Nanocrystallization of Cu₅₀Zr₄₅Ti₅ Metallic Glass Induced by Electron Irradiation

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The effect of electron irradiation on the structure of melt-spun Cu₅₀Zr₄₅Ti₅ metallic glass was investigated. Microstructural evolution during electron irradiation was examined by means of conventional and high-resolution transmission electron microscopy (CTEM and HRTEM) equipped with X-ray energy dispersive spectroscopy (EDS). The glassy phase was not stable under electron irradiation and crystalline nanoparticles with the monoclinic CuZr structure were formed. The volume fraction of the nanocrystalline phase increased with the electron dose while the average grain size remained at about 7 nm. This result indicates that electron irradiation is effective in producing nanocrystalline structures from the metallic glass. [doi:10.2320/matertrans.47.1930]

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1. Introduction

Metallic glasses have received much attention in recent years and have been considered as a new class of structural materials owing to their attractive physical and chemical properties such as high strength, high corrosion resistance and soft magnetic properties. However, monolithic metallic glasses exhibit poor ductility at room temperature, which limits their technical application as structural materials. In order to improve the ductility of metallic glasses, a number of studies have been carried out. It has been demonstrated that the formation of a nanocomposite structure, which is prepared by nanocrystallites dispersed in glassy alloys, is an effective method for improving the ductility. The nanocrystalline composites have exhibited excellent mechanical and functional properties which cannot be realized by conventional crystalline materials, nor by single-phase glassy materials.

Some glassy-nanocrystalline composites of enhanced ductility have been developed by proper alloying with the elements of non-negative mixing enthalpy with the major component in, for example, Cu-based and Zr-based alloys. The nanocrystallites can be formed by controlling the cooling rate upon solidification or by annealing of glassy alloys. Recently, it was found that Zr–Cu-based metallic glasses could form the nanocomposite structure through crystallization of the glassy phase via heat treatments. However, the expansion of the supercooled liquid region induces high stability of the glassy phase against crystallization and results in an increase in the crystallization temperature and/or changes in the crystallization mode, which make controlled nanocrystallization difficult. Therefore, only limited metallic glasses can form the nanocomposite structure through crystallization of the glassy phase via heat treatments.

Cryocrystallization of the glassy phase is induced not only by heat treatments but by other methods such as electron irradiation, ion irradiation, electropulsing and high pressure. It has been demonstrated that electron irradiation can induce nanocrystallization in metallic glasses in which nanoscale structures cannot easily be realized by heat treatments. However, there are few reports on electron irradiation effects on structural changes in metallic glasses. In this study, we investigate the microstructural changes of a Cu₅₀Zr₄₅Ti₅ metallic glass under electron irradiation.

2. Experimental Procedures

A master ingot of the Cu₅₀Zr₄₅Ti₅ alloy (composition is given in nominal atomic percentages) was prepared by arc melting, where mixtures of pure Cu, Zr and Ti were melted in an argon atmosphere purified using a titanium getter. From the obtained alloy ingot, ribbon-shaped samples of about 20 µm in thickness and 1.5 mm in width were prepared by rapid solidification of the melt on a single copper roller at a peripheral velocity of 42 m s⁻¹ in an argon atmosphere. The thermal stability against the glass transition and crystallization was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K s⁻¹.

The structure of as melt-spun ribbons was examined by X-ray diffractometry with a monochromatic Cu Kα radiation, conventional and high-resolution transmission electron microscopy (CTEM and HRTEM). Thin foils for TEM observations and electron irradiation were cut out from the melt-spun ribbons, followed by mechanical thinning and then argon ion milling to electron transparency. A low-energy ion milling at about 2.0 kV was used. Electron irradiation was carried out at room temperature using an electron microscope (JEM-2010) at the accelerating voltage of 200 kV with the electron beam of about 1500 nm in diameter. The current density of the electron beam was about 1.3 × 10⁷ A/m², or a dose rate of 8.0 × 10⁻²⁵ m⁻²s⁻¹. The total dose was 5.8 × 10²⁶ m⁻² at the highest. The microstructure of the as-irradiated specimens was observed and analyzed in-situ or after irradiation using the TEM and the X-ray energy dispersive spectrometer (EDS) attached to this TEM. The diameter of electron beam for the EDS analysis was about 5 nm. All the experiments were carried out at room temperature.

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3. Results

3.1 Structure and thermal properties of as melt-spun ribbons

Figure 1 shows the XRD pattern of a melt-spun ribbon before electron irradiation. The diffraction pattern consists only of broad diffuse peaks, and no diffraction peaks corresponding to a crystalline phase are observed. No crystalline phases were observed in TEM either in as melt-spun ribbons. Figure 2 shows an HRTEM image (a) and the corresponding SAD pattern (b) of the melt-spun ribbon sample before electron beam irradiation.

Figure 3 shows a DSC curve of an as prepared ribbon traced at a heating rate of 0.67 K s$^{-1}$. The glass transition temperature ($T_g$) estimated is 678 K. The onset temperature of the first-stage crystallization ($T_X$), corresponding to the primary exothermic peak, is 737 K. The supercooled liquid region ($\Delta T_X = T_X - T_g$), which is regarded as an indicator for the thermal stability against crystallization, is 59 K.

3.2 Nanocrystallization induced by electron irradiation

Figure 4 shows a series of in-situ TEM micrographs of a specimen during electron irradiation. The specimen was irradiated at a dose rate of $8 \times 10^{22}$ m$^{-2}$ s$^{-1}$ at room temperature up to the dose of $2.9 \times 10^{25}$ m$^{-2}$. Figures 4(a)–4(c) characterize the specimen before irradiation. Only halo rings were observed in the corresponding SAD pattern in Fig. 4(b). Figure 4(c) is a dark-field (DF) image of the same area as in Fig. 4(a) taken with the ring A indicated in Fig. 4(b), where no crystalline phase is observed. In the specimen irradiated to the dose of $2.4 \times 10^{25}$ m$^{-2}$, crystalline nanoparticles were observed as shown in Fig. 4(d). The nanocrystallites were homogeneously dispersed in the glassy matrix. Discontinuous Debye rings and/or sharp diffraction spots together with the broad halo rings are seen in the SAD pattern. New diffraction spots appeared during irradiation indicating that the electron-irradiation induced crystallization. With further irradiation, the intensity of the Debye rings increased, accompanied by weakening of the halo rings, and the area with granular contrast in the BF image extended. Figures 4(f), (g) and (h), (i) show DF TEM images and their corresponding SAD patterns for the specimen irradiated to the doses of $9.6 \times 10^{25}$ m$^{-2}$ and $2.9 \times 10^{26}$ m$^{-2}$, respectively. The amount of the nanocrystalline precipitates increased with the dose, although no significant changes in size and morphology of the nanocrystalline precipitates were observed. By analyzing the SAD patterns, the crystalline nanoparticles were identified to the monoclinic CuZr phase (Pearson symbol: mP4). The average particle size ($D$) was estimated from TEM micrographs. Figure 5 and it was plotted as a function of irradiation time ($t$) or irradiation dose in Fig. 5. The result shown in Fig. 5 indicates the non-linear growth of the nanoparticles with a decrease in the growth rate. It is noted that the data observed could not be fit with a power function like $D = a + bt^c$. 

![Fig. 1 XRD pattern of the melt-spun Cu$_{50}$Zr$_{45}$Ti$_5$ ribbon sample before electron beam irradiation.](image1)

![Fig. 2 An HRTEM image (a) and the corresponding SAD pattern (b) of the melt-spun Cu$_{50}$Zr$_{45}$Ti$_5$ ribbon sample before electron beam irradiation.](image2)

![Fig. 3 DSC trace of the melt-spun Cu$_{50}$Zr$_{45}$Ti$_5$ ribbon sample before electron beam irradiation.](image3)
Further characterization of the crystalline nanoparticles was performed using HRTEM, nano-beam electron diffraction (NBD) and EDS. Figure 6(a) shows an HRTEM image of the specimen irradiated to a dose of $2.9 \times 10^{26}$ m$^{-2}$. One of the nanoparticles formed during irradiation is indicated with an arrow in Fig. 6(a). Figure 6(b) shows the NBD pattern taken from the crystalline nanoparticle indicated by the arrow in Fig. 6(a), and Fig. 6(c) is the corresponding EDS spectrum. The chemical composition of the crystalline nanoparticle is determined to be Cu$_{50}$Zr$_{48}$Ti$_{5}$ by quantitative analysis of the EDS spectrum. By analyzing HRTEM image and the NBD pattern, the nanoparticles are identified as the monoclinic CuZr crystalline phase from the fringe spacing, the geometry of crossed-fringe image and the composition of the nanoparticles.

4. Discussion

As shown above, crystalline nanoparticles precipitated in the melt-spun glassy Cu$_{50}$Zr$_{48}$Ti$_{5}$ ribbon during electron irradiation. In general, there are two important factors in irradiation-induced crystallization: (1) promotion of atomic diffusion; and (2) the stability of the nanocrystalline phase against growth which helps to maintain the crystalline structure. Heating of the sample by the electron beam was found to be negligibly small. When the two conditions are meet simultaneously, electron irradiation induces nanocrystallization of the glassy phase. In this study, the crystalline nanoparticles with the monoclinic CuZr structure in the Cu$_{50}$Zr$_{48}$Ti$_{5}$ alloy specimen have been observed under electron irradiation, indicating that the monoclinic CuZr phase is highly stable against electron irradiation. On the
other hand, in the Cu$_{50}$Zr$_{45}$Ti$_{5}$ alloy specimen a Cu-rich oC68 Cu$_{10}$Zr$_{7}$ crystalline phase was formed by nucleation and interface-controlled growth after isothermal annealing at the temperature of the first exothermic peak, 747 K, in a vacuum of $10^{-3}$ Pa. The isothermal calorimetry performed at 710 K exhibited an incubation period related to nucleation. The existence of some weak unidentified peaks in the XRD pattern indicates that a small amount of some other phases was formed simultaneously. The CuZr$_2$ phase could thermally form together with the Cu$_{10}$Zr$_7$ phase according to the Cu–Zr phase diagram. Since the observed XRD peaks were too weak and the strongest diffraction peaks of the CuZr$_2$ phase were overlapped with those of the Cu$_{10}$Zr$_7$ phase, formation of the CuZr$_2$ phase cannot be confirmed precisely from the present result. However, these indicate that the crystallization process upon thermal annealing is different from that upon the electron irradiation.

It is also demonstrated that no significant change in the size of the crystalline nanoparticles takes place during electron irradiation at the higher doses. Similar results have been obtained in the studies on Zr-based and Fe-based metallic glassy alloys.\textsuperscript{10,11,16} CuZr particles exhibited a non-linear growth with time, where the growth rates at time $t > 1200$ s became to an order of $1 \times 10^{-13}$ m s$^{-1}$ in Fig. 5 and the particle size saturated at about 8 nm (Fig. 5). The strong retardation in the grain growth may be due to the small compositional difference between the glassy matrix and CuZr phase (Fig. 6(c)). Further, Fig. 5 shows that an incubation period of about 200 s is required for the irradiation-induced precipitation of the CuZr phase. In general, formation of the nanocomposite structure in amorphous alloys requires both the ease of homogeneous nucleation of the crystalline phase and difficulty of the subsequent crystal growth.\textsuperscript{11,16} The activation process of atomic diffusion under electron irradiation affects the nucleation and growth rates of crystalline phases. Considering atomic species and direction in atomic movement, highly frequent homogeneous atomic displacement in a glassy phase can be induced by electron irradiation. Highly dispersed homogeneous nucleation may occur under electron irradiation. The crystal growth can be discussed from the adsorption and dispersion of atoms at the liquid-solid interface.\textsuperscript{18} The growth rate is determined by the difference between the adsorption and dispersion rates. Under electron irradiation, the rates of adsorption and dispersion strongly depend not only on atomic interaction nature, but also on the interaction between high energy electrons and constituent atoms. The difference between these rates under electron irradiation is believed to be small.\textsuperscript{11,16} This is one reason for the subsequent low growth rate of the monoclinic CuZr under electron irradiation. In addition, interstitials and vacancies are continuously produced by electron irradiation in crystalline precipitates. Grain refinement of crystalline precipitates may occur through the rearrangement of a large amount of defects produced by electron irradiation.\textsuperscript{19} This may have certain effect on the nanocrystalline structure produced under irradiation. The present result suggests that electron irradiation is a possible method to prepare nanocrystalline-glassy composite structures in metallic glasses.

5. Conclusions

The effect of electron irradiation in melt-spun Cu$_{50}$Zr$_{45}$Ti$_{5}$ ribbon specimens was investigated. Microstructural evolution during electron irradiation was observed and analyzed using TEM and EDS. Crystalline nanoparticles with the monoclinic CuZr structure were precipitated by irradiation, where the fraction of the nanocrystalline precipitates increased with the dose. No significant changes in size and morphology of the nanocrystalline precipitates were observed during irradiation except for the initial stage of nanocrystallization. The present result suggests that the electron irradiation to metallic glasses has potential for producing the nanocrystalline-glassy composite structure.

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REFERENCES