Journal of Alloys and Compounds 663 (2016) 340–344

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Atomistic mechanism of nano-scale phase separation in fcc-based high entropy alloys

C.Y. Yu [a, b], X.D. Xu [c], M.W. Chen [c, d], C.T. Liu [a, *]

[a] Center for Advanced Structural Materials, Department of Mechanical and Biomedical Engineering, College of Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong, China
[b] College of Physics Science and Technology, Shenzhen University, Shenzhen 518060, China
[c] WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
[d] State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200030, China

ARTICLE INFO

Article history:
Received 6 July 2015
Received in revised form
27 October 2015
Accepted 3 December 2015
Available online 10 December 2015

Keywords:
High entropy alloys
Phase separation
Atomistic mechanism

ABSTRACT

Nano-scale phase separation and precipitation play a vitally important role in strengthening multi-component alloys, such as high entropy alloys (HEAs), which exhibit excellent physical and mechanical behaviors. Investigating their underlying atomistic mechanism is of great importance in understanding the strengthening mechanism of these complex alloy systems. In the present study, simplified atomic models have been developed to investigate the physical mechanism of the nano-phase separation in the *fcc*-based $Al_xCoCrCuFeNi$ HEAs at the atomic level. Furthermore, the modeling results agree well with the experimental observations from the state-of-the-art scanning transmission electron microscopy (STEM).

1. Introduction

Nano-scale phase separation and precipitation play a vitally important role in the mechanical behavior of multi-component alloys. Through controlling the size and distribution of nano-precipitates, substantial strengthening of the alloys for structural applications can be acquired without harmful embrittlement effects [1–3]. Therefore, investigation of the underlying physical mechanism of nano-scale phase separation and precipitation is of great importance in understanding the phase stability and strengthening mechanism of multi-component alloys. High entropy alloys (HEAs), also known as multi-principal-elements alloys, have recently received great attentions because of their extraordinary properties for potential industrial applications [4–8]. Distinguished from conventional multi-component alloys with one or two major elements, HEAs contain five or more principal metallic elements with equi-atomic or nearly equi-atomic ratios. The random mixing of components contributes to the high configurational entropy of mixing. Simple disordered phases (*eg. bcc* or *fcc*), rather than intermetallic compounds or other complex phases, are more likely to form in HEAs [9–12]. On the formation of simple solid solution matrix phases, nano-scale phase precipitation and separation have been often observed in *fcc* or *bcc*-based HEAs, and this nano-scale structure has been claimed playing an important role in the extraordinary mechanical behavior of HEAs [11,13–17]. The most extensively studied alloy system is $Al_xCoCrCuFeNi$, which exhibit *fcc* or *bcc* phase with different Al concentrations. The nano-scale phase precipitation in $Al_xCoCrCuFeNi$ HEAs has been considered mainly attributed to the positive mixing enthalpy between Cu and other alloying elements and has been argued to be thermodynamically favorable. However, the direct atomic mechanism controlling the nano-scale phase stability is still lacking at present. Therefore, in this study, we have selected *fcc*-based $Al_xCoCrCuFeNi$ HEAs as the model system to investigate the underlying physical mechanism of nano-scale phase separation and precipitation in the multi-component alloy systems.

Computational simulations are powerful and efficient in investigating the atomic mechanisms behind experimental observations. However, it is hard to tackle multicomponent alloy systems (HEAs) from the conventional computational modeling techniques, due to the lacking of atomic potentials describing the interactions between elements. The first-principles calculation based on the density functional theory (DFT) only needs some basic physical parameters of the elements to calculate the ground state electronic structure and total energy of the system, manifesting its power in

* Corresponding author.
E-mail address: chainliu@cityu.edu.hk (C.T. Liu).

http://dx.doi.org/10.1016/j.jallcom.2015.12.004
0925-8388/

dealing with the complex multicomponent alloy systems. In fact, the first-principles calculations based on the DFT have been applied in investigating phase stabilities and stacking fault energies of HEAs, and consistent results with the experiments have been reported [18,19]. In the present study, we investigated the atomic mechanism of coherent nano-scale phase separation in the *fcc* type $Al_xCoCrCuFeNi$ HEA from the DFT-based first-principles calculation. Furthermore, in order to verify the simulation results and understand the complex phenomenon of nano-scale phase separation and precipitation more clearly, scanning transmission electron microscopy (STEM) investigations have been also conducted.

2. Models and methods

In the DFT-based first-principles investigations of HEAs, the special quasi-random structure (SQS) [20] and the Korringa-Kohn-Rostocker-coherent potential approximation (KKR-CPA) [21] methods have been used to model the random solid solutions. In the present study, we are aiming at investigating the coherent nano-scale phase separation in the *fcc*-based $Al_xCoCrCuFeNi$ HEAs, then chemical partitioning and ordered phases such as L12 structure are involved. Therefore, the SQS and KKR-CPA methods which are powerful in investigating entirely random solid solutions are not applicable in the present case. Thus, considering about different atomic configurations, we applied the supercell method and developed simplified models to mimic the nano-scale phase separation in the *fcc* type $Al_xCoCrCuFeNi$ HEAs. In order to investigate the effects of different Al contents, and to ensure the atom number of each element in the supercells is integer, x was set to be 0.02, 0.12 and 0.45, respectively. Three kinds of supercells with $4 \times 4 \times 4$ unit cells for each alloy were established as the initial models for calculations, named as model S1, S2 and S3 respectively, the models with the composition of $Al_{0.45}CoCrCuFeNi$ are shown as examples in Fig. 1. In the model S1, all the Al, Co, Cr, Cu, Fe and Ni atoms are randomly distributed in the *fcc* lattice based on their concentrations to mimic the random solid solutions without any phase separation. In the model S2, there is a Cu-rich core in the center of the supercell, and all of the other atoms are distributed randomly around the Cu-rich core. The size of the *fcc* Cu-rich core was set based on the number of copper in the system and restricted by the lattice arrangement. This model is applied to mimic the nano-scale Cu-rich precipitation, while the atom structure around the precipitated core remains random. The model S3 also has a Cu-rich core in the center, and in difference with the model S2, the atom distribution of it exhibits Ni_3Al-type L12 ordering with Al atoms occupying the corner sites in the Cu-depleted area. The setting in model S3 is for mimicking the nano-scale chemical partitioning with a Cu-rich zone and Fe–Co–Cr–Ni-rich surroundings with the L12 ordering.

The first-principles total energy calculations were performed on all of the models based on the Vienna *ab initio* Simulation Package (VASP) [22]. The accurate total energies for all kinds of the models were determined based on their initial configurations. Projector augmented wave (PAW) potential [23,24] was used to describe the coulomb interaction of ion cores with the valence electrons, and the generalized gradient approximation (GGA) refined by Perdew, Burke and Ernzerhof (PBE) [25] was applied to describe the electronic exchange and correlation. A plane-wave energy cutoff was set as 400 eV to all the structures for consistency. Brillouin zone integrations were performed using the Γ centered Monkhorst-Pack grids [26], and the k-point meshes were set as $1 \times 1 \times 1$ for all of the supercells. For each initial configuration, equilibrium cell volumes and all atomic positions were fully relaxed until convergence with the total energy tolerance of 10^{-4} eV by using the conjugate

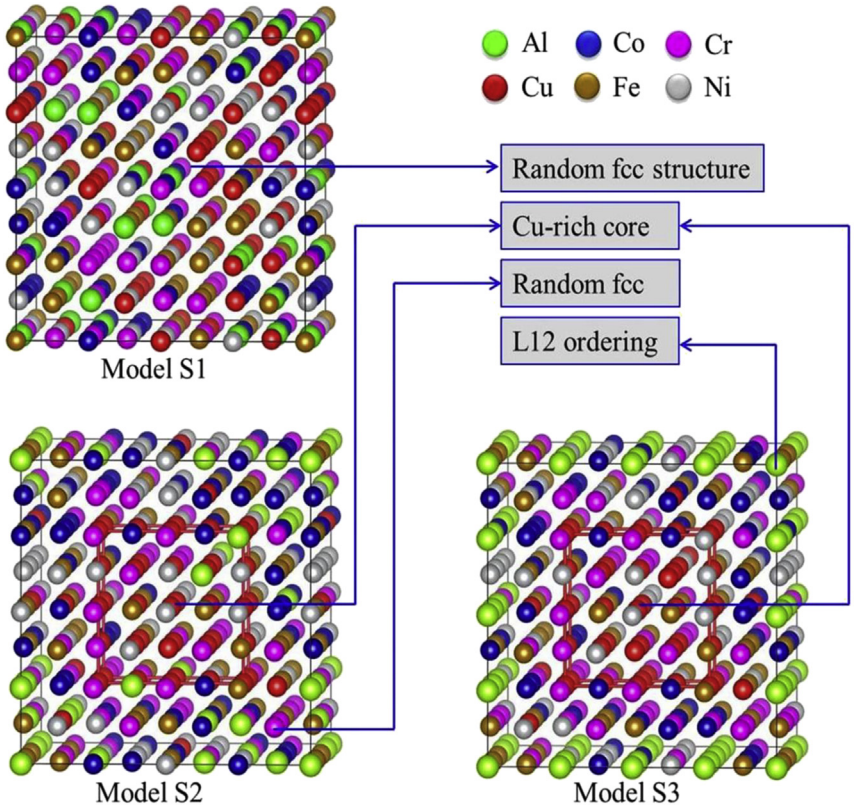

Fig. 1. Atomic models mimicking the nano-scale phase separations of the $Al_{0.45}CoCrCuFeNi$ alloy system.