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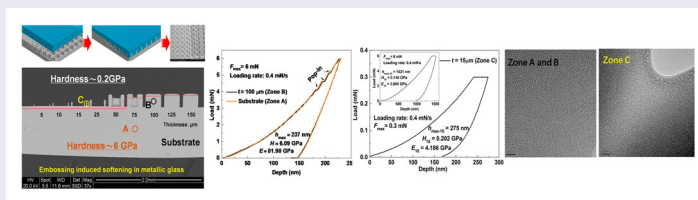
Pronounced softening of a Zr-based metallic glass in micro annular gap flow

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ABSTRACT

While shear softening is widely acknowledged inflow of metallic glasses (MGs), the underlying structural origin remains obscure. Here a $\text{Zr}_{35}\text{Ti}_{30}\text{Be}_{26.75}\text{Cu}_{8.25}$ MG was squeezed into annular gaps of an exterior diameter of 300 μm and widths of 5 ~ 150 μm by thermoplastic embossing. Pronounced softening was detected for MG flowing in gaps smaller than 50 μm , showing a hardness value $\sim 1/30$ of MG outside the gap. Nanofoam-like feature was observed in the atomic structure of softened MG. This is attributed to the increased shear in MG flowing in smaller gaps and proposed to be the main cause for the pronounced softening.



IMPACT STATEMENT

The effects of shear in micro annular gap flow on the structure and mechanical properties of metallic glass were revealed.

ARTICLE HISTORY

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KEYWORDS

Metallic glass; annular gap flow; deformation structure; softening

1. Introduction

Softening in metallic glasses (MGs) induced by flow was early recognized in the 1970s [1] and has attracted widespread attentions since then [2–9]. However, the origin of softening in MGs remains under debate [10–12] for insufficient information about structural evolution of MGs inflow. This is mainly for the high propensity to softening of MGs which causes the plastic deformation of MGs at ambient temperature to rapidly (in micro-to-milliseconds) localize into thin (10 ~ 50 nm) shear bands [3,13]. These temporal and spatial limitations largely hamper examination on structural evolution inside shear bands [5–9,14–16].

With the difficulties faced above, the supercooled liquid state of MGs exhibiting excellent micro and even nanoscale formability in imprinting, embossing and molding [17], provides an alternative approach to examine the structure of MGs inflow. By squeezing MG

in supercooled liquid state into micro gaps could partially simulate the flow of MG inside shear bands while avoiding the above limitations, especially noting the micrometer-sized shear band affected zones [15,18,19]. Meantime, examining the effect of flow in thin gaps on the structure and mechanical properties of MGs which determine the integrity and robustness of MG microstructures is critical to the application of the formed MG microparts [20–24]. Also, it is noteworthy that although nano-and-micro pillar samples of MGs have been widely investigated in past decades [25], it was found that the manufacture path of these small samples would have an important effect on their deformation behaviors [21,26,27]. Thereby, research on the effect of flow in micro gaps on MG could as well be a necessary complement to previous works [25] on nano-and-micro-sized MG specimens. In this work, by thermoplastic embossing (as will be illustrated in Figure 1), a $\text{Zr}_{35}\text{Ti}_{30}\text{Be}_{26.75}\text{Cu}_{8.25}$

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MG was squeezed into annular gaps of an exterior diameter of 300 μm and different widths to realize micro gap flow. Annular gaps are selected for convenient flow analysis due to rotational symmetry.

2. Material and methods

Annular gaps were fabricated on a silicon wafer of 0.5 mm in thickness and 4 in. in diameter via deep reactive ion etching. Individual silicon mold for embossing was a square piece of $4.5 \times 4.5 \times 0.5 \text{ mm}^3$ in size, as shown in Figure 1(a). Each silicon mold contains an array of annular gaps of an exterior diameter of 300 μm and different widths of 5, 10, 15, 25, 50, 75, 100, 125 and 150 μm (i.e. pillar). The annular gaps are of an increasing depth between 170 and 350 μm with increased width, and a spacing of 50 μm along both transversal and longitudinal directions.

$\text{Zr}_{35}\text{Ti}_{30}\text{Be}_{26.75}\text{Cu}_{8.25}$ (at.%) MG was chosen for its excellent anti-oxidation capability and thermal stability [28], showing a glass transition temperature T_g of 305 $^{\circ}\text{C}$ and a crystallization temperature T_x of 445 $^{\circ}\text{C}$, i.e. a wide supercooled liquid region of 140 $^{\circ}\text{C}$. MG specimens for embossing were $4.5 \times 4.5 \times 1.5 \text{ mm}^3$ in size. According to ref. [28], embossing was performed at 380 $^{\circ}\text{C}$ at a loading rate of $0.0015 \text{ mm}\cdot\text{s}^{-1}$ on a materials testing machine (Zwick/Roell 020). For embossing, MG was stacked onto silicon mold (Figure 1(b)). After embossing, the MG was squeezed into the annular gaps (Figure 1(c)) and could be released by etching away the mold in KOH solution. Annular features of MG flowing into the gaps were observed with scanning electron microscopy (SEM, FEI Sirion 200) and a transmission electron microscope (TEM, Tecnai G2 F30). As shown in Figure 1(d), the annular features show no obvious defects. Nanoindentation was performed on the annular features embedded

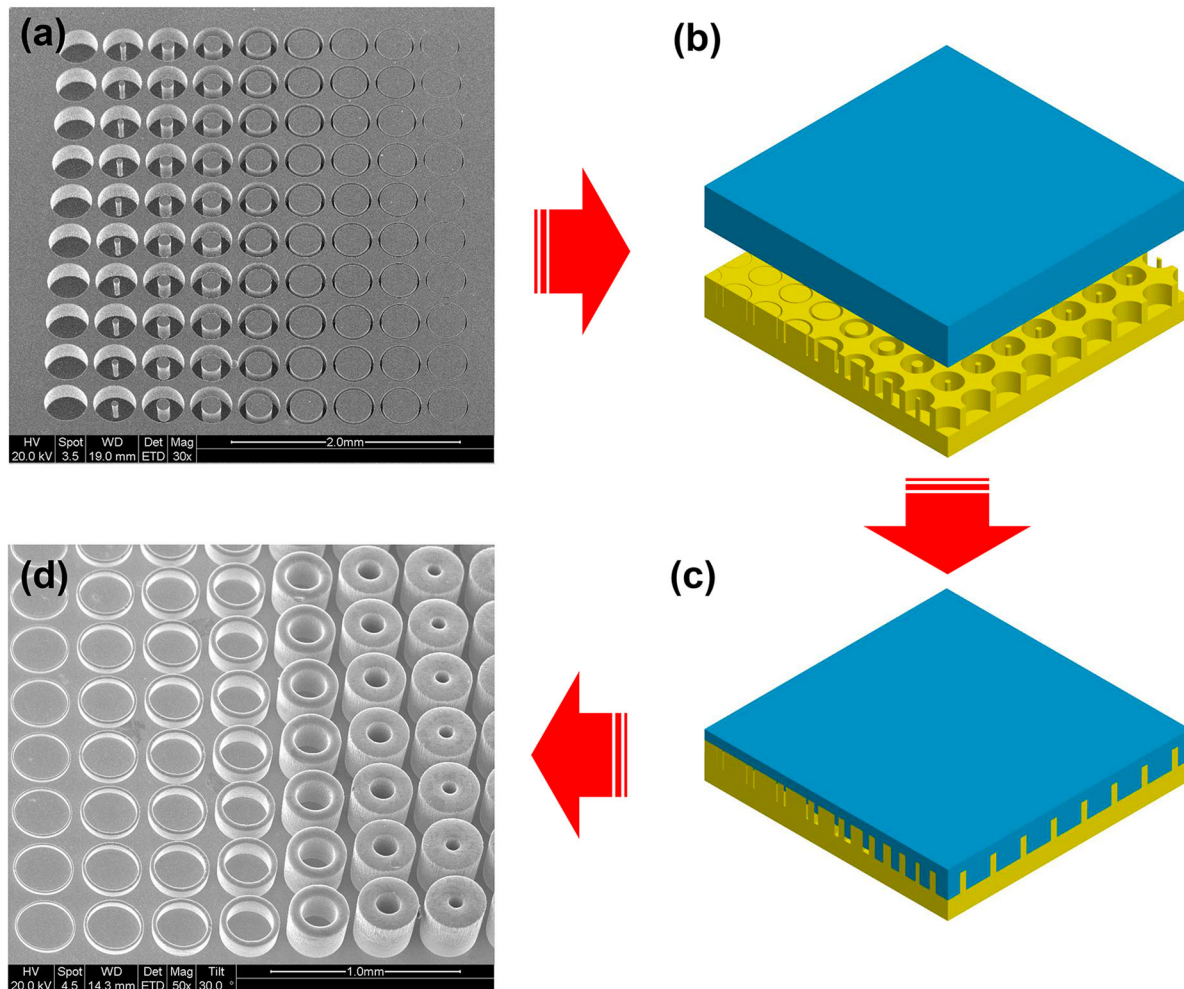


Figure 1. Illustration on thermoplastic embossing of metallic glass (MG) by which MG was squeezed into annular gaps. (a) Silicon mold fabricated with annular gaps; (b) Laying MG (blue) atop silicon mold (yellow); (c) MG squeezed into annular gaps after embossing; (d) Annular features embossed on MG by squeezing MG into the annular gaps, with the silicon mold etched away in KOH solution.

in an epoxy resin base with a Hysitron Triboindenter (Hysitron TI 750) using a Berkovich-type tip.

3. Results and discussion

Figure 2(a) shows cross-section of the annular features of $\text{Zr}_{35}\text{Ti}_{30}\text{Be}_{26.75}\text{Cu}_{8.25}$ MG squeezed into the annular gaps. Thickness of annular features corresponds to the annular gap width. Filling depth of annular features into the gap increases with the gap width, indicating the increased filling ability of MG into gaps of larger width. Figure 2(b) shows the high-resolution TEM image of $\text{Zr}_{35}\text{Ti}_{30}\text{Be}_{26.75}\text{Cu}_{8.25}$ MG outside the gap (i.e. the substrate) after embossing. The inset shows the selected area electron diffraction pattern. The disordered atomic packing and the appearance of a halo ring indicate that the MG maintained amorphous after embossing. Figure 2(c and d) shows the representative load (P) vs. displacement (h) curves in nanoindentation for Zone A, B and C (i.e. MG substrate, annular feature of a thickness of $100\text{ }\mu\text{m}$ and annular feature of a thickness of $15\text{ }\mu\text{m}$, as indicated by circles in Figure 2(a)). In Figure 2(c), the

P vs. h curves for Zone A and B showing a maximum depth of $\sim 235\text{ nm}$ and a maximum load of 6 mN almost overlap with each other, indicating that MG substrate and MG annular feature of a thickness of $100\text{ }\mu\text{m}$ exhibited similar mechanical properties. The hardness and reduced modulus are 6.09 and 81.98 GPa , respectively. Figure 2(d) shows the P vs. h curve showing a maximum depth of 275 nm and a maximum load of 0.3 mN for zone C, suggesting a hardness value of 0.20 GPa and a modulus of 4.18 GPa . The inset is the P vs. h curve showing a maximum load of 6 mN and a much increased maximum depth of 1520 nm for zone C, suggesting a hardness value of 0.15 GPa and a modulus of 3.0 GPa . This result indicates that flow in annular gap of $15\text{ }\mu\text{m}$ in width led to pronounced softening of MG.

To chart the softened region, Figure 3(a) shows the P - h curves for annular features of thicknesses ranging from 10 to $50\text{ }\mu\text{m}$ (P_{10} - P_{50}), top part of the annular feature of a thickness of $150\text{ }\mu\text{m}$ ($P_{150\text{-top}}$), and edge of the MG substrate (P_{s-e}). For these tests, a maximum load of 0.3 mN was adopted. The indent depth, hardness, and modulus are $\sim 279\text{ nm}$, $\sim 0.2\text{ GPa}$, and

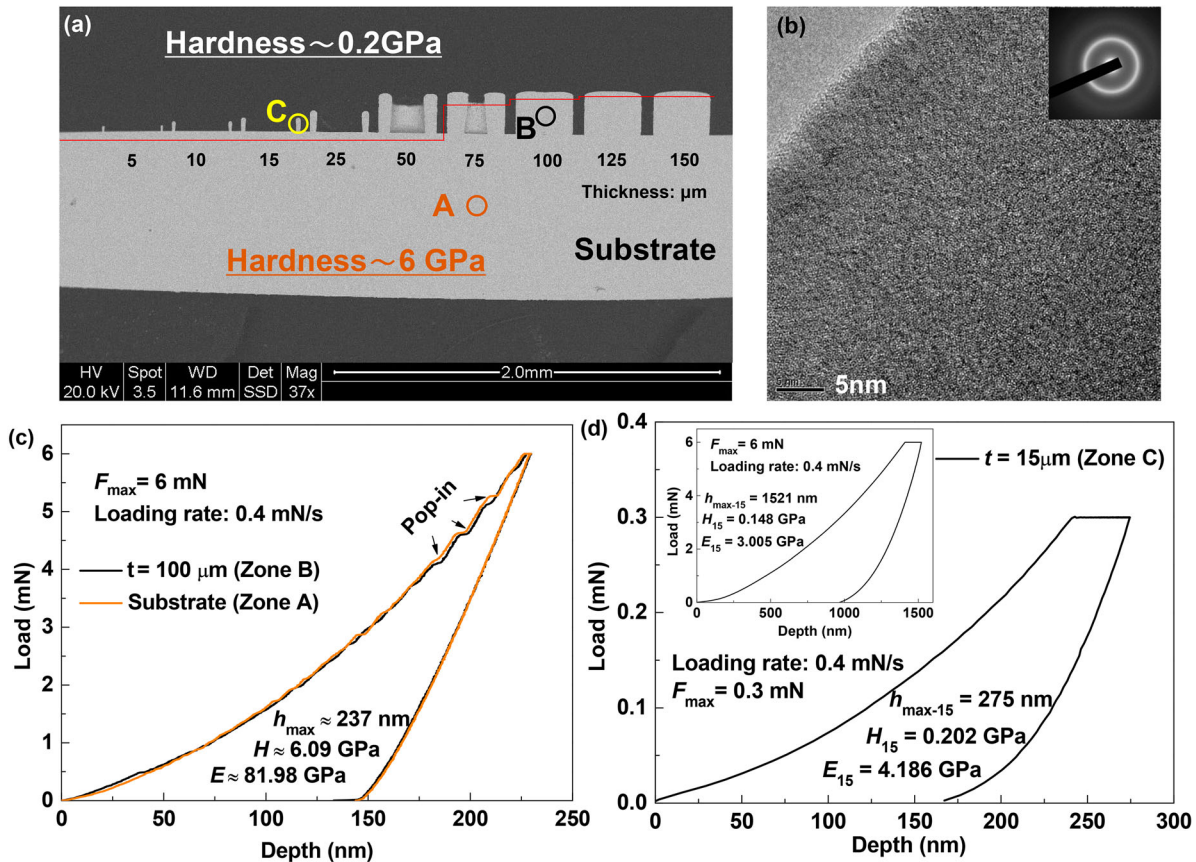


Figure 2. Nanoindentation and softening. (a) Cross-section of annular features of MG squeezed into annular gaps with various widths from 5 to $150\text{ }\mu\text{m}$ (i.e. a pillar). (b) High-resolution TEM images of atomic structure of the MG substrate. Inset shows the SAED pattern. (c) Load-displacement (P - h) curves of zone A (substrate) and B (annular feature with a thickness of $100\text{ }\mu\text{m}$). (d) The P - h curve for zone C (annular feature of $15\text{ }\mu\text{m}$ in thickness). Thickness of annular features corresponds to annular gap width.

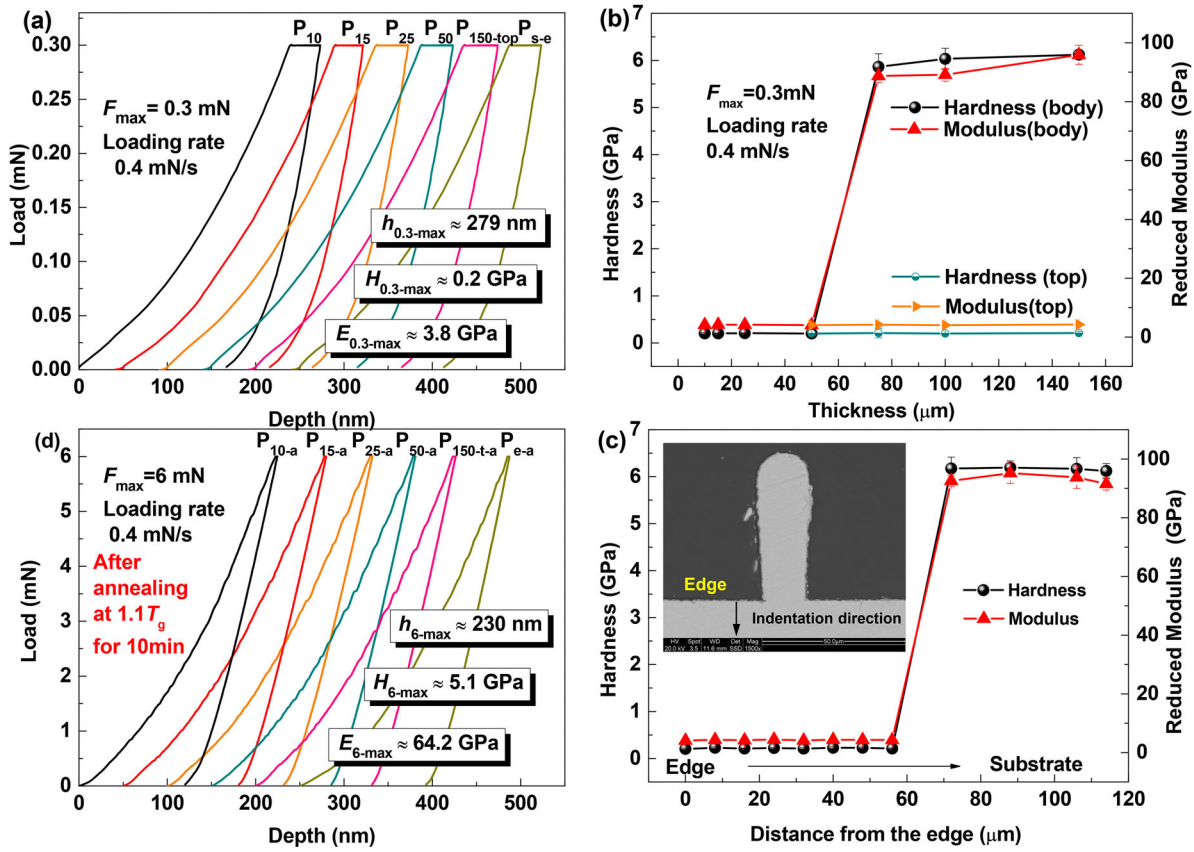


Figure 3. Nanoindentation on annular features. (a) Load-displacement (P - h) curves of annular features with various thickness (10–50 μm , P_{10} – P_{50}), top part of annular feature of 150 μm ($P_{150\text{-top}}$), and edge part (P_{s-e}) of substrate. (b) Hardness and modulus for the body part and top part of annular features. (c) Hardness and modulus for the edge part of MG substrate, indicating a softened region of $\sim 50 \mu\text{m}$. Inset shows the annular feature embedded in epoxy resin and the direction from edge to interior of MG substrate. (d) P - h curves for annealed annular features, demonstrating the removal of softening after annealing.

$\sim 3.8 \text{ GPa}$, respectively, indicating the occurrence of softening. Figure 3(b) shows the variation of hardness and modulus for the top part and body part of annular features with increasing thickness. It is seen that the top part of annular feature exhibits softening for all thickness, while the softening phenomenon disappears in the body part for annular features of a thickness greater than 50 μm . Similarly, Figure 3(c) provides the variation of hardness and modulus with increasing distance from the edge to the interior of MG substrate. It is seen that there is a softened region of a width of about 50 μm from the edge. The inset shows the annular feature embedded in epoxy resin and the direction from edge to the interior of MG substrate.

To confirm the softening effect, nanoindentation was also performed on MG annular features thermally annealed at 360°C ($\sim 1.1T_g$) for 10 min. Figure 3(d) presents the P - h curves for annular features of thicknesses ranging from 10 to 50 μm (P_{10-a} – P_{50-a}), top part of the annular feature of a thickness of 150 μm ($P_{150-t-a}$) and edge of the MG substrate (P_{e-a}). It is noted that the hardness and modulus recovered to 5.1 and

64.2 GPa, respectively, indicating the removal of softening. Thereby, a boundary can be drawn as the red line in Figure 2(a) for the softened region. Above the line, the hardness is $\sim 0.2 \text{ GPa}$, while below the line, the hardness is $\sim 6 \text{ GPa}$. Critical size of the geometric feature for softening could be identified as 50 μm . Namely, when the thickness of the annular feature is less than 50 μm , the whole feature exhibits softening. For annular features of a thickness larger than 50, the softened region was located at the top part with a distance less than 50 μm from the surface. With increasing thickness of the annular feature, the softened region shrinks rapidly.

Generally, the softening of MGs in flow stems from shear as in shear bands [13,29]. Here, due to the decreased gap width, the strong viscous traction effect on the surface of the silicon mold would lead to strong shear in the annular gap flow of MG. To calculate the flow state of MG in the annular gap, it is first assumed that the capillary force is negligible as the gap width is well above 100 nm [30]. Moreover, for the high viscosity of MG (approximately $2 \times 10^7 \text{ Pa s}$), the flow kinetics involves simple laminar flow [31]. Figure 4(a) shows the

illustration of the velocity distribution of MG on the cross-section of the annular gap. Assuming a non-sliding boundary condition, the strain rate at the surfaces of the gap could be obtained from the velocity distribution u on the radial cross-section of the annular gap:

$$u = \frac{\Delta P}{4\eta l} \left(\frac{R^2 \ln((t+r)/R) - r^2 \ln((t+r)/r)}{\ln(R/r)} - (t+r)^2 \right) \quad (1)$$

where η is viscosity, l is filling depth into the annular gap; R and r are the exterior and interior radii of the annular gap. t is the distance from the inner cylindrical surface along the radial direction. ΔP is the squeezing pressure and could be estimated with the Hagen–Poiseuille equation, where τ is filling time,

$$\Delta P = \frac{8\eta}{\tau} \cdot \frac{l^2}{R^2 + r^2 - \frac{R^2 - r^2}{\ln R/r}} \quad (2)$$

It is reasonable to consider that the filling times of all the annular features are the same and equal the duration period of the embossing process. Figure 4(b) shows the dimensionless forming pressure ($\Delta P\tau/8\eta$) required for the annular features and the corresponding filling depth. It is seen that the annular feature of a thickness of $d = 5 \mu\text{m}$ with a filling length $l = 30 \mu\text{m}$ requires a forming pressure ~ 10 times of that of the annular feature of a thickness $d = 125 \mu\text{m}$ with a filling length $l = 230 \mu\text{m}$. Thereby, more significant shear occurs inside annular gaps with a smaller width. The distribution of shear strain rate reads:

$$\dot{\gamma} = \frac{du}{dt} = \frac{\Delta P}{4\eta l} \left(\frac{R^2 - r^2}{(t+r) \ln(R/r)} - 2(t+r) \right) \quad (3)$$

and the maximum strain rates occurred at the exterior and interior surfaces of the annular gap. The $\dot{\gamma}$ at the interior and exterior surfaces respectively reads:

$$\dot{\gamma}|_r = \frac{\Delta P}{4\eta l} \left(\frac{R^2 - r^2}{r \ln(R/r)} - 2r \right) \quad (4)$$

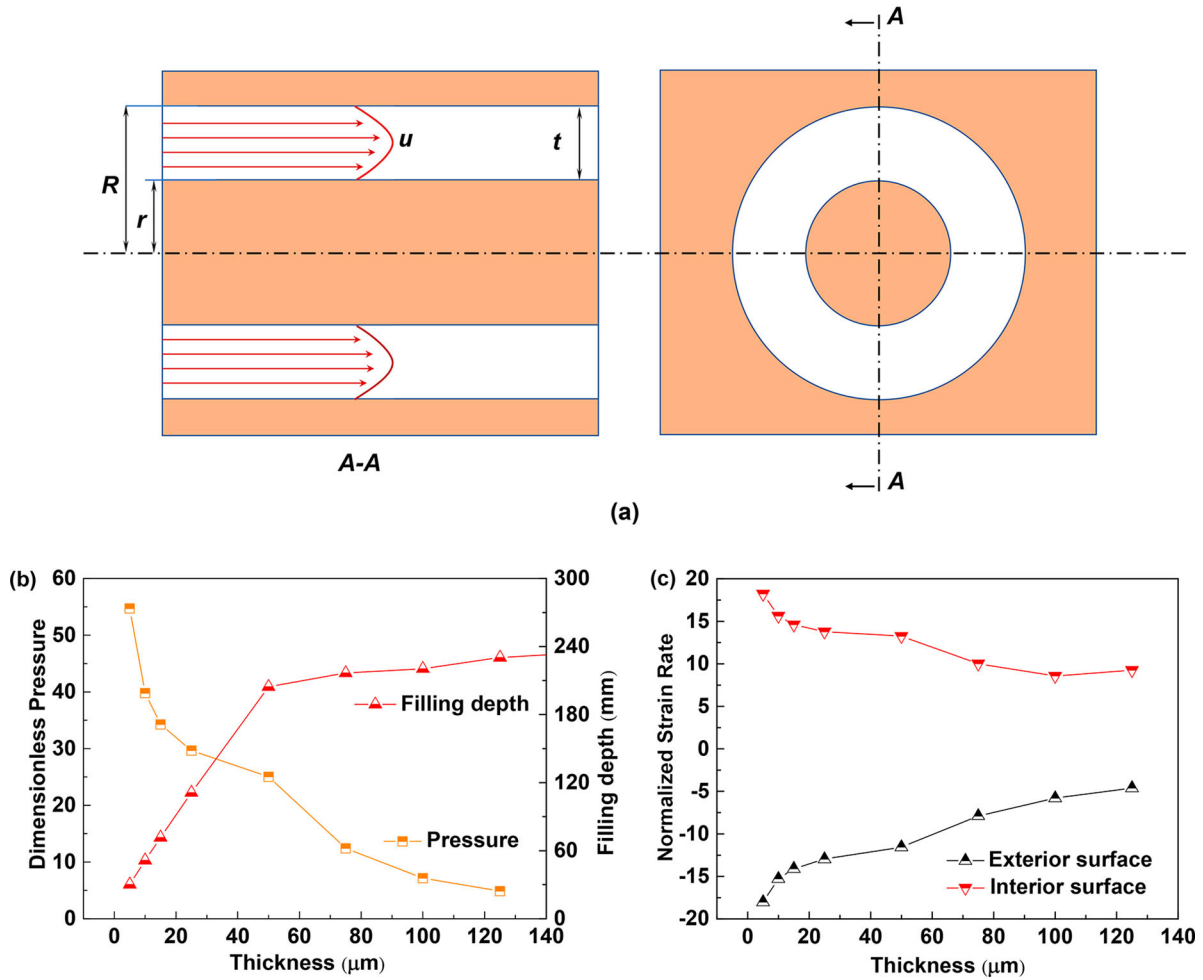


Figure 4. Theoretical calculation on the annular gap flow. (a) Velocity distribution on the cross-section of annular gap; (b) dimensionless filling pressure for annular features of different thickness; (c) normalized shear strain rate at the surface of annular gaps.

$$\dot{\gamma}|_R = \frac{\Delta P}{4\eta l} \left(\frac{R^2 - r^2}{R \ln(R/r)} - 2R \right) \quad (5)$$

Based on the above equations, the strain rate normalized as $(\frac{1}{2}\dot{\gamma} \cdot \tau)$ at the surfaces of the annular gaps of different thickness is shown in Figure 4(c). It is seen that with decreased width, the strain rate increases rapidly. The total embossing time is approximately 500 s. However, the filling time τ is less than this for the ramping loading process. The lower limit of the strain rate in the annular gap of 50 μm in width is $\sim 0.05 \text{ s}^{-1}$ and roughly the critical strain rate for shear thinning in the $\text{Zr}_{35}\text{Ti}_{30}\text{Be}_{26.75}\text{Cu}_{8.25}$ supercooled liquid at 380°C [32]. This result reasonably interprets the observed softening with decreasing gap width.

The critical thickness of $\sim 50 \mu\text{m}$ of the annular features for softening could also be partially understood based on the annular gap flow of MG. The normalized strain rate $(\frac{1}{2}\dot{\gamma} \cdot \tau)$ in Figure 4(c) is actually half the strain at the surface of the annular gap. It is seen that the accumulated strain for annular features thinner than 50 μm is greater than ~ 20 , while that for the thicker ones is less than ~ 20 . This critical strain near 20 coincides with the observation made by Liu et al. [8] that the accumulated strain inside shear bands starts to progressively reduce the density (*i.e.* increase the volume) of MGs. Liu et al. [8] also showed that a shear strain of the order of 10^1 would increase the volume by $\sim 2\%$ inside shear band. Evaluation on the specific volume of MGs shows that with a volume increase of $\sim 1.5\%$ the amorphous structure of

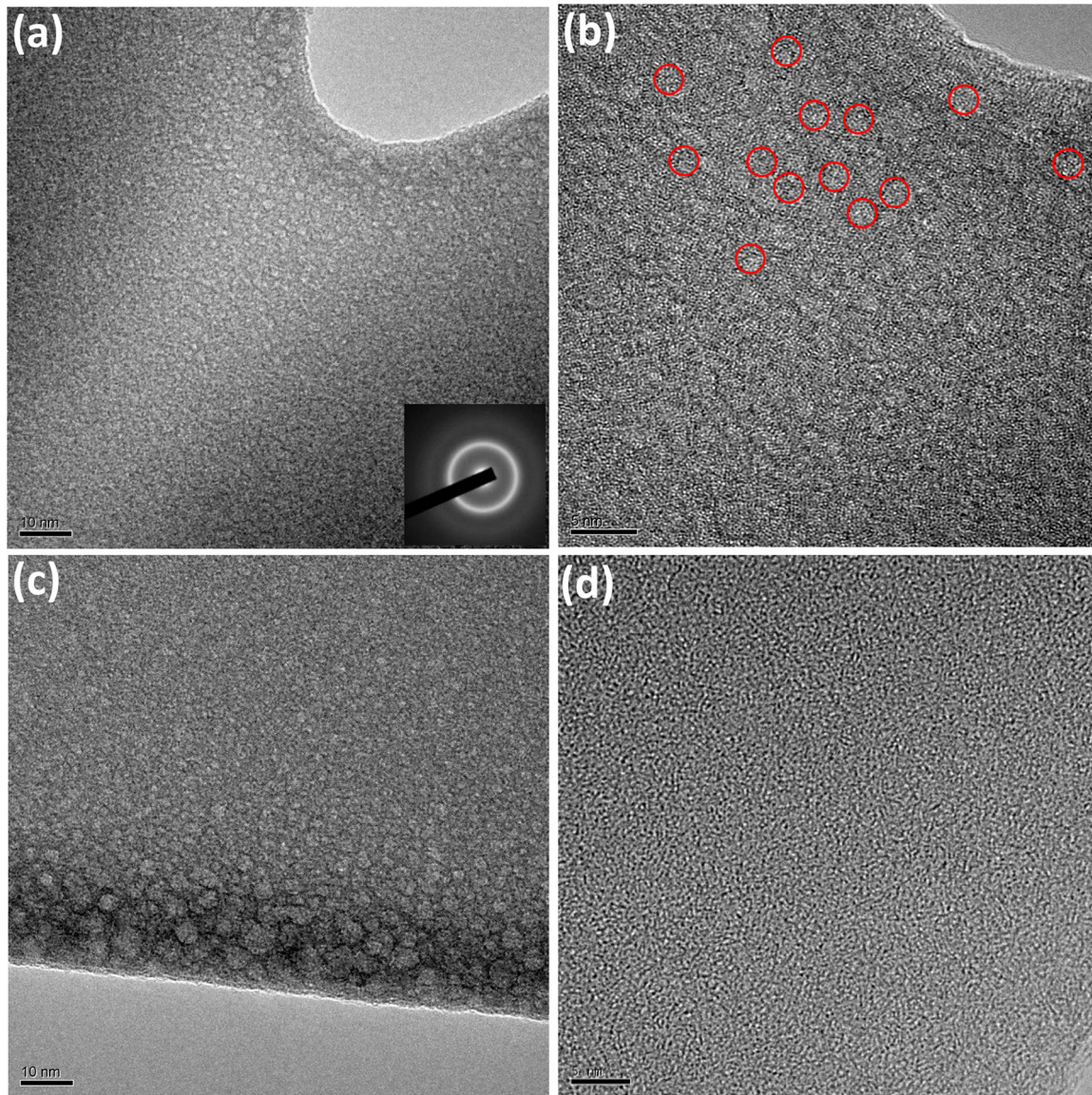


Figure 5. High-resolution TEM images on the atomic structure of annular features embossed on Zr-based MG. (a) Annular feature of a thickness of 25 μm , (b) zoom-in of (a); (c) the edge of MG substrate; (d) annular feature of a thickness of 100 μm . The scale bars in (a) and (c) are 10 nm, in (b) and (d) are 5 nm.

MGs would rise into the supercooled liquid state [33]. Here, the hardness of MG is as low as 0.2 GPa with a modulus of ~ 4 GPa. According to the mechanical relaxation spectroscopy of $\text{Zr}_{35}\text{Ti}_{30}\text{Be}_{26.75}\text{Cu}_{8.25}$ MG [34], the modulus corresponds to a state in the supercooled region at $360 \sim 370^\circ\text{C}$. Thereby, the softening of MG observed here is likely an equivalent to the softening of MG inside the core of shear bands. The observed softening on the edge of MG substrate and at the top of annular features may also be due to shear at the surface of MG.

To rationalize the observed softening, HRTEM images of the MG after annular gap flow are shown in Figure 5. In contrast to the substrate shown in Figure 2(b), it is seen in Figure 5(a–c) that spots with low contrast can be observed for annular features of a thickness of $25\ \mu\text{m}$ and the edge of MG substrate. For the low contrast, these spots are highly likely containing sub-nanovoids [35,36] (i.e. of low densities) and lead to the observed softening, resembling nanofoams. While for annular feature of a thickness of $100\ \mu\text{m}$, no such spots exists, as shown in Figure 5(d). The precipitation of nanofoam-like structures in the softened annular feature is in alignment with and corroborates the shear-thinning theory proposed by Furukawa and Tanaka [10] that the softening in MGs originates from simple shear flow-induced density fluctuation, as the viscosity of MGs is highly density-dependent (i.e. free volume-dependent). Nevertheless, for in-depth understandings, more works on the structure evolution in MG amid microscale shear flow are required.

4. Conclusions

In summary, micro annular gap flow leads to pronounced softening in $\text{Zr}_{35}\text{Ti}_{30}\text{Be}_{26.75}\text{Cu}_{8.25}$ MG when the annular gap is smaller than $50\ \mu\text{m}$. The softened MG shows a hardness value $\sim 1/30$ of MG outside the gap, equaling a softened state inside shear bands. The observed softening could be removed by thermal annealing at temperatures above T_g . The pronounced softening could be rationalized with the formation of atomic level nanofoam-like features which was probably caused by higher strain rate and larger accumulated shear strain in MG flowing in smaller gaps. Our work supports the scenario of shear softening induced by density fluctuation under simple shear flow.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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