Critical obstacle size to deflect shear banding in Zr-based bulk metallic glass composites

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The Zr53Cu22Ni9Al8Ta8 bulk metallic glass composite (BMGC) rods have been reported to present superior plastic strain up to 30% at room temperature. The remarkable plasticity is demonstrated to be contributed by the in-situ Ta-rich precipitates in micro-sized (10–20 μm) plus nano-sized (5–15 nm) scales, homogeneously distributed in the amorphous matrix. These Ta-rich particles act as discrete obstacles, separating and restricting the highly localized shear-banding, avoiding catastrophic shear-through of the whole sample and dramatically enhancing plasticity, as compared with the ZrCuNiAl monolithic BMG. To explore the critical particle size that can effectively deflect the shear banding, the Zr-based BMGC rods were plastically deformed to different strain levels (3–25%) before fracture for investigating the interaction between the Ta-rich particles (micro- and nano-sized) and shear banding. The results suggest that the critical size of single particle or particle cluster for deflecting the shear band is greater than 20 nm and less than 100 nm. The best estimation suggests about 80 ± 20 nm.

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1. Introduction

The Zr-based bulk metallic glass (BMG) has been considered to be one of the most promising metallic glass materials and has attracted much attention because of its exceptional mechanical as well as thermal properties [1–5]. However, the Zr-based monolithic BMGs usually present highly inhomogeneous deformation and tend to fracture in brittle nature before yielding below the glass-transition temperature [2,5–7]. To amend the weakness of low plasticity, the glassy microstructure with micro- or nano-scaled chemical inhomogeneity [8–13] or the bulk metallic glass composites (BMGCs) have been developed. BMGCs can be prepared by two main approaches; one is to precipitate in-situ crystalline phases in the BMG matrix, and the other is to add ex-situ foreign particles or micrometer-sized pores into the BMG matrix [14–21]. The advantage of the in-situ composites over the ex-situ ones in terms of sample preparation is that they can attain a finer crystalline precipitates with strong interface bonding by simply adjusting the alloy composition or cooling rate.

To prevent the formation of brittle intermetallic compounds [22] in the in-situ composites, some ductile refractory metals, such as Nb, Ta, and Hf, are added because they can form extended solid solution with Zr [23]. Recently, several ductile Ta-added Zr-based BMGCs were developed and presented significant plasticity improvement [24,25]. In such Ta-added BMGCs, the Ta-rich particles appear to act as obstacles in the amorphous matrix, arresting and diverting the propagating shear bands, and thus enhancing plasticity drastically. In our previous reports [24,26,27], the micro-sized Ta-rich particles can be observed directly from the surface of plastically deformed sample, absorbing the dynamic energy of shear banding and branching the principal shear bands into multiple shear bands. Since the thickness of typical shear bands was widely reported to be about 20 nm, thus the minimum obstacle size is generally postulated to be around or somewhat larger than this fine range about 20 nm. But the exact critical size of obstacles which are capable to effectively deflect shear bands in BMG is still unclear. Therefore, in this study, the Zr53Cu22Ni9Al8Ta8 BMGC is plastically deformed to different strains to systematically examine the interaction between the Ta-rich particles and shear bands.
2. Experiment procedures

The Zr$_{53}$Cu$_{22}$Ni$_{9}$Al$_{8}$Ta$_{8}$ BMGC rods with a diameter of 2 mm were prepared via two-step melting processing. At first, the raw metals of Zr and Ta, which have the highest melting temperatures in this alloy system, were melted together to form a homogeneous solid solution ingot. Then the binary ingots were re-melted with the remaining metals of Cu, Ni, and Al to obtain the target alloy composition in an arc furnace under a purified argon atmosphere. After complete melting, the liquid alloy was suction-cast into the water-cooled Cu mold to form alloy rods with a diameter of 2 mm. The differential scanning calorimeter (DSC) with a heating rate of 20 K/min and X-ray diffraction (XRD, Bruker D8A X-ray diffractometer, Cu-K$_\alpha$ radiation) were used to ascertain the amorphous nature of the as-cast alloys. The rod specimens with an aspect ratio of 2:1 (height/diameter) were tested in compression under an initial strain rate of 5 $\times$ 10$^{-4}$ s$^{-1}$ at room temperature by using an MTS 810 universal testing machine. The compression loading was stopped at engineering plastic strains of 3, 8, 15, 20, and 25% for microstructure examinations. The surfaces of the deformed specimens were examined by scanning electron microscopy (SEM, Hitachi S4700 FESEM) with energy-dispersive X-ray spectroscopy analysis (EDS). Transmission electron microscopy (TEM, Philip, Tecnai G2 at 200 keV) coupled with the EDS were conducted on the deformed specimens strained to 15%–25% to systematically examine the interaction between the Ta-rich particles and shear bands of the deformed samples. Two methods were conducted to prepare the TEM specimens, one is prepared by twin jet polishing and the other is sliced by dual beam focused ion beam system (FIB, FEI Versa 3D FEG system, operated at 30 kV) with special care to minimize the ion damage to samples. Both specimens were taken from the area with many traces of shear banding in the plastically deformed BMGC samples with strain of 15% and 25%, respectively.

3. Results and discussion

Fig. 1 presents the XRD patterns demonstrating the amorphous matrix with a broadened hump in the 2θ range of 30°–50° and accompanied with the high intensity crystalline peaks originated from the body centered cubic (BCC)-structured Ta-rich particles for the as-cast Zr$_{53}$Cu$_{22}$Ni$_{9}$Al$_{8}$Ta$_{8}$ BMGC samples. The room-temperature true stress–strain curves at a strain rate of 5 $\times$ 10$^{-4}$ s$^{-1}$ of the Zr$_{53}$Cu$_{22}$Ni$_{9}$Al$_{8}$Ta$_{8}$ BMGC samples plastically deformed to different plastic strain levels (3–30%) before fracture are shown in Fig. 2. The insert images show the appearance of deformed samples still intact with swollen diameters.

![Figure 1](image1.png)  
**Fig. 1.** XRD scans of the as-cast monolithic Zr$_{53}$Cu$_{22}$Ni$_{9}$Al$_{8}$ BMG and the as-cast Zr$_{53}$Cu$_{22}$Ni$_{9}$Al$_{8}$Ta$_{8}$ BMGC, with micro- and nano-scaled Ta particles.

Fig. 2. Stress-strain curves of the Zr$_{53}$Cu$_{22}$Ni$_{9}$Al$_{8}$Ta$_{8}$ BMGC samples, plastically strained to various strain levels before fracture. The insert shows the deformed specimens to different plastic strain levels.

The microstructures of the deformed BMGC examined by SEM and TEM are shown in Figs. 3 and 4, respectively. It can be seen that there are many micro-scaled Ta-rich particles in the SEM micrographs in Fig. 2, measuring about 10–20 μm. The volume fraction is measured to be about 10%. These particles are confirmed to be the BCC Ta-rich phase by SEM/EDS and TEM in our previous report [24]. Under TEM, there are abundant nano-scaled particles as seen in Fig. 4a, measuring ~5–10 nm. According to TEM/EDS, these nano particles are also the BCC-structured Ta-rich phase. The volume fraction is measured to be about 2%, assuming a TEM foil thickness of about 100 nm. Note that some of the nano particles show some clustering tendency, and the clusters or aggregates of these nano particles typically measure about 80 nm.

The SEM observations reveal that the shear band density on the specimen surface exhibits an increasing trend with increasing plastic strain, as shown in Fig. 3. There are only few shear bands interacting with the Ta-rich particles at 3% plastic strain (Fig. 3a). At this stage, some of the Ta-rich particles were sheared off by shear banding, indicating that the energy of shear banding was absorbed by these Ta-rich particles. Later on, a few traces of multiple shear banding attached at the Ta-rich particle can be seen in the 8% strain specimen, as presented in Fig. 3b. With increasing the plastic strain, more shear bands appear on the specimen surfaces, and they gradually become wavy and interwoven as shown in Fig. 3c and d. Under SEM, the small particles that are still capable to effectively induce branching of the shear bands are of the size ~5 μm, as indicated in the circle of Fig. 3d.

However, it is not easy to resolve the detailed interaction of shear bands with finer particles less than 1 μm. TEM characterization is necessary. Fig. 4a shows the representative TEM bright field image taken from the deformed specimen subject to 15% strain. The wavy and deflection shear bands are marked by arrows in these images. Note that the width of shear bands are consistently about 15–25 nm. It is noticed that most of the shear band deflection points are associated with the nano-particle clusters (measuring about 80 nm). For uniformly dispersed 5 nm individual nano particles, they are not effective to impose the capability to deflect the propagating shear bands. But the 80 nm particle clusters do. Similar phenomena have been observed numerously by TEM, as illustrated in Fig. 4b. Whenever the aggregates reach or more than the size of about 80 nm, the associated shear bands are deflected at that position. Since the TEM thin foil thickness is always less than 100 nm for the foil specimens prepared by twin-jet thinning, therefore the Ta-rich particles with sizes more than 80 nm become hardly remained inside the thin foil due to the jet erosion during specimen preparation. Accordingly, the FIB method was applied to save the
larger Ta-rich particles size (more than 100 nm) in the thin foil for TEM examination. As a result, when the size of nano-particle reaches to a level about 100 nm (as shown in a TEM bright field image example, taken from the 25% strain specimen prepared by FIB), the associated shear bands are restricted and blocked in front of the particles, as illustrated in Fig. 4c. This phenomena is quite different from the suppression of crack propagation by ductile particles dispersion in the cermet composite materials. The minimum

Fig. 3. SEM micrographs show the increasing shear band density with increasing plastic strain: (a) 3%, (b) 8%, (c) 15%, and (d) 25%.

Fig. 4. Some representative TEM micrographs show the deflection or blocking of shear bands in the deformed specimens subject to plastic strain of 15% (Fig. 4a and b) and 25% (Fig. 4c), respectively. The insert images at upper right side of each micrograph are the associated electron diffraction patterns. The insert images at lower right side of Fig. 4a and b are the enlarged images at the area indicated by arrow.
effective size of reinforcement is around several µm. In most cases, the micro-sized ductile particles in the BMGC also impose an effective blocking effect against the propagating shear bands. But in most BMGCs, the micro-sized particles would exist in a small amount (or a low quantity), making the shear bands sometimes penetrating from the empty region between two neighboring particles. Even more, once the micro-sized particles are unevenly distributed forming some clustered regions and some depleted regions, the overall shear band blocking effect would be appreciably reduced.

In comparison, the nano-sized particles are formed as a precipitation-like mechanism. The nano-sized particles are predominantly distributed uniformly, making the inter-spacing between two neighboring particles very small. The uniform distribution, the large amount (or a high quantity), and the small inter-particle spacing would in fact lead to an overall more effective blocking effect. Based on our previous reports on the Zr53Cu30Fe8Al8.5Ni9.5 (containing in-situ and ex-situ Ta particles) system, the nano-sized Ta particles can be observed in samples containing 2 at% Ta and the micro-sized Ta particles can be found in samples containing 4 at% Ta. For this Ta-4% sample, there is only a small amount of micro-sized Ta particles (less than 2 vol% and very low number density) precipitated from the amorphous matrix. Their number density was not high enough to form an effective confinement zone to restrict the shear bands. We observed that the nano-sized particles appeared to play a better role in limiting the propagating shear bands. In addition, some other reports also demonstrated significant plasticity enhancement by the nano-sized precipitate clusters [28,29].

If the particle size is about the similar range as the shear band width, say about 20 nm, the propagating shear band might only need to make very slight deflection to avoid or to shear through such small particles. This is particularly true for those shear bands which are not exactly encountering the center of a 20 nm particle. But for a particle measuring about 80 nm, even when the shear band that is not exactly heading on the center of the 80 nm particle, the propagating shear band is still likely to be blocked. It is for this reason that the critical particle size needs to be larger than the shear band width.

Taken altogether, for the current Ta particles in BMGC, the critical size for imposing effective blocking capability is demonstrated to be greater than 20 nm and less than 100 nm. The best estimation suggests about 80 ± 20 nm.

4. Conclusion

According to the results of systematic SEM and TEM characterizations on the plastically deformed Zr53Cu32Ni6Al8.5Ta8 BMGC samples to 3–30%, with micro-sized Ta-rich particles (10–20 µm for ~10% in volume fraction but very low number density) and nano-sized Ta-particles (5–10 nm for ~2% in volume fraction but much higher number density), the shear bands in the current BMGC were revealed to be blocked by both of the micro-sized and nano-sized particles (or particle clusters). The smallest critical size that can still provide an effective blocking capability is concluded to be about 80 ± 20 nm. This result might offer useful information in designing ductile BMGCs for practical applications.

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