Significant plasticity enhancement of ZrCu-based bulk metallic glass composite dispersed by in situ and ex situ Ta particles

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Using two-step arc melting process and suction casting, the Zr 47.3Cu 12Al 12Ag 6Ta 4Si 17-based bulk metallic glass composites (BMGCs) rods with ex situ added micro-sized Ta particles have been successfully fabricated. The structure and thermal properties of these BMGCs samples were examined by differential scanning calorimeter (DSC) and X-ray diffraction (XRD). It was found that these BMGCs with ex situ added Ta exhibit similar thermal properties in comparison with their base alloy counterpart, with relatively high glass forming ability (GFA). For the mechanical study, the results of compression test show that more than 25% compressive plastic strain and 1800 MPa fracture strength at room temperature can be obtained for the 2 mm diameter rod of the ZrCu-based BMGC ex situ added 6 and 9 vol.% Ta particles, respectively. Images from SEM on the fractured surfaces show that the homogeneously distributed Ta particles (20 ± 8 μm) would form semi-uniform confinement zones to restrict the shear band propagation. In other words, the inter-particle free space and the size of confinement zone (mean free path of shear bands) is apparently the controlling factor in affecting the plasticity of BMGCs.

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1. Introduction

Among the recently developed bulk metallic glasses (BMGs), Zr-based BMG has been considered to be one of the most promising materials and has attracted much attention due to its exceptional properties, such as a high strength, high hardness, high elastic strain up to 2%, good wear resistance, and near perfect as-cast surfaces, exceptional glass-forming ability (GFA) and an extremely wide supercooled liquid region (ΔTg is above 50 K, ΔTg is defined as the difference between the glass transition temperature Tg and the onset crystallization temperature Tc) [1–8]. However, almost all monolithic Zr-based BMGs fail catastrophically without obvious macroscopic plasticity due to the formation of highly localized shear bands [1,5–9]. In order to improve the plasticity of monolithic Zr-based amorphous alloy, both micro- or nano-scaled chemical inhomogeneities [10–19] and the bulk metallic glass composites (BMGCs) [20–29] have been developed.

Apart from forming phase-separated amorphous phases, two main approaches of synthesizing BMGCs have been developed so far, one is to in situ precipitate crystalline phases in the BMG matrix, the other is to ex situ introduce foreign particles or micrometer-sized pores into the BMG matrix. Though the ex situ composites can be synthesized from any bulk amorphous alloy composition, they have problems of a limited size of dispersoids and the bonding strength at interface between the dispersoids and the matrix. On the contrary, the in situ composites contain finer crystalline precipitates by simply adjusting the alloy composition or cooling rate. However, some added elements may form the intrinsically brittle intermetallic compounds, which often reduces the ductility of materials [30]. Only a few refractory metals, such as Nb and Ta can form ductile crystalline phases (such as Nb-rich or Ta-rich solid solution phase) in the Zr-based BMGs according to their binary phase diagram [31]. However, these in situ BMGCs have limited compositions and are very sensitive to their fabrication process, such as cooling rate.

In our previous report, it was found that the size distribution of in situ Ta-rich precipitate randomly varies from 20 nm to 30 μm with the increasing Ta content [29]. This reveals an opportunity to fabricate new BMGCs by combining in situ and ex situ to create more volume fraction of micro-size Ta particles with
a controllable and uniform distribution. Therefore based on our previous results, we choose Zr_{47.3}Cu_{32}Al_{8}Ag_{4}Ta_{4}Si_{0.7} as the matrix to form a new composite with ex situ added micro-sized Ta particles (about 20 μm); Zr_{47.3}Cu_{32}Al_{8}Ag_{4}Ta_{4}Si_{0.7} was selected for its substantial plasticity (~5%) due to in situ micro-sized Ta-rich precipitates [29]. The microstructures and mechanical behaviors of this new ZrCu-based BMGC will be investigated in detail.

2. Experimental details

The alloy ingots with different compositions of Zr_{47.3}Cu_{32}Al_{8}Ag_{4}Ta_{4}Si_{0.7} and Zr_{47.3}Cu_{32}Al_{8}Ag_{4}Ta_{4}Si_{0.7} were prepared by arc melting the appropriate mixture of high purity Zr, Cu, Al, Ag, Si, and Ta under a Ti-gettered argon atmosphere, respectively. In order to make the composition homogeneous, a two-step melting process was carried out; at first, 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. This binary ingot was re-melted with the remaining metals, i.e. Cu, Si, Ag, Al to obtain the target alloy composition in an arc furnace under argon atmosphere. Then the newly formed alloy ingot was melted once again with 3–9 vol.% Ta particles (average particle size of 20 ± 8 μm). After complete melt, the liquid alloy was suction cast into a water-cooled Cu mold to form alloy rods with diameters of 2–4 mm.

Thermal properties and microstructures of the sample rods were examined by the differential scanning calorimeter (DSC) at heating rate of 20 °C/min, X-ray diffraction (XRD, Scintag X-400 X-ray diffractometer, Cu Kα radiation) and transmission electron microscopy (TEM, Philip, Tecnai G2 at 200 keV) to ascertain the amorphous nature of the as-cast alloys. Thin foil specimens for TEM observation were electrochemically prepared at a potential of 30–40 V in a digital Fischione Twin-Jet Electro Polisher (model 110), with a solution of 10 vol.% perchloric acids and 90 vol.% methanol at −20 °C.

The hardness of alloys was examined by micro-hardness tester (Akashi MVK-H11). Compression test on specimen rods at room temperature were carried out by a MTS 810 universal testing machine under an initial strain rate of 1 × 10^{-4} s^{-1}. In the test, both ends of the specimens were polished to make them parallel. Multiple compression tests were conducted to ensure the reproducible trend and the scattering of the stress and strain was less than ±5%. After compression, cross-sectional microstructures of as-cast samples and the fracture surfaces of the deformed specimens were examined by scanning electron microscopy (SEM, Hitachi S4700 FESEM) with the energy-dispersive X-ray spectroscopy analysis (EDS). To estimate average inter-particle space between Ta precipitates, there are 100 selections measured in the SEM images is statistically estimated by the softer ware of Image-Pro Plus.

3. Results and discussion

3.1. Thermal properties of the as-cast ZrCu-based BMGC

The DSC scans on the Zr_{47.3}Cu_{32}Al_{8}Ag_{4}Ta_{4}Si_{0.7} rods with 0, 3, 6 and 9 vol.% ex situ added Ta particles are shown in Fig. 1. All samples exhibit a clear glass transition followed by a region of supercooled liquid phase before crystallization. Values of glass transition (T_g), crystallization (T_c), and supercooled liquid range (ΔT_x), GFA indicators γ = T_g/(T_g + T_c) [32] and χ_m = (2T_m − T_c)/T_c [33] are listed in Table 1. Variations of T_g, T_c and ΔT_x of sample rods with ex situ added Ta are not significantly different from that of the base alloy. This similarity in thermal properties of different alloys is due to the fact that Ta particles from ex situ only physically mixed with other metals during fabrication. The ultra high melting temperature of Ta and its low solubility to Zr in this alloy system are able to keep the ex situ Ta as separate phases. The GFA indicators γ and χ_m = (2T_m − T_c)/T_c also confirm this claim since all specimens have GFA indicator within a very narrow range (0.38–0.41 for γ and 0.73–0.77 for χ_m). Values of the GFA indicator nearly guarantee these Zr-based BMGCs to form shining 4 mm rods with ease. Nevertheless, the decreased range of supercooled liquid region with the increase volume fraction of ex situ Ta particles is an important indication of the increase heterogeneous nucleation sites, i.e. the more nucleation sites the faster and easier of crystallization.

3.2. Microstructure of the as-cast Zr-based BMGCs

XRD patterns of the BMGC rods of 4 mm in diameter are shown in Fig. 2. The amorphous phase of matrix can be confirmed with broadened humps in the 2θ range of 30–50° for all samples except the peak of (1 1 0) crystalline BCC structure of Ta particles. In parallel, the metallographic examination by SEM in Fig. 3(a)–(d) also reveals the existence of micro size Ta-rich particles. The volume fractions and inter-particle space of micro-sized Ta that statistically estimated from these SEM images are tabulated in Table 2. Total volume fraction of Ta particles increased from 1.9% to 10.4% as the added ex situ Ta changed from 0% to 9%. The inter-particle space decreases from 72 ± 8 μm to 32 ± 8 μm. The sizes of Ta particles are around 5–30 μm when the ex situ Ta content is more than 3 vol.%. As the volume fraction of ex situ Ta particles increasing, the confinement zone among particles also shrinks as illustrated in

![Fig. 1. DSC plots of Zr_{47.3}Cu_{32}Al_{8}Ag_{4}Ta_{4}Si_{0.7} based BMGC rods (2 mm in diameter) with ex situ added 0–9 vol.% Ta particles with heating rate of 20 K/min.](image-url)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Thermal properties of Zr_{47.3}Cu_{32}Al_{8}Ag_{4}Ta_{4}Si_{0.7}-based BMGC rods (2 mm in diameter) with ex situ added 0–9 vol.% Ta particles.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zr_{47.3}Cu_{32}Al_{8}Ag_{4}Ta_{4}Si_{0.7}</td>
</tr>
<tr>
<td>Base</td>
<td>694</td>
</tr>
<tr>
<td>3 vol.% Ta</td>
<td>699</td>
</tr>
<tr>
<td>6 vol.% Ta</td>
<td>698</td>
</tr>
<tr>
<td>9 vol.% Ta</td>
<td>707</td>
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</table>
Fig. 2. XRD plots of the Zr_{47.3}Cu_{32}Ag_{8}Al_{8}Ta_{4}Si_{0.7}-based BMG rods (4 mm in diameter) with ex situ added 3–9 vol.% Ta particles.

Fig. 3(b)–(d). This shrinking confinement can limit the propagation of shear bands to prevent brittle failure of materials.

In addition to SEM, the TEM observation revealed the existence of in situ nano-sized precipitates around 10–100 nm embedded in the amorphous matrix. Fig. 4(a) and (b) shows the bright and dark field TEM images of the as-cast Zr_{47.3}Cu_{32}Ag_{8}Al_{8}Ta_{4}Si_{0.7} with ex situ added 9 vol.% Ta particles where Ta precipitates can be clearly seen. The SAD pattern in Fig. 4(c) and (d) indicates that these Ta-rich nanoparticles have crystallinities of B[110] and B[013].

3.3. Mechanical properties

The macro hardness for Zr_{47.3}Cu_{32}Ag_{8}Al_{8}Ta_{4}Si_{0.7} with ex situ added 3–9 vol.% Ta particles were measured to be around 530–550 in Hv. The hardness does not change much by the ex situ addition of Ta.

Results from compression tests show a similar trend in yield strength. The yield strength of these BMGCs all keep at the same level, around 1770–1800 MPa as shown in Fig. 5. On the other hand, the plastic strains show a dramatic increase as the Ta content increases. More than 40% plastic strain were obtained for samples (2 mm in diameter) with 9 vol.% ex situ added Ta. SEM images of fractured specimens with ex situ added 3 and 9 vol.% Ta exhibit a high density of weaves which are the inter-connected shear bands on the rod outer surfaces. This is in contrast to the samples of monolithic BMG, which were brittle fractured by simple shear as shown in Fig. 6(a).

High magnifications on the fracture surface by SEM further confirm different patterns of failure. For monolithic Zr-based BMG

<table>
<thead>
<tr>
<th>Zr_{47.3}Cu_{32}Ag_{8}Al_{8}Ta_{4}Si_{0.7} based BMG</th>
<th>Final vol.% of micro-sized Ta particles (statistical cal.)</th>
<th>Mean inter-particle spacing of micro-sized Ta (µm)</th>
<th>True plastic strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.9</td>
<td>72 ± 8 µm</td>
<td>5.8</td>
</tr>
<tr>
<td>3</td>
<td>4.8</td>
<td>65 ± 8 µm</td>
<td>27.3</td>
</tr>
<tr>
<td>6</td>
<td>6.5</td>
<td>58 ± 8 µm</td>
<td>36.7</td>
</tr>
<tr>
<td>9</td>
<td>10.4</td>
<td>32 ± 8 µm</td>
<td>44.0</td>
</tr>
</tbody>
</table>
(Fig. 7(a)), only very small areas in the fractured surface have primary shear bands along the direction of maximum shear stress [29]. For other specimens with/without ex situ added Ta, all have different degrees of interactions between multiple shear bands and Ta particles as seen from Fig. 7(b)–(d). These interactions are evidences of energy release from local stress concentration in the matrix but hindered by the ductile Ta particles which can be plastically deformed to absorb the energy.

The entire fracture surfaces of the Zr<sub>47.3</sub>Cu<sub>32</sub>Ag<sub>8</sub>Al<sub>8</sub>Ta<sub>4</sub>Si<sub>0.7</sub>–based BMGC rod with ex situ added 3–9 vol.% Ta particles have a quite different morphology, consisting of vein-like pattern and highly rough regions, as shown in Figs. 8(b) and (c). This mixture of vein-like pattern and rough regions is not consistent with some other investigations [34,35], the vein-like pattern is the main part of the compressive fracture surfaces for most monolithic BMGs (as shown in Fig. 8(a)). In this BMGC case, the locally melted region on the fracture surface is suggested that a large amount of strain energy release following the shear banding led to local melting before fracture. In addition, the highly rough region of fracture surface implies that the shear bands are highly branched and propagate in a rather wavy way, indicating that a strong interaction occurs between shear bands and Ta-rich particles.

Plastic deformation in both monolithic BMG and the current BMG are mainly caused by shear banding in the amorphous matrix. Particularly in the composites, shear bands cannot travel freely or run away but are often arrested at the glassy matrix-Ta interfaces. The traveling distance, i.e. mean free path, of shear bands is limited by the inter-particle spacing of Ta particles. For a given Ta particles size, larger volume fraction of particles would lead to more interfacial areas, shorter inter-particle spacings, and smaller mean free path. This inter-particle spacing is an effective index for the mean free path of shear banding. The smaller mean free path results in higher plasticity.

A correlation between the fracture toughness, \( K_C \), and the length scale of plastic process zone, \( R_p \), for various brittle and tough BMGs using the equation:

\[
R_p = \left( \frac{1}{6\pi} \right) \left( \frac{K_C}{\sigma_f} \right)
\]

where \( \sigma_f \) is the yield stress, has been proposed by Xi et al. [36]. For tougher Zr<sub>41</sub>Ti<sub>14</sub>Cu<sub>23</sub>Ni<sub>10</sub>B<sub>2</sub>BMG, with \( K_C = 86 \) MPa√m and \( \sigma_f = 1800 \) MPa, exhibit a large scale of plastic zone size about 60 \( \mu \)m [36], significant crack bifurcation and branching, and then leading to a high toughness. Conversely, brittle Mg<sub>65</sub>Cu<sub>25</sub>Tb<sub>10</sub> BMG, with \( K_C = 2 \) MPa√m and \( \sigma_f = 660 \) MPa, only gave a much small plastic zone size about 0.2 \( \mu \)m.

For the present monolithic (Zr<sub>48</sub>Cu<sub>36</sub>Al<sub>8</sub>Ag<sub>8</sub>)<sub>99.25</sub>Si<sub>0.75</sub> base BMG (without ex situ Ta particles), yield strength \( \sigma_f \) and assumed
fracture toughness $K_C$ are about 1800 MPa and 70 MPa $\sqrt{m}$, respectively [37]. The plastic zone size calculated by the above equation is about 80 $\mu$m and apparently larger than the mean inter-particle spacings of Ta particles (confinement zone size of 65 $\pm$ 8 $\mu$m and 58 $\pm$ 8 $\mu$m, and 32 $\pm$ 8 $\mu$m for ex situ 3, 6, and 9 vol.% Ta, respectively, as shown in Table 2). Thus, the confinement zone of Ta particles would provide a plastic shielding of an opening crack tip to restrict shear band extension and avoid catastrophic crack propagation [23]. Therefore, fracture is primary controlled by shear bands movement between Ta particles, the crack propagation will be deflected into a wavy path and so as to increase the plasticity dramatically.

Fig. 6. SEM images of the fractured specimens of (a) monolithic Zr$_{47.3}$Cu$_{36}$Ag$_{8}$Al$_{8}$Si$_{0.7}$ BMG, (b) Zr$_{47.3}$Cu$_{32}$Ag$_{8}$Al$_{8}$Ta$_{4}$Si$_{0.7}$ BMGC, (c) Zr$_{47.3}$Cu$_{32}$Ag$_{8}$Al$_{8}$Ta$_{4}$Si$_{0.7}$ BMGC with ex situ added 3 vol.% Ta, and (d) Zr$_{47.3}$Cu$_{32}$Ag$_{8}$Al$_{8}$Ta$_{4}$Si$_{0.7}$ BMGC with ex situ added 9 vol.% Ta.

Fig. 7. SEM images of the specimen surface near the fracture area for (a) monolithic Zr$_{47.3}$Cu$_{36}$Ag$_{8}$Al$_{8}$Si$_{0.7}$ BMG, (b) Zr$_{47.3}$Cu$_{32}$Ag$_{8}$Al$_{8}$Ta$_{4}$Si$_{0.7}$ BMGC, (c) Zr$_{47.3}$Cu$_{32}$Ag$_{8}$Al$_{8}$Ta$_{4}$Si$_{0.7}$ BMGC with ex situ added 3 vol.% Ta, and (d) Zr$_{47.3}$Cu$_{32}$Ag$_{8}$Al$_{8}$Ta$_{4}$Si$_{0.7}$ BMGC with ex situ added 9 vol.% Ta.
fabricated in this study. It was found that shear bands are arrested at the amorphous matrix-Ta interfaces in these ZrCu-based BMGCs. The traveling distance, i.e., mean free path, of shear bands is limited by the mean inter-particle spacings of Ta particles. For a given size of Ta particles, the higher volume fraction of particles would lead to shorter inter-particle spacings and smaller mean free path of shear bands. The plastic zone size of present ZrCu-based BMG (~50 µm) is much larger than the average inter-particle space of Ta particles (confinement zone size). Therefore, the confinement zone among Ta particles would provide effective obstructions to shear bands extension and result in improved plasticity up to 44% plastic strain for BMG with ex situ added 9 vol.% Ta particles.

Acknowledgments

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References


Fig. 8. SEM images of different type vein pattern at some area of the fracture surface for the sample of (a) monolithic ZrCu3Al8Ag8Si0.7 BMG, (b) ZrCu3Al8Ag8Ta3Si0.7 BMG with ex situ added 3 vol.% Ta, and (c) ZrCu3Al8Ag8Ta3Si0.7 BMG with ex situ added 9 vol.% Ta after compression test (note: the arrow indicates the slip direction).