phase diagram shows the typical eutectic-type phase diagram without intermetallic compounds.²⁶⁾ The absolute values of $\Delta H_{i,j}$ in Fe–La and Ag–Cu pairs were smaller than those of Cu–Fe, Ag–Fe, Cu–La, and Ag–La pairs. The enthalpy map focusing on $\Delta H_{i,j}$ in Cu–Fe, Ag–Fe, Cu–La, and Ag–La pairs implies the occurrence of liquid-phase separation and the formation of the Cu–Ag–La-rich and Fe-rich liquids through the liquid-phase separation. Figure 1(b) shows the predicted Cu–Ag–La–Fe phase diagram based on the *ab initio* calculation. There are no intermetallic compounds in binary Ag–Fe, Cu–Fe, and La–Fe alloy systems, ternary Ag–Cu–Fe, Ag–La–Fe, and Cu–La–Fe alloy systems, and the quaternary Ag–Cu–La–Fe alloy system. The available thermal-equilibrium phase diagrams^{7,20–26)} and predicted phase diagram based on the Materials Project^{18,19)} indicate that the liquid-phase separation of the liquid phase to Cu–Ag–La-rich and Fe-rich liquid was not prevented by the formation of intermetallic compounds composed of Cu–Ag–La and Fe elements.

The alloy composition of quaternary Cu–Ag–La–Fe alloys was determined by the following procedure. (1) The alloy composition with the highest GFA in ternary Cu–Ag–La alloy¹⁶⁾ was selected. Cu₅₄Ag₄₀La₆ [at%] was chosen in this study. (2) The free energy of the liquid phase in (Cu_{0.54}Ag_{0.4}La_{0.06})_{100–x}Fe_x alloy, which was a combination of Cu₅₄Ag₄₀La₆ and Fe, was evaluated by thermodynamic calculation. The composition in alloys having the possibility of liquid-phase separation was selected. The thermodynamic calculation results are shown in Fig. 2 using FactSage (version 6.4) and the SGTE 2007 database.²⁷⁾ Figure 2(a) shows the temperature dependence of the Gibbs-free-energy curves of (Cu_{0.54}Ag_{0.4}La_{0.06})_{100–x}Fe_x alloy. The Gibbs free energy of the single-liquid phase (indicated by the solid line) was higher than that of two-liquid state (indicated by the broken line) at 1000, 1500, and 2000 K with a wide x range in (Cu_{0.54}Ag_{0.4}La_{0.06})_{100–x}Fe_x alloys. This indicates

Fig. 2 Thermodynamic calculation of the Gibbs free energy of liquid phase and the calculated phase diagram focusing on the liquid-phase separation in $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 0 \sim 100$) alloys: (a) Gibbs free energy of 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 Cu–Ag-rich side).

Table 1 Thermodynamic calculation results of the atomic composition of the separated liquids in $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloys: (a) Cu–Ag-rich liquid and (b) Fe-rich liquid.

(a) Cu–Ag-rich liquid

Temp. [K]	Cu [at. %]	Ag [at. %]	La [at. %]	Fe [at. %]
500	54.3	40.3	5.4	0.0
1000	54.3	40.4	5.1	0.3
1500	52.7	40.1	4.9	2.3
2000	49.3	39.1	4.8	6.9

(b) Fe-rich liquid

Temp. [K]	Cu [at. %]	Ag [at. %]	La [at. %]	Fe [at. %]
500	0.0	0.0	2.5	97.5
1000	0.8	0.0	3.7	95.5
1500	6.0	0.1	4.5	89.5
2000	16.3	1.0	4.9	77.8

the occurrence of liquid-phase separation in $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ alloys at temperatures at and below 2000 K. The liquid miscibility gap in $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ alloys constructed by the Gibbs free energy is shown in Fig. 2(b). The mixture of the separated Cu–Ag–La-rich and Fe-rich liquids was more stable than the single-liquid state with a wide x range in $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ alloys. Table 1 shows the composition of the separated two liquid phases evaluated by the thermodynamic calculation. The composition of the Cu–Ag-rich liquid phase (Table 1(a)) was close to $\text{Cu}_{54}\text{Ag}_{40}\text{La}_6$, and the solubility of Fe in the Cu–Ag-rich liquid phase was significantly low. This indicates the high GFA of the separated Cu–Ag-rich liquid phase formed through the liquid-phase separation. The thermodynamic calculation results showed that the solubility of Cu and Ag in the minor Fe-rich liquid phase (Table 1(b)) decreased with

the decrease in temperature, and it is extremely small at and below 1000 K. Based on the above prediction and calculation results, the $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 2, 10, 20$) alloys, namely, $\text{Cu}_{59.52}\text{Ag}_{39.2}\text{La}_{5.88}\text{Fe}_2$, $\text{Cu}_{48.6}\text{Ag}_{36}\text{La}_{5.4}\text{Fe}_{10}$, and $\text{Cu}_{43.2}\text{Ag}_{32}\text{La}_6\text{Fe}_{20}$ (at%) alloys, were prepared. For the comparison, a $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 0$) alloy without Fe, namely, $\text{Cu}_{54}\text{Ag}_{40}\text{La}_6$ (at%), was also prepared as a reference.

3. Experimental Procedures

The alloy ingots of $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 0, 2, 10, 20$) alloy were fabricated by arc melting of the mixture of Cu wire cuts (purity, 4N), Ag shots (4N), electrolytic Fe (3N), and La cutting scrap (2N). The cooling rate of the arc-melting process in the present study was estimated at approximately 2000 K s^{-1} by experimental evaluation via the secondary dendrite arm spacing measurements in Al–Cu alloy.²⁸⁾ The total amount of the arc-melted ingots was approximately 20 g. The melt-spun ribbons were prepared from the arc-melted ingots by single-roller melt-spinning methods. In the melt-spinning process, the arc-melted specimens were melted by high-frequency induction heating in a quartz nozzle; then, the thermal melt was ejected to a Cu roll whose circumferential velocity was 42 ms^{-1} . The formation of an amorphous phase in the melt-spun ribbons was evaluated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). 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 (VSM) mode of the Physical Properties Measurement System (PPMS).

4. Results

Figure 3 shows the optical microscopy (OM) picture and the SEM back-scattering electron (BSE) image of the cross

Fig. 3 The OM picture and the SEM-BSE image of the cross section of the arc-melted ingot in $(\text{Cu}_{0.54}\text{Ag}_{0.40}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy: (a) OM picture and (b) SEM-BSE image focusing on the interface between Fe-rich and Cu.

section of the arc-melted ingot in $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy. In the sectional OM image (Fig. 3(a)), the lower side corresponds to the bottom side that was in contact with the copper hearth. The formation of a macroscopically phase-separated interface, which was formed through liquid-phase separation and the aggregation of the separated liquid, was observed. Figure 3(b) shows the SEM-BSE image focusing on the interface between Fe-rich (upper part) and Cu–Ag rich (lower part) regions. The interface between the Fe-rich region and Cu–Ag-rich region was macroscopically smooth. Spherical regions with white contrast dispersed in the Fe-rich matrix with dark gray contrast was observed, as shown by black arrows. These features in the solidification microstructure indicate the occurrence of liquid-phase separation during the arc-melting process in $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy.

Figure 4 shows the outer appearance of the rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 0, 20$) alloys. In the $x = 0$ alloy without Fe (Fig. 4(a)), continuous ribbons were formed. The formation of continuous ribbons was also confirmed in $x = 20$ alloy with Fe (Fig. 4(b)). This result shows that the Cu–Ag–La–Fe alloys possessed high ribbon-forming ability together with ternary Cu–Ag–La alloys without Fe.

Figure 5 shows XRD patterns of the rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 0, 2, 10, 20$) alloys. Figure 5 shows the XRD patterns obtained from the free-surface side in melt-spun ribbons. In the present study, no difference in XRD patterns was found between the free-surface side and wheel-contacted side, regardless the Fe concentration. This result indicates that the formation of a macro phase separation structure^{8–10)} reported in the Fe–Ag-based liquid-separation-type amorphous alloy

Fig. 4 Outer appearance of the rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.40}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 0, 20$) alloys: $x =$ (a) 0 and (b) 20.

was not observed in the Cu–Ag–La–Fe alloys. In the XRD pattern of the $x = 0$ alloy without Fe and the $x = 2$ alloy containing a small amount of Fe, only a broad peak having a peak at approximately $2\theta = 41^\circ$ was observed. In contrast, sharp diffraction peaks were observed in $x = 10$ and 20 alloys with Fe, overlapping the broad peak. Sharp diffraction peaks could be indexed as FCC–Ag, FCC–Cu, and BCC–Fe. These results indicate that an amorphous phase was formed in $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 0, 2, 10, 20$) alloys, regardless of the Fe content, and a composite of an amorphous phase and crystalline phases was formed in $x = 10$ and 20 alloys.

To evaluate the solidification microstructure of the Cu–Ag–La–Fe alloys with the composite of amorphous and crystalline phases, TEM and STEM observations were performed of the rapidly solidified melt-spun ribbons in $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloys. The results are shown in Figs. 6 and 7. Figure 6 shows TEM microstructures of rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy. In the bright field (BF) image (Fig. 6(a1)) and magnified BF image (Fig. 6(a2)), the spherical crystalline phase whose diameter was approximately 50 nm (indicated by the black arrows) was embedded in the featureless contrast matrix. An amorphous-phase formation was confirmed by the featureless contrast region in TEM-BF images (Figs. 6(a1), 6(a2)) and the halo rings in the selected area electron diffraction (SAD) pattern (Fig. 6(b)). The crystalline phases embedded in an amorphous matrix were not dispersed independently, and several crystalline phases were aggregated. Figure 7 shows STEM microstructures of rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy. In the STEM-BF image (Fig. 7(a)) and the STEM high-angle annular dark field (HAADF) image (Fig. 7(b)), spherical

Fig. 5 XRD patterns of the rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.40}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 0, 20$) alloys.

Fig. 6 TEM microstructures of rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.40}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy: (a1) BF image, (a2) magnified BF image, and (b) corresponding SAD pattern.

crystalline phases were dispersed in an amorphous matrix. The results of element mapping (Figs. 7(c1)–7(c4)) show the following features: (1) Fe concentrates in the spherical crystalline phases embedded in the amorphous matrix, (2) the solubility of Ag, Cu, and La in the spherical Fe crystalline phases is much lower than those in an amorphous matrix, (3) the spherical Fe crystalline phases are surrounded by Cu-rich crystalline phases, and (4) Cu, Ag, and La concentrate in the amorphous matrix, while the solubility of Fe in the amorphous matrix is significantly small. The XRD analysis (Fig. 5) and the TEM (Fig. 6) and STEM (Fig. 7) observations indicate the formation of a composite structure with spherical BCC-Fe nanocrystals, Cu-rich crystalline phases around the spherical BCC-Fe nanocrystals, and an Cu–Ag–La-rich amorphous matrix in the rapidly solidified

Fig. 7 STEM microstructures of rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.40}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy: (a) BF image, (b) HAADF image, (c1) Cu image, (c2) Ag image, (c3) La image, and (c4) Fe image.

melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy.

Figure 8 shows the magnetic properties of rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy. The magnetization–magnetic-field (M – H) loop (Fig. 8(a)) and its inset of the magnified image show that the rapidly solidified melt-spun ribbon of Cu–Ag–La–Fe alloy has typical ferromagnetism. The coercive force was on the order of 100 Oe. The magnetic susceptibility was reduced at a magnetic field of at and above approximately 5000 Oe, and this was considered to be the effect of the diamagnetism of Cu and/or Ag. In the curves of zero-field cooling (ZFC) and field cooling (FC) shown in Fig. 8(b), the difference between ZFC and FC was observed at and below approximately 170 K, as indicated by the black arrow. This was thought to be caused by the pinning of the domain wall. In general, magnetic metal nanoparticles are known to exhibit superparamagnetism; however, the magnetic properties in rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy did not show superparamagnetism. The above-described results show that spherical BCC-Fe nanocrystals on the order of 50 nm dispersed in a Cu–Ag–La-rich amorphous matrix do not exhibit superparamagnetism and have ferromagnetism similar to general bulk BCC-Fe.

Fig. 8 Magnetic properties of rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.40}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy: (a) M–H loop and (b) ZFC and FC curves.

5. Discussion

The formation of liquid-phase-separation-type amorphous alloys with spherical BCC-Fe nanocrystals and a Cu–Ag–La-rich amorphous matrix was confirmed by XRD analysis (Fig. 5) and TEM (Fig. 6) and STEM (Fig. 7) observations in the rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy. The thermodynamic calculation results of the liquid miscibility gap (Fig. 2(b)) showed that the temperature of the liquid miscibility gap was much higher than the melting point of pure iron (1811 K) in the $x = 20$ alloy. This implies that spherical BCC-Fe nanocrystals were formed through the following process: (1) the liquid-phase separation occurred during rapid cooling of the thermal melt, resulting in the formation of the main Cu–Ag–La-rich and minor Fe-rich liquids, (2) the main Cu–Ag–La-rich liquid was frozen as a Cu–Ag–La-rich amorphous matrix, and (3) the minor Fe-rich liquid globules crystallized to spherical BCC-Fe nanocrystals. There is a possibility of the formation of spherical BCC-Fe nanocrystals through the nucleation and growth mechanism with a polymorphic-type precipitation reaction from the single Cu–Ag–La–Fe amorphous phase. However, a polymorphic-type reaction without the distribution of elements was not applicable in Cu–Ag–La–Fe alloys because of the significant difference in the chemical composition between spherical BCC-Fe nanocrystals and Cu–Ag–La-rich amorphous matrix. The formation of minor Fe-rich liquid globules formed by liquid-phase separation is considered to be an important factor for the formation of a particular solidification microstructure with spherical BCC-Fe nanocrystals embedded in a Cu–Ag–La amorphous matrix.

STEM observation (Fig. 7) clarified that Cu-rich crystalline phases were formed around spherical BCC-Fe nanocrystals, resulting in the cluster of crystalline phases embedded in an amorphous matrix in the rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy. The clusters of crystalline phases embedded in an amorphous matrix were also observed by TEM (Fig. 6). These indicate that the distribution of Cu-rich crystalline phases was not homogeneous, whereas spherical BCC-Fe

nanocrystals were randomly distributed, because the spherical BCC-Fe nanocrystals formed through the liquid-phase separation. The Cu-rich cluster become the nucleation site of spherical BCC-Fe nanocrystals in the Fe-rich Fe–Zr–B–Cu amorphous alloy containing Cu as a minor element.^{29,30} The nucleation and growth of BCC-Fe may have progressed based on the Nishiyama–Wassermann relation and/or the Kurdjumov–Sachs crystallographic orientation relationship.³⁰ These reports also imply that Cu-rich crystalline phases can be easily formed based on the BCC-Fe crystalline phase. The formation of the crystalline clusters composed of spherical BCC-Fe nanocrystals surrounded by Cu-rich crystalline phases embedded in a Cu–Ag–La-rich amorphous matrix was explained by the liquid-phase separation and the formation of Cu-rich crystalline phases based on the spherical BCC-Fe nanocrystals.

In this study, a Cu–Ag-rich liquid-phase-separation-type amorphous alloy composed of a Cu–Ag-rich amorphous matrix and minor spherical BCC-Fe nanocrystals was successfully developed. The alloy design⁶ based on (1) alloy prediction using the mixing enthalpy map and the predicted phase diagram obtained by *ab initio* calculation, shown in Fig. 2, and (2) thermodynamic calculation focusing on the liquid miscibility gap, shown in Fig. 3, was applicable not only in Fe-rich Fe–Cu-based alloys,^{3–6} Fe-rich Fe–Ag-based alloys,^{8–10} Co–Cu-based alloys,^{31–33} and Al–Pb rich alloys,³⁴ but also in Cu–Ag-rich Fe–Cu–Ag-based alloys. In the rapidly solidified melt-spun ribbons of the $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy, the solidification microstructure showed spherical BCC-Fe nanocrystals on the order of 50-nm diameter embedded in the Cu–Ag-rich amorphous matrix. The magnetic properties of the rapidly solidified melt-spun ribbons of Cu–Ag–La–Fe alloys showed the typical ferromagnetism (Fig. 8) and can be explained by magnetic properties of 10-nm-ordered spherical BCC-Fe nanocrystals similar to those of bulk BCC-Fe. Further reduction of the size of spherical BCC-Fe nanocrystals may lead to superparamagnetism in the rapidly solidified melt-spun ribbons in Cu–Ag–La–Fe alloys, and these are future research challenges. The alloy design combined with the mixing enthalpy map based on the empirical alloy design methods,

predicted phase diagram obtained by *ab initio* calculation, and thermodynamic calculation for developing the liquid-phase-separation-type amorphous alloy⁶⁾ is effective for developing alloys with fine spherical BCC-Fe nanocrystals using the liquid-phase-separation phenomenon.

6. Conclusions

Cu–Ag-rich Cu–Ag–La–Fe liquid-phase-separation-type amorphous alloys, which were designed as a combination of Cu–Ag–La alloy with high GFA and Fe, were developed. The microstructure and magnetic properties of melt-spun ribbons in $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ alloys were investigated. The obtained results and conclusions are summarized as follows.

- (1) Amorphous phase formation was detected in $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 0, 2, 10, 20$) alloys.
- (2) Spherical BCC-Fe nanocrystals on the order of 10 nm were dispersed in a Cu–Ag–La-rich amorphous matrix in rapidly solidified melt-spun ribbons in $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy. Spherical BCC-Fe nanocrystals were surrounded by the Cu-rich phases. The particular solidification microstructure of the composite of spherical BCC-Fe nanocrystals and a Cu–Ag–La-rich amorphous matrix was considered to be formed via liquid-phase separation.
- (3) Rapidly solidified melt-spun ribbons of $(\text{Cu}_{0.54}\text{Ag}_{0.4}\text{La}_{0.06})_{100-x}\text{Fe}_x$ ($x = 20$) alloy showed typical ferromagnetism.
- (4) Alloy design using the mixing enthalpy map, the predicted phase diagrams constructed by *ab initio* calculation, and thermodynamic calculation was effective to obtain the Cu–Ag-rich Cu–Ag–La–Fe liquid-phase-separation-type amorphous alloys.

Acknowledgments

A part of this research was carried out with the support of the 24th research grant from the Kansai Research Foundation for Technology Promotion (KRF). The authors are grateful to Prof. T. Tanaka and Prof. M. Suzuki at the Osaka University for their help with the thermodynamic calculations.

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