Transformation-induced plasticity in bulk metallic glass composites evidenced by in-situ neutron diffraction

Y. Wu¹, D. Ma^{2,*}, Q. K. Li¹, A. D. Stoica², W. L. Song¹, H. Wang¹, X. J. Liu¹, G. M. Stoica², G. Y. Wang³, K. An², X. L. Wang⁴, Mo. Li¹, Z. P. Lu^{1,*}

¹State Key Laboratory for Advanced Metals and Materials, University of Science and Technology
Beijing, Beijing 100083, People's Republic of China

²Chemical and Engineering Materials Division, Spallation Neutron Source, Oak Ridge National
Laboratory, Oak Ridge, Tennessee 37831, USA

³Department of Materials Science and Engineering, University of Tennessee-Knoxville, Knoxville,
Tennessee, USA

⁴Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Ave.,
Kowloon, Hong Kong

Abstract

Transformation-induced plasticity in a strain-softening amorphous matrix consisting of austenite B2 was studied by *in-situ* neutron diffraction, coupled with molecular dynamic simulation. It was found that the martensitic transformation from B2 to B19' upon loading commenced at the macroscopic yielding which increased with the decrease of the fraction of the parent austenite B2 phase, and the threshold lattice strain for the martensitic transformation is almost the same in different samples, suggesting that the martensitic transformation in the current glassy matrix is strain-controlled. Analysis of load partition and strain accommodation unveiled that B2 has elastic anisotropy, and the desirable elastic match between B2 and the amorphous matrix ensures a good cooperative deformation. Additionally, molecular dynamic simulation revealed that atoms at the interface between B2 and the amorphous matrix deviated from the standard B2 lattices and acted as nucleation site for the martensitic transformation, eventually giving rise to the strain-controlled martensitic transformation. Our findings provide new insights into the mechanism of phase transformation-mediated plasticity at the microscopic level, and have useful implications for developing novel, high-performance bulk metallic glass composites.

Keywords: Bulk metallic glass composite; neutron scattering; transformation induced plasticity; martensitic transformation; molecular dynamic simulations.

*Corresponding author: DM at dongma@ornl.gov or ZPL at luzp@ustb.edu.cn

1. Introduction

Transformation-induced plasticity (TRIP) has been proven to be an effective way to enhance plasticity and toughness of engineering materials [1-5], such as TRIP steels^{1,2} and shape memory alloy composites [3,4]. The basic principle is to embed a metastable transforming phase into a strain-hardening matrix, and then the back stress effect and the cooperative deformation between transforming phase and matrix lead to extraordinary increases in strength and plasticity [6,7]. Recently, the TRIP concept has also been introduced into bulk metallic glasses (BMGs) which has the characteristic of strain-softening, to overcome room-temperature brittleness and strain-softening of BMGs [8-10]. In fact, by applying this strategy to CuZr and Ti-based BMGs through introducing an *in situ* B2 phase into the glass matrix, large tensile ductility and work-hardening capability have been achieved in the resultant BMG composites [11-13]. However, the reinforcing mechanism of TRIP in strain-softening media is far from being well understood. Furthermore, due to the difficulties in characterizing deformation behaviors and phase transformation kinetics simultaneously, an in-depth understanding of the TRIP effects in an amorphous-crystalline composite is still missing.

In this study, we have conducted an *in situ* neutron diffraction study of deformation behavior of CuZr-based BMG composites upon compressive loading. Due to the high penetration capability of neutrons, neutron diffraction measurements can provide structural information representative of the bulk material, rather than the surface. As such, loading studies monitored by *in-situ* neutron diffraction are able to

correlate macroscopic deformation behaviors directly with the accompanying microstructure (and/or phase) evolution. As will be discussed below, this study reveals a martensitic transformation from B2-CuZr to B19'-CuZr during loading and a partially reversible phase transformation during subsequent unloading. Furthermore, this work also shed light on the microscopic mechanism of the TRIP effect in BMGs by probing the evolution of lattice strains in B2 and microscopic strains in the amorphous phase.

2. Experimental procedures

2.1 Sample preparation

Master alloy ingots with a nominal composition of $\text{Cu}_{47.5}\text{Zr}_{48}\text{Al}_4\text{Co}_{0.5}$ (at.%) were prepared by arc-melting a mixture of constituent elements with a purity of >99.9% [14]. Cylinders with a diameter of 2 to 5 mm were prepared by suction casting of the melt master alloy into water-cooled copper molds. The volume fraction of B2-CuZr can be controlled by changing the applied cooling rates (i.e., the casting diameter and casting atmosphere) during casting. Yield strength and Young's modulus for BMG composites with a different amount of B2 were determined by compressive loading experiments, and detailed information about the sample preparation and mechanical testing can be found in reference 11. Cross-section surfaces of the as-cast samples were examined in a ZEISS SUPRA 55 scanning electron microscope (SEM). Volume fractions of the crystalline phases were estimated from the SEM images with an Imagetool software. Transmission electron microscopy (TEM) was conducted in a JEM 2010F instrument with a field emission gun. The TEM samples were first

mechanically ground to a 50 μm thick plate and then twin-jet electropolished using a solution mixed in the ratio $\text{HNO}_3: \text{CH}_4\text{O} = 1:3$. Two distinct BMG composites, referred to as T1 and T2, were selected for neutron diffraction measurements, and their microstructures contained spherical B2 micro-crystallites with a volume fraction of $\sim 75\%$ and $\sim 25\%$, respectively.

2.2 *In situ* neutron diffraction measurements

Specimens of 3mm diameter and 10 mm long were electro-discharge machined from the as-cast rods of T1 and T2. *In situ* neutron diffraction investigations of these specimens upon compressive loading were conducted using a MTS load-frame on the VULCAN diffractometer, at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL) [15,16]. VULCAN is equipped with two detector banks positioned at $\pm 90^\circ$ diffraction angles, which are designated as Bank 1 and Bank 2, respectively. An incident neutron beam of 3 mm high and 3 mm wide, together with a pair of 5 mm radial collimators, were used for defining the sampling volume during the diffraction experiments. The compression specimens, as well as the loading axis, were orientated at 45° from the incident beam. As such, Bank 1 records diffraction patterns corresponding to the lattice planes whose normals are parallel to the loading axis, whilst Bank 2 probes lattice planes whose normals are perpendicular to the loading axis. The neutron diffraction data were reduced and then analyzed by single peak fitting using the VDRIVE program [17]. The hkl -specific lattice strain, ϵ_{hkl} , was determined from the relative change in the d -spacing of the (hkl) reflection in the diffraction pattern, i.e., $\epsilon_{hkl} = (d_{hkl} - d_{hkl}^0)/d_{hkl}^0$, where d_{hkl} and d_{hkl}^0 are the

d -spacings of the (hkl) plane obtained under a finite and zero load, respectively [18,19]. To evaluate microscopic strains of the amorphous phase, diffuse diffraction patterns due to the amorphous phase were obtained by subtracting the crystalline peaks from the total scattering patterns of a BMG composite, as implemented in the Generalized Structure Analysis Software (GSAS) [20]. This was followed by analyzing the shift of the first sharp diffraction peak (FSDP) position in the reciprocal space relative to the stress-free value [21,22], which gave rise to the axial ($\epsilon_{\parallel}$) and transverse ($\epsilon_{\perp}$) strain components of the amorphous phase.

2.3 Molecular dynamic (MD) simulation

Molecular dynamic (MD) simulation was conducted using the program package LAMMPS [23], and the system parameters in the interatomic potential can be found in Ref. 24. The MG samples were first prepared by cooling the equilibrated liquid from 2000 K to 10 K with a cooling rate of 1 K/ps and a time step of 10^{-3} ps. MG samples containing 864000 atoms ($24 \times 24 \times 24 \text{ nm}^3$) were investigated. After obtaining the equilibrated MG samples, the B2 particles with 25% and 75% volume fractions and various orientations were inserted into the bulk MG samples with the overlapped MG atoms being deleted. Then, while keeping the inserted B2 phase fixed, we gradually increased the composite samples up to 600 K, relaxed the composites for about 100 ps, then slowly cooled the samples to 10 K. Later on, tensile tests were performed with the prepared samples. The atomic bonding length and lattice angle distributions were examined, and various other properties were analyzed. To quantify plastic deformation at the atomic level, we used the atomic local strain

$\eta_i^{Mises} = \sqrt{\eta_{yz}^2 + \eta_{xz}^2 + \eta_{xy}^2 + \frac{(\eta_{yy}-\eta_{zz})^2 + (\eta_{xx}-\eta_{zz})^2 + (\eta_{xx}-\eta_{yy})^2}{6}}$, as a measure of local inelastic deformation according to Shimizu et al. [25].

3. Results

3.1 Microstructure and mechanical properties of the TRIP-reinforced BMG composites

Yield strength and Young's modulus for BMG composite with different volume fractions of the B2-CuZr phase were shown in Figure 1. As the amount of B2-CuZr increases, both of them gradually decreases. It was known that yield strength and Young's modulus of composite materials can usually be estimated from properties of the constituent phases by the "rule of mixtures (ROM)" principle. Based on the yield strength of the monolithic amorphous matrix and pure B2-CuZr phase [26,27], the estimated values of these BMG composites are also shown as the dashed line in Figure 1. It can be seen that the variation trend of the experimental data roughly agrees with the predication by the ROM principle, and samples T1 and T2 are on the two ends of the correlation line, representative for TRIP-reinforced BMG composites with a different volume fraction of B2.

SEM micrographs and distribution profile of grain size of T1 and T2 are shown in Figs. 2a-2d, respectively. Sample T1 shows not only a higher volume fraction and larger average particle size of B2, but also a wider distribution profile of the B2 size, as compared with T2. The difference in the volume fraction leads to the variation of yielding stress while that in the distribution profile may cause the fluctuation of

yielding stress around the ROM line. Both of them affect local stress field [28] and thus influence the martensitic transformation upon loading, which will be addressed in detail later on.

TEM image and the corresponding selected area electron diffraction (SAED) patterns of the as-cast and deformed samples of T1 are shown in Fig. 3. The B2 crystals embedded in the amorphous matrix transformed to martensitic laths, as clearly confirmed by the SAED patterns of the as-cast and deformed samples.

3.2 *In situ* neutron diffraction loading of TRIP-reinforced BMG composites

Figure 4 shows the stress-displacement curves and the diffraction patterns collected, with respect to the loading direction, at various stresses for T1 and T2. It is noted that T1 underwent a loading-unloading cycle (Fig. 4a), whilst T2 was loaded up to fracture (Fig. 4c). As can be seen from Figs. 4b and 4d, the diffraction patterns obtained at low stresses all exhibit a diffuse hump characteristic of the amorphous phase, and a series of Bragg peaks due to the presence of B2 [29,30]. Owing to a large volume fraction of B2, T1 shows much stronger crystalline peaks. In response to initially increased compressive loading, diffraction patterns of both T1 and T2 show slight B2-peak shifts but keep the peak intensities nearly unchanged prior to the macroscopic yielding. Notably, right after the macroscopic yielding at ~550 MPa for T1 (or at ~1200 MPa for T2), the intensities of the B2 peaks start to decrease and a few new peaks (indexed as B19') appear [29,30]. Evidently, a martensitic transformation from B2 to B19' accounts for the macroscopic yielding; this is also clearly demonstrated in Fig. 5,

which shows the variation in the relative peak intensities of B2 and B19' as a function of applied stress. There appears to be a specific crystallographic orientation relationship between B2 and the newly transformed B19' as $(110)_{B2} // (020)_{B19'}$; this can be seen from Figs. 4(b, d) and Fig. 5, in which the $(110)_{B2}$ reflection shows the largest reduction in intensity among all the B2 reflections, whereas the $(020)_{B19'}$ reflection exhibits the most pronounced gain in intensity during the transformation. It is also noted that the phase transformation was partially reversible during subsequent unloading, as indicated by the increase in intensities of the B2 peaks [e.g., $(211)_{B2}$ and $(110)_{B2}$] in Fig. 4b.

4. Discussion

4.1 Load transfer and cooperative deformation behavior

Microscopically, cooperation between deformation of amorphous matrix and martensitic transformation of B2 crystals can be characterized by the evolution of hkl -specific lattice strains (along the loading direction) in B2, as shown in Figs. 6a and 6b. Here, the generic hkl indices denote not only a reflection in the diffraction pattern, but also refer to a specific family of grains or crystallites whose plane normal $\langle hkl \rangle$ lies along the loading direction (LD) or the transverse direction (TD); these grains/ crystallites are designated as $\langle hkl \rangle // LD$ or $\langle hkl \rangle // TD$, respectively. For instance, figure 6a depicts the variation of lattice strains of two representative families of B2-crystallites in T1, i.e., $\langle 200 \rangle // LD$ and $\langle 110 \rangle // LD$, which are determined from the 200 and 110 reflections of B2 with respect to the loading direction. One

immediate observation from Fig. 6a is that, below the macroscopic yield stress (i.e., 550 MPa for T1), each hkl -specific lattice strain varies linearly in response to the applied stress, indicative of elastic deformation behaviors; whereas, the slopes of the applied stress versus lattice strain curves, termed as diffraction-specific elastic constants that represent effective Young's moduli, are strongly dependent on the hkl orientation (*see* Table 1). This phenomenon is known as elastic anisotropy, owing to the crystallographic orientation-dependent elastic stiffness in a single crystal [31], and will be discussed in more detail in a following section. Another salient feature of the evolution of lattice strains in B2 (*see* Fig. 4a) is that, beyond the yield stress, the $\langle 200 \rangle$ //LD B2-crystallites exhibit significant deviations from the linearity in the applied stress versus lattice strain curve, whilst other families of B2-crystallites, e.g., $\langle 110 \rangle$ //LD, show much less non-linearity. This implies that, as the martensitic transformation proceeds, the $\langle 200 \rangle$ //LD B2-crystallites take additional loads transferred from those B2-crystallites which undergo the phase transformation; thus, the deviation point in the applied stress-lattice strain curve of $\langle 200 \rangle$ //LD is indicative of the start of the martensitic transformation and, in turn, the macroscopic yielding. Accordingly, one may notice that $\langle 200 \rangle$ is likely the least favorable orientation of B2 for the martensitic transformation, whereas $\langle 110 \rangle$ is among the most favorable ones.

Martensitic transformation-induced plasticity in the BMG composites is characterized by load transfer and cooperative deformation among the B2 crystallites, the newly transformed B19' crystallites and the amorphous phase. This mechanism is elaborated in the following by taking T1 as an example. As shown in Figs. 6a and 6b,

the first yield point at ~550MPa can be identified by two indicators: one is the observation of the B19' phase at this stress level signifying the onset of martensitic transformation (as shown by the blue diamond symbols in Fig. 6b), and the other is the concurrent deviation of $\langle 110 \rangle_{B2}$ lattice strain from its elastic linearity beginning from this stress level [as indicated by the purple dash line (labeled as “a”) in Fig. 6b].

When the stresses are beyond the macroscopic yielding (at ~550 MPa), two deformation stages, one below and the other above 1200 MPa, are discernible and evidenced by the sharp slope change in the microscopic strain of the amorphous phase vs. applied stress curve, as depicted by the arrow and the purple dash line (labeled as b) in Fig. 6b. At stresses between 550 MPa and 1200 MPa, as the martensitic transformation proceeds, untransformed B2 crystallites and the amorphous phase sustain additional loads transferred from the transforming B2-crystallites. Since the newly formed B19' crystallites are much stiffer [9], they start to share the load as well. At stresses above 1200 MPa, as the transformation continues, a significant amount of B19'-crystallites (e.g., $\langle 020 \rangle // LD$) have been formed at the expense of B2 and take more loads. Meanwhile, the amorphous phase appears to yield, e.g., by the initiation of shear bands at the interface between rigid B2 (and/or B19') crystallites and the amorphous phase [9], as indicated by the substantially small changes in the microscopic strains measured at stresses above 1200 MPa (see the dash line labeled as “b” in Fig. 6b). Thus, the untransformed B2 crystallites (e.g., $\langle 200 \rangle // LD$), together with the completely transformed B19' crystallites, will take and share the load transferred from the yielding amorphous phase and the transforming B2-crystallites;

these are indicated by even greater deviations of the $(200)_{B2}$ lattice strains from the extrapolated elastic response at stresses above 1200 MPa, as shown in Fig. 6b. It is anticipated that, the rigid B2 and B19' crystallites will “block” the shear band propagation in the glass to a significant extent until fracture, at which the strain accommodation capability of the amorphous phase is exhausted.

4.2 Elastic anisotropy and strain-controlled martensitic transformation

It is interesting to note that, for elastic deformation of T1 and T2, the proportionality of the B2 hkl -specific lattice-strain response to the applied stress, i.e., the reciprocal of the hkl -specific diffraction elastic constant ($1/E_{hkl}$), is found to depend strongly on the anisotropy parameter Γ_{hkl} $[= (h^2k^2 + h^2l^2 + l^2k^2)/(h^2 + k^2 + l^2)^2]$ (see Fig. 7 and Table 1). This is a manifest of strong elastic anisotropy of B2-CuZr, as characterized by its rather large Zener's anisotropy factor $A [= 2C_{44}/(C_{11} - C_{12})]$ of 3.5, in which C_{11} (= 138 GPa), C_{12} (= 112 GPa) and C_{44} (= 45 GPa) are the single-crystal elastic constants [32]. Also shown in Figure 7 are the predicted values of $1/E_{hkl}$ from the Reuss, Kröner and Voigt models for a hypothetical polycrystalline aggregate of B2-grains (or crystallites) [33]. Based on these models, the single-crystal elastic constants can be determined via the diffraction elastic modulus through Γ_{hkl} . In addition, the elastic anisotropy behavior of the composites can be evaluated and particularly, the confinement effect from surrounding of a specific orientated grain can be evaluated based on the deviation of experimental values from the predictions derived from these models. In the Reuss

modeling schemes, all B2-grains/crystallites are assumed to experience the same stress, and the hkl -specific elastic moduli are given to be identical to those of a single-crystal B2. The Voigt model, on the other hand, assumes that all B2-grains/crystallites experience the same strain; thus, the calculated elastic moduli are isotropic and the same for all hkl . In contrast, the Kröner model allows both stresses and strains to vary among grains/crystallites, thus rendering elastic properties more realistic. Nevertheless, the experimentally determined $1/E_{hkl}$ values of T1 and T2 are systematically smaller than the Kröner predictions, indicative of a significant strengthening effect on the local environments of B2-crystallites as a result of the inclusion of an isotropic, stiffer amorphous phase in the composite. Specifically, for T1 that contains ~75% B2 and ~25% glass, the B2 crystallites are impinged or interconnected such that each B2 crystallite interacts with a majority of other oriented B2 crystallites and a minority of the amorphous phase (see Fig. 2a); this explains why the $1/E_{hkl}$ values of T1 are only slightly smaller than those calculated by the Kröner model and, essentially, exhibit a rather similar slope with the variation of Γ_{hkl} . In contrast, T2 contains only ~25% B2 in which each B2 crystallite interacts essentially only with the stiffer amorphous phase (see Fig. 2c); as such, the $1/E_{hkl}$ values of T2 are significantly smaller than the Kröner predictions, indicating a much larger confinement from the surrounding amorphous matrix. The plot also yields a much steeper slope in the $1/E_{hkl}$ vs Γ_{hkl} curve, resembling that for a single-crystal B2 as predicted by the Reuss model.

Although large anisotropy and different confinement were observed in T1 and T2, it can also be seen that the threshold lattice strain for the martensitic transformation (Fig. 8) is similar, in spite of different threshold stresses, suggesting that the martensitic transformation in the current TRIP-reinforced BMG composite is likely strain-controlled, rather than stress-controlled [34]. In T2 with a lower volume fraction of B2, higher stress was required for producing the same threshold strain due to the larger confinement effect from the surrounding amorphous matrix, which led to a higher yield strength, and vice versa for T1 with a higher B2 fraction.

In conventional TRIP-reinforced materials, such as TRIP steels, strain-induced martensitic transformation was usually attributed to the numerous martensitic nucleation sites resulted from plastic strain [35]. In the current TRIP-reinforced BMG composite, however, the strain-controlled MT occurred even before plastic deformation and thus highly-potent sites for easy nucleation of martensite, which is usually required for a strain-induced MT [36], are not identified. Our results clearly reveal that in the current TRIP-reinforced BMG composites, the intrinsic lattice response to the applied loading, instead of the external stress, is the determinative factor for the martensitic transformation. This finding sheds critical insights into understanding what controls yielding of the austenitic phase in the TRIP-reinforced BMG composites and has important implications in improving the overall mechanical properties of these glassy materials. To further discuss the underlying mechanisms of the confined martensitic transformation, we carried out molecular dynamic (MD) simulation and the corresponding results are presented as follows.

4.3 Mechanisms of confined martensitic transformation

Two composite samples containing 864000 atoms ($24 \times 24 \times 24 \text{ nm}^3$) with a different volume fraction of B2-CuZr (75%, termed as T1, 25%, termed as T2) were constructed, and tensile tests were performed with the prepared samples. Yield strength of the sample with 25% B2-CuZr was much higher than that of the sample with 75% B2-CuZr (Fig. 9a), which is consistent with the experimental results. It should be noted that the absolute value of stress and strain of the MD simulation is different from that of the bulk samples, which is due to the size effects of deformation behavior of BMGs [37].

To identify the martensitic transformation process more clearly, atomic bonding length and lattice angle distribution of each atom in the crystalline phase were analyzed. The CuZr martensite has a monoclinic structure by shearing the (011) planes of cubic B2 in the [100] direction, thus altering the atomic bonding distance and forming a monoclinic angle of 103.88° [29,30]. Therefore, there should be a change of atomic bonding length (such as Zr-Zr, Zr-Cu, Cu-Cu) and a 13.88° deviation of lattice angle from 90° after the martensitic transformation. In this case, the change of atomic bonding length and also the angle deviation from 90° with a 13.88° can be regarded as an indicator of martensitic transformation.

The distribution and variation of atomic bonding length with deformation of the two BMG composites are shown in Figs. 9b and 9c, respectively. The atomic bonding length in the B2-CuZr phase was found to increase with deformation. A small hump

on the distribution curve was also found to occur and became stronger with deformation, which can be attributed to the atomic bonding length in the transformed martensite and can thus be taken as an indicator of the martensitic transformation. The small hump started to appear at a different loading strain of 3% and 2% for the BMG composites with 25% and 75% crystalline phase, respectively, implying that the martensite transformation seemingly occurred at a different macroscopic strain. The bonding length of the B2-CuZr phase was then normalized with that in the underformed sample to get the bonding extension $\varepsilon_d = (d - d_0)/d_0$, where d and d_0 are atomic bonding length during and before deformation, respectively. Surprisingly, the martensitic transformation was found to occur at the same bonding extension for both BMG composites (Fig. 9d). The lattice strain was actually a result of atomic bonding extension, thus the current result indicates that the martensitic transformation would take place at a critical lattice strain regardless of the volume fraction of crystallites, which is consistent with the experimental results and indicates a strain-controlled martensitic transformation.

Furthermore, it was found that the martensitic transformation initiated at the interface between the B2-CuZr and amorphous matrix. Atoms with a 13.88° deviation from 90° for both composites were screened out at the strain that the martensitic transformation started to take place, as shown in Fig. 10. The illustration was focused on the martensitic transformation in crystalline phase, therefore, only atoms in the crystalline phase are shown (Zr and Cu atoms are in blue and brown, respectively) while those in the amorphous matrix are neglected. To show the

martensitic sites more clearly, two slices with a thickness of 5 nm were cut from both the samples, i.e., Figs. 10b and d, from which small martensites could be found at the interface between the crystallite and amorphous matrix, indicating that interface may act as nucleation site for the subsequent martensitic transformation. In fact, due to the lattice mismatch between B2 and the amorphous matrix, atoms at the interface has large deviation from the standard cubic B2 lattice, which may be one of the reason why the interface acted as the nucleation sites for the martensitic transformation. In other words, the martensitic transformation was initiated from the interface at the initial stage and gradually moved to the inside of B2 as the deformation proceeded.

In addition, the martensitic transformation of B2 correlates closely with not only the lattice mismatch, but also the elastic mismatch between B2 and the amorphous matrix. Evolution of local strain field on a representative cross-section of the composites with 25% crystalline phase was shown in Figs. 11 as an example. At the initial deformation stage, the amorphous matrix has a larger local strain and fluctuation in comparison with the B2 phase. The amorphous matrix actually took more external load due to its high stiffness, and the loading was transferred to the B2 phase through the interface, which resulted in a relative larger local stress/strain concentration on the interface and led to the initiation of martensitic transformation [38].

Therefore, it can be seen that the interface connecting the crystalline B2 phase and amorphous matrix acts as not only the nucleation sites of martensitic

transformation but also load transfer media upon loading. The atoms at the interface have large deviation from the standard cubic B2 lattice, which formed during rapid quenching of TRIP-reinforced BMG composites, provide substantive nucleation sites for martensitic transformation even before plastic deformation. Moreover, martensitic transformation occurred at the same threshold value of lattice strain in both T1 and T2 samples, but different macroscopic stress/strain was required to reach this critical lattice strain, which resulted in the different macroscopic strength and plastic strain observed for martensitic transformation in T1 and T2.

The findings in the present work have important implications for understanding the deformation mechanism of bulk metallic glass composites. Firstly, Our neutron diffraction results on T1 provide clear, microscopic-level evidence for the first two yielding phenomena in the triple yielding phenomenon of TRIP-reinforced BMG composites [39]. Secondly, the partial reversibility of the martensitic transformation, as observed in the present work, implies that conventional characterization of specimens obtained after interrupted deformation would inevitably underestimate how the transformation proceeds. This discrepancy may give rise to inconsistent experimental results and mislead the data interpretation and theoretical modeling. In this regard, *in situ* characterization of deformation by neutron or synchrotron diffraction is in urgent need to provide direct evidence of structural evolution of both the amorphous and crystalline phases upon loading. Furthermore, TRIP reinforcement mechanism in the strain-softening amorphous matrix was found to be distinct from that in the strain-hardening media, such as TRIP steels. The interface which connects

amorphous matrix and B2 not only effectively transferred the stress/strain between the amorphous and crystalline phase, but also acted as the nucleation sites initializing martensitic transformation.

5. Conclusions

In summary, a martensitic transformation and the transformation-induced plasticity in CuZr-based bulk metallic glass composites upon loading have been observed by *in-situ* neutron diffraction and MD simulation. Two yielding phenomena are revealed by the evolution of lattice strains in B2 and microscopic strains in the amorphous phase, providing microscopic evidence for the proposed triple-yielding mechanism. The transformation-induced plasticity is characterized by the elastic and plastic anisotropies of B2, load transfer and cooperative deformation between B2 and the amorphous phase. The interface between crystalline and amorphous phase was found to not only act as the loading transfer media, but also substantive nucleation sites for martensitic transformation, which give rises to the characteristic of strain-controlled martensitic transformation in strain-softening amorphous phase. Any factors that favor shearing of crystallographic planes to reach the threshold strain would promote martensitic transformation of the austenitic phase, and eventually alter the global mechanical behavior of the composite. These findings offer new, microscopic insights into the TRIP effect, and help to design stronger and tougher amorphous-crystalline composites.

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Table and figure captions

Table 1. Experimentally determined hkl -specific diffraction elastic constants of B2 (E_{hkl}) and the reciprocal ($1/E_{hkl}$), with respect to the loading direction, in T1 and T2, compared with those determined from the 020 reflection of B19' and from the first sharp diffraction peak (FSDP) of the amorphous phase in T1.

Fig. 1 (a) and (b) represent measured macroscopic yield stress and Young's modulus as a function of volume fraction of B2 in the CuZr-based TRIP-reinforced BMG composites, respectively, where values of T1 and T2 are marked.

Fig. 2 (a) and (c) are the representative SEM micrographs of T1 and T2, respectively. (b) and (d) are distribution profiles of grain size of T1 and T2, respectively.

Fig. 3. TEM images of the as-cast (a) and deformed BMG composites (c), and the corresponding selected area electron diffraction (SAED) of the B2 (b) and B19' (d) crystals.

Fig. 4. The stress-displacement curves and the corresponding diffraction patterns recorded, with respect to the loading direction, at various stress levels for T1 (a, b) and T2 (c, d).

Fig. 5. Evolution of relative peak intensities of $(110)_{B2}$ and $(020)_{B19'}$, with respect to the loading direction, as a function of applied stress in T1 and T2.

Fig. 6 (a) Evolution of $(200)_{B2}$ and $(110)_{B2}$ lattice strain component parallel to the loading axis as a function of applied stress during loading and subsequent unloading of T1. (b) Evolution of lattice strain (or microscopic strain) components parallel ($\epsilon_{\parallel}$) and perpendicular ($\epsilon_{\perp}$) to the loading axis, in terms of $(200)_{B2}$, $(110)_{B2}$, the amorphous phase and $(020)_{B19'}$ ($\epsilon_{\parallel}$ only), as a function of applied stress during loading of T1. The dashed lines “a” and “b” are for distinguishing the deviation from linearity of the

microscopic. The arrow points to the start of the substantially small change of microscopic strains in the amorphous phase.

Fig. 7. The reciprocal of experimentally determined hkl -specific elastic constant of B2 as a function of cubic anisotropy parameter (Γ_{hkl}) for T1 and T2, compared with predictions from the Reuss, Kröner and Voigt models.

Fig. 8. Plots of applied stress vs. microscopic strains of the {100}B2 and {020}B19' crystallites in T1 and T2. Martensitic transformation was found to occur at the same threshold lattice strain in both samples T1 and T2.

Fig. 9. Tensile stress-strain curve of the modeled BMG composites with 75% and 25% volume fraction of B2-CuZr (a), distribution of atomic bonding length and its evolution with loading strain for the BMG composite with 75% (b) and 25% (c) B2-CuZr, evolution of normalized bonding length with loading strain for both composites (d),

Fig. 10. Screening of atoms with 13.88° deviation from 90° in the crystalline phases (atoms in red) at the strain that the martensitic transformation started to take place in BMG composites with 75% (a, b) and 25% (c, d) crystalline phase, only atoms in crystalline phase were shown (blue, Zr, brown, Cu), atoms in the amorphous matrix are neglected to highlight atoms in the crystalline phase. (b) and (d) are slices with a thickness of 5 nm cut from the position indicated by the dashed line in (a) and (c), respectively, from which martensite nucleus can be clearly seen on the interface in both samples.

Fig. 11 Evolution of atomic local strain field (as defined in Ref. 25) on a cross-section of BMG composite containing 25% B2-CuZr phase with deformation at different loading strain, (a) 2%, (b) 4%, (c) 6%, (d) 8%, and local strain was represented by both the color and the size of the atoms. Large local strain and fluctuation were found

in the amorphous matrix and was transferred into crystalline phase through the interface.

Fig. 1

Figure 1 Wu *et al.*

Fig. 2

(a)

(b)

(c)

(d)

Figure 2 Wu *et al.*

Fig. 3

Figure 3 Wu *et al.*

Fig. 4

Figure 4 Wu *et al.*

Figure 4 Wu *et al.* (continued)

Fig. 5

Figure 5 Wu *et al.*

Fig. 6

Fig. 7

Figure 7 Wu *et al.*

Fig. 8

Figure 8 Wu *et al.*

Fig. 9

Figure 9 Wu *et al.*

Figure 9 Wu *et al.* (continued)

Fig. 10

(a)

(b)

(c)

(d)

Fig. 11

Figure 11 Wu *et al.*

Table 1

Phase	<i>hkl</i>	Γ_{hkl}	T1		T2	
			E_{hkl}	$1/E_{hkl}$	E_{hkl}	$1/E_{hkl}$
B2	200	0	66.4	0.0150	78.4	0.0128
	310	0.09	75.3	0.0133	86.0	0.0116
	110	0.25	91.8	0.0109	163.0	0.0061
	211	0.25	92.3	0.0108	165.1	0.0061
	321	0.25	92.5	0.0108	148.2	0.0067
	222	0.33	106.7	0.0094	-	-
B19'	020		104.6		-	
Amorphous phase	FSDP		84.5		-	

Note that E and 1/E are in units of GPa and GPa⁻¹, respectively.