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Atomistic simulation of nanoformed metallic glass

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ABSTRACT

The effects of forming speed and temperature on the forming mechanism and mechanics of $Cu_{50}Zr_{25}Ti_{25}$ metallic glass are studied using molecular dynamics simulations based on the second-moment approximation of the many-body tight-binding potential. These effects are investigated in terms of atomic trajectories, flow field, slip vectors, internal energy, radial distribution function, and elastic recovery of nanoimprint lithography (NIL) patterns. The simulation results show that a shear transformation zone (STZ) forms at the substrate surface underneath the mold during the forming process. The STZ area increases with mold displacement (D). The movement speed of substrate atoms underneath the mold increases with increasing D value. The movement directions of substrate atoms underneath the mold are more agreeable for a larger D value. The stick-slip phenomenon becomes more obvious with increasing D value and imprint speed. The substrate energy increases with increasing imprint speed and temperature. Great NIL pattern transfer is obtained with unloading at low temperatures (e.g., room temperature).

1. Introduction

With progress in micro- and nanosystems, the requirement for high-resolution patterns on micro- and nanometer scales has greatly increased. Nanoimprint lithography (NIL) [1,2] is one of the most popular nanopatterning technology. It's easy operation, high resolution (sub-10-nm feature size) [3,4], high throughput (patterning on a large substrate), and low cost have led to its application in various fields, such as data storage devices [5], flexible electronics [6], microelectronics [7], and biological devices [8]. NIL is a mechanical deformation process operated under suitable temperature and pressure, in which a mold with nanoscale patterns is directly replicated onto a polymer or thin metal film through imprinting and release.

Metallic glass, also known as amorphous metal alloy, is a solid metallic material. It has a disordered atomic arrangement (noncrystalline structure) and thus lacks the typical defects found in metals, such as dislocations and grain boundaries [9]. Metallic glass has recently been applied for nanomolds [10,11] due to their unique physical properties, such as high strength and hardness [12–14], low friction, good corrosion resistance [15], and minimal shrinkage.

Metallic glass is considered as an alternative to traditional materials [10], such as silicon and quartz, for nanomolds. However, few studies have been conducted on the forming mechanism and mechanics of metallic glass. Molecular dynamics (MD) simulation is a powerful tool for studying nanoscale material interactions. Atomic simulation avoids experimental noise and turbulence problems and can be used to analyze atomic trajectories, thermodynamics, and mechanical properties. Many nanosystems have been analyzed using MD, such as nanoscratching [16], nanoforming [17–19], and the bending of nanowires [20,21].

This work investigates the effects of forming speed and temperature on the forming mechanism and mechanics of $Cu_{50}Zr_{25}Ti_{25}$ metallic glass using MD simulations. The simulation results are discussed in terms of atomic trajectories, slip vectors, flow field, internal energy, radial distribution function, and elastic recovery of NIL patterns.

2. Model and methodology

The amorphous structure of $Cu_{50}Zr_{25}Ti_{25}$ metallic glass (substrate) at a temperature of 300 K was simulated with the following parameter settings and heat treatments. First, 120,000 atoms were placed in a cubic box and arranged as a perfect face-centered cubic (fcc) single crystal. Each fcc unit cell consisted of two Cu atoms, one Zr atom, and one Ti atom. Three-dimensional periodic boundary conditions were applied. The simulations were carried out in the isobaric–isothermal ensemble (NPT) and the Nosé-Hoover thermostat was used to control the temperature and to maintain the external pressure at zero. The system was heated from 0 to 1700 K at a constant heating rate of 0.5 K/ps to simulate the melting process (to obtain a well-equilibrated liquid state). Before the cooling

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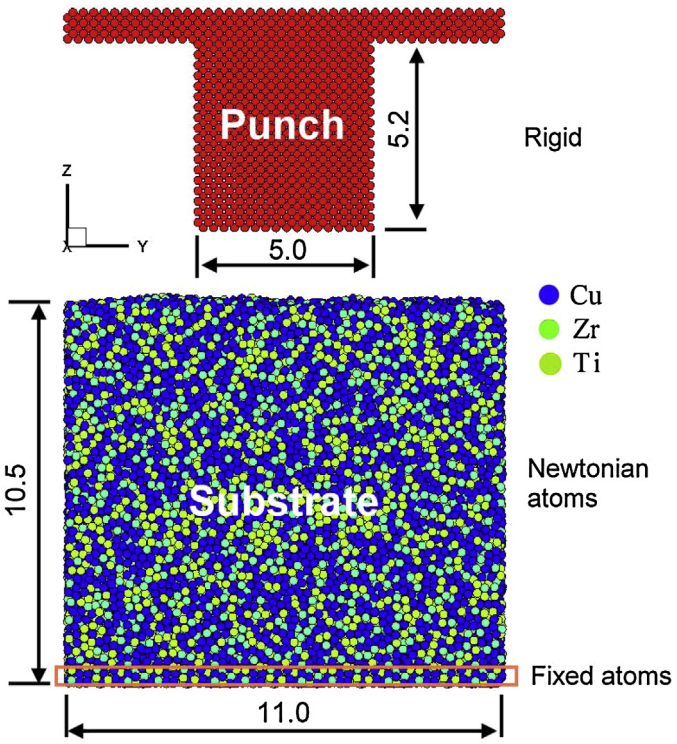

Fig. 1. Schematic of nanoforming model of $Cu_{50}Zr_{25}Ti_{25}$ metallic glass (unit: nm).

process began, the melting system was equilibrated at 1700 K for 300 ps. Finally, the system was cooled from 1700 to 300 K at a high cooling rate of 5 K/ps and then equilibrated at 300 K for 300 ps. The radius distribution function of the obtained amorphous structure is in good agreement with that reported by Dalgic et al. [22].

Samples for the forming test were cut from a large cubic-shaped amorphous sample, as shown in Fig. 1, in which the substrate atoms are colored according to the element type. The substrate dimensions are 11.0 nm (length) × 2.5 nm (width) × 10.5 nm (height). The mold, made of tungsten (W), consisted of a perfect body-centered cubic single crystal with a lattice constant of 0.316 nm. The feature size of the mold was 5.0 × 5.2 nm. The whole mold was assumed to be an ideally rigid object to simplify the forming problem and focus on the deformation of the substrate. Two kinds of atoms were set in the substrate, namely Newtonian atoms and boundary atoms (fixed atoms). The boundary atoms of the four layers at the substrate bottom were used to support the whole system. Periodic boundary conditions were applied in the X and Y directions in the model. The NTV ensemble was employed in the simulation. The equations of motion were integrated with steps of 1 fs using Gear's fifth-order predictor-corrector method [23]. A constant displacement of 3×10^{-5} nm per time step along the Z-axis was set for the mold for imprinting, followed by a holding process for 50 ps. Finally, the mold was instantly unloaded to simulate an ideal unloading process without adhesion action between the mold and the substrate.

The second-moment approximation of the many-body tight-binding (TB) potential [22] was adopted to describe the ternary Cu–Zr–Ti system. The TB potential can effectively predict the glass transition temperature for the ternary Cu–Zr–Ti system [22] via the change of the radial distribution function (g(r)) and the volume with temperature. The TB potential (E_s) is expressed as:

$$E_S = \sum_i \left({E_R}^i + {E_B}^i \right) \tag{1}$$

Table 1
Tight-binding potential parameters used in simulation [22].

Parameter	A (eV)	ξ (eV)	p	q	$r0$ (Å)
Cu–Cu	0.0855	1.2240	10.960	2.278	2.56
Ti–Ti	0.1519	1.8122	8.6200	2.390	2.890
Zr–Zr	0.1934	2.2792	8.2500	2.249	3.170

where E_B^i and E_R^i denote the bond-structure energy and repulsive energy of atom i, respectively; they are respectively expressed as:

$${E_B}^i = -\left\{ \sum_{j \neq i} \xi^2 \cdot \exp\left(-2q \left(\frac{r_{ij}}{r_0} - 1 \right) \right) \right\}^{\frac{1}{2}} \tag{2}$$

$${E_R}^i = \sum_j A \cdot \exp\left(-p \left(\frac{r_{ij}}{r_0} - 1 \right) \right) \tag{3}$$

where r_{ij} is the distance between atoms i and j, r_0 is the first-neighbor distance, and ξ is an effective hopping integral. The parameters A, p, q, and ξ are determined from experimental data of cohesive energy, lattice parameter, bulk modulus, and two shear elastic constants (C_{44} and $C' = \frac{1}{2}(C_{11} - C_{12})$), respectively. The TB potential parameters are listed in Table 1 [22]. A cut-off radius of 0.65 nm was used for the TB potential.

3. Results and discussion

3.1. Forming mechanism

Fig. 2 shows snapshots of the nanoforming process of the metallic glass at a temperature of 300 K at mold displacements (D) of 0.9, 3.3, 4.5, 5.0, 5.3, and 5.8 nm, respectively. The substrate atoms are colored according to the magnitude of their slip vectors. The slip vector of an atom was evaluated as the difference of the atomic positions between a specific time step and the time step after the equilibration at 300 K, which provides a clear description of the strain field for a deformed nanomaterial. At D = 0.9 nm (Fig. 2(a)), a few surface atoms of the substrate adsorbed onto the mold due to van der Waals (VDW) attractive forces, leading to a slight expansion at the substrate surface. When D increased to 3.3 nm (Fig. 2(b)), a shear transformation zone (STZ) formed at the substrate surface (light blue atoms) underneath the mold. The STZ, whose structure is independent and disordered, is the fundamental unit of plastic deformation in metallic glasses [24]. The STZ is considered as a point defect with high stress. However, for metallic crystals, the deformation mechanism originates from the nucleation and propagation of dislocations (line defects). Therefore, there is no formation of dislocations [25] in Fig. 2. When D further increased, as shown in Figs. 2(c)-(f), three main domains with high slip vector values appeared at the surface: one underneath the mold and the others at the two sides of the mold, respectively. The former is subjected to compressive stress from the mold whereas the latter are subjected to tensile stress, which leads to the atoms being extruded upwards. Interestingly, some surface atoms at the two sides of the mold have extremely low slip vector values, which indicates that they remained almost stationary during the forming process, forming a dead metal area, due to adhesion interaction with the mold. The slip vector of atoms significantly increases with D value.

Fig. 3(a)–(d) show snapshots of the flow field of the surface atoms of the substrate underneath the mold at D = 3.3, 4.5, 5.0, and 5.8 nm, respectively. In Fig. 3, the length of the arrows is proportional to the magnitude of the flow speed of atoms and their direction indicates the flow direction at the present time step during the forming process. At a shallow imprint depth of 3.3 nm (Fig. 3(a)), the atoms moved irregularly at low speed. With an