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Elimination of porosity in bulk metallic glass castings using hot isostatic pressing

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ABSTRACT

This study presents design and implementation of a systematic method to remove the pores in as-cast bulk metallic glass using hot isostatic pressing, without changing the amorphous structure of the samples. The supercooled liquid region of $Zr_{44}Cu_{40}Al_8Ag_8$ was characterized using differential scanning calorimetry and dynamic mechanical analysis. This enabled informed choice of the range of hot isostatic pressing process variables likely to result in successful reduction of the porosity in the glassy alloy. The operating pressure in hot isostatic press processing was relatively less influential than either the temperature or the dwell time in controlling the porosity. It was shown that the dwell time should be longer than the average relaxation time in the glass transition range. With the specific bulk amorphous alloy under study, the optimized temperature, pressure and dwell time are 475 °C, 50 MPa and 3 min, respectively. Excess dwell times will result in crystallization.

1. Introduction

Recently, it has been reported that Zr-Cu based bulk metallic glass (BMG) alloys possess large critical casting thickness, good strength, good corrosion resistance, low shrinkage upon cooling to room temperature and enhanced ductility at room temperature, making them potential contenders for advanced structural materials [1–4]. They have also exhibited high thermal stability as a supercooled liquid, above the glass transition temperature, and hence they offer better thermoplastic forming ability [4]. BMGs, unlike crystalline materials, have structural order that is limited to a few nanometers only and therefore sub-micrometer and nanoscale features can be made with precision on BMGs [5]. The possibility of plastic-like flow of a high strength material makes them suitable candidates for prospective industrial applications such as precision-shaped durable materials with complex surface features and patterns for micro-fluidic applications [4–9]. BMGs that are patterned with micro-features are being considered as inverted micro-structured tools for microinjection molding, which is one of the most popular mass production technologies for manufacturing relatively large thermoplastic polymer parts with small surface details and/or excellent surface finish, such as single-use micro-fluidic devices and micro-lenses [8,9]. However, defect-free surfaces are needed for such high precision applications. If microporosity is present in as-cast BMG materials, the pores result in spherical voids at the surface of machined BMG prior to patterning [10]. A typical example of such a surface-breaking pore is shown in Fig. 1. It is known that micropores form during the process of rapid solidification [11,12], yet that rapid solidification is the key process to successfully produce amorphous castings. The solution proposed here is to try to reduce, or preferably remove, the porosity formed during the casting of BMGs, using appropriate post-casting treatment.

Hot Isostatic Pressing (HIPping) is a process that can be used to effectively close the pores of metallic materials—e.g. biomedical alloys [13]—and hence to achieve higher density. The key operation of HIPping involves pressuring the material with a high pressure inert gas at elevated temperature in a sealed enclosure. However, in the case of BMG, the processing window, in terms of time and temperature, is very restricted in order to avoid potential crystallization. This is due to the fact that BMG is relatively unstable at elevated temperature. To date, research reported on HIP treatment of BMGs is very limited. To the authors' knowledge, only Chen et al. [14] have presented the use of a HIPping technique to control the porosity of BMG. However, during their HIP processing, sample crystallization occurred and so the amorphous state of the BMG was destroyed.

In order to thermoplastically shape BMGs i.e. by processing in the regime in which the BMG behaves like a thermoplastic polymer, an understanding of the supercooled liquid region (SCLR) is of utmost importance. A metallic melt below the solidus temperature is a super-

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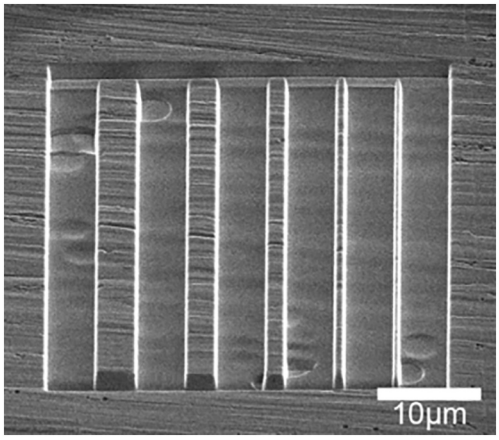

Fig. 1. Surface-breaking pores on $Zr_{47}Cu_{45}Al_8$ BMG on which a series of channels and ridges of depth/height ~ 2 μm were machined using Focused Ion Beam milling.

cooled liquid and it can become metallic glass if it cools below a glass transition temperature (T_g) without crystallization. This temperature is a dynamic temperature that depends on the cooling and heating rates during processing. A higher cooling or heating rate results in higher glass transition temperature. Near T_g, the supercooled liquid shows visco-elastic behavior, i.e. if the supercooled liquid is perturbed around T_g, the high frequency (short time) response can be elastic whereas the low frequency (long time) response can be viscous [4,15–17]. Therefore, understanding of the supercooled liquid's relaxation time is very important when considering the stability of BMG. It has been observed that the relaxation time increases quite rapidly as the temperature is lowered [15,17]. The viscosity, which is a macroscopic measure of its resistance to flow, gives a good idea of relaxation time. The viscosity is found to be closely correlated to the relaxation time and they both increase as the temperature decreases [18]. This temperature dependence of the viscosity (and relaxation time) of supercooled liquids is often described by the Vogel-Fulcher-Tammann (VFT) equation in metallic glasses [16,17]. Because metallic glasses have non directional metallic bonds, their viscosity rapidly increases with decreasing temperature, and hence they follow the VFT equation.

In this work, we report a systematic study of applying HIPping to the treatment of BMG alloys in an attempt to completely remove the pores that are formed during casting. We discuss the effect of HIPping process parameters viz. pressure, temperature and dwell time on reducing the porosity in BMGs.

2. Experimental method

An alloy of composition $Zr_{44}Cu_{40}Al_8Ag_8$ was prepared by melting pure constituent elements of purity > 99.99% in an arc melter in an argon gas atmosphere. The ingot was melted multiple times to ensure good compositional homogeneity of the alloy. This alloy was used to synthesize bulk metallic glass in the form of a rod, using a drop casting technique into a cooled copper mould in an argon gas atmosphere. The BMG rod was of 5 mm in diameter and 45 mm long. The amorphous nature of BMG was confirmed using X-ray diffraction; Siemens Kristalloflex with Cu-Kα radiation and Zeiss LIBRA 200 FE transmission electron microscope (TEM). Samples for TEM were prepared using Technoorg linda IV4 ion milling unit, at 4 KeV.

2.1. Characterization of materials

The viscosity of the BMG was measured at a variety of temperatures between 450 °C and 470 °C using dynamic mechanical analysis (DMA); Netzsch DMA 242 E Artemis. BMG samples were prepared with dimensions 55 mm × 2 mm × 3 mm machined from a separately cast BMG plate of the same composition. DMA was carried out using a 50 mm 3-point bending method in a nitrogen atmosphere.

Thermo-analytical studies were carried out in order to characterize the supercooled liquid (SCL) region of the BMG, using differential scanning calorimetry (DSC), Netzsch DSC 200f3. A continuous heating experiment at a constant rate of 10 K/min was performed in the temperature range between 300 °C and 525 °C using the DSC, in order to characterize the key temperatures of the BMG such as T_g and the crystallization temperature T_x. For the purpose of testing the thermal stability of the BMG at elevated temperature, the BMG was also isothermally tested at temperatures of 460 °C, 465 °C, 470 °C and 475 °C using the DSC.

2.2. Processing as-cast BMG

In order to conduct the HIP treatment and measure the porosity of the BMG, the 5 mm diameter rods were cut (through the cross-section) into discs of 3 mm thickness. These discs were subjected to mechanical grinding using grit sizes of P220, P320, P600, P1200, P2000, P2500, followed by diamond polishing via a conventional routine of preparing metallographic samples.

Following the characterization of the SCL region of the alloy, the temperature-time process window for HIPping of the amorphous BMG samples was determined. HIPping was carried out in an EPSI hot isostatic press at the Advanced Materials and Processing Laboratory of the University of Birmingham, UK, at various temperatures between 460 °C to 480 °C, under pressures ranging from 50 MPa to 180 MPa, and for different durations: ranging from 1 min to 10 min, in an argon atmosphere. The details of the experiments are given in Table 1.

Each HIPping experiment was performed in five stages, as follows.

- Samples were heated to 430 °C at a maximum possible heating rate of 20 K/min.
- Heating rate was then set to 10 K/min until the temperature reached 450 °C.
- Heating rate was changed to 5 K/min until the target temperature was reached. The pressure of 10 MPa was applied at the start of the second segment and the rate of increase of pressure was selected in such a way that the target pressure was achieved at the end of this third segment so that target temperature and target pressure were reached simultaneously.

Table 1
HIPping experimental parameters, and their effect on porosity and the percentage change (M) in pore area fraction.

Experiment number	Temperature (°C)	Applied pressure (MPa)	Dwell time (minutes)	Number of surfaces examined	Number of pores identified	m (%)
1	460	50	10	20	121	84.5
2	460	150	10	17	44	86.9
3	465	50	5	15	32	87.2
4	465	150	5	15	24	93.0
5	472	180	3	15	0	100.0
6	475	50	3	15	0	100.0
7	475	180	1	19	123	80.0
8	480	180	1	19	20	96.8