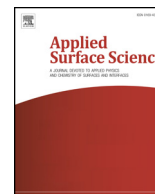




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Atomic simulation of melting and surface segregation of ternary Fe-Ni-Cr nanoparticles

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ABSTRACT

Knowledge of thermodynamics of multimetallic nanoparticles is of great importance in prediction and advancing the understanding of synthesis, characterization, and applications of metal nanoparticles. In this work, molecular dynamics simulations were performed to investigate the melting characteristics and behaviors of a ternary Fe-Ni-Cr nanoparticle (19.17 wt.% Cr, 11.72 wt.% Ni, and the rest Fe). It was found that the melting of the nanoparticles starts from the surface and proceeds gradually inwards to the core, indicating a liquid nucleation and growth melting mode. During heating, severe Cr segregation with increasing temperature were observed, and the nano Cr clusters prefer to aggregate mostly at the surface due to lower surface energy and stronger cohesive interactions of Cr atoms than Fe and Ni. Moreover, the melting temperature of the nanoparticles decreases as the particle radius decreases, and there exists a linear relationship between the melting point and the inverse of the radius. This signifies the feasibility of the linear depression effect for the size-dependent melting of Fe-Ni-Cr nanoparticles accompanying surface segregation and aggregation. The findings in this work are believed to provide the atomic scale understanding of mechanisms of melting and surface segregation of ternary Fe-Ni-Cr nanoparticles.

1. Introduction

Metal nanoparticles exhibit unique thermodynamic, mechanical and electronic properties different from those of the conventional coarse-grained metal powders ascribing to their large surface area to volume ratios. They have drawn wide attention in numerous potential applications such as actuators, catalysis, sensing and imaging, drug delivery, solar cells, and microstructural engineering, etc. [1–9]. For instance, Ag and Au noble metal nanoparticles exhibit high sensitivity, activity, and enhanced optical absorption and scattering making them attractive in catalysis and sensing applications [3]. Bimetallic nanoparticle catalysts such as *M*-Pt, where *M* = Ni, Fe, Co or Pd, offer exceptional catalytic activity based on structural sensitivity and high surface area when compared to their bulk counterparts [9]. In addition, Fe-based nanoparticles with superior magnetization and biocompatibility are

frequently used as magnetic drug-targeting carriers for controlled drug release and enhancement agents in magnetic resonance imaging [4]. Since the key to all the applications is related to their small size and inherent nanostructure, knowledge and control of the size, shape, surface composition, and crystalline structure of the metal nanoparticles is of significant importance to understand synthesis, processing, and performance of the metal nanoparticles from both scientific and technical viewpoints.

Recently, considerable efforts have been dedicated to investigate thermodynamics and kinetics of growth and stabilization of nanoparticles under thermal and other stresses. Experimental and theoretical studies have revealed characteristic size-dependent thermo-physical features such as depression of melting and sintering temperatures of the nanoparticles [10–15]. As the particle size decreases beyond a critical value, the melting temperature of the nanoparticle with free surface

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deviates from that of its corresponding bulk phase. The depression and deviation effect is mainly associated with the excess energy of the large percentage of weakly bound surface atoms that are less constrained in their thermal motion. Moreover, the kinetics and melting mechanisms of the nanoparticles have been investigated using computational techniques [16–22]. Earlier molecular dynamics (MD) simulations of the melting behavior of spherical Au nanoparticles showed that the pre-melting begins with the outer layer signaling the approach of the melting point, and proceeds inwards toward the core [16]. The thermal behavior of Na nanoclusters was examined using orbital-free density functional MD method [17]. It was revealed that isomers of Na_{142} and Na_{92} (both incomplete 3-shell icosahedrons) would melt in two steps: surface premelting and homogenous melting involving diffusion of all the atoms across the cluster. On the contrary, only a single transition was observed for perfect 2-shell icosahedron Na_{55} . Moreover, in bi-metallic core-shell systems such as Cu-Ni and Pd-Pt nanoparticles, structural changes accompanying the thermal evolution exhibited a characteristic two-stage melting: a dynamical premelting at the surface followed by homogenous melting of the core [18,19]. In particular, Cu/Pd atoms tend to diffuse and segregate to surface distributing on unsaturated edge sites prior to melting due to their lower surface free energy. Another MD simulation of Co-Pt and Co-Au core-shell structured nanoparticles suggested the existence of a strong dependence of the thermal stability on the structure of the core and the element of the shell [20]. It demonstrated a typical two-stage melting for Co-Au nanoparticles, while the Co core and Pt shell were found to melt concurrently.

In contrast to numerous investigation of monometallic and bimetallic nanoparticles [16–24], far less attention has been devoted to understanding the kinetics and melting behaviors of multimetallic nanoparticles. The additional interatomic interactions and coupling could make thermodynamic phenomena, i.e., surface melting and segregation, more complicated. Therefore, in this work, we employ MD simulation method to investigate the dynamic and melting behaviors of ternary Fe-Ni-Cr nanoparticles. The Fe-Ni-Cr alloy model has been chosen as it is the main constituent of a widely used structural alloy, 316L stainless steel. More importantly, microstructural characterization using electron backscatter diffraction (EBSD) and energy dispersive spectroscopy (EDS) has revealed that Cr atoms accumulate around the edges of the cellular structure, signifying Cr diffusion and segregation to the grain boundaries [25]. The distinct interface/surface segregation is of vital importance since it can affect most the physical and chemical properties. It was reported that the Cr segregation deteriorates the magnetic properties of Fe-Cr and Ni-Cr nanoparticles, thereby minimizing their potential applications [26]. However, knowledge and understanding of the mechanisms of Cr segregation in metal nanoparticles is incomplete and limited. In our MD simulations, the melting characteristics and behaviors of the Fe-Ni-Cr nanoparticles will be studied. The physical metallurgical reasons of Cr segregation and aggregation are explored and clarified. Furthermore, the effect of the particle size on the structural evolution and phase transition of the Fe-Ni-Cr nanoparticles during heating will be investigated.

2. Molecular dynamics simulation and methodology

2.1. Molecular models

The Fe-Ni-Cr nanoparticles were initially constructed in a spherical morphology with a face-centered cubic (FCC) crystal structure. All the Fe, Ni, and Cr atoms were distributed stochastically in the lattice sites across the nanoparticles to provide a clear insight on how Cr segregates at different temperatures. Fig. 1 shows a typical equilibrated Fe-Ni-Cr nanoparticle with a radius of $R = 60 \text{ \AA}$ at $T = 300 \text{ K}$, signifying a rather smooth surface structure. Clearly, the nanoparticles cannot be perfectly spherical and would, even in their ground state, exhibit some minor facets [16]. To study the effect of the particle size on the melting

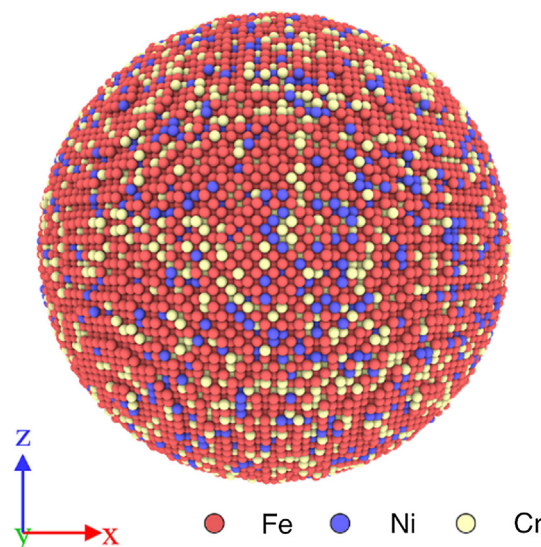


Fig. 1. Atomic distribution of a typical equilibrated Fe-Ni-Cr alloy nanoparticle of $R = 60 \text{ \AA}$ at $T = 300 \text{ K}$.

behavior, we prepared a range of nanoparticles with varying radii from 30 to 70 \AA , comprising around 10,000 to 126,000 atoms. The composition of all the Fe-Ni-Cr nanoparticles was chosen as 19.17 wt.% Cr, 11.72 wt.% Ni, and the remaining to be Fe to mimic a 316L austenitic stainless steel model alloy [25].

2.2. Simulation method

To characterize the interatomic interactions for Fe-Ni-Cr nanoparticles, we adopted an embedded atom method (EAM) potential proposed by Bonny et al. [27]. This potential model has been successfully proven to describe static and dynamic properties of metal alloys containing Fe, Ni and Cr, such as lattice parameters, phase transformation, diffusion coefficient, vacancy forming and dislocation, and thermal conductivity, etc. [28–30]. To verify the applicability of Bonny's EAM potential, we have also simulated the lattice parameter and stacking fault energy for the bulk Fe-Ni-Cr alloys. The simulation results, shown in Table S1, are in good agreement with the experimental data [31–33].

In addition to pair interactions V , the EAM potential contains an embedding energy F dependent on the local electron density ρ . The latter term approximates the many-body contribution from all nearby atoms. The total energy within EAM is thus given as

$$E = \frac{1}{2} \sum_{\substack{i,j=1 \\ j \neq i}}^N V_{it_j}(r_{ij}) + \sum_{i=1}^N F_{it_i}(\rho_i) \quad (1)$$

where N represents the total number of atoms in the system, r_{ij} is the distance between atoms i and j , and t_i denotes chemical species (Fe, Ni or Cr), respectively. The local electron density around atom i contributed from its neighbors is depicted as

$$\rho_i = \sum_{\substack{j=1 \\ j \neq i}}^N \varphi_{t_j}(r_{ij}) \quad (2)$$

where φ denotes the electron density function of the considered element. The details of the parameters of the EAM potential can be found in Ref. [27].

Initially, the Fe-Ni-Cr nanoparticles were equilibrated in a cubic simulation box with a side length of 28 nm at $T = 300 \text{ K}$ for a period of 600 ps. The temperature of the system was maintained constant using the Nose-Hoover thermostat with a relaxation time of 0.2 ps. After

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