Irradiation induced nanocrystallization of Cu-based metallic glass

Guoqiang Xie [1], Lin Shao [2], D.V. Louzguine-Luzgin [3] and Akihisa Inoue [1,3]

[1] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
[2] Department of Nuclear Engineering, Texas A&M University, Texas 77843, USA
[3] WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Metallic glasses (MGs) exhibit many interesting physical and chemical properties. They have attracted increasing attention, and are considered as promising candidates for the next generation of structural and functional materials. However, monolithic metallic glasses exhibit poor ductility under stress, which limits the extensive practical application. It has been demonstrated that nanocrystal-dispersed MGs can effectively improve ductility. Such partial crystallization can be realized by bending, annealing and indentation. However, bending and indentation are destructive and cannot be used in practical applications. Recently, electron and ion irradiation have been explored as means to introduce nanocrystals [1-4]. In the present study, we investigated the nanocrystallization behavior of a Cu-based ($Cu_{50}Zr_{45}Ti_5$) metallic glassy alloy under electron and He ion irradiation, as well as upon thermal annealing. The crystallization kinetics and structure changes on heating were also discussed.

$Cu_{50}Zr_{45}Ti_5$ (nominal at.%) alloy ribbon samples with about 20 μm in thickness and 1.5 mm in width were prepared by rapid solidification of the melt-spun method. The thermal stability was examined by differential scanning calorimetry (DSC). Some samples were annealed at 710 K in a vacuum for 7.2 ks. The structure of the samples was examined by X-ray diffractometry (XRD), conventional and high-resolution transmission electron microscopy (CTEM and HRTEM). Electron irradiation of the samples was carried out at room temperature using a JEM-2010 electron microscope. The accelerating voltage was 200 kV. The current density of the electron beam for irradiating the samples was about 1.3×10^4 A m^{-2}, which corresponds to a dose rate of 8.0×10^{22} m^{-2} s^{-1}. The size of electron beam during irradiation was about 1500 nm. The largest total dose of electron irradiation was 5.8×10^{26} m^{-2}. The microstructures of the as-irradiated samples were observed and analyzed *in-situ* or after electron irradiation using the TEM and an X-ray energy dispersive spectroscope (EDS) attached to this TEM. Ion irradiation was also carried out with 140 keV He ions to a dosage of 1.7×10^{21} m^{-2} at room temperature.

Based on the microstructure observation by TEM and the analyses by XRD and DSC, the $Cu_{50}Zr_{45}Ti_5$ alloy samples of as melt-spun ribbons before irradiation are composed of a glassy phase (Fig. 1(a)). Microstructural changes induced by electron irradiation of the $Cu_{50}Zr_{45}Ti_5$ alloy ribbon samples were observed with TEM. It is demonstrated that the nanocrystallites precipitated during electron irradiation. The amount of the nanocrystalline precipitates increased with the dose of electron irradiation, while no significant changes in size and morphology of the nanocrystalline precipitates were observed. Figure 1(b) shows the TEM micrographs of the $Cu_{50}Zr_{45}Ti_5$ ribbon samples irradiated by electron beam to a dose of 4.8×10^{25} m^{-2}. The crystalline nanoparticles with an average grain size of about 8 nm are observed. They are homogenously dispersed in the glassy matrix of the electron beam irradiation region. Discontinuous Debye rings and/or sharp diffraction spots together with the broad halo rings are seen, as shown in Fig. 1(b). By analyzing the SAD patterns (in Fig. 1(b)) and the corresponding to nano-beam diffraction (NBD) patterns as well as the HRTEM images, the nanocrystalline precipitates are identified to a monoclinic CuZr phase (Pearson symbol: mP4) [5].

The nanocrystalline precipitates are also observed with a size range from several nanometers to several ten nanometers for the samples irradiated by He ions to a dosage of 1.7×10^{21} m^{-2}, as shown in Fig. 2. Furthermore, a number of He bubbles (white spots in Fig. 2) are seen in the irradiated samples. A hardness enhancement associated with nanocrystal formation has been demonstrated [4].

On the other hand, the equilibrium oC68 $Cu_{10}Zr_7$ and tI6 $CuZr_2$ crystalline phases with the grain size ranged from several nanometers to about 200 nm were precipitated from the glassy phase of the $Cu_{50}Zr_{45}Ti_5$ glassy alloy upon thermal annealing, while no CuZr phase was observed in the annealed samples [6,7]. The crystallization process took place by nucleation and growth mechanism, and an Avrami exponent of about 3.3 may indicate a three-dimensional interface-controlled growth of nuclei with a decreasing nucleation rate.

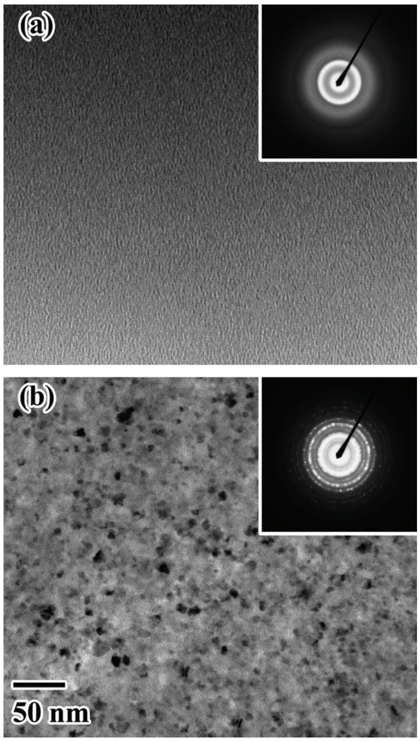

FIG. 1. Bright field-TEM images and the related SAD patterns showing the microstructure evolution of the $Cu_{50}Zr_{45}Ti_5$ alloy sample during electron irradiation: (a) before irradiation, (b) to a dose of 4.8×10^{25} m^{-2}.

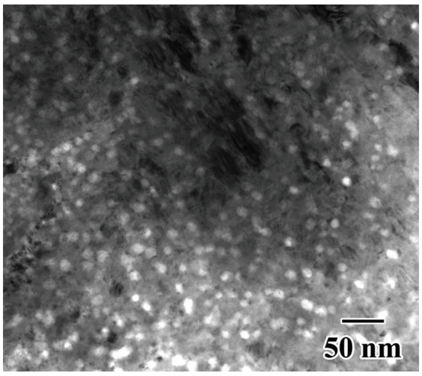

FIG. 2. Bright field-TEM image of the $Cu_{50}Zr_{45}Ti_5$ alloy sample irradiated by 140 keV He ions to a dosage of 1.7×10^{21} m^{-2}.

References

[1] G. Q. Xie et al., Mater. Trans. 47 (2006) 1930.
[2] T. Nagase et al., Intermetallics 15 (2007) 211.
[3] J. Carter et al., Scripta Mater. 61 (2009) 265.
[4] G. Q. Xie et al., Surf. Coat. Technol. 206 (2011) 829.
[5] A. V. Zhalko-Titarenko et al., Phys. Status Solidi B 184 (1994) 121.
[6] G. Q. Xie et al., Mater. Sci. Forum 561-565 (2007) 2045.
[7] G. Q. Xie et al., J. Alloys Compd. 483 (2009) 24.