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Synthesis and characterization of copper fiber reinforced $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ bulk metallic glass

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Abstract

Highly conductive Cu fibers were introduced into $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vitreloy1) Bulk Metallic Glass (BMG) of poor conductivity to produce a composite with a thermal anisotropy. The composites with circular and square cross-sections with the volume fraction ranging from 7 to 60% were processed successfully by pressure-gravity infiltration. Differential Scanning Calorimetry (DSC) showed that the BMG matrix remained predominantly amorphous after adding up to 60 vol.% of Cu fibers. The limited crystallization at the Cu/Vitreloy1 interface was observed under optical microscope. This crystallization is attributed to heterogeneous nucleation starting from the Cu/Vitreloy1 interface followed by the growth in the region with higher Cu concentration around the copper fibers. A combination of two-dimensional triangular and square ordering of the fibers was observed in the composite samples. X-ray diffraction patterns of the composites showed the peaks from the reinforced fibers and crystals around the Cu/Vitreloy1 interface superimposed on the broad diffuse maxima from the amorphous phase. Best processing parameters in terms of processing time and temperature were determined for the composite reinforced with 60 vol.% fibers.

Keywords: Amorphous materials; Liquid quenching; X-ray diffraction; Anisotropy; Thermal analysis

1. Introduction

Bulk Metallic Glasses (BMGs) are formed when crystallization is prevented by quenching the molten metal from the liquid disordered state. In particular, Zr based BMG's [1,2] are of great interest to the engineering community because of their superior mechanical properties, lower thermal conductivity and high corrosion resistance. The high resistance of these multi-component alloys against crystallization enables the formation of an amorphous structure which is responsible for the superior properties. Their low melting points, low solidification shrinkage and higher supercooled liquid region make these BMG's a good candidate as a matrix for processing composites. It has been shown earlier that BMG reinforced with metal or ceramics particulates [3–5] as well as fibers [6,7] can be successfully processed while retaining the glassy matrix.

To tailor the thermal conductivity of BMG based composite, this paper will show the synthesis and characterization of BMG matrix composites resulting in thermal anisotropy. As a matrix material, BMG with the composition, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$, commercially known as Vitreloy1™, is used. Copper is used as a reinforcement material due to its high thermal conductivity of 391 W/m K [8] which is significantly higher than Vitreloy1 with the thermal conductivity of 6.9 W/m K at the room temperature. The composites are characterized by optical microscopy, X-ray diffraction and differential scanning calorimetry.

2. Experimental methods

Ingots of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (Vitreloy1) were obtained from Liquid Metal Technology, Lake Forest, CA and 80 mm long Cu fibers with the diameters of 250 μm were purchased from Alfa Aesar, Ward Hill, MA. Prior to a pressure-infiltration run, the fibers were cleaned by ultrasonic cleaning first in a bath of acetone followed by ethanol. These fibers were annealed in a quartz tube using the ATS vertical split resistive tube furnace at 773 K under high vacuum conditions ($<10^{-5}$ mbar). After the material preparation, the final synthesis of composite was done in a quartz tube with a diameter of 7 mm

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based on Dandliker and Choi's work [9,10]. Molten Vitreloy1 was infiltrated into the copper fibers using pressure-gravity method, with the help of Argon at a pressure of about 50 kPa. Quenching was done within 60 s in a water bucket to ensure the cooling rate higher than the required critical cooling rate of 1 K/s for Vitreloy1. The optimum time and temperature for the process of infiltrating the matrix is 25 s at 1175 K. 80 mm long cylindrical specimens with varying copper fiber volume fraction ranging from 7 to 60 vol.% were obtained by this method.

Cross-sections of cast rods were examined by X-ray diffraction. The glass transition and crystallization of all samples was studied with a differential scanning calorimeter (DSC) (Perkin-Elmer—Pyris 1). Heating rate of 0.25 K/s was used for the DSC analysis. The fiber/matrix interface and fiber distribution in the composite specimens were investigated by optical microscopy. Compression tests were performed on an Instron 4505, at a strain rate of 0.00846 mm/s. The rods for compression tests were cut to the lengths that provided an aspect ratio of 0.5 and 2.0, respectively. The ends of the rods were ground flat and perpendicular to the loading axis.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns with Cu Kα radiation of pure amorphous Vitreloy1, pure copper fiber (bottom), and a composite sample. The X-ray diffraction pattern of the composite exhibits a superimposition of broad maximum from the glassy phase with several sharp Cu peaks and small peaks characteristic of other crystalline phases. The less dominant peaks were identified as a Zr_2Cu lattice pattern. However, peak shift towards higher angle by 1° was seen for this compound. This shifting of peaks to the higher angles is due to the reduction of the interatomic spacing in the Zr_2Cu crystal lattice. Therefore, the formation of an intermetallic compound like $(ZrTi)_2(CuNi)$ is expected, where Ni substitutes for Cu and Ti substitutes for Zr.

The fibers appear to arrange either in square or 2D triangular packing as shown in Fig. 2. However, they tend to cluster in one area, resulting in a closer distance than necessary. An investigation of the fiber distribution shows a peak around 250 μm. Furthermore, a second, less dominant peak exists at 400–450 μm for a volume fraction of wires of less than 45% and 300–330 μm for >45 vol.%. With increasing volume fractions, the range of distribution decreases and both peaks get closer to the theoretical minimum of 250 μm.

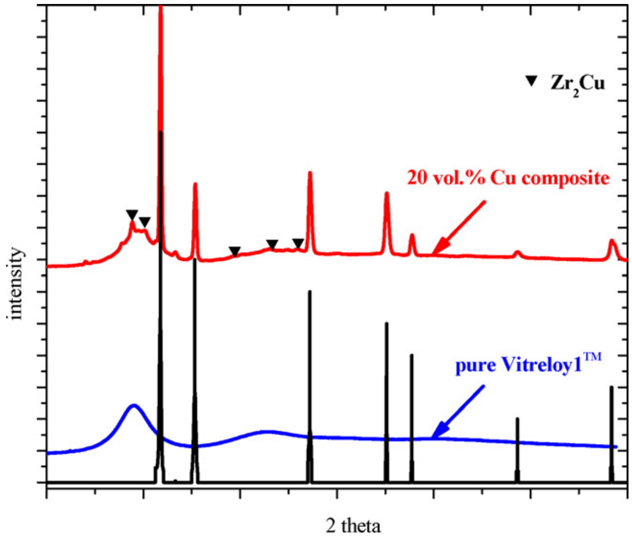

Fig. 1. X-ray diffraction patterns of amorphous Vitreloy1™, of its composite with 20 vol.% copper-fiber, and of pure copper (bottom).

Fig. 3 shows optical photomicrographs at two magnifications of 50× and 500× for a composite with 40 vol.% copper-fibers. Optical micrographs show a clear separation between the copper and Vitreloy1 interface with no macroscopic dissolution of copper into the Vitreloy1 can be seen. However, crystallization occurred at the interface between Vitreloy1 and copper-fiber, which is seen at higher magnification of 500×. Careful examination indicates that average thickness of the crystalline layer for most samples lies between 10 and 15 μm. This crystalline layer can be co-related with the heterogeneous nucleation and deteriorated glass forming ability of matrix around the fibers. This is done by simulating the two-dimensional concentration profile of copper into the matrix between two copper-fibers by using [11]

$$\frac{C - C_0}{C_s - C_0} = \sum_{n=0}^{\infty} \frac{2(-1)^n}{(n+1/2)\pi} \exp^{-(n+1/2)^2\pi^2(Dt/L^2)} \times \cos\left(n+\frac{1}{2}\right)\pi\left(\frac{x}{L}\right) \tag{1}$$

where C is concentration of copper at a distance x between the copper-fibers in at.%, L the distance between the two copper-fibers, C_0 the nominal matrix copper concentration which is 12.5 at.%, C_s the copper concentration at the copper-fiber/matrix interface which is 100 at.%, t the time for diffusion and D is the diffusivity of copper into the matrix. D was calculated from the

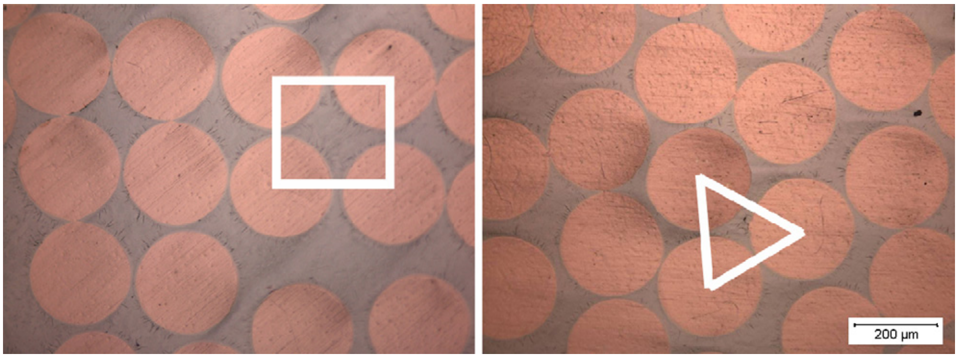

Fig. 2. Optical micrograph showing two-dimensional triangular and square ordering of fibers within the same sample.

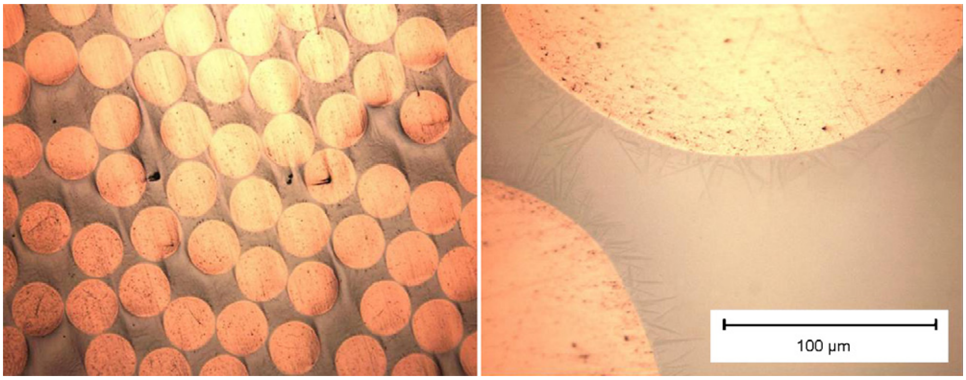

Fig. 3. Optical photomicrographs of a polished surface of the composite with 40 vol.% copper-fiber with diameter of 250 μm at 50× and 500× magnification.

relaxation time, τ, using the equation for random walk [12],

$$D = \frac{l^2}{6\tau} \tag{2}$$

We estimate the relaxation time, τ, as the time for the successful displacement of an average atomic diameter l of 3.2×10^{-10} m. This relaxation time is calculated by using Eq. (3) [12] from the viscosity data as a function of shear rate shown in Fig. 4 [13]. The relaxation time is given by

$$\tau = \frac{\eta}{G_\eta} \tag{3}$$

where η is the viscosity in Pa s and G_η is the high frequency shear modulus equal to 5.5×10^8 Pa. Fig. 5 shows a simulation done for a sample processed at 1175 K in 25 s at a shear rate of $1.0\,\mathrm{s}^{-1}$. The simulated concentration profile in Fig. 5 shows that copper diffuses to 16 μm. This diffusion length is close to the crystalline layer thickness shown in Fig. 3. Fig. 3 also shows that the growth of crystals ceases as the distance from the copper-fiber/Vitreloy1 interface increases. This indicates that the crystallization starts at the copper-fiber/Vitreloy1 interface due to heterogeneous nucleation and further grows into the Cu enriched matrix around the fiber. This simulation shows that the success in making the composite can be attributed not

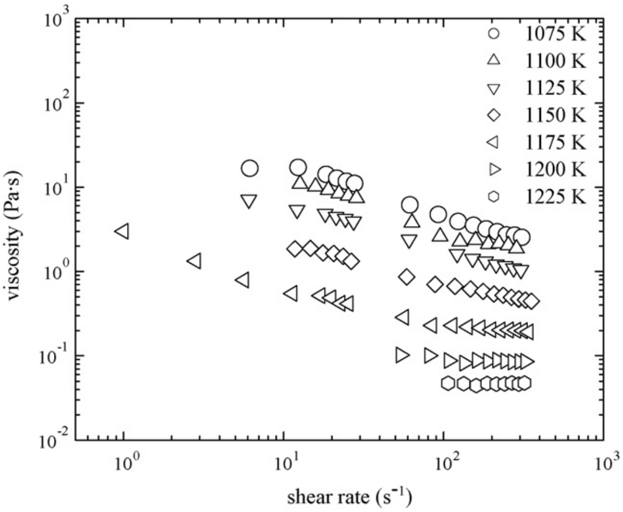

Fig. 4. Plot showing viscosity as a function of shear rate.

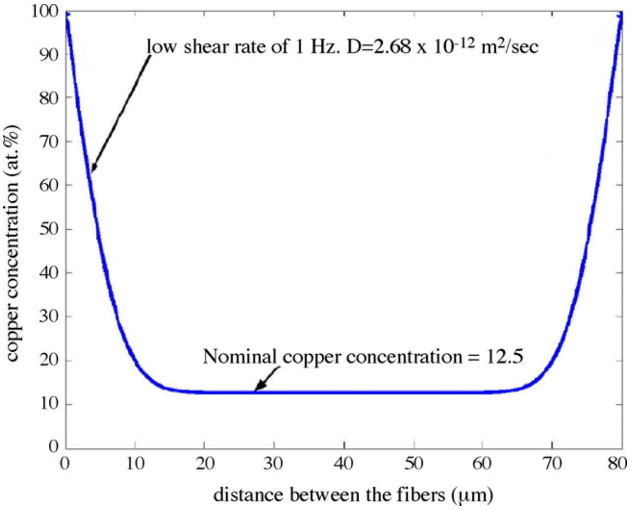

Fig. 5. Concentration profile of Cu into the matrix starting at Cu wire/Vitreloy1$^{\mathrm{TM}}$ interfaces from both sides. Location of two wire/matrix interfaces is at 0 and 80 μm on x-axis. Processing time is 25 s and processing temperature is 1175 K at shear rates $1.0\,\mathrm{s}^{-1}$.

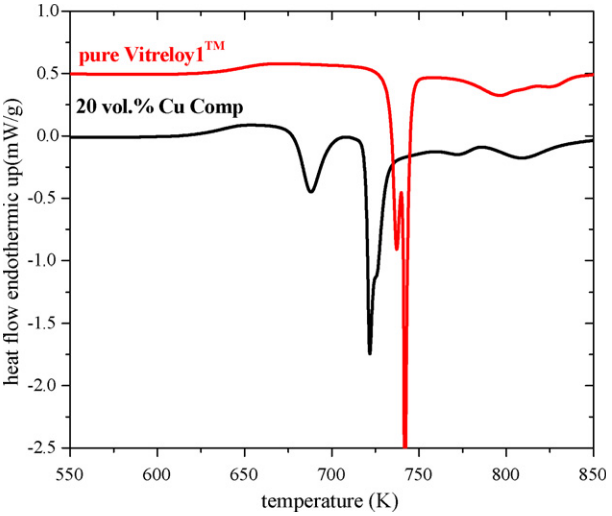

Fig. 6. DSC thermogram of pure Vitreloy1$^{\mathrm{TM}}$ and its composite with 20 vol.% of copper-fiber.

Fig. 7. Compression specimen fractured at a shear band at 45°.

only to the right processing time and temperature but also to the low shear rates involved in the processing. Shear rates were determined by the experimental parameters like casting pressure, diameter of fibers and the quartz tube.

To investigate the amount of amorphous phase in the matrix, DSC is used. Fig. 6 shows DSC scans of the pure amorphous Vitreloy1 and a 20 vol.% copper-fibers composite using a heating rate of 0.25 K/s. The composite sample exhibits an endothermic heat event characteristic of the glass transition followed by multiple exothermic heat release events indicating successive transformations from supercooled liquid state to crystalline phases. As expected, the area under the crystallization peaks is smaller for the composite due to crystallization at the copper-fiber/Vitreloy1 interface. The optimum processing condition for the composite with 60 vol.% copper-fibers was found out to be 1175 K in 25 s. The DSC analysis showed that for this composite sample, the metallic glass matrix retained up to 80% amorphous state.

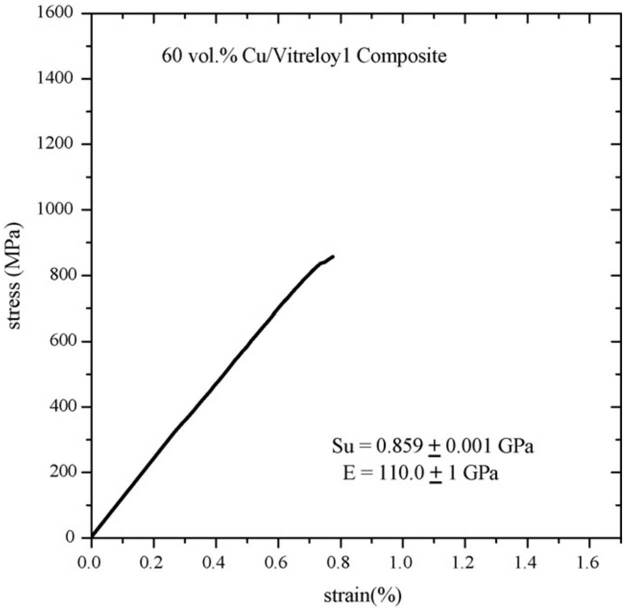

Fig. 8. Quasi-static compression stress–strain curve of the composite reinforced with 60 vol.% copper-fiber.

Compression tests exhibited an elastic behavior of the specimens. Since there is no lattice with fixed slip planes, the material deforms by the formation of 45° shear band as shown in Fig. 7. The compression tests revealed a Young's modulus of 110 ± 1 GPa and the yield strength of 0.859 ± 0.001 GPa for a 60 vol.% copper-fibers composite as depicted in the stress–strain curve shown in Fig. 8. This drop in yield strength by 54.8% compared to Vitreloy1 is due to the small yield strength of pure annealed Cu (<70 MPa) [14], so that its strength can virtually be neglected compared to the Vitreloy1 (<1.89 ± 0.01 GPa) [15]. These values are different than those calculated by the rule of mixtures for the expected Young's modulus and fractions for the ultimate strength. This difference is due to the partly crystalline matrix which has a higher Young's modulus than amorphous Vitreloy 1.

4. Conclusion

Copper-fiber reinforced Vitreloy1 composites were successfully processed even though Cu has a negative heat of mixing with the various components of Vitreloy1 and relatively small difference in the melting temperature with Vitreloy1. Volume fractions of reinforcement fibers from 7 to 60% were added without crystallizing the matrix completely. The utilization of relatively low processing temperature, time and smaller shear rates prevent excessive reaction between Cu fibers and glass matrix, thus allowing the matrix to retain the amorphous state.

The composites were characterized with respect to their microstructure, structure and thermal stability and the mechanical properties. The best processing parameters for time and temperature were determined for the composite reinforced with 60 vol.% Cu fibers. This composite was selected because of its uniform fiber distribution and distinct anisotropy. The DSC showed that the metallic glass matrix retained the 80% amorphous state for the composite synthesized at 1175 K in 25 s with 60 vol.% Cu fibers.

Optical microscopy confirmed that there is no macroscopic dissolution of Cu atoms from the wires into the matrix. However, at the interfaces between the matrix and fibers, a crystalline layer was observed. This crystalline layer is formed by heterogeneous nucleation at the interface followed by the growth in the region with higher Cu concentration around the copper-fibers. However, the matrix did not crystallize completely due to growth controlled crystallization in Vitreloy1 because of sluggish kinetics. Optical photomicrographs at low magnifications revealed clustering of fibers in particular regions.

The compression tests demonstrated that the material behaves elastically and fails in a brittle manner. However, the deviations in the observed values of the Young's modulus and the ultimate strengths indicate that the matrix crystallinity at the interfaces has to be taken into consideration in the rule of mixtures. One promising application of this metallic glass matrix composite could be in the meso and micro scale heat exchanger, where high heat transfer in one direction is required.

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