

# The Superplastic Forming of Bulk Metallic Glasses

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*Superplastic forming (SPF) is introduced in this article as a net-shape processing method for bulk metallic glasses (BMGs), commercially known as Liquidmetal® alloys. This method decouples fast cooling and forming of the BMG. Forming takes place in the supercooled liquid region, where the BMG exists as a highly viscous liquid and increases its fluidity with increasing temperature. The SPF method is very similar to techniques used for processing thermoplastics. In this work, a simple flow law is used to quantify the forming ability and to estimate both the potential and the limitations of the SPF method. This process is especially well suited to replicate small features and thin sections with high aspect ratios, which makes this process appropriate for microelectromechanical systems, nano- and microtechnology, jewelry, medical and optical applications, and data storage.*

## INTRODUCTION

During the last two decades, bulk metallic glasses (BMGs) have been discovered in a wide range of alloys.<sup>1–10</sup> The unique properties of BMGs, such as high strength, high specific strength, large elastic strain limit, and high corrosion resistance, along with unusual combinations of other engineering properties, make them interesting structural materials. Recently, BMGs were discovered that also exhibit a pronounced ductility.<sup>11,12</sup>

Most commercial applications of BMGs, such as electronic casings, medical devices, jewelry materials, and sporting goods, require a net-shape manufacturing process. Currently, for commercial applications, die casting is used as a net-shape process. Die casting, a common technique for net-shape

processing of metals, is subject to several limitations when used for the production of BMGs. Due to the metastable nature of the amorphous structure, BMGs must be cooled quickly to avoid crystallization. Conditions needed to obtain high-quality casts, on the other hand, are slow cooling and small temperature gradients. In a die-cast process, the liquid BMG must fill the entire mold cavity and at the same time be cooled fast enough to avoid crystallization. This makes casting of complex geometries (i.e., parts with thin sections and large aspect ratios) a challenging undertaking. In order to increase the fluidity during the casting process, the mold must be heated, which degrades the cooling efficiency. Only a very careful balance of processing parameters such as casting temperature, mold temperature and pressure, and mold design results in good quality casts.

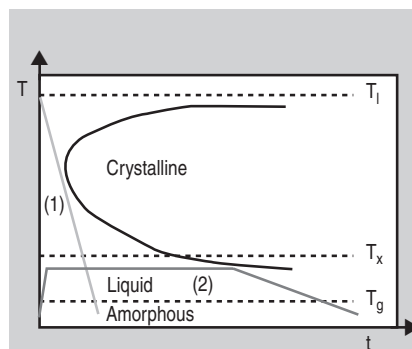


Figure 1. A schematic TTT diagram that shows the processing methods of (1) die casting and (2) superplastic forming (SPF). During die casting, the forming takes place simultaneously with fast cooling which is necessary to avoid the crystallization nose. (2) In SPF, the amorphous BMG is reheated into the supercooled liquid region where the available processing window is much larger than during die casting, resulting in better controllability of the process. This process does not require fast cooling to avoid crystallization during cooling.

The supercooled liquid region—the temperature region where the amorphous phase first relaxes into a highly viscous metastable liquid before it eventually crystallizes—is a manifestation of the extraordinary stability against crystallization of BMG alloys. This unique crystallization behavior permits an alternative net-shape processing method. The viscosity of the BMG in the supercooled liquid region can vary between  $10^{12}$  Pa s at the glass transition temperature,  $T_g$ , down to  $10^5$  Pa s<sup>13</sup> at the crystallization temperature,  $T_x$ , the high-temperature limit of the supercooled liquid region. Liquids with such viscosities can undergo substantial plastic strain under an applied pressure. Superplastic forming (SPF) of an amorphous BMG involves heating it into the supercooled liquid region and forming it under an applied pressure. The method is similar to processing of thermoplastics, where the formability, which is inversely proportional to the viscosity, increases with increasing temperature. In contrast to thermoplastics, however, the highly viscous BMG liquid is metastable and eventually crystallizes.

Crystallization of the BMG has to be avoided for several reasons. First, it degrades the mechanical properties of the BMG. From a processing point of view, crystallization limits the processing time for a hot-forming operation since the flow in crystalline materials is orders of magnitude higher than in the liquid BMG. Summarized in time-temperature-transformation (TTT) diagrams,<sup>14,15</sup> crystallization kinetics for various BMGs allow processing times between minutes and hours in the described viscosity range. This makes the SPF method a finely tunable process for BMGs that can be performed at convenient time scales, enabling the net-shaping of complicated geometries. Since similar processing

pressures and temperatures are used in the processing of thermoplastics, techniques used for thermoplastic processing such as compression molding, extrusion, blow molding, and injection molding might be applicable for the processing of BMGs.<sup>16</sup>

The ability to plastically form metallic glasses in the vicinity of  $T_g$  was recognized in the very early days of metallic glass research (see References 17 and

18). Inoue and co-workers were some of the first to notice that the described process can be used as a net-shape processing method for BMGs.<sup>19–22</sup> Initially, they focused on relatively simple features in the 500  $\mu\text{m}$  range and used Pd-Ni-Cu-P, a BMG with excellent glass-forming ability and a large supercooled liquid region. With very little applied pressure, this alloy could be formed into gear-shaped geometries. More recently, research was directed toward generating smaller features. Saotome, et al. used zirconium-based<sup>20</sup> and PtPd-based<sup>22</sup> alloys, and Pryds focused on magnesium-based BMGs<sup>23</sup> to replicate small features down to the submicrometer range. The ability to deform a BMG in the supercooled liquid region was also used to produce amorphous metallic foam<sup>24</sup> and to hot-isostatic press<sup>25</sup> and extrude<sup>26–29</sup> amorphous powder.

This article introduces SPF as a net-shape processing method for BMGs and discusses and quantifies its challenges and potentials.

### NET-SHAPE PROCESSING METHODS FOR BMGS

The processing conditions for SPF and die casting are shown in Figure 1 on a schematic TTT diagram. During die casting, the sample has to be cooled fast enough to avoid crystallization. This is indicated in Figure 1 by path 1, where the cooling curve does not intersect the “crystallization nose.” At the same time, the entire mold has to be filled. The cooling condition limits the filling time. Furthermore, during cooling the BMG’s viscosity rapidly increases, which drastically retards the filling of the mold.

In the SPF process, rapid cooling and forming are decoupled. To form the BMG it has to be in its amorphous state, which means that amorphous feedstock material has to be processed according to path 1. However, during this step the BMG alloy is not formed into its final shape but is cast into simple geometries such as cylinders, pellets, or powder. Since the production of powder or pellets allows for high cooling rates, bypassing the crystallization nose is trivial for most BMGs. Even the production of amorphous cylinders is less challenging compared to complicated geometries since no mold heating is required, which results in faster cooling. To hot-form the BMG it has to

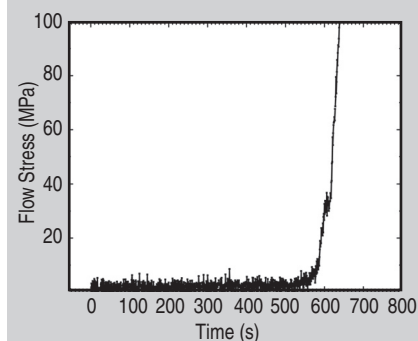


Figure 3. A flow-stress experiment to determine the flow stresses and processing time measured on  $\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$  (LM1b) BMG, which is deformed at a temperature of 445°C under a strain rate of  $10^{-2} \text{ s}^{-1}$ . The sharp increase in flow stress at approximately 550 s is due to the onset of crystallization. This means that LM1b can be formed for a maximum of 550 s at a temperature of 445°C.

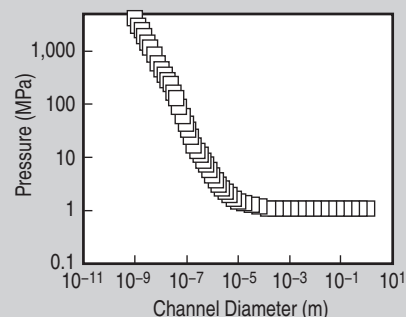


Figure 4. The required filling pressure for  $\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$  (LM1b), calculated according to Equation 3 for an aspect ratio  $L/d=5$  at a forming temperature of 460°C with a viscosity of  $9.8 \cdot 10^8 \text{ Pa s}$ , a processing time of 255 s, and a surface tension of 1 N/m. For large-diameter features, the influence of the surface energy contribution is negligible, but it becomes increasingly crucial for a feature size of less than 100  $\mu\text{m}$ .

be reheated into the supercooled liquid region where it is typically formed under isothermal conditions. This is indicated by path 2, where the amorphous phase relaxes into a highly viscous metastable liquid that can be formed under applied pressure. The processing window available through path 2 is much larger than that afforded by path 1, resulting in better control over the process. After forming and during cooling of the part, the avoidance of crystallization is trivial since the crystallization nose no longer has to be bypassed.

Figure 2 shows examples of BMG alloys that have been superplastically

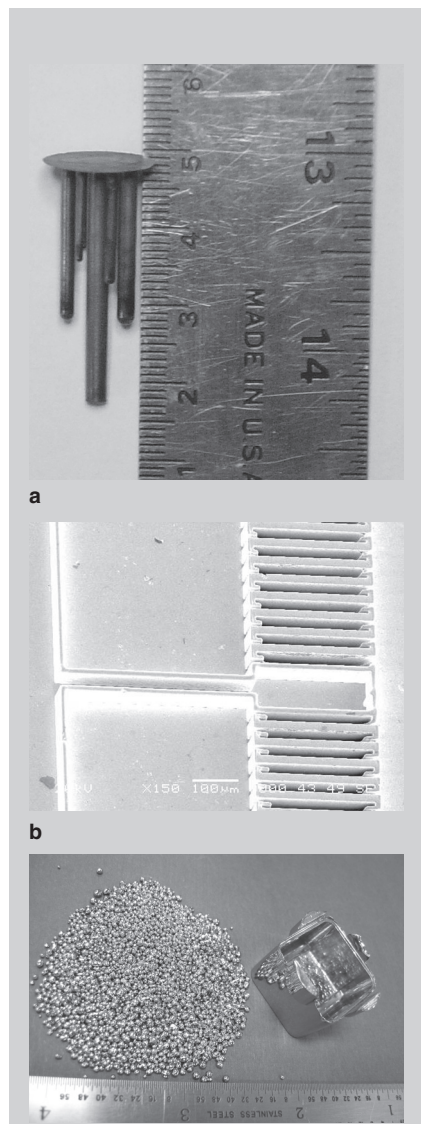


Figure 2. Examples of superplastically formed articles. (a)  $\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$  deformed at 460°C under a pressure of 10 MPa for 200 s. (b) Microfeatures replicated with  $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$  deformed at 260°C for 100 s under a forming pressure of 30 MPa. (c)  $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$  pellets that were used as feedstock material to form the part on the right-hand side. The part was formed at 260°C for 100 s under a forming pressure of 20 MPa. Note that the part is as-formed; overflow and flash are not removed.

formed into various geometries. Cylindrical-shaped feedstock material was used in Figure 2a ( $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ ) and Figure 2b ( $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ ). In Figure 2c,  $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$  pellets of about 1 mm in diameter were used. The samples were formed in air and maintained their amorphous structure after forming.

The required processing parameters for forming the BMG in its supercooled liquid region are determined by deformation experiments. This is shown in Figure 3, where a  $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$  (LM1b) BMG is deformed at a temperature of 445°C under a strain rate of  $10^{-2} s^{-1}$ . The flow stress can be determined from the measurement and can be correlated with the viscosity through  $\sigma_{flow} = \eta \cdot \dot{\epsilon}$  ( $\dot{\epsilon}$ : strain rate) for Newtonian liquids. At typical forming temperatures, BMG liquids exhibit Newtonian behavior at typical strain rates for SPF processing of  $10^{-2} s^{-1}$  or less (see Reference 30).

The other processing parameter is the maximum processing time given by the time to reach crystallization. The sharp increase in flow stress at approximately 550 s is due to the onset of crystallization, which means that LM1b can be formed for a maximum of 550 s at 445°C. Even though a strain-rate effect on the crystallization process of BMG-forming liquids can be expected in general, it should be negligible for strain rates typically used for SPF of  $10^{-2}$  or less.

The formability of a BMG in the supercooled liquid region can be quantified with the Hagen-Poiseuille-equation:

$$p = 16v \cdot \eta \cdot \frac{L}{d^2} \quad (1)$$

with  $p$  as the required pressure to move a liquid with viscosity,  $\eta$ , at a velocity,  $v$ , through a channel of thickness,  $d$ , and length,  $L$ . This equation assumes stick conditions (i.e., zero velocity of the liquid at the channel/liquid interface). The maximum time available for the forming process is given by the time to reach crystallization,  $t_{cryst}$ . In Equation 1, substituting  $v = L/t_{cryst}$  gives the maximum length that can be filled:

$$L = \sqrt{\frac{p \cdot t_{cryst} \cdot d^2}{16\eta}} \quad (2)$$

This filling length can be used to quantify the formability and to determine the opti-

imum processing conditions. It depends on both the viscosity and the filling time given by  $t_{cryst}$ . The filling length was calculated for LM1b, an ideal BMG for SPF with its large supercooled liquid region ( $\Delta T = 114^\circ C$ ).<sup>31</sup> Viscosity, crystallization time, and temperature data were taken from Waniuk, et al.<sup>32</sup> The filling pressure was taken to be 100 MPa. In the supercooled liquid region,  $t_{cryst}$  decreases with increasing temperature which results, according to Equation 2, in a reduction of the formability. On the other hand, the viscosity of a metallic liquid decreases with increasing temperature, leading to an increase in formability. For the filling of a channel, the decrease in viscosity is the dominant contribution, which can be concluded from the fact that the calculated filling length continuously increases with increasing temperature from 2.7 mm at 370°C to 21 cm at 510°C. This dramatic increase in formability with increasing forming temperature suggests that to obtain conditions of maximum formability the processing temperature should be as high as possible, as long as crystallization can be avoided during the forming process.

### MINIMUM SIZE LIMITATIONS OF THE SPF PROCESS

Small features are of particular interest for nano- and micro-applications,

microelectromechanical systems, data storage, and optical and medical devices. The ideal material for small geometries is BMG since it is homogeneous even on the nanoscale. This is due to the fact that no intrinsic limitation, such as the grain size in crystalline materials, is present. When considering small sizes, an additional pressure contribution resulting from the surface energy has to be taken into account. The pressure increase is given by  $p = 2\gamma/d$ , where  $\gamma$  is the energy of the liquid-vacuum interface. Considering this contribution to Equation 1 gives:

$$p = 16\eta \cdot v \cdot \frac{L}{d^2} + \frac{4\gamma}{d} \quad (3)$$

Equation 3 can be used to calculate the minimum feature size that can be hot formed for a given set of processing parameters. Figure 4 shows the required filling pressure for LM1b, calculated according to Equation 3 for an aspect ratio  $L/d = 5$  at a forming temperature of 460°C. A viscosity of  $\eta = 9.8 \cdot 10^6 Pa/s$ <sup>32</sup> and a typical value for the surface energy of metals, 1 N/m,<sup>33</sup> were used. For large-diameter features, the influence of the surface energy contribution is negligible, but it becomes increasingly crucial for a feature size of less than 100  $\mu m$ . To test the model's prediction, some SPF experiments were conducted. Figure 5 shows protrusions perfectly replicated by SPF of  $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$  at 270°C

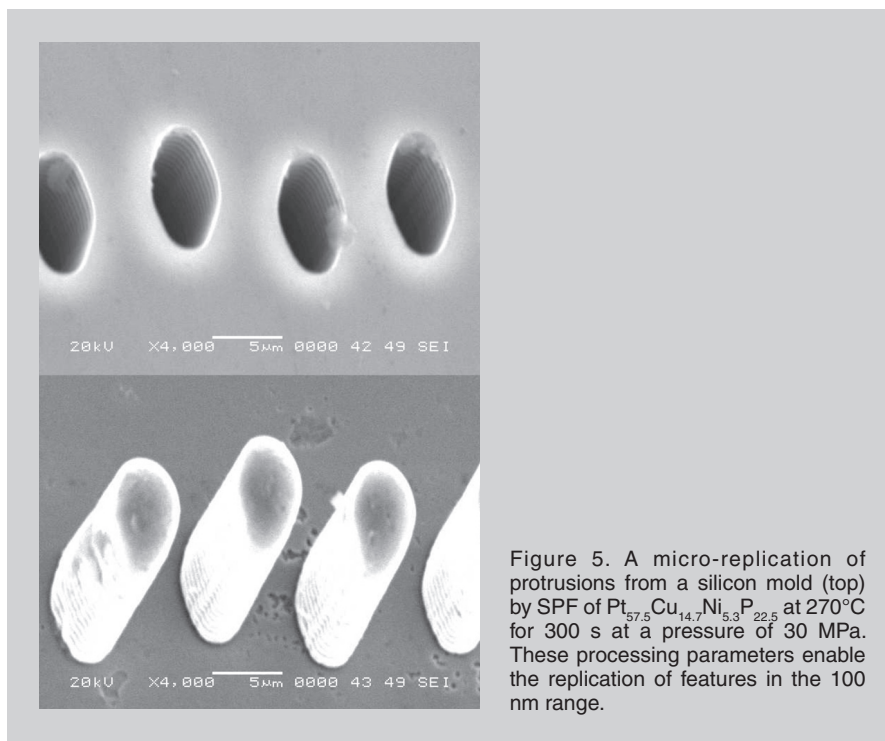


Figure 5. A micro-replication of protrusions from a silicon mold (top) by SPF of  $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$  at 270°C for 300 s at a pressure of 30 MPa. These processing parameters enable the replication of features in the 100 nm range.



for 300 s at a pressure of 30 MPa. The protrusions are 4  $\mu\text{m}$  thick and 12  $\mu\text{m}$  long. On the side of the protrusions, features of about 100 nm are replicated from the mold. This size fits the minimum feature size predictions shown in Figure 4. During SPF, a pressure on the order of 100 MPa, easily applied in this process, would result in the replication of features as small as 10 nm. Indeed, similar feature sizes were replicated with  $\text{Pt}_{48.75}\text{Pd}_{9.75}\text{Cu}_{19.5}\text{P}_{22}$  by Saotome, et al.<sup>22</sup>

## A COMPARISON BETWEEN SPF AND DIE CASTING

Superplastic forming of BMGs is, in many ways, an ideal processing method.

Since it is done isothermally and the subsequent cooling can be rather slow, thermal stresses can be reduced to a negligible level. Stresses or porosity resulting from solidification shrinkage are also much smaller than in other metal processing methods. Solidification shrinkage in crystalline materials originates from both thermal contraction and phase-transition shrinkage. The latter accounts for about 5% in typical casting alloys. The absence of a phase transition during solidification of BMGs thus dramatically reduces solidification shrinkage. LM1b, with an approximate thermal expansion coefficient of 5  $\mu\text{m}/\text{m}^\circ\text{C}$ ,<sup>34</sup> experienced approximately

0.4% solidification shrinkage during casting. During SPF of the same alloy, the shrinkage is only 0.2%.

The SPF process is very robust. This stems from the fact that the crystallization in the supercooled liquid region is a well-determined, growth-controlled process, in contrast to the crystallization mechanism at high temperatures<sup>15,35</sup> which defines the processing window for die casting. It was demonstrated that in BMG-forming liquids, at high temperatures crystallization is nucleation controlled, and its statistical nature only allows the use of a crystallization probability as a process parameter.<sup>15</sup> Typically, the upper part of the TTT diagram represents the average time to reach crystallization, and each individual crystallization event can deviate from this time considerably.<sup>15</sup> The statistical nature of the crystallization process can result in uncontrolled crystallization, making quality control an important issue for die casting. On the other hand, SPF basically eliminates the risk of unpredictable crystallization due to the deterministic nature of the crystallization process in the temperature region where SPF is performed.

For various BMGs, a strong dependence of the glass-forming ability on the oxygen content was observed.<sup>36–39</sup> At temperatures above the nose of the TTT diagram, the influence of the oxygen content is most pronounced, whereas at temperatures below the nose, where SPF takes place, the oxygen content has only minor influence on the crystallization kinetics.<sup>37</sup> This enables SPF to be carried out for most BMGs in air. Die casting, on the other hand, has to be carried out in vacuum or in an inert environment because the presence of oxygen reduces the processing time and even slight variations in oxygen content can have drastic effects on the crystallization kinetics.

For most geometries, the filling of the mold cavity is less challenging in an SPF process than it is for die casting. This is, to a large extent, due to the fact that the SPF process decouples fast cooling and forming, forming is carried out under isothermal conditions, and the processing window for SPF is orders of magnitude larger.

The degree of porosity in die-cast parts scales with the complexity of the geometry of the part. The feedstock

### DESIRABLE BMG PROPERTIES FOR SPF

From a processing point of view, a supercooled liquid region in which a material can exhibit a small flow stress is desired for superplastic forming (SPF) of bulk metallic glasses (BMGs). Alloys with a large supercooled liquid region provide lower processing viscosities. The glass-forming ability, a property of crucial importance for casting of BMGs, is of lesser importance. In some systems, a positive correlation between the glass-forming ability and  $\Delta T$  is found<sup>40,41</sup> whereas in other systems good glass-forming ability is accompanied by a small  $\Delta T$ .<sup>31,42</sup> As a rule of thumb, for zirconium-based BMGs, the viscosity in the supercooled liquid region decreases by an order of magnitude for every 20°C temperature increase. This results in an order of magnitude increase in formability, or in other words, an order of magnitude increase in  $L$ , according to Equation 2. In the literature, a large  $\Delta T$  is often associated with good formability of the BMG.<sup>43,44</sup> However,  $\Delta T$  should be normalized to the width of the undercooled liquid region,  $T_l - T_g$  ( $T_l$ : liquidus temperature;  $T_g$ : glass transition temperature), especially when comparing

the formability of different alloy systems. The parameter  $S = \frac{\Delta T}{T_l - T_g}$  shows better correlation with the formability, even though the assumption of identical viscosity at  $T_l$  is an oversimplification.<sup>34</sup>

The  $S$  parameter also does not consider the temperature dependence of the viscosity, which can be described within Angell's fragility concept.<sup>45</sup> Strong liquids show nearly Arrhenius behavior (i.e., a straight-line dependence of  $\log(\eta)$  on  $1/T$ ), whereas fragile liquids have a low viscosity at  $T_l$ , which raises sharply close to  $T_g$ . This behavior makes fragile BMG liquids highly desirable for the SPF process,

since for the same  $\frac{\Delta T}{T_l - T_g}$  value a fragile liquid exhibits a lower viscosity.

Another property that is desirable from a processing point of view is a low  $T_g$ . A low  $T_g$  implies a low processing temperature since it facilitates processing. No expensive high-vacuum equipment is required to reduce oxidation. Production costs are further reduced as a consequence of a low  $T_g$  by minimizing heating and cooling cycles and thermal cycling of the mold, which limits the mold life. Among various BMGs,  $T_g$  varies between ~550°C for iron-based BMGs,<sup>9</sup> ~350°C for zirconium-based BMGs,<sup>6,31</sup> ~300°C for palladium-based BMGs,<sup>3</sup> ~230°C for platinum-based BMGs,<sup>7</sup> down to ~130°C for gold-based BMGs.<sup>10</sup>

Heating some zirconium-based amorphous BMGs into the supercooled liquid region was found to result in a dramatic reduction of the fracture toughness.<sup>46,47</sup> This behavior would prevent such a BMG from being used in the SPF process. Even though the embrittlement is not fully understood, it was found that a slight composition change can prevent such behavior. For example, after changing the composition from  $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$  to  $\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$ , the fracture toughness is no longer affected by reheating into the supercooled liquid region and the supercooled liquid region even increases from 65 K to 114 K, respectively.<sup>32</sup>

material used for SPF is cast in very simple geometries. Any existing porosity in the feedstock material is dramatically reduced during SPF. If, for example, a feedstock material with 2% porosity and pores of 10  $\mu\text{m}$  or larger is formed under a pressure of 200 MPa, the porosity after SPF is reduced to 0.001%.

The maximum dimensions of a die-cast part (in its smallest dimension) are dictated by the critical casting thickness. Size restrictions in SPF are more relaxed. The geometry of the feedstock material can be substantially altered during SPF. More dramatically, powder or pellets can be used as a feedstock material, by which any size limitations are eliminated. This not only allows for the production of BMG parts exceeding its critical casting thickness, but opens up the opportunity to choose from a larger pool of BMGs in order to find an optimal combination of materials properties and costs.

The main disadvantage of SPF over die casting is that an additional processing step is required. This results from the decoupling of cooling and forming in the SPF process, both of which are performed simultaneously during die casting. While the additional processing seemingly adds to production costs, the combined advantages of this process, as discussed previously, still may result in lower overall production costs. See the sidebar for details on desirable BMG properties for SPF.

## CONCLUSION

The large resistance of some bulk metallic glasses to crystallization results in a supercooled liquid region that is accessible on a convenient time scale for processing. This allows for a net-shape process, where the BMG behaves like a plastic and similar processing methods can be used. During superplastic forming of BMGs, fast cooling, required to maintain the amorphous structure during solidification, and forming are decoupled. This results in a robust process that produces high-quality parts

with low porosity and high dimensional accuracy. An ideal BMG for SPF would be identified by a large S parameter, fragile liquid behavior, no embrittlement during heat treatment, and a low  $T_g$ .

The combinations of processing advantages suggest that SPF has the potential to replace die casting as a net-shape processing method for BMGs and might even lead to new applications for the use of BMGs.

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