Entangled Duplex Structure and Polycrystalline Globule Formation through Multistep Liquid-Phase Separation in Cu–Fe–Zr–B Alloys

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A unique entangled duplex structure was formed in rapidly solidified Cu–Fe–Zr–B alloys with Cu/Fe ratio = 1/1 and 6/1. Polycrystalline globules, embedded in a Cu crystalline matrix, were also observed in Cu60Fe20Zr10B20 and Cu60Fe60Zr10B20 alloys; this rapidly solidified structure was drastically different from that of Cu–Fe–Zr–B alloys enriched in Fe. Multi-step liquid phase separation can lead to unique microstructure formation during rapid solidification. [doi:10.2320/matertrans.F-M2013837]

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1. Introduction

The development of new materials with superior structural and functional properties from inexpensive alloy systems and/or common metals is important for the sustainable advancement of human society and the preservation of the global environment. The rapid solidification technique has attracted great interest for material processing in order to develop such materials. Rapid solidification can modify the microstructure of an alloy via amorphous phase formation, change in phase selection during solidification, change in the solidification mode (dendrite formation, eutectic reaction, liquid phase separation, and so on), grain refinement, and/or suppression of phase segregation. Simultaneous occurrence of liquid phase separation and amorphous phase formation, and/or multi-step liquid phase separation in alloys was recently shown to form unique features in the microstructure of rapidly solidified melt-spun ribbons; for example, ultra-fine globules and/or entangled duplex structures (marble structures) with amorphous phase formation were reported in various alloy systems through multi-step liquid phase separation. The repeated occurrence of liquid phase separation during the meltspit process results in the formation of unique structures that cannot be obtained by other processes.

The Fe–Cu alloy system shows a metastable liquid miscibility gap below the liquidus temperature; the occurrence of liquid phase separation in this system has been the subject of much interest. Regarding the microstructure of Fe–Cu-based alloys formed through multistep liquid phase separation with amorphous phase formation, previous studies have reported the formation of emulsions (in Fe–Cu–Zr–B2, Fe–Cu–Si–B4, and Fe–Cu–Ni–Si–Sn–B1, Y2), and Cu-crystalline nanoglobules embedded in an Fe-based amorphous matrix (observed in Fe–Cu–Zr–B2,6). These results are strictly limited to Fe-rich alloy compositions in Fe–Cu-based alloys. In the present study, the microstructure of Cu-rich Fe–Cu–Zr–B alloys upon rapid solidification was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), electron probe microanalysis (EPMA), transmission electron microscopy (TEM), and thermal analysis. We found that the formation of entangled duplex structures and polycrystalline globules occurred through multi-step liquid phase separation without an amorphous phase formation.

2. Experimental Procedure

Master ingots of Cu70–xFe xZr10B20 (x = 0, 10, 20, 30, 35, 40, 50, 60, and 70) alloys were prepared from Fe, Cu, B, and Fe–B prealloy on a water-cooled Cu hearth by arc melting in purified Ar atmosphere. The weight of each master ingot was approximately 10 g. Conventional single roller melt-spinning technique was used to produce rapidly solidified ribbons from the master alloy ingots. The experimental conditions of melt-spun ribbon preparation have been described in detail elsewhere. The structure of the melt-spun ribbon was examined by XRD using Cu–Kα radiation (RIGAKU RINT-2000), back-scattering electron imaging (BEI) using an SEM (JEOL JSM-5600), and electron probe microanalysis (EPMA) (JEOL JXA-8800R). OM images were obtained using non-polished samples, while SEM-BEI images were obtained using polished samples. Thermal properties of the ribbon were determined by differential scanning calorimetry (DSC) (MAC-SCIENCE DSC-3100S) performed at a heating rate of 0.67 K s−1 in Ar atmosphere from room temperature to 1023 K. Solidification analysis was performed by differential thermal analysis (DTA) (MAC-SCIENCE TG-DTA2000SA) with the following temperature program: room temperature to 1773 K at a heating and cooling rate of 0.33 K s−1 under Ar atmosphere. TEM specimens were prepared by ion-thinning (Fischione ion mill, Model 1000). TEM observation was performed on a JEOL JEM-2010 and a Hitachi H-800 with an acceleration voltage of 200 kV.

3. Results

3.1 Specimen preparation

Figure 1 shows the outer appearance of ingots obtained by arc melting of alloys Cu60Fe20Zr10B20 (x = 0, 10, 20, 30, 35, 40, 50, 60, and 70) (Fig. 1(a)) and melt-spun ribbons of Cu60Fe5Zr10B20 (Fig. 1(b)), Cu60Fe10Zr10B20 (Fig. 1(c)), and Cu10Zr10B20 (Fig. 1(d)) alloys. The ingots of Cu60Fe20Zr10B20 alloys (Fig. 1(a)) show a tendency toward...
irregular shapes with increasing Cu composition in quaternary alloys, corresponding to the difficulty of specimen preparation by arc melting. The color of the ingot changes from metallic silver to copper on increasing the Cu content. In the case of Cu-rich Cu$_{70}$Fe$_{30}$Zr$_{10}$B$_{20}$ ($x = 35$, 40, 50, and 60) alloys, the preparation of the melt-spun ribbon is significantly challenging because of the difficulty of the ejection of the melt from the quartz nozzle and the breakage of the quartz tubes. Melt-spun ribbons of Cu$_{60}$Fe$_{20}$Zr$_{10}$B$_{20}$ and Cu$_{50}$Fe$_{20}$Zr$_{10}$B$_{20}$ alloys could not be obtained in the present study. On the other hand, they were obtained in some Cu$_{70}$Fe$_{30}$Zr$_{10}$B$_{20}$ alloys whose Cu/Fe ratio was $\geq 1$ ($x \geq 35$); e.g., Cu$_{35}$Fe$_{35}$Zr$_{10}$B$_{20}$ (Fig. 1(b)) and Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$ (Fig. 1(c)). Note that it was impossible to eject all melts into the quartz nozzle, and residual ingots were produced in these alloys; as a result, the quantity of melt-spun ribbon was smaller than that in Cu$_{70}$Zr$_{10}$B$_{20}$ alloys (Fig. 1(d)). The melt-spun ribbons of Cu$_{70}$Fe$_{30}$Zr$_{10}$B$_{20}$ (Fig. 1(b)), Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$ (Fig. 1(c)), and Cu$_{50}$Zr$_{10}$B$_{20}$ (Fig. 1(d)) were Cu-colored because of the formation of face-centered-cubic (fcc) Cu phase as the main constituent of these alloys (this will be mentioned in the following sections). In the present study, the microstructure was investigated only in Cu$_{35}$Fe$_{35}$Zr$_{10}$B$_{20}$, Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$, and Cu$_{35}$Fe$_{35}$Zr$_{10}$B$_{20}$ alloys. The XRD patterns in Fig. 2 correspond to the melt-spun ribbons of Cu$_{70}$Zr$_{10}$B$_{20}$, Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$, and Cu$_{35}$Fe$_{35}$Zr$_{10}$B$_{20}$ alloys, together with a melt-spun ribbon of Fe$_{70}$Zr$_{10}$B$_{20}$ alloy as a reference. The XRD pattern of the Fe$_{70}$Zr$_{10}$B$_{20}$ melt-spun ribbon shows broad peaks typical for an amorphous single phase, while such peaks cannot be seen for the Cu$_{70}$Zr$_{10}$B$_{20}$, Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$, and Cu$_{35}$Fe$_{35}$Zr$_{10}$B$_{20}$ alloys. In melt-spun ribbons of Cu$_{70}$Zr$_{10}$B$_{20}$, Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$, and Cu$_{35}$Fe$_{35}$Zr$_{10}$B$_{20}$ alloys, fcc-Cu is the main constituent phase. A composite structure comprising fcc-Cu and B$_2$Zr was formed in the Cu$_{70}$Zr$_{10}$B$_{20}$ alloy. The replacement of Cu by Fe suppresses the B$_2$Zr formation and promotes the formation of a body-centered-cubic (bcc)-Fe phase. This can be seen in the XRD pattern of Cu$_{70}$Fe$_{30}$Zr$_{10}$B$_{20}$ alloy. Exothermic peaks can be seen at the temperature below the melting temperature of pure Fe as well as pure Cu. These two peaks are not direct evidence of the liquid phase separation; however, these imply the possibility that Fe and Cu have separated into distinct liquid phases and solidified separately. Microstructure analysis after solidification is mandatory for clarifying whether the liquid phase separation occurred during the cooling of the melt; this is mentioned in the following sections.

### 3.2 Microstructure analysis

XRD, SEM, EPMA, and TEM analyses were performed on the melt-spun ribbons in order to investigate in more detail the liquid phase separation and microstructure formation during rapid solidification. Figure 4 shows the trans-scale observation of melt-spun ribbons of Cu$_{35}$Fe$_{25}$Zr$_{10}$B$_{20}$ (Figs. 4(a)–4(d)) and Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$ (Figs. 4(e)–4(h)) alloys obtained by optical microscopy (OM) and SEM-BEI, where “trans-scale observation” means the combination of images at various magnifications by using OM, SEM, TEM, HVEM, HREM, and so on. The observation direction in OM, SEM, EPMA and TEM was perpendicular to the ribbon surface. In the case of both the alloys, typical structures formed through liquid phase separation could not be seen either at the millimeter or at the 100-µm scale (Figs. 4(a), 4(b), 4(c), and 4(f)). In the case of the Cu$_{35}$Fe$_{25}$Zr$_{10}$B$_{20}$ alloy, the SEM-BEI images (Figs. 4(c) and 4(d)) show the formation of an entangled duplex structure composed of dark and bright gray regions with structures of the order of 10–100 µm. As shown in Fig. 4(d), dark gray globules embedded in a bright gray matrix and bright gray globules embedded in a dark gray matrix can be seen. The size of globules is of the order of 1 µm. In contrast, the formation of an entangled duplex structure with 1-µm-sized globules can be seen in the case of the Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$ alloy (Figs. 4(g) and 4(h)). In this case, the size of dark and bright gray regions was slightly larger than those of the Cu$_{35}$Fe$_{25}$Zr$_{10}$B$_{20}$ alloy. Figure 5 shows trans-scale observation of melt-spun ribbons of the Cu$_{70}$Zr$_{10}$B$_{20}$ alloy obtained by OM (Figs. 5(a) and 5(b)), SEM-BEI (Figs. 5(c) and 5(d)), and TEM-BF (Fig. 5(e)) images. The OM images show the difference in the surface morphologies of the quaternary Cu–Fe–Zr–B and ternary Cu–Zr–B alloys. SEM-BEI images show black precipitates with a faceted structure embedded in a white gray matrix. The precipitates can be attributed to B$_2$Zr. Figure 5(e) shows the TEM-BF image corresponding to the white gray matrix from the SEM images. Coarse crystalline grains larger than 1 µm are indicated by the letter A, and a typical dendritic structure can be seen. These coarse grains can be identified as crystalline Cu with an fcc structure, based on the SAD pattern (Fig. 5(e)’). The occurrence of a liquid phase separation cannot be detected in ternary Cu–Zr–B alloy.

Figure 6 shows the EPMA analysis of the duplex structure in Cu$_{35}$Fe$_{25}$Zr$_{10}$B$_{20}$ (Figs. 6(a)–6(e)) and Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$ (Figs. 6(f)–6(j)). The dark regions in BEI images (Figs. 6(a) and 6(f)) are enriched in Fe (Figs. 6(b) and 6(g)), while the bright gray regions in BEI images (Figs. 6(a) and 6(f)) are enriched in Cu (Figs. 6(c) and 6(h)). In addition, the Fe-rich
regions are also enriched in Zr and B (Figs. 6(d), 6(e), 6(i), and 6(j)), which are absent in the Cu-rich regions. SEM-BEI images under higher magnification (Figs. 4(d) and 4(h)) show spherical regions (globules) embedded in an entangled matrix. EPMA analysis and SEM observation result (the spherical shape of the globules, as well as their smooth interface with two phases in an entangled duplex structure), indicate the liquid phase separation with Fe–Zr–B-rich and Cu-rich regions. Figure 7 shows the BF images and the corresponding SAD patterns for the melt-spun ribbons of Cu$_{35}$Fe$_{35}$Zr$_{10}$B$_{20}$ (Figs. 7(a)−7(d)), Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$ (Figs. 7(e)−7(h)) alloys, obtained by TEM. In the Cu$_{35}$Fe$_{35}$Zr$_{10}$B$_{20}$ alloy, BF images show globules as indicated by the letter B in Fig. 7(a) and the letter C in Fig. 7(b). The SAD pattern obtained from the white matrix (indicated by the letter A in Fig. 7(a)) can be attributed to the [001] of fcc-Cu (Fig. 7(c)). In contrast, Debye rings can be seen in the SAD pattern (Fig. 7(d)) obtained from the globule indicated by the letter B in
Fig. 3 Differential scanning calorimetry (DSC) (a) and differential thermal analysis (DTA) (b) curves of melt-spun Cu_{35}Fe_{35}Zr_{10}B_{20}, Cu_{60}Fe_{10}Zr_{10}B_{20}, and Cu_{60}Fe_{10}Zr_{10}B_{20} alloys, together with those of melt-spun amorphous ribbon in Fe_{50}Zr_{10}B_{50} alloy.26 DSC was performed at a heating rate of 0.67 K s^{-1} under Ar atmosphere. DTA was performed at a heating and cooling rate of 0.33 K s^{-1}; only the cooling curve is shown in the figure.

Fig. 7(a). Rather than single-crystalline contrast, the globules show polycrystalline structure, as indicated by the letter C in Fig. 7(b). Based on the position of the Debye rings, the constituent phases of the globules can be attributed to the bcc-Fe and unknown phases. The polycrystalline globules embedded in the fcc-Cu matrix can also be seen in the Cu_{60}Fe_{10}Zr_{10}B_{20} alloy. This is indicated by the letters E and F in the BF images (Figs. 7(e) and 7(d)), from the SAD pattern (Fig. 7(g)) obtained from the letter D in Fig. 7(e) and that (Fig. 7(h)) from the index E in Fig. 7(e). In Fe-rich alloys, e.g., Cu_{70-50}Fe_{50}Zr_{10}B_{20} (x = 50 and 60), single crystalline fcc-Cu globules embedded in Fe–Zr–B-based metallic glass were obtained.20 The globules in the Fe-rich and Cu-rich Cu_{60}Fe_{10}Zr_{10}B_{20} alloys exhibit a significant difference in the size and the constituent phases. The results of both the trans-scale observation, EPMA and TEM analyses indicate that liquid phase separation promoted the formation of entangled duplex structures on the order of 10 µm, and micro- and 100 nm order-polycrystalline globules of Fe–Zr–B– and Cu-rich phases, in Cu_{60}Fe_{10}Zr_{10}B_{20} and Cu_{60}Fe_{10}Zr_{10}B_{20} alloys.

4. Discussion

4.1 Amorphous phase formation in quaternary Cu–Fe–Zr–B alloys

In the present study, amorphous phase formation could not be detected by XRD (Fig. 2), thermal analysis (Fig. 3), and TEM measurements (Figs. 5 and 7) of Cu_{60}Fe_{10-70}Zr_{10}B_{20} (x = 35, 60, and 70) alloys; however, an amorphous phase was reported in the Fe-rich Cu_{60}Fe_{10}Zr_{10}B_{20} (x = 0, 10 and 20) alloys.2,6 The heat of mixing (ΔH_{mix}) and the difference in atomic radii (Δr) are two useful parameters for evaluating the glass forming ability (GFA) of multi-component alloys.30,31 Figure 8 summarizes ΔH_{mix} and Δr of each constituent element in quaternary Cu–Fe–Zr–B alloys, where Δr is defined by the difference of their respective Goldschmidt atomic radii (Δr = (r_{large} − r_{small})/r_{small}). Based on Fig. 8(a), the ΔH_{mix}–rel.ation map can be written as shown in Fig. 8(b). The repulsive relationship between Cu–Fe and Fe–Zr, and the large attractive relationship between Zr–B indicates the separation of Fe–Zr–B-based and Cu-based liquids after the liquid phase separation. This prediction is in good agreement with the EPMA analysis (Fig. 6). The large negative ΔH_{mix} and large Δr among Fe, Zr, and B indicate their high GFA in ternary Fe–Zr–B alloy system when mixed, and hence, the Fe_{50}Zr_{10}B_{50} alloy shows an amorphous single phase (see Figs. 2 and 3). On the other hand, the quantity of Cu-rich liquid in Cu_{60}Fe_{10}Zr_{10}B_{20} alloys increased with an increase in the value of x. The heat release caused by the crystallization of Cu-rich liquid during rapid solidification in the Fe-rich Cu–Fe–Zr–B alloys is too small to induce the crystallization of Fe–Zr–B-based liquid or amorphous phases, resulting in the formation of Cu crystalline globules dispersed in Fe–Zr–B amorphous alloys. In contrast, in Cu_{60}Fe_{10}Zr_{10}B_{20} (x = 35, 60, and 70) alloys, the heat released during the cooling of melt enhances the solidification and/or crystallization of the Fe–Zr–B-based liquid or amorphous phase, resulting in the formation of polycrystalline Fe–Zr–B-based globules.

4.2 Microstructural differences between Fe-rich and Cu-rich ternary Cu–Fe–Zr–B alloys

The SEM images (Figs. 4(c), 4(d), 4(g), and 4(h)) and EPMA analysis (Fig. 6) show the formation of entangled duplex structures of the order of 10 µm in both the Cu_{60}Fe_{10}Zr_{10}B_{20} and Cu_{60}Fe_{10}Zr_{10}B_{20} alloys. The size of the globules varied widely, ranging from the micro- to the nanoscale (1 µm to 100 nm), as shown in the magnified SEM (Figs. 4(c), 4(d), 4(g), and 4(h)) and TEM (Figs. 7(a), 7(b), 7(e), and 7(f)) images. The identification of some minor phases could not be achieved; however, the present trans-scale observations clarified the occurrence of liquid phase segregation during rapid solidification. Figure 9 shows typical examples of (a) one-step liquid phase separation and (b) multi-step liquid phase separation. The entangled duplex structure and the variations in the size of globules can be explained in terms of multi-step liquid phase separation.
In the Fe-rich alloys (Cu$_{70-x}$Fe$_x$Zr$_{10}$B$_{20}$), the entangled duplex structures could not be seen, and nanocrystalline fcc-Cu globules, dispersed in Fe–Zr–B-based metallic glasses, were formed during rapid solidification.$^{2,6}$ These nanocrystalline globules, with diameters of the order of 10 nm, could not be obtained in the Cu-rich Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$ alloys. The formation mechanism of micrometer-sized entangled duplex structures and the differences in microstructure between the Fe-rich and Cu-rich alloys can be explained by the model of multi-step liquid phase separation; however, the other mechanism can be considered to affect the rapidly solidified structure.

Fig. 5 Trans-scale observation of melt-spun ribbon in Cu$_{35}$Zr$_{10}$B$_{20}$ alloy. (a)(b) OM images, (c)(d) SEM-BEI images, and (e) TEM-BF image.

Fig. 6 EPMA analysis of melt-spun ribbon in Cu$_{35}$Fe$_{35}$Zr$_{10}$B$_{20}$ (a) and Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$ (b) alloys.

In the Fe-rich alloys (Cu$_{70-x}$Fe$_x$Zr$_{10}$B$_{20}$ ($x = 50$ and 60)), the entangled duplex structures could not be seen, and nanocrystalline fcc-Cu globules, dispersed in Fe–Zr–B-based metallic glasses, were formed during rapid solidification.$^{2,6}$ These nanocrystalline globules, with diameters of the order of 10 nm, could not be obtained in the Cu-rich Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$ alloys. The formation mechanism of micrometer-sized entangled duplex structures and the differences in microstructure between the Fe-rich and Cu-rich alloys can be explained by the model of multi-step liquid phase separation; however, the other mechanism can be considered to affect the rapidly solidified structure.
In Cu\textsubscript{x}Fe\textsubscript{70-x}Zr\textsubscript{10}B\textsubscript{20} (x = 35, 60, and 70) alloys, the formation of entangled duplex structure from the macroscopic view point (on the order of 10–100 µm) and that of globules from the microscopic view point (on the order of 1 µm) was observed. The formation of globules can be explained by the liquid phase separation and surface energy; for minimizing the surface energy and superficial area, a separated liquid phase with a spherical shape formed and solidified during cooling, resulting in the formation of globules. The formation of an entangled duplex structure can
be explained by the liquid phase separation with micrometer-order size and deformation of the separated liquid during the melt-spinning processes. The separated liquid with low viscosity and micrometer-order size can change their shape and be drawn out before the solidification, resulting in the formation of the entangled duplex structure. Above-mentioned microstructure formation processes in Cu$_{70-}$Fe$_{10}$Zr$_{10}$B$_{20}$ ($x = 35, 60$, and $70$) alloys are different from those in the Fe-rich alloys (Cu$_{70-}$Fe$_{10}$Zr$_{10}$B$_{20}$ ($x = 50$ and $60$)), resulting in the microstructural differences between Fe-rich and Cu-rich quaternary Cu–Fe–Zr–B alloys.

Alloy systems exhibiting an amorphous phase can maintain their liquid state over a wider temperature range above the glass transition (liquid-to-glass) temperature. This allows liquid phase separation to occur repeatedly, because solidification owing to crystallization of the liquid is suppressed in alloys. Amorphous phase formation during rapid solidification is effective for obtaining finer globules and/or finer entangled duplex structures. The results showed the occurrence of liquid phase separation, while an amorphous phase formation was not detected. The difference in the size of globules of Fe-rich and Cu-rich alloys in Cu$_{70-}$Fe$_{10}$Zr$_{10}$B$_{20}$ subjected to multi-step liquid phase separation could be explained by the differences in an amorphous phase formation as well as their Cu/Fe ratios. The general criterion for the multistep liquid phase separation is not clarified now; however, the present study indicates that an amorphous phase formation is not necessary and sufficient condition for the multistep liquid phase separation in Fe–Cu based alloys. Further systematic research work is necessary for clarifying the dominant factors for the occurrence of multistep liquid phase separation.

5. Conclusions

Melt-spun ribbons of Cu$_{70-}$Fe$_{10}$Zr$_{10}$B$_{20}$ ($x = 35, 10$, and $0$) alloys were characterized with respect to their rapidly solidified microstructure and the influence of liquid phase separation. The obtained results can be summarized as follows:

1. Entangled duplex structures, namely marble structures, were formed in the Cr$_{33}$Fe$_{55}$Zr$_{10}$B$_{20}$ and Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$ alloys, while such structures cannot be seen in Fe-rich Cu$_{70-}$Fe$_{10}$Zr$_{10}$B$_{20}$ alloys.

2. The formation of polycrystalline globules embedded in an fcc-Cu matrix can be seen by TEM observation. The constituent phases and microstructures of globules differed significantly in Cu-rich alloys from those of the Fe-rich alloys of Cu$_{70-}$Fe$_{10}$Zr$_{10}$B$_{20}$.

3. Amorphous phase formation cannot be detected in Cr$_{33}$Fe$_{55}$Zr$_{10}$B$_{20}$ and Cu$_{60}$Fe$_{10}$Zr$_{10}$B$_{20}$ alloys. The rapidly solidified microstructure of the Cu$_{70-}$Fe$_{10}$Zr$_{10}$B$_{20}$ alloy strongly depends on the Cu/Fe ratio, while both the Fe-rich and Cu-rich alloys show multistep liquid phase separation during rapid solidification.

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