Microstructure Feature of Bulk Glassy Cu$_{60}$Zr$_{30}$Ti$_{10}$ Alloy in As-cast and Annealed States

Yantang Chen$^1$, Tao Zhang$^2$, Wei Zhang$^1$, Dehai Ping$^3$, K. Hono$^3$, Akihisa Inoue$^2$ and Toshio Sakurai$^2$

$^1$Inoue Superliquid Glass Project, ERATO, Sendai 980-0807, Japan
$^2$Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
$^3$Materials Physics Division, National Institute for Materials Science, Tsukuba 305-0047, Japan

The microstructures of a bulk glassy Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy in as-cast state and annealed at glass transition temperature ($T_g$), i.e., 440°C, have been studied using an electron transmission microscope (TEM) and a high-resolution transmission electron microscope (HRTEM). Nanocrystals with a size of 4 nm were observed in the cast rod with a diameter of 4 mm. The nanocrystal was determined to be CuZr, which is primitive cubic structure with a lattice parameter of $a = 0.3262$ nm by analyzing its nano-beam electron diffraction pattern, suggesting that such nanocrystals have a positive effect on mechanical properties. Obviously distinguished interval dark and bright regions were observed in the cast rod with a diameter of 4 mm has been formed for Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy by the cop-molding technique using an electron beam, which is equipped with a three-dimensional atom probe field ion microscopy (3DAP-FIM). It was found that the Cu and Zr elements fluctuated along depth direction while the Ti element remained almost unchanged. It is therefore interpreted that the annealing-induced nanocrystalline phase results from nucleation and growth at the sites of the Cu-rich and/or Zr-rich regions as well as from growth of the cast-in nanocrystals.

(Received May 17, 2002; Accepted August 28, 2002)

Keywords: microstructure, glassy Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy, cast, anneal, glass transition temperature

1. Introduction

It has been reported that annealing-induced nanostructure alloys containing nanoscale particles in a glassy alloy matrix exhibit improved properties as compared with the corresponding glassy single-phase alloys. For example, the mechanical properties have been improved by homogeneous dispersion of nanoscale compound particles into glassy matrix in Zr-based and Al-based glassy alloys. The finding has generated considerable research interest in developing nano-composites in glassy alloys by heat-treatment prior to crystallization and studying the microstructure feature of nanocomposite because the microstructure evolution before and after heat treatment is an important factor in understanding the crystallization mechanism and the relationship between microstructure and property. However, little has been reported about the microstructure feature in bulk glassy crystalline composites in as-cast state and annealed at the temperature near $T_g$.

Recently, a new bulk metallic glass with a diameter up to 4 mm has been formed for Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy by the copper mold casting method and the bulk glassy alloy exhibits good mechanical properties. The Young’s modulus ($E$), tensile yield strength ($\sigma_y$), tensile fracture strength ($\sigma_f$) and fracture elongation including elastic elongation ($\varepsilon_{ef}$) are 114 GPa, 1780 MPa, 2000 MPa and 1.9%, respectively. In the present work, we present microstructure feature and decomposition behavior in the glassy Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy in as-cast state and annealed for 10 min at $T_g$.

2. Experimental Procedures

The glassy alloy with a nominal composition of Cu$_{60}$Zr$_{30}$Ti$_{10}$ was prepared by arc melting the mixtures of pure Cu, Zr and Ti metals in an argon atmosphere. Bulk glassy alloy rod in a cylindrical shape with a length of 70 mm and a diameter of 4 mm was produced by the copper mold casting method. The glass transition temperature ($T_g$) and crystallization temperature ($T_x$) of the bulk glassy alloy were described elsewhere. Heat treatment was subjected in vacuum ($\sim 10^{-3}$ Pa) for 10 min at $T_g$. TEM and HRTEM were carried out to observe the microstructure in the glassy Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy before and after annealing using Philips CM200, JEOL JEM 4000EX and JEM 3000F. To produce TEM specimen, disks with a thickness of about 0.5 mm were cut from the rod. Samples for TEM analysis were prepared first by mechanical grinding to be about 50 μm thick and finally thinned by ion milling. During TEM sample preparation, ion radiation does not hurt microstructure. The concentration distribution determination was performed with 3DAP-FIM, which is equipped with a Cameca tomographic atom probe detection system. The atom probe analyses were carried out at 70 K in an ultra-high vacuum ($< 1.0 \times 10^{-9}$ Pa) with a ratio of 20% between pulse voltage and permanent applied voltage on tip. To produce tips, bars with a square cross section of 0.5 mm x 0.5 mm were cut from the 4 mm diameter rod. The sharp needle shaped specimens for 3DAP-FIM examination were prepared by first mechanical grinding to be square of about 20 μm x 20 μm cross section followed by micro-electropolishing with 2% perchloric acid in 2-butyloethanol at 10 – 20 V dc.

3. Results and Discussion

Figure 1 shows the TEM image and electron diffraction pattern of the as-cast glassy Cu$_{60}$Zr$_{30}$Ti$_{10}$ rod. It seems that the alloy rod is a completely glassy single phase from the
broad diffraction pattern. Although no obvious crystals are observed in the bright-field TEM image in Fig. 1, the scattered dark and bright zones may imply that the composition in the alloy is not ideally uniform. Since the microstructure was not discerned in detail by TEM, HRTEM was used to clarify the microstructure of the bulk alloy. Figure 2 shows the HRTEM image of the alloy in the as-cast state. Nanocrystals with a size of ~4 nm are clearly seen and their volume fraction is estimated as about 3% in the HRTEM observation. In order to identify the phase and structure of the nanocrystals, nano-beam electron diffraction technique with a diameter of 2.4 nm was used. The nano-beam electron diffraction pattern of one crystal in area A in Fig. 2 is given in Fig. 3. Referred to the concentration of the alloy, the crystalline phase is identified to be a CuZr phase with a primitive cubic structure and its lattice parameter is 0.3262 nm.

It has been reported that the cast glassy Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy has good mechanical properties, especially has satisfactory ductility. Apart from the contribution of the atomic banding nature among Cu, Zr and Ti atoms, the cast-in crystals dispersing within the glassy matrix have also positive effect on the mechanical properties. During the action of external stress, the nanocrystals may absorb a part of energy from external forces and hinder the crack propagation. As a result, the strength and ductility of the alloy are increased. Such a glassy alloy may be classified to be a cast nanocrystal-glassy composite.

In order to study the microstructure evolution of the crystal-glassy composite, the alloy was annealed for 10 min at $T_g$ (58°C below the first crystallization peak temperature). Figure 4 shows the bright-field TEM image and electron diffraction pattern of the alloy. The morphology in the annealed samples exhibits some unusual contrast. Phase separation due to the fluctuation of Cu and Zr concentrations revealing a distinct regular contrast of darker region with a length scale of about 30 nm surrounded by brighter regions is recognized in the micrograph. The diffraction pattern shows two halo rings, indicating that the sample annealed at $T_g$ consists of some nanocrystalline regions embedded in the glassy matrix. It is believed that this is the first evidence of such a microstructure in the glassy Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy annealed at $T_g$. Ganopadhyay et al. reported a similar microstructure in the amorphous Al$_{88}$Gd$_6$Laz$_2$Ni$_4$ alloy annealed at 220°C for 1 min and such microstructure was interpreted to result from a nucleation and growth mechanism. Figure 5 shows HRTEM image of the alloy annealed for ~10 min at $T_g$. One can see nanocrystalline phases with a size of about 10 nm embedded in the glassy matrix (some crystals are marked with arrows). The crystal was identified as CuZr phase with X-ray diffraction pattern.
Microstructure Feature of Bulk Glassy Cu$_{60}$Zr$_{30}$Ti$_{10}$ Alloy in As-cast and Annealed States

Fig. 4 Bright-field TEM image and electron diffraction pattern of the as-cast crystal-glassy Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy.

Fig. 5 HRTEM image of the as-cast crystal-glassy Cu$_{60}$Zr$_{30}$Ti$_{10}$ composite annealed for 10 min at $T_g$.

It is difficult to determine exactly the composition in the bright and dark regions because of their small size and the problem of beam spreading by TEM techniques. The composition distribution of Cu, Zr, and Ti in the alloy annealed at 440°C for 10 min was examined by using the 3DAP-FIM techniques. Figure 6(a) shows 3DAP-FIM elemental mapping of Cu, Zr and Ti taken from an analyzed volume of 40 nm x 8 nm x 7 nm. Each dot corresponds to the position of atom. Figure 6(b) shows the concentration distribution profiles of Cu, Zr, and Ti. It is seen that the concentrations of Cu and Zr fluctuate as a function of analysis depth. The periodicity of Cu-rich and Zr-rich regions is detected. However, the distribution of Ti is uniform, indicating that the fluctuation of Cu and Zr concentrations may cause the periodic contrast of the darker and brighter regions in Fig. 4. The phase reaction containing Ti may occur at higher temperatures.

The present work has revealed clearly the dispersion of nanocrystals embedded in the glassy matrix of the cast alloy rod with a diameter of 4 mm. The nanocrystals were identified to be the CuZr phase by the nano-beam electron diffraction technique. Furthermore this result suggests that the crystalline particles have a significant contribution to good mechanical properties of Cu-based bulk glassy alloy. After heat treatment for 10 min at $T_g$, the unusual microstructure showing interval dark and bright regions was observed and the composition was not well-distributed. The contrast with a length scale of about 30 nm (in Fig. 4) approximately corresponds to the fluctuation of Cu and Zr concentration (shown in Fig. 6). The periodicity of the contrast may be due to the compositional fluctuation. The 3DAP-FIM data show that the elements of Cu and Zr do not distribute uniformly in the analyzed volume of the annealed sample while the concentration of Ti is almost uniform. It is reasonable to deduce that the nanocrystalline structure formed upon annealing at $T_g$ is due to the concentration fluctuations of Cu and Zr. If the concentrations of Cu and Zr are available for the formation of phase CuZr due to short distance diffusion at $T_g$, crystallization reaction may occur heterogeneously at the sites of Cu-rich and/or Zr-rich in this alloy. On the other hand, the crystals formed after annealing can also result from the growth of cast-in crystals since the size of crystal in the annealed sample is larger than that in the cast specimen.
4. Conclusions

Based on the study of the as-cast crystal-glassy composite using TEM, HRTEM and 3DAP-FIM, we conclude the following results:

(1) Nanocrystals of \( \sim 4 \text{ nm} \) in size in the as-cast Cu\(_{60}\)Zr\(_{30}\)Ti\(_{10}\) rod with a diameter of 4 mm were found and were identified to be a CuZr phase, which is a primitive cubic structure with a lattice parameter of \( a = 0.3262 \text{ nm} \). Such a glassy alloy may be classified to be a nanocrystal-glassy composite.

(2) Distinctly distinguished contrast consisting of interval darker and brighter region due to the fluctuation of Cu and Zr concentration, which was interpreted by phase separation, was observed in the alloy annealed for 10 min at \( T_g \).

(3) The composition fluctuation of Cu and Zr atoms was detected in the alloy annealed for 10 min at \( T_g \). The crystals formed at \( T_g \) were interpreted to result from the nucleation and growth at the Cu-rich and Zr-rich regions and/or the growth of the cast-in nanocrystals.

REFERENCES