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Article

Large Compressive Plasticity in a La-Based Glass-Crystal Composite

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Abstract: $La_{55}Al_{25}Cu_{10}Ni_{10}$ metallic glass has been reinforced with 325-mesh Ta particles to obtain *ex situ* glass-crystal composites. The composites show a high compressive plasticity (40%) with a minor reduction (~8%) in yield strength—a combination unprecedented for La-based systems and even surpassing some Zr-based glassy composites that utilize a tougher matrix. However, it is also found that the plastic strain is apparently sensitive to defects, like oxides, in the glassy matrix.

Keywords: plasticity; bulk metallic glasses; composites; toughness

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1. Introduction

The limited global plasticity exhibited by bulk metallic glasses (BMGs), because of highly localized shear banding and ways to improve their plasticity, are issues that have seen much attention in recent years. The addition of ductile crystalline phases to a glassy matrix is a popular way of proliferating shear bands in metallic glasses and, thus, improving their toughness/plasticity. The reinforcement in such BMG matrix composites (BMGCs) can be either intrinsic (crystals that form via devitrification of the glass) or extrinsic (where the crystalline phase is added to a melt that later congeals into a glass).

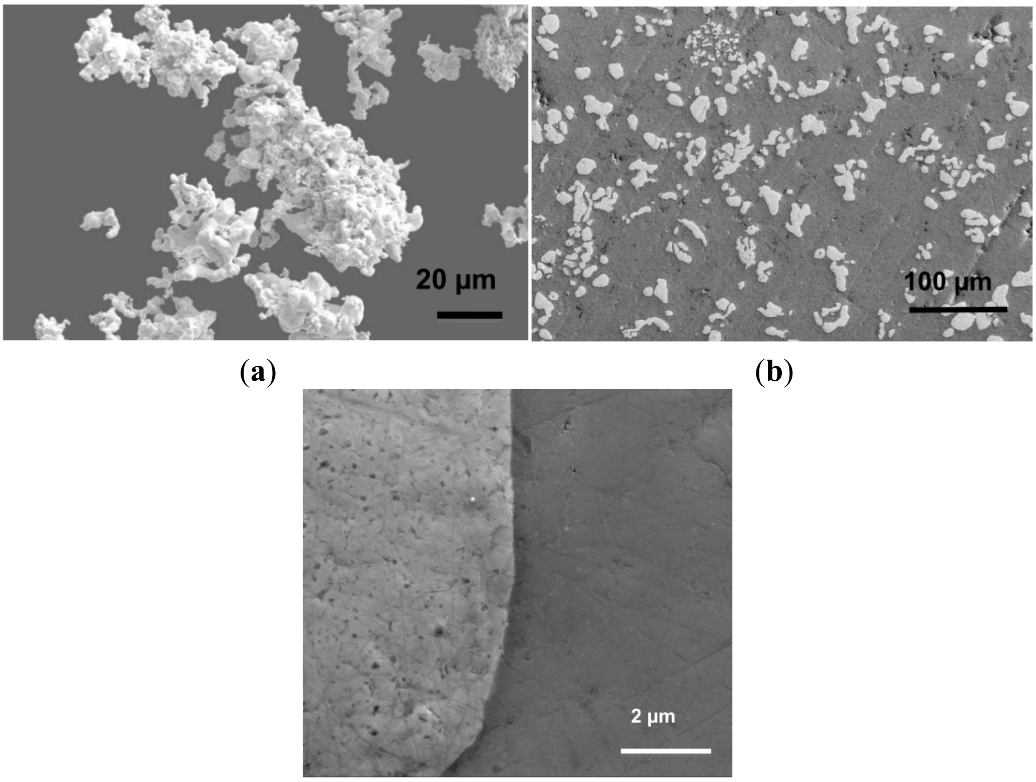
Monolithic BMGs have varying degrees of toughness, with those based on Zr, Cu or Pd being intrinsically tougher, whereas glasses based on rare earth metals, Fe or Mg, are less tough [1,2]. Although composites have been synthesized in a variety of alloy systems, like Zr [3–7], Cu [8,9], Mg [10,11] and La [12–15], a major part of the work has focused on the tougher glasses, since these are more likely to exhibit desirable combinations of strength and toughness. In particular, Zr-based BMGCs are the most extensively studied, as the glassy matrix is inherently tough, and in fact, *in situ* composites that consist of Zr-Ti-Nb dendrites dispersed in a glassy matrix can even show tensile ductility [5,6]. The idea of having ductile dendrites precipitating in a glassy matrix was also extended to the La-based compositions, and the *in situ* composites did show some enhancement in toughness, including tensile elongation of ~6%. The compressive plasticity was a modest 6%, but was accompanied by ~50% reduction in yield strength [12,13]. Further work using 20 vol.% of coarse Ti powder (150 μm spheres) as an extrinsic reinforcement in La-based glasses [16] led to the development of composites with a much higher strength (only 10% reduction compared to the glass) with much improved compressive plasticity (10%–15%). Of scientific interest is whether the properties of these less-tough La-based glassy materials can be improved any further, thus motivating the current study. As mentioned in [12], the key to improving plasticity is to increase the volume fraction of the soft ductile phase. Another way—the approach used in the present work—could be to use finer reinforcement particles, while keeping the volume fraction relatively unchanged, so that the average inter-particle spacing decreases. The current work uses 20 vol.% of −325 mesh (40 μm) ductile Ta particles as extrinsic reinforcement for the $La_{55}Al_{25}Cu_{10}Ni_{10}$ metallic glass. Ta was selected because it is immiscible with La [17] and is unlikely to readily react with the melt and, thus, leaves its glass-forming ability unchanged. The current BMGCs can show a compressive plastic strain of ~40%, with only a marginal (<10%) reduction in the yield strength. The combination of properties achieved seems better than any known La-based glassy material and, surprisingly, is even superior to some Zr-based glassy composites.

2. Results and Discussion

Figure 1a is an SEM image of the rounded Ta powder particles used as reinforcement. Figure 1b shows the microstructure of the composite specimens—the Ta particles retain their shape, suggesting they do not dissolve/extensively react with the molten alloy and are uniformly distributed in the $La_{55}Al_{25}Cu_{10}Ni_{10}$ glassy matrix. Figure 1c also shows that no interfacial reaction is detectable, at least by SEM and EDX. Figure 2a shows the corresponding XRD pattern that consists of Ta peaks superimposed on an amorphous halo; no additional crystalline phases are detectable, indicating that Ta particles do not trigger devitrification of the glass. The differential scanning calorimetry (DSC) traces (Figure 2b) for the glass and the composite are not significantly different.

Figure 3a shows the compressive stress-strain curves for the monolithic glass and the composite samples. The glass fails upon reaching its yield strength of about 780 MPa, with little plastic strain, but the composite sample shows a significant failure strain of about 40%, while maintaining a yield strength of 720 MPa. To our knowledge, such large plasticity has previously not been reported in any La-based glassy composite. Figure 3b shows that the composite specimens fail through shear on a plane ~45° to the loading axis, unlike the monolithic glass that fails by breaking into many pieces. The sides of the compressive specimens show that the large plasticity is a result of multiple shear band formation in the material (Figure 3c), induced by the ductile Ta particles.

Figure 1. (**a**) SEM image showing the morphology of Ta particles. (**b**) SEM backscattered electron image showing a uniform dispersion of Ta particles in a $La_{55}Al_{25}Cu_{10}Ni_{10}$ glassy matrix. (**c**) A higher magnification image showing the interface between Ta and the glassy matrix, which seems to be devoid of reaction products.



(**c**)

Figure 2. (**a**) XRD data showing Ta peaks superimposed on the amorphous pattern. (**b**) Differential scanning calorimetry (DSC) traces from $La_{55}Al_{25}Cu_{10}Ni_{10}$ and its composite containing 20 vol. % Ta particles.

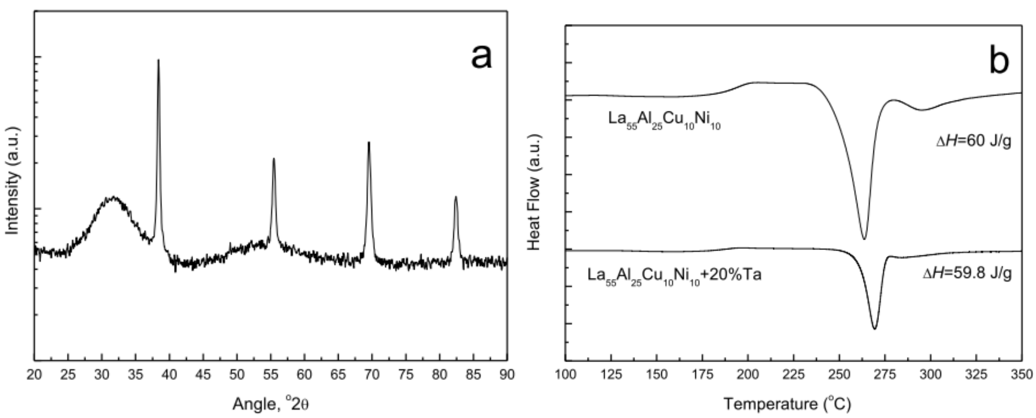
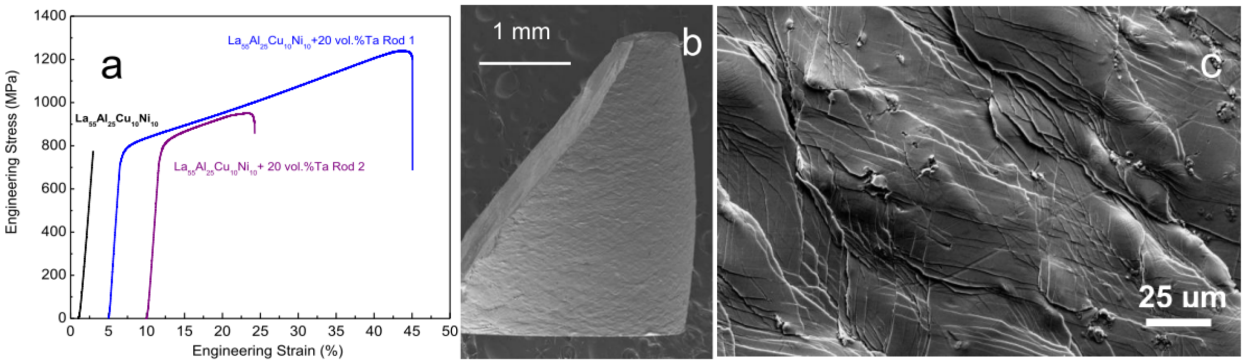


Figure 3. (**a**) Compressive stress-strain curves for the monolithic $La_{55}Al_{25}Cu_{10}Ni_{10}$ bulk metallic glasses (BMG) and the Ta-reinforced glassy composite, showing the enormous increase in plasticity. (**b**) Shear failure in the composite specimen. (**c**) Shear band proliferation is seen on the sides of the compressive specimens.



However, some samples can show lower plastic strain, exemplified by data for rod 2 in Figure 3a. For both rods, XRD reveals no obvious differences, such as the formation of brittle intermetallic compounds that may compromise plasticity. The interface between Ta and the glassy matrix also seems free from obvious intermetallics for both the rods (Figure 1c). But, the micrographs of the two rods show subtle differences, as seen in Figure 4a,b. Three phases are visible in the optical micrographs—the glassy matrix, Ta particles and black particles that are La oxides (verified by EDX analysis)—and it is evident that rod 2 has a higher fraction of these oxides, compared to rod 1 specimens. Image analysis also reveals that the volume fraction of oxides in rod 1 is 1.9% ± 0.3%, while for rod 2, it is 5.1% ± 0.5%. Most of the other rods studied have shown an oxide content similar to rod 1. The deleterious effect of oxygen on plasticity and toughness has been reported for a variety of other glasses, like those based on Zr-, Cu- and even La-based systems [18–21]. In these, the oxygen-containing phases, being brittle, crack readily and, thus, drastically reduce the toughness of these materials. Presumably, oxides act similarly in the current composites, thus accounting for the lower plastic strain for rod 2. The extreme reactivity of La-based alloys makes it difficult to avoid oxides completely.

Although the idea of enhancing plastic strain by introducing ductile crystalline phases in a glassy matrix is known, the large increase in plasticity for the present La-based glass is remarkable and warrants a comparison of the properties achieved with those reported for other BMG matrix composites. Figure 5 is a chart showing strength *versus* compressive failure strain for various BMG composites and monolithic glasses. Two classes of composites are represented, those based on intrinsically tougher and stronger glasses, like Cu- and Zr-based, and those based on glassy matrices that are less strong and tough, *i.e.*, Mg- and La-based. Both *in situ* and *ex situ* composites are included. The highest strength and plastic strain (up to 34%) are seen for the Ta-reinforced, Zr [7] and Cu-based *in situ* composites [8,9]. The Zr-Ti-Cu-Ni-Be β-phase composites [5,6], however, show only a modest compressive plasticity of about 8%. Interestingly, the Zr-based *ex situ* composites utilizing particulates of Ta, Mo, Nb or steel wires show a rather low strength, as well as plastic strain [3,4]. The low strength is evidently due to the high volume fraction of the softer reinforcement.

Figure 4. Optical micrographs of ($La_{55}Al_{25}Cu_{10}Ni_{10}$)-Ta composites from (**a**) rod 1 and (**b**) rod 2. The black particles are La oxides, and they are more numerous in rod 2 specimens.

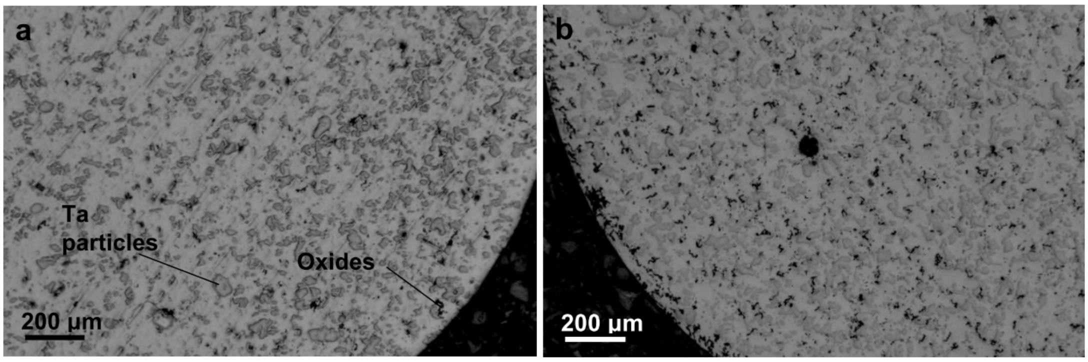
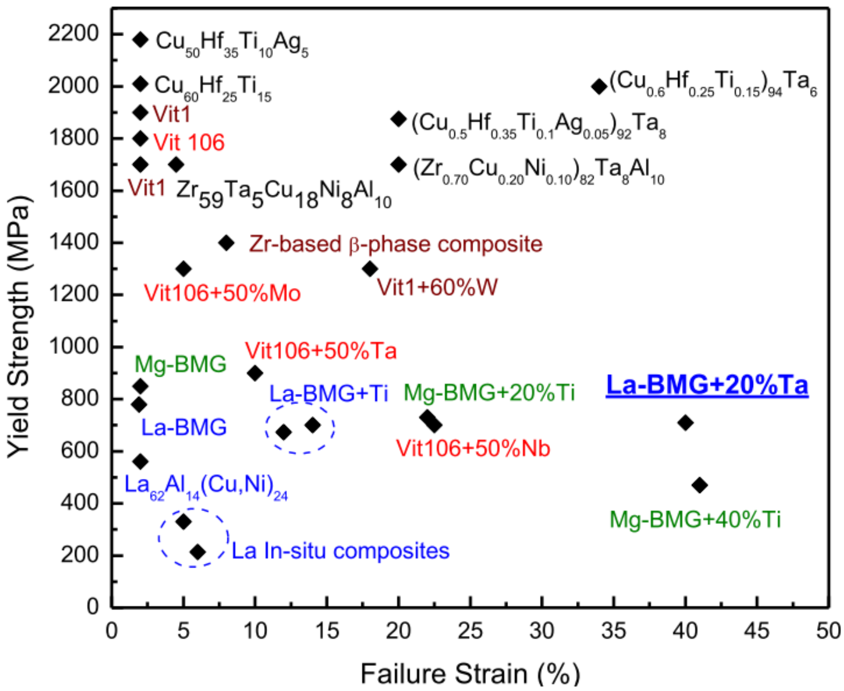


Figure 5. A chart comparing the yield strength and failure strain of various BMG composites. The compositions and the references wherefrom the data are taken are as follows—Vit1: $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ [4]; Vit106: $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$ [3]; β-phase composite: $Zr_{56.2}Ti_{13.8}$ $Nb_{5.0}Cu_{6.9}Ni_{5.6}Be_{12.5}$ [5,6]; $Cu_{50}Hf_{35}Ti_{10}Ag_5$ [9]; $(Cu_{0.6}Hf_{0.25}Ti_{0.15})_{94}Ta_6$ [8]; $(Cu_{0.5}Hf_{0.35}Ti_{0.1}Ag_{0.05})_{92}Ta_8$ [9]; $(Zr_{0.7}Cu_{0.2}Ni_{0.1})_{82}Ta_8Al_{10}$ [7]. La-BMG: $La_{55}Al_{25}Cu_{10}Ni_{10}$; Mg-BMG: $Mg_{65}Cu_{25}Gd_{10}$ [11]. In general, the *in situ* composites show toughening, but with a large reduction in strength. The current composite, La-BMG + 20% Ta appears to possess the best combination of strength and plasticity among all La-based composites and even surpasses some of the Vit106-based *ex situ* composites.



In contrast, the La-based BMGs are weaker, as well as less tough, but still, their composites can show significant plasticity. Previous work on La-based materials has focused on *in situ* composites [12–15] and Ti-reinforced *ex situ* composites [16]. The *in situ* composites have a high volume fraction of La dendrites (~50%), and although they show some plastic strain (5%–6%), it is accompanied by a significantly reduced strength. The La-based *ex situ* composites utilizing 150 µm-sized Ti spheres [16] show a much better combination of strength and plasticity, although the failure strain is still limited to ~15%. The current Ta-reinforced alloys, however, show properties better than previously reported La- or Mg-based glassy materials. The Mg-based BMG reinforced with 40% Ti [11] does exhibit a high strain, but has a much lower strength. Interestingly, the present La-based glassy composites have both a higher strength, as well as plasticity, than even certain Zr-based *ex situ* composites, e.g., Vit 106 reinforced with 50% Nb or 50% Ta [3]. Considering the lower strength and toughness of La-based glasses, these properties are noteworthy, especially for a relatively low volume fraction of reinforcement used (20%). Further work in this area may focus on optimizing the Ta particle size and volume fraction to achieve large tensile ductility, as well as yield strength. The nature of the glass-crystal interface is also expected to be important in controlling plasticity and could be one reason why the present composites are tougher compared to the Ti-reinforced, La-based glass reported earlier [16]. Detailed transmission electron microscopy (TEM) studies are in progress to investigate the interface in La-based composites, e.g., to see whether a thin nanometer-scale reacted layer forms, which controls mechanical behavior.

3. Experimental Section

$La_{55}Al_{25}Cu_{10}Ni_{10}$ ingots were prepared by arc-melting under a high purity Ar atmosphere. Composites were prepared by induction melting the ingot with the appropriate amount of Ta powder (–325 mesh) in a BN crucible. In order to avoid reaction between Ta and the molten alloy, care was taken to keep the temperature below 700 °C. Pieces of the composite ingot were remelted and injection-cast into a copper mould to obtain 3 mm rods. X-ray diffraction (XRD) measurements were carried out using CuKα radiation. The crystallization of the glassy alloys was studied using a Perkin Elmer DSC at a heating rate of 20 °C/min. Samples for compression testing were cut from the rods and polished in a jig designed to ensure that the ends of the samples were parallel to each other and orthogonal to the specimen axis. The compression tests were performed on samples with a 2:1 aspect ratio at an engineering strain rate of 5×10^{-4} s^{-1}. The fracture surfaces were examined with a Hitachi S4300 high-resolution scanning electron microscope, and compositional analysis was performed using energy-dispersive X-ray (EDX) analysis. The Clemex Vision PE image analysis software was used for estimating the volume fraction of oxide particles from polished specimens of the as-cast rods.

4. Conclusions

In summary, the $La_{55}Al_{25}Cu_{10}Ni_{10}$ glass has been reinforced with 325 mesh Ta particles, and the composites show a combination of high yield strength (720 MPa) and large plasticity (40%) not observed in previous La-based glass-crystal composites. The strength-plasticity combination of these composites can even surpass some of the Zr-based *ex situ* composites. Apparently, however, the plasticity of these La-based composites can be compromised by oxide inclusions, necessitating careful processing of these materials. The large plasticity observed in this work tends to support recent claims that the La-based glasses, though previously believed to be intrinsically brittle, are actually tougher [21], since a truly brittle glassy matrix is not expected to show a high strain, even if reinforced with ductile particles. The authors believe that this composite system is worthy of further scientific study, e.g., fracture toughness measurements, as well as potential applications.

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Conflict of Interest

The authors declare no conflict of interest.

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