Journal of Alloys and Compounds 650 (2015) 342–350

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Microstructure of rapidly solidified Co–Cu–Si–B immiscible alloys with an amorphous phase

Takeshi Nagase [a], [b], *, Yukichi Umakoshi [b]

[a] Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, 7-1, Mihogaoka, Ibaraki, Osaka 567-0047, Japan
[b] Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1, Yamada-Oka, Suita, Osaka 565-0871, Japan

ARTICLE INFO

Article history:
Received 27 April 2015
Received in revised form
23 July 2015
Accepted 25 July 2015
Available online 4 August 2015

Keywords:
Rapid solidification
Liquid phase separation
Amorphous materials
Electron microscopy

ABSTRACT

The microstructure of Co–Cu-based $(Co_{0.75}Si_{0.10}B_{0.15})_{100-x}Cu_x$ alloys was investigated for a wide range of Co/Cu ratios, with a focus on liquid phase separation and amorphous phase formation. The simultaneous occurrence of liquid phase separation and amorphous phase formation was confirmed in rapidly solidified $(Co_{0.75}Si_{0.10}B_{0.15})_{100-x}Cu_x$ ($x = 10$–50) alloys. Nano-scale emulsion-like structures were found in the macroscopically phase-separated Co-rich region in the $(Co_{0.75}Si_{0.10}B_{0.15})_{100-x}Cu_x$ ($x = 30, 50$) alloys. The microstructure in the Co–Cu–Si–B alloys strongly depended on the solidification process and the Co/Cu ratio.

1. Introduction

Nano-scale emulsion-like microstructures composed of Cu-based crystalline globules and an Fe-based amorphous matrix have been found in various Fe–Cu-based alloy systems [1–15]. In these alloys, liquid phase separation leads to the formation of a liquid mixture consisting of a dispersed Cu-rich liquid and a continuous Fe-based liquid during rapid solidification. The dispersed Cu-rich liquid is then solidified as crystalline globules and the continuous Fe-based liquid changes to an amorphous phase through a liquid-to-glass transition. The simultaneous occurrence of liquid phase separation and amorphous phase formation in a continuous liquid is thus linked to the formation of such unique nano-sized emulsion-like structures. It is well known that emulsion-type structures are widely observed in cosmetics, food engineering products such as milk and mayonnaise, skin-care creams, and cutting fluids used in metal working. However, such emulsion-type structures are less commonly found in metallic materials. The reports about nano-scale emulsion-like structure formation in Fe–Cu-based alloys may offer a unique opportunity to develop a new technique for controlling the microstructure in metals.

Co–Cu alloys are well known in alloy systems that have a flat liquidus line in the thermal phase diagram and a metastable miscibility gap in the undercooled liquid state, similar to the Fe–Cu-based alloy system [16]. The simultaneous occurrence of amorphous phase formation and liquid phase separation was reported in some Co–Cu based alloy systems. A macroscopically phase-separated dual-layer melt-spun ribbon composed of a Cu-rich crystalline phase and a Co–Si–B-based amorphous phase was obtained by a conventional single-roller melt-spinning method [17,18], and a Cu-rich crystalline/Co–Si–B-rich amorphous composite powder with a core–shell-like structure was formed by gas atomization [19]. The formation of bulk metallic glass composites in Co–Cu-based immiscible alloys was reported in Cu–Cu–Zr–Al alloy systems of $(Cu_{46}Zr_{46}Al_8)_{100-x}Co_x$ [20] and $(Cu_{47.5}Zr_{47.5}Al_5)_{100-x}Co_x$ [21]. In melt-spun ribbons of Co–Cu–Zr–B alloys, a macroscopically phase-separated structure was not observed [22]. Fragmentary reports have focused on amorphous phase formation and the possibility of obtaining superior magnetic and mechanical properties in Co–Cu-based amorphous phase with a phase-separated structure; however, the dominant factors affecting the microstructure of rapidly solidified Co–Cu-based immiscible alloys with an amorphous phase were not clarified. There is little information regarding the microstructure and simultaneous occurrence of liquid phase separation and amorphous phase formation in Co–Cu-based alloys upon rapid cooling of the thermal melt. The objective of the present study was to investigate the

---

* Corresponding author. Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, 7-1, Mihogaoka, Ibaraki, Osaka 567-0047, Japan.
E-mail address: t-nagase@uhvem.osaka-u.ac.jp (T. Nagase).

http://dx.doi.org/10.1016/j.jallcom.2015.07.230

microstructure of rapidly solidified melt-spun ribbons prepared by a single-roller melt-spinning method in $(Co_{0.75}Si_{0.10}B_{0.15})_{100-x}Cu_x$ alloys over a wide range of Co/Cu ratios, focusing on (1) the occurrence of liquid phase separation, (2) amorphous phase formation, and (3) the microstructure formed through liquid phase separation and amorphous phase formation simultaneously, especially for the formation of an emulsion-like structure.

2. Experimental procedures

Ingots of $(Co_{0.75}Si_{0.10}B_{0.15})_{100-x}Cu_x$ (x = 0–90 at%) alloys were prepared from Co, Cu, Si, B, and a Co–B prealloy on a water-cooled Cu hearth by arc melting in a purified Ar atmosphere. The $(Co_{0.75}Si_{0.10}B_{0.15})_{1-x}Cu_x$ alloys were designed as a combination of pure Cu and a $Co_{75}Si_{10}B_{15}$ alloy system with a high glass-forming ability [23–25] in the Co-based alloy system. Rapidly quenched ribbons were produced from the ingots by a conventional melt-spinning method. A fused quartz nozzle measuring 14 mm in diameter with an orifice approximately 1.0 mm in diameter was used to apply radio frequency heating. The roller surface velocity was approximately 42 m s^{-1}. The structure of the melt-spun ribbon was examined by X-ray diffraction (XRD) using Cu Kα radiation. Scanning electron microscopy (SEM)–backscattered electron image (BEI) observation was performed using a JEOL JEM-5600. Transmission electron microscopy (TEM) observations were carried out using a Hitachi H-800. High-resolution transmission electron microscopy (HRTEM) and nano-beam energy dispersive X-ray spectrometry (EDS) were carried out using a Hitachi HF-2000 with a cold-type field-emission electron (FEG) gun. Thin films for TEM and HRTEM observations were prepared by an ion-thinning method using a Gatan precision ion-polishing system (PIPS™), model 691. Thermal analysis was performed by differential scanning calorimetry (DSC) using a Mac Science DSC-3100S system.

3. Results

The liquid phase separation behavior in arc-melted ingots of $(Co_{0.75}Si_{0.10}B_{0.15})_{100-x}Cu_x$ alloys was evaluated, although amorphous phase formation is unlikely in an arc-melted ingot. Fig. 1a and b shows XRD patterns and optical microscope (OM) images, respectively, of the cross-sectional area of arc-melted ingots of the $(Co_{0.75}Si_{0.10}B_{0.15})_{100-x}Cu_x$ alloys for a wide range of Co/Cu ratios. In the XRD patterns, the sharp intensity peaks corresponding to *fcc*-Cu can be seen in specimens with x = 10–90, and that of *hcp*-Co was seen in specimens with x = 0–70. Both *fcc*-Cu and *hcp*-Co peaks can be seen in the Co–Cu–Si–B specimens over a wide range of Co/Cu ratios. In the cross-sectional images of Fig. 1b, a phase-separated interface on the scale of millimeters between the metallic silver core and the copper-colored shell layer is clearly seen in the specimens with x = 20–90. The interface between the metallic silver and copper-colored regions is smooth. These observations indicate the occurrence of liquid phase separation to form Cu-rich and Co-rich liquids during the arc-melting process in $(Co_{0.75}Si_{0.10}B_{0.15})_{100-x}Cu_x$ alloys with a wide range of Co/Cu ratios.

Fig. 2 shows the outer appearance of melt-spun ribbons made from $(Co_{0.75}Si_{0.10}B_{0.15})_{100-x}Cu_x$ alloys with a wide range of Co/Cu ratios. Continuous ribbons were obtained regardless of the Co/Cu ratio. The color of the melt-spun ribbon depended on the Cu content. The color changed from metallic silver to copper-colored with increasing Cu content. To identify the occurrence of liquid phase separation and the formation of an amorphous phase in the alloys, XRD and DSC analyses were performed; the results are shown in

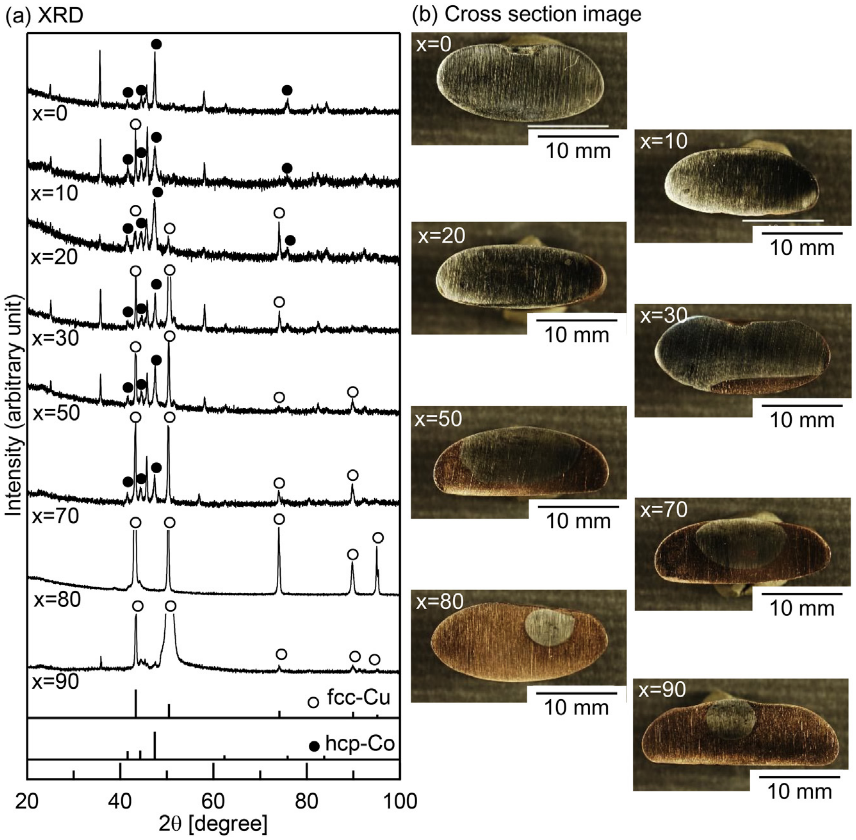

Fig. 1. (a) XRD patterns and (b) cross-sectional images of arc-melted ingots of $(Co_{0.75}M_{0.10}B_{0.15})_{100-x}Cu_x$ alloys of varying Co/Cu ratios.