

# Precision Molding of Metallic Micro-Components

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## Abstract

The micro-molding of bulk amorphous metal to create sub-micrometer to sub-millimeter surface features was investigated. The goal was to demonstrate the reproduction of such features in a metallic material from a master. The bulk metallic glass material was embossed at temperatures between the glass transition and crystallization temperatures. Silicon wafers patterned by deep reactive ion etching were used as masters. The patterns were designed to test the effects and interactions of aspect ratios, geometry, and spatial proximity. In addition to these patterns, a master was developed to mold two-dimensional channel geometries. Comparisons between the replicated features and the molds are provided.

## Introduction

The steady trend towards the miniaturization of a wide variety of mechanical devices and systems has been restricted by the limitations of the manufacturing technology and available materials, including limits on the types and range of component geometries which can be produced. In order to realize these devices, alternate fabrication technologies suitable to these complex micro-scale and meso-scale component geometries and materials must be developed. Successful development and commercialization of this technology will enable numerous new classes of microdevices.

One class of materials that enables the advances of micro-devices is amorphous metals, or bulk metallic glasses. Their unique combination of properties make amorphous metals ideal for forming high strength, high precision micro-components. Several of these alloys have strength properties which equal or exceed those of existing high strength crystalline alloys. The alloy commercially known as Vitreloy-1, for example, has a room-temperature yield strength of 1.90 GPa and a Young's modulus of 96 GPa [1]. Unlike crystalline metals, however, metallic glass can be molded to produce micrometer or smaller features at temperatures near 400° C. This low glass transition temperature allows molds to be made of conventional materials such as tool steel, or even aluminum or copper. It also suggests that conventional thermoplastic molding equipment may be able to be modified for this application, resulting in low capital costs for manufacturers.

Their unique atomic structure leads to a set of characteristic properties for some amorphous metals which include: very high yield strength, high hardness, superior strength/weight ratio, superior elastic limit, and high wear resistance. These alloys have several fundamental characteristics that make them ideal for net shape molding of micro-components. Since no phase change occurs, there is relatively little shrinkage as the material cools below the glass transition temperature. This enables tight tolerance control of cast and molded features. Also, due to lack of crystallinity, bulk amorphous metal alloys tend to develop good surface finish upon vitrification, which is important because options for secondary-finishing operations are limited.

Control of the viscosity of the material via temperature in its "supercooled liquid" state will allow additional flexibility in determining optimal processing parameters when molding fine features with high aspect ratios, where the high surface area to volume ratios lead to high heat transfer rates. The components that result will have exceptional mechanical strength properties, very high flexibility, good fracture toughness and fatigue strength, and will be electrically conductive.

Research has been conducted to investigate mold forming ability by several groups. Zumkley *et al.* studied forging of bulk metallic glass at relatively low pressures and temperatures into microparts up to 200  $\mu\text{m}$  in width and 500  $\mu\text{m}$  in height [2]. However, this study was conducted with Vitreloy-4 and the parts were pressed for extended times. A.A. Kündig *et al.* performed experiments by heating Vitreloy-4 to the melt temperature of 1350 K, allowing the material to flow into 20  $\mu\text{m}$  high, 8  $\mu\text{m}$  widths, then cooling at 20 K/s [3]. Further research by A.A. Kündig *et al.* studied wetting effects during molding of metallic glass [4].

## Experimentation

### Instrumentation

A MTS Q-Test 5 load frame with a 5000 N load cell was adapted for the micro-molding experiments. A multi-step process consisting of a pre-load, molding load, and cool-down load was employed. The molding force, controlled dynamically by the MTS machine, determines the applied pressure. Molding temperature was achieved with 20 computer controlled cartridge heaters. The cartridge heaters had a combined power of 5 kW allowing for the quick heating necessary to avoid

crystallization. A centrifugal pump provided forced water flow and the rapid cooling necessary to avoid crystallization after molding. Data acquisition was used to record temperatures in the top and bottom mold platens. Applied force from the MTS machine was also recorded and used to calculate the average applied pressure from the sample area. In addition to temperature and force, crosshead position during the tests was recorded.

### Silicon Wafer Mold Design

A master silicon mold was designed to test the effects and interactions of aspect ratio (A), geometry (G), and feature proximity (P). Experiments were conducted to test the sensitivity of the moldability of the amorphous alloy to these process variables. Applied pressure, temperature, and molding time were also studied through process variation.

A 100 mm diameter x 0.1 mm thick silicon wafer was divided into 4.75 mm x 4.75 mm square sections patterned with sets of through holes. Within each section, 0.95 mm x 0.95 mm subsections with specific parameter combinations were randomly distributed. The parameter combinations included: A, G, P, AG, AP, GP, and AGP. For example, an “AG” section included holes with variations in aspect ratio and geometry while holding the proximity of the features constant. To examine the pressure profile of the molding operation over the surface of the mold, a separate 4.75 mm x 4.75 mm section was designed with a radial pattern of holes.

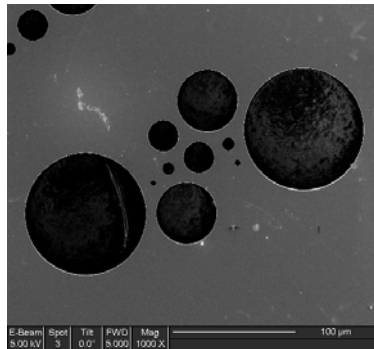


Figure 3: SEM micrograph of Aspect Ratio section on AGP silicon wafer mold

### Test Conditions

A series of 64 tests were run over a range of temperatures, pressures, and molding times. Test conditions are provided in Table 1. The temperature range coincides with the bulk metallic glass “supercooled liquid” region, i.e., the temperature range above the glass transition temperature and below the crystallization temperature. The glass transition temperature for Vitreloy-1 is approximately 350° to 375° C, so a temperature of 400°C was chosen as the first molding

temperature to ensure the material would exhibit the required decrease in viscosity. Applied pressure and molding time values were chosen based on experimentation for bulk deformation of the material.

Temperature [°C]	Pressure [MPa]	Time [s]
400	100	15
425	115	30
450	130	45
475	150	60

Table 1: Experimental test matrix

Samples of bulk metallic glass were first melted into small buttons in an arc-melter furnace to reduce porosity. These buttons were then placed in a copper funnel and once again melted into a 5 mm X 5 mm square cross sectioned pin. The metallic glass pin was then cut into 1 mm slices using a low-speed diamond saw. X-ray diffraction was performed on the sliced samples to check for crystallization. Assuming no crystallization was found, the sides of the samples were then polished to fit the sample into the mold pocket. The bulk metallic glass was then readied for the molding process by cleaning with acetone and methanol and drying with compressed air.

Following molding, the silicon wafer master was removed from the molded bulk metallic glass by a two step wet etch process. First, the silicon wafer and bulk metallic glass were placed in a 20% (by volume) acetic acid – 80% ethyl alcohol solution. This removed any oxide layer that may have formed on the surface of the silicon during the molding process. With the oxide layer removed, the silicon and bulk metallic glass were placed in a 20% concentration potassium hydroxide – water solution at 70° to 80° C, which dissolved the silicon completely. The elevated temperature increased the etch rate allowing for complete removal of the silicon wafer in about 2 hours.

### AGP Results

Initial results show excellent moldability and reproducibility. Aspect ratios as high as 12 to 1 have been observed. See Figure 4d.

Over the entire range of prescribed temperatures, bulk flow of the metallic glass occurred. The best flow occurred at 450°C with higher pressures and molding times. At 475°C, for the two largest molding

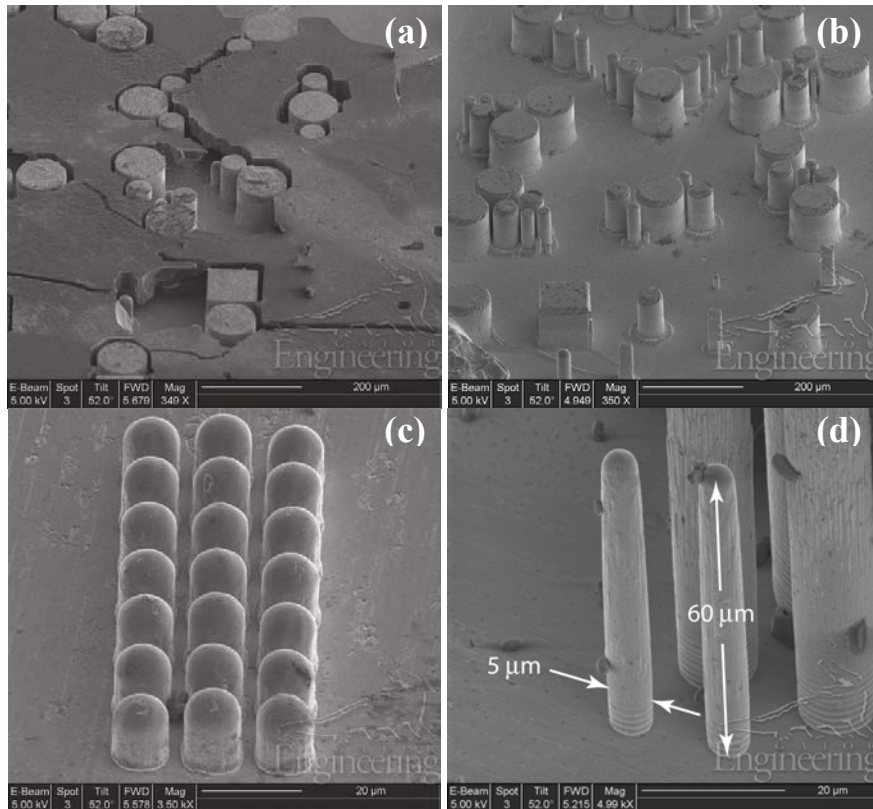


Figure 4: SEM micrographs of molded metallic glass features. (a) silicon master partially dissolved, (b) silicon master fully dissolved, (c) 10 μm holes partially filled at lower molding temperatures, (d) 5 μm holes filled to a depth of 60 μm.

times of 45 and 60 seconds, a darker gold tone was observed on the surface of the bulk metallic glass. This could occur from surface oxides or may be an effect of crystallization. Since this material is temperature, time, and oxygen dependent, sustaining elevated temperatures for extended times can lead to crystallization. Also, crystallization is more likely at higher temperatures because it takes longer to cool below the glass transition temperature causing the cooling rate to be a crucial factor.

Proximity and Geometry showed little effect on the molding of the metallic glass. Aspect ratio results were determined by measuring the same set of two 10 μm diameter features on every sample. The results are plotted in Figure 5. Temperature dominated applied pressure and molding time because the material is very temperature dependent; i.e. small changes in temperature result in large changes in viscosity.

The 450°C and 475°C experiments resulted in 10 μm holes being completely filled to the full mold depth of 100 μm. These results are not plotted in Figure 5. The mold limit aspect ratio was 10 as the silicon wafer was approximately 100 μm thick.

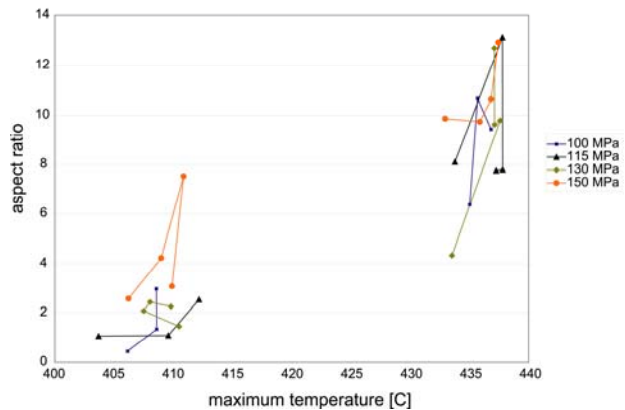


Figure 5: Aspect ratio results for 400°C and 425°C tests

X-ray diffraction was used to determine if any oxidation or crystallization occurred in the bulk metallic glass at several random test conditions. A diffraction pattern reports the x-ray intensity in counts as a function of 2θ angle. Diffraction tests indicate that most of the material has remained amorphous. An example of a x-ray diffraction graph can be seen in Figure 6.

Broad diffuse peaks suggest that the material has remained amorphous. Sharp peaks would suggest crystallization in the material because evidence of atomic structure would increase the intensity. As can be seen in

Figure 6, the broad diffuse peaks can be seen over the entire angle range; however, some sharp peaks exist that may suggest localized crystallization.

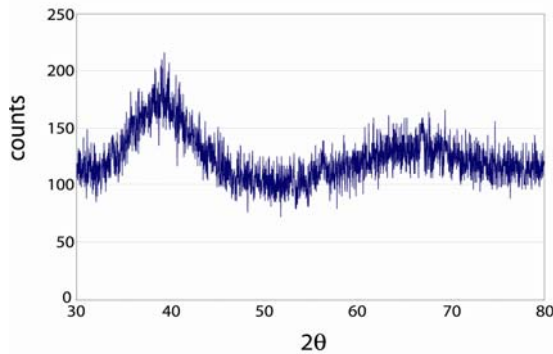


Figure 6: X-ray diffraction results suggesting amorphous molded bulk metallic glass

Excellent reproduction of the molds can be seen in the bulk metallic glass. For example, the deep reactive ion etching process produces scallops along the sidewalls of the silicon mold. These scallops are created because it is a two step process of etching and passivation in cycles of 1  $\mu\text{m}$  to 2  $\mu\text{m}$  in depth. The cycles provide for nearly 90 degree sidewalls which allow for high aspect ratio features. A scanning electron micrograph of the replicated scallops in the molded bulk metallic glass can be seen in Figure 7.

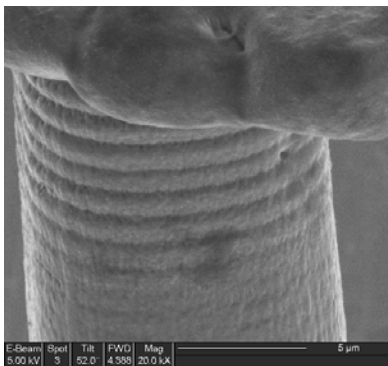


Figure 7: Reproduced scallops on molded bulk metallic glass

Non-line-of-sight flow has also been observed in the molded bulk metallic glass, suggesting that more complex three-dimensional geometries could be filled. During the deep reactive ion etching process, a “footing” is created on one end of the feature in the silicon wafer mold. Footing refers to a small gap between the end of the etched holes and the top surface of the silicon wafer. This small void has been filled in Figure 8. Flow around corners is specific to molding processes and isn't characteristic of many other fabrication techniques.

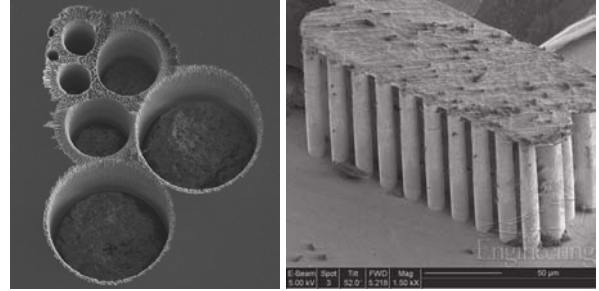


Figure 8: Non-line-of-sight flow. Top: Silicon wafer mold with footing. Bottom: Molded bulk metallic glass with filled footing.

## Conclusions

A micro-molding platform has been designed, constructed, and tested. Experiments were carried out to demonstrate micro-molding of micrometer scale features in bulk metallic glass. A range of temperature, pressure, and molding time combinations were tested and successful reproduction of a variety of amorphous, high aspect ratio features from silicon masters was observed. Additionally, non-line-of-sight flow was seen, which suggests the potential for the production of three-dimensional geometries by this method.

## Acknowledgements

This material is based upon work supported by the National Science Foundation under Grant No. DMI-0245589, "Precision Molding of Metallic Micro Components" and the NASA Hydrogen Research at Florida Universities Program. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation or NASA.

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