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Structural and bonding transformation of $Al_{0.67}CrCoCuFeNi$ high-entropy alloys during quenching

Kun Zhang [a, b], Shaopeng Pan [c], Weiqi Tang [a, b], Yating Zhang [a, b], Bingchen Wei [a, b, *]

[a] *Key Laboratory of Microgravity (National Microgravity Laboratory), Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China*
[b] *School of Engineering Science, University of Chinese Academy of Sciences, Beijing 101408, China*
[c] *College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan, 030024, China*

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ABSTRACT

Structural and bonding transformation of the $Al_{0.67}CrCoFeNi$ high-entropy alloys (HEA) during quenching is investigated by molecular dynamics simulations. At a high cooling rate, some short-ranged ordered clusters, such as FCC, HCP and BCC crystalline clusters are already present in the almost amorphous HEAs. When the cooling rate decreases, the atoms become packed more orderly and ultimately form a nano-polycrystalline structure dominated by FCC structures. The BCC structures appear only as an intermediate state acting on the course of crystallization, while the HCP structure can be viewed as the precursor of the malposed FCC structure due to the identical first neighbor distances. In liquid HEAs, the low-symmetry and low-coordination bond pairs, either transform to high-symmetry and high-coordination 1551 bond pairs, or transform to 1(5,4)41 bond pairs for FCC structure and 1661 bond pairs for an HCP structure, depending on the cooling rates. This study will contribute to a better understanding of the essential phase change in HEAs.

1. Introduction

High entropy alloys (HEAs) have attracted considerable research interests due to their high strength, ductility, toughness and corrosion resistance compared with traditional alloys [1–4]. The solidified structure of HEAs is generally simple, even though they are comprised of five or more than five elements. Their simple crystal lattices exhibit both the individual characteristics of their constituents and collective features. Nowadays, HEAs have been shown to have a wide application prospect in various fields, such as in the aerospace industry or in the fabrication of tool and damage resistant materials [5–8]. In earlier work on HEAs, numerous studies focused on the study of single-phase HEAs. Indeed, most of the described HEAs contained multiple phases instead of a single solid-solution phase [1,9]. The formation of multiphases in HEAs is strongly associated with the local atomic stress/strain environment, thermal-equilibrium behavior, and interatomic interactions among the constituent elements [10,11]. Understanding the underlying thermodynamic characteristic of HEAs through integrated experiments and thermodynamic modeling can provide an insight into the design of multiphase HEAs [12]. Especially, with little Al addition, CrCoCuFeNi HEAs are composed of a simple FCC solid-solution structure. As the Al content reaches $x = 0.8$, a BCC structure appears, which consisted of mixed FCC and BCC eutectic phases [13]. It is believed that excessive Al is capable of triggering diffusive transformations from a molten to a crystalline phase via an intermediate amorphous structure [14]. However, the basic understanding of the structural stability and transformation properties is still lacking, due to the complicated elemental diffusion and atomic-bonding environments [11,14]. Recently, transformation-induced plasticity has been successfully employed in HEAs to overcome the strength-ductility trade-off [15,16]. In addition, altering the cooling conditions is another effective pathway to achieve multiphase structures. Nevertheless, how the HEA liquid changes into the solid as well as the evolution of intermediate states during a rapid quenching process need to be further investigated. In addition, the relation between the structural transformation and bonding characteristic should also be elucidated.

First principle simulation based on the density functional theory is useful to investigate the physical and structural property of HEAs [17–19]. Such calculations can provide accurate descriptions of the

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* Corresponding author. Key Laboratory of Microgravity (National Microgravity Laboratory), Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China.

E-mail address: weibc@imech.ac.cn (B. Wei).

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binding energies and bonding characteristic among the atoms. However, the technique is limited to a small number of atoms. Motivated by the above concerns, in this work, the classical molecular dynamics (MD) simulation is used to examine the bonding characteristic and origins of the structural transformation in $Al_{0.67}CrCoFeNi$ HEAs. A possible nucleation mechanism in liquid HEAs is proposed. The findings of this study can pave new paths for guiding the future development of promising single-phase and multiphase HEAs.

2. Simulation details

The highly parallelized Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) MD simulation package [20] is employed for computations, while the visual analysis and post-processing of molecular trajectories are performed with the open visualization tool (OVITO) [21]. The simulations are conducted using the classical Lenard-Jones (LJ) pair-potentials with parameters obtained from the literature [14]. These LJ force-field parameters have been found to agree well with previous results, where a maximum deviation of ~11% is observed [22–24]. An FCC lattice of 9.2 nm × 9.2 nm × 9.2 nm composed of randomly distributed Al, Co, Cr, Cu, Fe and Ni atoms, as shown in Fig. 1, is constructed. The cuboidal simulation cell contains 37,044 atoms with periodic boundary conditions imposed in all the directions. First, the energy minimization of the structure is performed using the steepest descent algorithm with an energy tolerance of 10^{-6} and force tolerance of 10^{-8} (eV/Å). Then, this model is initialized at 5300 K under an isothermal-isobaric (NPT) ensemble at zero pressure for 100 ps. Subsequently, the alloy is rapidly quenched to 300 K at different cooling rates (0.05 K/ps; 0.34 K/ps; 0.5 K/ps; 5 K/ps). A time step of 0.001 ps is maintained throughout all our simulations. In order to record the averaging structural information at each given temperature, we create five atomic trajectories using slightly different integration time steps starting from the same initial configuration.

3. Results and discussions

The pair correlation functions (PCF) curves of the $Al_{0.67}CrCoFeNi$ HEAs are shown in Fig. 2. It is worth noting that the main peak height of the PCFs, which represents the nearest-neighbor shell, increases significantly with the decrease of the temperature, and the second peak begins to split. At the cooling rates of Q = 5 K/ps and 0.5 K/ps, the second peak begins to split into two subpeaks at 300 K, where the ordered structure in the short range appears. With the decrease of the cooling rate to Q = 0.34 K/ps, the splitting occurs at 1300 K. Additionally, a small shoulder peak between the first and second peaks arises on the left, which indicates that the length of the ordered structure is further extended to a large scale. At the cooling rate of Q = 0.05 K/ps, the left shoulder peak becomes more prominent than the subpeak at the right, suggesting that the orientation of crystalline structures becomes more consistent. The results indicate that the shoulder peak at the left side of the second peak is due to the appearance of short- or medium-range ordered structures [25].

To achieve a better characterization of the internal structural evolution, common neighbor analysis (CNA) is implemented to obtain the general characteristic signature by computing the topology of the bonds that connect the surrounding neighbor atoms [26]. The adaptive CNA with variable cut-offs automatically determines the threshold radius for phase identification of the atoms in the multicomponent environment of the HEA lattice. The CNA parameters of the quenched HEAs with different cooling rates are shown in Fig. 3. The detailed fractions of various crystal structures are listed in Table 1. When the cooling rate is Q = 5 K/ps, some short-ranged ordered clusters, such as FCC, HCP and BCC crystalline clusters are already present in the HEAs, which are difficult to observe in experiments due to the resolution limit. The crystallites distribute discretely at random locations, which makes the crystalline clusters seem more stable and compact than their surroundings due to the dense packing. Further reducing the cooling rate (Q = 0.5 and 0.34 K/ps) will aggregate more crystalline clusters which become larger. An evident characteristic is that FCC and HCP structures alternate with each other. Instead, when the cooling rate continues to reduce (Q = 0.05 K/ps), the atoms become packed more orderly and ultimately form a nano-polycrystalline structure dominated by FCC structures. Compared with the conventional alloys, the severely distorted lattice in HEAs may make the atoms more difficult to diffuse. Xue reported that the high-cooling HEAs favored the formation of FCC and BCC phase respectively, rather than the dual-phase structure, due to the cooling rate-related sluggish diffusion effect [27]. It should be emphasized that BCC structures appear only as an intermediate state acting on the course of crystallization, which initially increase from 0.3% to 2.0% when the cooling rate decreases from 5 K/ps to 0.34 K/ps, and eventually

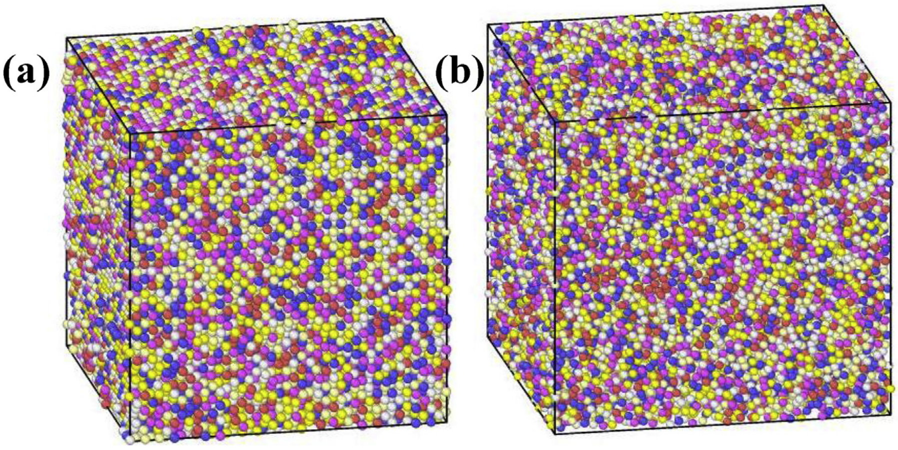

Fig. 1. Elements are randomly distributed in (a) an FCC lattice then (b) kept at 5300 K for 100 ps under a NPT ensemble. The various colors represent the different elements: Al in red, Co in blue, Cr in green, Cr in pale yellow, Cu in white, Fe in yellow, and Ni in purple. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)