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

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ABSTRACT

The $La_{55}Al_{25}Cu_{10}Ni_{10}$–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.

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 ν 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 was found to be effective

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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 Eq. (1) given by Zhang et al. [24], which is based on the Varshni relations [25].

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

where $C(T)$ is the elastic constant at temperature T, T_R is room temperature (293 K), s is a fitting parameter and θ_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 1.

3. Results and discussion

Fig. 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. Fig. 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). Fig. 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]. Fig. 2 shows the estimated change in elastic moduli and ν with temperature. The ν 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 (ν) in Fig. 2c. For this purpose, the following relations were used:

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

Table 1
Relevant data for the $La_{55}Al_{25}Cu_{10}Ni_{10}$ (at.%), bulk glass — the average melting temperature (T_m), density (ρ), shear modulus (G), bulk modulus (B), Debye temperature (θ_D) and the Varshni parameters s_G and s_B.

Alloy	T_m (K)	ρ (g/cm^3)	G (GPa)	B (GPa)	θ_D (K)	s_G (GPa)	s_B (GPa)
$La_{55}Al_{25}Cu_{10}Ni_{10}$	1198.09	5.822	15.25	43.42	179.98	1.217	1.616

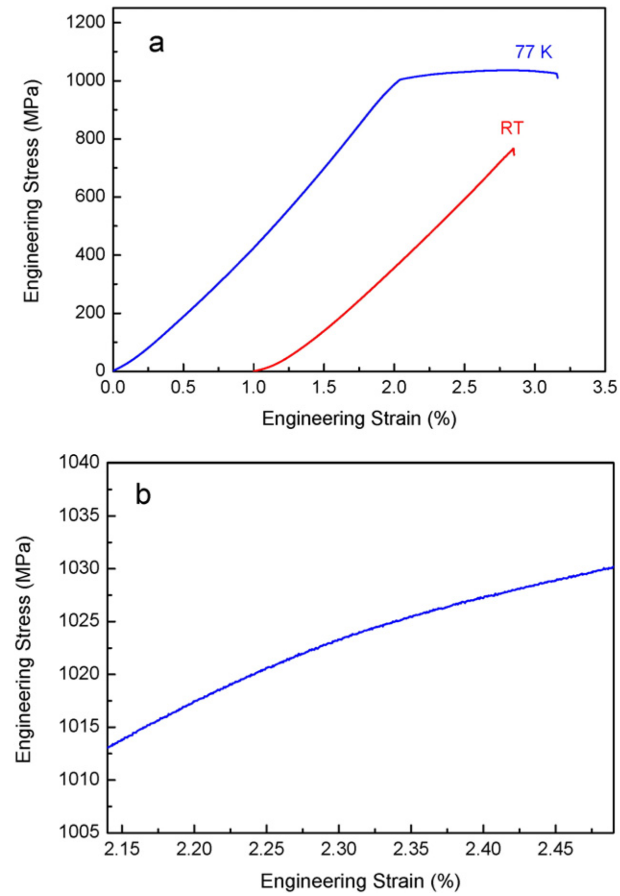

Fig. 1. (a) Compressive stress–strain curves for the monolithic $La_{55}Al_{25}Cu_{10}Ni_{10}$ glass at RT and 77 K. (b) A magnified view of the plastic portion of the stress–strain curve at 77 K in (a), showing a lack of serrations.

and

$$B = \frac{E}{3(1-2\nu)}. \tag{3}$$

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

Fig. 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 Fig. 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 Eq. (4), following reference [29]. The fracture energy (G) is calculated using Eq. (5):

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

$$G = \frac{K^2_{IIc}}{E}(1-\nu^2). \tag{5}$$