

Effects of Nanoparticle Geometry and Temperature on the Structural Evolution in FeCo Nanoalloys

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Effects of nanoparticle size (2.0–6.0 nm) and shape (spherical and cubic) on structural characteristic of atomic ordering processes and order-disorder transformation in B2-type ordered equiatomic-FeCo nanoalloys have been studied by combining electronic theory of alloys in the pseudopotential approximation with Ising-type Hamiltonian site exchange Monte Carlo simulation method. Structural evolutions in amorphous nanoparticles (2–6 nm) of Fe₅₀Co₅₀ alloy have been utilized via molecular dynamic simulations from room temperatures to 1700 K temperatures. It has been shown that disordering starts at surface and propagates into volume of nanoparticles with increasing temperature. FeCo nanoparticles with critical dimensions more than 5 nm have order-disorder transformation behavior almost similar with bulk B2–FeCo alloys irrespective of their shape. Molecular dynamic analyses indicate that short- and medium-range ordered atomic structures exist in quenched Fe₅₀Co₅₀ nanoparticles at room temperature. Deformed bcc structures and deformed icosahedron structures are most probable atomic configurations for 2, 4, 6 nm particles of Fe₅₀Co₅₀ nanoalloy.

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1. Introduction

Multifunctional binary FeCo and ternary FeCo–X nanoparticles with high magnetic moments have potential to be used in biomedical applications such as drug delivery, hyperthermia, magnetic resonance imaging, etc. [1, 2]. There are recent progresses in direct synthesis of FeCo and FeCo–X core-shell nanoparticles with narrow size distribution and controllable shapes [3]. However, many physico-chemical and magnetic properties of these nanoparticles are strongly dependent on particle geometry, degree of retained long range order (LRO) and order-disorder transition (ODT) phenomena which have not been fully understood yet. ODT phenomena (B2 ↔ A2 transformation) in bulk FeCo and FeCo–X alloys have been studied extensively. In this present study, first-principle pseudo-potential theory combined with Ising-type Hamiltonian site exchange Monte Carlo (MC) simulation method have been used to disclose the effects of nanoparticle geometry, i.e. particle size (2.0–5.0 nm) and shape (spherical and cubic), on the structural evolution of B2–FeCo nanoalloy from room temperature to higher temperatures. Also embedded atom method (EAM) has been combined with molecular dynamic (MD) simulation in order to investigate the effects of temperature and particle size on the evolution of various atomic configurations in amorphous FeCo nanoparticles.

2. Methodology

Investigations of the stochastic nature of atomic evolutions of FeCo crystalline nanoparticles have been done via site-exchanging lattice gas Monte Carlo simulations.

MC method combined with electronic theory of alloys in the pseudo-potential approximation have been extensively and successfully utilized in simulations of atomic short-range ordering (SRO), LRO and ODT processes for number of crystalline intermetallics at wide temperature range, because of their ease of application, rapid convergence, and lack of the diffusion barrier at lower temperatures [4–7]. In this study, the same method was applied to investigate the response of degree of LRO parameter to varying particle size and shape in equiatomic Fe₅₀Co₅₀ nanoparticles from room temperature to 1500 K temperatures. The common canonical ensemble Metropolis MC method has been employed by using an Ising-type Hamiltonian

$$H = H_0 + \sum_{\ell} n_{AB}^{\ell} \omega_{AB}^{\ell}. \quad (1)$$

The parameters ω_{AB}^{ℓ} and n_{AB}^{ℓ} reveals the atomic ordering energy and number of nearest-neighbor A–B pairs at ℓ -th coordination spheres (CSs), respectively. The calculation of atomic ordering energy in FeCo alloy, $\omega_{Fe-Co}(R)$, as a function of interatomic distances R has been provided via electronic theory of alloys in the pseudo-potential approximation up to first five CSs, which successfully takes many-body effects partially into account and yields effective interaction fields [7]. Periodic boundary conditions have been applied in bulk simulations, while nanoparticles have free boundaries and no additional treatments was provided for surface potentials. First five CSs have been taken into account in order to increase the accuracy of energy calculations. Lattice parameter of alloy was taken to be 2.8571 Å and the change in the magnitude of lattice parameter with temperature was ignored. Magnitude of ordering energies, $\omega_{Fe-Co}(R)$, was used as an input data in MC simulation of structural evolutions of Fe₅₀Co₅₀ crystalline nanopar-

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ticles. The number of the MC steps applied to obtain equilibrium in system varies in between 10^4 and 10^7 MC steps depending on alloy composition, size, and shape of nanoparticles.

MD simulations have been performed, by using interatomic interaction potentials and electron densities calculated via EAM method whose parameters for binary Fe–Co alloy system were tabulated in literature [8–10]. Based on constant temperature and constant pressure (NPT) MD method, a cubic bulk B2–Fe₅₀Co₅₀ alloys system containing 21296 atoms were heated up to 3000 K and stabilized for 10^6 time steps. Then it was quenched to room temperature and stabilized at 200 K temperature to get amorphous FeCo alloy and the overall cooling rate was 5×10^{12} K/s. The time step was 1 fs and the motion of atoms was integrated by using Verlet algorithms. Long time relaxations were performed at different temperatures to stabilize the atomic structure and to analyze the kinetic evolution of the Voronoi structures. The pressure of surrounding environment was set to zero. Spherical nanoparticles with different sizes (2–5) nm were extruded from bulk amorphous alloy at room temperature.

3. Results and discussion

Although it is impossible to fully equilibrate the systems of limited number of atoms, LRO parameter fluctuations attained during MC simulations were minimal enough to extract surface-to-core ordering profiles in FeCo alloy with 2.0–6.0 nm sized nanoparticles and in bulk form. Nanoscale systems with free surfaces are not able to undergo phase changes. Therefore LRO parameter of FeCo nanoparticles in any size and shape show diffusive responses to temperature. Nanoparticles with free boundaries show lower degree of LRO with varying particle size and also ODT temperature, T_{odt} , decreases with decreasing particle size in comparison with the well-defined $T_{\text{odt}} \approx 1015$ K of bulk FeCo alloys, Fig. 1.

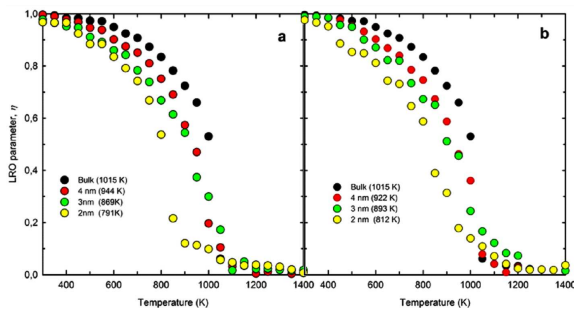


Fig. 1. Variation of LRO parameter with temperature for equiatomic FeCo nanoparticles in (a) spherical and (b) cubical forms. Corresponding T_{odt} values are shown in parenthesis.

It is evident from Fig. 1 that T_{odt} of binary FeCo nanoparticles are not extensive for both spherical and

cubic shape nanoparticles, which is in a good agreement with experimental observations [11]. Magnitude and temperature dependence of LRO parameter for nanoparticles having a size approximately 5 nm (and above) show almost similar character with bulk B2–FeCo alloys irrespective of their shape, Fig. 1.

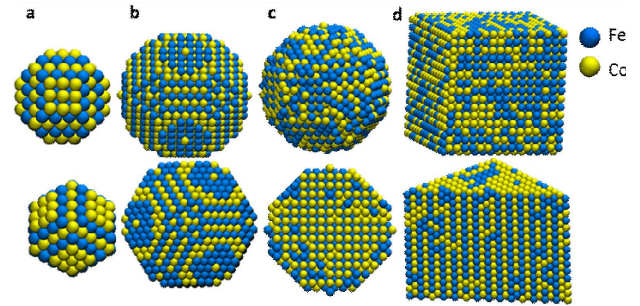


Fig. 2. Snapshots of fully and partially ordered Fe–Co nanoalloys having various size and shape at different perspectives. (a) Fully ordered spherical 2 nm nanoparticles (NP) at room temperature, (b) fully ordered spherical 4 nm NP at room temperature, (c) partially ordered spherical 4 nm NPs, and (d) partially ordered cubic 4 nm NPs.

Moreover, MC simulations show that disordering process initiates mainly at surfaces of nanoparticles and propagates inwards as temperature increases, Fig. 2. It is evident that surfaces of NPs are completely disordered, while the ordered arrangement of Fe and Co atoms are directed toward the center of both spherical and cubic NPs.

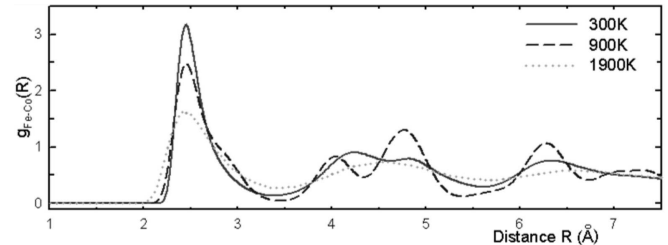


Fig. 3. PPDF of Fe–Co atomic pairs in 4 nm Fe₅₀Co₅₀ amorphous nanoalloy at different temperatures calculated via MD simulations.

Figure 3 displays the calculated partial pair distribution function (PPDF) for Fe–Co atomic pair in 4 nm amorphous Fe₅₀Co₅₀ nanoalloy at different temperatures. PPDFs of Fe–Fe and Co–Co atomic pair's shows the almost identical behavior with PPDF of Fe–Co atomic pair at all calculated temperatures of Fe₅₀Co₅₀ amorphous nanoalloy. Such an identical behavior of PPDF for different atomic pairs have been observed also for amorphous Fe₅₀Co₅₀ nanoparticles having different sizes ranging from 2 nm to 6 nm, indicating that in both Fe- and Co-centered clusters these atoms are surrounded by equal number of nearest-neighbor Fe and Co atoms. Moreover, calculated PPDF at different temperatures shows

that the main peak position of each pair does not show any significant change in decreasing temperature. PPDFs of quenched Fe₅₀Co₅₀ nanoparticles indicate that short- and medium-range ordered (MRO) atomic structures are still existing at room temperature. MD simulations show that amorphous nanoparticles having different sizes were completely melted below 1500 K during heating process. Peak separation at second and third nearest-neighbor distance for 4 nm and 6 nm nanoparticles designate the crystallization of nanoparticles at approximately 900 K.

The three-dimensional (3D) atomic configurations for MRO structured amorphous Fe₅₀Co₅₀ nanoalloys have been identified by using the Voronoi analysis. The Voronoi analysis yields a statistical distribution of polyhedron, each formed around a certain kind of atom by its nearest-neighbor atoms [12]. Calculated via MD simulations, the Voronoi diagrams of Fe-centered polyhedrons in amorphous Fe₅₀Co₅₀ nanoparticles at liquid and glassy states indicate that $\langle 0, 3, 6, 4, 0 \rangle$, $\langle 0, 2, 8, 4, 0 \rangle$ and also their derivatives of $\langle 0, 3, 6, 5, 0 \rangle$ and $\langle 0, 3, 6, 6, 0 \rangle$ configurations, which are “so-called” deformed bcc (d-bcc) structures and $\langle 0, 1, 10, 2, 0 \rangle$ deformed icosahedron (ico) structures are most probable atomic configurations for 2, 4, 6 nm particles of Fe₅₀Co₅₀ nanoalloy.

4. Conclusions

In summary, a detailed structural investigation of both amorphous and crystalline nanoparticles of Fe₅₀Co₅₀ alloy having 2–6 nm size have been conducted by MC and MD simulation methods from room temperature to higher temperatures. In MC simulation of crystalline nanoalloys, it is observed that disordering starts at surface and propagates into volume of nanoparticle with increasing temperature. Also FeCo nanoparticles with critical dimensions over 5 nm have ODT behavior not different than bulk alloys. MD analyses indicate that MRO and SRO structures exist in glassy nanoalloys at room temperatures. Those structures are mainly deformed-bcc, and deformed-icosahedron clusters.

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