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Micro thermoplastic forming of a Pd-based metallic glass: theory and applications

Can Yang, Le-ming Lu, Zhi-wu Zhao, Jia-hao Li, Feng Gong, Jiang Ma*

Guangdong Provincial Key Laboratory of Micro/Nano Optomechatronics Engineering, College of Mechatronics and Control Engineering, Shenzhen University, Shenzhen 518060, Guangdong, China

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ABSTRACT

Metallic glasses (MGs) are considered as the ideal materials for miniature fabrication because of their excellent micro thermoplastic forming ability in the supercooled liquid region. The understanding and controlling of micro filling process are fundamental for miniature fabrication and their applications, yet presently remain unresolved issues. A universal kinetic equation was proposed to describe the filling kinetics of viscous metallic glass supercooled liquid in micro molds with general cross sectional shapes by using a Pd-based MG as the modeling material and a series of potential applications based on the micro thermoplastic forming of the MG were developed.

1. Introduction

An increasing demand for miniature parts and components on the length scale of micrometers to centimeters is required due to the advancements in technologies such as micro-electromechanical systems (MEMS), electronics devices, and microfluidic devices[1-10]. One of the most commonly used miniature-fabrication method for miniature parts and components is LIGA, an acronym that stands for Lithographie, Galanoformung and Abformung. Although it is a mature technology that allows a variety of geometries with high-aspect-ratio and good precision to be manufactured on length scales ranging from about 10 μm up to about 1 mm[11], the range of materials that can be used by such technology is limited, of which the main drawback is very expensive and time-consuming. There are also some methods of direct structuring on the material surface, such as mechanical micro machining (including turning, drilling or milling and so on), laser structuring and electric discharge machining (EDM); however, these methods cannot ensure the desired dimensional accuracy when doing this job[6,12].

Metallic glasses (MGs) have triggered a flood of research since they were discovered in 1960[13]. Now, the study and development of MGs are at the leading edge of metal research because the materials are creating more and more new opportunities for both fundamental studies and commercial applications. The initial interest and purpose for developing MGs are aiming at engineering applications because of their attractive mechanical properties, such as high strength, high elasticity, high corrosive resistance and good tribological behavior[14-17]. Then, more and more excellent properties in certain MG systems were found, for example, good soft magnetic property, catalytic property, as well as bio-compatibility which make it feasible to use some MGs as implants[16,18-22]. Besides the above, one of the most attractive properties of MGs is their thermoplastic forming (TPF) ability. When heated into its supercooled liquid region (SLR, a temperature window between glass transition temperature T_g and crystallization temperature T_x), the viscosity of MG drops drastically with the increase of temperature, driving the transition of metallic-like to plastic-like behavior for them[15,23,24]. Therefore, the MG can be conveniently processed like viscous plastics. Furthermore, owing to the absence of crystalline defects (e.g., dislocations) and a first-order phase transition during the solidification, the shrinkage in the MG formers is only approximately 10% of conventional crystal alloys, and thus they show high dimensional accuracy when being processed by the TPF method[23-26]. As a result, MGs are considered as

* Corresponding author. Prof., Ph.D.
E-mail address: *majiang@szu.edu.cn* (*J. Ma*).

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the ideal materials for miniature-fabrication through micro thermoplastic forming (MTPF) and have promising applications in the fields of MEMS, micro mold inserts, biomedical devices and implants, microrobotics, micromanipulators and so on[16,23,25,27-29]. Much work has been done to show that various micro- and nano-scale structures can be fabricated on the surface of MGs by the MTPF method[23,25,30,31], and this approach is proved to be a more effective and low-priced miniature-fabrication method compared with the LIGA techniques[23,25,31], as well as a much more precise method in contrast with the direct structuring ways[12,23,31]. Although the superior properties of MGs over conventional materials used for miniature applications have triggered significant effort, few achievements have been obtained and as a key issue of MTPF of MGs, the forming kinetics in such process is also far from being understood. In present work, the mold filling kinetics of MGs during MTPF is studied by using a modeling Pd-based MG and efforts are made to develop structured MG for applications in different fields.

2. Experimental

To choose a proper MG for MTPF, some characteristics should be considered. The MG should have good flow properties and thermal stability in its SLR. The main challenge during MTPF is to avoid crystallization. The PdNiCuP bulk glassy alloy is chosen for present study, due to that the MG is proved to have excellent glass-forming and thermoforming ability, wide SLR and good resistance to oxidation and crystallization[32,33]. The PdNiCuP bulk MG samples which were used to conduct MTPF were prepared from a master alloy with nominal composition of Pd 40 at. %, Ni 10 at. %, Cu 30 at. %, and P 20 at. % by conventional water-cooled copper mould casting process. The as-cast glassy samples are cut and sawed into required dimension. In order to perform MTPF, a clean and flat surface of MG sample is needed. The specimens are first polished by hand with abrasive papers up to 1200 grit and then 1.5 μm diamond paste on the polishing machine.

The amorphous nature of the as-cast and MTPF treated Pd-based MG samples was ascertained by X-ray diffraction (XRD) with CuKα radiation and differential scanning calorimetry (DSC, Perkin-Elmer DSC-7) at a heating rate of 10 K/min, showing a glass transition temperature of 573 K and a crystallization temperature of 653 K.

To fabricate microstructures on the surface of MGs, the corresponding master molds are required. In this study, the silicon molds with different microstructures which were fabricated by the photoetching technique are used. First, the polished silicon wafer of about 10 mm×10 mm was coated with S1813 photo resist. It was followed by Ultraviolet exposure using a UV lithography system (MA6) in order to define the designed micro pattern, which was fabricated on the exposure mask, on the resist. After development, the wafer was etched using an Inductively Coupled Plasma (ICP) system (PlasmaLabSystem100), and the pattern was finally transferred from the exposure mask to the silicon wafer. The MTPF process of MG can be illustrated by Fig. 1(a). The MG plate was firstly heated into its SLR (620 K) by a resistance heating stage; then, a required force P is provided by the electromechanical INSTRON 3384 equipments and held for a time t of several seconds.

The surface features of the structured silicon mold and MG sample were examined by scanning electron microscopy (SEM, Philips XL30) observation and atomic force microscopy (AFM) measurements on SPA-400.

3. Results and Discussion

Fig. 1(b, c) presents the XRD patterns and DSC traces of the as-cast and MTPF treated Pd-based MG samples. One can see that they remain fully amorphous after the MTPF process, which proves the good crystallization resistance of this Pd-based MG.

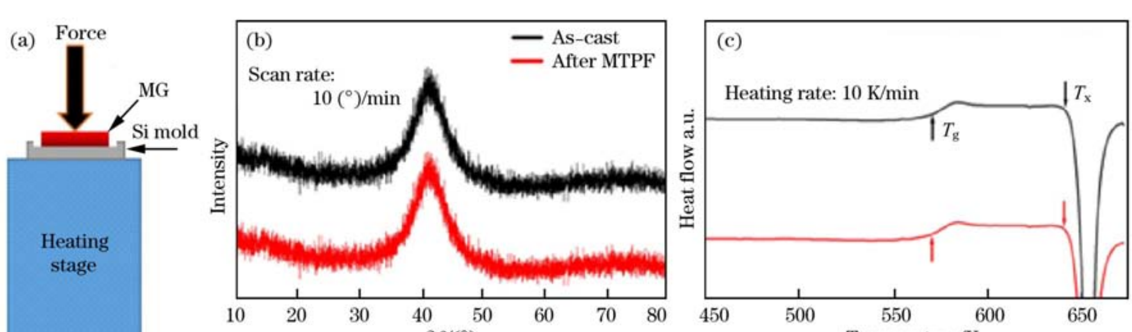


Fig. 1. Schematic illustration of MTPF process of MG in silicon micro mold (a), XRD patterns (b) and DSC traces (c) of as-prepared and MTPF treated Pd-based metallic glass samples.

3.1. Mold filling kinetics

The mold filling kinetics plays a critical role during the MTPF process of MG. The understanding and controlling of micro filling are crucial for miniature fabrication and applications, yet remain unresolved. Although the filling kinetics of MG fluid in the cylindrical mold has been studied in early researches[23,25,34,35], when the constitutional unit of the microstructure on the silicon mold is not a cylindrical one which is a common situation in practical use, the filling kinetics is still unknown and thus a universal kinetic equation is necessary to describe the micro mold filling process.

According to the fluid mechanics[36], when the viscous fluid fills a uniform channel with non-circular cross section, the channel can be equivalent to a circular one (Fig. 2(a)) with a hydraulic equivalent diameter $D_e = 4A/g$, where A and g are the area and perimeter of the non-circular channel's cross section, respectively. To investigate the mold filling kinetics of viscous MG in its SLR, three different silicon molds (circular, rectangular and triangular ones) are fabricated. The SEM images of the silicon molds and corresponding MG replicas after MTPF are presented in Fig. 2(b). Based on the above equation, the hydraulic equivalent diameter D_e of the different silicon molds was calculated (see the bottom column in Fig. 2(b)). With D_e, the dimensionless Reynolds number Re, which is pivotal and used to determine the flow state, can be expressed as follows[36]:

$$Re = \frac{\rho \cdot v \cdot D_e}{\eta} \tag{1}$$

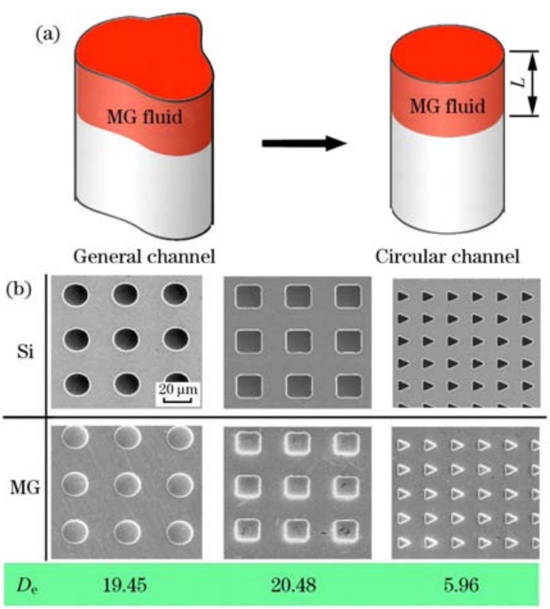


Fig. 2. Illustration of equivalence of flow channel for MG liquid in a general channel and a tube (a) and SEM images of silicon molds and corresponding MG replicas after MTPF (b).

where, ρ, v and η are the density, velocity and viscosity of a fluid, respectively. For miniature-fabrication of MG using MTPF method, the η (about $10^6 - 10^{12}$ Pa·s) is large, v is in the order of μm/s and D_e is in the μm order, then Re is estimated to be far below 1 by Eq. (1). In consequence, a conclusion can be drawn that the supercooled MG liquid exhibits steady laminar flow in the mold filling process during the MTPF based on the theory of fluid mechanics[36], and this process can be described by the D_e-modified Hagen-Poiseuille equation:

$$L = \sqrt{\frac{PD_e^2}{32\eta} \cdot t} \tag{2}$$

with L as the filling length under a certain pressure P to move a liquid with η through a channel of D_e, in a given time t. Despite the capillary force $f = \frac{4\gamma\cos\theta}{D_e}$[37], where γ is the MG-vacuum interfacial energy (about 1 N·m^{-1})[38] and θ is the dynamic contact angle between the supercooled liquid and the mold, may play a critical role in the mold filling process, the micro scale MTPF is mainly focused on in this paper under the cases of $D_e > 5$ μm; hence, the maximum capillary force f could only be as large as 0.8 MPa, which is very small compared with the force that is needed during the MTPF; therefore, the effect of wetting behavior between MG liquid and the mold can be ignored.

Eq. (2) describes the filling kinetics of supercooled MG liquid into a microstructured mold with non-circular constitutional unit. To verify the availability of Eq. (2), the filling behavior of MG fluid in different silicon molds (Fig. 2(b)) was investigated. The MTPF process of this Pd-based MG was conducted at 620 K ($\eta = 5 \times 10^7$ Pa·s[33]) under a typical constant pressure P of 10 MPa, and the filling length L of different D_e and filling time t were characterized. The L in different t for triangular, circular and rectangular molds is presented in Fig. 3(a). It can be seen that L is proportional to $t^{1/2}$ for a mold with a specific D_e value, which is in good coincidence with Eq. (2). The slopes of linearly fitted L versus $t^{1/2}$ are 1.524, 1.648 and 0.480 for the corresponding circular, rectangular and triangular molds, respectively, and the results are in good consistence with the theoretical scaling factors between L and $t^{1/2}$ obtained from Eq. (2). In addition, the relationship between L and $D_e \cdot t^{1/2}$ for the three different molds is plotted in Fig. 3(b), where the slope of fitted line is 0.07897, which is very close to the calculated coefficient $\left(\frac{P}{32\eta}\right)^{1/2} = 0.07906$ obtained from Eq. (2), suggesting that L is only related to D_e and t under constant pressure and temperature condition. These results indicate the rationality of using the

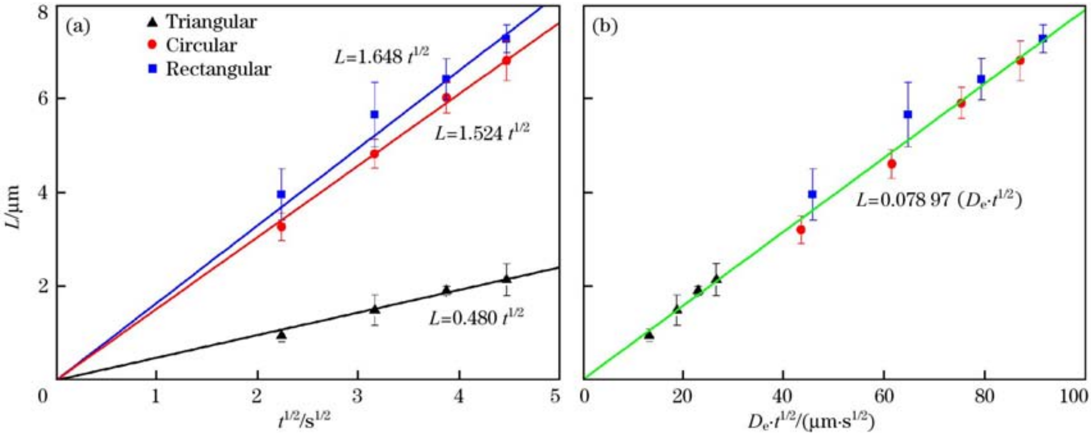


Fig. 3. Plots of L versus $t^{1/2}$ for triangular, circular and rectangular molds and linear-fitted line (a); plots of L versus $D_c \cdot t^{1/2}$ for three molds and fitted line of data (b).

universal Eq. (2) to describe the filling kinetics of MG in non-circular cross section mold channels for the MTPF, and the establishment of such equation may help us in theory to design and produce micro products of high qualities with MG, which have been proved to be ideal candidate of miniature-fabrication materials for high precision and ready preparation[39-41].

Based on the theory of MTPF, a series of applications are developed because of their superior properties and convenient microstructure fabrication method of MGs.

3.2. MG mold insert for hot embossing of polymers

Molding of micro components from thermoplastic polymers (TPs) has become one of the most promising fabrication techniques for non-electronic micro devices[42,43]. The essential part in this industry is to find hard, ductile and durable material for mold insert, which is used to define pattern on the surface of TPs and responsible for the primary microstructures. Another challenge for the TPs miniature fabrication techniques is to develop a convenient and low-priced method to prepare the mold insert[6]. As known, MGs have excellent mechanical properties and they can be easily thermoformed in their SLR by MTPF, which exactly meet the requirements of a mold insert for hot embossing of polymers.

They were employed as the mold insert material for hot embossing of polymers in order to produce polymer micro components and devices. The surface morphology and profile of the MG mold inserts which are prepared by MTPF are examined through the SEM observation and AFM measurement, as shown in Fig. 4(a－d). 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 Cyclic olefin copolymer

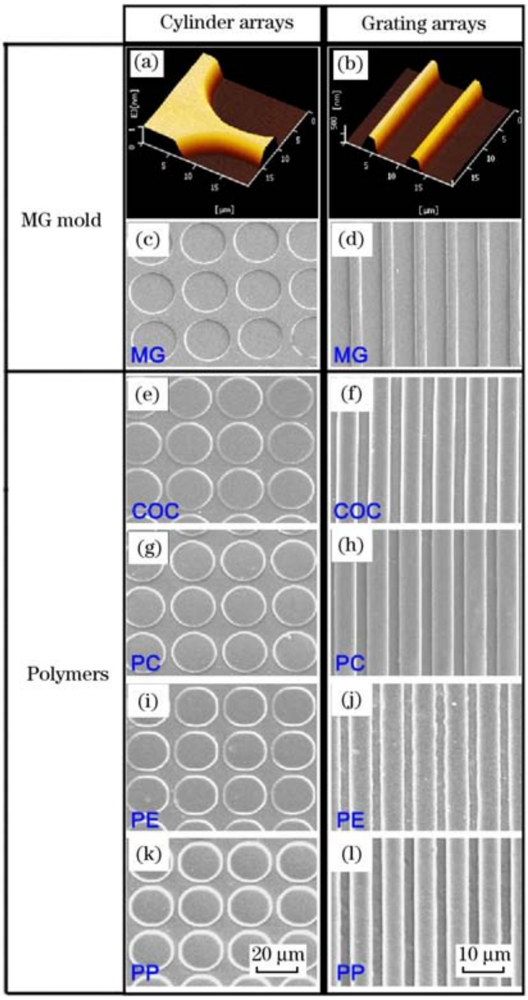
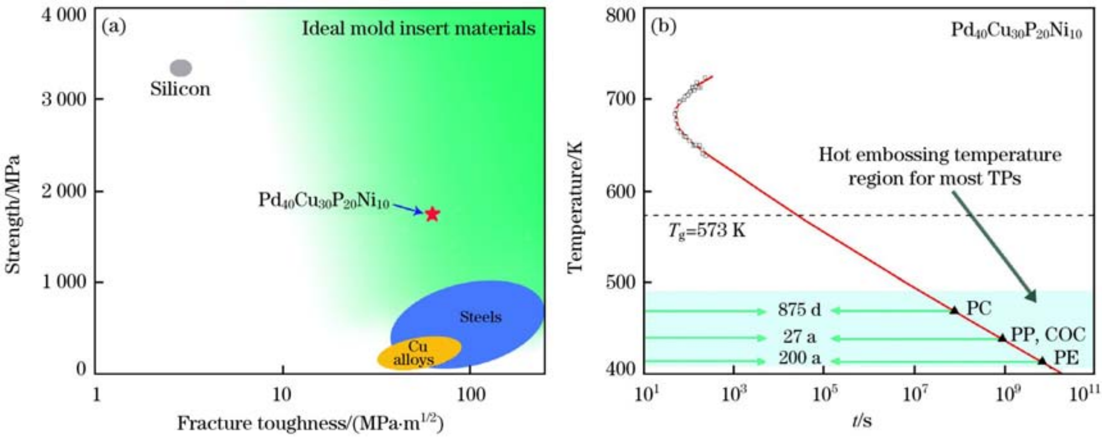


Fig. 4. AFM images of MG mold inserts with hole arrays and grating arrays after MTPF (a, b), SEM morphology of mold inserts (c, d), and SEM microscopy of typical polymer products by hot embossing using MG mold insert (e－l).

(COC). The SEM images of polymer products (for the convenience of conducting SEM observation, an ultrathin conductive gold layer of less than 20 nm was deposited on their surfaces) after hot embossing are also presented in Fig. 4(e-l).

Compared with conventional mold insert materials and fabrication technology, MG has several advantages. Mechanical performance is the first issue that should be concerned about to avoid the mold insert break, deformed or weared during being used. Fig. 5(a) presents the mechanical performance (strength versus fracture toughness) of the Pd-based MG and currently available materials for the mold insert. As for a mold insert, the stronger and tougher the better, so the materials in the green region are regarded as the ideal mold insert materials. It is obvious that the Pd-based MG has big mechanical advantages compared with the conventional materials such as silicon, steels and copper alloys.



Red plot which is extrapolated to 400 K shows trend of TTT curve.

Fig. 5. Mechanical properties of metallic glasses compared with common mold insert materials (a); TTT diagram of $Pd_{40}Cu_{30}P_{20}Ni_{10}$ MG that is used to estimate the service life of this MG mold insert (b).

The surface quality is also important when it comes to a mold insert, because it not only relates to the quality of polymer products but also makes great sense for the demolding process. The AFM observation on MG mold insert with periodic hole arrays and grating arrays (see Fig. 4(a, b)) shows that the surface roughness is 12.49 and 6.94 nm, respectively, which is much smaller than the mold insert fabricated by CNC machine (about 300 nm for steels)[12].

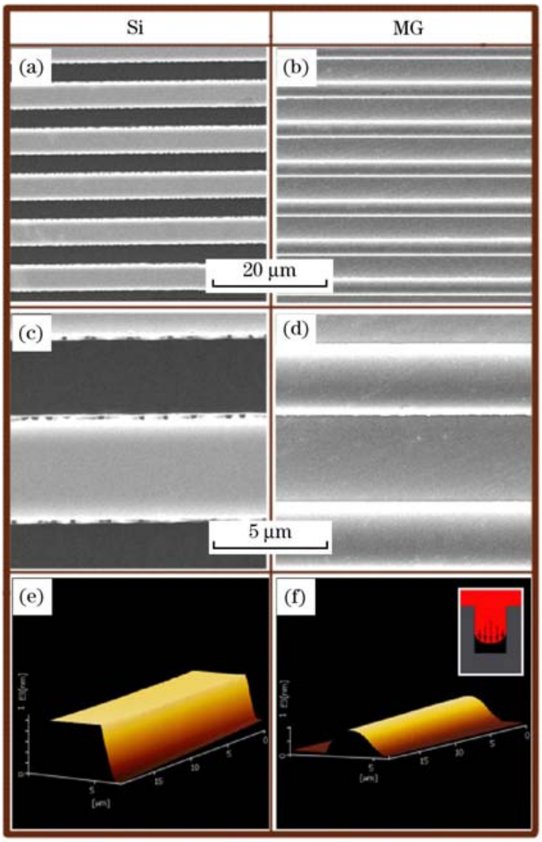
During the hot embossing of TPs, the crystallization of MGs which may result in brittleness, dimensional change and even increase in the surface roughness of the MG mold insert should be avoided[44]. Fortunately, the hot embossing temperature for most TPs is below 473 K, which is far less than the crystallization temperature of the Pd-based MG. The time span before crystallization is defined as the service life of a MG mold insert, and it can be estimated by the temperature-time-transformation (TTT) diagram which was performed by isothermal crystallization studies. Fig. 5(b) shows the TTT diagram of this Pd-based MG which is extrapolated to 400 K. It can be seen that the service life of the MG mold insert is 875 d, 27 a, 27 a and 200 a for the hot embossing of PC, PP, COC and PE, respectively and if the cooling step during the hot embossing cycle is taken into account, the service life should be even longer.

Besides above, MG has high thermal conductivity and small thermal expansion coefficient, which could reduce the heating and cooling time, increase the production efficiency, and improve the dimensional accuracy of polymer products. All these factors indicate that MGs are the desired candidate for the mold insert materials.

3.3. *MG grating*

Recently, owing to the rapid development of spectroscopic analysis and sensor technology, optical gratings with excellent properties are urgently required. However, currently available methods of manufacturing gratings such as mechanical ruling and replicating are both easy to bring in defects (e.g., target patterns) or with too complicated structures which makes them fragile and inconvenient for practical application. Furthermore, these methods are expensive and time consuming (it may need several weeks or months)[45]. Therefore, it is necessary to develop new grating fabrication method with proper materials and the discovery of MGs gives us inspiration.

MG is also used to fabricate grating which is a crucial component in the spectrum analysis due to its extraordinary surface finish after MTPF and the ready fabrication method that could greatly improve the production efficiency over conventional approaches. The SEM images of a Pd-based MG grating which is prepared by the MTPF method are shown in Fig. 6(a-d). It can be seen from Fig. 6(d) that the polishing marks, which exist before MTPF, disappear after the treatment and the grating constant shrinks from 8.0 μm of Si die to 7.9 μm of the MG



(c) and (d) are the close-up views of (a) and (b). The inset in (f) demonstrates the filling velocity distribution on the cross section.

Fig. 6. SEM photographs of Si mold and MG grating by MTPF (a－d); and AFM images of silicon mold and MG replica (e,f).

replica with a slight shrinkage of about 1.25%, indicating that it is a good fabrication method with excellent dimensional accuracy.

The AFM measurement (Fig. 6(e,f)) shows that the surface roughness is less than 3 nm, reflecting the superior surface quality of MG grating after the MTPF. The inset of Fig. 6(f) illustrates how the viscous MG is squeezed into silicon mold during the MTPF, and according to the Hagen-Poiseuille law for creeping flow[36], the filling velocities are different for different zones on the cross sections; this inset demonstrates the velocity profile on the cross section, and the parabolic corresponds to the actual shape which is characterized by AFM observation.

It is known that gratings can diffract light into certain angles obeying grating equation[45]. When compound light (e.g. sunlight) shines upon grating, each monochromatic light which composes the compound light is separated towards certain direction and the rainbow-like colorful spectrum can be observed. Fig. 7(a,b) shows the MG samples which were shined by fluorescent lamp light. The colorful rainbow-like MG plate with grating structure fabricated by MTPF is in contrast with the polished one which only has metallic luster (Fig. 7(a)). In addition, due to the high reflectance (which is due to the ultra smooth surface and the metallic nature), the MG replica is even more brilliant than silicon grating mold as can be seen in Fig. 7(b). Fig. 7(c) presents the reflective spectrums of Pd-based MG, silicon and BK7 glass (which is used as a reference). It can be seen that the MG has a relatively higher reflectance than silicon,

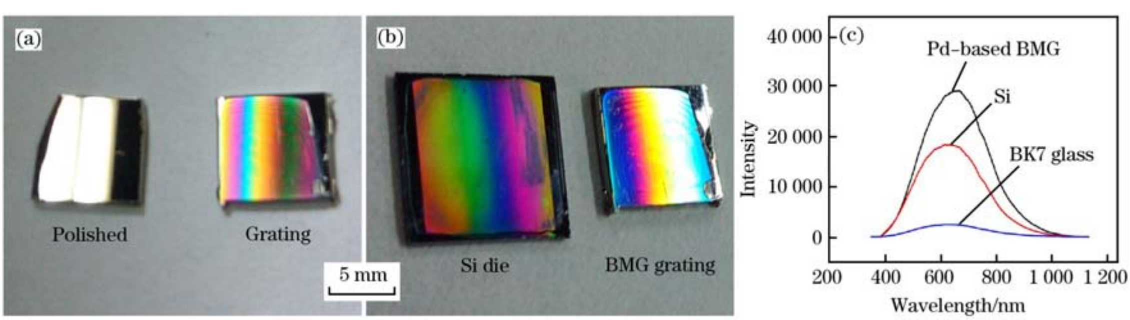


Fig. 7. Photographs of polished MG plate (left) and MG grating (right) when fluorescent lamp light shines upon them (a); photographs of Si grating (left) and MG grating (right) under the shine of fluorescent lamp light (b); reflective spectrums of BK7 glass, Si and $Pd_{40}Cu_{30}P_{20}Ni_{10}$ MG in visible light region (c).

indicating a better diffraction efficiency of MG grating than silicon master grating.

Using MGs as the candidates for the production of gratings may cast a new light on the fabrication of integrated optical components such as diffractive optical microstructured elements. They can be easily net-shape formed by the MTPF method and have a much higher fabrication efficiency (the cycle time could be less than 30 s) compared with the conventional method. Furthermore, as demonstrated above, these replicated MG gratings can also be used as molds to further create the second-generation replicas on thermoplastic polymers.

4. Conclusion

In present work, a universal kinetic equation was proposed which can describe the filling kinetics of viscous MG supercooled liquid in micro molds with irregular shapes during the MTPF by using a Pd-based MG as the modeling material. The availability of the universal kinetic equation was verified by fabricating three different shapes of silicon molds (circular, rectangular and triangular ones). Based on the MTPF theory and the unique and desirable physical characteristics of the MG, a series of applications such as MG mold insert for hot embossing of polymers and MG grating are developed.

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References

[1] H. Becher, Anal. Bioanal. Chem. 390 (2008) 89-111.
[2] D. Erickson, D. Li, Anal. Chim. Acta 507 (2004) 11-36.
[3] H. Becker, L. E. Locascio, Talanta 56 (2002) 267-287.
[4] A. E. Kamholz, A. Schilling, P. Yager, Biophys. J. 80 (2001) 1967-1972.
[5] Y. Jiang, P. C. Wang, L. E. Locascio, C. S. Lee, Anal. Chem. 73 (2001) 2048-2053.
[6] M. Heckele, W. K. Schomburg, J. Micromech. Microeng. 14 (2004) R1.
[7] L. Martynova, L. E. Locascio, M. Gaitan, G. W. Kramer, R. G. Christensen, W. A. MacCrehan, Ann. Chem. 69 (1997) 4783-4789.
[8] R. M. McCormick, R. J. Nelson, M. G. Alonso-Amigo, D. J. Benvegnu, H. H. Hooper, Ann. Chem. 69 (1997) 2626-2630.
[9] G. B. Lee, S. H. Chen, G. R. Huang, Y. H. Lin, W. C. Sung, Sensors Actuators B 75 (2001) 142-148.
[10] W. K. Schomburg, R. Ahrens, W. Bacher, J. Martin, V. Saile, Sensors Actuators A 76 (1999) 343-348.
[11] W. Menz, Sensors Actuators A 54 (1996) 785-789.
[12] G. Fu, S. B. Tor, N. H. Loh, D. E. Hardt, J. Micromech. Microeng. 20 (2010) 085019.
[13] W. Klement, R. H. Willens, P. Duwez, Nature 187 (1960) 869-870.
[14] A. L. Greer, E. Ma, MRS Bull. 32 (2007) 611-619.
[15] W. H. Wang, C. Dong, C. H. Shek, Mater. Sci. Eng. R 44 (2004) 45-89.
[16] W. H. Wang, Prog. Mater. Sci. 52 (2007) 540-596.
[17] A. R. Yavari, J. J. Lewandowski, J. Eckert, MRS Bull. 32 (2007) 635-638.
[18] C. A. Schuh, T. C. Hufnagel, U. Ramamurty, Acta Mater. 55 (2007) 4067-4109.
[19] A. Inoue, Acta Mater. 48 (2000) 279-306.
[20] U. Koster, D. Zander, Triwikantoro, A. Rudiger, L. Jastrow, Scripta Mater. 44 (2001) 1649-1654.
[21] J. Schroers, G. Kumar, T. M. Hodges, S. Chan, T. R. Kyriakides, JOM-US 61 (2009) 21-29.
[22] B. Zberg, P. J. Uggowitzer, J. F. Loffler, Nat. Mater. 8 (2009) 887-891.
[23] J. Schroers, Adv. Mater. 22 (2010) 1566-1597.
[24] W. H. Wang, Adv. Mater. 21 (2009) 4524-4544.
[25] J. Schroers, JOM 57 (2005) 35-39.
[26] B. Zhang, D. Q. Zhao, M. X. Pan, W. H. Wang, A. L. Greer, Phys. Rev. Lett. 94 (2005) 205502.
[27] O. Rötting, W. Röpke, H. Becker, C. Gärtner, Microsyst. Technol. 8 (2002) 32-36.
[28] X. J. Shen, L. W. Pan, L. Lin, Sensors Actuators A 97 (2002) 428-433.
[29] M. Heckele, W. Bacher, K. D. Müller, Microsyst. Technol. 4 (1998) 122-124.
[30] G. P. Zhang, Y. Liu, B. Zhang, Adv. Eng. Mater. 7 (2005) 606-609.
[31] J. Ma, X. Zhang, W. H. Wang, J. Appl. Phys. 112 (2012) 024506.
[32] J. Yi, X. X. Xia, D. Q. Zhao, M. X. Pan, H. Y. Bai, W. H. Wang, Adv. Eng. Mater. 12 (2010) 1117-1122.
[33] R. Busch, J. Schroers, W. H. Wang, MRS Bull. 32 (2007) 620-623.
[34] H. M. Chiu, G. Kumar, J. Blawzdziewicz, J. Schroers, Scripta Mater. 61 (2009) 28-31.
[35] G. Kumar, A. Desai, J. Schroers, Adv. Mater. 23 (2011) 461-476.
[36] K. P. Kundu, M. I. Cohen, Fluid Mechanics, 4th ed., Academic Press, Waltham, 2008.
[37] G. Kumar, H. X. Tang, J. Schroers, Nature 457 (2009) 868-872.
[38] T. Iida, R. I. L. Guthrie, The Physical Properties of Liquid Metals, Clarendon Press, Oxford, 1988.
[39] J. Q. Wang, W. H. Wang, H. Y. Bai, Appl. Phys. Lett. 94 (2009) 041910.
[40] J. P. Chu, C. L. Chiang, H. Wijaya, R. T. Huang, C. W. Wu, B. Zhang, W. H. Wang, T. G. Nieh, Scripta Mater. 55 (2006) 227-230.
[41] X. F. Liu, R. J. Wang, D. Q. Zhao, M. X. Pan, W. H. Wang, Appl. Phys. Lett. 91 (2007) 041901-041903.
[42] M. Heckele, W. Bacher, K. D. Müller, Microsyst. Technol. 4 (1998) 122-124.
[43] H. Becker, C. Gärtner, Electrophoresis 21 (2000) 12-26.
[44] J. Basu, N. Nagendra, Y. Li, U. Ramamurty, Philos. Mag. 83 (2003) 1747-1760.
[45] C. Palmer, Diffraction Grating Handbook, 6th ed., Newport Corporation, New York, 2005.