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Ion milling-induced micrometer-sized heterogeneities and partial crystallization in a TiZrCuFeBe bulk metallic glass

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ABSTRACT

The $Ti_{36.2}Zr_{30.3}Cu_{8.3}Fe_4Be_{21.2}$ (at.%) bulk metallic glass (BMG) exhibits a regular micrometer-sized pattern in the transmission electron microscope (TEM) after ion milling. Quantitative energy-dispersive X-ray spectroscopy (EDX) results show that the compositions in the bright and dark regions are distinctly different, and the compositions gradually change with the contrast of the pattern. In the intermediate regions (with grey contrast) preferential crystallization is observed and this confirms that microscale heterogeneities exist in the ion-milled TEM specimens. On the contrary, the specimens prepared by focused ion beam and by electrolytic thinning show featureless microstructures in the TEM. Moreover, EDX results and the secondary ion mass spectroscopy show that the constituent elements are homogeneously distributed. An ion milling-induced compositional fluctuation mechanism is proposed, and the partial devitrification can be explained based on this mechanism. The present findings may lead to a deeper understanding of the occurrence of micrometer-sized heterogeneities in BMGs induced by ion milling.

1. Introduction

Bulk metallic glasses (BMGs) are considered to be potential engineering materials because of their unique properties, such as high strength, high hardness, large elastic limit and excellent corrosion resistance [1–5]. However, most BMGs show very little macroscopic plastic deformation at room temperature due to the highly localized deformation in thin shear bands, which restricts their widespread application as structural materials [3–5]. An effective way to improve the plastic deformability of BMGs is to introduce structural heterogeneities, for example by designing compositions containing constituents with positive enthalpy of mixing, like Ni-Cu [6–8], Cu-Co [9,10], Ni-Ag [11], and Fe-Cu [12–14]. During plastic deformation, the heterogeneities can restrain the propagation of shear bands and multiply the number of shear bands, resulting in enhanced plasticity [2,7,15]. Additionally, structural heterogeneities have been suggested as the source for the "work hardening-like" behavior of BMGs [7]. Although some heterogeneities observed in BMGs with limited glass-forming ability (GFA) are attributed to artifacts introduced during sample preparation [16,17], cluster-scale and nanoscale heterogeneities are quite common in BMGs [7,18,19] and often play an important role in determining their physical and mechanical properties [7,18].

Since the cooling rate required for the vitrification of melts into bulk specimens is relative high (usually above 10 K/s) [1,4], the time window for constituent atoms to diffuse during solidification is very small and compositional fluctuations are generally limited to the nanometer scale [7,12,18]. Thus, micrometer-sized heterogeneities have been believed to be unlikely to form in monolithic BMGs, until Liu et al. [6] reported micrometer-sized soft and hard regions with a different contrast in transmission electron microscopy (TEM) images of $Zr_{61.88}Cu_{18}Ni_{10.12}Al_{10}$ (at.%) and $Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10}$ (at.%) BMGs. They explained the observed "super plasticity" of these Zr-Cu-Ni-Al BMGs on the basis of hard and soft glassy regions [6]. However, energy-dispersive X-ray (EDX) analysis gave no indications for compositional variations in both the hard and soft regions [6,20]. Hence, the formation of micrometer-sized hard and soft glassy phases with identical

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chemical compositions in $Zr_{61.88}Cu_{18}Ni_{10.12}Al_{10}$ and $Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10}$ BMGs has attracted much interest and has not yet been completely understood [20–27].

Recently, a $Ti_{36.2}Zr_{30.3}Cu_{8.3}Fe_4Be_{21.2}$ (at.%) BMG was found to possess exceptional glass-forming ability and remarkable compressive plasticity [28]. Its critical size for glass formation is estimated to exceed 50 mm [14,28], and the compressive plastic strain is about 8% [28]. This bulk metallic glass is subjected to detailed TEM investigations in the present work. STEM (scanning transmission electron microscopy) and TEM observations of the ion-milled ingot (150 g) and an as-cast rod (diameter: 2 mm) show very regular patterns of a bright and dark contrast with a typical length scale of 1–2 μm. The chemical compositions in these micrometer-sized bright and dark regions are different as revealed by quantitative EDX analysis. Additionally, when the TEM specimens are prepared by ion milling without cooling, the intermediate regions (with grey contrast) crystallize more readily, which indicates that the different regions show a different resistance against crystallization. However, TEM specimens obtained by a focused ion beam (FIB) or prepared by electrolytic thinning only show a featureless microstructure. EDX and secondary ion mass spectroscopy (SIMS) measurements indicate that all constituent elements are distributed homogeneously in the as-cast material. In other words, the micrometer-sized compositional fluctuations observed in the TEM are caused by ion milling. Based on these results, a mechanism is proposed to explain the evolution of these heterogeneities during ion milling and the reasons for preferential partial crystallization are elucidated.

2. Experimental procedures

A 150 g mixture of pure metals with nominal composition of $Ti_{36.2}Zr_{30.3}Cu_{8.3}Fe_4Be_{21.2}$ (at.%, the purity of each metal is over 99.8 wt.%) was melted under a Ti-gettered high-purity argon atmosphere in an arc furnace (Hotstar). After melting the alloy four times, the melt solidified into a semi-spherical ingot with a diameter of 50 mm (denoted as 150 g ingot). The as-cast rod with a diameter of 2 mm (denoted as 2 mm rod) was prepared by induction melting and sucking it into a copper mold in a high-purity argon atmosphere (Edmund Bühler). Samples were cut from the center of the 150 g ingot and from the rod for X-ray diffraction (XRD, Phillips PW1050, Cu-Kα) characterization. TEM specimens of the 150 g ingot were again cut from the center of the ingot and then mechanically ground into 20 μm thick discs with a diameter of 3 mm. Twin-jet electrolytic thinning of the (S)TEM specimens was performed in 30 ml perchloric acid + 175 ml 1-butanol + 295 ml methanol at 248 K. Ion-milling of the (S)TEM specimens was done in a JZLB-280B (Juzhi Vacuum Equipment) device with or without sample stage refrigeration ($T = 240$ K). The samples were milled at 4 kV, 0.4 mA and a beam inclination angle of 20°, followed by 30 min of milling at 3.5 kV, 0.4 mA, 8° after the occurrence of a small hole. The TEM specimens of the 2 mm rod were transversely cut from the rod and also mechanically ground into 20 μm thick discs, and then sandwiched between two copper rings with an outer diameter of 3 mm and an inner diameter of 1.5 mm. These specimens from the 2 mm rod were first ion-milled at 4 kV, 10 μA and a beam inclination angle of 8° in a Gatan 691 precision ion polishing system with liquid nitrogen cooling, then followed by 5 min milling at 3.5 kV, 10 μA under an angle of 3.8° after the occurrence of a small hole. The TEM observations were carried out using a JEM-2100 (JEOL) electron microscope equipped with an energy-dispersive X-ray spectroscopy system (EDX, Oxford), and STEM observations combined with EDX line scans were carried out using a FEI Tecnai F20 electron microscope equipped with a high angle annular dark field (HAADF) detector. Moreover, thin lamellae with a size of 50 μm × 200 μm × 100 nm were cut from the samples using a "lift out" method by a focused ion beam (FIB, 30 keV, Ga^+ ions, Zeiss). Samples with a size of 10 × 10 × 2 mm^3 were selected for secondary ion mass spectroscopy (SIMS, ION-TOF), which were cut from the center of the 150 g ingot, followed by mechanical grinding, and then, the samples were polished using a suspension of 50 nm-sized SiO_2 particles and ion-cleaned at 4 kV, 2 mA and an oscillating angle of 30° in a Leica EM RES101.

3. Results

The XRD results of the 150 g ingot and the 2 mm rod are shown in Fig. 1 and the broad diffraction maxima as well as the absence of sharp reflections indicates that both samples are fully glassy. This is in agreement with previous reports [28], which showed that no lattice fringes can be found in the high-resolution TEM images of electrolytically thinned specimens of this alloy.

3.1. Specimens prepared by ion milling at low temperatures

Fig. 2 shows a bright-field TEM (BF-TEM) micrograph of the 150 g ingot. The TEM specimen was prepared by ion milling with sample stage refrigeration. This BF-TEM image shows a gradually changing bright and dark contrast. The regions with a dark contrast form a sort of matrix in which the bright regions are embedded. This microstructure is reminiscent of the microscale heterogeneities found in $Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10}$ BMG [6,21,24]. From Fig. 2, the typical size of this regular pattern (average distance between two adjacent bright regions) is extracted to be about 1–2 μm, comparable to the length scale of the features observed in the $Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10}$ BMG [6,21,24]. The insets in Fig. 2 display the corresponding selected area electron diffraction (SAED) patterns of the bright and dark regions, which are broad rings in both cases, indicating that both dark and bright regions are amorphous.

Fig. 3 depicts the TEM micrographs of a specimen taken from the 2 mm rod, which was prepared by ion milling with liquid nitrogen cooling. Also for the 2 mm rod, a regular bright and dark contrast similar to that found in the 150 g ingot (Fig. 2) is detected. The typical size of these patterns is also about 1–2 μm and no nanocrystals could be found. The holes in the bright regions indicate that the contrast fluctuation is mainly caused by a variation in the

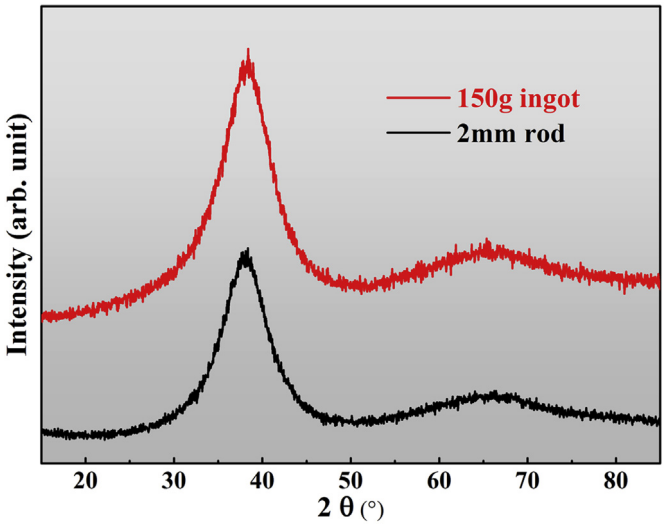

Fig. 1. The XRD results of the 150 g ingot and the 2 mm rod. Only a broad maximum can be found indicative of fully glassy samples.