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Microstructure identification of devitrified Cu–Ti–Zr–Ni bulk amorphous alloy

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ABSTRACT

The microstructures of devitrified Cu–Ti–Zr–Ni bulk amorphous alloy were identified by X-ray diffractometry (XRD) and transmission electron microscope (TEM). XRD and TEM examinations show that the deep eutectic structures of the tested alloy consist of $CuTi_2$–$Cu_{10}Zr_7$, Cu_3Ti–CuZr, Cu_3Ti–$Cu_{10}Zr_7$–CuZr low-order eutectics. Moreover, short-range ordering clusters in the melt with configuration similar to that of $Cu_{10}Zr_7$ compound may contribute to the glass forming ability of bulk amorphous Cu–Ti–Zr–Ni alloy.

1. Introduction

Cu-based bulk metallic glasses (BMGs) have been drawing increasing attentions in recent years due to their high mechanical properties as well as good glass forming ability (GFA) and relatively lower materials cost. Considerable efforts have been devoted to exploring new Cu-based BMGs, such as Cu–(Zr, Hf)–Ti [1], Cu–(Zr, Hf)–Al [2,3], Cu–Zr–Ti–Ni [4] etc. Particularly, $Cu_{46}Zr_{42}Al_7Y_5$ [5] and $Cu_{44.25}Ag_{14.75}Zr_{36}Ti_5$ [6] with the critical diameter of 10 mm were successfully fabricated by appropriate minor alloying additions of Y and Ag, respectively. Recently, Fu et al. [7] have successfully produced the glassy rod with a maximum sample thickness of 11 mm and larger supercooled liquid region of 108 K by substituting Cu with minor amount of Ag in Cu–Zr–Al–Gd alloy system. Remarkable achievements in GFA of Cu-based BMGs are attributed to significant atomic size mismatches and negative heats of mixing between the constituent elements, and closing to deep eutectics of the multi-component alloy systems. Previous work proves that alloy, which is close to the deep eutectic composition and far away from the compositions of intermetallic compounds with high melting temperatures, can be easily quenched to amorphous state [8]. Therefore, elaborate examination on the crystalline structures of devitrified amorphous alloy concerning the varieties and morphologies of the precipitated compounds would be significant for composition optimization of high GFA alloy and the design of new amorphous alloy. Nevertheless, relatively little has been reported on the mechanism of solidification kinetics and resultant solidification microstructures of Cu-based BMGs. In current paper, therefore, an investigation focused on the issues above-mentioned is conducted with respect to the slowly solidified Cu–Ti–Zr–Ni amorphous alloy.

2. Experimental procedure

The alloy $Cu_{52.5}Ti_{30}Zr_{11.5}Ni_6$ (at.%, hereafter referred to as Cu52.5) ingot was prepared by arc melting mixture of pure Cu (99.9 wt.%), Ti (99.9 wt.%), Zr (99.5 wt.%) and Ni (99.9 wt.%) in a Ti-gettered argon atmosphere. Alloy ingot was re-melted three times to ensure chemical homogeneity. Bulk cylindrical rods of 5, 6 and 8 mm in diameter and of 40 mm in length were produced by conventional copper mold casting method. The microstructure was examined by X-ray diffractometry (XRD) with Cu-Kα radiation and transmission electron microscope (TEM) with energy dispersive X-ray (EDX) spectrometer operated at 200 kV.

3. Results and discussion

Amorphous Cu52.5 alloy exhibits higher reduced glass transition temperature T_{rg} ($T_g/T_l = 0.603$) with deep eutectic among the alloy series designed, which can be quenched into glassy sample up to 5 mm diameter by the copper mold casting method [9]. In current experiment, samples with diameters of 6 and 8 mm were also prepared aiming to identify the crystalline compounds precipitated from the amorphous matrix. Fig. 1 shows typical X-ray diffraction patterns of Cu52.5 alloy rods with different diameters. XRD examinations indicate that broad halo typical of amorphous structure decomposed distinctly and crystalline peaks were detected when the size of sample rods exceed the critical diameter of amorphous Cu52.5 alloy. The dominating precipitated compounds were determined to be Cu_3Ti, $Cu_{10}Zr_7$, $CuTi_2$ and CuZr. Part diffraction peaks superimposed on each other due to a great deal of crystalline phases form in the amorphous matrix. Although X-ray diffraction

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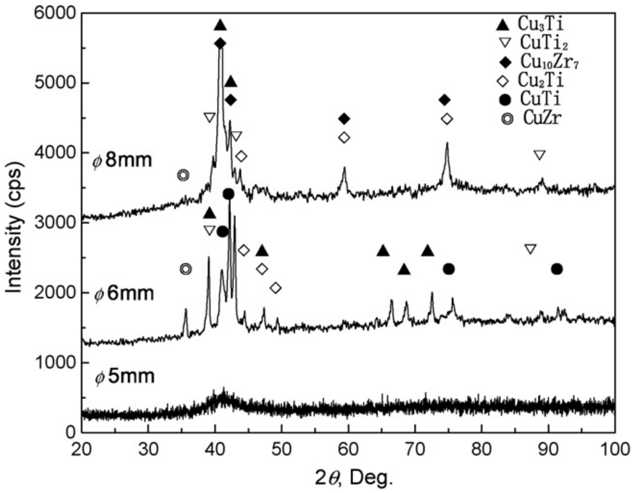

Fig. 1. XRD patterns of as-cast $Cu_{52.5}Ti_{30}Zr_{11.5}Ni_6$ samples with different diameters.

intensity of 8 mm sample is higher apparently than that of 6 mm sample, the number of crystalline peaks decreases. On the one hand, the diffraction peaks of crystals overlap with increasing number and varieties of the precipitated compounds. On the other hand, the crystalline peaks corresponding to CuTi compound detected in 6 mm sample are nearly disappeared in 8 mm sample. The crystallization behavior of amorphous $Cu_{40}Ti_{30}Ni_{15}Zr_{10}Sn_5$ alloy shows that the precipitated CuTi phase at low annealing temperature disappears gradually with prolonged annealing time or increased annealing temperature [10]. Thus, CuTi compound in the devitrified Cu–Ti–Zr–Ni alloy system is considered to be a metastable phase. In the well-known $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy, metastable Cu–Ti phase (composition is determined approximately to be $Cu_{85}Ti_{15}$) is also reported to form prior to other compounds when isothermally annealed at 623 K [11]. Concerning the CuTi phase might hold a small unit cell with structure possibly similar to that of some short-range ordering clusters in the matrix, it is easier for CuTi phase to form firstly when external activation energy is exerted, which requires no long-range diffusion for different atoms to simultaneously rearrange their spatial positions.

The microstructures of as-cast Cu52.5 samples with diameters of 6 and 8 mm were observed by TEM. Yet the microstructure of Cu52.5 alloy with a 8 mm diameter exhibits rather coarse dendrite-like morphology, the whole TEM images presented in the current paper originate from the cast sample of 6 mm in diameter. Fig. 2(a) shows the transitional area just demonstrating the formation of primary crystalline structure (dark contrast) from the decomposed amorphous matrix (bright contrast). In the centre of the sample with decreasing cooling rate, typical eutectic microstructure was observed following the glassy matrix entirely decomposed. Lamellar eutectic microstructure is clearly observed though the lamellae are not ideally aligned and not completely uniform in thickness. The eutectic structure consists of bright regions and grey regions alternatively, and the majority of the bright regions exhibit approximately ellipse shape and the minority are strip-bands (as is shown in Fig. 2(b) and (c)). The different growth directions of some lamellar sheets with respect to the plane of cross-section account for the observed different profiles of the bright crystalline phase in Fig. 2(c). The bright grains are distinguished to be tetragonal $CuTi_2$ phase, and the residual greys to be orthorhombic $Cu_{10}Zr_7$ phase, corresponding selected area electron diffraction patterns (SADPs) are shown in Fig. 2(d) and (e), respectively.

Another typical eutectic morphology, mostly showing elongated and striated strip-bands, is shown in Fig. 3(a). The striated strip-bands may grow separately, or grow combining with bright strip-bands. The SADPs of the bright strip-bands, grey regions and striated strip-bands are shown in Fig. 3(b), (c) and (d), respectively. The examinations reveal that they are Cu_3Ti, $Cu_{10}Zr_7$ and CuZr phases with orthorhombic ordered structures, respectively. It can be inferred from the results that one phase is Ti-rich and the other is Zr-rich concerning their coupled growth constituents ($CuTi_2$–$Cu_{10}Zr_7$, Cu_3Ti–CuZr and Cu_3Ti–$Cu_{10}Zr_7$). The enrichments of Ti or Zr in the concomitantly formed compounds imply that solutes redistribution occurs evidently when solidification proceeds. The formation of leading phase excludes superfluous atoms, which changes the composition of the surrounding matrix. Thus, the compositional fluctuation facilitates the formation of the vicinal phase enriched the ejected atoms. Based upon the integrated results of XRD and SADPs, the solidified microstructure of Cu52.5 alloy with decreasing cooling rates can be approximately pictured as follows:

$$\begin{aligned} Am &\rightarrow Am' + \mathrm{CuTi(Metastable\ Phase)} \\ &\rightarrow \mathrm{Eutectic\ Structure}(Cu_3Ti + CuTi_2 + Cu_{10}Zr_7 + CuZr + Cu_2Ti) \end{aligned}$$

However, the constituent element Ni appears to leave invisible traces all along in either detected compounds. The essential of minor Ni addition is to enhance the complexity and confusion of the designed alloy system as a few Cu is substituted by according to atomic size effect [12]. It is known that Cu and Ni is located in the same family in the element periodic table with infinite mutual solubility, as is the case for Ti and Zr. Naturally, substitutions of Cu by Ni and Ti by Zr on the lattices occur as crystalline phases form. Thus, the precipitated compounds from the Cu–Ti–Zr–Ni amorphous matrix are commonly described as $(Cu,Ni)_x(Ti,Zr)_y$ (solid solutions of Ni, Ti or Zr elements in the Cu–Zr or Cu–Ti phases). Partial substitutions mutually induce the calculated lattice parameters to deviate slightly from those precise values of binary compounds, though not indicated in the paper. For instance, Ti dissolved in $Cu_{10}Zr_7$ phase may shrink its lattice parameters as Ti atoms are smaller than Zr. The concentration of Ni in the alloy is relatively little, and most is dissolved replacing Cu in the unit cell. Fig. 4 shows the EDX spectrum result indicating the element contents of a characteristic particle CuZr observed above.

Previous literatures [5,8] have pointed out that near deep eutectic, there are multiple ordered crystalline phases competing with each other, especially in multi-component alloy system. Thus, the crystallization of liquid should necessitate the simultaneous rearrangement of different species of atoms via long-range diffusion, which limits the crystallization kinetics significantly for the cooperative growth reactions of more than three kinds of crystalline phases. The opinion about BMG is approved by the fact that the morphology of the devitrified Cu52.5 alloy demonstrates distinct eutectic microstructure, and numerous precipitated crystalline phases with comparatively complex configurations present in the decomposed Cu52.5 alloy matrix. The crystallization process of Cu52.5 alloy can be frustrated consequently for achieving good GFA upon rapidly quenching. Some melting curves of the multi-component amorphous alloys show that the deep eutectics possibly consist of different low-order eutectics, such as binary or ternary eutectic with close melting points [13]. The examination of the decomposed Cu52.5 alloy reveals that there exists visible $CuTi_2$–$Cu_{10}Zr_7$, Cu_3Ti–CuZr and Cu_3Ti–$Cu_{10}Zr_7$ eutectic structures, which is consistent with the above argument about deep eutectics of multi-component amorphous alloys.

Otherwise, it is worth noting that $Cu_{10}Zr_7$ phase may play an important role in the formation of bulk glassy alloy as well as the stability of supercooled liquid against crystallization. Inoue