Metallic glass mold insert for hot embossing of polymers

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Metallic glass mold insert for hot embossing of polymers

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Molding of micro components from thermoplastic polymers (TPs) has become a routinely used industrial production process. To find hard, ductile and durable material for mold insert and to fabricate the mold insert are two big challenges for the thermoplastic polymers fabrication techniques. We report that a Pd-based metallic glass (MG) mold insert was readily fabricated in its supercooled liquid region, and the atomic force microscope measurement and time-temperature-transformation analysis show that the metallic glass mold insert has very fine surface quality and long service life. We show that the metallic glasses, which have remarkable mechanical properties and excellent thermoplastic forming ability, are new ideal materials for hot embossing mold insert of thermoplastic polymers. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4737484]

I. INTRODUCTION

Recent years, the increasing demand for polymer-based micro-scale devices has resulted in a flood of research on the micro-scale fabrication of polymer products. Many polymer-based micro-fabrication techniques have been explored for applications in bio-, chemical, and optical MEMS (micro-electro mechanical system).[1–3] Micro molding of thermoplastic polymers (TPs) especially hot embossing is one of the most promising fabrication techniques for non-electronic micro devices.[4,5] To perform micro molding of TPs, molding tools, which are used to define pattern on the surface of TPs, are required and the essential part of the tools is the mold insert, which is responsible for the primary micro structure.[4,5] In order to preserve the micro structure over as many molding cycles as possible and withstand lateral force during molding, the materials of the mold insert should be hard and ductile enough.[6] People have developed many different kinds of materials such as metals, polymers, and even ceramics to fabricate mold insert, however, they are either not strong enough or not sufficiently ductile.[7]

Besides the problem of choosing a suitable material for mold insert, another big challenge is how to fabricate the mold insert.[8,9] The current available methods include direct structuring, including mechanical micro machining, laser structuring, electric discharge machining (EDM), and lithographic processes with x-rays or UV radiation combined with electroplating, and so on.[6] Nevertheless, the existing disadvantages of these technologies such as low dimension precision, unsatisfactory surface quality or time consuming, and so on leave much to be desired for the fabrication of novel mold insert.[6,7,10]

Bulk metallic glasses (MGs) exhibit superior mechanical properties like high yield strength, hardness and fracture toughness, high wear and corrosion resistance,[11,12] which exactly meets the requirements of material needed for the mold insert. Figure 1 compares the mechanical properties (yield strength versus fracture toughness) of some typical MGs[11] with the commonly used mold insert materials. It can be seen that some MGs are ideal for the fabrication of the mold insert, the MGs are stronger than steel and copper alloys and tougher than the very fragile silicon. Nickel is also an important mold insert material, however, it needs the electroplating process and the electrodeposited Ni goes soft dramatically (from ~1800 MPa at room temperature decrease to about 100 MPa at 600 K) when the temperature is higher than 423 K,[13] making it not suitable for some polymers which need higher processing temperature. What is worse, the essential process for producing the mold is very expensive and requires long production cycle (more than several weeks). Besides excellent mechanical properties, bulk MGs also have desirable thermoforming ability in their supercooled liquid region (SLR),[14–16] which is a temperature window between glass transition temperature T_g and crystallization temperature T_x. Therefore, the MG mold insert can be net-shape formed with precise micro even nano-scale structure owing to their amorphous nature.[16–18] The above-mentioned features could make MGs the ideal material for mold insert of polymer micro molding. Computer-numeric-controlled (CNC) milled MGs insert had been used in the micro molding of cyclic-olefin-copolymer (COC), however, the minimum feature size of the micro structure was limited by the cutting tool, and the passable surface quality which was induced by mechanical milling resulted in uneven surface on the polymer samples.[16] In present work, we show that thermoformed bulk MGs are suitable for the fabrication of mold insert which can be used in hot embossing of polymers. The MG mold insert is demonstrated to be durable and towards to ideal hot embossing mold insert of thermoplastic polymers.

II. EXPERIMENTAL

$Pd_{40}Cu_{30}P_{20}Ni_{10}$ (at.%) MG possesses admirable mechanical properties,[18] as depicted in Fig. 1. Other MGs also

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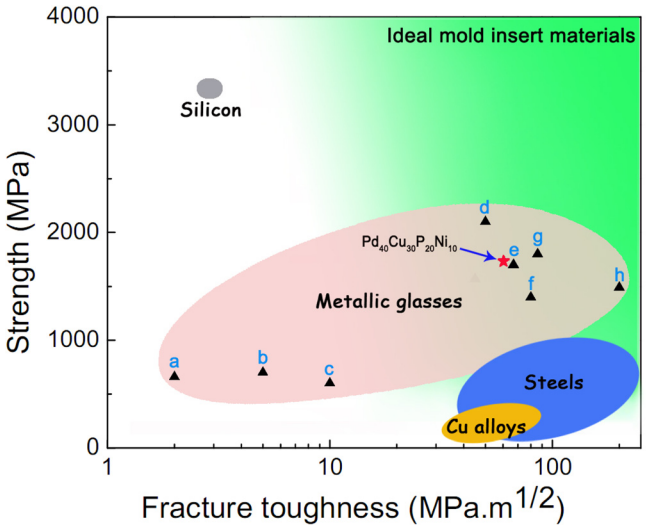

FIG. 1. Mechanical properties of metallic glasses compared with common mold insert materials, data for typical metallic glasses[11] (a: $Mg_{65}Cu_{25}Tb_{10}$; b: $La_{55}Al_{25}Ni_5Cu_{10}Co_5$; c: $Ce_{60}Al_{20}Ni_{10}Cu_{10}$; d: $Ti_{50}Ni_{24}Cu_{20}B_1Si_2Sn_3$; e: $Cu_{60}Zr_{20}Hf_{20}Ti_{10}$; f: $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$; g: $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$; h: $Pd_{79}Ag_{3.5}P_6Si_{9.5}Ge_2$) designated by solid triangle and $Pd_{40}Cu_{30}P_{20}Ni_{10}$ designated by red solid five-pointed star. The materials in the green region are regarded as the ideal mold insert materials.

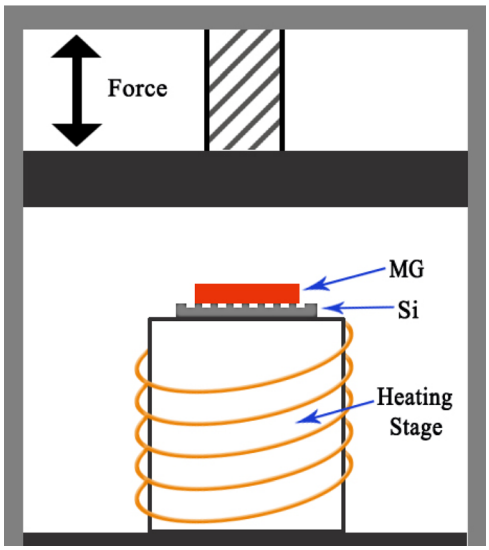

FIG. 2. Schematic drawing of the thermoforming process of MG mold insert.

have good mechanical properties and thermoforming ability.[19,20] In the work, we chose the typical Pd-based MG as model system owing to its relative large SLR and good resistance to oxidation and crystallization.[21,22] Moreover, it still keeps strong and tough below its T_g temperature (about 573 K[23]), which is enough for molding most polymers. To thermoform a mold insert, $Pd_{40}Cu_{30}P_{20}Ni_{10}$ MG plates with a thickness of 1 mm and width of 8 mm were prepared by conventional water cooled copper mould casting process. The Si die, which was used to thermoform micro structures on the surface of MG plate, was fabricated by photoetching technique. Figure 2 shows the schematic diagram of the thermoforming process of the bulk MG mold insert using Si die. The MG plate was heated to 620 K (the temperature is in the supercooled liquid region of the MG) by a resistance heating stage, and then a force of 20 MPa was applied and held for 20 s. Owing to the viscous state in its SLR, the MG plate replicated the micro structures of Si die. For comparison, two different micro structures of the periodic hole arrays and grating arrays were made.

III. RESULTS AND DISCUSSIONS

The atomic force microscope (AFM) observation was taken on SPA-400 to examine the profile and surface quality of the hot embossed MG mold insert. In order to evaluate the thermoforming quality of $Pd_{40}Cu_{30}P_{20}Ni_{10}$ MG, a smooth surface was hot embossed with a polished silicon wafer. Figure 3(a) shows the AFM image of the MG smooth surface, and surface roughness of the scanning area ($20 \times 20\ \mu m^2$) is 2.76 nm, even smaller than the polished silicon which is about 5 nm. The small surface roughness indicates good thermoforming ability and glassy nature of the $Pd_{40}Cu_{30}P_{20}Ni_{10}$ MG, and this ensures excellent surface quality of polymer products made by the MG mold insert.

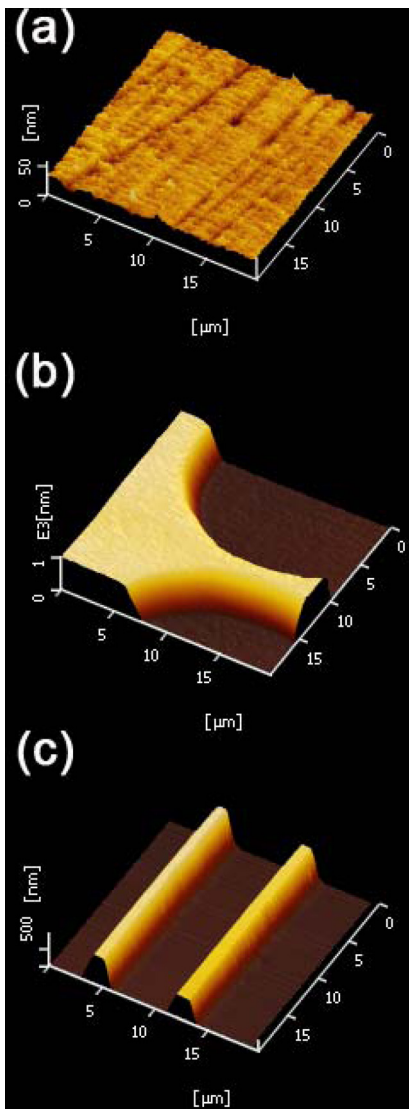

FIG. 3. AFM images of $Pd_{40}Cu_{30}P_{20}Ni_{10}$ MG surface after hot embossing. (a) is a flat surface embossed by a polished silicon wafer, (b) and (c) are the embossed hole arrays and grating arrays, respectively.

This also makes great sense for the demolding process when being used as the mold insert. Figures 3(b) and 3(c) present the AFM images of MG surfaces with different micro structures hot embossed on them. The surface roughness of the periodic hole arrays (Fig. 3(b)) and grating arrays (Fig. 3(c)) are 12.49 nm and 6.94 nm, respectively, which is much smaller than the mold insert fabricated by CNC machine (about 300 nm for steels).[17]

To characterize the performance of the Pd-based MG mold insert, several typical polymers were hot embossed with it. The chosen polymers were polyethylene (PE), polycarbonate (PC), polypropylene (PP), and COC, and the hot embossing parameters are summarized in Table I. Figure 4 presents the scanning electron microscope (SEM) images of the MG mold insert with two different micro structures and the polymers after hot embossing. An ultrathin conductive gold layer (less than 20 nm) was deposited on the surfaces of polymers to conduct SEM observation. It can be seen that the polymers perfectly replicated the micro structures on the surface of the MG mold insert. To evaluate the forming quality of the polymers, an f parameter, which describes the periodicity differences between the MG mold insert and the polymer replicas, is proposed as

$$f = \frac{\Lambda_{MG} - \Lambda_{polymer}}{\Lambda_{MG}} \times 100\%, \quad (1)$$

where $\Lambda_{polymer}$ and Λ_{MG} are the periodicity of the polymer product and MG mold insert, which can be obtained from the SEM measurement. The calculated f value for PE, PC, PP, and COC are 0.053, 0.033, 0.028, and 0.030, respectively, which are mainly caused by the thermal expansion of these polymers. The small values of the parameter indicate excellent filling ability when conducting hot embossing.

MGs will crystallize at certain temperature for some time, which is determined by the nucleation and growth mechanism.[24,25] The crystallization may result in brittleness, dimensional change, and even increase the surface roughness of the MG mold insert.[26] To avoid such process, the temperature which is needed for the hot embossing of polymers should not be very high. Fortunately, for most TPs, this temperature is below 473 K, which is far less than the crystallization temperature T_x (about 675 K[23]) of the $Pd_{40}Cu_{30}P_{20}Ni_{10}$ MG. The temperature and time dependent transformation from amorphous to crystalline state of this MG can be summarized in a temperature-time-transformation (TTT) diagram which was performed by isothermal crystallization studies,[24] as presented in Fig. 5. The light green region is the temperature range for hot embossing of most TPs. Data in

TABLE I. Hot embossing parameters for different polymers.

Acronym	Full name	Embossing temperature (K)	Pressure (MPa)	Hold time (s)
PE	Polyethylene	413	2	3
PC	Polycarbonate	468	2	3
PP	Polypropylene	438	2	3
COC	Cyclic olefin copolymer	438	2	3

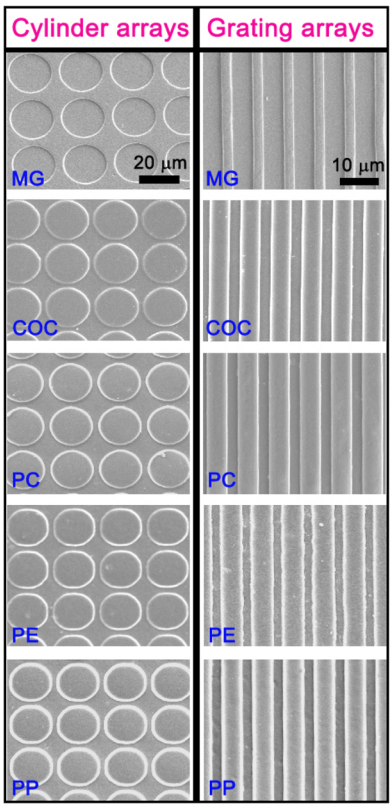

FIG. 4. SEM images of $Pd_{40}Cu_{30}P_{20}Ni_{10}$ MG mold insert with two different structures and thermoplastic polymer products after hot embossing.

Fig. 5 (open square) were taken from Ref. 19 and the red line plots the trend of the TTT data, which is extrapolated to 400 K. From the plot in Fig. 5, it can be easily estimated how much time it takes to crystallize a $Pd_{40}Cu_{30}P_{20}Ni_{10}$ MG mold insert. The solid triangles stand at the temperature that is required to hot emboss corresponding thermoplastic polymer. We define the time span before crystallization as the service life of a MG mold insert, then the service life of the $Pd_{40}Cu_{30}P_{20}Ni_{10}$ MG mold insert estimated from the TTT diagram is 875 days, 27 yr, 27 yr, and 200 yr for the hot embossing of PC, PP, COC, and PE, respectively. Actually,

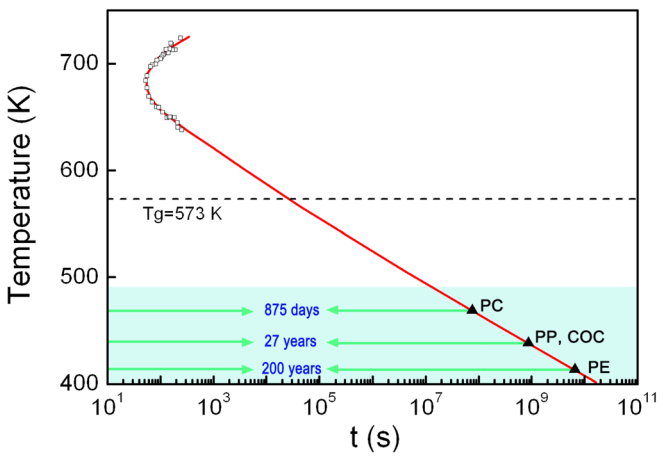

FIG. 5. TTT diagram of $Pd_{40}Cu_{30}P_{20}Ni_{10}$ MG. The open square data points are taken from Ref. 23. The red plot which is extrapolated to 400 K shows the trend of the TTT curve.

in consideration of the cooling step during the hot embossing cycle, the actual service life should be longer than the estimated above.

As metallic alloys, MGs have high thermal conductivity compared with the nonmetallic materials such as silicon, which will reduce the heating and cooling time and increase the production efficiency when they are used as the mold insert materials. Furthermore, due to their unique amorphous structure, the typical thermal expansion coefficient of them is several times smaller than that of the crystalline metals and alloys, suggesting a much higher dimensional accuracy.[15] Moreover, the lack of crystalline defects makes MGs have fine chemical corrosion resistance.[27] Therefore, the addition of release agent to the surface of mold insert would not damage the micro structures on it. All these factors indicate that MGs are the desired candidate for the mold insert materials of TPs. In our future work, we will fabricate complex structures by hot-embossing and compare the performance of metallic glass mold with that made of other mold materials.

IV. CONCLUSIONS

We demonstrate that MGs were ideal mold insert materials for hot embossing of TPs owing to their remarkable mechanical properties and excellent thermoforming abilities in their supercooled liquid region. $Pd_{40}Cu_{30}P_{20}Ni_{10}$ MG mold insert with different micro structures were fabricated by hot embossing. The analysis shows that the MG mold insert has outstanding surface quality and long service life for typical TPs. Our results may open a route for application of metallic glasses.

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