

Casting metal microstructures from a flexible and reusable mold

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Abstract

This paper describes casting-based microfabrication of metal microstructures and nanostructures. The metal was cast into flexible silicone molds which were themselves cast from microfabricated silicon templates. Microcasting is demonstrated in two metal alloys of melting temperature 70 °C or 138 °C. Many structures were successfully cast into the metal with excellent replication fidelity, including ridges with periodicity 400 nm and holes or pillars with diameter in the range 10–100 μm and aspect ratio up to 2:1. The flexibility of the silicone mold permits casting of curved surfaces, which we demonstrate by fabricating a cylindrical metal roller of diameter 8 mm covered with microstructures. The metal microstructures can be in turn used as a reusable molding tool.

(Some figures in this article are in colour only in the electronic version)

Introduction

Metals have attractive properties for microelectromechanical systems (MEMS) because of their high thermal and electrical conductivity, optical properties, high mechanical toughness and ductility [1, 2]. Some metals such as titanium are biocompatible [3] and can also operate at very high temperature. Metal microstructures and nanostructures are attractive for manufacturing molds for nanoimprint lithography (NIL) [4], as they can be reused many times more than silicon or quartz. Published articles report fabrication of metal submillimeter, micro- and nanostructures using forging [5–12], electroplating [4, 13–16] and casting [17, 18].

Forging can produce small-scale structures in ductile metals. In one demonstration of metal forging, 40 nm wide grooves were embossed into free-standing aluminum thin film at elevated temperatures by silicon carbide (SiC) mold templates [12]. Similarly, 300 nm grooves were fabricated into aluminum films on silicon [7]. Another study reported sub-10 nm grooves embossed into a thick nickel film using a diamond mold template [11]. Silicon can be used as a mold for metal forging [5, 6, 9, 10, 19, 20], although silicon does not have the compressive strength of SiC or diamond, and so silicon mold templates require lower forging pressures

and more ductile metals. For example, silicon molds forged 250 nm wide and 1 μm tall structures into flat gold and silver [6], where the silicon was sacrificed in a lost mold process. Surface oxidation was also a challenge in working with these metals. It is not necessary to sacrifice the silicon under all circumstances; it was possible to demold a silicon mold template following forging of 50 μm structures into a thin film of aluminum on a silicon substrate [9]. Molecular dynamics (MD) simulations of small-scale metal forging [20] found that the pile-up of excess material cannot be avoided and that forging pressure increases for decreased metal film thickness.

Microscale metal electroplating avoids pile-up of excess material and is less expensive than forging, but it is slower and sample size can be limited. Several recent reports have shown that flexible nickel sheets can be electroplated onto a polymer structured by NIL after sputtering a seed layer onto the structured polymer [13, 16, 21]. After dissolving the polymer in a lost mold process, the flexible nickel can be wrapped around a roller that can emboss continuous sheets of polymer with 1 μm wide holes 250 nm deep [4]. Electroplated Ni–Co has also been used to hot emboss Mg–Cu–Y bulk metallic glass (BMG) that then embossed polymethylmethacrylate (PMMA) microlenses [22, 23].

Somewhat less work has been reported on the manufacture of metal microstructures by casting. One strategy for

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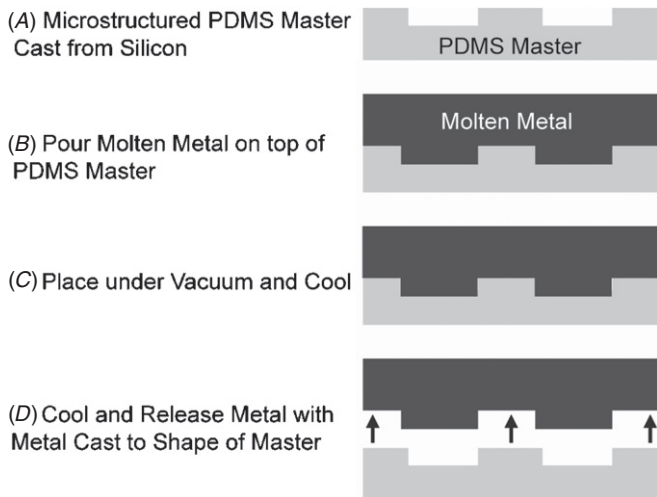


Figure 1. Process for microcasting metal. (A) Begin with a microstructured silicone master that was cast from silicon. (B) Pour molten metal on top of the silicone master. (C) Place molten metal and silicone under vacuum to release entrapped gas. Then vent to atmosphere to reduce the size of any remaining gas bubbles. (D) Cool and release metal with metal cast to the shape of the silicone master.

submillimeter casting of either aluminum–bronze or gold alloy is to cast into small plaster molds that were themselves cast from injection-molded PMMA gears [17, 18]. One strategy for microscale metal casting of one-dimensional structures is to cast microstructures into wax, cast ceramic into the wax, cure the ceramic in a lost wax method and finally cast metal into the microstructured ceramic [24].

These recent techniques that can produce metal microstructures are mostly limited to metal that is flat in a thin film. There is a need for inexpensive, parallel processes for producing metal microstructures on curved surfaces. This paper describes using an inexpensive, reusable, flexible mold with three-dimensional microstructures to meet that need.

Experiment and results

The metals for microcasting were selected to have a eutectic melting temperature below the maximum working temperature range of our microstructured silicone molds, which was about 350 °C. The metals were commercially available alloys CerroTru and CerroBend. CerroTru was composed of 58% bismuth and 42% tin, had a melting point of 138 °C, a compressive strength of 62 MPa sustainable for 5 min and a Brinell Hardness of 22. CerroBend was composed of 50% bismuth, 26.7% lead, 11.3% tin and 8.5% cadmium. CerroBend melted at 70 °C, had a compressive strength of 28 MPa sustainable for 5 min and a Brinell Hardness of 9.2 [25].

Figure 1 shows the casting process, which was adopted from a previous approach to produce microstructures on curved ceramic [26]. The process begins with a flexible microstructured polydimethylsiloxane (PDMS) silicone master, Sylgard 184 by Dow Corning. The silicone

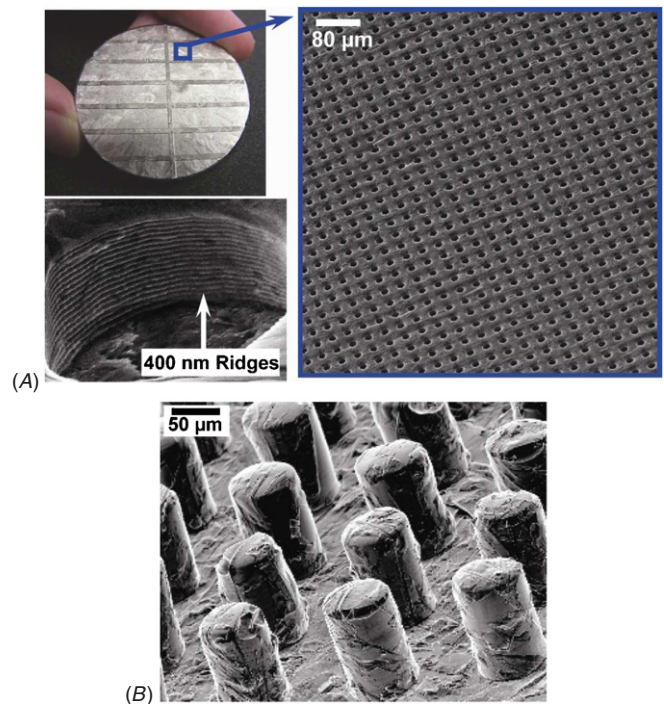


Figure 2. Microcast metal. (A) Metal with 10 μm diameter holes 15 μm deep. 400 nm ridges from the Bosch process are viewable in the picture showing a single 25 μm diameter hole. (B) Metal pillars 50 μm diameter and 100 μm tall.

master itself was vacuum cast from a silicon master etched with the Bosch process. A vacuum oven heated the silicone master to 20 °C above the melting point of the metal. Molten metal was poured onto the silicone master. The vacuum oven degassed the molten metal for 5 min while maintaining a temperature 20 °C above the melting point to keep the metal hot enough to remain liquid while air bubbles degassed. After the degassing step, the vacuum oven was vented to atmospheric pressure to decrease the size of any remaining gas bubbles within the metal. The metal solidified upon cooling and the silicone master was easily released.

Figure 2 highlights results from the metal casting process. Figure 2(A) shows an array of 10 μm diameter holes in metal that are 15 μm deep. Figure 2(A) also shows the 400 nm ridges inside a hole. The 400 nm ridges came from the Bosch process that etched the original silicon master that cast the silicone master. Figure 2(B) shows cast metal pillars that are 50 μm in diameter and 100 μm tall. Metal solidification may induce wrinkling in the silicone, which results in the observed surface finish of the metal microstructures.

A systematic study showed that high fidelity metal microstructures can be replicated from master microstructures of size between 400 nm and 100 μm , and with a height:width aspect ratio of up to 2:1. Figure 3 shows the set of master silicone micropillars used, which were of diameters 100, 50, 25, 15 and 10 μm . On the right-hand side of figure 3, the master pillars were all 15 μm tall. On the left-hand side of figure 3, the master pillars were all 50 μm tall. This set of master microstructures has sizes ranging from 10 to 100 μm and aspect ratios ranging from 1:7 to 5:1.

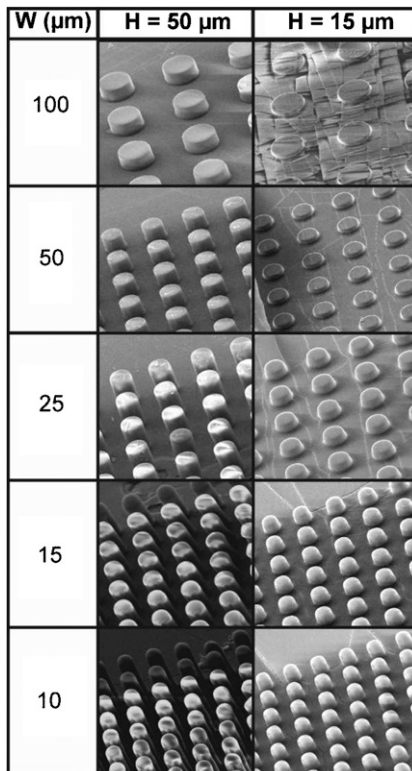


Figure 3. Set of microstructures in the silicone master. Matrix showing master pillars with height 50 and 15 μm and structure widths of 100, 50, 25, 15 and 10 μm .

Figure 4 shows metal microstructures cast from the silicone master. All of the 15 μm tall master microstructures cast well into both metals, forming 15 μm deep holes that range in aspect ratio from 1:7 to 3:2. Of the 50 μm tall master microstructures, the 100, 50 and 25 μm diameter master microstructures replicated well. The 15 μm diameter \times 50 μm tall master microstructures partially replicated. Holes next to metal cast to the shape of buckled master pillars are evidence of the partial replication. The 10 μm diameter \times 50 μm tall master pillars did not replicate well—metal cast to the shape of buckled master pillars is evidence of poor replication. For the 50 μm tall master microstructures, aspect ratios ranging from 1:2 to 2:1 replicated well. Figure 5(A) shows the 400 nm wide lines on the side of the master silicone pillars and figure 5(B) shows the 400 nm wide structures that replicated into both the 70 $^{\circ}\text{C}$ and 138 $^{\circ}\text{C}$ melting point metals. The two metals used in this study cast microstructures equally well.

One application of metal microstructures is for use as an embossing tool, and so the metal microstructures were used to emboss a polymer. Figure 6 shows the embossing process, in which a metal master is pressed into a polymer. When the polymer is a thermoplastic, heat is applied to soften the polymer, allowing the master to emboss the polymer with less force. In this work, a hot plate heated a thermoset polymer precursor to partially cure the precursor instead of softening it. Sylgard 184 base and accelerant were mixed in a 10:1 ratio by weight, and the mixture degassed under vacuum for

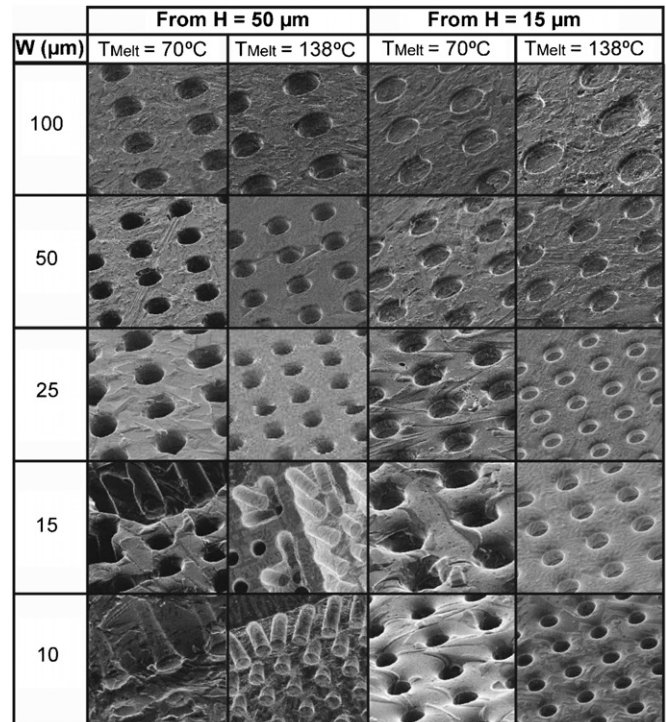


Figure 4. Set of metal microstructures cast. Matrix showing quality of casting from master pillars with height 50 and 15 μm , two metal alloys with melting points 70 $^{\circ}\text{C}$ and 138 $^{\circ}\text{C}$, and structure widths of 100, 50, 25, 15 and 10 μm .

5 min. A hot plate at 180 $^{\circ}\text{C}$ heated the silicone for 2 min to partially cure the silicone. Then 138 $^{\circ}\text{C}$ melting point metal that was cast into a microstructured embossing die embossed the partially cured silicone. The silicone fully cured for 1 min at an embossing pressure of 200 kPa. When the microcast metal released the silicone, the holes from the microcast metal had embossed pillars into the silicone as shown in figure 7.

The molding fidelity was of sufficient quality and homogeneity to produce a macroscopic effect. The embossed micropillars enhanced the hydrophobicity of the silicone by mimicking the structure of the lotus plant, shown in figure 7(B) [27, 28]. Figure 7(B) shows a 5 μl water droplet on flat silicone. The angle the water droplet makes with the solid is denoted as the contact angle and is 92 $^{\circ}$. Figure 7(B) shows that the contact angle increased to 152 $^{\circ}$ after embossing the silicone with the microcast metal. The contact angle is a static measure of hydrophobicity and the slide angle is a dynamic measure. The slide angle is measured by placing a droplet on a surface and then tilting that surface until the droplet slides. 10 μl water droplets cling to flat silicone even when it tilts to 90 $^{\circ}$, but the pillars shown in figure 7(B) reduce the slide angle to 48 $^{\circ}$.

Because the silicone mold is flexible, it is possible to mold microstructures onto curved surfaces [26]. Metal microstructures were cast into a macro cylindrical roller that could be used as a roller. Figure 8 shows the process of microcasting a metal roller. The process begins with a round macro master. A microstructured polymer such as silicone

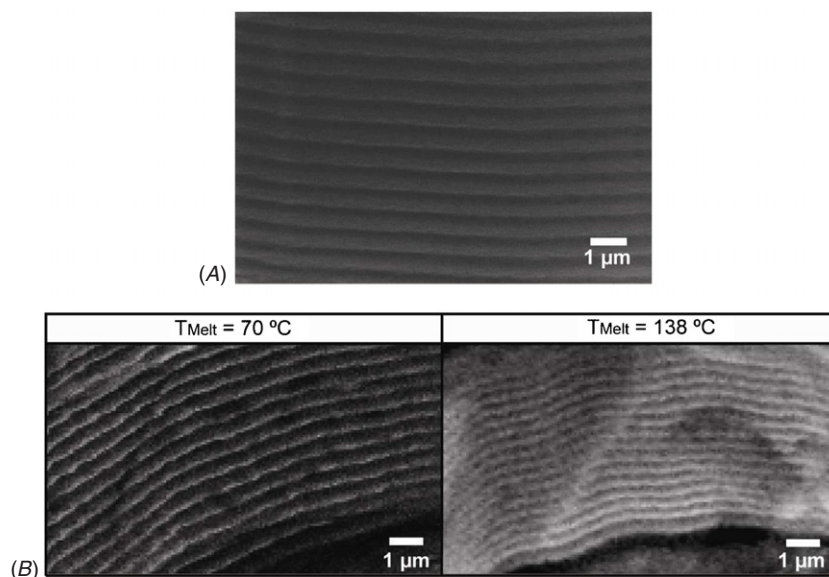


Figure 5. 400 nm wide structures in sidewall of (A) silicone master pillars and (B) metal holes cast from the silicone master.

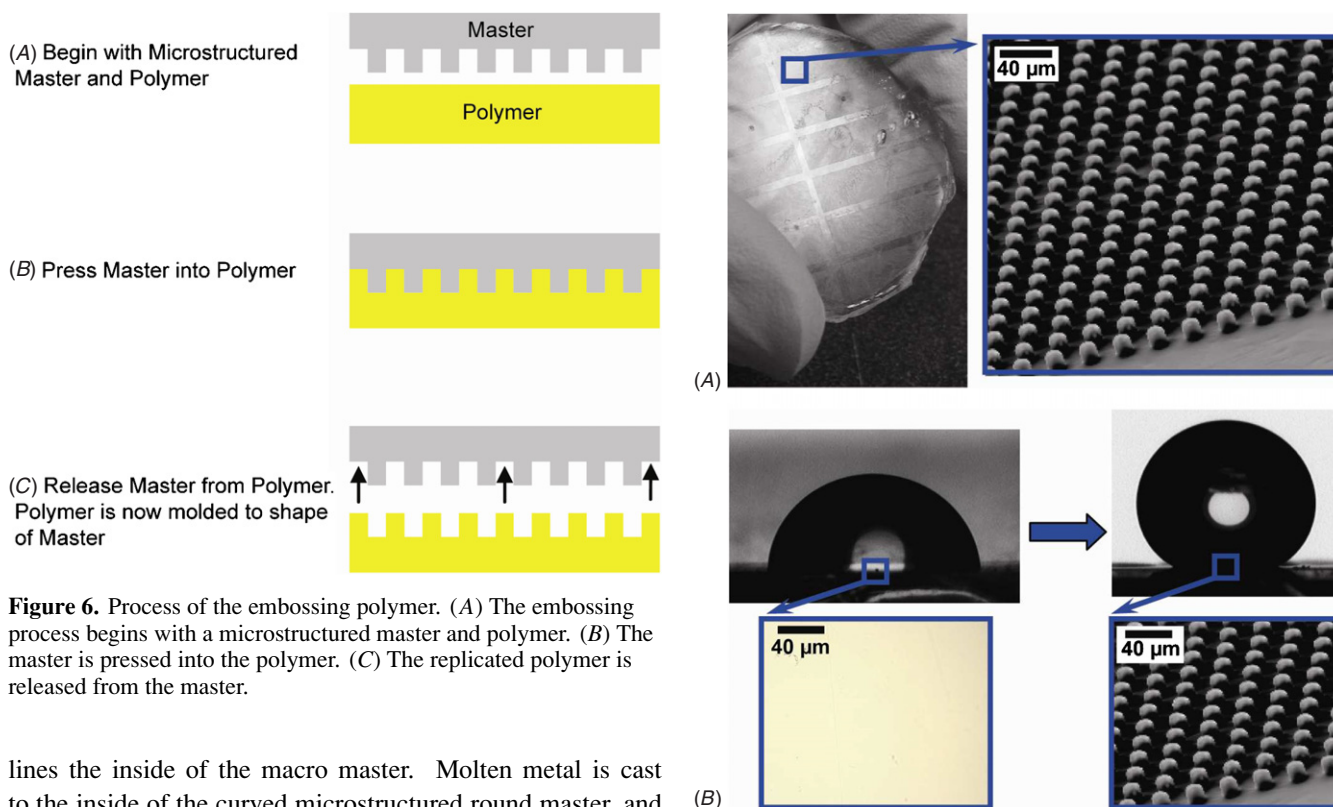


Figure 6. Process of the embossing polymer. (A) The embossing process begins with a microstructured master and polymer. (B) The master is pressed into the polymer. (C) The replicated polymer is released from the master.

lines the inside of the macro master. Molten metal is cast to the inside of the curved microstructured round master, and when the macro master and microstructured liner release the metal, a microstructured metal roller results. Figure 9 shows the resulting microstructured metal roller that could be used in industrial roll-to-roll processes. The roller is 8 mm in diameter, and the curvature of the roller is limited by the height and spacing of the structures on the flexible master. If the structures are sufficiently tall and in sufficient proximity that they touch when they are flexed to the curvature of the macro mold, then the resulting metal roller will have distorted structures, and demolding may also be difficult.

Figure 7. Microcast metal used as an embossing master. (A) Silicone embossed by microcast metal. (B) Left: 5 μl water droplet on flat silicone with contact angle 92°. Right: 5 μl water droplet on silicone embossed with microstructured metal alloy with contact angle 152°. The silicone pillars have a diameter of 10 μm, a pitch of 20 μm and a height of 15 μm.

Discussion

Previous techniques to produce metal microstructures have been mostly limited to flat surfaces and thin films. Inexpensive,

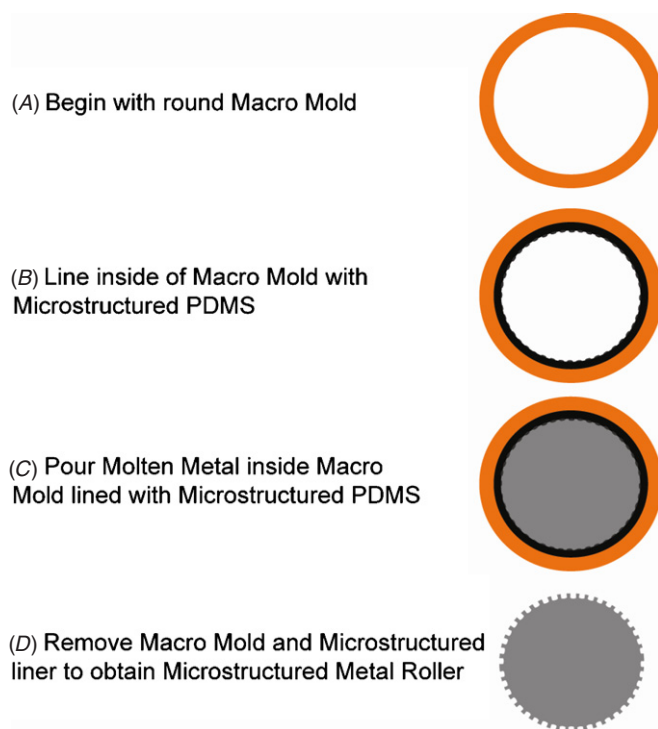


Figure 8. Process of microcasting a metal roller. (A) The process begins with a round macro master. (B) Microstructured polymer such as silicone lines the inside of the macro master. (C) Molten metal is cast to the inside of the curved microstructured round master. (D) When the macro master and microstructured liner release the metal, a microstructured metal roller results.

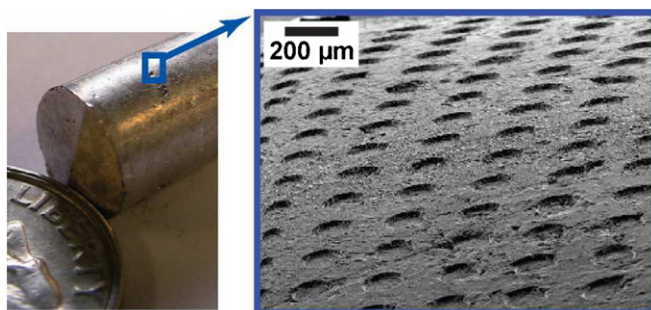


Figure 9. Microcast metal roller showing $100\ \mu\text{m}$ diameter holes $15\ \mu\text{m}$ deep. The roller could be used to emboss sheets of polymer in roll-to-roll processes.

parallel processes that lack caustic chemicals do not currently exist for producing curved, bulk metal with three-dimensional metal microstructures. Much of the forging work to date has used SiC or diamond molds patterned by electron beam lithography to forge thin metal films deposited on silicon. A metal film bonded to a second material has the general disadvantage of being constrained by the properties of the second material. In this specific case, one constraint is flatness of the forged metal. Molds made of SiC and diamond are expensive because of material and processing techniques.

While using silicon molds can reduce the mold material and fabrication expense, silicon die wear and failure problems exist because of the brittle nature of silicon [5]. Designing the molds with sloped sidewalls lacking sharp edges and corners

can mitigate mold wear and failure. Using maximum aspect ratios of 1:1 in mold structures also reduces mold wear and failure. One previous report used finite element analysis (FEA) to investigate microscale room temperature imprinting of aluminum with silicon, and it suggests that silicon mold wear occurs because of misalignment during molding and demolding, causing uneven tensile stresses and frictional tractions [10]. Ductile metals such as platinum, gold and silver are often used in forging processes to mitigate die wear and failure. While precious metals are ductile, they are also much more expensive than the alloys used in the present study. Casting can be used to microstructure metals, but previous work has used lost mold techniques and brittle plaster molds to fabricate three-dimensional submillimeter structures and one-dimensional microscale structures. Compliant polymer molds have an advantage over silicon in terms of wear, over lost molding techniques because polymer molds are reusable and also lack the wax and ceramic casting steps which introduce defects, and over brittle plaster in terms of demolding ease. Also, replacing a worn polymer mold is inexpensive.

Replication fidelity depended upon relative temperatures between the molten metal and the silicone and also the thickness of the silicone master, apparently due to the thermomechanical deformation of silicone. In the first trials, molten metal $30\ ^\circ\text{C}$ above the silicone temperature was poured onto $0.7\ \text{mm}$ thick silicone masters. While the silicone microstructures replicated into the metal, the silicone contracted and deformed the metal macrostructure. Decreasing the temperature of the molten metal to equal the temperature of the preheated silicone and increasing the thickness of the silicone masters to $2\ \text{mm}$ enabled the silicone masters to withstand the thermal stresses of casting and produced the results presented here. We speculate that thin silicone would work well if adhered to a stiff surface. Another challenge to casting the metal with high fidelity was the high surface tension of the molten metal. Surface tension caused the liquid metal to be suspended on the tops of the silicone pillars rather than be in intimate contact with the spaces between the silicone pillars. Applying mild pressure to the liquid metal caused the suspended liquid to collapse into the spaces between the silicone pillars.

Conclusions

The present work explores casting of low melting temperature metal alloys directly to microstructured silicone. A systematic study showed that metal is reliably cast to ridges with periodicity $400\ \text{nm}$ and holes or pillars with diameter in the range $10\text{--}100\ \mu\text{m}$ and aspect ratio up to 2:1. The casting techniques required no solvents, and the mold used in this process is highly flexible in two dimensions, enabling fabrication of metal microstructures into surface curvature in two dimensions. Using silicone molds allows a route to metal microcasting that does not require microfabrication equipment. This paper demonstrates the usefulness of microstructured low melting temperature alloys by casting an embossing die that then embosses micropillars into the polymer, enhancing the hydrophobicity of the polymer.

Another demonstration casts a microstructured cylindrical metal roller that could emboss sheets of polymer in roll-to-roll processes. A roll-to-roll process could also be developed where a polymer roller micromolds a continuous sheet of metal. Molten metal could enter a cold polymer roller, and the roller could press the metal into its microstructures, outputting solidified microstructured metal in a continuous sheet. Similarly, a microstructured polymer conveyor could be a mold for a continuous stream of molten metal that cools once the molten metal is cast to the polymer microstructures and is removed as a continuous sheet. Future work will explore the minimum structure size attainable with the present casting technique and casting metals with higher melting points to silicone.

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