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Injection molding metallic glass

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Advances in alloy development have produced the $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$ alloy with a crystallization–glass transition temperature, ΔT, of 165 °C. This alloy's large supercooled liquid region provides the longest processing times and lowest processing viscosities of any metallic glass and was injection molded using tooling based on plastic injection molding technology. Injection-molded beams and die-cast beams were tested in three-point bending. The average modulus of rupture (MOR) was found to be similar, while injection-molded beams had a smaller standard deviation in MOR.

Keywords: Metallic glasses; Bulk amorphous materials; Thermoplastic forming; Injection molding

Bulk metallic glasses (BMGs) are high strength, high hardness, highly elastic, low modulus and low melting temperature materials with no crystalline order that have been the subject of extensive research in recent years [1–4]. Because of their low melting temperature they are easily processed using conventional vacuum die- and suction-casting techniques. These methods require processing that is sufficiently fast to avoid crystallization, and alloys with high glass-forming ability are generally preferred. Die-cast parts have somewhat unreliable mechanical properties because of porosity that often exists in the specimens due to the high flow velocities required to fill the mold cavity [5]. The cooling requirements of die-casting restrict the dimensions of die-cast parts to being no larger than can be cooled sufficiently fast to avoid crystallization and no smaller than can be quickly filled. Parts with complex geometries, thin sections and high aspect ratios are difficult to obtain via die-casting.

Thermoplastic forming decouples the forming and cooling processes because it is carried out in the supercooled liquid region (SCLR) between the glass transition temperature, T_g, and the crystallization temperature, T_x. In the SCLR a BMG-forming alloy exists as a viscous, deeply undercooled liquid. The viscosity of the alloy follows a hyper-Arrhenius function of temperature [6] and crystallization is forestalled due to the sluggish kinetics in the deeply undercooled liquid. Much longer processing times are available in the SCLR than are available when casting from the molten state because the alloy is resistant to crystallization below T_x. Die-casting processes must shape and cool the alloy in seconds to tens of seconds while processing in the SCLR allows hundreds to thousands of seconds for forming and cooling. Time–temperature transformation (TTT) diagrams measure the time to crystallization of an alloy held isothermally at a given temperature. Viscosity plots measure the Newtonian viscosity of an alloy held isothermally at a given temperature. Figure 1 combines data from these two kinds of plots to show attainable viscosity for a given processing time for three alloys commonly used in thermoplastic forming experiments and the alloy used in this experiment, $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$ [6–9]. It is clearly seen that the $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$ alloy has the lowest processing viscosity for a wide range of processing times. Interpolation of viscosities not directly measured was done using the fit suggested by Johnson et al. [6].

The decreasing viscosity and longer processing times available in the SCLR allow metallic glasses to be processed in ways similar to plastics which are not possible with crystalline metal alloys. Nanometer-scale features with high aspect ratios have been formed in the SCLR by pressing metallic glasses into etched wells of semiconductor materials [10]. Glassy powders have been consolidated in the SCLR to form net-shaped parts [11]. Hot extrusion has been demonstrated using Zr-based alloys [12] and blow molding experiments using relatively low

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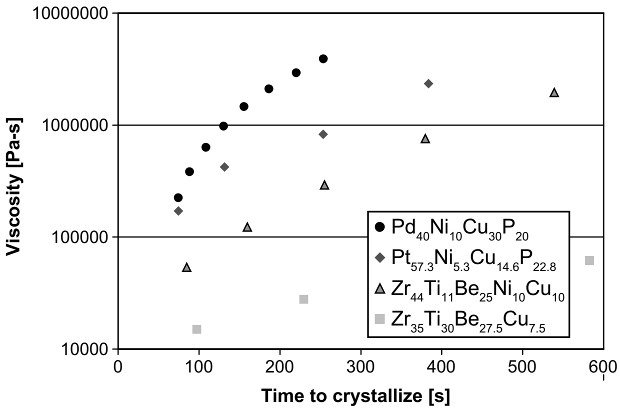

Figure 1. Time to crystallization vs. viscosity plot for four thermoplastically processable alloys. This plot combines TTT and viscosity vs. time data found in Refs. [6–9] to show available processing time for a given viscosity for the alloys.

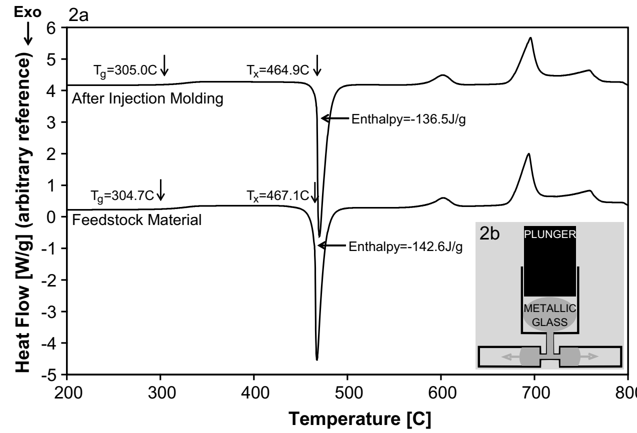

Figure 2. (a) 20 °C min^{-1} DSC scans of feedstock material and injection-molded specimen. The injection molding process appears to have had little effect on the thermodynamic properties measured in the DSC. (b) Schematic drawing of the modified injection molding setup consisting of a plunger, gates, and a heated mold and reservoir. The dimensions of the mold cavities are 2 mm × 10 mm × 20 mm and 1.5 mm × 10 mm × 20 mm.

pressures yielded hemispheres with a high-quality surface finish [13]. An additional benefit to processing BMGs in the SCLR is the decoupling of forming and cooling steps which allows formation of parts larger than the critical casting thickness of the alloy.

A conventional processing method used in the plastics industry that has not previously been successfully demonstrated with BMGs is injection molding. This is in part due to the limited viscosities and processing times available in the SCLR of known alloys. Recent discovery of alloys with SCLRs ($\Delta T = T_x - T_g$) as high as 165 °C makes BMG injection molding a possibility [14].

A basic injection molding machine has a heated reservoir in which plastic feedstock is softened, a piston or plunger to apply pressure to the feedstock, a nozzle or gate to restrict the flow of plastic when necessary, and a mold into which the plastic is forced to form a part. A schematic drawing of the setup used in this experiment is shown in Figure 2b. Typical operating temperatures and pressures are 175–350 °C and 35–150 MPa, respectively. Softened plastics used for injection molding usually have a viscosity of $\sim 10^3$ Pa-s.

$Zr_{44}Ti_{11}Be_{25}Cu_{10}Ni_{10}$, $Pd_{43}Ni_{10}Cu_{27}P_{20}$ and $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$ are among the most thermoplastically processable alloys known, reaching viscosities of $\sim 10^5$ Pa-s in the SCLR before the onset of crystallization. The alloy used in this experiment, $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$, can reach viscosities in the SCLR of $\sim 3 \times 10^4$ Pa-s at 420 °C with ~230 s available for thermoplastic processing at that temperature [15]. This is an order of magnitude lower viscosity than is attainable in the SCLR of previously reported metallic glasses [16–18]. However, it is an order of magnitude higher than the viscosity of plastics used for injection molding. A modified injection molding setup was created to accommodate the higher temperatures and pressures necessary to force the more viscous $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$ supercooled liquid into a mold cavity.

The $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$ feedstock material was made using >99.9% pure elements and melted thoroughly in an arc-melter under a Ti-gettered argon atmosphere. Each ingot was flipped and remelted multiple times to ensure chemical homogeneity. Ingots with more than 0.1% deviation from initial weighed mass after melting were discarded. Die-casting was done by radiofrequency heating the alloy in a quartz nozzle and injecting the molten alloy into a copper mold using argon pressure. The amorphous nature of all material was determined using X-ray diffraction and differential scanning calorimetry (DSC). Mechanical testing was performed on an Instron 4204 loadframe at a constant displacement rate of 0.5 mm min^{-1} in a three-point bending geometry to determine modulus of rupture.

A schematic drawing of the modified injection molding setup can be found in Figure 2b. The experimental setup consisted of a plunger used to apply force, a 19 mm diameter × 20 mm tall heated reservoir in which BMG feedstock material was brought to the processing temperature, and an 8 mm diameter × 3 mm tall vertical channel opening into two perpendicular channels with dimensions 5 mm × 2 mm × 2 mm long which restricted the flow of material into the mold cavity. The heated mold cavity on the left in Figure 2b is 10 mm × 2 mm × 60 mm long and the one on the right is 10 mm × 1.5 mm × 60 mm long. A photograph of injection molding attempts is shown in Figure 3. The most successful run was accomplished when the mold and glassy feedstock material were heated to 420 °C with a force of 300 MPa applied to the material in the reservoir for 2 min. The material completely filled the larger mold cavity and a 0.2 mm diameter flashing was formed along the perimeter due to insufficient clamping pressure. The material that filled this cavity underwent more than 1000% strain. Minimal polishing with 320 grit sandpaper removed the surface oxide layer and the beam formed in the large mold cavity was found to be glassy using X-ray diffraction. The flow was terminated in the smaller cavity due to crystallization of material near the heating element. Figure 3c shows the most successful metallic glass part; Figure 3a and b illustrate two less successful attempts, and Figure 3d is a part made of