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Work toughening effect in $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass

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Work hardening is a well-known phenomenon occurring in crystalline metals during deformation, which has been widely used to increase the strength of metals although their ductility is usually reduced simultaneously. Here we report that the plastic strain of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ (at.%) bulk metallic glasses has been increased from 0.3% for the as-cast sample to 2.5%–8.0% for samples that have experienced pre-deformation under constrained conditions. The pre-deformed glassy alloys possess more free volume and abundant introduced shear bands, which are believed to promote the activation of shear bands in post-deformation and result in an increase in plasticity. The orientation of the pre-introduced shear bands relative to the loading direction will affect the deformation behavior of pre-deformed samples. The present results show that pre-deformation of this glassy alloy will result in work toughening. This work toughening effect can be removed by isothermal annealing at a sub-T_g (glass transition) temperature, which causes annihilation of free volume and healing of shear bands.

metallic glass, mechanical properties, shear bands

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It is well known that most bulk metallic glasses (BMGs) possess super-high strength but very low global plasticity. The accepted reason for the limited plasticity of BMGs is that BMGs possess a tendency to form highly-localized shear bands which result in early fracture of the materials. It is obvious that deformation behavior of BMGs is quite different from crystalline metals, in which plastic deformation corresponds to the generation and motion of large numbers of dislocations. As the dislocation density increases with the plastic deformation, the interactions among dislocations are also increased, resulting in an increase in the resistance to dislocation movement. Then, further deformation requires an increase in the applied stress. This is the so-called "strain hardening" or "work hardening". However, since there are no dislocations in glassy alloys, absolutely no strain hardening resulting from interactions among dislocations can be observed in BMGs. So it is very difficult for glassy alloys to deform uniformly. Instead, highly localized shear bands [1] form easily during the deformation process, resulting in limited global plasticity of BMG.

So to enhance the plasticity of BMGs, it is necessary to promote the activation of multiple shear bands [2–10] and hinder the localization and rapid propagation of shear bands [11–19]. Indeed much important progress has been made in enhancing the ductility of BMGs by various ways [2–19], such as by introducing second phase particles on the nanoscale/microscale [2–5] or solid solution particles [6] which restrict the severe localization and rapid propagation of shear bands, the as-prepared BMG composites could exhibit a global plasticity of about 7% [7]. Because the partially relieved local heating and hindrance of the propagation of shear bands, both the strength and the ductility of a Zr-based BMG are enhanced at cryogenic temperatures [12]. A compressive strain as large as 80% for a previously brittle BMG was obtained under constrained conditions, by tuning the strain rate and aspect ratio [13]. Large plasticity has also been obtained by shot-peening [16], electrodeposition [17, 18] and use of a metal sleeve [19]. Very recently it has been

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found that introducing a uniform distribution of shear bands by rolling and pre-deformation can improve the plasticity of BMGs [20,21]. To understand the effects of pre-introduced shear bands on the subsequent deformation behavior of BMGs, the compressive behavior of pre-deformed $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vit1) BMGs has been studied in the present work. Factors which may affect the plasticity of the pre-deformed BMGs have been discussed.

1 Experimental

Master alloy ingots with nominal composition $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vit1) were prepared in an arc furnace under argon atmosphere. They were remelted several times to ensure compositional homogeneity. Rod shaped samples with diameters of 4, 7 and 10 mm were suction-cast into copper molds. For the pre-deformation experiment under compression, samples with small aspect ratios (h/d=0.4 and h/d=0.5) were cut out from the as-cast rods using a diamond saw. The uniaxial compression tests of samples with h/d=0.4 and all the post-deformation tests were carried out at a strain rate of 1×10^{-4} s^{-1}, while samples with h/d=0.5 were initially compressed at a strain rate of 1×10^{-3} s^{-1}. Samples before and after the pre-deformation experiments were carefully examined by XRD analysis using a Rigaku D/max diffractometer with monochromated Cu$K\alpha$ radiation, and the thermal behavior associated with glass transition temperature was measured by DSC at a constant heating rate of 20 K/min. Since the samples had small aspect ratios, they could be deformed to large plastic strains because the geometrical constraint. Then, the deformation behavior of the pre-deformed Vit1 BMG was studied by use of standard compressive specimens (with aspect ratios of 2.0) cut from the pre-deformed samples. According to the angle between the pre-loading axis and secondary loading (or post-loading) axis, three different cutting methods were employed to cut the vertical (Figure 1(a)), parallel (Figure 1(b)) and inclined (Figure 1(c)) compressive specimens from the pre-deformed samples. The size of these vertical, parallel and inclined orientation specimens was about 1.5 mm×1.5 mm×3 mm to 2 mm×2 mm×4 mm (Figure 1). For comparison, isothermal annealing at 573 K for 3600 s was applied to some pre-deformed samples before secondary deformation. The side-views of all deformed specimens were observed using a LEO1530 scanning electron microscope (SEM) integrated with a field emission gun.

2 Results and discussion

To understand the influence of pre-deformation on the mechanical properties of glassy alloys, BMG samples with small aspect ratio were pre-deformed to designated plastic strains of ~5%, ~10%, ~15%, ~20%, ~25%, ~35% and ~50%, respectively. X-ray analysis confirmed that all the pre-deformed samples, including those that had experienced pre-deformation and isothermal annealing, possess fully amorphous structures. Figure 2 shows continuous DSC traces for some of the pre-deformed, or pre-deformed plus isothermally annealed Vit1 BMGs at a heating rate of 20 K/min. Their characteristic parameters are listed in Table 1, including the relaxation enthalpy and supercooled liquid region. Both the pre-deformed and pre-deformed plus isothermally annealed samples exhibit kinetic characteristics of amorphous alloys, in agreement with the reported results in [13]. However, careful examination of the section of the DSC curves near T_g showed that the relaxation enthalpy of the BMGs has been increased by the pre-deformation, but decreased by the isothermal annealing (see the inset of Figure 2). For the BMG sample pre-deformed by 15%, the relaxation enthalpy was enhanced to ~0.81 W/g, which is much larger than that of the as-cast sample (~0.28 W/g). But when the BMG sample pre-deformed by 15% was annealed at 573 K for 3600 s, its relaxation enthalpy was reduced to nearly 0 W/g. Based on Beukel's theory [22], the value of relaxation enthalpy is related to the amount of free volume existing in the BMGs. Therefore, the total amount of free volume could be increased by the pre-deformation, in agreement with the result reported for rolling of BMG [23]. But this effect could be recovered by isothermal annealing at a temperature about 70 K below T_g. Moreover, the isothermal annealing at 573 K for 3600 s resulted in a slight decrease in T_g (see the inset of Figure 2), which eventually

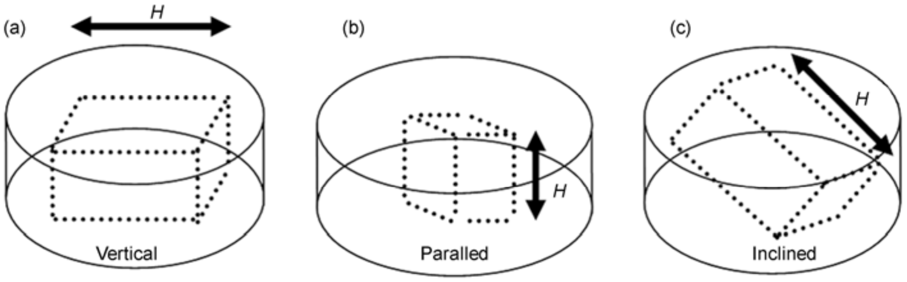

Figure 1 Three different cutting methods of the pre-deformed Vit1 BMG samples. (a) Vertical sample with loading axis vertical to the pre-compressing direction; (b) parallel sample with the loading axis parallel to the pre-compressing direction and (c) inclined sample with the loading axis inclined 45° to the pre-compressing direction.

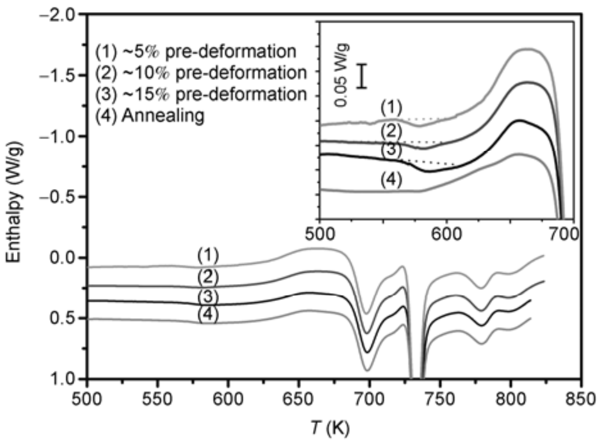

Figure 2 DSC scans of the pre-deformed Vit1 BMG samples.

Table 1 The thermal and mechanical properties of Vit1 BMGs

	A	*B*	*C*
Relaxation enthalpy *H* (W/g)	0.28	0.81	0
Supercooled liquid region ΔT (K)	58	60	95
Yield strength σ_y (MPa)	1804	1910	1830
Compressive strength σ_c (MPa)	1815	2190	1870
Plastic strain ε_p (%)	0.31	8.9	1.9

a) *A*, As-cast sample; *B*, with 15% pre-deformation; *C*, with 15% pre-deformation plus isothermal annealing at 573 K for 3600 s.

enhanced the supercooled liquid region ΔT by 37 K when compared with that of as-cast Vit1 BMG. Why ΔT was significantly increased is still not clear.

In the secondary deformation (or called post-deformation) process of the pre-deformed BMGs, the loading direction for vertical orientation specimens, parallel orientation specimens and inclined orientation specimens is vertical to, parallel to and inclined at 45° to the loading axes of the samples in pre-deformation, respectively (Figure 1(a), (b), (c)). Figure 3(a) shows the engineering strain-stress curves of the as-cast specimen and pre-deformed plus annealed specimens. The as-cast Vit1 BMG exhibits a yield strength of about 1800 MPa and a plastic strain of 0.3%, in agreement with the reported result [12–15]. When the BMG samples were pre-deformed by 5%, 10% and 15%, respectively, in a constrained state, vertical orientation specimens cut from the pre-deformed samples exhibited plastic strains of ~2.5%, ~5.0% and ~8.0%, respectively (Figure 3(b)). This indicates that mechanical pre-deformation in the constrained condition has significantly enhanced the plastic deformation ability of BMGs in post-deformation. Since the plasticity is closely related to the toughness of materials, it shows that the pre-deformation or working results in a work toughening phenomenon in glassy alloys.

As shown in Figure 3(b), the plasticity of the pre-deformed Vit1 BMGs increases with the pre-deformation amount for $\varepsilon_p \leqslant 15\%$. When the pre-deforming amount increases to 20%, however, the plastic strain of the pre-deformed BMG is decreased sharply to ~3.2%. Further increases in pre-deformation amount to ~25% and to ~50%, still result in plastic strains of the pre-deformed Vit1 BMG of around 3.2%. This indicates that the optimum pre-deformation amount, ε_p, to enhance the plastic deformation ability of the pre-deformed Vit1 BMGs in the vertical orientation is around 15%. A similar phenomenon has also been found for pre-deformed Vit4 BMGs but the optimum pre-deformation amount was different [21]. As shown in Figure 3(a), the yield strength of pre-deformed samples in vertical orientation is slightly larger than that of as-cast samples (1.80 GPa, Figure 3(a)). Especially, the maximum compressive strength of all the pre-deformed samples, which range from 2.00 to 2.20 GPa, is obviously larger than that of the as-cast ones (1.81 GPa, Figure 3(a)). This indicates that mechanical pre-deformation in a constrained condition has a significant influence on the strength of the pre-deformed BMGs in post-deformation. But the reason is still not clear.

Figure 3(c) shows the strain-stress curves of the samples deformed in the directions parallel to and inclined to the loading direction in pre-deformation. Both the yield strength and maximum compressive strength of the pre-deformed samples loaded in parallel or inclined directions remain nearly the same as that of the as-cast alloy, but the plastic strains of the BMGs have been enhanced significantly by pre-deformation. The plastic strain for samples pre-deformed by 5% is about 7% (Figure 3(c), I), while the plastic strains for samples pre-deformed by 10% and 15% are about 2.0%–4.0% (Figure 3(c), II and III), less than that obtained with smaller pre-deformation. For the sample loaded in the inclined direction, the plastic strain at fracture for 5% pre-deformed samples is about 6.9%, but when the plastic strain is larger than ~5%, the stress clearly decreases. Comparing Figure 3(b) with 3(c) shows that for the samples that had experienced the same pre-deformation (such as 5%) the plastic strains of the samples with different orientations show quite different plasticity. For samples with low pre-deformations (such as 5%), parallel samples show better plasticity than that of vertical orientation samples and inclined orientation samples. In contrast, for samples with high pre-deformation (such as 15%), vertical samples show better plasticity than parallel samples or inclined samples. That is the plasticity of pre-deformed samples in post-deformation is closely related to the loading orientation with respect to the pre-deformation loading direction. It is known that for the samples pre-deformed by the same amount, the angle between pre-introduced shear bands and the loading direction of parallel samples is quite different from that of vertical samples. This then means that the resolved shear stress on the pre-existing shear bands in post-deformation must be different for the samples with different orientation, resulting in different possibility of reactivation of the shear bands and subsequently affecting the plasticity of the pre-

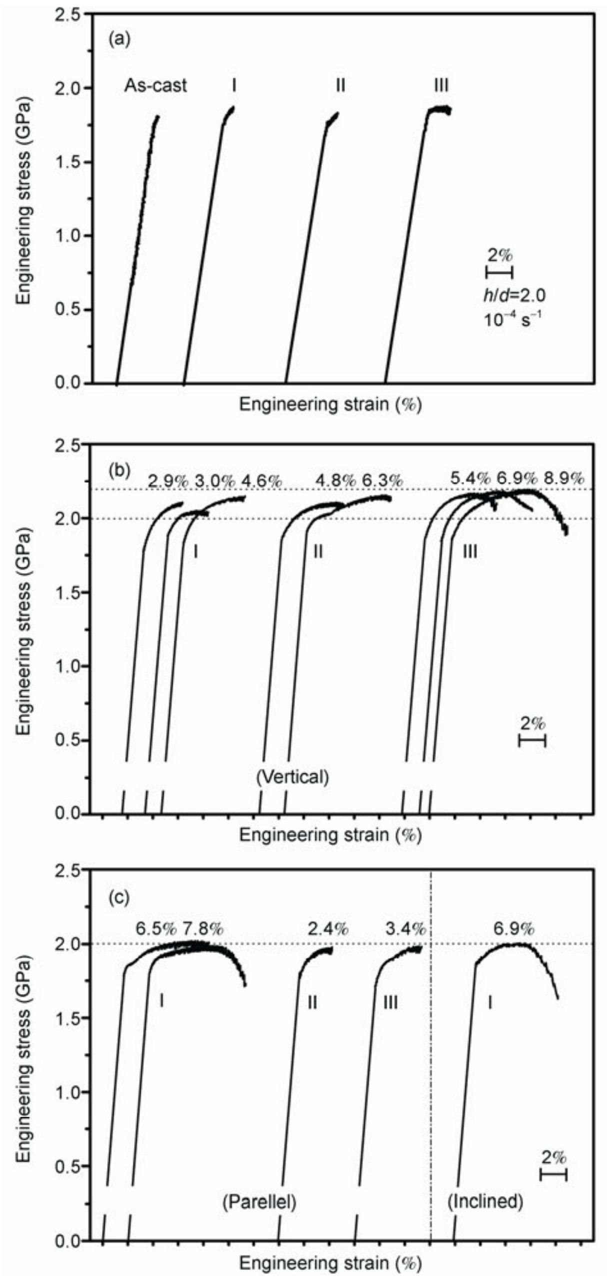

Figure 3 Engineering strain-stress curves for Vit1 BMGs. (a) As-cast and pre-deformated plus annealed. I, II and III denote 5%, 10% and 15% pre-deformation, respectively; (b) post-deformation in the vertical direction; (c) post-deformation in parallel and inclined directions.

deformed samples in post-deformation. It is worth noting that if microcracks have been formed along the pre-existing shear bands, the microcracks would induce stress concentration, which is harmful to the subsequent deformation, and would result in premature fracture of the pre-deformed samples.

Some samples that had experienced 15% pre-deformation were isothermally annealed at 573 K (about 70 K lower than T_g) for 3600 s. Test samples, 2 mm×2 mm×4 mm, were cut from these annealed samples in the vertical orientation (Figure 1(a)). The strain-stress curves of these pre-deformed plus annealed samples are shown in Figure 3(a). They indicate that after annealing all of the pre-deformed samples exhibit lower yield strength (<1.86 GPa) and less plastic strain (<2.0%) than those prior to isothermal annealing (Figure 3(b)). Among these annealed samples, those that experienced larger pre-deformation displayed larger plastic strains than those that had experienced smaller pre-deformation (III:1.9%>II:0.8%>I:0.6%). The mechanical properties of the as-cast sample, the 15% pre-deformed sample, and the sample with 15% pre-deformation plus isothermal annealing, are listed in Table 1 for comparison. This indicates that the work toughening effect in glassy alloys resulting from the pre-deformation process in the constrained condition could be removed by isothermal annealing at a sub-T_g temperature.

Figure 4(a) and (b) presents SEM side-view images of the specimen secondary-deformed in the vertical direction. The shear fracture angle measured in the fractured specimen is 48.9°, which is larger than 40.5°, the original shear angle of Vit1 BMG under compression. Two main groups of parallel shear bands (zones I and II) can be clearly observed on the surface, and the angle between shear planes in zone I and the loading direction is approximately 42.6°. In the vicinity of the interaction area of zones I and II, in addition to primary shear bands (P.S.B) with spacing of ~60 μm, some secondary shear bands (S.S.B) with interspacing of ~5 μm (Figure 4(b)) are observed. The orientation of S.S.B shown in Figure 4(b) is parallel to the loading direction in pre-deformation, and thus they could not have resulted from the pre-deformation. Figure 5(a) and (b) presents SEM side-view images of the specimen secondary-deformed in the inclined direction. Since the angle between pre-loading and secondary loading is approximately 45°, the orientation of P.S.B introduced by the pre-deformation process should be nearly vertical or parallel to the secondary loading. Accordingly, they could not be reactivated under the secondary loading, and the main shear planes can not be clearly distinguished on the surface in Figure 5(a). The angle between the fracture plane and secondary loading direction is approximately 41.9°, which is close to the original shear angle of Vit1 BMG under compression. Interestingly, one can see

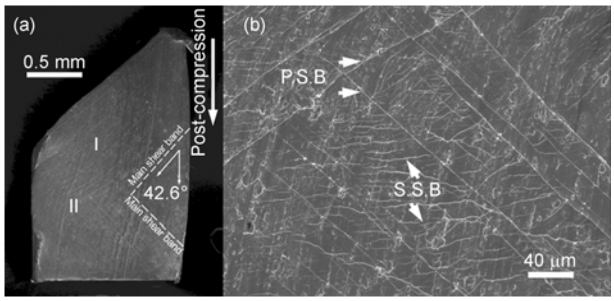

Figure 4 SEM side-view images of the secondary-deformed specimen in the vertical direction.

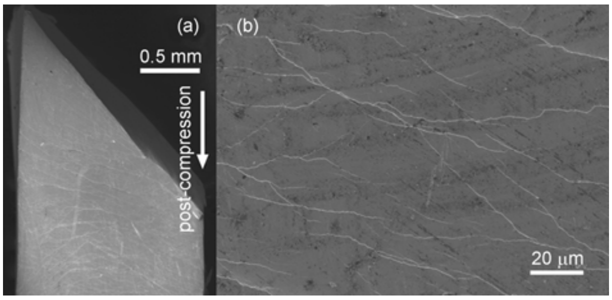

Figure 5 SEM side-view images of the secondary-deformed specimen in the inclined direction.

that shear bands in Figure 5(b) propagated in a winding manner, not straight like the ones introduced in the pre-deformation process, and the average spacing between the flexural shear bands is ~50 μm. The enhanced activation of the shear bands is in good agreement with the improved plasticity of pre-deformed samples showed in Figure 3(b) and (c).

Based on the above results, the plasticity of metallic glasses under uniaxial compression can be effectively enhanced by pre-deformation processing. Furthermore, XRD analysis found no apparent difference in the specimens prior to and after pre-deformation. Therefore, the enhanced plastic strain did not result from deformation-induced nano-crystallization. The activation and multiplication of shear bands would be promoted by both the increased amount of free volume and the pre-introduced shear bands, which are believed to act as activation sources of shear bands. This then means that the severe shear localization during the early stages of deformation can be avoided by the generation of lots of shear bands and the reactivation of pre- introduced shear bands when the resolved shear stress on the shear band is suitable (except in the case of inclined orientation specimens). It is generally thought that discrete atomic jumps in glassy alloys are favored near sites with more free volume [1], and thus shear deformation would be activated more readily in the high free-volume-containing area. In fact, in some cases S.S.Bs have been observed to have originated directly from the P.S.B (Figure 5(b)), and more than one shear banding event can occur on the same shear plane [24]. In the present research, multiple S.S.B have been observed to originate from the primary shear bands (see Figure 4(b) and Figure 5(b)) because of the increased free volume as a result of shear deformation from the pre-deformation process.

To sum up, the work toughening effect in glassy alloys results from the introduced free volume and shear bands. Similar toughening effects in BMGs were also reported in [21,25]. For instance, the cold rolling technique was successfully applied to introduce profuse shear bands in glassy alloys, and the as-rolled samples indeed displayed enhanced ductility under bending deformation [20,25]. The effective multiplication of shear bands during post-deformation was observed in samples with ~29% pre-deformation amount in Vit4 BMG [21]. The compressive deformation of glassy alloys with small aspect ratio is close to the case of cold rolling, so the work toughening effect in BMGs shows good consistency with the reported results. Although some ductile metallic glasses have been found to exhibit large plasticity [8–12], they are limited to sample sizes not larger than 2 mm, and most other amorphous alloys appear to be inherently brittle. Consequently, the work toughening effect may be employed as a practical way to improve the plasticity of brittle glasses or ductile glasses with large sample size.

3 Conclusions

In summary, it was found that with pre-introduced shear bands, Vit1 BMGs exhibited large plastic strains ranging from ~2.5% to ~8.0% and high strength in the post-deformation process. In other words, the pre-deformed BMGs exhibit a work toughening effect. The pre-deformed specimens with large plasticity showed enhanced amounts of free volume and increased densities of shear bands, which are beneficial for the activation of multiple shear bands and hindering shear localization in the subsequent deformation. The orientation of pre-introduced shear bands with respect to the loading direction would influence the plasticity of the pre-deformed samples. This toughening effect can be removed by isothermal annealing at sub-T_g temperature, which results in the annihilation of free volume and the healing of shear bands. The present results suggest a promising way for enhancing the plasticity of BMGs.

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