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Blow molding of bulk metallic glass

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Blow molding is introduced as a net-shape process for bulk metallic glass (BMG). The forming takes place in the supercooled liquid region, where the viscosity of the BMG permits forming pressures that can be created with the force exerted by the human lung alone. The absence of external friction during the initial stages of forming allows large forming tangential strains. A simple model suggests strains of up to 10,000% are achievable under suitable processing conditions.

Keywords: Bulk metallic glass; Superplastic forming; Thermoplastic forming; Blow molding; Net-shape processing

It was discovered more than 2000 years ago that glass can be formed under forming pressures achievable solely with the human lung when heated above its softening temperature [1]. About 40 years ago, it was recognized that synthetically developed plastics can be processed in a similar way [2]. Blow molding became the terminology for plastic processing which allows the net-shaping of complex geometries consisting of thin sections with a vast aspect ratio.

In a separate development, superplastically formable (SPF) metallic alloys were found to exhibit large plastic deformations far beyond the plasticities normally associated with metals, which were usually expected to be less than 10–25%. When stable two-phase microstructures with grain sizes of less than 10 μm were processed in an environment, where the temperature was around $0.5T_\mathrm{m}$ and at the same time subjected to gas pressures of up to 5 MPa in a controlled manner, outstanding plasticities of ∼500% [3,4] were observed. The flow stresses of these SPF alloys are, however, significantly higher than those in plastic or glass at their respective processing temperatures.

Bulk metallic glasses (BMGs) are a new class of materials with attractive properties for structural applications, including very high strength and elasticity, and high corrosion resistance [5–7]. With the exception of a new class of BMGs [8,9], no or very limited plasticity has been observed, which has limited BMG applications [7]. However, it was recognized that in small dimensions BMGs can show significant plasticity. Conner et al. [10] have shown that the plasticity of beams in bending increases significantly when the beam thickness is decreased below 1 mm. Also, it was observed that for the majority of BMGs the plastic zone shielding a crack tip is less than 1 mm [7]. These results suggest that an ideal geometry for BMG applications should be limited in at least one dimension to below 1 mm for the BMG to express its full potential properties.

To date, the achievable geometries with BMG are still quite limited. Two fundamentally different processing routes are used [11]. The first is direct casting, where the BMG is simultaneously fast cooled to avoid crystallization during solidification and filled into the entire mold cavity. This makes the production of thin sections with high aspect ratio particularly challenging. Only a careful balance of process parameters makes this process commercially useful for some geometries [12].

The sluggish crystallization kinetics in BMGs provide a unique processing opportunity. During heating, the amorphous BMG first relaxes at the glass transition temperature into a supercooled metastable liquid before eventually crystallizing. The temperature region in which the BMG exists as a supercooled liquid is called the supercooled liquid region (SCLR). Here viscosities down to 10^5 Pa s can be measured [13–16]. Even though metastable in its SCLR, a processing window which includes minutes to hours without crystallization exists [14,17,18]. For some BMGs the viscosity and processing

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temperatures that define the flow stress for plastic forming are comparable to plastics [12,19–21]. This suggests that similar processing methods can be applied [11]. The ability to plastically form BMGs in their supercooled liquid region was recognized in the early days of metallic glass research [22,23] and various terminologies are used, including superplastic forming, thermoplastic forming and hot-forming. This processing opportunity has been used for a wide range of applications, including net-shape processing [12,24], micro- and nanoreplication [11,25–27], extrusion [28–30], synthesis of amorphous metallic foams [31], superplastic forming of sheet material [32–34], and synthesis of BMG composites [35,36].

Even though during TPF of BMG fast cooling and forming are decoupled [12], thin sections with a high aspect ratio are challenging to create when using techniques, where the BMG is in physical contact with the mold. This is due to stick conditions between the BMG and the mold under plane-strain conditions, which retards radial movement (parallel to the mold) of the BMG. This effect can be reduced to some degree by using lubricants, which results in some slippage. The improvement is quite limited and the use of lubricants also sacrifices the otherwise excellent achievable surface finish. In order to eliminate external friction, physical contact between the BMG and the mold has to be avoided at least whilst significant tangential strain is accomplished. In this case, the required minimum pressure for forming is solely defined by the flow stress of the BMG. This concept is introduced in this article.

The setup used for blow molding of BMG is schematically shown in Figure 1. Disks used as feedstock material for the blow molding are 60–80 mm in diameter and about 1 mm in thickness. $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ alloy is used as a BMG material for its good thermoplastic formability [11,27]. Its preparation is described in detail elsewhere [14]. For the blow molding, the entire setup is heated to the processing temperature using resistance heating. A pressure gradient between the top and the bottom sides of the disks is applied to form the BMG. This can be achieved either by applying pressure from the top side of the disk or by reducing pressure in the mold cavity, or a combination of the two. The forming process is terminated either once the BMG touches the entire mold cavity or by releasing the pressure difference. Thermal analysis was performed using a Netzsch DSC 404c differential scanning calorimeter (DSC). X-ray diffraction (XRD) was carried out on an Inel XRG 3000 using Cu Kα radiation. The results were utilized to verify the amorphous structure of the material before and after blow forming.

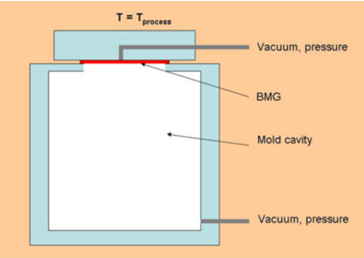

Figure 1. Schematic sketch of the blow molding setup. The entire setup is heated to the processing temperature. The driving force for expansion in the blow molding process is generated by a pressure difference between the top and the bottom side of the BMG disk. Blow molding can be terminated by equalizing the pressure on both sides or once the entire BMG surface is in physical contact with the mold.

The low forming pressure required in the blow molding of a BMG in its SCLR is demonstrated in Figure 2a. A 0.8 mm thick $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ disk was formed through a circular opening of 4 cm at a temperature of 460 °C. The disk section covering the opening was formed into a hemisphere under a pressure, which was generated with the sole power of the human lung ($\sim 10^4$ Pa). The forming process took less than 100 s which corresponds to a ‘ $\dot{\varepsilon} \geqslant 10^{-2}\ s^{-1}$. XRD and DSC results of the blow-molded material confirmed their amorphous structure. This characterization was carried out for all blow-molded BMG specimens. At the 460 °C processing temperature used in this study, crystallization becomes detectable after 255 s [14] compared with the processing time of 100 s.

The cross-sectional area revealed barely discernible thinning of the material. For example, at the edge of the opening the material is 0.72 mm thick compared with its minimum value of 0.69 mm at its pole. An extrapolation of viscosity measurements [37] suggests a strain-rate-sensitivity exponent, $m = \frac{d\sigma_{flow}}{d\dot{\varepsilon}}$ (σ_{flow} as the flow stress), of 1 for the processing parameters used here for the blow molding. As a comparison, the strain-rate-sensitivity exponent for SPF titanium alloys is between 0.3 and 0.8, with specific measurements dependent on the material, the strain rate, the temperature at which deformation takes place and the stability of the microstructure [38]. The high m values recorded for the BMGs under the above-described conditions suggest that thinning, in particular for large strains, is more uniform in BMGs than for many SPF crystalline metals because, as m increases, the rate of change of the cross-sectional area becomes less dependent on the magnitude of that area and any neck will grow more slowly [38]. Of course, the strain

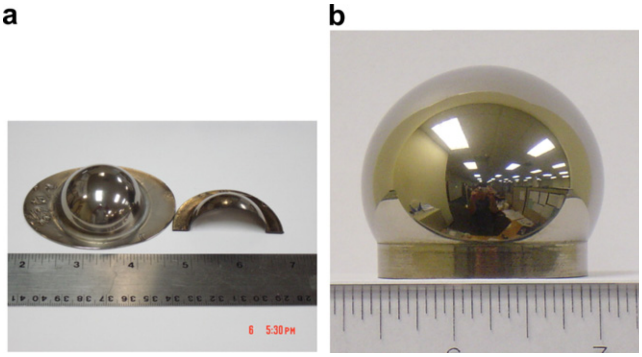

Figure 2. Free expansion of $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ using blow molding. (a) A 0.8-mm-thick $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ disk was formed through a circular opening of 4 cm at a temperature of 460 °C. The disk section covering the opening was formed into a hemisphere under a pressure exerted by the human lung of about 10^4 Pa. The forming process took less than 100 s (compared with the crystallization time at this temperature of 255 s [14]), which corresponds to a strain rate of $\dot{\varepsilon} \geqslant 10^{-2}\ s^{-1}$. (b) $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ disk with a diameter of 3.5 cm and a thickness of 0.8 mm was processed using a pressure difference of 2×10^5 Pa, which was applied for 40 s at a temperature of 460 °C. The achieved deformation corresponds to a strain of about 400% under a strain rate of 0.1 s^{-1}.