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Enhanced plasticity in a Zr-based bulk metallic glass composite with *in situ* formed intermetallic phases

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An *in situ* formed intermetallic phase/bulk metallic glass composite with high strength and good plasticity was fabricated by casting $Zr_{55.0}Cu_{29.0}Ni_{8.0}Al_{8.0}$ melts. *In situ* formed tetragonal structured $(Zr,Ni,Al)_2(Cu,Ni,Al)$ intermetallic particles with a hardness of 9.6 ± 0.3 GPa improve the fracture strength of the composite. Micrographs of the fractured samples reveal that the shear band spacing is smaller than the intermetallic particles, indicating that they can effectively block shear band propagation before catastrophic fracture.
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Monolithic metallic glasses in bulk forms normally deform by shear localization and show macroscopically brittle failure at ambient temperature.[1,2] Increasing the plasticity or malleability of bulk metallic glasses (BMGs) has attracted extensive interest recently. Excellent plasticity has been achieved in some "ductile" BMGs with nanometer scaled structural chemical heterogeneity,[3] phase separation,[4] or increased free volumes.[5,6]

Another way to increase the plasticity of BMGs is to fabricate *in situ* formed dendrite/BMG composites through solidification. Appreciable plastic strains under compression have been achieved in Zr-based,[7–15] Mg-based,[16,17] La-based,[18] Cu-based,[19,20] and Pd-based[21] BMG composites containing micrometer-sized dendritic phases. Total strains of 9.6%–13.1% under tension were reported in Zr-based BMG composites.[7] It is noted that most dendritic phases in BMG composites are ductile solid solution (ss) phases, e.g., body centered cubic (BCC) phases (β-Zr,[2,8,10,11] Nb_{ss},[20] α-Fe,[16] and Ta_{ss}[12]), face centered cubic (FCC) phase (α-Pd [21]), and hexagonal close packed(HCP) phases (Mg_{ss},[17] α-La,[18] and Ti_{ss}[22]) or nanocrystalline phases.[23–25]

Previous studies showed that intrinsically brittle intermetallic compounds or quasicrystalline precipitates were apparently harmful to the ductility of BMGs.[26,27] For example, very fine Zr_2Cu intermetallic phase was deleterious to the plastic deformation of BMGs.[26] *In situ* formed TiC particles have been found to increase the hardness by 25% in $(Cu_{47}Ti_{33}Zr_{11}Ni_6Sn_2Si_1)_{100-x}C_x$, which has very limited plasticity (~0.6%).[28] Here, we report that obvious yielding is observed and plastic strain of 4.4% is achieved in an *in situ* formed intermetallic phase reinforced Zr-based BMG composite under compression testing. The mechanism of improved plasticity in this intermetallic phase/BMG composite will be discussed based on microstructural observation.

Ingots with a nominal composition of $Zr_{55.0}Cu_{29.0}Ni_{8.0}Al_{8.0}$ were prepared by arc-melting with high-purity elemental metals (99.5%Zr, 99.99%Ni, 99.99%Cu, 99.99%Al). The ingots were remelted several times to ensure a homogeneous distribution of alloying elements under a Ti-gettered Ar atmosphere. Then the arc-melted button was drop cast into rods 6.7 and 10 mm in diameter under He atmosphere. A differential scanning calorimeter (DSC) was used to investigate thermal properties of specimens at a heating rate of 20 K/min. X-ray diffraction (XRD) was used to identify the phases present in the specimen. The microstructure was examined in a scanning electron microscope (SEM) and phase compositions were determined by microprobe analysis. Compression samples 2.5 mm in diameter and ~5.0 mm in height were cut from the as-cast rods. Uniaxial compression tests were conducted at room temperature at an initial strain rate of $2 \times 10^{-4}\ s^{-1}$. The yield strength was determined by using 0.2% offset plastic strain method.

XRD patterns from the cross section of as-cast rods showed that specimens with a diameter of 6.7 mm exhibit only broad diffraction humps with no detectable crystalline Bragg peaks, indicating a fully glassy state. For specimens with a diameter of 10 mm, three crystalline peaks were found, corresponding to the tetragonal $(Zr,Ni,Al)_2(Cu,Ni,Al)$ phase, in addition to the broad amorphous humps. DSC curves of both the 6.7 and 10 mm specimens showed a distinct endothermic peak corresponding to the glass transition and exothermic peaks indicating crystallization. But the exothermic heat of the 10 mm sample is smaller than that of the 6.7 mm sample, indicating that the former had partially crystallized during casting.

Figure 1(a) shows the microstructure of the 10 mm diameter casting of the intermetallic/BMG composite. Spherical intermetallic particles with a diameter of 60–530 μm were found to be homogeneously distributed in the BMG matrix. The volume fraction of the spherical phase in the composite is 33%–42%, as estimated from DSC curves and SEM images. Since the intermetallic particles were *in situ* formed during the casting process, the interface between the spherical phase and the metallic glass matrix is smooth, and

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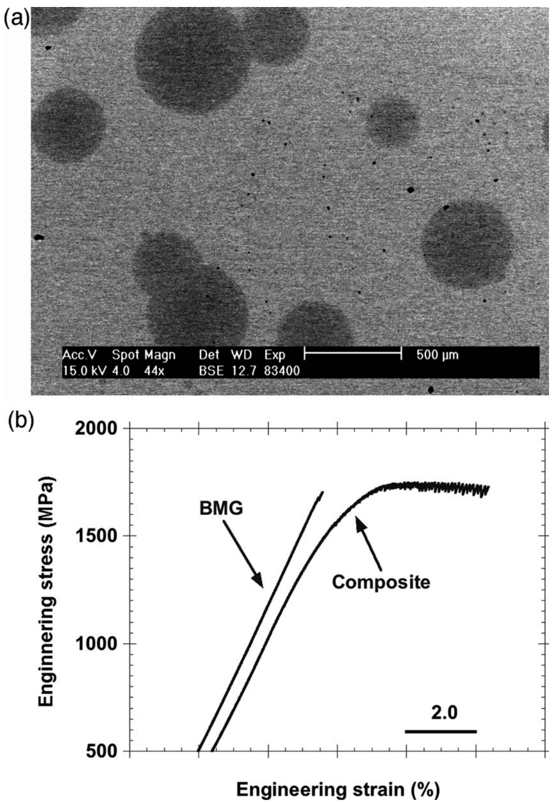

FIG. 1. (a) Backscattered electron image, and (b) compressive engineering stress-strain curve for $Zr_{55.0}Cu_{29.0}Ni_{8.0}Al_{8.0}$ intermetallic/BMG composite with a diameter of 10 mm. For comparison, a monolithic BMG with same composition is also included.

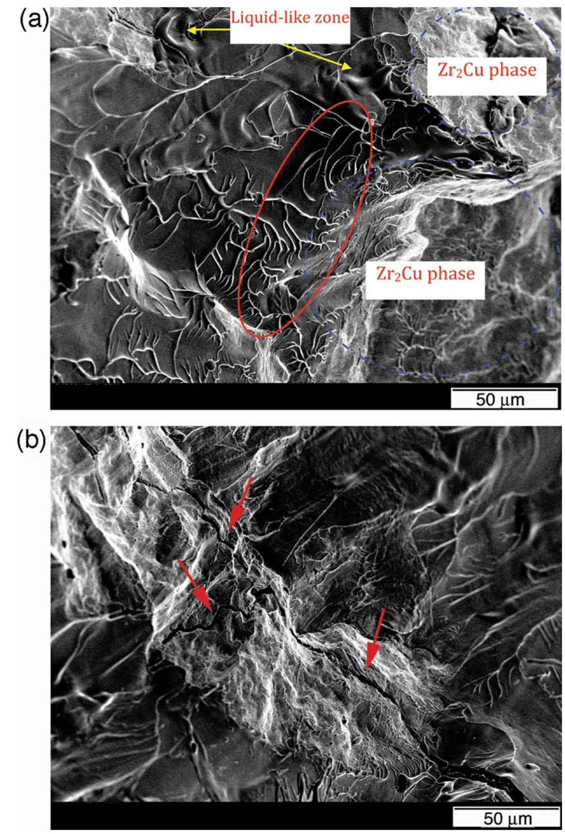

FIG. 2. (Color online) SEM fracture surface of the $Zr_{55.0}Cu_{29.0}Ni_{8.0}Al_{8.0}$ intermetallic/BMG composite: (a) Veinlike patterns in the glassy matrix, and (b) cracks in the intermetallic phase.

no other phases or cracks were found in this composite.

Microprobe analysis shows that measured compositions of spherical precipitates and the BMG matrix are $Ni_{8.0}Cu_{28.8}Al_{7.9}Zr_{55.3}$ and $Ni_{8.0}Cu_{29.1}Al_{7.9}Zr_{55.0}$ (at. %), respectively. Note that no significant composition difference between the two phases is detected, indicating that no solute redistribution occurred during the formation of spherical intermetallic particles. This observation suggests that the precipitated particles were formed at quite low temperature during the Cu-mold casting, and that atomic diffusion over long distance was suppressed. Therefore, the formation mechanism of the spherical $(Zr,Ni,Al)_2(Cu,Ni,Al)$ phase is apparently different from spherical β-Zr solution phase which formed from the agglomeration of β-Zr dendrite.[11]

Surprisingly, this composite material shows both high strength and plasticity. Figure 1(b) shows the comparison of the engineering stress-strain curves for fully bulk metallic glass and *in situ* formed intermetallic/BMG composite. All curves of the fully glass specimens showed only linear elastic deformation, and no noticeable yielding was found before fracture. For the intermetallic/BMG composite specimens, yielding was clearly observed, followed by significant plastic deformation.

Effect of intermetallic phases on mechanical properties of BMGs is not fully understood.[26,29] He *et al.*[26] found that larger samples had a lower plasticity in $Zr_{52.25}Cu_{28.5}Ni_{4.75}Al_{9.5}Ta_5$, and they attributed it to an increased fraction of very fine brittle Zr_2Cu phase. Sun *et al.*[29] reported an increased plasticity in BMG composites containing nanometer scaled *B*2-structured phase. In general, it was believed that brittle intermetallic was harmful to the plasticity of BMGs.[26,30] However, here, improved plasticity was found in the intermetallic/BMG composite, where spherical shaped $(Zr,Ni,Al)_2(Cu,Ni,Al)$ phases with diameters larger than 60 μm were *in situ* formed.

Nanoindentation tests showed that the Young's modulus and hardness of $(Zr,Ni,Al)_2(Cu,Ni,Al)$ phases were 121 ± 2 and 9.6 ± 0.3 GPa, while those of the glassy matrix were 112 ± 2 and 7.6 ± 0.1 GPa, respectively. If we assume that the value of yield strength is proportional to its hardness,[31] the yield strength of $(Zr,Ni,Al)_2(Cu,Ni,Al)$ phase is much higher than that of monolithic Zr-based BMG. During loading, deformation was initiated in the "soft" BMG matrix and then transmitted to hard spherical intermetallic particles. The fracture surface is shown in Fig. 2. As can be seen, veinlike patterns with a stochastic distribution of liquidlike droplets were observed on the fracture surface of the glassy matrix. The liquidlike droplets might result from melting due to local heating. Stress concentrations around the vicinity of intermetallic spheres induced more veinlike patterns, as shown in the red circle in Fig. 2(a). During the shear deformation, hard intermetallic particles would serve as the reinforced phase. Intermetallic spherical islands block the propagation of shear bands, resulting in the formation of multiple shear bands and improved plasticity in the composite material. Because of the brittle nature of the intermetallic phase, final fracture of the composite occurred most likely at $(Zr,Ni,Al)_2(Cu,Ni,Al)$ particles. Arrows in Fig. 2(b) show the crack propagation in intermetallic phases.

Figure 3 shows the SEM and backscattered electron images of shear bands near spherical intermetallic particles after fracture. Primary shear bands were deflected at the inter-

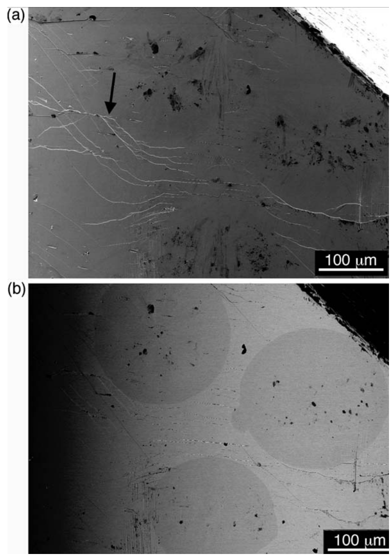

FIG. 3. (a) SEM image showing shear bands near intermetallic particles in the $Zr_{55.0}Cu_{29.0}Ni_{8.0}Al_{8.0}$ intermetallic/BMG composite, and (b) backscattered electron image (BSE) showing the position of intermetallic spheres in the same sample.

face between the glassy matrix and intermetallic particles, as shown by the arrow in Fig. 3(a). Besides the circumambulation effect, shear bands divided into double subbands and further divided into several tiny bands around the spheres. The "blocking effect" of hard particles improved the compressive plasticity. To effectively block the propagation of shear bands, the size of "hard" phases should be large enough to avoid by-pass. The mechanism for improved plasticity in this study appears to be different from the BMG composites containing nanometer scale or very fine intermetallic phases. In those materials, the second phase is not big enough to block the propagation of shear bands. However, if second phases are fine enough and homogeneously distributed over the entire material, they may act as stress concentration points and stimulate abundant nucleation of shear bands, which can also result in macroscopic plastic deformation.[24,25] Pronounced geometry effect has been demonstrated in compression testing of low aspect ratio samples[32] and in bending tests.[33] Since the shear band spacing in compression shows strong correlation with the geometry and distribution of second phases for a fixed composition, further investigations are needed to reveal effects of particle size and distribution on plasticity in BMG composites.

Composites consisting of *in situ* formed intermetallic particles in a BMG matrix have two advantages: (1) since the second-phase particles are formed during casting, temper-induced embrittlement can be avoided; (2) because of the high hardness of intermetallic particles, the composites can gain additional fracture strength as compared with solid-solution phase/BMG composites.

In summary, *in situ* formed tetragonal structured $(Zr,Ni,Al)_2(Cu,Ni,Al)$ intermetallic spheres with diameters of 60–530 μm were found to increase plasticity of a Zr-based BMG. In contrast to soft second phases, intermetallic particles with a higher hardness also have a beneficial effect on the fracture strength of the composite. Based on previous and current studies, the role of intermetallic phases on the plasticity of BMGs may be divided into three categories according to their sizes and distribution: (1) Homogeneously distributed intermetallic particles with sizes in the nanometer range (2–5 nm) can stimulate shear band nucleation, resulting in macroscopic plastic deformation.[24,25] (2) Intermetallic particles with sizes that are not in the nanometer range, but not large enough to block shear-band propagation effectively, resulting in no obvious enhanced macroscopic plasticity. (3) Intermetallic particles that are large enough to effectively block shear band propagation, resulting in improved plasticity.

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