Shaping of Bulk Metallic Glasses by Simultaneous Application of Electrical Current and Low Stress

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ABSTRACT

Using the intrinsic materials properties of bulk metallic glasses (BMG), namely electrical resistivities two orders of magnitude higher than good conductors and a Newtonian viscous-flow regime of deformability, a new electromechanical process has been developed for shaping, joining and engraving of BMGs. The wider the liquid supercooled region between the glass transition temperature $T_g$ and the crystallisation temperature $T_x$ of the bulk metallic glass, the easier the application of the new process. In this range, the undercooled liquid deforms in a quasi-Newtonian way, allowing thermomechanical shaping in the low viscosity range as for oxide glasses. The new electromechanical processing technology has been used for economical and rapid shaping at low applied stresses by eliminating the thermal mass of the furnace and the need to heat the deformation dies. The process parameters are adaptable for the full maintenance of the glassy state or when desired, for appropriate compositions, for nanocrystallisation during the joining or shaping operation.

INTRODUCTION

The first bulk metallic glasses were Pd-based alloys developed by the team of David Turnbull at Harvard in the early 1980s (see for example [1]). With thicknesses of about 3 mm, PdNiP-type glass demonstrated that the previous thickness limits were surmountable but did not attract much attention due to the high cost of palladium. The real breakthrough came from 1989 onwards when A. Inoue discovered multicomponent liquid alloys with very deep eutectics capable of freezing to a glassy state several mm to several cm thick by conventional cooling such as in copper die casting (for a review, see [2]). Beginning with La- and Mg-based quaternary alloys, Inoue extended BMG formation to Zr, Fe, Ni and other alloy families. W.L. Johnson et al. developed ZrTi-based BMGs with up to 25% beryllium [3-4] and other thick glassy alloys.

Bulk metallic glasses have been proposed for a range of applications that include dies, ornaments, solders (deep eutectic compositions), electrodes, medical and dental implants and tools, bullet-proof jackets, tank armour perforators, coatings and more. Fe-based BMGs have saturation magnetisations up to 1.3 T (which is in the application range) together with very high permeabilities (see for example [5]) and can be introduced in ring-shaped form into small motors. Due to their 2% elastic strain range (as compared to 0.2% for crystalline materials), BMGs currently have the best known values for the Ashby performance index $\sigma^2/E$ (where $\sigma$ and $E$ are the yield strength and Young’s modulus). High values of this performance index (reversible storing of elastic energy) open applications in sporting goods materials (golf clubs, skis, other high elasticity equipment), cutting, writing, punching and printing tools, springs, gears for micromachines (MEMS parts). Elastic limits are higher than high performance steels giving high toughness values inspite of plastic instability under tension. BMGs show low...
shrinkage in mold casting, high impact resistance, promising tribological and wear properties, low surface roughness and high resistance to stress corrosion and hydro-thermal corrosion (no grain boundaries). Given these potential applications, technologies for their shaping, assemblage and other manipulations are important and possibly determining for their future use.

TECHNOLOGICAL APPROACHES TO SHAPING OF BULK METALLIC GLASSES

In addition to metallic hardness and toughness, BMGs have the formability of polymers in their supercooled liquid region’s temperature window $\Delta T$ between the glass transition and the crystallisation temperatures $T_g$ and $T_x$ respectively. This “superplastic” range can be used to create various shapes such as reported in [6].

As early as 1978, S. Kavesh and G. R. Bretts [7] proposed welding of glassy metallic materials using Joule heating but at that time available glass forming compositions required very high critical cooling rates and their approach strictly specifies that at least 90% of the energy is delivered in less than about $4 \times 10^{-3}$ seconds and requires extracting heat from the welding bodies through the electrodes at a cooling rate at least about $10^3 \degree C/$second. Their approach may have been inspired by previous experiments on crystalline materials. However, deformation of metallic glasses is fundamentally different because of the absence of the crystalline lattice and Nabarro-Herring creep. In addition, while the resistivity of crystalline metals increases monotonously with temperature, that of glassy alloys drops sharply with crystallisation thus sharply modifying the Joule power as will be discussed later. In the early 1990s, Ballard et al [8] proposed the application of electrical current heating for hot shear, severing or cutting of amorphous alloy ribbons and ribbon stacks. However they made no mention of joining and assemblage above $T_g$ perhaps due to their primary concern with FeSiB-type electrical sheets (usually with no $T_g$).

Horimura [9] and Pekker et al [10], citing the work of Kawamura et al [6], proposed production of die-formed amorphous metallic articles such as golf club heads[10] by thermomechanical processing at temperatures between $T_g$ and $T_x$. However, the nature of thermomechanical shaping in the supercooled liquid region requires intimate contact between the BMG specimen and the shaping dies. This generates a large thermal mass that must be controlled closely in order to avoid crystallisation during shaping. More specifically, thermal shaping requires the heating and cooling of the BMG specimen as well as the deformation equipment, with the ensemble usually placed into a furnace. Thus the heating and cooling cycles are rather long while the time allowed to stay in the supercooled region before the onset of crystallisation is limited. This time can be prolonged by holding isothermally just above or at the glass transition temperature $T_g$ but in this case the glass’s viscosity will be higher and the shaping will require higher stresses thus requiring more expensive equipment and processing. If the shaping could be done well above $T_g$ but below $T_x$, shape changes could be achieved much faster but this requires the ability to heat up, deform and cool quickly. The possibilities and limits of conventional shaping of BMGs may be deduced from studies such as ref. [6].

ELECTROMECHANICAL PROCESSING OF BULK METALLIC GLASSES

This process introduces the use of Joule heating instead of conventional heating methods in the mechanical shaping of BMGs [11]. It may thus be referred to as electromechanical shaping instead of thermomechanical shaping.

Contrary to conduction, convection or radiation heating, Joule heating does not require heat transfer from the heat source to the specimen to be heated. Instead, the heat is generated directly
in the specimen by the passage of electrical current. Induction heating using high or radio frequency alternating magnetic fields also generates the heat directly in the specimen but is more difficult to apply as it also heats neighboring metallic pieces such as dies or press parts etc.

Our Joule heating technique takes advantage of the high electrical resistivity $\rho$ of bulk metallic glasses which are close to those of liquid alloys and of the order of 150 or 200 $\mu\Omega\cdot$cm. Current brought in by a good electrical conductor (electrode) in contact with the BMG will heat the BMG quickly but the electrode itself will not be heated much because it has a low electrical resistivity such as that of copper or copper-based alloys, of the order of 2 to 10 $\mu\Omega\cdot$cm. For equal dimensions of such materials, the power generated by a fixed current $I$ scales with the resistance $R$ equal to $\rho \cdot \frac{L}{S}$ where $L$ is the conductor’s length in the current flow direction and $S$ its cross-sectional area perpendicular to the current.

The external surfaces of the BMG specimen being shaped, whether in contact with the electrodes or with the ambient (inert) gas in the shaping chamber, will be slightly cooler than the inside as the heat generated by the current dissipates out of the sample by conduction, convection or radiation. On the other hand, the outer surfaces of samples heated by conduction, convection or radiation are slightly hotter than the inside. This is an important advantage for the present method as crystallisation and or oxidation of metallic glasses often begin first on outer surfaces and interfaces and if they are slightly below the temperature of the bulk, such undesirable surface crystal formation may be more easily avoided.

A particular advantage of electromechanical shaping of BMGs is that the copper or otherwise high-conductivity electrodes that supply the current and therefore the heat are also sinks for the same heat once the specimen is to be cooled after shaping. As soon as the current intensity drops or is interrupted, cooling will occur by heat flow from the shaped BMG sample into the cooler electrode mass. This procedure therefore allows both fast heating and fast cooling and the thermal mass to be heated and cooled is limited to the mass of the BMG sample and not the deformation or electrode equipment. This will allow the glass to be shaped faster at higher temperatures without crystallisation and using much lower applied loads and stresses intrinsic to thermomechanical shaping.

In addition, in many of our experiments, the electrode material is also the die or the part that applies the load to the BMG sample in order to change its shape. This is possible because in their superplastic supercooled liquid regime between $T_g$ and $T_x$, BMGs are softer than the electrode materials (such as copper and copper alloys). The latter can in addition be cooled by water cooling or otherwise in order to increase their temperature difference with the BMG sample during cooling after shaping.

The present process of application of moderate stresses during Joule heating has been successfully applied [12] for electromechanical shaping, electromechanical joining to form complex shapes, welding, electromechanical engraving, writing-ability or complex net-shaping, electromechanical shaping into BMG-based composites and electromechanical glass coating.

There are couplings between the sample shape and the Joule heating power, the power and the sample temperature, the temperature and the sample viscosity, the viscosity and the sample mechanical properties such that for many applications, the sample cools down and hardens at the desired shape for an appropriate choice of initial current.

The key parameter is the Joule power per unit volume $p = \frac{P}{v}$ where power $P = V \cdot I$ for voltage $V$. At steady state, $p$ would determine sample temperature due to trade-off between Joule heating and heat loss mainly by conduction through the contact surfaces. Since $P = R \cdot I^2 = \rho \cdot \frac{L}{S} \cdot I^2$, and for a simple shape volume $v = L \cdot S$, the specific power $p$ can be written as

$$p = \rho \cdot (\frac{I}{S})^2$$

(1)
In a shaping process that increases the contact surface such as crushing by the electrodes, $S$ increases as the sample undergoes deformation with strain given by $\varepsilon = \ln(S/S_0)$. In such cases the specific heating power decreases with increasing deformation with $S^{-2}$ while heat loss to the electrodes increases with $S$. Thus application of a fixed selected initial current, $I$, can heat the sample under load, produce a desired shape change which, in turn, will lead to sample cooling. As the sample cools, its viscosity increases sharply such that further deformation ceases. Thus the process is well adapted to industrial automation for fabrication of parts.

Another important application of the process is for simultaneous shaping and nanocrystallisation of bulk metallic glasses. It has been established that selected bulk metallic glass compositions can be heat-treated to a mixed nanostructure of nanocrystalline particles in a residual amorphous matrix. In several cases it has been shown that this type of reaction leads to improvement of mechanical properties provided that the nanoparticle volume fraction is limited [13] such that they do not percolate. Development of these new nanostructures is a task well suited for electromechanical processing because in addition to the previously mentioned automation possibilities, percolation of the nanocrystals will lead to a sharp drop in the resistivity and the resistance of the bulk metallic glass and hence a decrease of specific heating power $p$. (see figure 1). In addition, such percolation modifies the flow behaviour away from Newtonian viscous. Thus nanocrystal formation will lead to a power decrease and cooling as well as hardening and the cessation of the deformation.

In the present paper we will give examples of connecting amorphous pieces and mounting assemblies of amorphous and non-amorphous pieces. Consider two bulk metallic bars, each 10 mm long and 1x1 mm$^2$ in cross-section. We sandwich them between two large copper electrode plates with their lengths perpendicular to each other to form a cross as in the drawing of figure 2. The current to be applied is of the order of 130 A and it is to be noted that this current will go through the contact area of the super-imposed bars which has a cross-section of about 1 mm$^2$ for a current density just over $10^4$ A/cm$^2$. Prior to the application of the current, a uniaxial stress of 5x10$^7$ Pa is applied vertically to the sandwich (electrode plateA is pressed on B).

![Figure 1: Resistance R vs. current I curves during Joule heating of glassy Zr$_{65}$Al$_{17.5}$Ni$_{10}$Cu$_{7.5}$Pd$_{10}$. R values were normalized at 0.2 A.][1]

![Figure 2: Two bulk metallic bars sandwiched between copper electrode plates with their lengths perpendicular to each other to form a cross.][2]

When the current is applied, the bars deform to produce a cross shape as shown in figure 3. Here the central contact area can be seen to have been heated to melting temperature and surface tension forces have deformed the area near the contact or the hot zone. X-ray diffraction in transmission using high-energy synchrotron beam showed that some crystallinity had developed during this shaping process. When the procedure is repeated by using a lower current density, a
cross of the form of figure 4 can be obtained from the two glassy bars. The shape of the contact or hot zone is now quite different from that of figure 3 and no surface-tension induced rounding is observed. The bars have clearly been deformed in the supercooled region above \( T_g \) and transmission X-ray diffraction shows no residual crystallinity after the shaping operation. In order to control the extent to which the bars are to interpenetrate, a circuit breaker is placed at an appropriate height on the cross-head that drives electrode plate A.

The same procedure can be applied to press crystalline conductors into BMG specimen. For example, figure 5 shows how a steel needle can be assembled onto a glassy plate by electromechanical insertion. It is seen that only the amorphous plate is deformed. The stainless steel needle does not undergo significant heating or softening because it has a high melting temperature and its lower electrical resistivity generates less Joule heating power density \( p \) than in the BMG plate.

Figure 5 shows indentations by a sharp electrode to demonstrate the writing ability of the electromechanical process and the formation of net and sharp shapes and corners (the excess glass expelled during penetration has been polished off).
Figure 7 Shows the insertion of tungsten spheres into a metallic glass plate thus demonstrating the ease of fabrication of composites using the present electromechanical process.

CONCLUSIONS

Connecting and shaping of bulk metallic glass (BMG) pieces with other glassy pieces or assembling with crystalline alloys such as steel as well as writing ability or engraving have been successfully demonstrated using a new electromechanical process. The process takes advantage of the polymer-like superplastic deformation of BMGs above the glass transition temperature $T_g$ as in thermomechanical shaping but in addition, exploits the high electrical resistivity of metallic glasses in order to provide fast heating and cooling ramps using Joule heating. Controlled nanocrystallisation of some BMGs can be precisely accomplished during shaping operations due to the drop in resistivity at the percolation limit of the nanocrystal population distribution. Such processes are easily adaptable to industrial automation and should enhance prospects for application of bulk metallic glasses.

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REFERENCES


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