

Mechanical properties of La-based bulk amorphous alloy and composites

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Abstract

Influence of different microstructure of La-based fully amorphous samples and its composites on the impact fracture energy were investigated and discussed. Results showed improvement in fracture energy of glassy metals with the presence intermetallic phases, but deteriorated in the presence of dendrite phases and high volume % of crystalline phases.

1. Introduction

Some bulk metallic glasses exhibit high yield strength of up to 2GPa and yield strain limits of 2% but are accompanied by remarkably limited plastic deformation compared to polycrystalline metallic materials with similar compositions. Metallic glasses failed by highly localized shear flow [1]. Although the local plastic strain in a shear band is quite large, the overall strain is determined by the number of shear bands. Loaded in a state of uniaxial or plane stress, metallic glasses fail on one dominant shear band and show little overall plasticity, which makes the stress-strain curve appear similar to that of a brittle material. Under constrained geometries (e.g. plane strain), BMGs fail in an elastic, perfectly plastic manner by the generation of multiple shear bands. Multiple shear bands are observed when the plastic instability is constrained mechanically, for example in uniaxial compression, bending, rolling, and under localized indentation. This quasi-brittle deformation behavior limits the application of bulk metallic glasses as an engineering material.

The preparation of bulk metallic glass matrix composites with ductile metal or refractory ceramic particles as reinforcements has been used to improve the mechanical properties, especially toughness [2, 3]. It was proposed that the increase in toughness results from the particles restricting shear bands propagation and promoting the generation of multiple shear bands. This proposition suggests the possibility of producing an entirely new class of materials which

combine the high strength of metallic glass with large plastic deformations under confined loading conditions.

Thus the improvement of metallic glass matrix composites may involve adjusting the volume fraction and types of crystalline phases acceptable in the amorphous matrix without being detrimental to the mechanical performance and the deformation mechanisms controlling the composite's properties.

In this paper, four compositions of La-based bulk metallic glasses are presented. The monolithic amorphous $\text{La}_{62.42}\text{Al}_{15.89}\text{Cu}_{11.35}\text{Ni}_{11.35}$ (LA), dendrite-reinforced amorphous $\text{La}_{66}\text{Al}_{14}\text{Cu}_{10}\text{Ni}_{10}$ (LD1), intermetallic-reinforced amorphous $\text{La}_{57.60}\text{Al}_{17.46}\text{Cu}_{12.47}\text{Ni}_{12.47}$ (LI1) and nearly fully crystalline $\text{La}_{52.96}\text{Al}_{19.37}\text{Cu}_{13.84}\text{Ni}_{13.84}$ (LC) alloys were chosen as model in-situ composites. Their fracture behaviors under impact testing due to the different microstructures are investigated.

2. Experimental Procedure

The ingots were prepared by arc-melting a mixture of La (99.9%), Al (99.9%), Ni (99.98%) and Cu (99.999%) in a Ti-gettered argon atmosphere. The BMG alloy and its composites were prepared by remelting the master ingots at a temperature of 973K in an argon atmosphere and casted into copper mould with a 5mm diameter cavity.

Cross sections of the rods were examined by X-ray diffraction. The glass transition and crystallization of all the samples were studied with a differential scanning calorimeter at a heating rate of 40K/min. Analysis of as-cast microstructures and fracture surfaces were characterized by scanning electron microscopy (SEM).

Non-standard sized Charpy specimens with dimensions 60mm in height and 5mm in diameter were prepared and notched (notch depth of 0.5mm) with a low speed diamond saw. The Charpy impact tests were carried out with a tabletop, instrumented Charpy test machine. The drop hammer of the impact machine was calibrated to impact energy of 0.0585J at a velocity of 1.911m/s and the resulting impact fracture energy of the specimens were recorded.

3. Results and discussions

3.1 Materials Characterization

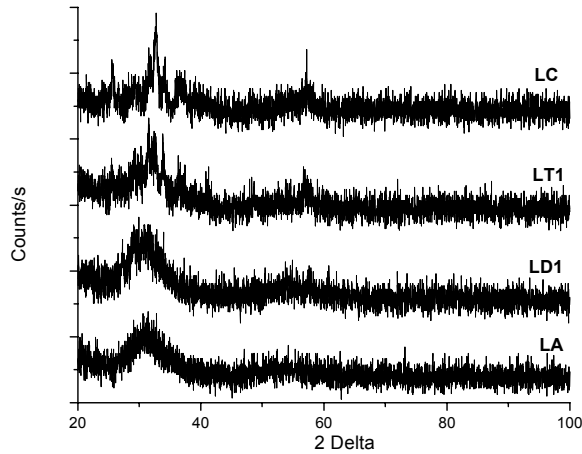


Figure 1: XRD scan of as-cast La-based bulk amorphous alloy and composites.

In Figure 1, the X-ray diffraction patterns of the monolithic amorphous alloy and composites were compared. Samples LA were fully amorphous and are verified by the absence of peaks in Fig.1. Some distinct peaks corresponding to crystalline phases can be seen for the diffraction pattern of the LD1 composite. Higher intensity of crystalline peaks can be observed when the LI1 and LC samples were scanned. The corresponding microstructures of the samples are shown in Figure 2. While the polished and etched microstructure of the LA sample was featureless, the in-situ composite LD1 microstructure revealed a presence of hcp α -La dendritic phases in a

glassy matrix. Intermetallic phases in glassy matrix were revealed for LI1 composites and an almost fully crystalline structure for LC. Table 1 summarizes these findings.

Table 1: Phase analysis by XRD

Sample	Composition	Phases
LA	$\text{La}_{62.42}\text{Al}_{15.89}\text{Cu}_{11.35}\text{Ni}_{11.35}$	BMG
LD1	$\text{La}_{66}\text{Al}_{14}\text{Cu}_{10}\text{Ni}_{10}$	BMG + hcp α -La
LI1	$\text{La}_{57.60}\text{Al}_{17.46}\text{Cu}_{12.47}\text{Ni}_{12.47}$	BMG + intermetallics
LC	$\text{La}_{52.96}\text{Al}_{19.37}\text{Cu}_{13.84}\text{Ni}_{13.84}$	Almost fully crystalline

3.2 Mechanical Properties

Charpy impact testing was carried out on these samples and their impact fracture energies are summarized in Table 2.

Average impact fracture energy, γ of 0.395J was obtained for the monolithic bulk metallic glass. The presence of hcp α -La dendrites in the glassy matrix reduced the fracture energy by 13% to 0.342J. However, introduction of intermetallics into the amorphous matrix improved the impact fracture energy by 11% to 0.440J but further crystallization leads to reduction of γ to 0.118J (70%). Thus, there is a crystallization fraction that maximizes toughness.

Macroscopic observations of the fracture surfaces reveal two distinct regimes of fracture in the specimens as shown in Fig 3. The material in the fully amorphous state (Fig.3a) shows a very jagged fracture surface. The surface roughness was very high near the notch root and decreases progressively away from the notch. The fractograph of the composite LD1 with dendritic phases, (Fig. 3b) appeared to be less jagged. However the composite LI1 with intermetallic phases, (Fig 3c) showed similar roughness to that of the amorphous alloy. Further increases in crystallinity (Fig 3d) leads to a quasi-cleavage appearance of the fracture surface.

SEM examination of the jagged fractured surfaces for the fully amorphous metal (Fig. 4a) showed vein-like fracture typically observed in tensile fracture of bulk metallic glass. It was also observed that the veins are much deeper in the very jagged surfaces near the notch root, similar to the ductile mode of failure observed in many metals [4, 5]. The depth of the veins became shallower with distance from the notch root [Figs 4b]. With the presence of a dendritic crystalline phase such as in the case of the LD1,

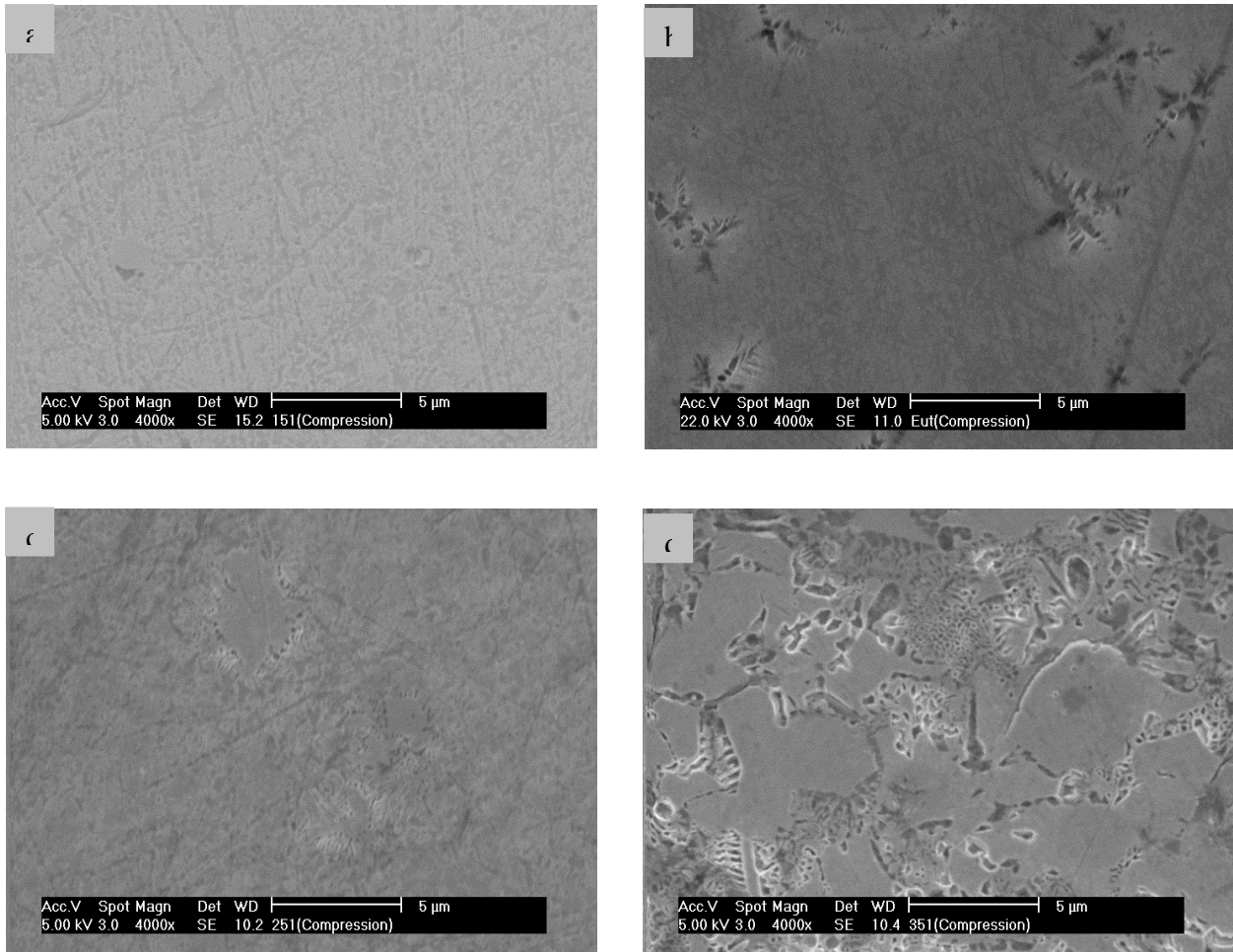


Figure 2: SEM images of amorphous and in-situ composite microstructures; (a) LA, (b) LD1, (c) LI1 and (d) LC alloys.

the veins tended to become shallower at the notch root and very often both shallow and deeper veins could be observed (Fig 4c). However, introduction of intermetallic phases into a glassy matrix, as in the case of LI1, the depth of the vein pattern is similar to those observed in the fully amorphous sample (Fig 4d). In the nearly fully crystalline material LC (Fig. 4e), the fracture was significantly more brittle in appearance.

3.3 Fracture Mechanism

The deformation mechanisms of amorphous metals were suggested to depend on the relative temperature (with respect to T_g), the rate of deformation, and the applied stress [6]. At low stresses (<0.01 times the yield strength) and high temperature ($\sim T_g$), homogenous flow occurs and can be characterized as Newtonian viscous flow. Homogenous flow, in which each volume element of the material

contributes to the strain, is the result of uniform deformation for a uniformly stressed specimen. Under high stresses, low temperature ($T < 0.7T_g$) or high strain rates, inhomogenous flow is observed. Inhomogenous flow occurs by deformation localized into discrete, thin shear bands, and leaves the rest of the material undeformed. The fracture process that terminates the flow is considered “ductile” as it occurs along a shear band (not normal to the tensile axis) and forms a very characteristic ‘vein’ or ‘river’ morphology on the fracture surface that involves extensive plastic flow. The density of the shear bands dictates the overall plastic strain accommodated by the metallic glass.

In metallic glasses, because of the viscous nature of the glass, a strong dependence between impact fracture energy and the imposed rate of deformation can be anticipated. Under high rates of deformation,

Table 2: Summary of impact testing results and observations

Sample	LA	LD1	LI1	LC
Microstructure	Amorphous	Dendrites	Intermetallics	Crystalline
γ , Impact fracture energy (J)	0.395	0.342	0.440	0.118
Observation	Spark	Spark	Spark	No spark

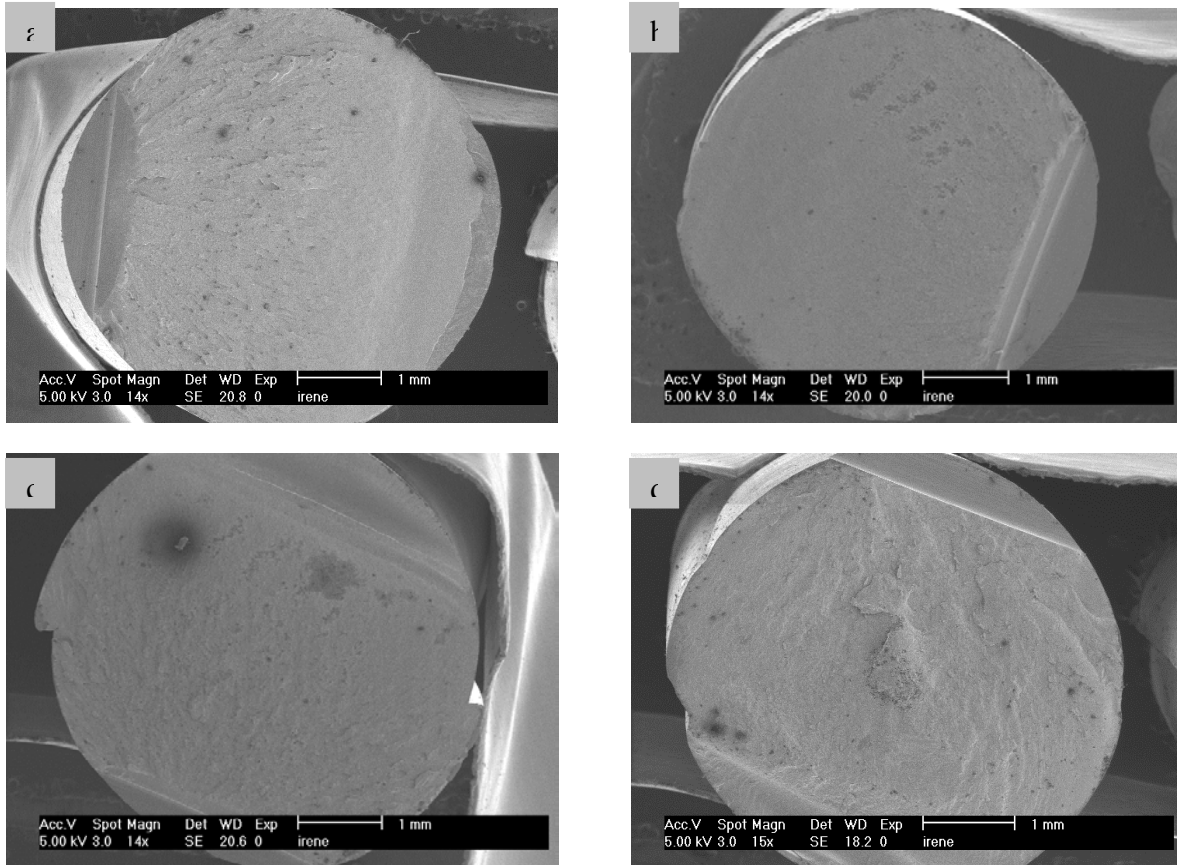


Figure 3: Macroscopic images of fracture surfaces of (a) LA, (b) LD1, (c) LI1 and (d) LC alloys.

localized melting associated with inhomogenous flow occurs during catastrophic fracture and often with the emission of bright sparks [7]. In the current work, except for the almost crystalline samples, visible bright sparks were emitted upon fracture, due to the generation of intense heat during plastic work. Evidence of localized melting phenomenon was also found on the fractographic surfaces when observed under SEM.

The high strain rate from impact loading and the high stress intensity at the notch root should promote localized shear band deformation. Farther away from the notch root, the stresses and the rates are much lower allowing for homogenous deformation. This conclusion is from the observation of vein patterns (a result of the localized flow of glass within narrow

bands) which are significantly deeper near than away from the notch root in the fully amorphous alloys. With the presence of crystalline phases, the veins become much shallower at the notch root, indicating less propensity for shear band formation. The marked decrease in toughness of the dendrite amorphous matrix composites suggests that crystallization decreases the propensity for shear band formation. This may be due to the solute redistribution during crystal growth that possibly increases the melting temperature of the diffusion zone and the amorphous matrix [8]. Because increasing melting temperature generally leads to higher viscosity, the average viscosity of the residual amorphous matrix can be assumed to increase with increasing crystallinity. This increase in viscosity leads to a suppression of

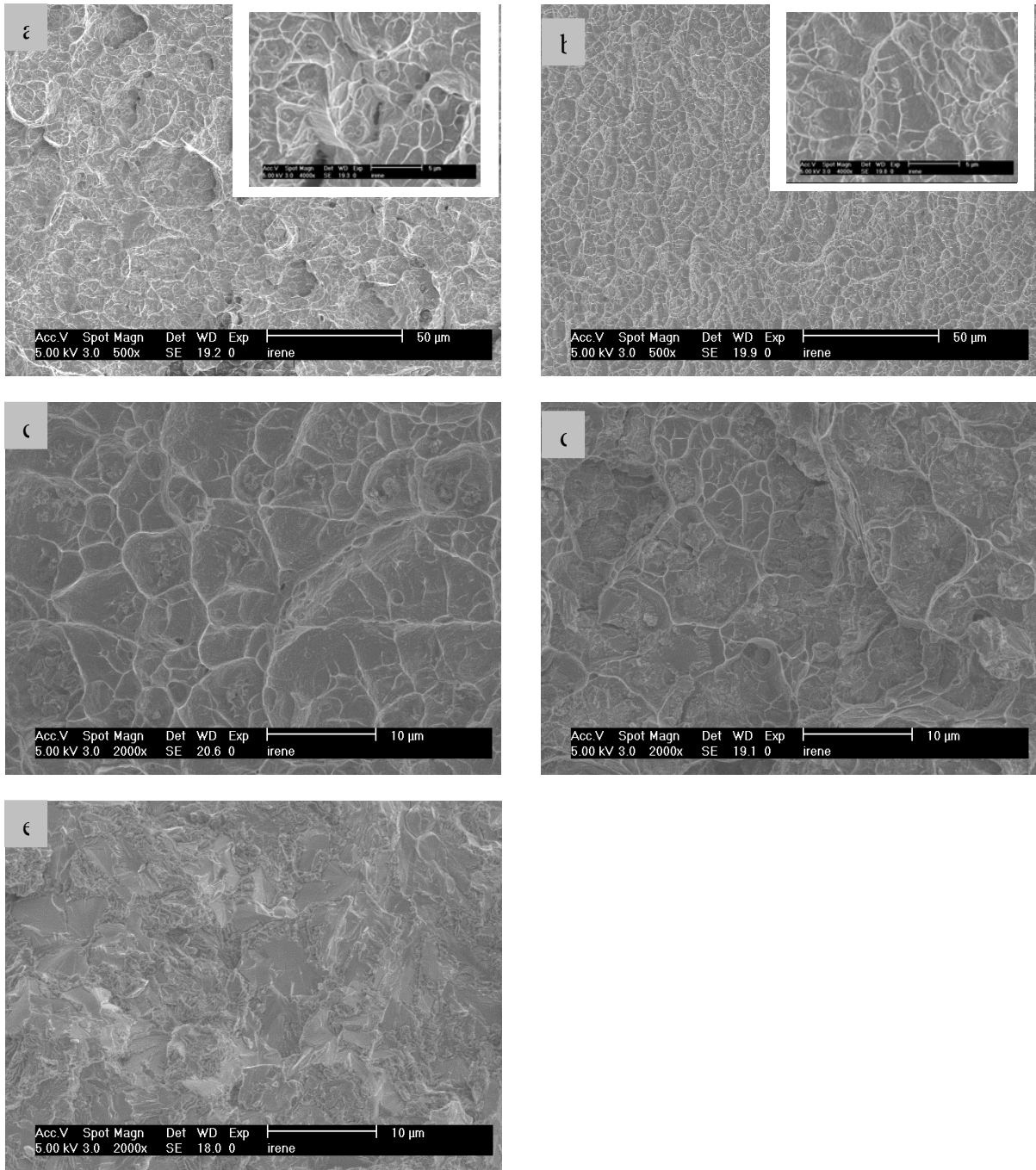


Figure 4: High magnification fractographs in specimens; typical “venous” pattern observed in the as-quenched alloy showing (a) deeper veins at the notch root, (b) shallower veins away from the notch root in the monolithic amorphous sample. (c) showed fracture features at the notch root for LD1 composite, showing shallower veins due to the presence of dendrites. (d) showed deeper veins pattern comparable to those seen in the amorphous sample suggesting the presence of intermetallic phases in glassy matrix improved the plastic flow of the system. Quasi-cleavage like brittle fracture was observed for the nearly crystalline sample shown in (e).

shear band nucleation and hence promotes brittle fracture.

On the other hand, there have been reports that the introduction of an optimum size of crystalline particles will improve the properties of the metallic glasses. Hays et al.[2] had reported a 250% improvement in Charpy impact toughness of ductile-dendrite reinforced bulk metallic glass composites over that of monolithic BMG specimens. This improvement in toughness was attributed to the ductile dendrite phases serving as heterogenous sites for the initiation of individual shear bands, while at the same time acting as pinning centers during shear band propagation. Similar explanations may apply to this present work where the impact fracture energy was improved for the intermetallic reinforced bulk metallic glass composite, even though the improvement was smaller. Pictures at higher magnification of the fracture surface also showed the classic vein-like fracture morphology characteristics of the monolithic glass mixed with regions of ductile fracture. This suggested higher overall plastic strain and hence larger energy required to fracture the composite. Characterization and modification to the microstructure of the intermetallic-reinforced glass matrix composite to further improve the fracture energy will be carried out.

The impact fracture energy of the almost fully crystalline sample was low and exhibited a quasi-cleavage like features implying a limited amount of viscous flow of glass interspersed with brittle cleavage fracture. In this case, the microstructure can be taken as crystalline matrix with glassy phases disperses in it. Hence it can be inferred that metallic glass phases will be the weak connecting regions among crystalline matrix where the nucleation and propagation of microcracks is easier. This means that microcracks will nucleate and propagate along the residual metallic glass and straight across the brittle crystalline matrix before flow deformation behavior of the remaining metallic glass alloy can take place. Hence microcracks propagated so rapidly that no shear bands can be formed before failure and resulting in brittle fracture.

4. Conclusion

The influence of different microstructures of La-based bulk amorphous alloys and in-situ composite microstructures on impact fracture energy was investigated. Vein-like fracture surfaces are observed on the monolithic amorphous alloy. With the present of dendritic phases in a glassy matrix, LD1, the impact fracture energy decreases. This might attributed to the microstructure decreasing the propensity for shear band formation and promoting brittle fracture. However, the introduction of intermetallic phases into a glassy matrix, LI1 showed a slightly improved fracture energy compared to the fully amorphous sample. The presence of this phase might act to hinder shear band propagation and promote generation of multiple shear bands thus improve the plastic flow of the material. Further increases in the amount of intermetallic phases, LC, resulted in brittle fracture of the specimen. This suggests a rational method for exploring microstructures to optimize toughness.

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