Sub-Micron Feature Patterning of Thermoplastics using Multi-Scale BMG Tooling

Dermot J. Stratton, Cormac Byrne, James Mulcahy and David J. Browne
Engineering & Materials Science Centre, University College Dublin, Belfield, Dublin 4, Ireland

ABSTRACT

One potential application for Bulk Metallic Glasses (BMGs) is in dies with micro- and nano-sized features. Three basic characteristic sets inherent to BMGs make them ideal materials for micro/nano-tooling applications: (1) excellent compressive strength, wear and corrosion resistance; (2) amorphous structure which presents no microstructural length scale limitation to cutting and forming operations; (3) the presence of a glass transition temperature above which they can be easily formed. There are many potential applications for multi-scale BMG tooling, including in production of microfluidic and other precision biomedical devices. In the current work, discs were cut from 5 mm diameter cylindrical specimens of $Zr_{44}Cu_{40}Al_8Ag_8$ BMG produced via arc melting and casting into water-cooled copper molds. The cylindrical specimens were then thermoplastically formed into thin coin-like disc samples. The thin disc-shaped plates were then ground and polished to create a smooth flat surface. Sub-micron-sized features were patterned into the plates via a focused ion beam. We demonstrated that such feature sizes are not achievable in conventional crystalline metallic tool materials. The patterned BMG tools were then set in a compression press where the platen temperature was precisely controlled and a series of load-controlled embossing trials were carried out in which the features of the BMG tooling were replicated in poly(methyl methacrylate) (PMMA) sheet. An exercise in mapping out the size limitation of such a multi-scale embossing operation is reported.

INTRODUCTION

In this paper, the focus is placed on three specific characteristics of the BMG material that make it an ideal material choice for micro- and nano-featured dies for use in production of polymeric devices: (1) excellent mechanical properties, (2) amorphous structure free of microstructural details, and (3) presence of a glass transition temperature.

The excellent mechanical properties of these alloys have been studied extensively [1]. The high compressive yield strength, large elastic strain limit, high wear resistance and good corrosion resistance of these BMGs are all properties ideal for a mold material. Another important characteristic of BMGs is their amorphous structure. In crystalline materials, the size of feature that can be milled or formed is limited by the size of the microstructural features (grain boundaries, lattice defects, etc.). Since such microstructural features are absent in BMGs, they can be milled or formed down to the nanoscale. Another characteristic resulting from the amorphous nature of BMGs is the presence of a glass transition. BMGs can be formed at relatively low pressures at temperatures above their glass transition temperature. As a result, BMGs can first be cast into simple cylindrical shapes (ideal for the uniform high cooling rates necessary to form a fully amorphous BMG) and subsequently thermoplastically formed into shapes matching the necessary end application [2].

A specific Zr-based BMG alloy, $Zr_{44}Cu_{40}Al_8Ag_8$, was chosen in this study because of its high glass forming ability and sufficiently wide super cooled liquid (SCL) region. In the alloy's

SCL region, the cylindrical samples can be compressed into thin disc shapes needed for a hot embossing tool. The ability to themoplastically form and then mill micro- and nano-sized features into this BMG will be illustrated in this paper. The ability to use this material as a die to transfer said patterns into a polymer will also be shown.

EXPERIMENT

Buttons of $Zr_{44}Cu_{40}Al_8Ag_8$ alloy were prepared by arc melting (figure 1a) of high purity Zr (99.95%), Cu (99.999%), Al (99.999%) and Ag (99.95%) elements under a partial argon atmosphere. All samples were re-melted at least 4 times to assure homogeneity. The buttons were then melted and drop cast into a water-cooled copper mold with casting dimensions of 5 mm diameter by 40 mm length. These rods were then cut into 5mm lengths via a high-speed diamond saw. These sections were then compressed into ~10 mm diameter by ~1 mm thick discs using a custom built heated platen set-up mounted onto a Hounsfield 50kN universal testing machine. Accurate temperature control was achieved using a closed loop Omega CN79000 PID controller. A schematic of the test setup is shown in figure 1b. The 5mm long sections were compressed at a temperature 490°C at a constant displacement rate of .01 mm/min. The resulting discs were then polished to a .05 micron finish with standard metallographic polishing techniques. The amorphous nature of these discs was verified by differential scanning calorimetry (DSC) and x-ray diffraction (XRD). The DSC scans were performed using a Perkin Elmer DSC at a heating rate of 20 K/min. XRD scans were performed using a Siemens D500 unit. The discs were then milled using a focused ion beam in a FEI Quanta 3D FEG DualBeam SEM. The BMG discs with milled patterns were then used as dies and pressed into 0.5 mm PMMA sheet at varying temperatures and pressures using the heated platen set-up referenced above. The BMG die and PMMA sheet were placed on the platens at embossing temperature above the T_g of the PMMA, but well below the T_g of the BMG, and allowed to equilibrate to this temperature for 60 seconds before pressure was applied. This pressure was held for 3 minutes before the heaters were turned off. The pressure was then held between the mold and PMMA and air cooled to below 90°C. The average cooling rate was approximately 5°C/min, so total holding time varied, depending on the embossing temperature used.

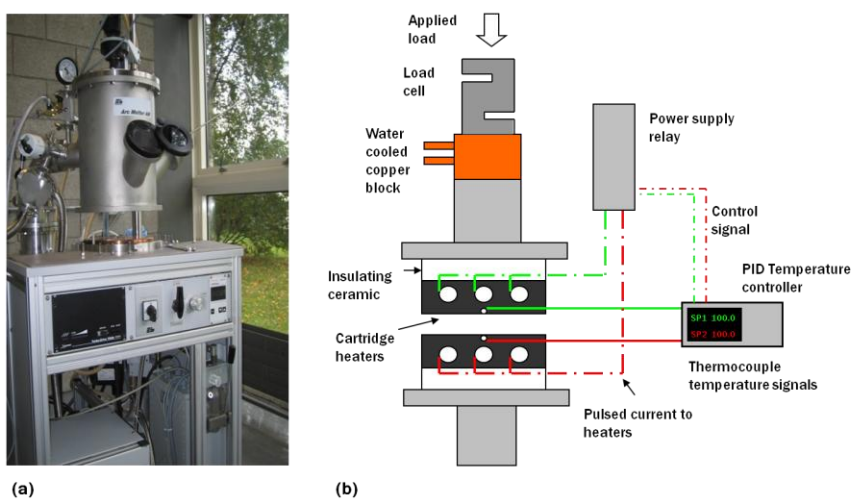


Figure 1. (a) arc melter used in production of alloy; (b) schematic of custom-made heated compression platens used for compression of BMGs and hot embossing of PMMA.

RESULTS & DISCUSSION

Casting and characterisation of BMG

The amorphous nature of the alloy was confirmed with the XRD scan, a portion of which is shown in figure 2a. The broad hump with no distinct crystalline peaks is indicative of an amorphous material. The DSC scan shown in figure 2b also confirms the presence of a glass transition temperature which is indicative of an amorphous material. The onset of glass transition temperature and onset of crystallisation temperature were determined to be 448°C and 513°C, respectively.

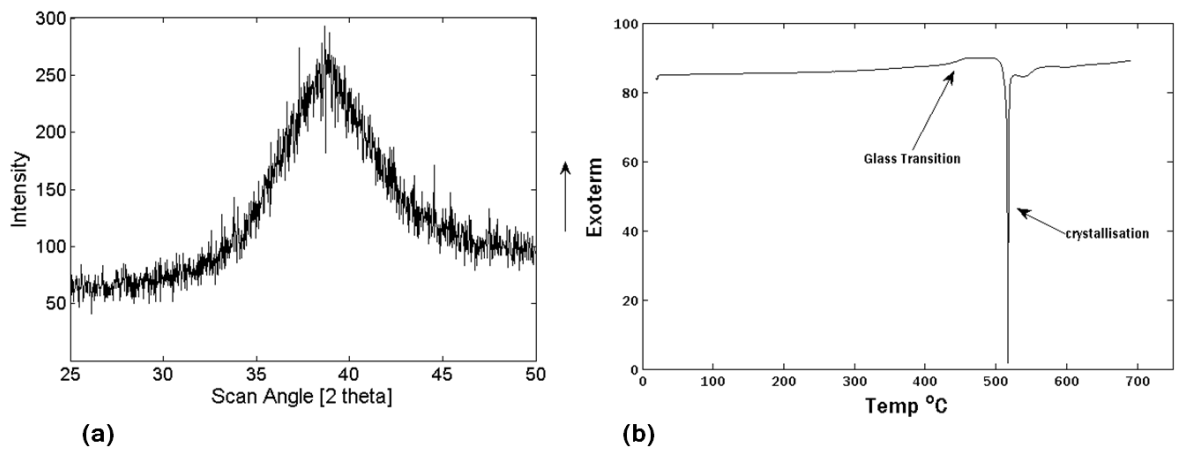


Figure 2. (a) XRD and (b) DSC scans confirming amorphous nature of the BMG alloy.

Thermoplastic forming of BMG

The initial cast BMG samples 5 mm in diameter and 5 mm in height were compressed into discs that were ~ 1 mm in thickness as displayed in figure 3a. The force vs. displacement curve of a BMG compressed at a constant crosshead displacement rate is shown in figure 3b. Looking at this curve, it can be seen that the BMG initially deforms with a very low force. The increase in force towards the end of the compression cycle is attributed to several factors including; the increase in the diameter of the BMG during compression, the friction forces between the BMG and platens and increased strain rate as the sample height decreased. The purpose of the compression testing was not to thoroughly examine the deformation mechanisms of the BMG in the SCL region, but rather to show that it is possible to form an initial cast shape into one suited for a specific end application. A closer study of the deformation mechanisms of $Zr_{44}Cu_{40}Al_8Ag_8$ in the super cooled liquid region will be pursued in future work.

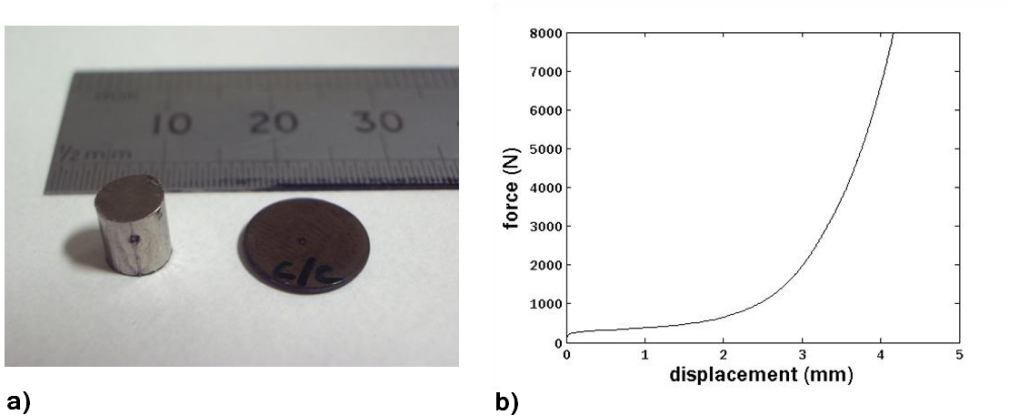


Figure 3. (a) BMG sample before compression in SCL region (left) and BMG sample after such compression (right); (b) force vs. displacement curve of compression test.

Nanopatterning of BMG

The unique ability to nanopattern BMG via focused ion beam (FIB) milling is clearly displayed in figure 4 – gear wheel cavity of ~ 20 μm diameter. For the sake of comparison, a piece of tool steel was FIB milled with identical parameters as showin figure 4a. The limits imposed by the microstructural features of the tool steel clearly show that it can not be FIB milled to the same precision as the amorphous BMG shown in figure 4b. With this FIB milling technique any complex bitmap can be imported and subsequently FIBed into the BMG substrate, which allows for arbitrarily complex 2-D images to be FIBed to a certain depth, as exhibited by the UCD crest logo shown in figure 5a. Figure 5 shows the various patterns that were milled and investigated in this study.

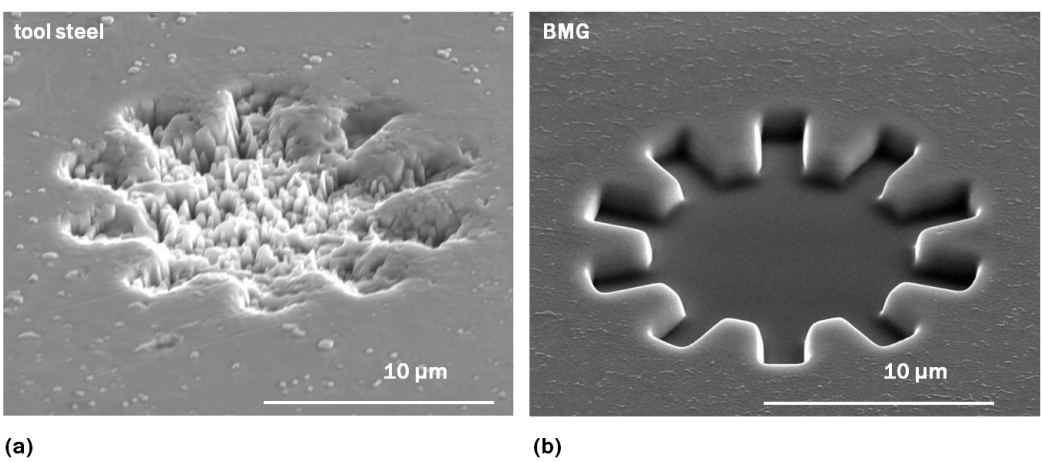


Figure 4. FIB milling trials in (a) tool steel and (b) BMG material.

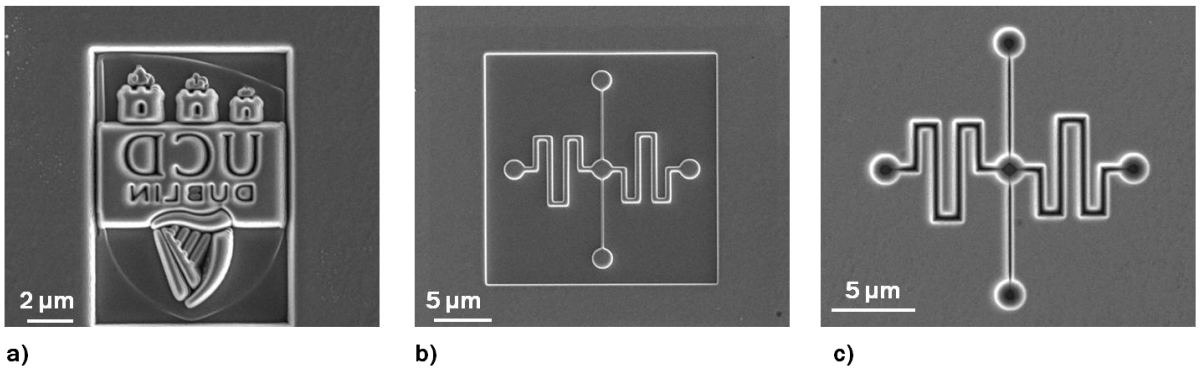


Figure 5. Patterns FIB milled into the BMG die material: (a) UCD crest; (b) sub-microfluidic pattern with negative channels; (c) sub-microfluidic pattern with positive ridges.

Hot embossing PMMA into BMG mold

Once the BMG tools were patterned, they were then used as dies into which PMMA sheet was hot embossed. A test matrix was set up which varied embossing temperature (110°C, 120°C, 130°C, 140°C) and embossing pressure (1.5 MPa, 2.0 MPa, 2.5 MPa, 3.0 MPa) in order to determine what combination of temperature and pressure was necessary to replicate the features FIBed into the BMG. It was noted that at 140°C the PMMA sheet would begin to degrade and bubbles would form within it, so this was determined to be above the upper allowable embossing temperature. There was some degree of replication of patterns throughout the entire test matrix. The lowest temperature (110°C) used in the test matrix resulted in a non complete fill of the mold features as shown in figure 6 (a - positive ridges; b – negative channels – in PMMA). The increase in pressure (from 2.0 MPa to 2.5 MPa) and temperature resulted in a better fill and replication of features in the microfluidic-like features showed in figure 7. Within the test matrix, the optimal processing conditions were determined to be a temperature of 120°C with a force of 2.5 MPa. These conditions resulted in the most consistent replication of features in the PMMA. The best replication of the crest features also occurred in this range, shown in figure 8. It should be noted that all of the embossing was done at atmospheric pressure. It is recorded in literature that it is recommended to do embossing of sub-micron features under vacuum [3]. The deformities seen on the filled channels are associated with the separation of the PMMA sheet and the BMG mold, which could not be precisely controlled due to limitations in the experimental setup.

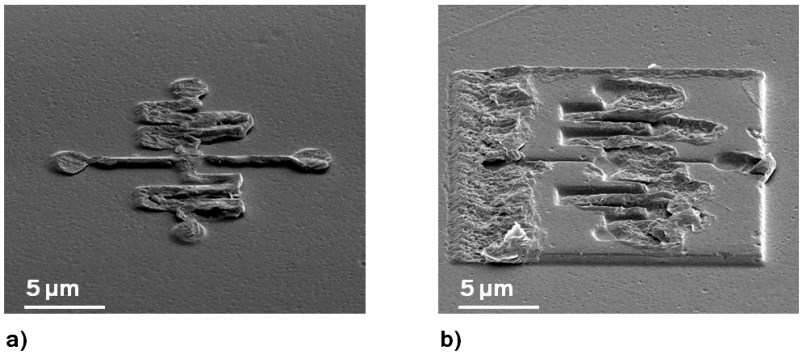
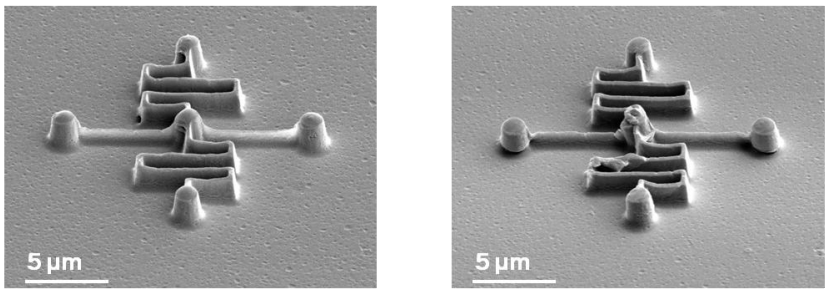
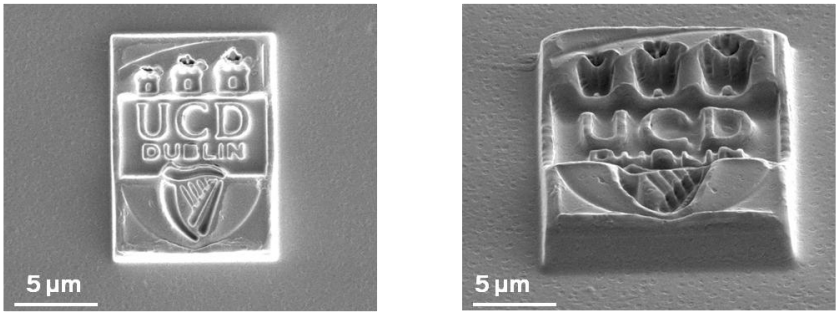


Figure 6. Patterns embossed into PMMA at (a) 110°C, 1.5 MPa; (b) 110°C, 1.5 MPa.



a) b)

Figure 7. Patterns embossed into PMMA at (a) 120°C, 2.0 MPa and (b) 120°C, 2.5 MPa.



a) b)

Figure 8. UCD crest embossed into PMMA (120°C , 2.5 MPa) (a) SEM image with no tilt; (b) SEM image with 52° tilt to show relief.

CONCLUSIONS

It has been shown that BMGs can be cast in relatively large sections which can subsequently be formed and milled to create micro- and nano-sized features. These BMG tools can be used as dies to transfer these submicron features into PMMA material via hot embossing. Process parameters were optimized for transferring patterns from the BMG tools to the PMMA. The complete process chain for using BMG tools to replicate features in polymers for applications such as micro/nano fluidics has been demonstrated. This process has great potential for enabling high volume replication of low cost nano-patterned polymer devices.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Ian Reid at Nano Imaging and Material Analysis Centre (NIMAC), University College Dublin, for assistance in FIB milling and imaging, and Enterprise Ireland who provided funding for this work via contract CTFD 06/IT/335.

REFERENCES

[1] C. A. Schuh, T. C. Hufnagel, and U. Ramamurty, *Acta Materialia* **55**, 4067-4109 (2007).
[2] J. Schroers, *JOM* **57,** 35-39, (2005).
[3] M. Worgull, *Hot Embossing:Theory and Technology of Microreplication*, 1st ed. (William Andrew, 2009) pp. 140-142.