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Steady-state tensile viscous flow forming of bulk metallic glass

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ABSTRACT

Tensile viscous flow is explored as a forming method for metallic glasses in their supercooled liquid temperature region. Bulk amorphous preforms with nominal alloy composition $Zr_{55}Cu_{30}Al_{10}Ni_5$ were produced by arc melting and tilt- and suction casting into a copper mould. A simple loading rig, in which the preform is suspended from a wire, combined with selective heating of the section to be deformed, avoids the need for complicated loading grips. Different strategies are evaluated to attach the sample to the rig and to selectively heat the central part of the specimen.

Finite element models were compared with experiments to verify the design of the induction heating coil and optimize process parameters. Differential scanning calorimetry and X-ray diffraction measurements show that the material is glassy before and after deformation. The rapid decrease of flow stress with increasing temperature means that the process can be controlled thermally at constant load instead of mechanically at constant temperature. An asymmetric configuration, where the selective heating zone is moved relative to the specimen during the deformation, allows to form rods into wire by a steady-state process. The effect of deformation on induction heating under constant tension was found to be inherently self-stabilizing, reducing the need for precise process control.

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1. Introduction

Bulk metallic glasses are amorphous metals, with a diameter larger than 1 mm, that have solidified without detectable crystallization. Upon heating from the solid state these alloys exhibit a glass transition, after which they remain metastable for a finite length of time in the super-cooled liquid region, before crystallizing. Increased stability against crystallization is usually achieved by alloying multiple elements with significant difference, greater than 12%, in atomic radius and negative heats of mixing among constituent elements [1].

The critical casting diameters of known BMG alloys typically range from 1 mm to several centimeters. BMG alloys have been found in many different alloy groups (Pd-, Mg-, Ln-, Zr-, Ti-, Fe-, Co-, Ni- and Cu-based systems) and new alloys have been discovered and reported with a variety of different properties. Complex shapes can be produced, with excellent mechanical properties in the as-cast stage: purely elastic deformation up to a yield strain of typically 2%, resulting in reported tensile or compressive strengths of 1500–5500 MPa, with Young's modulus of 70–275 GPa [1]. Accurate dimensions and surface finish can be achieved with BMG materials, due to the uniform shrinkage during solidification and the lack of grain boundaries. Several recent reviews testify to the

widespread interest in these materials both from a fundamental science perspective and for practical applications [1–3].

For practical applications, it is often necessary to form application specific shapes, such as wires. In general, the final shape in metallic glasses is obtained either during solidification from a molten state directly, or by reheating a glassy preform to allow thermoplastic forming [4]. Thermoplastic forming processes that have been successfully carried out with bulk metallic glasses include imprinting [5–8], extrusion [4], injection molding [9], friction welding [10], manipulation with forceps [6] and blow molding [11]. Usually the reheating process is limited to a temperature much lower than melting temperature to avoid crystallization. However, in some cases, with very high heating speeds, temperatures above melting temperature have also been achieved [12].

Previously reported metallic glass wire forming methods, operating directly from melt, use a rapidly spinning disk that comes into contact with arc-melted glass forming alloy melt [13,14]. Alternatively, the melt is poured onto a spinning disk with suitably sized groove for thicker wire formation [15]. The use of thermoplastic forming for metallic glass wire production is reported relatively seldom [16,17].

Thermoplastic forming of metallic glass is seen as a promising method for producing shapes that are difficult or impossible to cast. By decoupling the casting process from the final shaping, the cast specimen can be relatively simple to produce compared to the final shape. In practice, the preform material is alloyed and cast normally into a metallic glass by metal mold casting. Then, in the

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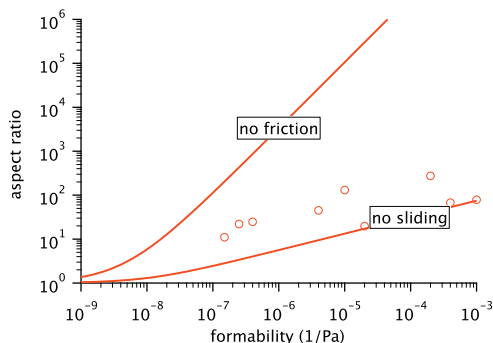


Fig. 1. Theoretical limits [19] to thermoplastic forming (solid lines) for flattening of cylindrical specimens with a force of 4450 N under constant heating at 20 K min⁻¹, and corresponding experimental data [18] for different alloys with different figures of merit for formability (open circles).

thermoplastic forming step, the cast sample is reheated between T_g and T_x temperatures, where a larger forming time is available before crystallization than in direct casting. The amount of thermoplastic deformation that can be achieved in constant heating of metallic glass, before crystallization puts an end to further deformation, depends on the alloy. It can be characterized by the figure of merit [18]

$$F = \frac{1}{3(\partial T/\partial t)} \int_{T_g}^{T_x} \frac{1}{\eta(T)} dT \quad (1)$$

where η , T_g and T_x are viscosity, glass transformation temperature and onset temperature of crystallization, respectively. However, as shown in Fig. 1, even for alloys with good formability the amount of deformation that can be achieved in constrained flow is limited. In fully constrained flow, such as injection molding into a long and narrow mold, the friction of the alloy surface against the mold wall requires shearing inside the alloy for continued deformation. In unconstrained flow, such as blow molding [11], the absence of metal-mold friction allows the material to deform by nearly uniform extensional flow, and much larger aspect ratios can be manufactured.

Here the idea of a simple setup for unconstrained thermoplastic forming of bulk metallic glass in uniaxial tension [17] is developed further. Through selective heating of that part of the material that is to be deformed, the temperature dependence of the viscosity of glass-forming alloys can be exploited to allow high mechanical stress in parts of the material that should not deform. In particular, this allows drastically simplified construction of the end grips for a tensile specimen. Furthermore, induction heating and convective cooling conspire to automatically switch from net heating to net cooling as a result of tensile deformation.

Ideally there is a balance between:

- The amount of heat that is extracted via convective cooling: the thinner the material at a given cross-section the more rapidly it cools (Newton's law of cooling).
- The amount of heat that is brought into a cross-section: the thinner the cross-section, the less it heats up from inductive currents. Excess heating must be avoided, as it leads to crystallization of the feedstock, which rapidly stops the wire pulling process.
- The amount of heat that is extracted along with the material making up the wire as it is pulled out of the deformation zone.

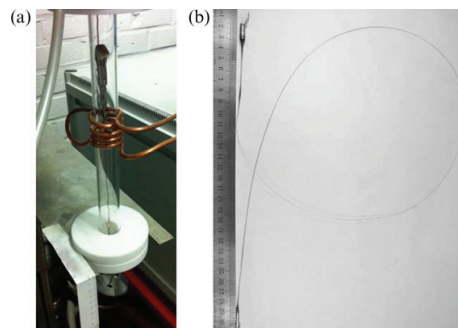


Fig. 2. (a) The constructed wire pulling apparatus. The preform specimen in the fused quartz chamber contains 20 mm long segments of 10, 7, 5, 3 and 1 mm diameters, and can be made without machining steps. Here this specimen type can only be used because the bucking coil prevents the top of the specimen from heating too much before the wire production begins from the smaller diameter portion. The wire production begins from the 5 to 3 mm diameter step similarly as if a specimen shown in Fig. 4b was used. (b) An example of produced glassy wire.

It is expected that when a balance between these factors is achieved, the process is essentially self-stabilizing. This allows a thermoplastic forming process for producing metallic glass wire without the need for high-vacuum chamber or high-end instrumentation. In addition, the induction heating and the preform geometry can be designed to minimize the number of process steps required. Preliminary experiments can be complemented by finite element calculations to evaluate suitable specimen geometries for different induction coils.

2. Experimental procedures

The Zr₅₅Cu₃₀Al₁₀Ni₅ (in at.%) bulk metallic glass specimens were prepared by copper mold casting. Alloy constituents for the target composition of Zr₅₅Cu₃₀Al₁₀Ni₅ (in at.%) were weighed from the elements with purity (in mass%) of 99.999% for Cu, and 99.99% for Zr(+Hf), Ni and Al. The cut and weighed pieces were melted and cast in a custom built combined arc melting and tilt casting furnace, under reduced pressure titanium gettered argon atmosphere, with the same process parameters as reported in more detail elsewhere [20].

The X-ray diffraction (XRD) patterns were measured with a Siemens Kristalloflex 710H X-ray generator and Inel CPS-120 position sensitive detector. A Netzsch STA 449F1 was used for the DSC measurements with 20 K min⁻¹ heating rate. The finite element modeling calculations were done with COMSOL Multiphysics 4.1.

The constructed forming apparatus, shown in Fig. 2a, consists of a fused quartz tube and two end pieces. At the upper end piece there is a connection for helium gas, which is used both to increase the convective cooling rate and to protect the deforming specimen from excess oxidation. The upper end piece includes a hook from which the specimen is suspended by a copper wire, and the lower end piece has an opening for a second copper wire which is used to pull the metallic glass specimen, until the formed metallic glass wire is pulled through the opening and the metallic glass wire can be pulled directly. A nominally constant force is applied by suspending a mass of 0.2 kg from the second wire. It should be noted that the ends of the specimen where the copper wires are attached must remain colder than the part of the specimen to be deformed, otherwise the copper wire is pulled out of the specimen instead of deforming the specimen. This is achieved by locally heating the part of the specimen to be deformed, using induction heating with an appropriate combination of specimen geometry and induction coil geometry. The apparatus is held in place by a support mechanism, which allows the induction coil to move up and down during the process, in effect gradually feeding the specimen into the induction coil.

Two induction coils were tested. One is regular solenoidal coil, with all loops conducting current in the same direction. The other coil, shown in Fig. 2a, is a bucking coil where the highest loop conducts current in the opposite direction of the lower loops. Depending on the induction coil used, different specimen geometries were required to successfully focus the induction heating. In the symmetric set-up with the regular solenoidal coil, the specimens are straight cylinders with slots machined into the ends and holes drilled to attach the wires. Starting from an as-cast cylinder, producing a specimen in this geometry, which is shown in Fig. 4a, required up to six machining steps. In contrast, specimens for the asymmetric set-up with the bucking coil are cylinders with a step change in diameter but no slots. This geometry, the relevant part of which is shown in Fig. 4b, was produced directly by copper mold casting. As can be seen in Fig. 2a, the actual

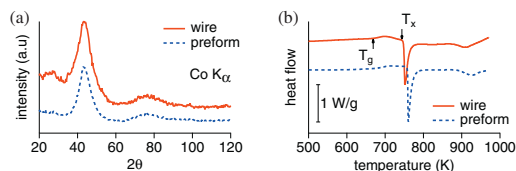


Fig. 3. (a) X-ray diffraction (Co K_{α}) patterns of drawn wire and preform, showing amorphous structure. (b) Differential scanning calorimeter (DSC) measurements of drawn wire, with its glass transition and crystallization temperatures $T_g = 668.6$ K and $T_x = 748.6$ K marked by arrows, and of a preform.

mold has several step changes in diameter. The need for drilling the gripping holes in the asymmetric set-up was avoided by placing the copper attachment wires into the mold prior to casting, and casting the metallic glass around them.

3. Experimental results and discussion

The amorphous structure of glassy as-cast preforms can be demonstrated [21] by combination of X-ray diffraction and differential scanning calorimeter (DSC) measurements. Fig. 3 shows a comparison of such measurements between a sample of one of the produced wires and a glassy preform, indicating that the thermal stability of the thermoplastically formed wire is reduced from the as-cast specimen— T_x is 10 K lower—whereas the diffraction patterns and the heats of crystallization do not differ significantly.

Two methods were tried for tensile viscous flow forming of copper mold cast $Zr_{55}Cu_{30}Al_{10}Ni_5$ preforms with induction heating, and both methods worked in practice. In the first method (symmetric set-up) the focusing of the induction heating was achieved by machining the preform specimen so that the inductive currents heated the middle of the specimen preferentially, as shown in Fig. 4a. In the second method (asymmetric set-up) the focusing

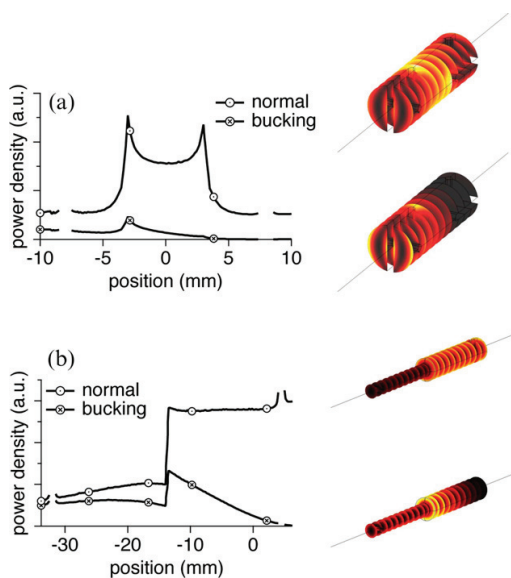


Fig. 4. A comparison of calculated power loss densities per sample length, with and without using a bucking coil, for both of the tested wire drawing preform geometries: (a) 7 mm cylinder with holes for attaching it to the wire drawing rig and slots cut into the ends to reduce the heating of the sample ends, where the bucking coil is not needed; and (b) specimen with step change in diameter from 5 to 3 mm, where the lower portion heats less because its diameter is smaller, and use of a bucking coil reduces heating of the upper end.

of the induction heating was accomplished with the use of smaller diameter at the lower end and by the use of a bucking coil in the upper end of the preform. This asymmetric set-up leads to a steady state, where high temperatures and thermoplastic flow remain essentially limited to the deformation zone, which is slowly moved up along the feedstock while newly formed wire is extracted from below. Examples of the successful asymmetric set-up are shown in Fig. 4b and in Fig. 2a. Notably in Fig. 2a the as-cast specimen was used as preform, without further machining steps.

Finite element modeling was used to evaluate the focusing of the induction heating using both approaches. A finite element model used in [17] was further developed to evaluate the various schemes to focus the induction heating away from the sample suspension wires. Experimentally, failure to focus the induction heating away from the sample grips was found to result in metallic glass wires of limited length and non-uniform, highly elliptical cross-section, where the attachment wires are pulled out of the specimen. Machining slots at both ends of the specimen—as shown in Fig. 4a—reduces the coupling of the ends of the specimen to the magnetic field of the induction coil, thereby focusing the electromagnetic power loss density, i.e., the induction heating effect, in the central part of the specimen. This is a workable solution, although it involves rather extensive sample preparation. The second approach, using a combination of using a bucking coil and a smaller diameter lower part sample, avoids the need to machine the slots at the ends of the sample. Fig. 4 shows the effect of using the bucking coil on the electromagnetic power loss density, and the effect of changing to a 40 mm long, 5–3 mm diameter sample. As shown in Fig. 4b, the combination of the bucking coil and the asymmetric sample focuses the induction heating effect near the step change in diameter, on the larger-diameter side, as desired. This observation is quantified in a plot along the length of the specimen, of the electromagnetic power loss integrated over the cross section and divided by the area of the cross-section. Thus, both approaches are effective in focusing the induction heating effect in the central part of the specimen, but the asymmetrical set-up allows much simpler sample preparation.

Another difference between the two approaches, is the possibility in the asymmetric set-up to continue the process by feeding more of the specimen into the induction coil. Because a steady state can be achieved, where a larger-diameter rod is continuously fed into the process zone and a smaller-diameter wire is continuously pulled out, producing wires of essentially unlimited length may be possible via this method; as long as the preform does not run out and does not crystallize, the process can continue indefinitely. As a result of the effect of wire diameter on the balance between inductive heating and convective cooling, and the effect of temperature on viscosity, the process is self-stabilizing both for mechanical and thermal perturbations. Issues of process control to control the diameter and thermal history of the thermoplastically formed wire, as well as the stability of dynamic perturbations are topics for further research. The effect of the force used to draw the wire was qualitatively analyzed by continuing to pull the wire by hand after the 0.2 kg weight had dropped the available 0.5 m height. The produced wire thickness was found to be very sensitive to the amount of force used, which could enable the tailoring of wire thickness profiles by changing the force and speed of the pulling during the process. Wires with such tailored thickness profile could be useful as non-linear springs, benefiting from the excellent spring properties of bulk metallic glasses [22].

4. Conclusions

Two methods were tried for tensile viscous flow forming of copper mold cast $Zr_{55}Cu_{30}Al_{10}Ni_5$ preforms with induction heating,

and both methods worked. The glassy microstructure of the drawn wire was verified with XRD and DSC measurements. Finite element simulation was used to evaluate the performance of the induction heating and specimen geometries.

In the first method (symmetric set-up) the focusing of the induction heating was achieved by machining the preform specimen so that the inductive currents heated the middle of the specimen. In the second method (asymmetric set-up) the focusing of the induction heating was accomplished by using preforms with smaller diameter at the lower end, in a bucking coil which minimizes heating in the upper end of the preform. The preforms used for the asymmetric setup are simpler to produce than those required for the symmetric set-up. Furthermore, the asymmetric set-up offers the possibility to continue the wire forming process indefinitely in a steady state, as long as the preform does not crystallize and the preform does not run out.

Unlike other glassy wire production methods, this method allows some real time control over the produced wire diameter, which can be very useful for the production of non-linear glassy springs. The presented asymmetric test set-up may also have some potential as a method to characterize thermoplastic forming behavior of different metallic glasses, if more instrumentation is added to monitor the temperature profiles and a more comprehensive numerical model is constructed to relate the resulting thickness profile to the material parameters.

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