Formation of Nanocrystalline Globules and Metallic Glass in Fe$_{70-x}$Cu$_x$Zr$_{10}$B$_{20}$ ($x = 0$–70) Alloys

Takeshi Nagase, Akimasa Yokoyama and Yukichi Umakoshi*

Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

The microstructure in rapidly-solidified Fe$_{70-x}$Cu$_x$Zr$_{10}$B$_{20}$ ($x = 0$, 10, 20, 30, 35, 60 and 70) alloy ribbons prepared by single-roller melt-spinning method was examined. In spite of the positive heat of mixing in Fe–Cu atom pair, metallic glass was formed in Fe–Cu–Zr–B ribbons. Size of the globules in nano-emulsion structure increased with increasing Cu concentration. In Fe$_{35}$Zr–Cu nano crystalline globules dispersed in Fe–Zr–B based metallic glass was formed in Fe–Cu–Zr–B alloys. Size of the globules in nano-emulsion structure increased with increasing Cu concentration. In Fe$_{35}$Cu$_{70}$Zr$_{10}$B$_{20}$ and Fe$_{35}$Cu$_{60}$Zr$_{10}$B$_{20}$ alloys, an entangled marble-like duplex structure composed of Fe-rich and Cu-rich crystalline phases was formed. Zr and B additions in Fe–Cu based alloys cause the formation of metallic glass and unique solidification structures in rapidly solidified melt-spun ribbons.

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1. Introduction

The glass-forming ability (GFA) of metallic materials is known to be large in a liquid stabilized alloy system where the free energy of liquid is lowered to a large extent by alloying. In such a case, a “deep eutectic” exists in the phase diagram. From the viewpoint of heat of mixing ($\Delta H_{\text{mix}}$), a large negative value is effective in forming the deep eutectic. Many binary metallic amorphous alloys were developed based on the strategy of “large negative $\Delta H_{\text{mix}}$”.$^{1}$ Recently, new amorphous alloys called metallic glasses were found in a lot of alloy systems.$^{2}$ Metallic glasses show a glass-to-liquid transition during conventional differential scanning calorimetry (DSC) measurement and a supercooled liquid region can be maintained in the range between the glass-to-liquid transition temperature ($T_g$) and crystallization temperature ($T_x$). Inoue et al. proposed three empirical rules for obtaining metallic glasses: (1) multi-component systems consisting of more than three elements, (2) significant difference above 12% in atomic size ratio among the three main constituent elements, and (3) negative $\Delta H_{\text{mix}}$ among these three main constituent elements.$^{2}$ The simultaneous satisfaction of these three empirical rules causes a topologically and chemically unique glassy structure with an extremely high degree of dense-random-packing (DRP). The negative $\Delta H_{\text{mix}}$ is necessary for obtaining not only conventional amorphous alloys but also metallic glasses.

Metallic glass is often formed in a composition close to a deep eutectic in multi-component system composed of elements with high negative $\Delta H_{\text{mix}}$. The atomic pair with a large positive $\Delta H_{\text{mix}}$ is believed not to be favorable for obtaining metallic glasses. Since it causes the flat liquidus and/or liquid miscibility gap in the phase diagram, the homogeneous mixture of alloying elements with DRP structure is difficult to achieve in alloy systems composed of elements with large positive $\Delta H_{\text{mix}}$, resulting in destabilizing the liquid phase and no formation of amorphous phase even by rapid solidification.

Recently, two-phase amorphous alloys were reported through liquid phase separation in La–Zr–Al–Ni–Cu,$^{3}$ Y–Ti–Al–Co$^{4}$ and Ni–Nb–Y.$^{5}$ Formation of two-phase amorphous alloy requires high GFA for the alloy and a demixing tendency of components. In such a multi-component alloy system, phase separation in liquid state occurs first and then each liquid region composed of elements with high negative $\Delta H_{\text{mix}}$ undergoes liquid-to-glass transition, resulting in the formation of a two-phase amorphous.

Fe–Cu alloy system is well known to have a metastable liquid miscibility gap below the liquidus because of the diminishing component of Fe–Cu atom pair.$^{6-18}$ The separation of Fe and Cu elements in melt-spun binary Fe–Cu and ternary Fe–Cu–B alloys was confirmed.$^{19}$ Considering the GFA of Fe-rich and Cu-rich phases based on three empirical rules,$^{2}$ Zr and B were selected for glass former multi-component alloys as an element with high negative $\Delta H_{\text{mix}}$ accompanied by a big difference in atomic size ratio.

Figure 1 shows $\Delta H_{\text{mix}}$ and atomic size ratio ($\Delta r$) among Fe, Cu, Zr and B atoms. Although the combination of Fe, Zr and B elements in a Fe-rich component system satisfies the three empirical rules, the Cu, Zr and B combination in the Cu-rich component system cannot satisfy them; the $\Delta H_{\text{mix}}$

(a) heat of mixing [kJ/mol]

(b) atomic radius ratio [%]

Fig. 1 Mixing enthalpy ($\Delta H_{\text{mix}}$) and atomic size ratio ($\Delta r$) among Fe, Cu, Zr and B atoms.

*Corresponding author, E-mail: umakoshi@mat.eng.osaka-u.ac.jp
value of Cu–B atom pair is strongly positive. In spite of one positive deviation of $\Delta H_{\text{mix}}$ in the Cu–B atom pair, the quaternary Fe–Zr–Cu–B alloy system is expected to form two phase amorphous regions.

In the present study, the microstructure of rapidly solidified Fe$_{70-x}$Cu$_{x}$Zr$_{10}$B$_{20}$ ($x = 0$–70) alloys was examined focusing on formation of amorphous phase in an alloy system having a metastable miscibility gap.

2. Experimental Procedure

The composition of Zr = 10 at% and B = 20 at% was selected from previous work; Fe$_{71}$Zr$_{9}$B$_{20}$ metallic glass shows the highest $\Delta T_\alpha$ ($= T_\alpha - T_g$, $T_\alpha$ is the onset temperature for crystallization) among Fe$_{71-x}$Zr$_{x}$B$_{20}$ alloys. Master ingots of Fe$_{70-x}$Cu$_{x}$Zr$_{10}$B$_{20}$ ($x = 0$, 10, 20, 30, 35, 60 and 70) alloys were prepared from Fe, Cu, Zr, B and ferroboron by arc melting under purified Ar atmosphere on a water-cooled copper substrate. Rapidly quenched ribbons with a cross section of about 2.0 mm $\times$ 0.02 mm were produced from the ingots by single-roller melt-spinning method. The quenching apparatus with a 200 mm diameter copper roller was operated in an Ar atmosphere. The rotation speed of the roller was 4000 min$^{-1}$ so that the roller surface velocity was about 42 ms$^{-1}$. A quartz crucible of 14 mm diameter with an orifice of about 1.0 mm was used. The gap between the crucible bottom and roller surface was controlled within 0.4 mm. The quantity of melt per run was about 5 g. The pressure of ejection gas was 0.04 MPa. The temperature of melt before ejection was around 1723 K. Structure of the melt-spun ribbon was examined by X-ray diffractometry using Cu-K$\alpha$ radiation, optical microscope (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HREM), electron probe micro analysis (EPMA) and TEM-energy dispersive X-ray analysis (TEM-EDX). Thin foil for TEM and HREM observation was prepared by ion milling. Thermal properties of the ribbon were determined by differential scanning calorimetry (DSC) and differential thermal analysis (DTA).

3. Results

3.1 Microstructure of rapidly solidified melt-spun ribbon

Figure 2 shows XRD patterns of rapidly solidified melt-spun ribbons. XRD patterns of the internal area of ribbons were obtained from the polished specimens. Melt-spin specimens in Fe$_{70}$Zr$_{10}$B$_{20}$ and Fe$_{60}$Cu$_{10}$Zr$_{10}$B$_{20}$ alloys show only a typical broad halo peak at around 2$\theta$ = 44 degree for an amorphous single phase. With the further increase in Cu content, sharp diffraction peaks corresponding to crystalline phases appeared. F.c.c.–Cu phase was observed in Fe$_{50}$Cu$_{35}$Zr$_{10}$B$_{20}$ alloy. The intensity of f.c.c.–Cu phase peak increased with increasing Cu concentration. In Fe$_{55}$Cu$_{15}$Zr$_{10}$B$_{20}$ alloy, not only sharp diffraction peaks of f.c.c.–Cu phase but also that of $\alpha$-Fe phase can be seen. Some diffraction peaks could not be indexed as f.c.c.–Cu phase and $\alpha$-Fe phase. The identification of the peaks was very difficult because of the few peaks or many candidates. In

![Fig. 2 XRD patterns of melt-spun Fe$_{70-x}$Cu$_{x}$Zr$_{10}$B$_{20}$ ($x = 0$, 10, 20, 30, 35, 60 and 70) alloys.](image)

![Fig. 3 DSC curves of melt-spun Fe$_{70-x}$Cu$_{x}$Zr$_{10}$B$_{20}$ ($x = 0$, 10, 20, 30, 35, 60 and 70) alloys. (b) is close-up of (a) at the temperature near glass transition temperature ($T_g$).](image)
Fe$_{60}$Cu$_{10}$Zr$_{10}$B$_{20}$ and Cu$_{70}$Zr$_{10}$B$_{20}$ alloys, sharp diffraction peaks corresponding to f.c.c.–Cu and B$_2$Zr phase are observed. No clear broad diffraction peaks corresponding to an amorphous phase are seen. An amorphous phase in the Fe-rich component system of Fe$_{70}$Zr$_{10}$B$_{20}$ alloy prepared by single-roller melt-spinning phase was confirmed, while that in the Cu-rich component system of Cu$_{70}$Zr$_{10}$B$_{20}$ alloy could not be obtained. The XRD results show the tendency for GFA to decrease with increasing Cu content. To confirm the amorphous phase, conventional DSC measurement at a heating rate of 0.67 Ks$^{-1}$ was performed. The results are shown in Fig. 3. The sharp exothermic peak which may correspond to crystallization can be seen in Fe$_{70}$Zr$_{10}$B$_{20}$, Fe$_{60}$Cu$_{10}$Zr$_{10}$B$_{20}$ and Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ alloys, which is in good agreement with the XRD analysis. The intensity of the exothermic peak decreases with increasing Cu content, while the position and the shape do not change. In Fe$_{40}$Cu$_{30}$Zr$_{10}$B$_{20}$, a small exothermic peak was observed. The position of the onset was almost the same as that in Fe$_{70}$Zr$_{10}$B$_{20}$, Fe$_{60}$Cu$_{10}$Zr$_{10}$B$_{20}$ and Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ alloys. A small amount of Fe-based amorphous phase may form in Fe$_{40}$Cu$_{30}$Zr$_{10}$B$_{20}$ alloy. No exothermic peaks exit in Fe$_{35}$Cu$_{35}$Zr$_{10}$B$_{20}$ or Fe$_{10}$Cu$_{60}$Zr$_{10}$B$_{20}$ alloys and there was no evidence of an amorphous phase from XRD analysis and DSC measurement. Cu$_{70}$Zr$_{10}$B$_{20}$ alloy showed an exothermic peak whose position was different from that in Fe-rich alloys; the intensity of this peak was much smaller than that of Fe$_{70}$Zr$_{10}$B$_{20}$ alloy. There are many reports on the formation of an amorphous phase in Cu–Zr binary alloys through a rapid solidification process, while little is known about
ternary Cu–Zr–B alloys. The origin of the exothermic peak in Cu_{70}Zr_{10}B_{20} alloy is not yet clear. Figure 3(b) shows a closeup of the exothermic peak in Fig. 3(a). In Fe_{70}Zr_{10}B_{20}, Fe_{60}Cu_{10}Zr_{10}B_{20} and Fe_{50}Cu_{20}Zr_{10}B_{20} alloys, an anomalous endothermic reaction was observed before the exothermic reaction corresponding to thermal crystallization. These three alloys showed a glass-to-liquid transition at \( T_g \) before crystallization.

Figure 4 shows a back electron scattering image (BEI) by SEM microstructure in rapidly solidified melt-spun ribbons. Fe_{60}Cu_{10}Zr_{10}B_{20} (a) shows weak contrast and an ultra fine grain structure in the BEI image. In Fe_{50}Cu_{20}Zr_{10}B_{20} alloy (b), the emulsion structure of globules with bright contrast homogeneously embedded in dark gray matrix is seen. Nano-
emulsion structure is formed through rapid solidification by single-roller melt-spinning method. The size of globules in the emulsion structure increases with increasing Cu concentration and the morphology of spherical bright globules changes to ellipsoidal morphology as shown in Fe$_{40}$Cu$_{30}$Zr$_{10}$B$_{20}$ alloy (c). There is a great difference in microstructure between Fe$_{40}$Cu$_{30}$Zr$_{10}$B$_{20}$ and Fe$_{35}$Cu$_{35}$Zr$_{10}$B$_{20}$ (d) alloys. Fe$_{35}$Cu$_{35}$Zr$_{10}$B$_{20}$ alloy formed not an emulsion structure but an entangled duplex structure, where the interface between Fe-rich and Cu-rich regions was very smooth and curved. This entangled duplex structure is reported to as a “marble-like structure” in the present study. Formation of the marble-like structure cannot be explained by dendritic growth and/or eutectic growth during the solidification process. Little is known about the marble-like structure former alloy systems or the formation mechanism. The unique marble-like structure can be seen in Fe$_{10}$Cu$_{60}$Zr$_{10}$B$_{20}$ alloy (e), where the size of the bright gray region and dark gray region is larger than that in Fe$_{35}$Cu$_{35}$Zr$_{10}$B$_{20}$ alloy. In Cu$_{60}$Zr$_{10}$B$_{20}$ alloy (f), the dark gray precipitates with facet interface were embedded in the white gray matrix. The dark gray precipitates were identified as B$_2$Zr phase from XRD, EPMA and TEM observation. The microstructure depended on Cu content in quaternary Fe–Cu–Zr–B alloys; the emulsion structure and marble-like structure were observed in rapidly-solidified specimens obtained by single-roller melt-spinning method.

3.2 Microstructure of Fe$_{60}$Cu$_{10}$Zr$_{10}$B$_{20}$ and Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ melt-spun ribbons with nano-emulsion structure

Fe$_{60}$Cu$_{10}$Zr$_{10}$B$_{20}$ and Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ alloys formed a metallic glass emulsion structure, while Fe$_{35}$Cu$_{35}$Zr$_{10}$B$_{20}$ and Fe$_{10}$Cu$_{60}$Zr$_{10}$B$_{20}$ alloys forming marble-like structure did not show the metallic glass formation during rapid solidification. In the present study, the microstructure of metallic glass former alloys was examined.

Figure 5 shows EPMA of rapidly solidified melt-spun Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ alloy with emulsion structure. Fe image (b) and Cu-image (c) show that dark gray matrix and bright globules in the bright filed image (BFI) (a) correspond to Fe-rich and Cu-rich regions, respectively. Zr atoms segregate in Fe-rich matrix rather than in Cu-rich globules. The distribution of B atoms was hardly detected by EPMA analysis. The EPMA results of Fe$_{40}$Cu$_{40}$Zr$_{10}$B$_{20}$, Fe$_{35}$Cu$_{35}$Zr$_{10}$B$_{20}$ and Fe$_{10}$Cu$_{60}$Zr$_{10}$B$_{20}$ alloys show the tendency that the B element segregates from Fe-rich region to Fe−Zr rich region.

Figure 6 shows TEM microstructures and corresponding SAD patterns of melt-spun Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ and Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ alloys. (a) BEI of Fe$_{60}$Cu$_{10}$Zr$_{10}$B$_{20}$, (b) BEI of Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$, (c) SAD pattern obtained from amorphous matrix and spherical crystalline precipitates in Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$, (d) SAD pattern obtained from spherical crystalline precipitates in Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$. TEM-EDX analysis was performed in rapidly solidified melt-spun Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ ribbon. The composition ratios of Fe:Cu:Zr for crystalline globules and an amorphous matrix were 0:97:3 and 88:1:11, respectively. Although the quantitative analysis of distribution of B atoms was difficult by TEM-EDX, B atoms showed a strong tendency to segregate in Fe−Zr rich amorphous matrix rather than in f.c.c.–Cu crystalline globules. These results indicate that emulsion structure in rapidly solidified melt-spun Fe$_{50}$Cu$_{10}$Zr$_{10}$B$_{20}$ and Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ alloys is composed of f.c.c.–Cu crystalline globules and Fe−Zr–B based metallic glasses. Size of the f.c.c.–Cu crystalline globules decreased with decreasing Cu content. Nanocrystalline globules with a diameter of about 20 nm were obtained in Fe$_{50}$Cu$_{10}$Zr$_{10}$B$_{20}$ alloy.

Figure 7 shows HREM images of a crystalline globule in melt-spun Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ alloy. Fe−Zr−B based matrix shows the salt-pepper contrast typical for an amorphous phase. The nanocrystalline cluster and/or the region of well-

![TEM microstructures and corresponding SAD patterns of melt-spun Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ and Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ alloys.](image-url)
developed medium range order (MRO) are not observed in the matrix. The morphology of f.c.c.–Cu crystalline globules seems to be perfectly spherical. Numerous stacking faults can be seen in f.c.c.–Cu crystalline globule. These are inhomogeneously distributed, and the majority of them do not break off in the crystalline globules, but it exists from the edge to the edge.

Figure 8 shows HREM images of crystalline globules in melt-spun Fe$_{60}$Cu$_{10}$Zr$_{10}$B$_{20}$ alloy. The f.c.c.–Cu crystalline globules are embedded in Fe–Zr–B metallic glass, and their size is smaller than that in Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ alloy. One can notice the formation of a core-shell structure in each globule which is surrounded by a salt-pepper contrast region. The salt-pepper contrast in the shell region of these globules is different from that in Fe–Zr–B amorphous matrix. There may be a difference in alloy composition of the amorphous phase between the shell of globules and matrix. To our knowledge, there is no report about formation of such nano core-shell structure during rapid solidification in metallic glass former alloy systems.
3.3 Change in microstructure of Fe\textsubscript{50}Cu\textsubscript{20}Zr\textsubscript{10}B\textsubscript{20} melt-spun ribbon with nano-emulsion structure

In order to investigate thermal stability of an emulsion structure composed of f.c.c.–Cu crystalline globules and Fe–Zr–B based amorphous matrix, \textit{in situ} observation of change in TEM microstructure during heating was performed in melt-spun Fe\textsubscript{50}Cu\textsubscript{20}Zr\textsubscript{10}B\textsubscript{20} alloy. The results are shown in Fig. 9. The glass-to-liquid transition temperature of \( T_g \) and crystallization temperature of \( T_x \) of Fe–Zr–B based amorphous matrix in melt-spun Fe\textsubscript{50}Cu\textsubscript{20}Zr\textsubscript{10}B\textsubscript{20} alloy were evaluated from the conventional DSC curve at a heating rate of 0.67 Ks\(^{-1}\) as shown in Fig. 2. The \( T_g \) and \( T_x \) were 887 and 964 K, respectively. Figure 9(a) shows the BF image and corresponding SAD pattern of Fe\textsubscript{50}Cu\textsubscript{20}Zr\textsubscript{10}B\textsubscript{20} specimen at 858 K. There is no significant difference in the morphology of f.c.c.–Cu crystalline globules between the melt-spun specimen and specimen annealed at 858 K. In SAD pattern, broad halo rings corresponding to an amorphous phase and discontinuous Debye rings can be seen, which is analogous to that of melt-spun specimen. At 883 K near \( T_g \) (b), the change in morphology of f.c.c.–crystalline phase from spherical to a polygonal shape can be seen as indicated by white arrows. The viscosity of Fe–Zr–B based metallic glass may drastically decrease during glass-to-liquid transition and the polygonal crystalline phase is formed due to aggregation of some Cu globules. Fig. 9(c) shows the BF image and corresponding SAD pattern of the specimen annealed at 1053 K; in the latter, broad halo rings have changed to Debye rings. The BF image shows that polygonal crystals about 100 nm in diameter are embedded in nano-granular matrix showing dark and bright contrast. The Fe–Zr–B based supercooled liquid matrix thermally crystallized resulting in the formation of a nano crystalline matrix.

Figure 10 shows the HREM image of f.c.c.–Cu phase in melt-spun Fe\textsubscript{50}Cu\textsubscript{20}Zr\textsubscript{10}B\textsubscript{20} alloy after \textit{in situ} observation of thermal annealing at 1053 K. Numerous stacking faults can be seen. There is no significant difference in the feature of stacking faults between the melt-spun specimen and the specimen annealed at 1053 K: (1) distribution of the stacking-faults is not homogeneous and (2) the majority of stacking faults does not break off in the crystalline globules, namely, they exist from edge to edge. The HREM image implies that the f.c.c.–Cu crystalline precipitate with polygonal shape forms through the aggregation of two f.c.c.–Cu globules. Some facet interface is observed in the f.c.c.–Cu crystalline precipitate as indicated by black arrows. Not only aggrega-
tion but also facet interface formation causes the change in morphology of f.c.c.–Cu globules. These results indicate that the emulsion structure is composed of f.c.c.–Cu crystalline globules and Fe–Zr–B based amorphous matrix shows high thermal stability and remains near \( T_g \). Above \( T_g \), there is another unique structure where f.c.c.–Cu crystalline precipitates with a high density of stacking faults were embedded in a Fe–Zr–B nanocrystalline matrix.

4. Discussion

The separation of Fe and Cu elements was observed in rapidly solidified quaternary Fe–Cu–Zr–B alloys prepared by single-roller melt-spinning method. B and Zr elements preferentially segregated in Fe-rich regions resulting in the formation of a Fe–Zr–B rich region and a Cu-rich region containing few Zr or B elements. The B and Zr segregation was discussed from the viewpoint of \( \Delta H_{\text{mix}} \) shown in Fig. 1(a). The \( \Delta H_{\text{mix}} \) of Cu–B pair is mostly positive among Fe–Cu, Fe–Zr, Cu–Zr, Fe–B and Cu–B pairs. Therefore, not only the separation of Fe and Cu elements but also that of Cu and B elements is expected in quaternary Fe–Cu–Zr–B alloys. The B element was previously confirmed to segregate from Cu-rich region to Fe-rich region in melt-spun ternary Fe–Cu–B alloys.

In the present study, the segregation of Zr element from Cu-rich region to Fe–B rich region occurred. The \( \Delta H_{\text{mix}} \) of Zr–B pair is mostly negative among all possible atomic pairs. This implies that the Zr element segregates to the B-rich region. The largest positive \( \Delta H_{\text{mix}} \) of Cu–B pair and negative \( \Delta H_{\text{mix}} \) of Zr–B pair cause the formation of the Fe–Zr–B rich region and the Cu-rich region containing little Zr and B elements in quaternary Fe–Cu–Zr–B alloys.

The Fe–Zr–B ternary alloy system is well known as a metallic glass former alloy system. The metallic glass in Fe\(_{70}\)Zr\(_{10}\)B\(_{20}\), Fe\(_{60}\)Cu\(_{10}\)Zr\(_{10}\)B\(_{20}\) and Fe\(_{50}\)Cu\(_{20}\)Zr\(_{10}\)B\(_{20}\) alloys was formed in the Fe–Zr–B phase region because of the high glass forming ability of this ternary component system. In contrast, the Cu-rich region did not transform to an amorphous phase from the liquid state because the composition of this region is not glass former alloy. In Fe\(_{75}\)Cu\(_{15}\)Zr\(_{10}\)B\(_{20}\) and Fe\(_{10}\)Cu\(_{20}\)Zr\(_{10}\)B\(_{20}\) alloys, an amorphous phase formation was not observed either in Cu-rich region nor in the Fe–Zr–B rich region. The following two effects may be the origin of crystallization in the Fe–Zr–B region during rapid solidification: (1) As Cu concentration increases in quaternary Fe–Cu–Zr–B alloy, the glass forming ability of the Fe–Zr–B alloy system decreases because of the increase in Zr and B concentration in Fe–Zr–B region. (2) The volume fraction of Cu-rich region increases with increase in Cu concentration. Crystallization of the Cu-rich region during rapid solidification provides heat to Fe–Zr–B region, and the provided heat, in turn, causes the crystallization of Fe–Zr–B based liquid and/or an amorphous phase during the solidification.

The two-phase amorphous alloys could not be obtained in Fe\(_{70}\)–Cu\(_{10}\)Zr\(_{10}\)B\(_{20}\) \((x = 10, 20, 30, 35, 60)\) alloys by single-roller melt-spinning method. Metallic glass formed in Fe\(_{60}\)Cu\(_{10}\)Zr\(_{10}\)B\(_{20}\) and Fe\(_{50}\)Cu\(_{20}\)Zr\(_{10}\)B\(_{20}\) alloys during rapid solidification. The melt-spun ribbons show a unique emulsion structure composed of f.c.c.–Cu globules containing numerous stacking faults embedded in Fe–Zr–B based amorphous matrix. The unique emulsion structure maintained its original structure at the temperature near \( T_g \) during heating. Little is known about the formation mechanism of such emulsion structure. Liquid phase separation may be an important factor for the emulsion structure formation in quaternary Fe–Cu–Zr–B alloy.

5. Conclusions

The microstructure of melt-spun Fe\(_{70}\)–Cu\(_{10}\)Zr\(_{10}\)B\(_{20}\), Fe\(_{60}\)Cu\(_{10}\)Zr\(_{10}\)B\(_{20}\) and Fe\(_{50}\)Cu\(_{20}\)Zr\(_{10}\)B\(_{20}\) alloy ribbons prepared by single-roller melt-spinning method.
In Fe$_{60}$Cu$_{10}$Zr$_{10}$B$_{20}$ and Fe$_{50}$Cu$_{20}$Zr$_{10}$B$_{20}$ alloys, the nano-emulsion structure composed of f.c.c.–Cu crystalline globules and Fe–Zr–B based metallic glass matrix is formed. Cu-rich crystalline globules show a high density of stacking-faults. The size of f.c.c.–Cu crystalline globules increases with increasing Cu concentration. The unique nano-emulsion structure shows high thermal stability until the glass-to-liquid transition temperature ($T_g$).

A unique marble type structure can be obtained in Fe$_{35}$Cu$_{35}$Zr$_{10}$B$_{20}$ and Fe$_{10}$Cu$_{60}$Zr$_{10}$B$_{20}$ alloys by single-roller melt-spinning method but an amorphous phase does not form.

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