Compressive plasticity of a La-based glass-crystal composite at cryogenic temperatures

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Abstract  The La\textsubscript{55}Al\textsubscript{25}Cu\textsubscript{10}Ni\textsubscript{10}–10 vol.% Ti glassy composites have excellent compressive strength and plasticity at room temperature (RT). At cryogenic temperature (77 K), neither the glassy matrix, nor the Ti particles undergo embrittlement, and the composite retains appreciable toughness. Surprisingly, despite significant shear band plasticity at 77 K, failure occurs in a mixed mode manner, with large areas showing quasi-cleavage features that appear to initiate from cracks at the glass-Ti interfaces, which also limit the overall plastic strain. Interface engineering is the key to further alloy development for even better properties.

Keywords: Bulk metallic glass, composites, toughness, cryogenic plasticity.
1. Introduction

Bulk metallic glasses (BMGs) have attractive properties such as high strength, low modulus [1] and have thus been extensively investigated. Toughness of BMGs is of clear practical interest and much effort has been devoted to understanding the factors controlling toughness [2], such as its correlation with elastic properties like Poisson's ratio [3], shear modulus [4, 5] or the critical fictive temperature [6]. Composites based on BMG matrices can show greatly improved toughness and are of interest for potential applications [7, 8]. The testing temperature can significantly affect toughness, which is fundamentally interesting as well as relevant to engineering applications, e.g. spacecraft components [9]. A major part of the work on cryogenic behaviour of BMGs has dealt with systems based on Zr [9-12], Ti [13] or Cu [14], with only a few reports on the less tough glasses such as Ce- [15] or Fe-based [16]. The rare earth based glasses have a lower Poisson's ratio than the Zr- or Cu-based BMGs, and they show correspondingly lower toughness [17]. Even so, the La$_{55}$Al$_{25}$Cu$_{10}$Ni$_{10}$ (at.%) glass, when reinforced with extrinsic particles of Ti or Ta, displays vastly improved compressive plasticity (15-40% strain), while retaining the high yield strength of the monolithic glass [18, 19]. The strength-plasticity combination of these composites is superior to in situ composites utilising La dendrites [20] and may even rival that of some Zr-based glassy composites [19], which is of clear relevance to emerging applications. Prior work on the Zr-based in-situ composites revealed a marked drop in toughness at cryogenic temperatures, attributed to a ductile-brittle transition (DBT) and consequent brittle fracture in the bcc Zr-rich dendrites that are dispersed in the glassy matrix [9-11]. In stark contrast, significant plasticity was still retained at cryogenic temperatures in a Ti-based glassy composite [13]. However, the cryogenic behaviour of La-based glassy composites has not yet been investigated, thus motivating the present study. The La-based glasses sit near a critical Poisson's ratio ($\nu$=0.31-
0.32) that was earlier proposed [3] to mark a transition from plasticity to brittleness. Even though the existence of a critical $v$ is now debated [17, 21-22], it is evident that Poisson's ratio of the glass will reduce at lower temperatures. Toughness of a Ce-based glass deteriorates at cryogenic temperatures [15], but the scenario for La-based glasses is not known. Also, the present La-based composites use $hcp$ Ti (>99.9 wt.% pure) as a reinforcement and a DBT is less likely in these crystals. The cryogenic properties of these otherwise attractive La-based BMG composites are not obvious and thus worthy of investigation.

2. Experimental Procedures

La$_{55}$Al$_{25}$Cu$_{10}$Ni$_{10}$ (at.%) ingots were prepared by arc-melting a mixture of pure elements (>99.9 wt.%) in a purified argon atmosphere. Pieces of the ingot were melted with 10 vol.% of spherical pure Ti powders (–100 mesh) in an induction furnace, while ensuring that the temperature stayed below 700 °C, to minimize dissolution/reaction of the Ti particles with the melt. The stirring during induction melting, together with manual shaking of the crucible were found to be effective in getting a uniform dispersion of Ti particles in the melt. The composite ingots were further melted and injection-cast into 3 mm diameter rods. As mentioned elsewhere [18], the interfaces between Ti particles and the BMG were found to be free of any reaction products, within the resolution of a field emission scanning electron microscope (FEGSEM). Samples with an aspect ratio of 2:1 were cut from the rods, for compression testing at room and liquid nitrogen temperatures. The tests were performed at a strain rate of $5 \times 10^{-4}$ s$^{-1}$ on a Shimadzu universal testing machine, equipped with a fixture for compressing samples in a liquid nitrogen container. The fractured specimens were examined in a Hitachi FEGSEM. Elastic constants are known to affect toughness, yet shear and bulk moduli for this exact composition are unavailable in the literature. Hence, the room
temperature moduli for the alloy were calculated from the elemental values using the approach given by Zhang and Greer [23]. These are found to be very close to data for very similar compositions and also, the experimentally measured Young's modulus provides a validation of the calculations. The variation in elastic constants with temperature was estimated from the room temperature data using equation (1) given by Zhang et al. [24], which is based on the Varshni relations [25].

\[
C(T) = C(T_R) + \frac{s}{e^{\theta_D/T_R} - 1} - \frac{s}{e^{\theta_D/T} - 1}
\]

where \( C(T) \) is the elastic constant at temperature \( T \), \( T_R \) is room temperature (293 K), \( s \) is a fitting parameter and \( \theta_D \) is the Debye temperature. The Debye temperature can be calculated from the alloy density and room temperature elastic constants, as stated in [24]. All relevant data are summarized in table I.

3. Results and Discussion

**Figure 1a** shows the compressive stress-strain data for the monolithic glass, at RT and 77 K. As expected, the yield strength increases, from 780 MPa to ~1000 Pa and the Young's modulus (\( E \)) changes, from 42 GPa to 48.8 GPa. Figure 1a shows that the plastic strain is zero at RT, typical of most La-based BMGs, which is because failure occurs through a mixture of crack propagation on a single shear band, combined with brittle fracture, which can originate from defects like oxide inclusions in the alloy [17]. In fact, many BMGs often show very limited plastic strain, although they can possess reasonable fracture toughness, because of localized deformation on a single shear band. The plastic strain at 77 K can increase up to 1% for some samples (Fig. 1a). **Figure 1b** shows a magnified view of the plastic part of the stress-strain curve for samples tested at 77 K – no serrations can be seen and neither are multiple shear bands visible on the sides of the compression specimens (not
shown here). This suggests that the small plastic strain is a result of retarded sliding on a single shear band [26, 27], in contrast to multiple shear banding seen in other BMGs, e.g. Cu$_{57}$Zr$_{43}$ [14]. Figure 2 shows the estimated change in elastic moduli and v with temperature. The v slightly reduces from 0.342 at RT to 0.336 at 77 K. To validate the use of the Varshni equation, we have estimated the shear ($G$) and bulk ($B$) moduli from the experimentally measured Young's moduli ($E$) in Fig. 1a and the Poisson's ratio ($v$) in figure 2c. For this purpose, the following relations were used:

$$G = \frac{E}{2(1+v)}$$

and

$$B = \frac{E}{3(1-2v)}$$

The estimated shear and bulk moduli are shown as diamonds on the plots in Figs. 2a and 2b – the experimental values are close to the predictions shown by the red lines. We believe the small difference should not affect the essential arguments in this work.

Figure 3 shows secondary electron images of the fractured specimens. The specimens typically break into many pieces, and show dual fracture modes, labelled as areas I and II in Figure 3a. Area I corresponds to shear failure, evidenced by the vein patterns on the fracture surface (Fig. 3b). Area II shows nanoscale features, associated with quasi-cleavage fracture, often initiating at the oxide particles in these reactive alloys, as discussed elsewhere [17]. When tested under liquid nitrogen, the fracture behaviour is very similar, with dual fracture modes. Fig. 3c shows the scale of vein patterns for a specimen tested at 77 K, which is almost unchanged, at ~20 µm. The mode II fracture toughness ($K_{IIc}$) is estimated from the
scale \((w)\) of vein patterns using equation (4), following reference [29]. The fracture energy \((G)\) is calculated using equation (5)

\[
w = 0.025 \left( \frac{K_{IIc}}{\sigma_y} \right)^2 \tag{4}
\]

\[
G = \frac{K_{IIc}^2}{E} (1 - \nu^2) \tag{5}
\]

Interestingly, \(K_{IIc}\) increases from 22 MPa.m\(^{1/2}\) at RT to 28.2 MPa.m\(^{1/2}\) at 77 K. Likewise, \(G\) shows a modest increase from 10.2 kJ/m\(^2\) to 14.3 kJ/m\(^2\). The key point is that unlike another rare earth-based glass (Ce\(_{68}\)Al\(_{10}\)Cu\(_{20}\)Co\(_2\)) [15], the La-based glass does not become brittle at 77 K (in fact, toughness increases), despite a relatively low Poisson's ratio. Toughening at cryogenic temperatures was also noted by Yoon \textit{et al.} [14] for a Cu-Zr glass and was attributed to the generation of extra free volume (rejuvenation) upon elastic loading at low temperatures. It is known that BMG toughness increases with the shear transformation zone (STZ) size [30], which in turn increases with the free volume fraction [31]. Hence, the extent of free volume generation in the current La-based glass can be a topic for further investigation. Structural rejuvenation is also reported to occur by thermal cycling from RT to 77 K, leading to higher plasticity [32]. The present glass will be of interest for plasticity enhancement through thermal cycling.

The behaviour of the La\(_{55}\)Al\(_{25}\)Cu\(_{10}\)Ni\(_{10}\)\(\sim 10\) vol.\% Ti composites will now be discussed. Figure 4a shows their typical microstructure, consisting of spherical Ti particles dispersed in a glassy matrix. Figure 4b shows the stress-strain curves at RT and 77 K. The strength increases from 800 MPa to 1000 MPa, with a reduction in plastic strain from 9\% to 4\%; the total strain energy at fracture (area under the curve) reduces from 76.7 MJ/m\(^3\) at RT to 51 MJ/m\(^3\) at 77 K. Thus, the composite still maintains significant toughness at liquid nitrogen
temperature, unlike the drastic embrittlement noted by Qiao et al. [11] for the β-phase reinforced in situ Zr-based glassy composites. Moreover, the fracture mechanisms in the present alloy are quite different from the previous literature. Figure 5a shows the SEM images of fractured specimens. At RT, the composites fail in the expected manner along a single shear band at ~45° to the loading axis, and the fracture surface shows vein patterns (not shown). At 77 K, however, the specimens fail by breaking into many pieces, with a small fraction of the fracture surface showing shear failure and the rest, brittle (quasi-cleavage) failure, akin to the monolithic glass. Figure 5b shows an example of a fragment, where areas I and II correspond to shear and brittle fracture respectively. This is unexpected, because of the significant plasticity preceding fracture. Indeed, the sides of the specimens show multiple shear offsets (Fig. 5c), reflecting the plastic deformation that has occurred in the specimens. Figure 5d shows area I in greater detail – the failure is ductile, with vein patterns and Ti particles that have undergone microvoid coalescence. Figure 5e shows area II, typical of brittle fracture (although not magnified here, the surface has sub-micron features, like Fig. 3c for the unreinforced glass). Importantly, the Ti particles are not fractured. So, in contrast to previous reports [9-11], it is not a case of the Ti particles undergoing cleavage fracture at low temperatures that triggers failure of the BMG composite. Rather, the BMG-Ti interface opens up and it appears that the cracked interfaces serve as sites for the initiation of brittle fracture in the composite. One such site showing conchoidal features is marked by an arrow in Fig. 5e – concentric rings reflecting brittle fracture in the BMG [33], originate from the cracked interface between Ti and the glassy matrix. Fig. 5f shows another initiation site (arrowed) and also reveals that some Ti particles fall off during fracture. When tested at RT (not shown here), all the Ti particles undergo ductile fracture, as in Fig. 5d. These findings suggest that beyond a certain strain (6%, Fig. 4b) at 77 K, the Ti particles are unable to deform along with the glassy matrix, i.e. there seems to be a strain incompatibility that causes
cracking at the interfaces, leading to relatively early failure of the composite. So, although the composite shows significant plastic strain, the fracture behaviour is similar to the unreinforced glass, with many areas failing in a brittle manner. This combination of plasticity followed by mixed mode fracture in the same material is not commonly seen for glass-crystal composites, where eventual fracture is instead fully ductile, occurring on a single shear band. It may be noted that in monolithic La-based glasses, brittle fracture was shown to occur due to the presence of oxide inclusions (which act as pre-existing cracks) in the glassy matrix [17] and the glass is otherwise capable of shear fracture. Similarly, oxygen-containing phases in a Cu-Hf-Al BMG were shown to trigger brittle fracture in an intrinsically tough material [28]. In the present composites, the cracked interfaces essentially have an embrittling effect similar to the oxides in the monolithic glass. Hence, further work on La-based ex situ composites may be directed towards finding suitable reinforcements that will more easily deform at cryogenic temperatures. Then, even better combinations of strength and plasticity may well be obtained at low temperatures. Potential reinforcements may include fcc metals (as they remain deformable at very low temperatures), or possibly Ta, which, although bcc, confers large cryogenic plasticity to some Zr-based glassy composites [34].

4. Conclusions

Compressive stress-strain behaviour of La\textsubscript{55}Al\textsubscript{25}Cu\textsubscript{10}Ni\textsubscript{10}−10 vol.% Ti ex situ glassy composites has been investigated and the main findings are:

1. At 77 K, the glassy matrix shows a minor reduction (from 0.342 to 0.336) in Poisson's ratio and yet its fracture toughness shows a modest increase, from 22 MPa.m\textsuperscript{1/2} to 28.2 MPa.m\textsuperscript{1/2}. This is likely due to increased generation of free volume upon loading at low temperatures, and is a topic for further work.
2. Unlike some Zr-based in situ composites, the reinforcing Ti particles themselves do not show brittle fracture at 77 K, although it is likely that their deformability reduces.

3. The composite exhibits legitimate plasticity, i.e. multiple shear banding at 77 K, with a failure strain of ~6%. Yet, surprisingly, failure occurs through mixed mode fracture – some areas show shear fracture, but most show quasi-cleavage features, triggered by cracking at the glass-Ti interfaces beyond a critical strain. Hence, further alloy development for an enhanced strength-plasticity combination may focus on identifying suitable (softer) reinforcements, where the interface can support a larger plastic strain.

**References**


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Table I Relevant data for the La$_{55}$Al$_{25}$Cu$_{10}$Ni$_{10}$ (at.%), bulk glass – the average melting temperature ($T_m$), density ($\rho$), shear modulus ($G$), bulk modulus ($B$), Debye temperature ($\theta_D$) and the Varshni parameters $s_G$ and $s_B$.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_m$ (K)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$G$ (GPa)</th>
<th>$B$ (GPa)</th>
<th>$\theta_D$ (K)</th>
<th>$s_G$ (GPa)</th>
<th>$s_B$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{55}$Al$</em>{25}$Cu$<em>{10}$Ni$</em>{10}$</td>
<td>1198.09</td>
<td>5.822</td>
<td>15.25</td>
<td>43.42</td>
<td>179.98</td>
<td>1.217</td>
<td>1.616</td>
</tr>
</tbody>
</table>
Figure 1  (a) Compressive stress-strain curves for the monolithic La$_{55}$Al$_{25}$Cu$_{10}$Ni$_{10}$ glass at RT and 77 K. (b) A magnified view of the plastic portion of the stress-strain curve at 77 K in (a), showing a lack of serrations.
Figure 2  Predicted data for the La$_{55}$Al$_{25}$Cu$_{10}$Ni$_{10}$ glass showing variation in (a) shear modulus \((B)\); (b) bulk modulus \((G)\) and (c) Poisson’s ratio \((\nu)\) with temperature. The superimposed diamonds in figures (a) and (b) represent the moduli calculated using Poisson’s ratio and the experimentally measured Young’s modulus in Fig. 1a.
Figure 3  SEM fractographs of monolithic La$_{55}$Al$_{35}$Cu$_{10}$Ni$_{10}$. (a) Fractured pieces typically exhibit two regions, I and II corresponding to shear and quasi-cleavage fracture. (b) Shear band vein patterns characterizing region I. (c) Sub-micron fracture surface features in region II, which indicate quasi-cleavage fracture. (d) An example of vein patterns also seen in specimens fractured at 77 K. Their scale is almost unchanged.
Figure 4  (a) An optical micrograph showing a typical microstructure of the Ti-reinforced composite. (b) Stress-strain data for the glass reinforced with 10 vol.% Ti particles, showing increased yield strength and reduced plastic strain.
Figure 5  SEM fractographs of La$_{55}$Al$_{25}$Cu$_{10}$Ni$_{10}$–10 vol.% Ti composite.  (a)  Shear fracture in the sample tested at room temperature.  (b)  At 77 K, the material breaks into many pieces, with some areas undergoing shear failure (marked I) but most failing through quasi-cleavage (II).  (c)  The sides of the specimen show multiple shear offsets, reflecting plastic deformation in the composite.  (d)  Area I shows vein patterns in the glassy matrix and the Ti particles fail in a ductile manner.  (e)  Area II shows typical features of brittle fracture, which seems to have originated at the cracked interfaces between Ti and the glassy matrix, indicated by the arrow.  (f)  Another initiation site, and regions where the Ti particles have completely debonded from the matrix.