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# High strain rate thermoplastic demolding of metallic glasses

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ABSTRACT

Silicon templates are ideal for thermoplastic patterning of metallic glasses but their thermal expansion mismatch prevents demolding without chemical etching. Besides limiting the template life, chemical exposure alters the surface chemistry and properties of metallic glasses. To overcome these issues, we develop thermoplastic demolding which enables template reusability and fabrication of pristine metallic glass structures. Chemical-free demolding allows decoupling of topographic and compositional effects on properties of metallic glasses. We show that mechanically and chemically demolded samples exhibit distinct wetting behavior despite similar topography. The versatility of demolding technique is demonstrated for structures of different shapes and metallic glass formers.

Patterning is an effective route to change the surface properties such as adhesion [1–4], cell-response [5,6], friction [7,8], reflectance [9,10], and wetting [3,11,12]. Numerous techniques such as lithography [13–15], embossing [16–18], self-assembly [19,20], electrochemical etching [21], and laser processing [22] have been developed for patterning of semiconductors and polymers. These methods are either not readily applicable to metals or require complex hardware. Metallic glasses (MGs) are unique alloys of metals which can be patterned by simple thermoplastic methods due to the existence of their supercooled liquid state [23–27]. This is achieved by molding of MGs against templates heated above the glass transition temperature ($T_g$) followed by cooling below $T_g$ and demolding [27]. MG surfaces textured with micro [28–30], nano [31–33], and hierarchical [34] structures have been synthesized by using suitable templates. Structures harvested from the patterned surfaces have also been used for characterization of size-effects in MGs [35]. However, in all these cases the templates are chemically etched away to release the MGs. Use of chemicals not only limits the template reusability but can also affect the properties of molded MGs. It has been reported that KOH typically used for wet etching of silicon and alumina templates can de-alloy some Zr-based MGs [36]. KOH is known to decrease the hydrophobicity of materials by altering the surface chemistry and topography [37]. Size-effects are also very sensitive to the processing conditions in MGs due to their metastable structure [38]. Therefore, chemical-free demolding of templates is essential to use thermoplastic fabrication for surface engineering and characterization of small structures in MGs.

Mechanical separation of templates and MGs after thermoplastic molding is prevented by their thermal expansion mismatch (Fig. 1). The coefficient of thermal expansion ($\alpha$) for MG formers is often higher than templates (Table 1). But any combination of mismatch in $\alpha$ ($\alpha_{MG} > \alpha_{template}$ or $\alpha_{MG} < \alpha_{template}$) results in thermal stress build up on the multiple MG-template interfaces during cooling below $T_g$ (Fig. 1a). To estimate the extent of residual thermal stress, a 2D thermomechanical analysis was performed using finite element method for the Pt-based ($Pt_{57.3}Cu_{14.6}Ni_{5.3}P_{22.8}$) MG molded against silicon (Si) template (Fig. 1b). Two rectangular Si cavities filled with Pt-based MG were cooled from 503 K ($T_g$ of Pt-based MG) to room temperature. The thermal stress distribution due to mismatch in $\alpha$ was calculated using the elastic constants of Pt-based MG and Si. The residual stress in thermoplastic operations develops only during cooling below $T_g$ above which the MG supercooled liquid can relax through fast structural rearrangement. Compressive stress as high as 177 MPa was observed on the interface due to different thermal shrinkage of Pt-based MG and Si (Fig. 1b). The stress is highest at the interface close to the MG substrate due to its large shrinkage. Similar analysis was performed for other MGs and Si templates and the resulting values of maximum thermal stress are listed in Table 1. This residual stress must be minimized for characterization of intrinsic mechanical behavior of MG structures prepared by thermoplastic molding.

Thus, there are three primary reasons why an alternative demolding method for thermoplastically formed MGs is required: (1) to produce chemical-free MG patterns for understanding the topographic effects, (2) to fabricate stress-free MG structures for mechanical testing, and (3) to enable reusability of expensive lithographic templates. In this paper, we describe a novel high temperature mechanical demolding of MGs by utilizing the strain rate effects. We show that thermoplastic

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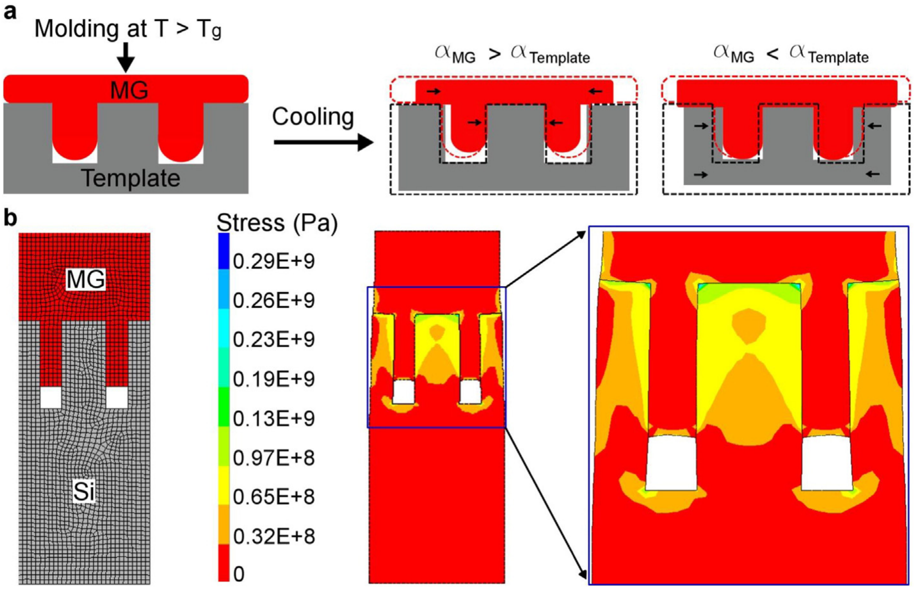

**Fig. 1.** Thermal stress development during thermoplastic molding of MGs. The schematic (a) illustrates that thermal stress is generated for any combination of mismatch ($\alpha_{MG} > \alpha_{Template}$ or $\alpha_{MG} < \alpha_{Template}$) in thermal expansion coefficients. Thermomechanical analysis for Si and Pt-based MG preformed using finite element method shows the distribution in thermal stress at MG-template interface (b).

molding and demolding of a MG supercooled liquid can be performed at the same temperature but varying strain rates without sacrificing the template or the MG features.

MG supercooled liquids exhibit a variety of flow behaviors depending on the temperature (viscosity) and strain rate (Fig. 2a). At low strain rates, the MG supercooled liquids flow homogeneously as Newtonian fluids [39–42]. At higher strain rates the viscosity of MG supercooled liquids becomes strain rate dependent and the flow becomes non-Newtonian but remains spatially homogeneous [40,43]. Further increase in strain rate results in solid-like yielding and inhomogeneous (shear-localized) deformation in MG supercooled liquids [40,41]. Low strain rates are used for thermoplastic molding because the Newtonian behavior of MG supercooled liquids can be precisely described using constitutive equations to model the shaping process [44,45]. In addition, low strain rate loading minimizes the risk of premature template failure. Ideally, the demolding should be performed above $T_g$ to avoid the thermal stress but it results in distortion of MG structures because their flow stress (cohesive strength) is lower than the adhesive strength. The flow stress of MG supercooled liquids increases with increasing strain rate in Newtonian and non-Newtonian regimes and becomes comparable to the room temperature yield strength in the shear-localized regime [40]. We propose to utilize this strain rate dependent strengthening of MG supercooled liquids for thermoplastic demolding (Fig. 2b). Thermoplastic molding is performed at a low strain rate whereas the demolding is performed at a higher strain rate but the same temperature. Above a critical strain rate, the flow stress of MG supercooled liquid exceeds its adhesive strength resulting in failure at the MG-template interface. Isothermal processing overcomes the issue of thermal stress while different strain rates invoke cohesive and adhesive failure in MG supercooled liquids during molding and demolding, respectively (Fig. 2b).

Fig. 3 demonstrates the feasibility of proposed thermoplastic demolding of MGs. Figs. 3a and b compare the SEM (scanning electron microscopy) images of patterned MG (Pt-based) released by chemical and mechanical demolding, respectively. The chemically demolded sample was prepared by molding against a Si template at 270 °C followed by etching of Si in KOH at room temperature. The mechanically demolded sample was prepared by slow pressing (~0.02 mm/s) and fast pulling (~12 mm/s) at 270 °C using a Si template. Similarity between the overall geometry of pattern features in the chemically and mechanically demolded samples demonstrates the capability of high strain rate mechanical separation. The SEM image of Si template after mechanical demolding shows that the template is free of cracks and MG residue (Fig. 3c). Therefore, the demolded template can be reused multiple times to enable cost-effective patterning of MGs. Although the critical strain rate for demolding is determined by the feature dimensions and the type of MG former, but a strain rate higher than $10^2$ s$^{-1}$ was sufficient to demold three MG formers considered here: Pd-based ($Pd_{43}Cu_{27}Ni_{10}P_{20}$), Zr-based ($Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$), and Pt-based. Square micro-pillars were mechanically demolded after

**Table 1**

The α, $T_g$, and Young's modulus for selected templates and MG formers. The maximum thermal stress is calculated from the thermomechanical analysis of MG formers cooled in Silicon from the $T_g$ to room temperature. The elastic constants of MGs are taken from Ref. [50].

| | Material | α ($\times 10^{-6}$ K$^{-1}$) | $T_g$ (K) | Young's modulus (GPa) | Maximum thermal stress (MPa) |
|---|---|---|---|---|---|
| Templates | Silicon | 2.8 [51] | | 169 | |
| | Nanoporous alumina | 16.7 [52] | | 100–125 | |
| | Electroplated nickel | 13 | | 165–205 | |
| MGs | $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ | 12.5 [53] | 503 | 94.8 | 177 |
| | $Pd_{43}Cu_{27}Ni_{10}P_{20}$ | 14.1 [53] | 588 | 93.4 | 289 |
| | $Z_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ | 9.3 [53] | 578 | 86.9 | 155 |
| | $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ | 9.9 [54] | 623 | 96 | 205 |
| | $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ | 11.3 [55] | 653 | 82 | 252 |