Chapter 2

Thermoplastic Forming of Metallic Glasses

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Abstract

Metallic glasses (MGs) are an unusual class of materials that possess an amorphous atomic-level structure and display a plethora of desirable mechanical, chemical and physical properties, which makes them one of the most promising engineering materials. However, the poor processability of metallic glasses greatly hindered their engineering applications. Though some techniques have been developed to fabricate metallic glass components, the unique superplasticity of supercooled liquid metallic glasses attracts enduring attentions, which allows thermoplastic forming of metallic glasses on length scales ranging from atomic-size to centimeter and especially offers an alluring prospect in the field of microfabrication. While some pivotal aspects during thermoplastic forming of metallic glasses should be addressed, for example, the evaluation of thermoplastic formability and its relationship with material flowing characteristic, the required thermoplastic forming techniques for processing MG components with high quality and the potential applications of these thermoplastic formed textures are compressively reviewed in this chapter.

Keywords: metallic glasses, thermoplastic forming, formability, supercooled liquid region, vibration loading, superhydrophobic

1. Introduction

Unlike crystalline metals where dislocations or grain boundaries carry the plastic deformation, metallic glasses (MGs) usually deform inhomogeneous plastic deformation at ambient temperature caused by high localization of shear stress, resulting in fail catastrophe with zero tensile plasticity [1], which severely constraints their structural applications in macro-scale. This challenge tends to be mediated by reducing the sample size or feature below a critical length scale (<1 mm), wherein large tensile-plasticity and enhanced strength could be observed [2, 3], exhibiting size-dependent deformation behavior. Furthermore, MGs also illustrate size-dependent crystallization kinetics at nano-scale, such as the crystallization temperature rapidly increases with reduction in the diameter of nanorods, disclosing the enhanced thermal stability [4]. Consequently, the potential applications of MGs in micro- and nano-fields such as micro and nano-electro mechanical systems (MEMS/NEMS) have attracted enduring attentions [5]. However, the poor manufacturing ability origins from the high strength and ambient-temperature brittleness has been the Achilles' heel to structural applications of MGs [6, 7]. In the past decade, efforts have been devoted to fabricate MGs components with precise and versatile geometries, though the main techniques mainly focus on mold casting [8], thermoplastic forming [5, 8–26] and additive manufacturing [27–29]. By comparing with mold casting and additive manufacturing, the superiorities of thermoplastic forming is worth noting, for example, (1) the existence of supercooled liquid regime (SCLR) between the glass-transition temperature (Tg) and the crystallization temperature (Tx) allows thermoplastic forming (TPF) of MGs under low-forming strength [6], which breaks through the limitations of poor processability of MGs at ambient temperature; (2) net-shaping of precise and versatile geometries with minimum size of atom-scale could be realized, that were previously unachievable with any conventional crystalline metals; (3) the absence of phase transition of MGs during solidification endows them small solidification shrinkage (1/20 of typical casting alloys) [30], which is beneficial to the net-shaping with high precision and (4)as mentioned earlier, MGs maintain more excellent mechanical properties than crystalline metals.

In investigating the thermoplastic micro-forming of MGs, formability, namely the filling ability of supercooled liquid MGs in the mold, has been proposed to the MGs processability in the supercooled liquid region [31]. For MGs with various alloy compositions, previous literatures have reported that the thermoplastic formability was related to fragility of the supercooled liquid MGs and the width of supercooled liquid region. While for an MG with certain composition, the low viscosity and the long processing time are always appreciated [8, 32], in which the viscosity of supercooled liquid MGs is determined by processing parameters such as temperature, stress and strain rate [33]. The forming parameters actually affect the materials flow characteristics (i.e. Newtonian and non-Newtonian flow) [34]; therefore, the fundamental understanding the correlation between materials flow characteristics and thermoplastic formability is attractive with great significance. To improve the thermoplastic formability of supercooled liquid MGs, various forming techniques have been developed; these novel methods could also hot-process MGs components with macro size. It is worth noting that the potential applications of these thermoplastic formed parts especially the micro-components/patterns have been probed, which would broaden the real application of MGs. On the basis of the above descriptions, this chapter reviews the related aspects and provides in-depth understanding of the fundamental issues.

2. Thermoplastic formability

In order to evaluate the filling ability of supercooled liquid MG, micro-nano imprinting experiments on geometrical transferability of V-grooved die shapes to the material was first

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carried out by Saotome et al. [35, 36], who regarded that the micro-nano formability of supercooled liquid MGs could be quantified by the percentage of flowed area (R_f), expressed as,

$$R_f = A_f / A_g \quad (1)$$

where, A_f is the flowed area into the V-groove, A_g is the area of the V-groove. They found that the supercooled liquid MGs exhibit superior formability on micro-nanometer scales. It is easy to find that the alloys used in thermoplastic forming are generally with wide temperature ranges of supercooled liquid region, $\Delta T_x = T_x - T_g$, to reduce the risk of crystallization. Large ΔT_x indicates that the MGs have opportunities to obtain low viscosity, long forming time, and enhance the thermoplastic formability. Accordingly, ΔT_x is also regarded as one of the important indicators of the formability [31, 37], similar to the normalized parameter (S) [30] that should reflect better the formability of a MG, particularly when comparing different MG alloy families,

$$S = \Delta T_x / \left(T_l - T_g\right) \quad (2)$$

in which T_l is the melting temperature. While for MGs with different compositions, fragility parameter (m) [38],

$$m = \partial \log\eta / \partial\left(T_g / T\right)\Big|_{T=T_g} \quad (3)$$

was proposed to measure the formability of supercooled liquid MG [37]. As the Angell plots of conventional MGs and high entropy MG as shown in **Figure 1**, wherein the temperature dependent viscosity among alloys exhibits various steepness index, that is, fragility parameter (m). A large steepness index corresponds to fragile liquid behavior, such as $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ MG shows the largest value of fragility, exhibits fragile liquids with the best micro-formability, is ideal candidate for near-net shape processing with fine printability. While a small index corresponds to strong liquid and exhibits poor formability, such as the thermoplastic forming of TiZrHfNiCuBe, high entropy MG becomes arduous with reducing mold size to tens micrometer, owing to the strong supercooled TiZrHfNiCuBe high entropy MG with small value of m [39]. Similar results are also observed by Schroers [31], who proposed a simple and precise standard to characterize the formability of BMGs, and the maximum diameter (d) of the hot-formed disc was taken as a measure of the MG's formability.

It is essential that all these parameters (such as R_f, ΔT_x, m and d) in evaluating the thermoplastic formability of MGs focus on amorphous alloys with various compositions. As for MG with certain composition, it is well understood that low viscosity is crucial to improve the thermoplastic formability of supercooled liquid MG. The viscosity of MGs not only depends on the temperature but is also sensitive to the strain rate. For example, with increasing strain rates under a certain temperature in the supercooled liquid region, there is a remarkable decrease in the viscosity, accompanied by the transitioning from Newtonian to non-Newtonian behavior [40]. In this case, thermoplastic forming becomes increasingly difficult, rather than enhancement [41]. In order to probe the physical origin of this phenomenon, Li et al. [34] established a

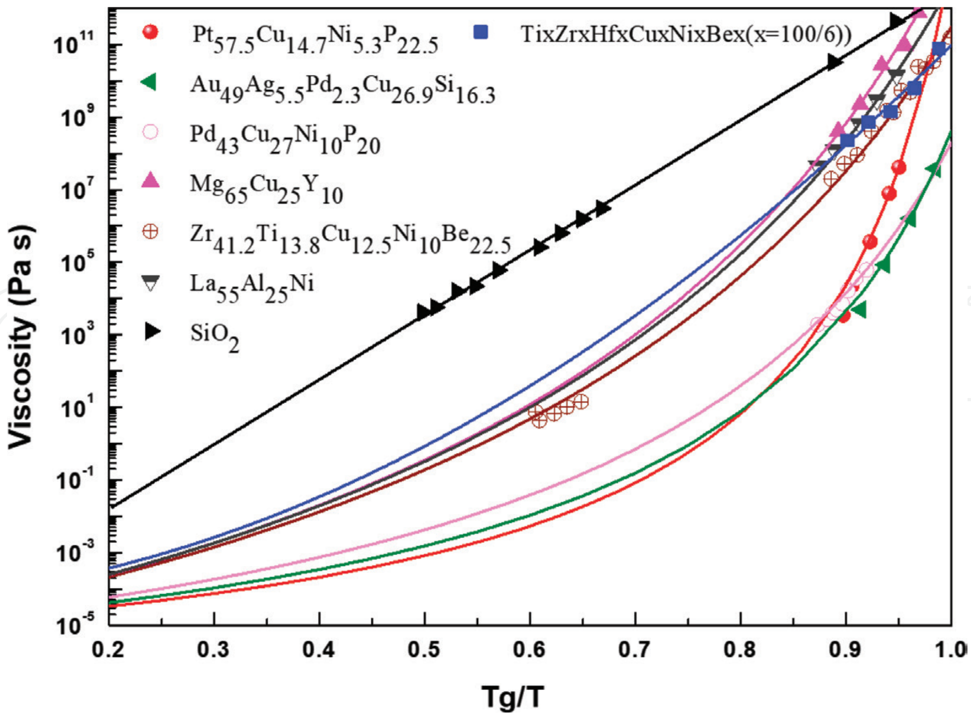

Figure 1. Angell plots of conventional MGs and high entropy MG [39].

thermoplastic forming map (see **Figure 2**), which reveals an inherent relationship between the thermoplastic formability and the flow characteristics, namely, Newtonian flow facilitates the forming capability, while the thermoplastic forming in a non-Newtonian flow regime tends to be difficult. Li et al. believe that this scenario is caused by the spatio-temporally homogeneous/inhomogeneous flow of MGs in Newtonian/non-Newtonian flow regime.

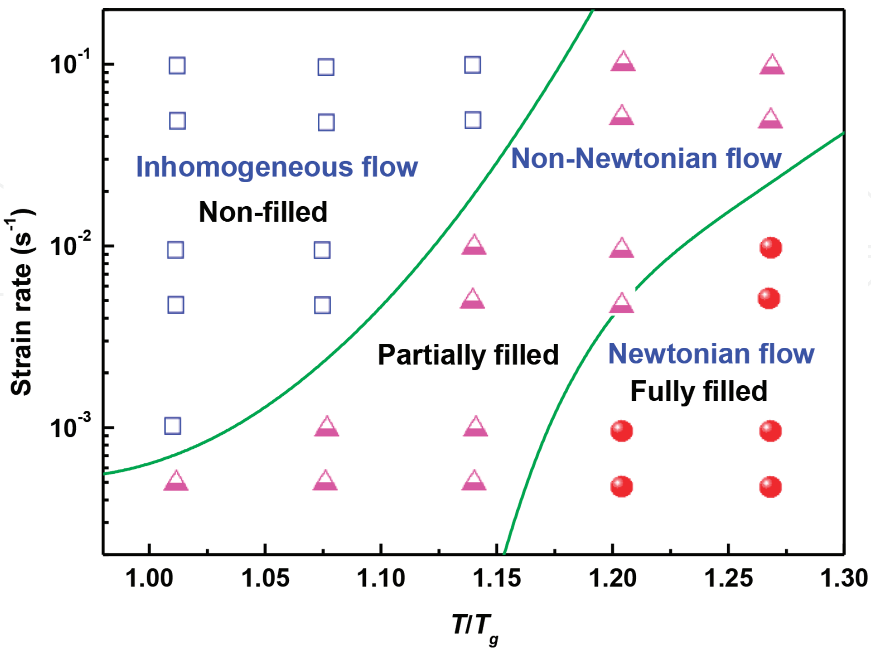

Figure 2. Thermoplastic forming map that reveals the relationship between the formability and the flow characteristics [34].

3. Thermoplastic forming techniques

Thermoplastic forming map clarifies the relationship between flow features and formability and provides the selection of processing parameters. However, the Newtonian flow usually locates at regions with high processing temperature and low strain rate, which would induce the crystallization of amorphous alloys. In addition, the interfacial effect between amorphous alloys and mold materials becomes prominent during micro- and nano-scale forming, which seriously hinders the forming of metallic glasses [5, 9]. In order to improve the formability of supercooled MGs, various forming techniques have been developed.

By comparison with the hot-embossing technique as mentioned earlier, injection molding [42] as a net-shaping method for MGs exhibits superiorities in development of commercial manufacturing processes with minimized production cycle and high-volume production. Wherein the feedstock melt is gathered and forced into the part forming mold cavity at high pressure and velocity. As a potential forming process for MG parts, the injection molding is conducted at temperatures much lower than direct casting, which can improve

Figure 3. These shapes were previously unachievable with any other metal processing method that can be fabricated by blow molding [46].

the lifetime of the mold. Furthermore, the processing is accomplished in the laminar flow regime; therefore, higher quality and reliable parts could be obtained by comparison with the current mold-casting technique [8, 42]. However, the viscosity of the supercooled liquid MGs is much higher than that of the plastics melt, which poses a challenge for mass production.

In order to improve the thermoplastic formability of supercooled liquid MGs, micro-back-extrusion was proposed by Wu et al. [14], and a three-dimensional cup-shaped object with wall thickness of 0.05 mm was successfully fabricated. To reduce the contact area between MGs and mold materials, rolling was developed by Schroers et al. [43] who not only hot-rolled high-quality MG sheets but also replicated micro-patterns with featured size of 300 nm. The micro-replication of MGs through hot-rolling is actually similar to hot-embossing process, wherein the high viscosity and interfacial effect are main reasons limit the processability. Subsequently, Schroers et al. [44, 45] developed blow molding (see **Figure 3**), which allows blowing hollow products by using gas pressure to inflate the thermoplastic MGs enclosed in the mold. The low-forming pressure and high-dimensional accuracy indicates that this net-shaping technology could bring economic and environmental benefits.

Recently, an ultra-fast MGs' hot-processing technique was probed by Johnson et al. [47], as illustrated in **Figure 4**. When rapidly and uniformly heating a metallic glass at rates of 10^6 K/s to temperatures spanning the undercooled liquid region, rapid thermoplastic forming of the undercooled liquid into complex net shapes is implemented under rheological conditions typically used in molding of plastics. Owing to the millisecond time window, this method is able to "beat" the intervening crystallization and successfully process even marginal glass-forming alloys with very limited stability against crystallization that are not processable by

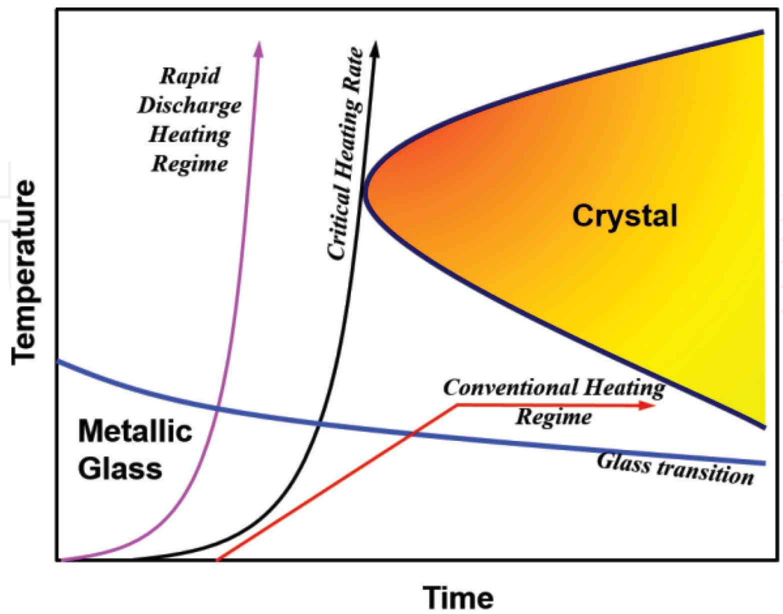

Figure 4. Using the rapid uniform heating approach with heating rates in the order of 10^6 K/s, the undercooled liquid is accessible at any temperature above the glass transition, through the melting point and beyond, where the liquid enters the equilibrium state.

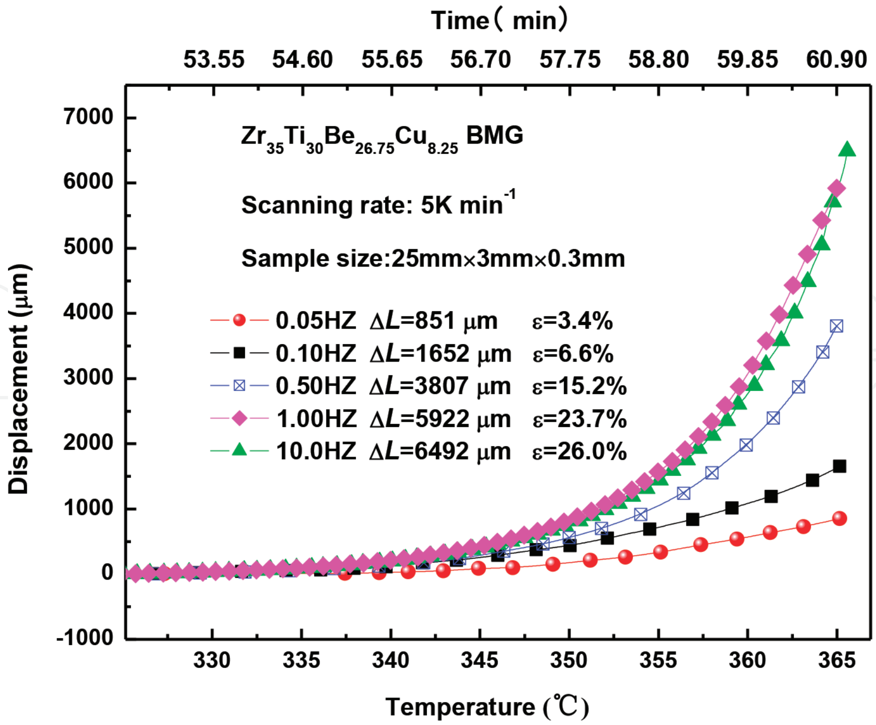

Figure 5. The displacement-temperature (time) curves of $Zr_{35}Ti_{30}Be_{26.75}Cu_{8.25}$ MG after vibrational tension under various loading frequencies ranging from 0.05 to 10 Hz (temperature rises from 23 to 365°C with scanning rate of 5°C/min^{-1}) [50].

conventional heating. Take advantage of unique rheological property along with the classic Lorentz force concept, electromagnetic coupling of electric current and a magnetic field was then thermoplastically shape a metallic glass without conventional heating sources or applied mechanical forces [48].

Based on improvements of formability made in the traditional metal formed by employing ultrasonic vibration [49], and considering that the viscosity is closely related to the dynamic relaxation of the alloy system, namely the shortening of the relaxation time, reduced viscosity is caused. Li et al. [50] introduced vibrational loading in thermoplastic forming of MGs; the intriguing finding was that the formability of supercooled liquid MGs is facilitated by vibrational loading (**Figure 5**). This technique exhibits potential applications in micro-/nano-scale forming of MGs. By increasing loading frequency to about 20 KHz, Ma et al. [51] used high frequency ultrasonic beating method to fabricate micro- to macro-scale structures, avoiding crystallization and oxidation of MGs.

4. Potential applications

The above thermoplastic forming techniques endow MGs with superiority in net-shaping precise and versatile structures comprising of macro-/micro-/nano-sized features. Through nanoimprinting, Schroers et al. [5, 8, 9] fabricated metallic glass nanowires with very high aspect ratios (>200); these nanorods not only exhibit enhanced thermal stability [4] but also display superb durability combined with high electrocatalytic activity toward methanol, ethanol oxidation and

CO, exhibiting great potential in energy conversion/storage and sensors fields [52]. The superb durability and high-surface area of these MG nano-structures motivate the generation of first functional proton exchange membrane micro fuel cells (MFCs). Such novel MFCs have been identified as a promising alternative power sources for portable electronics [53].

In addition to the potential applications in energy sector, the micro-/nano-gratings hot-imprinted on MGs surfaces also exhibit excellent spectroscopic performance [54, 55]. For example, Chu et al. [54] fabricated nano-scale gratings, and Ma et al. [55] hot-embossed micro-scale gratings with fine periodicity on Pd-based MGs surfaces, both surface exhibit beautiful optical properties such as rainbow-like spectrum when shone by fluorescent lamp light, as shown in **Figure 6**. Inoue et al. [56] pointed out that these nano-imprinted MG surfaces exhibit potential applications as anti-reflection materials, electrode materials, hologram technology, next generation ultra-high density of information data storage material and cell culture medium for bio-chips.

By integrating macro-, micro- and nano-scale features in a sequential order, Kumar et al. [13] hot-embossed hierarchical structures and displayed potential applications in optical devices, electrochemical activity and cellular response. Through micro-imprinting, some micro-lens arrays [57], micro-channel geometries [58] have been fabricated, showing potential applications in aspheric lens and fuel cell interconnect plates, respectively. Furthermore, the thermoplastic formed MG components have been used as a master mold (see **Figure 7**) to imprint polymers (such as PMMA) [10, 24, 59, 60], and an integrated PMMA micro-channel part was fabricated, implying that MG is a robust, attractive and viable mold material for thermoplastic imprinting of polymer devices [10]. Bardt et al. [23] thermoplastic formed some complex 3-D micro-topologies and envisaged potential application as high-Q micro-resonators, microwave waveguides, microsurgical tools and devices, connectors for higher frequency operations, micro-scale motors and transmission components, microfluidic arrays, and free-form reflective micro-optics.

The hot-embossed surface micro-components can be used in MEMS, biochips, such as micro-spring, micro-gear, micro-motor, micro-fan, micro-honeycomb structure, micro-gyroscope and micro-accelerometer structure and micro-turbines; some beautiful surface features such as micro-bats and micro-poetry of Tang Dynasty "Yellow Crane Tower" have also been fabricated

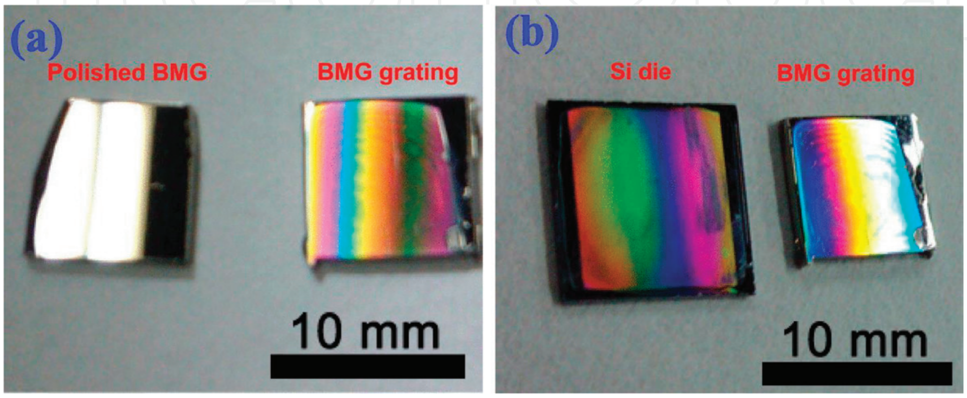

Figure 6. (a) Photographs of polished BMG plate (left) and BMG grating (right) when fluorescent lamp light shines upon them (b) photographs of Si die (left) and BMG grating (right) under the shine of fluorescent lamp light [55].

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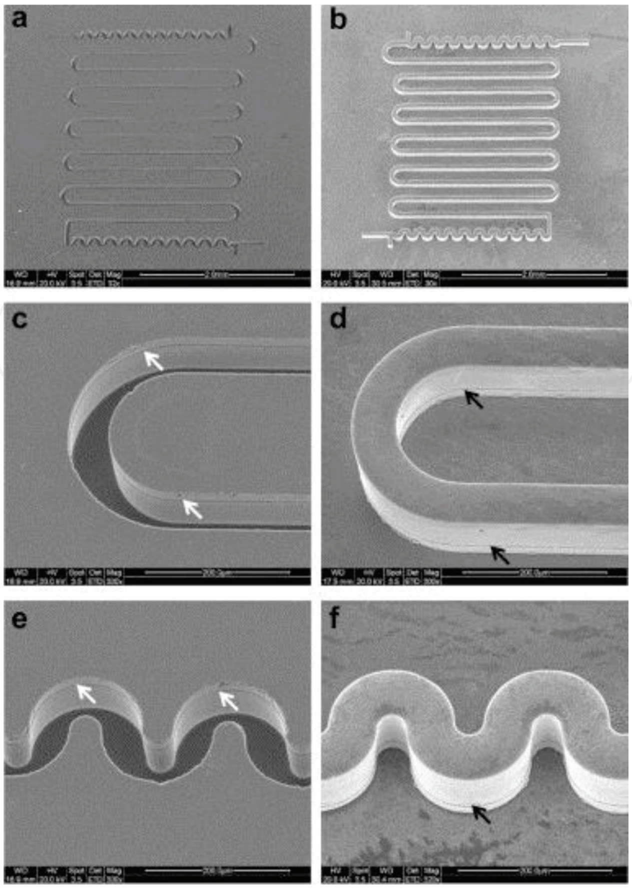

Figure 7. SEM micrographs of the silicon master (a) with single (c) and continuous bends structure (e); the corresponding hot-embossed metallic glass micro-channel structure (b, d, and f) [10].

by Li et al. [6] through thermoplastic forming. Similar to micro-/nano-scale hot-imprinting, the TPF-based blow molding has also been used to fabricate ultra-smooth and symmetric 3-D metallic glass resonators, which demonstrates precision over 5 orders of magnitude without the use of cleanroom facilities or traditional microfabrication techniques, displaying potential applications in future MEMS vibratory devices, such as accelerometers and gyroscopes, with reduced energy dissipation mechanisms, increased performance and low costs [61].

The thermoplastic micro-forming technique also exhibits great potential in fabrication superhydrophobic surfaces with long lifespan in service, as demonstrated by Li et al. [62, 63]. Who found that without any modification or post-treatment, superhydrophobic surfaces with good stability could be fabricated by hot-embossing honeycomb patterns on $Pd_{40}Cu_{30}Ni_{10}P_{20}$ MG [62]. By constructing micro-/nano-hierarchical structures on $Zr_{35}Ti_{30}Be_{26.75}Cu_{8.25}$ MG surface, Li et al. [63] not only fabricated superhydrophobic MG surface with water contact angle over 150°, but also found that these surfaces exhibit strong adhesion with water droplets. The combined properties of both superhydrophobicity and strong adhesion toward liquid exhibit promising applications as dry adhesives and transport of liquid micro-droplets, as well as desirable mechanical and corrosion resistance showing potential applications in modern industries [64]. Furthermore, Li et al. revealed that MGs surfaces with hot-embossed textures exhibit low friction coefficient especially under dry contact (see **Figure 8**), which indicates that the lifetime of the textured surfaces could be optimized by minimizing friction [65].

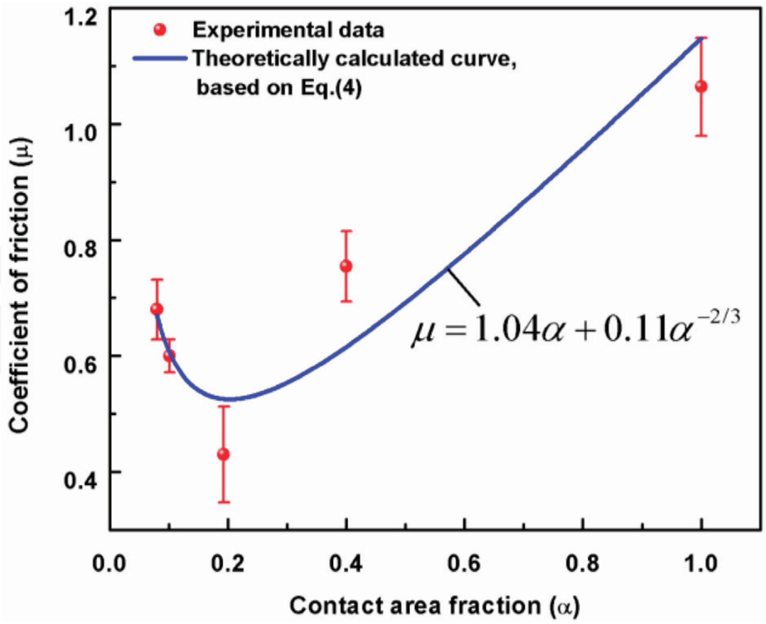

Figure 8. The experimental and theoretically calculated coefficients of friction with the contact area fraction [65].

5. Summary and outlook

Thermoplastic forming provides a promising method to fabricate MGs topological structures and components at various scale sizes, which provides alluring prospects in broadening the application of MGs. The chapter reviews some crucial issues such as the thermoplastic formability, processing techniques and potential applications. Some challenges still exist and impede the practical applications: (1) only few amorphous alloys with excellent glass forming ability, anti-oxidation ability and wide supercooled liquid region, and so on can meet the requirement of thermoplastic forming, (2) the current TPF techniques face challenges in fabricating complicated 3-D structures, (3) the material flow is seriously affected by the interfacial effect on the micro- and nano-scale and the root physical mechanism remains vaguely understood and needs to be settled, and (4) large-scale manufacture is necessary to improve productivity and reduce the cost, if the market of commercial application is developed. Therefore, developing a novel forming technique becomes urgently necessary to breakthrough the alloy systems' limitations. Recent literatures [27–29] have revealed that additive manufacturing (3D printing) is a promising technique for the production of bulk metallic glass (BMG) components without size and alloy system limitations. The authors believe micro-3D printing would provide new opportunities for the creation of small, complex and free-form MG components that were previously unachievable, which would open a new window for MGs fabrication.

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Conflict of interest

The authors declare that they have no competing financial interests.

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