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Letter

Formation of macroscopic phase-separated dual-layer melt-spun ribbon from Co–Si–B–Cu alloy

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ABSTRACT

A macroscopically phase-separated dual-layer ribbon can be obtained from $(Co_{75}Si_{10}B_{15})_{70}Cu_{30}$ alloy by using a conventional single-roller melt-spinning method, whereas such a structure cannot be obtained from $(Fe_{75}Si_{10}B_{15})_{70}Cu_{30}$ alloy. Liquid phase separation and amorphous phase formation take place simultaneously in Co–Si–B–Cu alloy, which leads to the formation of a unique structure during rapid solidification.

1. Introduction

The simultaneous occurrence of liquid phase separation and amorphous phase formation results in the formation of new metallic materials with unique structures, such as two-phase amorphous alloys in La–Zr–Al–Ni–Cu [1], Y–Ti–Al–Co [2], and Ni–Nb–Y systems [3] and multiscale globule crystal dispersed metallic glasses in Fe–Zr–B–Cu systems [4,5]. Such materials cannot be obtained using conventional material processing methods. The abovementioned multicomponent alloys, prepared by the conventional single-roller melt-spinning method, show phase-separated structures in the nanoscale. The microstructure of the melt-spun ribbon of $(Fe_{75}Si_{10}B_{15})_{70}Cu_{30}$ alloy (Fig. 1) is a typical example of a nanoscale emulsion-type structure. Recently, we investigated the formation of a macroscopically phase-separated core-wire/cover-layer structure in the Fe–Si–B–Cu alloy by the arc-melt-type melt-extraction method [6]. In terms of external appearance, the melt-extracted wire of the $(Fe_{75}Si_{10}B_{15})_{70}Cu_{30}$ alloy is copper colored, unlike conventional metallic materials that have a silver surface. The macroscopically phase-separated structure composed of a Fe-based alloy core and Cu-based alloy cover layer was formed during rapid solidification. However, the formation of such a macroscopically phase-separated structure by the conventional melt-spinning method has not been reported thus far.

The Co–Cu alloy has a metastable liquid miscibility gap below the liquidus temperature owing to the large heat of mixing [6–15]. In this paper, we report the preparation of a rapidly solidified ribbon of Co–Si–B–Cu alloy by the conventional single-roller melt-spinning method and the formation of a macroscopically phase-separated dual-layer structure. To the best of our knowledge, this is the first report on the formation of a melt-spun amorphous alloy with a macroscopically phase-separated structure by simultaneous liquid phase separation and amorphous phase formation.

2. Experimental procedure

The microstructures of rapidly solidified $Co_{75}Si_{10}B_{15}$ and $(Co_{75}Si_{10}B_{15})_{70}Cu_{30}$ alloys were investigated in this study. The alloy compositions are expressed in nominal atomic percentages. It is well known that $Co_{75}Si_{10}B_{15}$ exhibits the standard alloy composition of the previously developed Co-based melt-spun amorphous phase alloy [16]. Master ingots of Co–Si–B and Co–Si–B–Cu alloys were prepared from Co, Cu, Si, B, and the Co–B alloy on a water-cooled Cu substrate by arc-melting in a purified Ar atmosphere. A melt-spun ribbon was prepared from the ingots by the conventional single-roller melt-spinning method.

3. Results and discussion

A continuous melt-spun ribbon was prepared by the conventional single-roller melt-spinning method. The melt-spun ribbon did not exhibit a monotonous metallic silver color but a dual-layer pattern comprising a metallic-silver-colored region and a copper-colored region. The color of the free surface was different from that of the side surface of the substrate (roll side) [17]. Fig. 2 shows the microstructure of the melt-spun ribbon of the $(Co_{75}Si_{10}B_{15})_{70}Cu_{30}$ alloy, as obtained by SEM–BEI and EPMA analyses. Cross-sectional

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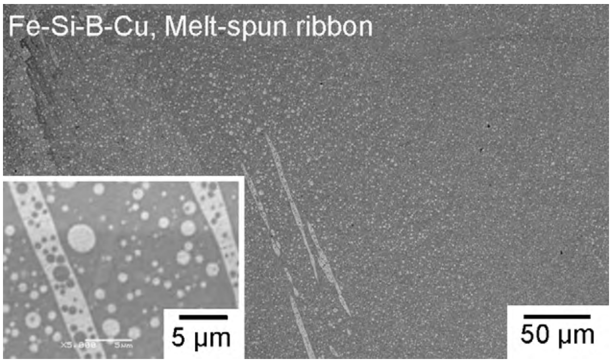

Fig. 1. SEM–BEI images of melt-spun ribbon prepared from $(Fe_{75}Si_{10}B_{15})_{70}Cu_{30}$ alloy by conventional single-roller melt-spinning method. The microstructure of this ribbon shows a typical example of a nanoscale emulsion-type structure.

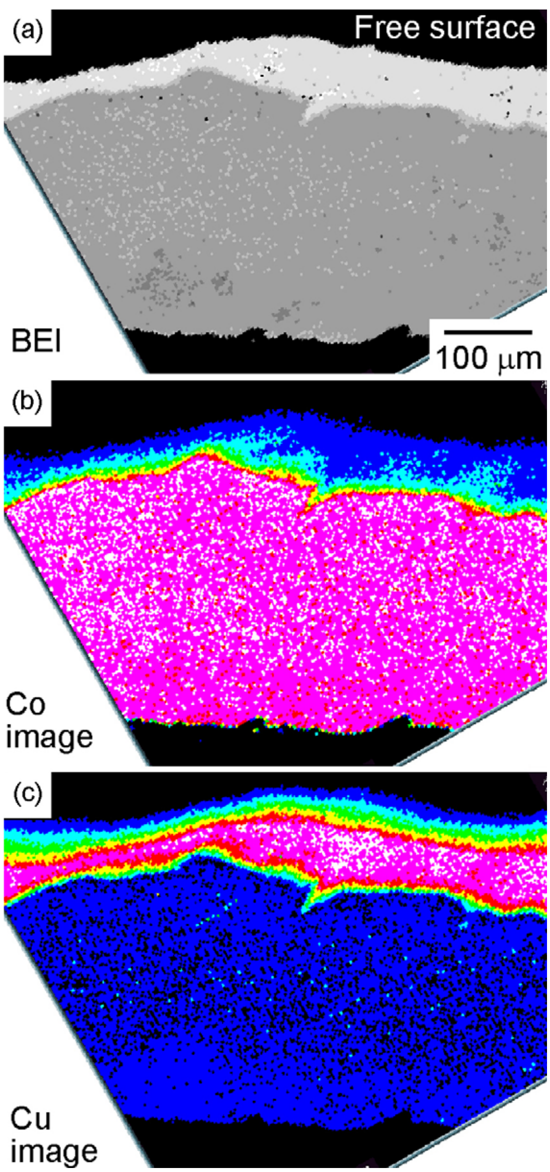

Fig. 2. EPMA analysis of melt-spun ribbon of $(Co_{75}Si_{10}B_{15})_{70}Cu_{30}$ alloy. The cross-sectional images were obtained at a tilted angle for easy observation. (a) SEM–BEI, (b) Co image, and (c) Cu image.

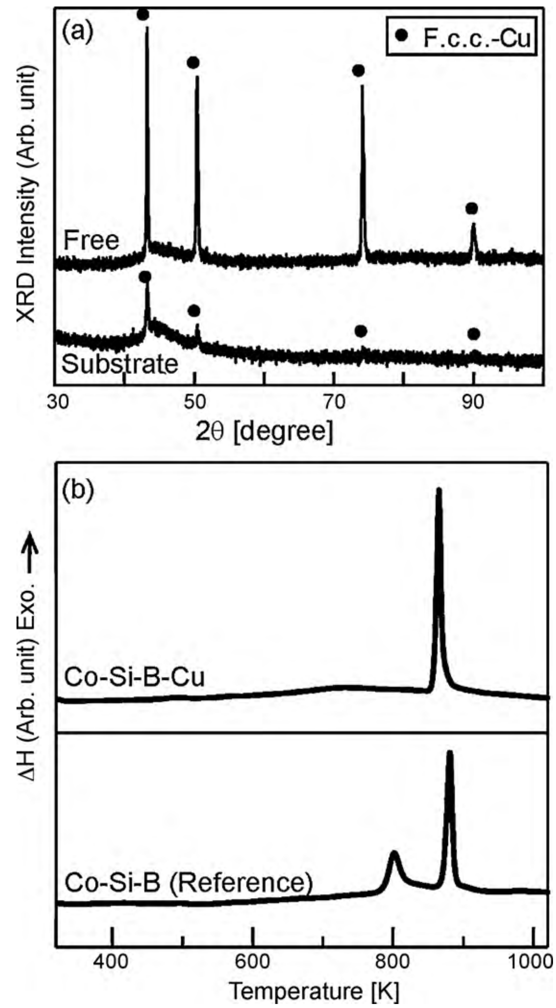

Fig. 3. XRD pattern and DSC curve of the melt-spun ribbon of the $(Co_{75}Si_{10}B_{15})_{70}Cu_{30}$ alloy. (a) XRD obtained by Cu Kα and (b) DSC obtained at a heating rate of 0.67 K s^{-1} together with the data of $Co_{75}Si_{10}B_{15}$ alloy as reference.

images are viewed at an angle for easy observation. The BEI and EPMA analyses of the Co- and Cu-image clearly indicate the formation of a dual-layer structure. The light and dark regions in the SEM–BEI image indicate the free surface and the substrate surface, respectively. The EPMA analysis of the average composition ratio Co, Cu, and Si in both layers was as follows: 18:80:2 for the free surface and 80:10:10 for the substrate surface. The copper-colored layer on the free surface is enriched with Cu, while Co is in abundance in the metallic-silver-colored layer on the substrate-surface. The macroscopically phase-separated structure has not been reported for a melt-spun ribbon obtained from the Co–Cu binary alloy [10] or for the rapidly solidified wire prepared from the Co–Cu–Be alloy by the in-rotation-water melt-spinning method [18]. This is, hence, the first report on the formation of the macroscopically phase-separated melt-spun ribbon.

Fig. 3 shows the XRD patterns of the melt-spun ribbon of $(Co_{75}Si_{10}B_{15})_{70}Cu_{30}$ alloy. The free surface of the Co–Si–B–Cu melt-spun ribbon shows sharp diffraction peaks corresponding to the fcc Cu crystalline phase, while the substrate surface of the ribbon shows both broad and sharp diffraction peaks corresponding to the fcc Cu crystalline phase. The intensity of the fcc Cu crystalline phase peak for the substrate surface is much lower than that for the free surface. The copper-colored alloy layer on the free-fright surface is identified as fcc Cu crystalline alloy. The position of the broad peak overlaps that of the fcc peak of Cu (1 1 1) at about 43°. The position

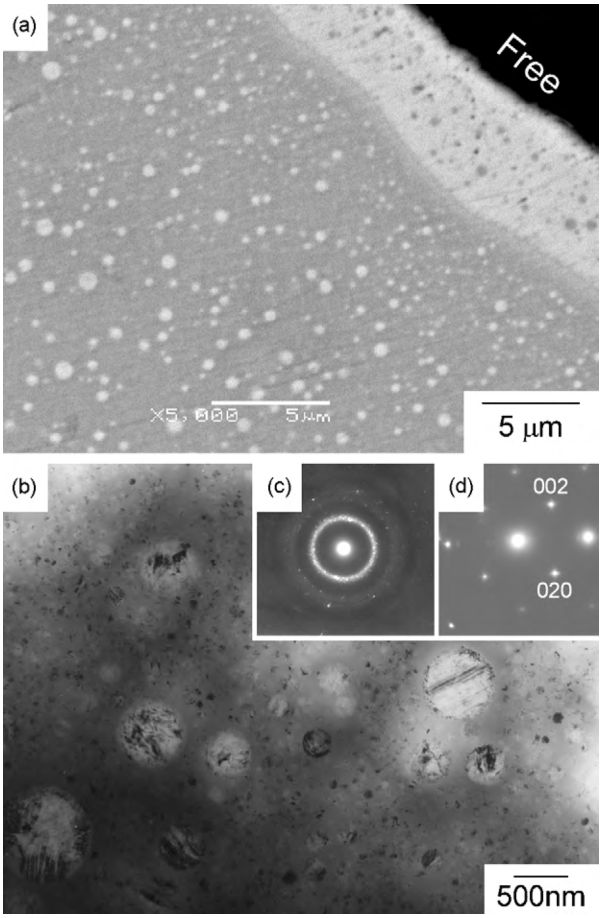

Fig. 4. SEM–BEI images of the interface between the Cu-rich alloy layer and Co-rich alloy layer (a), and UHVEM images of metallic-silver-colored Co-rich alloy layer on the substrate surface in the melt-spun ribbon of $(Co_{75}Si_{10}B_{15})_{70}Cu_{30}$ alloy. (b) BF image, (c) SAD pattern obtained for both the matrix and globules, and (d) SAD pattern obtained only for a globule.

of this broad peak is similar to that of the $Co_{75}Si_{10}B_{15}$ melt-spun ribbon [16]. To confirm the formation of the amorphous phase in the Co–Si–B–Cu melt-spun ribbon, DSC measurement was performed. Fig. 3(b) shows the result of this measurement together with the DSC curve of the $Co_{75}Si_{10}B_{15}$ melt-spun ribbon. Two exothermic peaks can be observed in the DSC curve of the Co–Si–B melt-spun ribbon; the lower peak corresponds to the precipitation of the MS-I phase (hcp), and the higher peak corresponds to the formation of the MS-II phase [19]. In the Co–Si–B–Cu melt-spun ribbon, a single exothermic peak is observed. The position, morphology, and heat release of the exothermic peak is similar to those of the higher peak corresponding to the crystallization of the Co–Si–B melt-spun amorphous phase. An amorphous phase formation in the Co–Si–B–Cu melt-spun ribbon can be confirmed by XRD and DSC analyses.

SEM–BEI observations with high magnification and UHVEM observations were carried out in order to closely study the microstructure of the dual-layer melt-spun ribbon. Fig. 4(a) shows the magnified images of the interface between the Cu-rich alloy layer on the free surface and the Co-rich alloy layer on the substrate surface. Gray-contrast globules can be seen in a white-contrast matrix for the Cu-rich alloy layer, while white-contrast globules can be seen in the gray-contrast matrix for the Co-rich alloy layer. A emulsion structure was formed in both layers. The Co-rich alloy layer was observed in detail by UHVEM and TEM–EDX analyses. In the present study, a UHVEM (Hitachi H-3000) operating at 2000 kV at Osaka University is used instead of the conventional TEM because of the large thickness of the specimen. The UHVEM provides a 15 times greater magnification than the 100 kV electron microscope [20]. TEM–EDX analysis was performed by conventional TEM JEOL JEM-2010 at 200 kV. The UHVEM results of the Co-based alloy layer with a metallic-silver-colored substrate surface are shown in Fig. 4(b)–(d). The bright field (BF) image in Fig. 4(b) shows crystalline globules in a featureless matrix. Fig. 4(c) shows the diffraction pattern obtained for the globules and the matrix. Both Debye and halo rings can be observed. The diffraction pattern of a globule having a diameter of about 500 nm (Fig. 4(d)) indicates that the globules have an fcc structure. The TEM–EDX analysis indicates that the composition ratios of Co, Cu, and Si in the crystalline globules and the amorphous matrix are 1:98:1 and 88:2:10, respectively. The XRD, DSC, SEM–BEI, EPMA, UHVEM, and TEM–EDX results reveal that the fcc crystalline globules of Cu are embedded in the Co–Si–B amorphous matrix in the Co-based layer having a metallic-silver-colored surface.

Multiscale globule formation indicates the concurrence of a liquid phase separation and an amorphous phase formation [5]. The mechanism of the formation of the phase-separated dual-layer structure is not clear and will be discussed in subsequent papers. However, there is no doubt that this structure was formed by liquid phase separation during rapid quenching of the thermal melt. The size distribution of globules in Co–Si–B–Cu alloys are scattered farther than in Fe–Zr–B–Cu [4,5] and Fe–Si–B–Cu alloys, which do not show the formation of any macroscopically phase-separated structure in their melt-spun ribbons. This explains the differences in the glass-forming ability, tendency of liquid phase separation, viscosity of separated liquids, and surface tension between the Co–Si–B–Cu alloy and the Fe-based alloys. These factors can be considered to be important parameters in the formation of a dual-layer structure.

4. Conclusion

In the present study, a rapidly solidified Co–Si–B–Cu ribbon was prepared by single-roller melt-spinning. The following conclusions were obtained:

(1) A continuous ribbon of Co–Si–B–Cu alloy with a macroscopically phase-separated dual-layer structure can be obtained by using a conventional single-roller melt-spinning method.
(2) The Co–Si–B–Cu melt-spun ribbon shows a Co–Si–B-based amorphous alloy layer with multiscale Cu crystalline globules on the metallic-silver-colored substrate surface and a Cu-based alloy layer on the copper-colored free surface. The concurrence of the liquid phase separation and amorphous phase formation is the most important reason for the formation of a unique phase-separated structure.

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