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Thermoplastic deformation and structural evolutions in nanoimprinting metallic glasses using molecular dynamics analysis

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ABSTRACT

We perform simulations on nanoimprinting metallic glasses to investigate the thermoplastic deformation and structural evolutions via molecular dynamics analysis. The atomic diffusion mechanisms, including single atomic and highly collective hopping, are observed in metallic glass block. Mold filling speed is significantly affected by the initial metallic glass film thickness, and the film with the thickness approaching the width of the pattern on mold is optimal to shorten mold filling time and save materials. With the support of a modified equation of plane Poiseuille flow, we analyze the resistance of boundary condition and capillary force, which have reasonably explained the thickness effect. We then show the structural evolutions to assess the impact of the mold filling process on the short-range and the middle-range orders in metallic glasses. Lower fractions of icosahedra and icosahedra-like clusters and smaller aggregated clusters have been detected in the processed structure than in the billets, showing that the processed metallic glasses are more symmetrical and have more disorder. The results further suggest that the mold filling process has broken the original structures in metallic glasses, resulting in less icosahedra and bond networks, which lead to a better plasticity in the processed metallic glasses.

1. Introduction

Nanoimprint possesses many advantages such as high resolution and low cost over other traditional methods in fabricating micro-/nano-structures, and has been a promising way to achieve micro-/nano-structure integration systems [1]. The polymer is the original material in nanoimprint [2,3], in which the ultimate feature size is fundamentally limited by the length of the resist molecule [4]. Metallic glasses (MGs), which have no size limiting factor, are superplastic in the super-cooled liquid region, showing the ability to replicate smaller features including nanoscale structures such as nano-grating [5]. With high strength, good surface quality, excellent wear and corrosion resistance in nanoscale compared with polymer, MGs can be used in nanoimprint and greatly improve the quality of micro-/nano-structures [6].

Till now, the effects of pressure, viscosity, temperature and dimensions of stamp on nanoimprint have been well analyzed through experiments [7], finite element analysis [8] and molecular dynamic (MD) analysis [9,10]. The imprint objects are mainly alloy or polymer and the influence of capillary force is rarely noted. Some works have been carried out to fabricate MG structures via nanoimprint, and good micro-/nano-sized structures are obtained [11–14]. The MGs show enormous potential in micro-molding. J. Schroers et al. reported 13 nm MG structures fabricated by nanoimprint and firstly combined the capillary contribution to Hagen-Poiseuille's law to describe nanoimprinting MGs [5]. Subsequently, they built a quantitative model for the thermoplastic compression molding process using lubrication theory [15]. Although the mold filling process is well studied, present understanding of atomic migration, which can reflect the influences of capillary contribution and may be helpful to optimize the nanoimprint parameters, is rather incomplete. Furthermore, MGs have low plasticity at room temperature, leading to obvious brittleness which is regarded as an intrinsic defect of MGs and severely limits their application [16]. Evidences are obtained that the inner atomic order can reflect the performance of MGs. The icosahedra (ICO) are considered to be the dominated short-range order in MGs [17]. It is reported that the ICO are resistant to the atomic migration and the MGs with low fraction of ICO readily accept the shear transformation [18,19]. The ICO clusters tend to overlap together forming the medium-range order in MGs and the network of aggregated clusters is also a significant influence factor on the mechanical property [20,21]. Thus, the research about structural evolutions in MGs during the mold filling process becomes very meaningful.

In this article, we construct a numerical nanoimprint model to investigate the atomic migration of MGs. The effect of the thickness of initial billet film (*TF*) on nanoimprinting MGs is discussed and a rule is proposed for selecting the thicknesses to perform an efficient and economical filling process. The boundary condition and the capillary contribution are observed playing important roles in the process. We

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Table 1
Parameters of LJ potential of Zr, Cu and Si.

Species	ε (eV)	σ (Å)
Zr	0.7382	2.9318
Cu	0.409	2.338
Si	0.0175	3.826
Si–Zr	0.1137	3.3789
Si–Cu	0.0846	3.082

also study the structural evolutions of MGs in the filling process, including the short-range order and middle-range order, to assess the change of performance of MGs during the thermoplastic deformation.

2. MD simulations

The model consisted of three types of atoms, Cu, Zr and Si, where three potential functions were used. The embedded atom model (EAM) potential was adopted to describe the interactions between Zr–Zr, Zr–Cu, and Cu–Cu, which was developed by Mendelev et al. and widely used [22,23]. The stamp composing of silicon atoms was introduced, where the interaction between Si–Si was determined by Tersoff potential [24]. The interaction between Si–Cu was evaluated by the Lennard-Jones (LJ) potential, and so did Si–Zr. The parameters of Zr, Cu and Si for LJ potential were listed in Table 1, where the pair parameters were obtained using the Lorenz–Berthelot mixing rule [25].

A configuration with the size of $67 \times 67 \times 67$ Å^3 consisting of 16,000 atoms was built to prepare MGs through a rapid cooling process, in which the atom ratio of Cu:Zr was 46:54. Periodic boundary condition was applied in three dimensions and the Nose–Hoover algorithm was used to control temperature and pressure. The time step was set as 1 fs. The $Cu_{46}Zr_{54}$ block was melted (at 2100 K) at first and then quenched to 300 K at a cooling rate of 2 K/ps under pressure of 0 Pa. The partial pair distribution functions of the $Cu_{46}Zr_{54}$ are plotted in Fig. 1a. The splitting of second peaks is observed in the Cu–Cu, Zr–Zr and Cu–Zr curves. The first-neighbor bonds calculated from the positions of first peaks are $r_{Cu-Cu} = 2.57$ Å, $r_{Zr-Zr} = 3.17$ Å and $r_{Cu-Zr} = 2.81$ Å, consistent with the experimental and emulational values [23,26], indicating that the potential is appropriate for describing the Cu–Zr MGs. The elastic coefficients are calculated using fluctuation formula [27] after equilibration of 10 ps. The shear modulus at temperature of 300 K is about 30 GPa, in good agreement with the results in reference [28]. The average atomic volume changes with temperature during the cooling process, as shown in Fig. 1b. The intersection point of the fitting lines locates the glass transition temperature T_g, about 839 K, higher than the experimental result of 696 K due to much higher cooling rate [29]. The inset in Fig. 1b shows the temperature dependence of the self diffusion coefficients for Cu and Zr. With a smaller atomic radius and mass, Cu always obtains a larger diffusion coefficient than Zr. The break of the lines corresponds to the glass transition region. Under this break the block turns to a solid amorphous alloy.

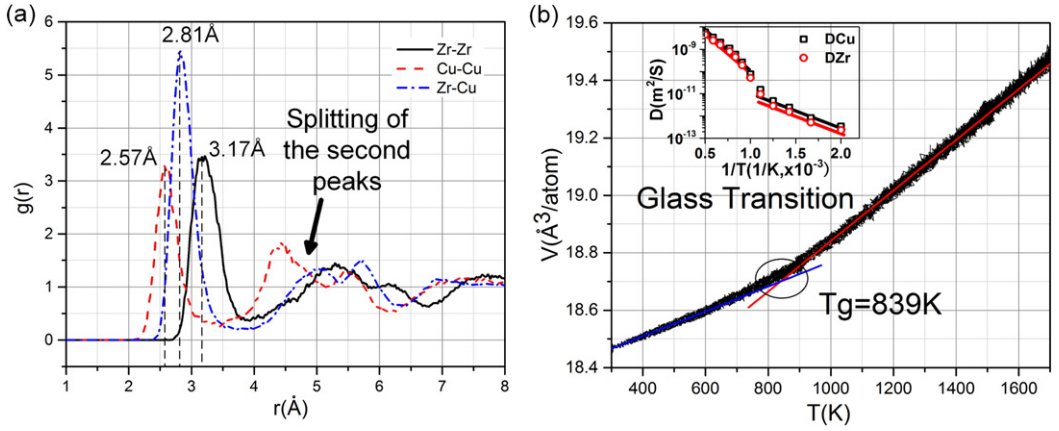

Fig. 1. (a) The partial pair distribution functions of the $Cu_{46}Zr_{54}$ block at 300 K and (b) the average atomic volume of the $Cu_{46}Zr_{54}$ block during the cooling process.

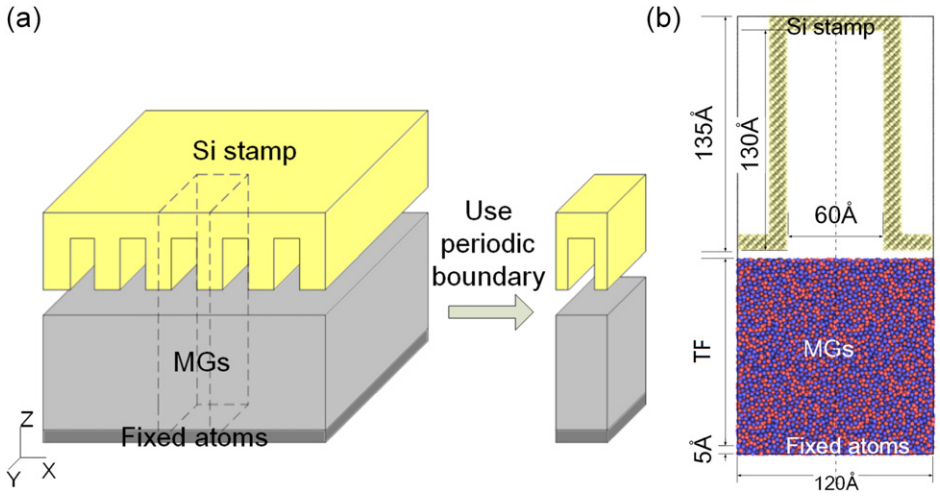

Fig. 2. The nanoimprint simulation model: (a) schematics diagram for simplification and (b) the atomic view with detailed dimensions.