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Effect of solute segregation on the intrinsic stacking fault energy of Co-based binary alloys: A first-principles study

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ABSTRACT

Segregation of solute atoms to stacking faults (Suzuki segregation) and their interactions are of long-standing attention since it has a deep impact on mechanical properties. In this study, we systematically investigate the segregation behavior of different solute atoms in fcc Co-based binary alloys and its effect on the intrinsic stacking fault energy (SFE) using first-principles density-functional-theory (DFT) calculations. Interestingly, while Mo, W, Cr, Mn and Al atoms have a strong tendency to Suzuki segregation with some significant energy barriers, Ni atom has no tendency of segregation and only Fe atom has extremely low energy barriers. A strong segregation effect on the intrinsic SFE was observed and it only extends at a few atomic layers in the vicinity of the intrinsic stacking fault plane. The results are consistent with observed solute segregation in similar alloys and commercial superalloys then it would be useful for SFE modeling and Co-based alloys design. Furthermore, the effect of solute concentrations and changes in the electronic features (charge density difference and density of states) are also investigated. A mutual interaction between solutes and stacking faults enhanced local bonding between the solute atom and the adjacent Co atoms, resulted in the lower intrinsic SFE, thus favoring Suzuki segregation.

1. Introduction

In multicomponent alloy systems (binary, ternary, etc.), segregation of solute atoms to crystalline defects (stacking faults, slip bands, etc.) or interfaces and their interactions are of longstanding attention, since they have deep impact on mechanical properties, such as grain boundary strength, yield strength, oxidation, and precipitate growth kinetics [1,2]. For instance, the strength of binary Co–Ni-based superalloys is improved after cold rolling followed by aging at intermediate temperature owing to the chemical interaction between solute and stacking faults (SFs), known as the Suzuki effect or Suzuki segregation [1,3]. Suzuki segregation, which was first considered by Suzuki in 1952, could reduce the stacking fault energy (SFE) and affect the plastic deformation of fcc alloys [3]. Decreasing SFE also increases the pinning effect (segregation of solid solution atoms to the partial dislocation core, known as Cottrell pinning) that suppresses dislocation and lowering the critical shear stress for deformation twinning [4]. Other phenomena such as flow stress, plastic flow behavior, dynamic strain aging and deformation twinning are frequently credited to the SFE reduction by Suzuki segregation and/or Cottrell pinning [2,5].

Numerous electron microscopy experiments to imaging the solute atoms distribution along the stacking fault area have been explored in order to understand Suzuki segregation and its impact on the mechanical properties [1,6]. The atom-probe field-ion microscope investigations in 1985 presented some evidence for the segregation of solute atoms to SFs in Co-0.96 at.%Nb and Co-0.98 at.%Fe alloys [7,8]. Recently, transmission electron microscope (TEM) investigations have produced some quantitative results. For example, the segregation distributions of Zn and Y along SFs in Mg–Zn–Y alloys have been characterized experimentally on the atomic level by Yang et al. using scanning transmission electron microscope (STEM) [2]. They conclude that the superior strength of Mg–Zn–Y alloys at elevated temperatures is owing to the solute segregation to the newly formed SFs together with the SFs formed during growth that could effectively hinder dislocation movement within the Mg grains. Han et al. have been detected the solute segregation to both stacking faults and slip bands in Co–Ni–Cr-

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based (MP159) superalloys using EDX line scans on a field emission gun (FEG) TEM [5]. They also found that the Suzuki segregation reduces the SFE and it can contribute to the continuous serrated plastic flow behavior of MP159 superalloys. However, due to the thickness of SF may only be a few atomic layers, then X-ray signals from these thin SF planes is extremely low, there are some difficulties to detect the solute segregation profile across the SF, such as the concentration analysis can fluctuate and the measurement must be repeated several times [1,5]. Koizumi et al. have tried to detect the solute segregation profile of Co–Ni-based superalloy by scanning TEM and EDS analysis, but it was not successful although the analysis was repeated several times across some different SFs [1]. They assumed that the similarity in the energies of the characteristic X-rays from the main elements in Co–Ni-based superalloys is responsible for the difficulty with EDS measurement.

Atomistic simulation using supercomputer facilities is a powerful device and an effective alternative for understanding mechanism and phenomena that is not possible to be measured or observed experimentally. Then, several studies using atomistic modeling to investigate the segregation behavior of solute atoms to SF and its effect to the SFE in some alloys have been studied [1,6,9–12]. Koizumi et al. have been detected the Suzuki segregation in Co–Ni-based superalloy using a phase-field simulation although it was not successfully detected by the experiment [1]. The simulation suggested that Ni atoms are depleted while Cr and Mo atoms are segregated at the SF, thus as a consequence of the Suzuki segregation, the SFE of Co–Ni–Cr–Mo alloy can become negative. Eurich et al. investigated the solute segregation to intrinsic and extrinsic SF in γ'-Ni_3Al using first-principles density-functional-theory (DFT) calculations, and show that the local alloying concentration together with its electronic structure could change the SFE [6]. Zhao et al. used first-principles calculations to study the Suzuki segregation of Mg impurities and its effect to the twinnability of Al–Mg alloys related to plastic deformation [9]. They conclude that Mg atoms are segregated to the SF plane and decrease the intrinsic SFE then improve the twinning tendency of Al. Furthermore, they also predicted that there is a mutual stimulation of the Suzuki segregation of Mg impurities and vacancies to the intrinsic SF of Al-Mg alloys [10]. First-principles simulation of FeNiCoCrMn high entropy alloy by Patriarca et al. shows that Co atoms are preferred near the SF plane and reduce the intrinsic SFE by almost 55% [11]. Additionally, they note that the simulation results would be inaccurate without applying the solute segregation effects. Meanwhile, Zhao et al. used the exact muffin-tin orbital (EMTO) method to prove that the local Mo segregation to the SF plane has a strong effect on the SFE and contributes to the twinnability enhancement of Ni-Mo alloys [12]. Conversely, atomic simulation of the solute segregation behavior in Co-based alloys (other than Cr and Mo segregation in Co–Ni–Cr–Mo alloy) has not been studied yet. Several intrinsic SFE simulations of Co-based binary alloys were assumed that the substitutional solute atoms are located in the SF area [13,14] or treated as random alloys used the coherent-potential approximation (CPA) technique. In this study, we systematically investigate the segregation behavior of solute atoms in fcc Co-based binary alloys and its effect on the intrinsic SFE using first-principles DFT calculations.

Based on experiments and atomistic simulations that have been mentioned above, it seems that the Suzuki effect can occur in all multicomponent alloy systems. Cui et al. used first-principles calculations to demonstrate that the Suzuki effect is not a universal phenomenon and different solute atoms reveal distinct behavior with respect to the SF regions [15]. They have been classified the solute atoms in binary Mg alloys into three types, such as anti-Suzuki segregation (solute atoms that have no tendency to segregate at SF), activated Suzuki segregation (solute atoms that have a strong Suzuki segregation tendency, but need to confront significant energy barriers when move toward the SF) and natural Suzuki segregation (solute atoms that have strong Suzuki segregation with extremely low energy barriers). In the present study, we identify and classify the behavior of different solute atoms in Co-based binary alloys (Cr, W, Mo, Ni, Mn, Al and Fe) when approaching to the SF regions and its tendency for Suzuki segregation. We also simulate the effect of solute concentrations on the segregation behavior and the intrinsic SFE using high concentration model. First-principles calculations by Chowdhury et al. reveal that there exists a non-uniform intrinsic SFE variation owing to the competition between the solid solution hardening and the solute segregation in Ni–Co alloys when Co concentrations are lower than 10% [16]. Furthermore, the features in the electronic structure (charge density difference and density of states) are analyzed to understand a detailed mutual interaction between solutes at different layers and SFs that affect the solute segregation behavior. An in-depth investigation of the Suzuki segregation in the present study would give a new insight to the SFE modeling and would be useful for the design of Co-based alloys.

2. Computational details

The atomic simulation cell (supercell) is created to consist of 11 closed-packed layers on the (111) glide plane with stacking sequences ABCABC][BCABC for the intrinsic SF structure. To plot the relative energy curve, one alloying atom was placed in each layer for each supercell structures with different alloying elements (Cr, W, Mo, Ni, Mn, Al and Fe) then the concentration was about 4.5 at.%. Several test calculations with supercells and atomic size variations are performed to ensure that the supercells are large enough to minimize the interaction of the SF with its periodic image. The intrinsic SF supercell which is periodic in all directions was used to calculate the layer-by-layer relative energy, charge density difference and density of states (DOS). In order to calculate the intrinsic SFE, a model of perfect or ideal fcc supercell structure is constructed, consist of 12 layers on the (111) plane with stacking sequences ABCABCABCABC as well as a vacuum spacing of 15 Å. An intrinsic SF supercell was created through a shear displacement of the atomic layers number 7–12 through [11–2] direction. The intrinsic SFE (mJ/m^2) was calculated by;

$$\gamma_{isf} = \frac{E_{isf} - E_0}{A} \tag{1}$$

where E_{isf} corresponds to the total energy of intrinsic SF supercell (in mJ), E_0 is the total energy of the ideal or perfect fcc structure (in mJ), and A is the cross-section region of the supercell or area of the SF plane (in m^2).

All first-principles DFT calculations in the present study were performed using CASTEP package [17]. The exchange-correlation functions were defined with the Generalized Gradient Approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [18]. Vanderbilt-type ultrasoft pseudopotential [19] was used with the plane wave kinetic energy cut-off was converged to 400 eV. The Brillouin zone was sampled using a k-points mesh sampling of $11 \times 11 \times 1$ in reciprocal space according to Monkhorst-Pack scheme [20]. The tolerances for the atomic relaxations were set as follows: the difference in total energy within 10^{-5} eV/atom, the maximum ionic Hellmann-Feynman force within 0.03 eV/Å, the maximum ionic displacement within 0.001 Å and the maximum stress within a component is 0.02 GPa. All total energy calculations used a spin-polarized approximation owing to the ferromagnetism of Co with the calculated spin magnetic moment for cobalt is 1.65 μ_B/atom.