Crystallization of supercooled liquid and glassy Fe thin films

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A R T I C L E   I N F O

A B S T R A C T

Isothermal crystallization of supercooled liquid and glassy Fe thin films has been studied via molecular dynamics (MD) simulations with a many-body potential of the embedded atom method (EAM). Supercooled liquid and glassy Fe thin films are obtained by cooling from the melts. Models at a given temperature are annealed for a long time in order to study crystallization process. Time dependence of various thermodynamic and structural quantities upon annealing is analyzed including potential energy, radial distribution function (RDF), coordination number distribution, fraction of atoms of various crystalline orders etc. We find that crystallization of supercooled liquid and glassy states exhibits a first-order behavior. Time–temperature-transformation (TTT) diagram is found for a wide temperature range from a supercooled liquid to a deeply glassy state and it exhibits a nose shape like that commonly found. Atomic mechanism of crystallization is studied in details via analysis of the spatio-temporal arrangements of crystalline atoms occurred during annealing and we find a quite new scenario of crystallization unlike that thought in the past. Crystalline atoms have a tendency to form clusters including a single extra-large percolation one. Crystalline phase is formed via enhancement of atomic population of the single largest percolation cluster by attachment of smaller clusters and newly formed crystalline atoms upon further annealing. We find that only one third of the 'naturally quenched-in' crystalline atoms remains stable and participates in the crystallization process. Free surface effects on structure and crystallization is also found and discussed.

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1. Introduction

Glassy state is unstable and eventually transforms into a more stable state – crystalline one after annealing at a given temperature for a sufficient long time. Crystallization of supercooled liquids and glasses is of great interest due to fundamental and technological importance of the phenomenon and it has been under intensive investigation by both experiments and computer simulations for a long time [1–21]. For certain practical applications, crystallization of glasses must be avoided entirely while for some applications partial crystallization of glasses is desired [10]. Glasses with a certain degree of crystallization are called glass-ceramic materials which have been widely used in practice [2,10]. Final state of crystallization of a glass may be an ordered crystal or a more complicated material such as quasicrystal [12]. Experimental works have been done mainly for studying of crystallization of silicate or multi-component metallic glasses, therefore, devitrification of glasses is too complicated and it is very difficult to get detailed insights of mechanism of the process. Primarily, three devitrification modes of glasses have been identified such as polymorphic, primary, and eutectic ones which are generally defined by the different resulting microstructures [12]. On the other hand, kinetic data obtained upon isothermal crystallization of glasses are often used for detecting nucleation and subsequent growth of crystalline phase in the glassy matrix. It is found that classical nucleation theory (CNT) does not accurately describe the crystal nucleation in common glasses [10]. It is important to describe the fraction of materials crystallized at a given time in terms of the nucleation and growth rates, and Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory is often used for this purpose (see [10,12,13] and references therein). JMAK theory has been intensively used for interpretation of crystallization experiments and for inferring crystallization mechanisms from the experimental results [10,12,13]. However, detailed information at the atomic level of crystallization of glasses can be obtained only by computer simulations [14–21]. Indeed, not only time or temperature dependence of various kinetic and thermodynamic quantities related to the crystallization process of supercooled liquids and glasses can be easily determined, but one can monitor evolution of any structural properties including fraction of materials crystallized at any time upon annealing of glasses by computer simulations. Therefore, the validity of CNT, JMAK theory or related

models of crystallization of glasses can be easily tested. In particular, isothermal crystallization of amorphous Ti–Al alloy has been studied via analysis of variation of internal energy, cell volume, RDF, bond pairs, atomic configurations and three-stage feature of crystallization process is defined [14]. Recently, similar analysis has been done for study on crystallization of amorphous Cu–Al–Ni alloy including testing of the JMAK theory via MD simulations [18]. Similar information can be found in other simulation works [15–17].

Although crystallization of supercooled liquids and glasses has been under intensive investigations for a long time, basic scientific questions regarding nucleation and subsequent growth of the crystalline phase in glassy matrix remain not fully understood. In the present work, we carry out a comprehensive study on the isothermal crystallization of supercooled liquid and glassy Fe thin films at various temperatures above and below a glass transition one (T_g). Motivations of the study are as follows: (i) amorphous Fe and Fe-based alloys are important metallic glasses and have various applications in science and technology as important magnetic and catalytic materials, therefore, understanding of their crystallization is important for more effective applications of materials in practice; (ii) using monatomic system is easier to detect the atomic mechanism of crystallization since one can focus attention only on topology of the atomic arrangements related to the phase transition rather on both topological and chemical orders if one uses a multi-component system; (iii) although some information related to the crystallization of supercooled liquid and glassy bulk Fe with the pair Pak–Doyam potential can be found [19–21], study of crystallization of supercooled liquid and glassy Fe thin films has not been found in literature yet. In practice, glassy Fe (with some percents of impurities) is often prepared in the form of thin films and surface effects cannot be ignored. Therefore, it is of great interest to carry out MD simulations of crystallization of supercooled liquid and glassy Fe thin films with a more realistic interatomic potential, i.e. a many-body EAM one. It is our main aim here in the present work. In addition, although crystallization of amorphous Fe-based alloys has been under intensive investigations by experiments [1,22–29], crystallization experiment of pure amorphous Fe has not been found yet with exception of information about the crystallization temperature (~585 K) of the amorphous Fe reported in Ref. [30].

2. Calculations

Our MD simulations of crystallization of supercooled liquid and glassy Fe thin films consists of two stages as follows: (i) obtaining supercooled liquid and glassy Fe thin film models at various temperatures by cooling from the melt; (ii) annealing of the obtained models at a given temperature above or below T_g for a long time in order to study annealing-induced crystallization. The second stage is our main task in the present work.

In the first stage, glass formation and related thermodynamics have been studied in models containing 31,250 Fe atoms interacted via the EAM potential, for which the total atomic potential energy of a system is as given below [31,32]:

$$E_{tot} = \frac{1}{2}\sum_{i,j}\Phi_{ij}(r_{ij}) + \sum_i F_i(\overline{\rho_i}) \qquad (1)$$

The energy in EAM potentials consists of two terms: a pair potential term, $\Phi_{ij}(r_{ij})$, represents the electrostatic core-core repulsion, and a cohesive term, $F_i(\overline{\rho_i})$, represents the energy the ion core gets when it is "embedded" in the "electron sea". This embedding energy is a function of the local electron density, which in turn is constructed as a superposition of contributions from neighboring

atoms. In Eq. (1), r_{ij} is the interatomic distance between atoms i and j, and $\overline{\rho_i}$ is the host electron density at the site i induced by all other atoms in the system which is given as follows:

$$\overline{\rho_i} = \sum_{i\neq j}\rho_j(r_{ij}) \qquad (2)$$

Note that various interatomic potentials have been proposed for crystalline Fe including the Morse pair potential, EAM potential, Stillinger–Weber type potentials, Finis–Sinclair potential, Pak–Doyam pair potential, etc. [33–41]. However, based on the fact that EAM potentials are more appropriate for 3d metals including Fe and have been widely used in MD simulations of metals, EAM potential is used for simulation of Fe thin films in the present work.

Initial bcc Fe crystal containing 31,250 atoms in cube of a length of $L = 76.254$ Å (i.e. at the real density of liquid Fe at 2500 K of 6.54 g/cm^3) under periodic boundary conditions (PBCs) has been relaxed at 2500 K for 300 ps in order to get an equilibrium melt. After that PBCs are applied only along the x and y Cartesian directions, while along the z Cartesian direction the non-periodic boundaries with an elastic reflection behavior are employed after adding the empty space of a length of 10 Å at $z = 0$ and at $z = L$, i.e. two free surfaces in the z direction are formed. We use NVT ensemble simulations for this new simulation cell including the empty space. This means the system is under zero pressure for the whole simulation procedure. The models with two free surfaces have been relaxed further for 300 ps before cooling down at the cooling rate of $\gamma = 5 \times 10^{13}$ K/s via velocity rescaling. The Verlet algorithm is employed and MD time step is 1.0 fs. For calculating of coordination number distribution in the supercooled liquid and glassy Fe, the cutoff radius $R_{C1} = 3.45$ Å is used which is equal to the first minimum after the first peak in RDF of a glassy state at 300 K.

In the second stage, atomic configurations obtained at various temperatures above and below $T_g = 900$ K have been annealed for 6 ns in order to study crystallization. For calculating of coordination number distribution in the crystalline Fe, the cutoff radius $R_{C2} = 2.75$ Å is used which is equal to the first minimum after the first peak in RDF of crystalline bcc Fe. We use VMD software [42] for 3D visualization of atomic configurations in the paper and LAMMPS software for MD simulations [43]. The Ackland's analysis method, a computation that calculates the local lattice structure based not only on the distance between particles but also on the bond-angles, is used for detecting fraction of various crystalline orders occurred during isothermal crystallization process [44]. In order to improve the statistics, we average the results over two independent runs.

3. Results and discussions

3.1. Glass formation in supercooled liquid Fe thin films

Some structural and thermodynamic quantities of glassy Fe thin films obtained by cooling from the melt are presented in Fig. 1. Temperature dependence of potential energy per atom in models can be seen in Fig. 1a, linear part of the curve in the low temperature region is related to a glassy state of the system and the point of deviation from linearity is a glass transition temperature, i.e. $T_g = 900$ K, which is smaller than that found for the bulk using the Pak–Doyam pair potential such as $T_g = 1180 \pm 80$ K (Refs. [45,46]) or $T_g = 1070$ K (Ref. [47]). However, it is close to that found for the bulk system with Johnson pair potential, i.e. $T_g = 900$ K (Ref. [48]) or for 5 nm Fe nanoparticles with the Pak–Doyam one ($T_g = 909$ K, see Ref. [49]). This means that our $T_g = 900$ K for Fe thin films has a reasonable value. On the other hand, evolution of RDF of Fe thin films upon cooling from the melt can be seen in Fig. 1b