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# Micro mold filling kinetics of metallic glasses in supercooled liquid state

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The unique thermoplastic forming ability of metallic glasses in their supercooled liquid state makes them the ideal embossing materials for miniature fabrication. However, the understanding and controlling of micro filling process that is crucial for miniature fabrication and their applications remain fundamental, yet presently unresolved issues. Here, the mold filling kinetics of a model Pd-based metallic glass in supercooled liquid state is studied using different Si micro molds with different channels. A universal kinetic equation, which can describe the filling kinetics of viscous metallic supercooled liquid in micro molds with irregular shapes, is obtained. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4795508]

## I. INTRODUCTION

Metallic glasses (MGs) with distinctive amorphous structure exhibit superior mechanical performances such as high yielding strength, high hardness, large elastic strain limit and fracture toughness as well as excellent wear and corrosion resistance.[1–5] On the other hand, the MGs can be thermoplastic formed (TPF) at an elevated temperature in their supercooled liquid region (SLR),[8,9] which is a temperature window between glass transition temperature, $T_g$ and crystallization temperature, $T_x$. The viscosity of MGs dramatically drops with the increase of temperature in their SLR, which drives the transition of solid-like to liquid-like behavior for them.[6,10] Therefore, the MGs can be conveniently processed like viscous plastics,[11] and the absence of a first-order phase transition during the solidification reduces shrinkage in the MG formers (approximately 10% of conventional crystal alloys),[8,11–13] and thus the MGs show high dimensional accuracy when conducting thermoform, which suggests that they are the desirable materials for miniature-fabrication and have promising applications in the MEMS (microelectromechanical systems), biomedical devices and implants, microrobotics, and micromanipulators fields.[14–16] Previous work has revealed that various surface patterns and three-dimensional micro- and nanoscale structures can be fabricated by thermoforming of bulk MGs.[8–10,17,18] And this approach is proved to be a more effective and low-price miniature-fabrication method compared with currently used Lithographie, Galanoformung, and Abformung (LIGA) techniques.[6] Great efforts have been made on the theoretical understanding of the TPF of MG such as the formability, the fragility and thermal stability, the mold filling process, the constitutive equations and the effect of surface tension or capillary force, and so on.[19–27]

Early researches which studied on the filling kinetics of MG fluid focused only on the cylindrical mold.[9,28] In practical cases, the most micro products are of irregular shapes, and the filling kinetics in corresponding irregular micro molds is unknown yet. Therefore, a universal kinetic equation is necessary for the micro mold filling process. In this letter, a universal kinetic equation is obtained to describe the filling process of the MG supercooled liquid. We study the mold filling process of MG fluid in various molds with different shapes of cross section and confirm that the universal kinetic equation can well describe the filling process of the supercooled liquid in different cross section shapes.

## II. EXPERIMENTS

The PdNiCuP bulk glassy alloy was chosen for the study of mold filling kinetics. This is due to that the MG was proved to have excellent glass-forming and thermoforming abilities, large SLR, and good resistance to oxidation and crystallization.[29,30] The PdNiCuP bulk MG rod with a diameter of 5 mm was prepared from a master alloy with nominal composition Pd 40 at.%, Ni 10 at.%, Cu 30 at.%, and P 20 at.% by the arc melting and copper mold suck-casting method.[5] In order to carry out the TPF, the glassy rod was cut into wafers with a thickness of 1 mm and then polished by abrasive paper and polishing machine. The Si molds, which were used as dies to thermoform micro structures on the surface of MG wafers, were fabricated by photoetching technique and etched for a depth of 20 $\mu$m. To investigate the generalized laws for filling process, three different Si molds with varied shapes of cross section, which were periodic circular, rectangular, and triangular arrays, were prepared. Figure 1 schematically illustrates the thermoforming process. The required force is provided by the electromechanical INSTRON 3384 equipments and the MG sample was heated into its SLR (=620 K) by a resistance heating stage, and the scanning electron microscope (SEM) observation was performed on Philips XL30 SEM instrument.

## III. RESULTS AND DISCUSSIONS

We try to understand the mold filling process of the metallic glass-forming supercooled liquids using the fluid mechanics. As illustrated in Fig. 2(a), when the viscous MG liquid fills a uniform channel with irregular cross section, the channel is equivalent to a circular channel with a diameter

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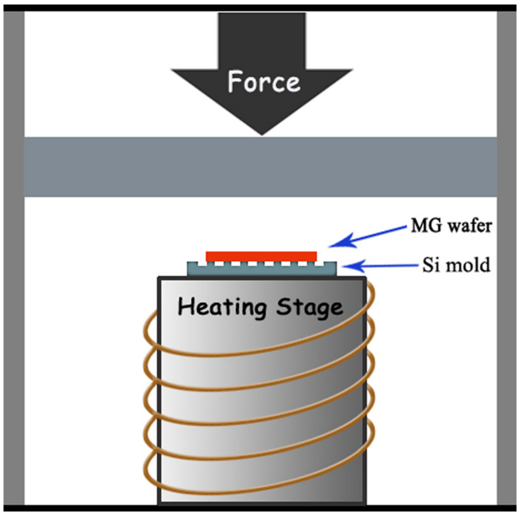


FIG. 1. Schematic illustration of the thermoforming process of MG in silicon micro mold.

$D_e$, which is called hydraulic equivalent diameter according to the fluid mechanics[31]

$$De = \frac{4A}{g}, \tag{1}$$

where $A$ and $g$ are the area and perimeter of the irregular channel's cross section, respectively. The dimensionless Reynolds number $Re$, which is pivotal and used to determine the flow state, can be expressed as follows:[31]

$$Re = \frac{\rho \cdot \mathrm{v} \cdot D_e}{\eta}, \tag{2}$$

where $\rho$, $v$, and $\eta$ are, respectively, the density, velocity, and viscosity of a fluid. When $Re$ is larger than 2300, the flow is turbulent which is very complex, in contrast, when $Re$ is smaller than 2300, the flow becomes laminar and therefore easier to be understood.[31] For miniature-fabrication of MG using TPF method, the viscosity $\eta$ ($\sim 10^6$–$10^{12}$ Pa·s) is large, the filling velocity $v$ is in the order of $\mu$m/s, and feature dimension $D_e$ is in the $\mu$m order, the $Re$ is estimated to be $\ll 1$. Therefore, from Eq. (2) we know that the supercooled liquid exhibits steady laminar flow. Assuming that the MG liquid fills in a general channel is equivalent to a tube as depicted in Fig. 2(b), the resultant force acting on a control volume (CV) with a length of $dx$ and a radius of $r$ the CV should be zero in steady laminar state,[31] then

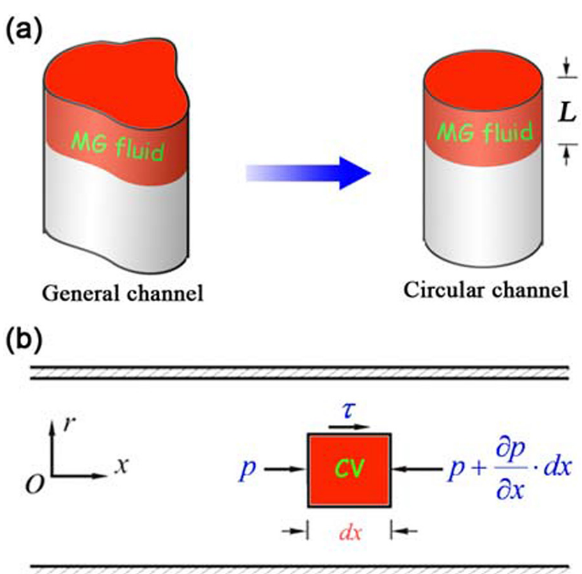


FIG. 2. (a) Illustration of the equivalence of the flow channel for MG liquid in a general channel and a tube. (b) The depiction the CV in the equivalent tube chosen for force analysis.

$$p\pi r^2 - \left(p + \frac{\partial p}{\partial x}\cdot dx\right)\pi r^2 + \tau \cdot 2\pi r \cdot dx = 0$$
$$\text{and} \quad \frac{dp}{dx} = \frac{2\tau}{r}, \tag{3}$$

here, $p$ is the pressure at the position of CV, and $\tau$ is the Newton viscous stress upon the surface of the CV. On the basis of Newton's law of viscosity, $\tau = \eta \cdot \frac{du}{dr}$,[31] where $u$ is the velocity of the fluid at a distance $r$ from central axis of the tube, we yield from Eq. (3)

$$\frac{du}{dr} = \frac{1}{2\eta}\frac{dp}{dx}\cdot r. \tag{4}$$

By integrating Eq. (4), one can obtain

$$u = \frac{1}{4\eta}\frac{dp}{dx}\cdot r^2 + C, \tag{5}$$

where C is an integration constant. According to the no-slip boundary condition for viscous flow, $u = 0$ at the inner surface of the tube, that is to say $u = 0$ when $r = \frac{D_e}{2}$.[31] So $C = -\frac{1}{4\eta}\cdot\frac{dp}{dx}\cdot\frac{D_e^2}{4}$, and Eq. (5) becomes

$$u = \frac{1}{4\eta}\frac{dp}{dx}\cdot\left(r^2 - \frac{D_e^2}{4}\right). \tag{6}$$

Equation (6) describes the radial velocity distribution of the MG liquid in the equivalent tube. By computing integrals of Eq. (6) along the whole cross section, we get the volume flow rate of MG liquid in the tube

$$Q = \int_0^{\frac{D_e}{2}} u 2\pi r dr = \frac{\pi}{2\eta}\frac{dp}{dx}\int_0^{\frac{D_e}{2}}\left(r^2 - \frac{D_e^2}{4}\right) r dr = \frac{\pi D_e^4}{128\eta}\frac{dp}{dx}. \tag{7}$$

For the filling length $L$ in the applied pressure $P_{total}$ and filling time $t$, $Q = \frac{\pi D_e^2 L}{4t}$, $\frac{dp}{dx} = \frac{P_{total}}{L}$, Eq. (7) becomes

$$\frac{\pi D_e^2 L}{4t} = \frac{\pi D_e^4}{128\eta}\frac{P_{total}}{L}$$
$$\text{or} \quad L = \sqrt{\frac{P_{total} De^2}{32\eta}t}. \tag{8}$$

Equation (8) is the obtained universal kinetic equation of the mold filling of metallic supercooled liquids.

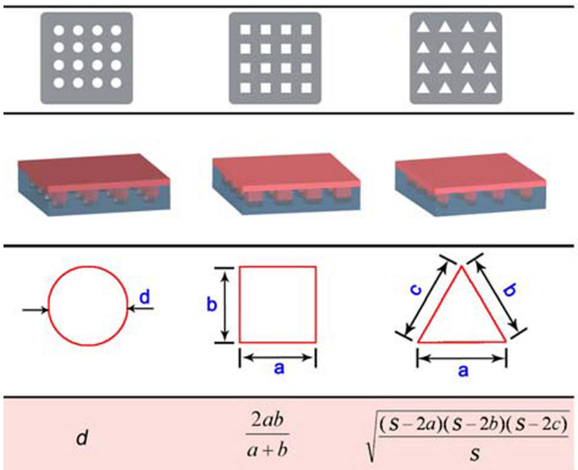


FIG. 3. Micro structures of Si molds and three-dimensional sketches of TPF. The top row is the three different micro structures of Si molds, the second row shows the filling state of MG (designated in red) into cavity of Si molds (designated in grey), third row presents the constitutional units with dimension marked in each structure, and the bottom row gives the $D_e$ calculation equation for above three structures.

To confirm the availability of Eq. (8) for the TPF of MGs, we used different Si molds with different cross section shapes to study the filling kinetics. Figure 3 illustrates the microstructure of the Si molds and three-dimensional sketches of TPF. The top row in Fig. 3 shows three different microstructure of Si molds, the second row exhibits the filling state of MG (designated in red) into cavity of Si molds (designated in grey), and the constitutional units with dimension marked in each structure were presented in the third row. Figure 3 shows the calculated values of $D_e$ of these circular, rectangular, and triangular silicon molds, and the results are also listed in Table I. It is noted that the area $A$ is figured out by Heron's formula and $s$ is equivalent to the perimeter in the $D_e$ calculation of triangular mold. The SEM images of Si molds and MG samples after TPF are shown in Fig. 4. It can be seen that the MG replicas fit the Si dies well and the dimension difference between them is less than 1%, suggesting excellent TPF ability of the Pd-based MG in its SLR and the fine feasibility of conducting present research with this MG.

The TPF process of the Pd-based MG was conducted at 620 K ($\eta = 5 \times 10^7$ Pa·s[30]) under a constant pressure of 10 MPa. The filling length $L$ can be determined by $t$ and $D_e$ according to universal kinetic equation. The surface profilometer (Dektak 8) was used to characterize the $L$ of

TABLE I. $D_e$ values and slopes of linearly fitted $L$ versus $t^{1/2}$ for different micro structures.

| Constitutional unit | Feature size (μm) | $D_e$ (μm) | Fitted slope of $L$ vs $t^{1/2}$ | $\frac{dL}{d(t^{1/2})} = \sqrt{\frac{D_e{}^2 \cdot P}{32\eta}}$ |
|---|---|---|---|---|
| Circle | $d = 19.45$ | 19.45 | 1.524 | 1.538 |
| Rectangle | $a = 20.65$<br>$b = 20.31$ | 20.48 | 1.648 | 1.619 |
| Triangle | $a = 10.61$<br>$b = 10.61$<br>$c = 9.85$ | 5.96 | 0.480 | 0.471 |

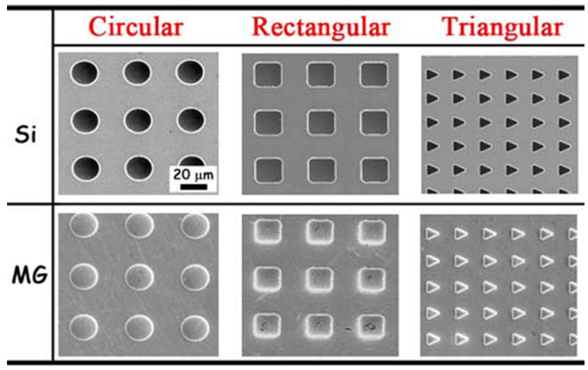


FIG. 4. SEM images of three different silicon molds and corresponding thermoformed MG samples.

channels with different cross sections and filling times. Despite the capillary force $f = \frac{4\gamma\cos\theta}{D_e}$,[7,19] where $\gamma$ is the MG-vacuum interfacial energy ($\sim$1 N m$^{-1}$)[6] and $\theta$ is the dynamic contact angle between the supercooled liquid and the mold, may play a critical role in the mold filling process; however, here we mainly focus on the micro scale TPF under the cases of $D_e > 5\,\mu$m; 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 TPF; therefore, the effect

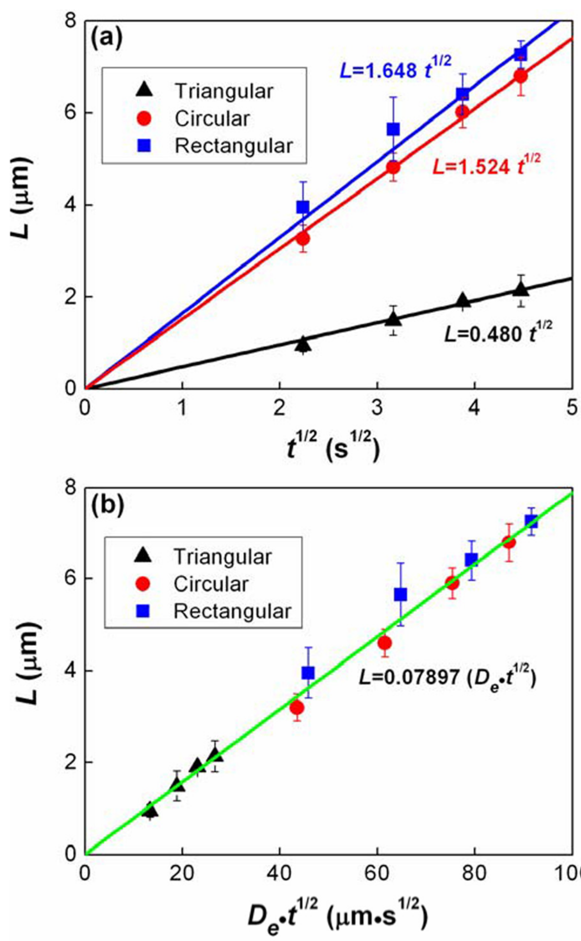


FIG. 5. (a) The plot of $L$ versus $t^{1/2}$ for triangular, circular, and rectangular molds and the solid line is the fit line. (b) The plot of $L$ versus $De \cdot t^{\frac{1}{2}}$ for three molds and fitted line of the data.

of wetting behavior between MG liquid and the mold can be ignored in present research.

Figure 5(a) presents the $L$ in different $t$ for triangular, circular, and rectangular molds. It can be seen that the filling length $L$ is proportional to $t^{1/2}$ for a mold with a specific $D_e$ value, and a larger $D_e$ means a larger $L$ in a given time $t$. The slopes of linearly fit $L$ versus $t$ are listed in Table I. For comparison, the theoretical scaling factors between $L$ and $t^{1/2}$ for different $D_e$ estimated by Eq. (8) are also presented in Table I. We can see that the fitted slopes of experimental data are consistent with the theoretically calculated scaling factors using Eq. (8). Figure 5(b) plots the relationship between $L$ and $De \cdot t^{\frac{1}{2}}$ for the three different molds and the slope of fitted line is 0.07897, which is very close to the calculated coefficient $(\frac{P_{total}}{32\eta})^{\frac{1}{2}} = 0.07906$ obtained from Eq. (8), suggesting that $L$ is only related to $D_e$ and $t$ under constant pressure and temperature condition. These results indicate the rationality of the universal kinetic equation for describing the filling kinetics in irregular cross section mold channels for the TPF process of MGs, which have been proved to be ideal candidate of miniature-fabrication materials for high precision and ready preparation.[32–37] We note that the stress distribution in the starting disc is a factor which could affect the filling.[20] However, in our case, as the sample is a very thin plate (less than 1 mm height), the stress on the sample has a relatively uniform distribution and is not significantly dependent on the position of the sample.

## IV. CONCLUSIONS

We proposed a universal equation which can describe the filling kinetics of viscous metallic supercooled liquid in micro molds with irregular shapes. The experimental data of the mold filling process are in good agreement with the theoretical analysis based on the universal equation for the circular, rectangular, and triangular molds. The results might provide an insight into the filling kinetic of viscous metallic supercooled liquid, and could help us to design and produce MG micro products with high qualities.

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[1]W. Klement, R. H. Willens, and P. Duwez, Nature **187**, 869 (1960).
[2]W. H. Wang, Prog. Mater. Sci. **52**, 540 (2007).
[3]Y. H. Liu, G. Wang, R. J. Wang, D. Q. Zhao, and W. H. Wang, Science **315**, 1385 (2007).
[4]J. J. Lewandowski, W. H. Wang, and A. L. Greer, Philos. Mag. Lett. **85**, 77 (2005).
[5]W. H. Wang, C. Dong, and C. H. Shek, Mater. Sci. Eng. R **44**, 45 (2004).
[6]J. Schroers, Adv. Mater. **22**, 1566 (2010).
[7]G. Kumar, A. Desai, and J. Schroers, Adv. Mater. **23**, 461 (2011).
[8]K. Zhao, X. X. Xia, H. Y. Bai, D. Q. Zhao, and W. H. Wang, Appl. Phys Lett. **98**, 141913 (2011).
[9]J. Schroers, JOM **57**, 35 (2005).
[10]W. H. Wang, Adv. Mater. **21**, 4524 (2009).
[11]B. Zhang, D. Q. Zhao, M. X. Pan, W. H. Wang, and A. L. Greer, Phys. Rev. Lett. **94**, 205502 (2005).
[12]B. Zhang and W. H. Wang, J. Non-Cryst. Solids **352**, 5687 (2006).
[13]B. Zhang, D. Q. Zhao, M. X. Pan, R. J. Wang, and W. H. Wang, Acta Mater. **54**, 3025 (2006).
[14]O. Rötting, W. Röpke, H. Becker, and C. Gärtner, Microsyst. Technol. **8**, 32 (2002).
[15]X. J. Shen, L. W. Pan, and L. Lin, Sens. Actuators, A **97**, 428 (2002).
[16]M. Heckele, W. Bacher, and K. D. Müller, Microsyst. Technol. **4**, 122 (1998).
[17]G. P. Zhang, Y. Liu, and B. Zhang, Adv. Eng. Mater. **7**, 606 (2005).
[18]J. Ma, X. Zhang, and W. H. Wang, J. Appl. Phys. **112**, 024506 (2012).
[19]G. Kumar, H. X. Tang, and J. Schroers, Nature **457**, 868 (2009).
[20]G. Kumar, J. Blawzdziewicz, and J. Schroers, Nanotechnology **24**, 105301 (2013).
[21]J. Schroers, Acta Mater. **56**, 471 (2008).
[22]H. Kato, T. Wada, M. Hasegawa, J. Saida, A. Inoue, and H. S. Chen, Scr. Mater. **54**, 2023 (2006).
[23]E. B. Pitt, G. Kumar, and J. Schroers, J. Appl. Phys. **110**, 043518 (2011).
[24]D. L. Henann and L. Anand, Acta Mater. **56**, 3290 (2008).
[25]G. Kumar and J. Schroers, Appl. Phys. Lett. **92**, 031901 (2008).
[26]D. L. Henann and L. Anand, J. Mech. Phys. Solids **58**, 1947 (2010).
[27]C. E. Packard, J. Schroers, and C. A. Schuh, Scr. Mater. **60**, 1145 (2009).
[28]H. M. Chiu, G. Kumar, J. Blawzdziewicz, and J. Schroers, Scr. Mater. **61**, 28 (2009).
[29]J. Yi, X. X. Xia, D. Q. Zhao, M. X. Pan, H. Y. Bai, and W. H. Wang, Adv. Eng. Mater. **12**, 1117 (2010).
[30]R. Busch, J. Schroers, and W. H. Wang, MRS Bull. **32**, 620 (2007).
[31]K. P. Kundu and M. I. Cohen, *Fluid Mechanics*, 4th ed. (Academic Press, Waltham, 2008), pp. 295–601.
[32]J. Q. Wang, W. H. Wang, and H. Y. Bai, Appl. Phys. Lett. **94**, 041910 (2009).
[33]J. P. Chu, C. L. Chiang, H. Wijaya, R. T. Huang, C. W. Wu, B. Zhang, W. H. Wang, and T. G. Nieh, Scr. Mater. **55**, 227 (2006).
[34]X. F. Liu, R. J. Wang, D. Q. Zhao, M. X. Pan, and W. H. Wang, Appl. Phys. Lett. **91**, 041901 (2007).
[35]Y. Saotome, K. Itoh, T. Zhang, and A. Inoue, Scr. Mater. **44**, 1541 (2001).
[36]Y. Saotome, K. Imai, S. Shioda, S. Shimizu, T. Zhang, and A. Inoue, Intermetallics **10**, 1241 (2002).
[37]Y. Saotome, Y. Fukuda, I. Yamaguchi, and A. Inoue, J. Alloys Compd. **434**, 97 (2007).