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Metallic glasses: viable tool materials for the production of surface microstructures in amorphous polymers by micro-hot-embossing

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Abstract
Metallic glasses possess unique mechanical properties which make them attractive materials for fabricating components for a variety of applications. For example, the commercial Zr-based metallic glasses possess high tensile strengths ($\approx 2.0$ GPa), good fracture toughnesses ($\approx 10–50$ MPa$\sqrt{m}$) and good wear and corrosion resistances. A particularly important characteristic of metallic glasses is their intrinsic homogeneity to the nanoscale because of the absence of grain boundaries. This characteristic, coupled with their unique mechanical properties, makes them ideal materials for fabricating micron-scale components, or high-aspect-ratio micro-patterned surfaces, which may in turn be used as dies for the hot-embossing of polymeric microfluidic devices. In this paper we consider a commercially available Zr-based metallic glass which has a glass transition temperature of $T_g \approx 350$ $^\circ$C and describe the thermoplastic forming of a tool made from this material, which has the (negative) microchannel pattern for a simple microfluidic device. This tool was successfully used to produce the microchannel pattern by micro-hot-embossing of the amorphous polymers poly(methyl methacrylate) ($T_g \approx 115$ $^\circ$C) and Zeonex-690R ($T_g \approx 136$ $^\circ$C) above their glass transition temperatures. The metallic glass tool was found to be very robust, and it was used to produce hundreds of high-fidelity micron-scale embossed patterns without degradation or failure.

1. Introduction
There is a growing demand in the biomedical industry for microfluidic devices made from amorphous thermoplastic materials. Currently, depending on feature sizes and part quantities, such devices are made either by micro-hot-embossing or by injection-molding methods (cf e.g. [1]). Both the micro-hot-embossing process and the injection-molding process require a tool containing the negative of the desired pattern to impart the pattern to a polymeric substrate. The tool must be robust and capable of producing many (thousands of) parts without any degradation of the pattern or failure of the tool. The property requirements for a material from which the tool is made include (i) high stiffness; (ii) high strength; (iii) reasonably high fracture toughness; (iv) good surface finish; (v) good wear and corrosion resistances; and importantly (vi) a straightforward method for the production of the desired features in the tool material over a wide range of length scales and aspect ratios. Thus, as with any other thermo-mechanical forming process, the following questions are always of major concern: (a) from what material should the tools be made? and (b) how to produce the tools from the chosen material?

A number of different materials have been used for making tools for thermo-mechanical forming of amorphous polymers [1]. By far, the most widely used tool material is as follows:
A single-crystal silicon wafer patterned by reactive-ion etching. The wide use of silicon as a tool material is primarily due to the existence of well-developed processing methods, such as deep-reactive-ion etching (DRIE), used in the production of integrated circuits and MEMS devices, which are easily adapted for making surface patterns on silicon wafers for thermo-mechanical forming of microfluidic devices. However, silicon is fatally flawed as a tool material in that it is very brittle ($K_{IC} \approx 1 \text{MPa}\sqrt{\text{m}}$) and rarely survives more than a handful of production cycles for micro-hot-embossing of polymers before failing catastrophically.

Other tooling options include the following:

- **SU-8 on silicon.** Tools made from SU-8 are primarily used for the casting of polydimethylsiloxane (PDMS) for making microfluidic devices, and are ill-suited for micro-hot-embossing or injection molding because (i) the SU-8 features tend to delaminate from the silicon substrate under repeated use, and (ii) the brittle silicon substrate tends to fracture.

- **Electroformed metallic tools.** Electroformed nickel microstructures on a metallic substrate as embossing tools for thermo-mechanical forming of polymers have gained substantial interest due to the dimensional precision and excellent surface finish with which the microscale features may be electroformed. The resulting tools possess most of the positive attributes of a desirable tool listed above. However, the electroforming process has several limitations: (i) it is slow and time consuming; (ii) it is difficult to produce high-aspect-ratio tools using this process; and (iii) electroformed features often fail by delamination from the substrate.

- **Micro-machined metallic tools.** Tools micro-machined from metals such as brass or stainless steel have good stiffness, strength, toughness and wear resistance. However, the micro-machining process is capable of accurately producing features which are only $\approx 50$ $\mu$m and larger. Further, the micro-machining process usually leaves machining marks and burrs, which can result in a poor surface finish.

It is the purpose of this paper to introduce metallic glasses and the thermoplastic hot-embossing of these glasses as a robust and attractive alternative to the existing materials and methods for making tools for thermo-mechanical forming of amorphous polymers by micro-hot-embossing or injection molding.

Metallic glasses possess unique mechanical properties which make them attractive materials for fabricating components for a variety of applications. For example, the commercial Zr-based alloys exhibit a reasonably high Young’s modulus ($\approx 90$ GPa), high tensile strength ($\approx 2.0$ GPa), good fracture toughness ($\approx 10–50$ MPa$\sqrt{\text{m}}$) and good wear and corrosion resistances (e.g. [2–4]). A particularly important characteristic of metallic glasses is their intrinsic homogeneity to the nanoscale because of the absence of grain boundaries. This characteristic, coupled with their unique mechanical properties, makes them ideal materials for fabricating nano/microscale components. Also, since metallic glasses are amorphous materials, they exhibit a glass transition, and at temperatures above this glass transition, they soften dramatically [5, 6] and are therefore amenable to net-shape thermoplastic forming processes (e.g. [7]).

We emphasize that:

- **the central idea reported in this paper is not limited to the use of Zr-based metallic glasses. Indeed any metallic glass with good thermoplastic formability may be used to manufacture dies for micro-hot-embossing of polymers, as long as the glass transition temperature of the specific metallic glass is well above that of the polymer being embossed.**

The plan of this paper is as follows:

(a) In section 2, we describe the micro-hot-embossing process that we have used to produce a wide variety of micron-scale patterns in the metallic glass Vitreloy-1b. We also describe a polymer embossing tool that we have made from this metallic glass, which has the (negative) microchannel pattern for a simple microfluidic device.

(b) In section 3, we describe the results of using the metallic glass tool to replicate the microchannel pattern by micro-hot-embossing of the amorphous polymers poly(ethyl methacrylate) ($T_g \approx 115$ °C) and Zeonex-690R ($T_g \approx 136$ °C) above their glass transition temperatures. The metallic glass tool was found to be very robust, and it was used to produce hundreds of high-fidelity micron-scale embossed patterns without degradation or failure.

(c) Lastly, in section 4, we describe the production of a microstructural pattern in Vitreloy-1b with substantially smaller dimensions ($\approx 1$ $\mu$m) than those of

1. SU-8 is an epoxy-based negative photoresist, commonly used in the microelectronics industry.

2. There is some cause for concern in the use of Vitreloy-1b because of the high beryllium content of this alloy. If this proves to be a serious problem, then either the Pd- or Pt-based metallic glass may be used instead, but these alloys are expensive, and not readily available commercially.
the channels (≈50 μm) produced for the microfluidic device embossing tool, and show that the smaller dimensioned pattern may also be successfully transferred to a polymeric substrate, thus demonstrating that our two-stage replication process is easily scaled in the 1–100 μm feature size range.

2. Micro-hot-embossing of metallic glasses

A materials-processing method for fabricating microscale features and components made from metallic glasses is the thermoplastic forming process conducted above the glass transition temperatures of these materials (e.g. [6, 7, 12–22]). In this process, a metallic glass is first obtained by traditional casting methods at a sufficiently high cooling rate so as to obtain an amorphous state. The material is not cast into intricate shapes but into simple geometries such as plates or rods. The metallic glass is then heated into the supercooled liquid region above the glass transition temperature of the material, where it may be isothermally formed to produce intricate microscale patterns and then slowly cooled. A typical thermoplastic forming process for a metallic glass is shown schematically in figure 1 on a time–temperature-transformation (TTT) diagram. Since metallic glasses in their supercooled region are metastable, they eventually crystallize; however, the crystallization kinetics in glass-forming alloys are sluggish, and this results in a relatively large temperature–time processing window in which thermoplastic forming may be carried out without crystallization. Further, since the forming is done isothermally and the subsequent cooling is rather slow, and since there is no phase change on cooling, residual stresses and part distortion may be minimized.

A specific thermoplastic forming process suitable for producing microscale, high aspect ratio, patterned features on metallic glass plates is micro-hot-embossing. This process has received considerable attention in the literature for producing metallic glass components for applications such as NEMS/MEMS [16, 19], optical gratings [17, 22] and micro-dies [12, 20]. In a typical process, a patterned silicon wafer is used as the master surface—a negative of the desired pattern is imparted to the silicon tool using deep-reactive-ion etching (DRIE), which is capable of producing nano-/microscale features with high-dimensional accuracy. A flat sheet of metallic glass is then placed along with the patterned silicon tool between parallel heated compression platens. The assembly is then heated to an appropriate temperature above the glass transition temperature of the metallic glass, and a desired pressure is then applied over a set amount of time, after which the load is removed and the assembly is cooled. It is important to remember that after a certain amount of time at a given temperature above the glass transition temperature, a metallic glass will eventually crystallize, which is undesirable because it substantially degrades the properties of the formed product. Accordingly, it is important to consider this constraint when selecting appropriate temperature–time processing parameters for the micro-hot-embossing process.

During the embossing process, the metallic glass substrate and silicon wafer become mechanically locked together. Thus, following the embossing process, the metallic glass is separated from the silicon mold by etching away the silicon in a heated KOH bath, leaving the embossed metallic glass part. Hence, the silicon tool used in this process is sacrificial. Finally, any flash occurring as a result of the micro-hot-embossing process may be trimmed at this point, leaving the final part.

We begin with a simple example of a micron-scale hot-embossing process: the embossing of a series of long raised ridges into a Zr41Ti17Be22Cu10Ni10 (Vitreloy-1b) substrate. The pattern consists of channels which are 55 μm wide, 43.5 μm deep and are spaced 92 μm apart. Figure 2(a) shows a schematic of the master pattern, and figure 2(b) shows a SEM micrograph of a portion of the silicon master produced through DRI etching. In order to determine appropriate processing parameters for this geometry, namely (i) the embossing temperature, (ii) the applied pressure and (iii) the hold time, a numerical simulation was carried out. In a recent paper [6], simulations of the micro-hot-embossing of Vitreloy-1 (Zr41.2Ti13.8Be22.5Cu12.5Ni10) were reported. Since the mechanical behavior of Vitreloy-1b is similar to that of Vitreloy-1, we use the simulation capability presented in that paper, along with the material parameters determined for Vitreloy-1, to simulate the current embossing of a Vitreloy-1b substrate.

Note that the mechanical behavior of a metallic glass is highly temperature dependent above its glass transition temperature, with the ‘viscosity’ of the material decreasing dramatically as the temperature increases; and, as such, selecting a high temperature as possible without risking crystallization is desirable. See Henann and Anand [6] for a detailed analysis and discussion of the mechanical behavior of a Zr-based metallic glass in the temperature range relevant to thermoplastic forming, and numerical simulations of the micro-hot-embossing of metallic glasses.

3 Thermoplastic forming of metallic glasses was first recognized by Patterson and Jones [11] in 1978.
4 Since metallic glasses can be extended to very large elongations at high temperatures above the $T_g$ of the material, such forming processes are sometimes also called superplastic forming processes.
Since the channels are long relative to their width, and there are a large number of them aligned in parallel, we employ a plane strain idealization in our numerical simulation and consider only a single half-segment with suitable boundary conditions. Figure 2(c) shows the initial finite element mesh. The metallic glass substrate is modeled using 4098 Abaqus-CPE4R plane strain elements, and the silicon master is modeled using an appropriately shaped rigid surface. Contact between the substrate and tool was approximated as frictionless. The displacement boundary conditions on the portions AD and BC of the mesh boundary are $u_1 = 0$, while on the portion CD of the mesh, $u_1 = u_2 = 0$ are prescribed.

The simulations were performed under typical conditions for micro-scale hot-embossing. We chose a temperature of 450 °C and a process time of 2 min; for Vitreloy-1b, the risk of crystallization and the subsequent deterioration of mechanical properties under these process conditions is expected to be minimal (e.g. [23]). In our numerical simulations, we sought to determine a molding pressure that will result in good replication. After a few trial simulations, it was found that for the geometry under consideration, at 450 °C, a pressure of 40 MPa would result in a filled mold after 2 min.

The corresponding hot-embossing experiment was carried out on a servohydraulic Instron testing machine equipped with heated compression platens. A 12 mm square sheet specimen of Vitreloy-1b, and a 12 mm square patterned silicon master were aligned and placed between the heated compression platens. The embossing experiment was conducted under nominally isothermal conditions at a temperature of 450 °C in air. The load was ramped up to produce a pressure of 40 MPa in 2 s, and thereafter held constant for another 2 min. Following the embossing process, the metallic glass substrate and silicon wafer, now locked together, are removed from the load frame, and the metallic glass is separated from the silicon mold by etching away the silicon in a heated KOH bath.

An SEM image of the embossed pattern is shown in figure 3(a), and a numerically predicted pattern is shown in figure 3(b). We further investigated the quality of the embossed features using a Zygo optical profilometer; figure 4 compares representative cross-sections of the embossed features in the metallic glass (circles), against the numerically predicted channel profile (dashed line). The final geometry of the embossed channels predicted by the numerical simulation agrees well with the results from the micro-hot-embossing experiment.

6 The numerical pattern has been mirrored and repeated during post-processing to ease comparison with the corresponding experimental result.

7 The optical profilometry method that we used to measure the channel profile is not capable of providing data for the sharp vertical features.
Figure 3. (a) SEM micrograph of the embossed pattern in the metallic glass, and (b) the corresponding numerical prediction. The plane strain simulation has been extruded and mirrored to make the comparison more clear.

Figure 4. Comparison of the experimentally measured (circles) and numerically predicted channel profile (dashed line).

Our results from two additional micro-hot-embossing experiments on the metallic glass Vitreloy-1b are shown in figure 5—since both patterns involve similar depths and aspect ratios as in the plane strain pattern above, the same processing parameters were utilized.

(i) Figure 5(a) shows SEM images of the silicon master and resulting metallic glass part and a corresponding optical profilometry trace of a set of concentric raised rings, each \( \approx 50 \mu m \) wide and \( \approx 45 \mu m \) high.
(ii) Figure 5(b) shows images of a simple gear-like pattern with a height of \( \approx 51 \mu m \).

Such embossed patterns in metallic glasses have also been previously reported in the literature (cf e.g. [7]).

Next, we report on our results of thermoplastic forming of a metallic glass tool made from Vitreloy-1b, which has the (negative) microchannel pattern for a simple micro-mixer, a schematic of which is shown in figure 6. The micro-mixer design has two inlets which converge into a single long serpentine mixing channel with a single outlet. The mixing channel is \( \approx 50 \mu m \) wide, and was DRI-etched to a depth of \( \approx 40 \mu m \) on a silicon tool. In addition to the serpentine micro-mixing channel, the pattern also has a number of micron-size
3. Micro-hot-embossing of amorphous polymers using metallic glass tooling

A number of different amorphous polymers have been used for making microfluidic chips. Some common choices are poly(methyl methacrylate) (PMMA), cyclo-olefin-polymers (such as Zeonex), cyclo-olefin-copolymers (such as Topas), polystyrene (PS) and polycarbonate (PC). Here, we focus our attention on PMMA and the cyclo-olefin polymer Zeonex-690R. The nominal glass transition temperatures of these two materials are

\[ \text{PMMA: } T_g \approx 115 \degree \text{C} \quad \text{and} \]
\[ \text{Zeonex – 690R: } T_g \approx 136 \degree \text{C}. \]

Details of the processes used to manufacture and test functional microfluidic devices made from PMMA are presented in [25, 26]. Briefly, the micro-hot-embossing process consists of applying a nominal pressure of 1.5 MPa while heating the PMMA substrate to a temperature of 150 \degree \text{C} over the course of 50 s and subsequently cooling to a temperature of 80 \degree \text{C} over the course of 80 s, at which point the pressure is removed, and the metallic glass tool and embossed polymeric substrate are separated. This process of demolding below the glass transition of the polymer is done so that the embossed geometries are locked-in and features are not damaged upon demolding [1]. The process has been designed such that the total cycle time is under 3 min, allowing for a high volume of parts (hundreds) to be produced in a relatively short amount of time [26].

SEM images of one of the resulting PMMA parts, before the part is capped, are shown in figure 8(a). As in figure 7, figure 8 shows close-ups of one of the straight portions, one of the bends, several straight portions and the Y-section where the two inlets meet.

Hundreds of PMMA microfluidic chips with this pattern were produced without any noticeable degradation in quality, indicating that the metallic glass tool withstood numerous thermal-mechanical loading cycles with negligible wear, and without failure [25]. As evidence of this claim, figure 9(a) shows an SEM image of one of the straight portions on a metallic glass tool that has not been used, while figure 9(b) shows the same section of a tool after it was subjected to \approx 350 embossing cycles. A comparison of these two figures (as well as images from several other sections of the used and unused tools, not reported here) shows that no observable degradation of the metallic glass tool has occurred after \approx 350 embossing cycles.

The micro-mixer pattern was also embossed in the cyclo-olefin polymer Zeonex-690R using a process cycle similar to that described above, but with a peak temperature of 160 \degree \text{C}, a nominal pressure of 2 MPa and a demolding temperature of 85 \degree \text{C}. Figure 8(b) shows SEM images of various portions of the resulting Zeonex part. Figure 10 shows a comparison of the straight portions of ridge/channel cross-sections between the metallic glass tool and the embossed Zeonex; the measurements were made with a Zygo optical profilometer. This figure clearly shows, in quantitative terms, that the desired pattern was faithfully reproduced in the Zeonex substrate.

4. Production of small-scale, high-aspect-ratio, high-density micropatterned surfaces

One of the major advantages of using a metallic glass tool is that the polymer hot-embossing procedure described above...
may be scaled to produce micropatterns which are much smaller in length scale, are of higher aspect ratio, and are of higher density than those in the micro-mixer pattern, by simply adjusting the temperature, pressure and time used in the micro-hot-embossing process.

We produced a silicon master with the pattern shown in figure 11(a). Note that the pattern is more complex than a simple array of square posts—a wavy geometry occurs at the bottom of the trenches on the silicon tool. The surface edge length of each nominally square feature on the silicon master is $\approx 1 \mu m$, and the depth of the ‘post’ is $\approx 10 \mu m$, yielding an aspect ratio of 1:10. This pattern was hot-embossed in a Vitreloy-1b substrate using a process cycle similar to that described in the previous section; but because of the density of the microstructure, the embossing pressure was increased to 50 MPa, and the hold time was increased to 4 min. Figure 11(b) shows a view of the embossed metallic glass substrate, and figure 11(c) shows the embossed metallic glass from a different angle, looking down into the resulting trenches. From this angle, it is clear that the posts from the top part of the silicon tool have resulted in an array of square wells at the bottom of the metallic glass part.

The high-density metallic glass tool was then used to emboss a PMMA substrate at a temperature of 130 °C, under a pressure of 50 MPa for 10 min, and demolded at a temperature of 85 °C. The resulting PMMA part is shown in figure 11(d). As is clear from this figure, the pattern in the original silicon

Figure 7. SEM micrographs of (a) features in the silicon master and (b) corresponding features in the metallic glass tool.
Figure 8. SEM micrographs of (a) features in a PMMA part and (b) features in a Zeonex part.

Figure 9. SEM micrographs of one of the straight portions on a metallic glass tool that has been (a) unused and (b) subjected to \( \approx 350 \) embossing cycles.
tool shown in figure 11(a) is faithfully replicated in the PMMA substrate.

This exercise demonstrates that the process of micro-hot-embossing a metallic glass substrate with a silicon tool, and then using the resulting metallic glass part as a tool to hot-emboss patterns on polymeric substrates is scalable in producing surface microstructural feature sizes ranging from 1 to 100 μm without any change in methodology, but by only changing the pressure and the hold times during the two successive embossing processes.

5. Conclusions

A tool with a micro-mixer pattern was produced by micro-hot-embossing a Vitreloy-1b metallic glass substrate with a sacrificial DRI-etched silicon master tool, and the resulting metallic glass part was used several hundred times as a robust tool to hot-emboss the micro-mixer pattern on PMMA and Zeonex-690R polymeric substrates. Further, we have demonstrated that the silicon-to-metallic glass tool spawning process is scalable in producing surface microstructural feature sizes ranging from 1 to 100 μm without any change in methodology, but by only changing the pressure and the hold times during the two successive embossing processes.

Thus, metallic glasses are robust, attractive and viable tool materials for micro-hot-embossing of polymeric substrates for use in the manufacture of microfluidic devices. Due to the superior combination of mechanical properties, good wear resistance and homogeneity to the atomic scale, tools made of Vitreloy-1b address the persistent problems of short tool life in polymer micro-hot-embossing processes.

Finally, we note that metallic glass tooling may also be used in other manufacturing methods used to produce polymeric microfluidic devices. Indeed, metallic glass tooling has been effectively used by Mazzeo [27] for high-volume production of PDMS microfluidic devices using centrifugal casting methods, and is currently being used by Tor et al [28] in high-volume production using injection molding of amorphous polymers.

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