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Evolution of atomic ordering in metallic glasses

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ABSTRACT

A new atomistic model involving quasi-ordered metastable structures has been proposed recently for nanocrystallization of metallic glasses (MGs). However, the physical driving force for such unique phase transformation has not been elucidated at present. In this paper, we firstly verify this unique model experimentally by HRTEM via a careful tilt operation. Secondly, atomistic simulations by molecular dynamics have led to identifying the strain energy term governing the step-by-step planar ordering in MGs. Thus, our study has provided a fundamental understanding of the atomic ordering and nanocrystallization mechanism in MGs and other amorphous materials.

1. Introduction

Metallic glasses (MGs) are of both fundamental and engineering interests for scientists due to their unique atomic structures and physical properties [1–4]. The knowledge of atomic arrangements and their migrations in the MGs are especially important because they provide clues for the basic issue. For example, the glass transition and/or the nanocrystallization mechanism in MGs might be discovered from these studies [5]. Substantial progress has been made in deciphering the short- and intermediate-range structure of MGs [6–9]. The nanocrystallization of MGs in the amorphous state has a significant importance in both scientific and technological fields [10], and thereby has been often investigated [11–15]. Previous investigations mostly focused on either the thermodynamic and kinetics of the transformation [16–20] or the microstructural evolution and property change during the transformation [21–24]. The atomic ordering process [25,26] and atomistic mechanisms during nanocrystallization, however, have been not well addressed.

Our studies revealed that the ordered atomic packing on the scale of 1–2 nm is imperfectly ordered packing (IOP) in as-cast MGs [27], and these structures can act as pre-existing nuclei and grow directly into nanocrystals when the crystallization takes place under a deep undercooling [26]. Moreover, in contrast to conventional solidification process where liquids crystallize into solids by directly forming spherical nuclei, three distinct steps of the structural evolution from the IOP to nanocrystal were observed when glassy samples were annealed below glass transition temperature (T_g) [28], i.e., from one-dimensional (1D) periodic structure to 2D periodic structure, and finally to 3D nanocrystal. Nevertheless, the physical driving force for this unique structural transformation has not been elucidated at present. Furthermore, there is a lack of a critical evidence to experimentally verify the formation of these quasi-ordered structures. This unique structural transformation is very interesting since it offers the knowledge to fundamentally understanding the nanocrystallization mechanism in atomic scales. In this paper, we firstly provide a clear experimental evidence for these quasi-ordered structures by high-resolution transmission electron microscopy (HRTEM) via a tilt operation, and then unveil the physical driving force for such transformation by molecular dynamics (MD) simulation and mathematical analysis. Eventually, a mechanistic explanation of this structural transformation has been provided.

2. Experimental

$Zr_{65}Ti_{10}Ni_{25}$ metallic glass was selected as the model alloy. The master alloys with a nominal composition of $Zr_{65}Ti_{10}Ni_{25}$ (at.%) were prepared by arc melting under a Ti-gettered pure argon atmosphere, using pure metals (≥99.9%, wt.%) as charge materials. Then the amorphous ribbons with a cross-section of 0.04 × 4 mm^2

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were produced by a single roller melt-spinning technique under argon atmosphere. The glass transition temperature of $T_g = 601$ K and the crystallization temperature of $T_x = 631$ K were determined by differential scanning calorimetry (DSC, Du Pont 2010) with a heating rate of 0.66 K/s. To investigate the nanocrystallization the samples were annealed in their supercooled liquid region (615 K) for different durations. Thin foil samples for high-resolution transmission electron microscopy (HRTEM) analysis were first prepared by twin-jet electrolytic polishing in a mixing solution of 90 vol.% methanol and 10 vol.% perchloric acid under 240 K. The electropolished and perforated samples were then cleaned by a brief (0.5 h) ion milling process to remove some residual surface contamination. The HRTEM observations were performed on a JEM-2010 field emission gun microscope operated at a voltage of 200 kV. The images were collected on a charge-coupled device (CCD) camera and image analysis was carried out using the software DigitalMicrograph 3.5.2 of Gatan Inc.

3. Molecular dynamics (MD) simulation

To further explore the atomic-scale structural evolution during this dynamic ordering process in the real 3D space, MD simulations of nanocrystallization in the amorphous Ni were performed. The selection of pure Ni as a model system is based on the following considerations: first, it can eliminate the interference of chemical composition on the intrinsic feature of the structure. Second, it is feasible and convenient for the simulation itself, because the empirical potentials for a multi-component system are the major problem in the classical MD simulation. *Ab initio* MD can overcome this problem, but its limited system size ($\sim$200 atoms) is another technical issue. Third, it is, in fact, not possible to simulate the crystallization of multi-component alloys at the vicinity of Tg by MD simulation due to its limited time scale.

The MD cell contains 4000 atoms, corresponding to a cubic box of side $\sim$3.5 nm. A many-body tight-binding potential based on the second-moment approximation of the density of electronic states was adopted to depict the interatomic interaction [29]. The total energy of the simulated model system is written in the form [29]

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

where E_B^i is the band-energy of atom i, which is written as

$$E_B^i = -\left\{ \sum_j \xi^2 e^{-2q\left(r_{ij}/r_0 - 1\right)} \right\}^{1/2} \tag{2}$$

and E_R^i is a repulsive interaction term which is described by a sum of Born-Mayer ion–ion repulsions

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

here r_0 is the equilibrium distance between atoms in the perfect crystal, and r_{ij} is the interatomic distance between the atom i and its neighbor j. The values of parameters A, ξ, p and q are: $A = 0.0376$ eV, $\xi = 1.070$ eV, $p = 16.999$ and $q = 1.189$, respectively [29]. In this work, the cutoff distance of the potential was set to be 0.50 nm.

The simulations were performed with the classical MD program XMD 2.5.32 [30]. Calculations were carried out in an *NPT* isobaric–isothermal ensemble with constant particle number, pressure (P) and temperature (T). The MD simulation was implemented with 5th Gear prediction-correction algorithm, using the "Pressure Clamp" method to maintain a constant P and the "Temperature Clamp" method to maintain a constant T. The MD time step was set as 1 fs to integrate Newton's equations of motion. During the simulation, the system was firstly heated from 300 K to 2000 K under a zero external pressure at a heating rate of 1.0×10^{12} K/s and then relaxed for 30,000 MD steps (30 ps) at 2000 K to get a full liquid. Subsequently, the system was cooled from 2000 K to 0 K at a cooling rate of 4.0×10^{13} K/s to form an amorphous Ni. The modeled T_g is found to be about 530 K. To investigate the structure evolution from disorder to order of amorphous Ni, the resultant amorphous configuration was annealed at 400 K for 1000 ps. The purpose that this low annealing temperature was chosen is to slow the crystallization kinetics and then to record the scenarios of atomic ordering conveniently. During the isothermal annealing, 1000 configurations were saved. For each configuration, the energy and position information were recorded. The periodic boundary conditions were used throughout the simulation.

4. Results and discussion

4.1. HRTEM identification of quasi-ordered metastable structures

The primary phase was identified to be an *fcc*-Zr_2Ni in the nanocrystallization of $Zr_{65}Ti_{10}Ni_{25}$ MG [26]. Fig. 1 shows the HRTEM images and their corresponding fast Fourier transformation (FFT) patterns of ordered structures formed during the nanocrystallization. Fig. 1a displays a typical 1D quasi-ordered structure with the scale of 2–3 nm, in which ordered atomic planes are parallel to each other and construct a planar array, resulting in the 1D periodicity. Its FFT pattern (the inset in Fig. 1a) shows two diffraction spots along one exclusive periodic direction (indicated with a red arrow), confirming the 1D periodicity of this structure. Actually, the 1D periodic structure was also observed in the primary crystallization of the $Al_{87}Ni_7Cu_3Nd_3$ amorphous alloy [31]; however, it was regarded as nanocrystals in Ref. [31]. The 1D periodic structure becomes further ordered as the crystallization proceeds, leading to the formation of ordered structures with a 2D periodicity (Fig. 1b). As compared with the 1D periodic structure, the 2D structure has two periodic directions demonstrated by its FFT pattern (the inset in Fig. 1b), which results from two ordered planar arrays (marked by two red arrows). Interestingly, the angle between these two periodic directions was measured to be $\sim$70.5°, corresponding to the angle between two {111}, the close-packed plane in an *fcc* lattice. Finally, the nanocrystals (Fig. 1c) with a 3D periodicity are developed due to the further ordering. In this study, a tilting operation has been conducted to further elucidate the characteristics of these ordered structures in the real 3D space. Note that the same defocus value was used before and after tilting operation to eliminate the effect of different imaging conditions on HRTEM images. Fig. 1a–c was carefully tilted with a tilt angle as small as 0.70°, leading to Fig. 1d–f, respectively. In these operations, the 1D and 2D periodic structures were turned into amorphous features (Fig. 1d and e) when the projection directions slightly deviate from the exclusive projection direction due to their imperfect periodic dimensionalities, while the 3D nanocrystal retains to have a 3D periodicity (Fig. 1f). This image change induced by the slightly tilting operation was verified by the sequent MD simulations. This HRTEM examination (Fig. 1) offered a direct evidence that two transition quasi-ordered structures (1D and 2D ordered structures) were formed during the nanocrystallization of MGs.

4.2. MD simulation reproducing the quasi-ordered metastable structures

To reproduce the scenario observed in the experiments and then further to reveal the nature of these quasi-ordered structures, MD