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Fabrication of metallic glass micro grooves by thermoplastic forming

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Abstract

Metallic glasses (MGs) are considered as ideal materials for miniature fabrication because of their excellent thermoplastic forming ability in the supercooled liquid region. We show that Pd-based MG micro grooves, which are essential for microdluidic devices, can be prepared by a highly efficient and precise fabrication method. The scanning electron microscope observation and surface profiler measurement show that the MG micro grooves have superior dimensional accuracy. The excellent corrosion resistance of MGs compared with silicon, which is the conventional microfluidic device material, is also proved by the weight-loss corrosion method. Our results indicate that MG can be a promising candidate material for the fabrication of microfluidic devices and may have broad applications in the biomedical areas.

Keywords: metallic glass, thermoplastic forming, micro grooves

(Some figures may appear in colour only in the online journal)

1. Introduction

Microfluidic devices, first developed in the early 1990s, are recently gaining more and more popularity. Microfluidics refers to a set of technologies that control the flow of small amounts of liquids or gases, which is typically measured in nano- or picoliters, in a miniaturized system, including a set of micro reservoirs and micro-channels [1, 2]. A variety of interesting measurements such as molecular diffusion coefficients, fluid viscosity, pH, chemical binding coefficients and enzyme reaction kinetics can be conducted by the usage of microfluidic devices [3–6]. Driven by their extensive applications, different methods have been developed to fabricate such structures [7, 8]. Applications for microfluidic devices also include capillary electrophoresis [9–11], immunoassays, flow cytometry, deoxyribonucleic acid (DNA) analysis, cell manipulation, cell separation, cell patterning [12], and pressure and flow sensors [13]. Microfluidic devices in current use are usually fabricated in silicon and glass using photolithography and etching techniques adapted from the microelectronics industry, which are precise but expensive and inflexible, or they can be fabricated in polymers by hot embossing and injection techniques, however, polymers have a large thermal expansion during thermoforming, resulting in poor dimensional accuracy. They also tend to degrade with time and temperature [12]. In addition, microfluidic devices usually refer to various chemical liquids, therefore, the compatibility between the material of microfluidic devices and chemical liquids is also a area of concern. Thus, a material with good corrosion resistance in its service environment is more favorable, and ideal for the fabrication of microfluidic devices.

Bulk metallic glasses (MGs) have attracted significant research since they were discovered in the 1960s [14]. They exhibit superior mechanical properties such as high yield strength, hardness and fracture toughness, high wear and corrosion resistance because of their unique amorphous

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structure [15–18]. Besides this, MGs can be thermoplastic, formed in the same way as plastics, and due to this their viscosity drops dramatically with the increase of temperature in their supercooled liquid region (SLR), a temperature window between the glass transition temperature T_g and crystallization temperature T_x [19–23]. Moreover, owing to the absence of crystalline defects, the solidification shrinkage of MGs during thermoplastic forming is only approximately 10% that of conventional crystal alloys [23], and thus the MGs show high dimensional accuracy when conducting thermoform, which suggests that they are the desirable materials for miniature-fabrication. In addition, the thermoplastic forming of MGs has been proved to be a convenient and low-priced miniature-fabrication [24, 25]. In the present work, we show that the micro grooves with fine feature size can be fabricated on the surface of MG by using the readily thermoplastic forming method, and the micro grooves are promising for the microfluidic devices, which may open a new application for this unique material.

2. Experimental details

To choose an appropriate MG for thermoplastic forming, some characteristics must be considered. The MG should have good flow properties and be stable under heat in its SLR. A PdNiCuP bulk glassy alloy was chosen for the present study, as the MG has been proven to have excellent glass-forming and thermoforming ability, large SLR and good resistance to oxidation and crystallization [26, 27]. The PdNiCuP bulk MG plate with a thickness of 1 mm and width of 8 mm was prepared from a master alloy with nominal composition Pd 40 at.%, Ni 10 at.%, Cu 30 at.%, and P 20 at.% by a conventional water cooled copper mould casting process [18]. For the convenience of thermoplastic forming, the plate was cut to a length of about 10 mm and then the surface was polished by the abrasive paper and polishing machine. The silicon molds, which have microfluidic patterns and were used as dies to thermoform micro structures on the surface of MG plate, were fabricated by the photoetching technique (the well known LIGA technique), as is illustrated in figure 1. The polished silicon wafer was coated with S1813 photo resist. It was followed by ultraviolet exposure using a UV lithography system (MA6) in order to define the micro grooves, which were fabricated on the exposure mask, on the photo resist. After development, the wafer was etched using an inductively coupled plasma (ICP) system (PlasmaLabSystem100), then the micro pattern was finally transferred from the mask to the silicon wafer and we obtained the silicon molds with micro grooves. The thermoplastic forming process of the MG micro grooves is illustrated by figure 2(a). The MG plate was heated into its SLR (=620 K) by a resistance heating stage, then a force of about 10 MPa was provided by the electromechanical INSTRON 3384 equipments and held for several seconds. Because the required temperature and force are relatively low in this process, the silicon mold can be reused many times without breaking, which helps significantly in reducing the cost. The whole process lasted for less than half a minute, indicating high efficiency of this easy fabrication method. Figure 2(b) illustrates the typical patterns for micro grooves and the areas of interest

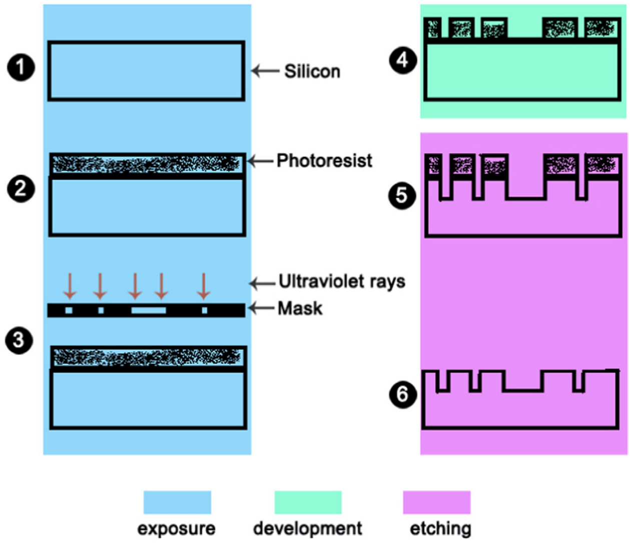

Figure 1. Schematic diagram of the silicon molds fabrication process.

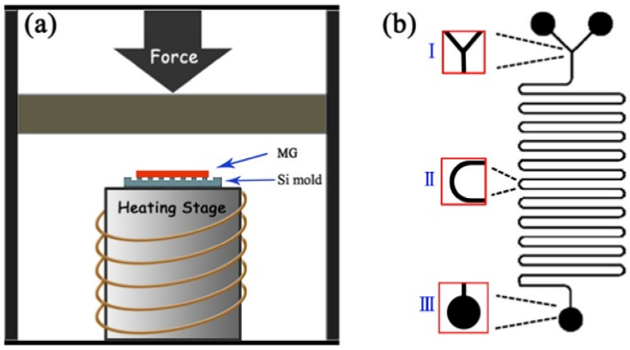

Figure 2. (a) Schematic diagram of the fabrication of micro grooves; (b) illustration of the microfluidic patterns (labeling denotes areas of interest).

are labelled by I, II and III. Usually, there are some defects in the labeled areas for micro grooves with poor quality, so the dimensional accuracy of the labeled areas can be regarded as an important index to evaluate the quality of micro grooves [12]. The surface features of the structured MG plate and silicon mold were examined by scanning electron microscopy (SEM) observation, performed on a Philips XL30 SEM instrument.

The height of the silicon mold and the corresponding depth of the MG product were investigated by a stylus surface profiler (Bruker, DektakXT). The corrosion resistance experiment was measured by the weight-loss method. The specimen with a surface area S and initial mass m_0 was immersed in a corrosion solution for a period of time t, the mass of the specimen became m', and the corrosion rate of the specimen in the corrosion solution can be calculated.

3. Results and discussion

Figure 3 shows the SEM images of silicon mold and MG micro grooves at concerned areas I, II and III respectively. It can be seen that MG perfectly replicates the micro structure

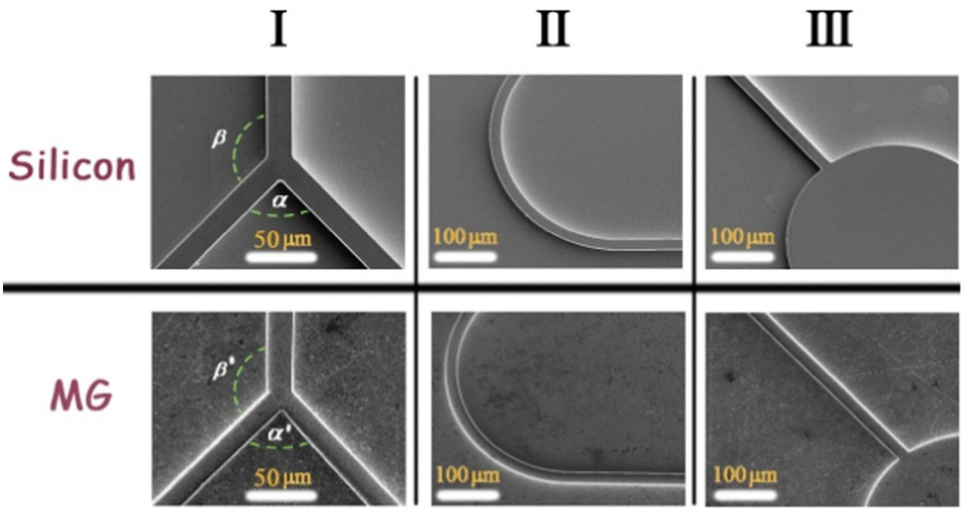

Figure 3. SEM images of silicon and MG micro grooves at concerned areas I, II and III.

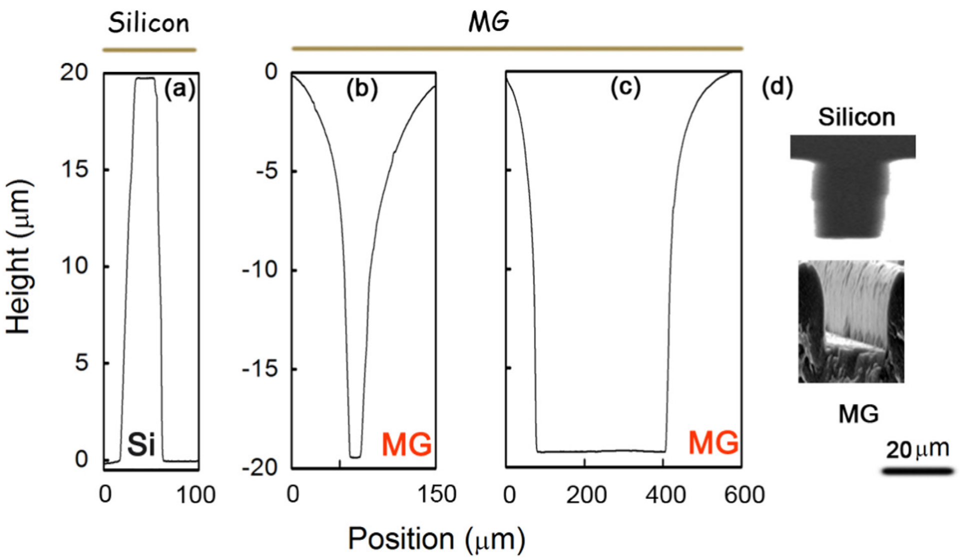

Figure 4. Cross-sectional views of silicon mold and MG product. (a) The height of the micro structure on silicon mold; (b) and (c) the corresponding depth of MG product at different positions; (d) the cross-sectional view of the silicon mold and the MG replica.

on the silicon mold. The width of the designed micro channel on the silicon mold is 18.50 ± 0.03 μm, and the MG product is 18.45 ± 0.05 μm with only a slight average error of about 0.27% compared with the silicon mold. However, this dimensional error could be as large as $>3\%$ due to the large thermal expansion coefficient, if we use polymers such as polyethylene (PE), polycarbonate (PC), polypropylene (PP) and cyclic olefin copolymer (COC), etc [24] Moreover, if we take a further close look at area I in figure 3, it is found that the included angles α and β on the pattern of the silicon mold are $90.1 \pm 0.2°$ and $135.9 \pm 0.3°$, and the corresponding angles α' and β' on the MG product are $90.0 \pm 0.2°$ and $135.9 \pm 0.4°$ respectively. This excellent accordance between the silicon mold and MG product indicates the high dimensional accuracy of MG when conducting thermoplastic forming, and can ensure good geometrical quality during the fabrication of micro grooves using this material.

Figure 4 presents the cross-sectional views of the micro features on silicon mold and MG replica. It is seen that the height of micro pattern on silicon mold (figure 4(a)) is 19.77 ± 0.06 μm and the corresponding depth of MG replica (figure 4(b)) is 19.35 ± 0.12 μm. For a contrast, the depth of the circle area shown in area III is also measured and presented in figure 4(c). It is 19.33 ± 0.09 μm, very close to the other positions, indicating good uniformity on the whole pattern area of the MG replica. To help the reader to understand the transfer accuracy of this method, the cross-sectional images of the silicon mold and the MG replica were provided in figure 4(d). It is worth mentioning that the depth of MG replica can be precisely adjusted by changing the parameters of thermoplastic forming such as the applied force, temperature and holding time, etc [19, 20, 23, 25].

As mentioned above, the microfluidic devices usually involve a series of chemical solutions such as the acid-base solution, so the corrosion resistance is of great importance for

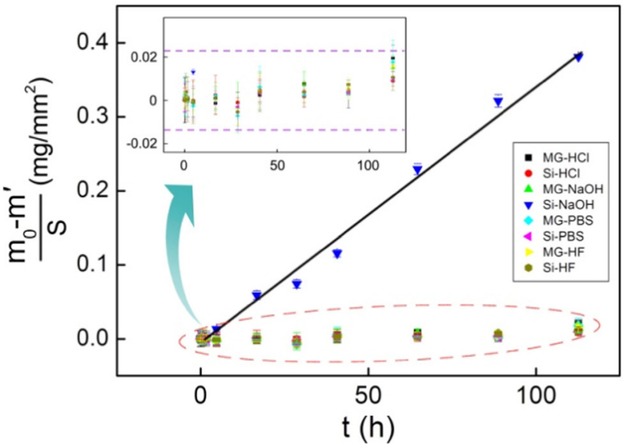

Figure 5. Mass loss of silicon and MG per unit area in different corrosion solutions with the increase of time. Inset shows the details in the red dotted ellipse region.

microfluidic device in such environment. To investigate the corrosion behavior of MG micro grooves (at room temperature), four different common solutions were prepared: 1 mol l^{-1} hydrochloric acid (HCl), 1 mol l^{-1} sodium hydroxide (NaOH), phosphate buffered saline (PBS) solution and 10 wt% hydrofluoric acid (HF). For comparison, the corrosion behavior of silicon, which is commonly used to fabricate micro grooves, is also studied. According to the weight-loss method, the corrosion rate v in certain chemical solution can be expressed as:

$$v = \frac{m_0 - m'}{S \cdot t} \quad (1)$$

where m_0 is the initial mass of a sample, m' is the mass after a corrosion time t and S is the area that is exposed in the corrosion environment. Obviously, a large v stands for a poor corrosion resistance. Figure 5 presents the mass loss of MG and silicon per unit area $\frac{m_0 - m'}{S}$ with the increase of soaking time t in the aforementioned corrosion solutions. It can be seen that both MG and silicon exhibit excellent corrosion resistance in HCl, PBS and HF solutions. The inset of figure 5 reveals the details of corrosion behaviour and the mass losses of MG and silicon are almost within the limits of experimental error in these solutions. However, as for the NaOH solution, silicon is not as stable as it is in others, the corrosion rate v calculated by equation (1) is about 0.003 42 mg $h^{-1} \cdot mm^{-2}$, which is much faster than MG in the same condition. Furthermore, if put into an elevated temperature environment, the corrosion rate of silicon in these solutions will become even larger. In contrast, due to the amorphous nature, MG shows strong corrosion resistance in a series of corrosion environments, which is favourable in the fabrication of microfluidic devices. This indicates that MG may be a promising candidate material for this field. Figure 6 shows the photograph of MG micro grooves.

Besides the advantages we have mentioned above, which make them suitable materials to fabricate micro grooves, MGs also have superior mechanical properties and a fine surface finish quality. Therefore, MG microfluidic products can be used as molding dies to further create the second-generation replicas on thermoplastic polymers, and they were proven to have better performance compared with the conventional molding tools [12, 24].

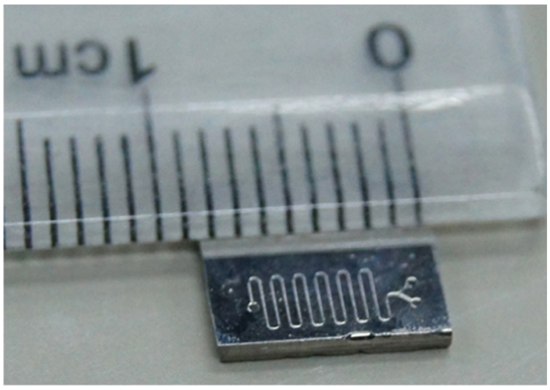

Figure 6. Photograph of a MG micro grooves.

4. Conclusions

In summary, we show that MG micro grooves can be fabricated by thermoplastic forming in their SLR. Because of their unique amorphous property, the preparation method is proven to be highly efficient and MG micro grooves show very good dimensional accuracy and excellent corrosion resistance. Our results may open a route for the application of MGs.

Acknowledgments

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