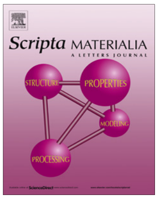
Scripta Materialia 111 (2016) 127–130

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat



Supercooled liquid fusion of carbon fibre-bulk metallic glass composites with superplastic forming properties

Karl F. Shamlaye*, Kevin J. Laws, Michael Ferry

Australian Research Council Centre of Excellence for Design in Light Metals, UNSW, Sydney, NSW 2052, Australia
School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia

ARTICLE INFO

Article history:
Received 13 July 2015
Accepted 3 August 2015
Available online 13 August 2015

Keywords:
Hot pressing
Bulk metallic glass
Carbon fibres
Superplasticity

ABSTRACT

Bulk metallic glasses (BMGs) are multicomponent metal alloys that form a glassy structure with relative ease upon cooling from the melt. Unique to glassy materials is a glass-transition (temperature), whereby the vitreous solid relaxes into a supercooled liquid state, leading to a dramatic decrease in viscosity. This softening behaviour allows novel thermoplastic forming and bonding processes to be carried out that are simply unachievable among conventional metal processing methods. The work presented herein utilises this supercooled liquid state by infiltrating carbon fibres within a Mg-based BMG to manufacture fully-dense carbon fibre reinforced BMGs which also exhibit unique secondary forming capabilities.

There is a growing trend in the technological and energy industries to favour lightweight, highly processable materials for both their economic and performance advantages. Of the current advanced high specific-strength and stiffness materials, carbon fibre-reinforced composites and advanced alloys based on magnesium, aluminium and titanium, have found growing market share, particularly in personal electronic devices, automotive and aerospace applications [1].

Bulk metallic glasses (BMGs) are relative newcomers to materials science and engineering applications, with a unique suite of mechanical and thermo-physical properties when compared to conventional crystalline alloys, including high-specific yield strength, elastic strain limit and wear resistance, as well as exhibiting glass-transition phenomena [2–5]. As a result of the softening associated with the glass transition, within specific temperature and time conditions metallic glasses may be processed into complex shapes in a manner similar to thermoplastic polymers or ceramic glasses [6–8], and have been deemed "*the most significant development in the material science world*" since the discovery of plastics over 50 years ago [9].

Despite BMGs closely approaching the theoretical maximum strength achievable by any material [3], such a glassy structure limits their ability to accommodate plastic deformation below the glass transition, with the only mechanism available being shear banding that is often rapid and catastrophic; this results in a material that is strong but often brittle. A useful solution for overcoming this material property shortfall is the development of metallic glass composites, whereby the most favourable properties of two or more different materials are combined to create a single product with properties broadly superior to those of each individual material component.

Albeit recent reports of ductile BMG/crystalline composites being created directly from the molten state (in-situ method) [10], the majority of BMG composites to date are ex-situ, in that the metallic glass is 'externally' combined with a secondary phase. This method typically involves the addition of a second phase to the BMG-forming melt that is then cast, or the infiltration of a pre-fabricated second phase network by the molten glass-forming alloy to generate a continuous BMG-matrix [11].

Carbon fibre (CF) as a reinforcement material in metal-matrix composites (CFMMCs) has gained significant importance in modern engineering. The fibre addition results in a component with increased strength and stiffness and a reduction in its density leading to both high specific strength and stiffness [12–14]. However, processing issues have constrained the use of such CFMMCs because of the difficulty of embedding these fibres into the metal matrix. Furthermore, the high melt temperature typically results in fibre degradation and the generation of undesired reaction products at the metal/fibre interface. Continuous CF reinforced BMG (CFBMG) composites have been fabricated by melt infiltration of a Zr-based BMG [15,16] and discontinuous short carbon-fibre BMG composites were produced by distributing fibres in a Zr-based BMG melt followed by copper mould casting [17]. Unfortunately, these processing methods resulted in a chemical

---

* Corresponding author at: School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia.

E-mail address: s9801051@unsw.edu.au (K.F. Shamlaye).

http://dx.doi.org/10.1016/j.scriptamat.2015.08.001

reaction between the carbon fibres and metal matrix to produce brittle zirconium carbide at their interface [15–17].

The aim of the present work is to produce low-density CFBMG composites superior to current CF-reinforced MMCs and polymers by utilising the low viscosity of the supercooled liquid (SCL) state found only in BMGs. A $Mg_{65}Cu_{25}Y_{10}$ BMG was selected as the matrix material for its relatively low density (3.28 g/cm^3), low glass transition temperature ($T_g \sim 140$ °C), large SCL region (with standard crystallisation temperature, T_X, of 210 °C) and well-known viscosity properties [18–22] for enabling easy processing within a temperature/time processing window comparable to the fabrication of CF-reinforced polymer composites.

In service, it is expected that the high elastic limit of the BMG matrix [23] (the ∼2% elastic strain is comparable to polymers and 2 to 3 times greater than conventional crystalline metals) will not be exceeded prior to the failure of the high-strength CF reinforcement (which also has an elastic strain limit to failure of ∼2.1% [24]). The fibres are expected to contribute significantly to the strength and stiffness of the material with a tailored fibre distribution within the metal matrix hindering the propagation of shear bands leading to an extended failure limit of the matrix material and, hence, the composite [11].

Amorphous ribbons of the $Mg_{65}Cu_{25}Y_{10}$ alloy ∼50 μm in thickness and 7 mm in width were produced by the melt spinning method (Edmund Buehler HV Melt Spinner), whereby a thin stream of molten metal is ejected on a rotating copper wheel with a surface speed of ∼20 m/s. The $Mg_{65}Cu_{25}Y_{10}$ ribbons were ultrasonically cleaned in acetone for 30 min in order to remove any surface contaminants or oxides (this method has proven to be a useful technique for removing the weak surface oxide found on Mg-based BMGs) in order to create a clean surface for the supercooled liquid fusion process.

The BMG composites developed in this work contain raw carbon fibres that are infiltrated directly by the metallic glass whilst in the supercooled liquid state. Here, CF tows (Torayca® T700S) were ultrasonically cleaned in acetone for 30 min to remove polymer sizing and coupling treatments and to promote separation of individual (7 μm diameter) fibres. Alternating layers of $Mg_{65}Cu_{25}Y_{10}$ BMG metallic glass ribbon and carbon fibre ribbon arrays were stacked in a holding fixture (100 mm × 10 mm area). Cyanoacrylate binder was placed at the ends of the fibre/ribbon stacks to hold the composite arrangement in place. After stacking, composite arrangements were inserted into a heated steel die (100 mm × 10 mm area) incorporated into a 12 ton Carver laboratory press (Model No. 2697) held at 180 °C (40 °C above T_g) at which the time for the onset of crystallisation, t_{Cryst} is approximately 15 min [19–22]. A pressure of 60 MPa was applied to sample stacks for a maximum of 7 min or until the nominal final sample thickness was reached. Fig. 1 shows a schematic representation of the process and the resulting composite microstructure. The total compressive strain was limited using shim plates of specific thicknesses; sample results shown herein were for samples with a final thickness of 1 mm that had experienced a total compressive strain of 20%. The fabricated samples were cooled and removed from the die. The mechanical performance of the materials was determined by four-point bend testing with a 20 mm load span and 10 mm support span (ASTM D6272-02) and was conducted on at least five specimens using an Instron 5565 test bed with a 1 kN load cell with a load rate of 0.1 mm/min. The semi-unconstrained loading generated by this testing method is regarded as the most common way that an engineering material would be loaded. As-prepared and fractured specimens were analysed by scanning electron microscopy (SEM) using a Hitachi S3400-x SEM. The density of the resultant CFBMG composites was determined using a Mettler Toledo Density test kit.

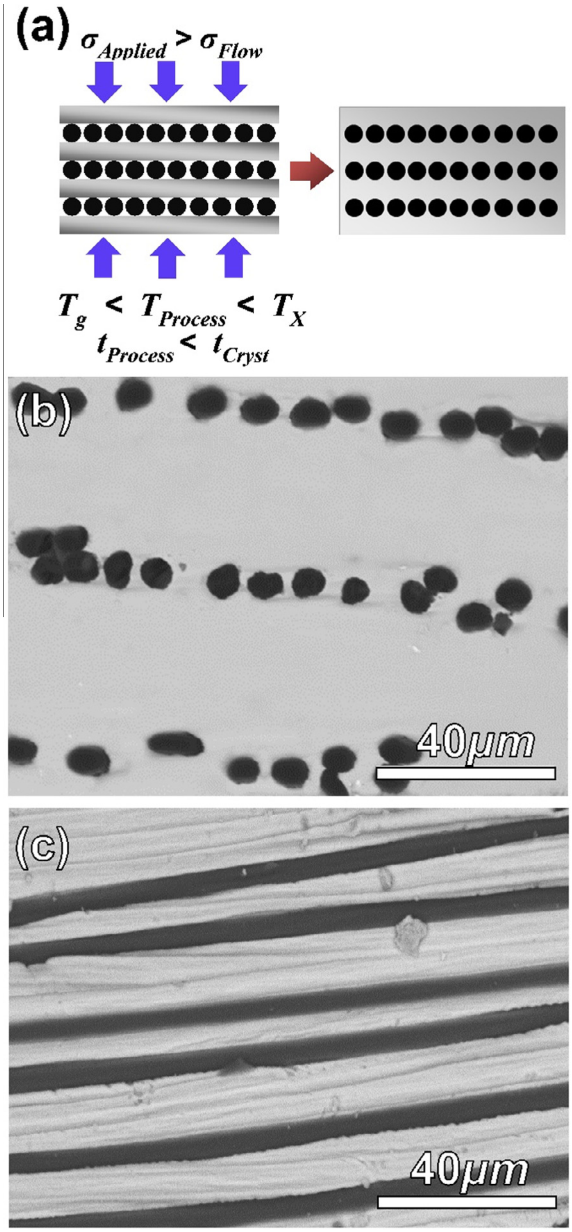


Fig. 1. (a) Schematic representation of the supercooled liquid fusion process. Backscattered SEM micrographs of the cross-section of as-fabricated carbon fibre-reinforced BMG composites in (b) the transverse and (c) longitudinal direction.

Fig. 1 shows a cross-section of a typical CFBMG composite produced by the supercooled liquid fusion technique. A CF volume fraction of 10 vol.% was achieved for these 1 mm thick composites. The figures clearly show the extent of metallic glass infiltration, distribution about the fibres and the excellent self-bonding/fusion characteristics of the metallic glass between ribbon layers. The lateral distribution of the carbon fibres shown here, although relatively consistent, is not equal to the longitudinal distribution. This is due to the fact that the metallic glass ribbon thickness is approximately 7 times the diameter of the fibres and the amount of strain applied during pressing essentially determines both the lateral and longitudinal distribution of the fibres. When pressure is applied to the arrangement, flow of the BMG is initiated, having a lateral strain component [$\varepsilon = \sigma \cdot t / 3\eta$] [25]. An additional strain component due to radial flow occurs [$\varepsilon = h/2R$], as the matrix also has to flow around a fibre for consolidation, therefore causing