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Crystallization kinetics and fragility of a metallic glass composite

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The crystallization behavior and viscosity of an in situ metallic glass composite was investigated using a non-contact electrostatic levitation technique. The width of the supercooled liquid region for the amorphous matrix was found to be 74 K, indicating its excellent stability against crystallization. The viscosity data follows the Vogel–Fulcher–Tammann relation, which was used to determine the fragility of the composite melt. The viscosity of the composite is compared to monolithic metallic glasses in the context of "strong-fragile" liquid behavior.

Keywords: Metallic glass composite; Crystallization; Kinetics; Fragility

Metallic glasses are fully amorphous metallic alloys with very high strength and elastic limit. However, metallic glasses fail catastrophically because of their limited plasticity [1,2]. To counter this limitation, metallic glass composites have been developed for structural applications; in these composites a ductile crystalline phase formed in situ is distributed in a fully amorphous matrix [3–5]. This microstructure leads to a remarkable improvement in impact toughness and plasticity. The mechanical behavior of metallic glass composites has been widely studied [4,6]. However, there are no reports on crystallization kinetics of these materials, which is critical to explain and control their thermal stability.

Viscosity is a kinetic parameter that describes the timescale for structural rearrangement of liquid atoms to form a crystalline nucleus. The temperature-dependent viscosities of a number of metallic glass systems have been reported earlier [7–9]. However, most of these studies are for monolithic metallic glasses and are limited to the temperature range close to the glass transition. There are no reports of viscosity measurements for metallic glass composites. It is important to determine the high-temperature viscosity in these systems as this dictates the critical cooling rate for glass formation [10]. The presence of highly reactive elements such as Ni, Ti, and Zr restricts the use of conventional viscosity measurement techniques such as the Couette viscometer at high temperatures.

In this paper, we report on the crystallization behavior and viscosity of a bulk metallic glass (BMG) composite, $Zr_{56.2}Ti_{13.8}Nb_{5.0}Cu_{6.9}Ni_{5.6}Be_{12.5}$, using a high-vacuum electrostatic levitation (ESL) technique. The microstructure for this composite consists of 25 vol.% of a body-centered-cubic (bcc) phase of composition $Zr_{71}Ti_{16.3}Nb_{10}Cu_{1.8}Ni_{0.9}$ embedded in 75 vol.% of an amorphous matrix of composition $Zr_{47}Ti_{12.9}Nb_{2.8}Cu_{11}Ni_{9.6}Be_{16.7}$ [5]. The crystallization kinetics for the in situ bcc phase was investigated by isothermal annealing at different temperatures. The viscosity of the composite-forming liquid was determined as a function of temperature and is discussed within the context of "strong-fragile" behavior.

A schematic of the ESL approach is shown in Figure 1a. Small samples (15 mg) were levitated and melted using a high-power, continuous-wave Nd-YAG laser. The temperature of the levitated sample was measured using a two-color pyrometer. To ensure temperature uniformity, a tetrahedral heating arrangement was used. A detailed description of the ESL facility itself was given in an earlier publication [11]. The crystallization kinetics for the in situ bcc phase was determined by isothermal annealing. The molten sample was cooled to a predetermined temperature by turning off the laser, which was subsequently turned back on at a preset power. Prior to each isothermal measurement, the alloy was subjected to melting and radiative cooling to ensure proper fluxing. The temperature fluctuations were within ±5 K during the isothermal period.

Viscosity measurements were done by the drop oscillation technique, in which alternating current (AC) voltage was applied to the levitated molten drop. An excitation pulse of sine-wave cycles was applied at the resonant frequency of the drop and the ensuing transient signal was recorded. The viscosity (η) of the liquid drop was calculated from the decay time constant (τ) of free oscillation that followed the excitation pulse and is given as [12,13]: $\eta = \frac{\rho r^2}{5\tau}$, where ρ is the density and r is the radius of the spherical drop. A detailed description of the viscosity measurement technique is given

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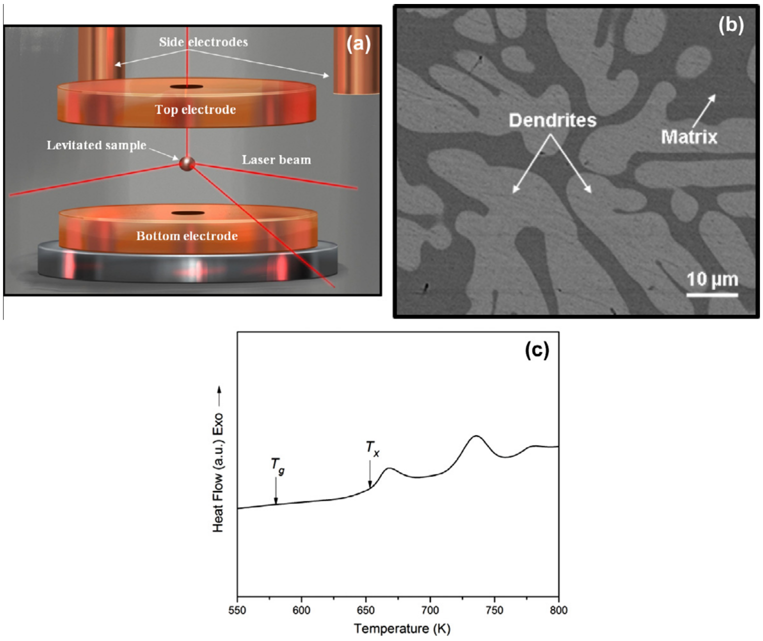

Figure 1. (a) Schematic of electrostatic levitation (ESL). (b) Backscatter SEM image. (c) DSC curve for the metallic glass composite $Zr_{56.2}Ti_{13.8}Nb_{5.0}Cu_{6.9}Ni_{5.6}Be_{12.5}$. The glass transition and crystallization temperatures are indicated by T_g and T_x, respectively, on the DSC curve.

elsewhere [13]. Images of the levitated molten sample were captured by a charge-coupled device video camera with a telescopic head [14]. Microstructural studies were done by scanning electron microscopy (SEM). Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g) and the crystallization temperature (T_x).

A backscattered SEM image of the BMG composite is shown in Figure 1b. The microstructure comprises of in situ ductile crystalline dendrites distributed in the amorphous matrix. The average size of the crystalline dendrites in the BMG composite was determined by ImageJ software to be nearly 22 µm. The DSC curve for the as-cast BMG composite is shown in Figure 1c. Two crystallization events are seen, a pattern that is a typical signature of phase separation in Zr-based metallic glasses [15–17]. The glass transition temperature (T_g) was found to be 578 K and the crystallization temperature (T_x) around 652 K. The width of the supercooled liquid region ($T_x - T_g$) is 74 K, indicating good glass-forming ability of the matrix.

Free radiative cooling curves obtained for the composite under two different conditions are shown in Figure 2a. Overheating the melt to a temperature greater than 1420 K prior to free radiative cooling resulted in two recalescence events: a sharp peak at 1055 K and a broad peak around 915 K. However, for overheating below 1420 K, only a single broad recalescence event was observed. The melting point of the crystalline bcc phase was indirectly determined from viscosity measurements to be around 1420 K. The crystallization times for the bcc phase during isothermal annealing at different temperatures are shown in Figure 2b. Crystallization is indicated by recalescence, i.e. the sharp rise in temperature due to release of latent heat of fusion. The crystallization time at 1083 K is 736 s, which reduces to <1 s at 1055 K. This indicates that the driving force for nucleation of the bcc phase reduces dramatically with increase in temperature above 1055 K. The complex chemistry of the in situ crystalline phase likely results in stabilization of the liquid and suggests a very sharp liquidus curve for the corresponding multicomponent phase diagram.

The specific volume data obtained for the two different processing conditions, along with the cooling/heating curves, are shown in Figure 3a and b. Although the starting temperature in both the cases is different, the temperature profile and specific volume data are given for the same temperature range for ease of comparison. The dashed line represents the point where laser was turned back on to reheat the sample. From the heating curve and corresponding specific volume data, the melting point of the matrix was identified to be close to 1030 K and matches with the value obtained from DSC. For overheating above the crystalline bcc phase melting temperature (Fig. 3a), there is severe distortion of the sample upon nucleation (first sharp recalescence). The nucleation of highly directional crystalline dendrites at the first recalescence peak causes severe distortion of the sample, as shown by the large scatter in the volume data in Figure 3a. For overheating below the crystalline bcc phase melting temperature (Fig. 3b), the sample remains fairly spherical even after the broad recalescence. The second recalescence, likely from phase separation prior to glass formation, does not change the noise level in the volume data appreciably.

The transient signals obtained from a molten levitated drop at two different temperatures are shown in Figure 4a. High-pass filtered data in the time domain along with the fast Fourier transform (FFT) spectrum was used for the analysis. The signal follows the function:

$$y = Ae^{-t/\tau}\sin(2\pi ft + \phi),$$

where A is the amplitude, t is the time, τ is the decay time constant, f is the resonant frequency, and ϕ is a constant phase factor. The decay time at the lower temperature of 1093 K is smaller ($\sim$0.3 s) compared to that at the higher temperature of 1448 K (> 1 s) as shown in Figure 4a.

The temperature variation of viscosity for the metallic glass composite is shown in Figure 4b. The viscosity could be measured down to the temperature slightly below that at which the bcc in situ phase nucleates. The level of noise in the measured viscosity gets larger with lowering of