Molecular simulation of freestanding amorphous nickel thin films

T.Q. Dong [a], V.V. Hoang [b],*, G. Lauriat [a]

[a] *Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, UMR 8208 CNRS, 5 Boulevard Descartes, 77454 Marne-la-Vallée, Cedex 2, France*
[b] *Department of Physics, Institute of Technology, National University of Ho Chi Minh City, 268 Ly Thuong Kiet Street, District 10, Ho Chi Minh City, Viet Nam*

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ABSTRACT

Size effects on glass formation in freestanding Ni thin films have been studied via molecular dynamics simulation with the *n*-body Gupta interatomic potential. Atomic mechanism of glass formation in the films is determined via analysis of the spatio-temporal arrangements of solid-like atoms occurred upon cooling from the melt. Solid-like atoms are detected via the Lindemann ratio. We find that solid-like atoms initiate and grow mainly in the interior of the film and grow outward. Their number increases with decreasing temperature and at a glass transition temperature they dominate in the system to form a relatively rigid glassy state of a thin film shape. We find the existence of a mobile surface layer in both liquid and glassy states which can play an important role in various surface properties of amorphous Ni thin films. We find that glass formation is size independent for models containing 4000 to 108,000 atoms. Moreover, structure of amorphous Ni thin films has been studied in details via coordination number, Honeycutt–Andersen analysis, and density profile which reveal that amorphous thin films exhibit two different parts: interior and surface layer. The former exhibits almost the same structure like that found for the bulk while the latter behaves a more porous structure containing a large amount of undercoordinated sites which are the origin of various surface behaviors of the amorphous Ni or Ni-based thin films found in practice.

1. Introduction

Amorphous Ni is a magnetic material which has been under intensive investigations by both experiments and computer simulations (see [1–12] and references therein). The samples obtained in practice are often in the form of a thin film [1,2,4] and limited information related to the structure and properties of amorphous Ni is found by experiments [1,2,4,5,7]. Experimental evidence shows that amorphous Ni has a dense random packed structure and a typical radial distribution function (RDF) of metallic glasses: the splitting of the second peak [2,5]. The existence of local icosahedral order in deeply undercooled Ni melts is also discovered experimentally, ensuring that amorphous Ni should also contain a local icosahedral order [10]. More detailed information of structural properties of amorphous Ni at the atomic level can be obtained via computer simulations. In literature, a limited number of simulation works have been done involving the bulk material based on models under periodic boundary conditions (PBCs). Indeed, molecular dynamics (MD) simulations and systematic analysis of the local atomic structure of liquid and amorphous models containing 256 Ni atoms interacted via *n*-body Gupta potential have been presented [8]. Both the RDFs of liquid and amorphous Ni are in good agreement with the experimental data including the splitting of the second peak in amorphous samples. The crystalline and icosahedral orders are

found with almost the same proportion in the amorphous Ni [8]. Similar properties were also observed in other study on models containing 500 Ni atoms using an embedded atom method (EAM) interatomic potential [9]. Although the splitting of the second peak is not as strong as in the previous work, the RDF in the liquid state is in good agreement with the experiment [9]. Via the Honeycutt–Andersen analysis [13], local icosahedral order in the amorphous Ni has been found together with other ones such as fcc, hcp and bcc [9]. Recently, the equation of state for Ni glass has been studied via MD simulations [12] and crystallization of the amorphous Ni thin film on a singular Pd(100) surface has been examined [11]. However, systematic simulations of structural properties of the amorphous Ni thin films have not been found in literature yet. Thin films, systems with free surfaces, possess behaviors different from the bulk. Therefore, understanding of structure and properties of amorphous Ni thin films is of fundamental and technological importance since it is widely produced for practical purposes. For the simple monatomic systems with Lennard–Jones–Gauss (LJG) interatomic potential, it is found recently that atomic mechanism of glass formation in thin films is quite different from that of the bulk [14,15]. Hence, it motivates us to carry out the research in this direction for Ni thin films since the results can be generalized for a popular class of glasses, i.e. metallic ones.

The paper is organized as follows. After the Introduction, calculation parameters and models are introduced in Section 2. Detailed results and discussions about the thermodynamics, structure evolution of free standing films are given in Section 3. Finally, the last section of the paper is dedicated to some concluding remarks.

* Corresponding author. Tel.: +84 8 38647256; fax: +84 8 38656295.
  E-mail address: vvhoang2002@yahoo.com (V.V. Hoang).

2. Calculations

Glass formation and thermodynamics of Ni thin films have been studied in models containing 32,000 Ni atoms interacted via the same n-body Gupta potential previously used in [8], which has the form:

$$V = \varepsilon \sum_{j=1}^{N} \left[A \sum_{i(\neq j)=1}^{N} \exp\left[-p\left(r_{ij}/r_0 - 1\right)\right] - \sqrt{\sum_{i(\neq j)=1}^{N} \exp\left[-2q\left(r_{ij}/r_0 - 1\right)\right]} \right].$$

$$(1)$$

The parameters of potential are taken as follows: $A = 0.101$, $\varepsilon = 1.7$ eV, $p = 9$, $q = 3$, $r_0 = 2.49$ Å (see [8] and references therein). The Verlet algorithm is employed with a time step of $dt = 0.75$ fs. The cutoff is applied to the potential at $r_c = 3r_0$ [8]. Initial fcc structure models are melted in a cube of a length $L = 70.72$ Å corresponding to a real density of fcc Ni (e.g. $\rho_0 = 8900$ kg/m³) and under PBCs at the temperature as high as $T_0 = 1970$ K via MD relaxation for 2×10^5 MD steps (i.e. above the experimental melting point of fcc Ni). The melted state of model obtained at $T_0 = 1970$ K is confirmed via checking RDF. 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 $\Delta z = 2r_0$ at $z = L$. Due to using the elastic reflection boundaries, an additional free surface will occurs at $z = 0$ during further MD simulations. The systems are left to equilibrate further for 2×10^5 MD steps at $T_0 = 1970$ K at a constant volume of the simulation cell of the new size, i.e. NVT ensemble simulation. Then the system is cooling down at the constant volume of the new simulation cell at the cooling rate of $\gamma = 10^{13}$ K/s, and temperature is decreased linearly with time as $T = T_0 - \gamma \times t$ via the simple atomic velocity rescaling (t is a cooling time). This means that atomic configurations of thin film shape have been under zero pressure during the simulations. Note that if a lower cooling rate is used for simulation, the spontaneous crystallization of Ni is observed. For comparison, the initial liquid system containing 32,000 atoms under PBCs is quenched at the same cooling rate under zero pressure. This system is referred

as the "bulk" one. In order to study the size effects, glass formation and thermodynamics of models containing 4000, 11,000 and 108,000 Ni atoms have been investigated by the same procedure like that done for models containing 32,000 atoms described above. In order to improve statistics, we average the results over two independent runs.

3. Results and discussions

3.1. Thermodynamics

Temperature dependence of various thermodynamic quantities of the system upon cooling from the melt can be seen in Fig. 1 which presents the inherent intermediate scattering function, $F_S(Q,t)$, potential energy per atom (PEA), diffusion constant D and surface energy. The quantities such as $F_S(Q,t)$ and D at a given temperature have been computed after relaxation of models for 5×10^5 MD steps. In the present work, $F_S(Q,t)$ is calculated for $Q = 3.1986$ Å⁻¹ which is the location of the first peak in structure factor of the bulk amorphous Ni, $S(Q)$. The inherent intermediate scattering function is defined as follows:

$$F_S(Q,t) = \frac{1}{N} \sum_{j=1}^{N} \left\langle \exp\left(iQ.\left[r_j(t) - r_j(0)\right]\right) \right\rangle \qquad (2)$$

where $r_j(t)$ is the location of the j-th atom at time t and Q is a wave-vector. From Fig. 1a, one can see that $F_S(Q,t)$ is typical for the glass-forming systems. At high temperature, we observe a ballistic regime at a short time followed by a relaxation regime at a longer time. The latter is exponential and decays to zero within 1 ps. However, at low temperature, a plateau regime is found after the ballistic one due to the caging effects, i.e. temporary trapping of the atoms by their neighbors. On the other hand, the long time behavior of $F_S(Q,t)$ is non-exponential, like typical glass-forming systems (see [14,15] and references therein). This means that glass formation has occurred in the liquid Ni models. The influence of the free surfaces on PEA can be seen in Fig. 1b, i.e. PEA in thin films is higher than that of the bulk due to the free surface effects. The deviation from the linearity of a low temperature region of PEA starts
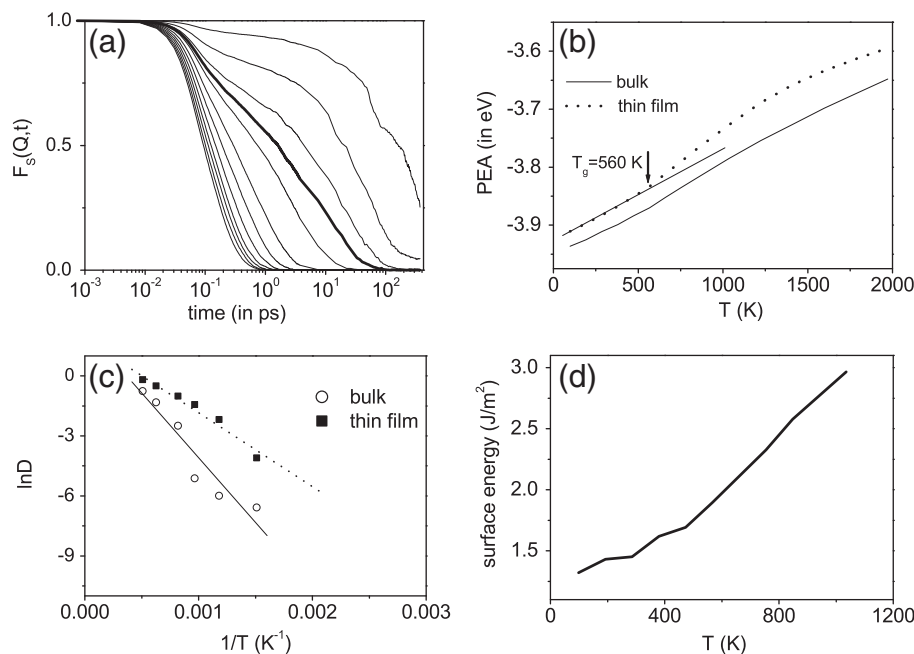
Fig. 1. (a) Inherent intermediate scattering function, $F_S(Q,t)$, from left to right for temperatures: 1970 K, 1785 K, 1600 K, 1400 K, 1220 K, 1040 K, 850 K, 660 K, 560 K, 470 K, 290 K, 100 K, respectively and the bold line is for $T_g = 560$ K; (b) potential energy per atom (PEA), the straight line serves as guide for eyes; (c) inverse temperature dependence of the logarithm of diffusion constant (ln D) in the system, the straight lines serve as guide for eyes; (d) temperature dependence of surface energy of Ni thin film. All figures of thin films are associated with models containing 32,000 atoms.