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Regular article

The origin of negative stacking fault energies and nano-twin formation in face-centered cubic high entropy alloys

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ABSTRACT

The secrets behind the exceptional mechanical properties of high entropy alloys (HEAs) at cryogenic temperatures have drawn much attention in recent years. In this work, the negative stacking fault energy of FCC CrNiCo and FeCrNiCo alloys are disclosed by first-principles calculations. We found that the negative SFEs originate from the thermodynamic metastability of FCC stacking sequence and heavily influenced by the local atomic environment, which in turn affects the formation of stacking faults and nano-twins.

1. Introduction

High entropy alloys (HEAs) have drawn much attention due to the simultaneous improvement of strength, ductility, and toughness at cryogenic temperature [1]. In HEAs, stacking faults and nano-twins are of great research and technology interests, as they contribute to the astonishing improvements of mechanical properties [2,3]. Understanding their formation is significant for conquering the trade-off between strength and toughness in metallic alloys.

A great deal of theoretical studies has focused on the low stacking fault energies (SFEs) in HEAs. The pioneering work of Zaddach et al. [4] predicted the stacking fault energy of two- to five-component alloys using a combination of experimental measurements of microstrain and *ab initio* calculations of elastic moduli. They concluded that the stacking fault energy would decrease with the number of components increasing. Bhattacharjee et al. proposed that the low SFEs in HEAs were due to the combined effect of the high energy level of the distorted matrix and the relieving of strain energy by *in situ* adjustment of solute atoms in the stacking faults, but not due to the Suzuki mechanism [5]. Later on, the Suzuki mechanism was emphasized by Patriarca et al. [6]. They studied the role of solute segregation effects on SFE by first-principles calculations and claimed that the presence of Co atoms was favored near the stacking faults, reducing the SFE by almost 55% (from 38 mJ/m^2 to 17 mJ/m^2) when compared to the presence of Co atoms away from stacking faults.

In the present work, the stacking fault energies in certain FCC (CrNiCo, FeCrNiCo) and HCP (FeCrNiCo) HEAs were calculated using the first-principles method in combination with the special quasi-random structure (SQS) technique [7,8]. We predicted the SFEs of intrinsic stacking faults for HEA alloys with FCC or HCP structures at 0 K. Furthermore, we found that the local atomic environment would influence heavily on the SFEs. The thermodynamic results indicate the formation of intrinsic stacking faults in FCC HEAs could be a spontaneous process at low temperatures if no significant kinetic barrier. A positive energy input is not necessarily required when introducing defective structures in HEAs, especially intrinsic stacking faults in FCC HEAs. Moreover, those defective structures are intrinsically stable in HEAs. These results would help in the design of novel HEA alloys with low SFEs and excellent mechanical properties.

2. Methodology

Density functional theory (DFT) calculations were performed by using Vienna *ab initio* simulation package (VASP) [9,10] with the projector augmented wave (PAW) method [11,12]. The exchange-correlation functional was chosen as the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) [13]. The semicore p states of all elements were treated as valence electrons, and plane-wave energy cutoff of 600 eV and Monkhorst–Pack [14] k-point spacing of 0.2 $Å^{-1}$ were used for all calculations. The energy and the force tolerance were 1.0×10^{-7} eV and 1.0×10^{-3} eV·$Å^{-1}$, respectively. To determine the equilibrium lattice constants, the geometry optimization was done using SQS supercells with 108 and 96 atoms for FCC and HCP structures, respectively. Simulation of random HEA alloys using SQS method, allows the atomic relaxation to reproduce the severe lattice distortion in HEAs.

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Our calculations were mainly performed on non-magnetic structures (*i.e.*, non-spin-polarized). The theoretical calculation of Ma et al. [15] suggested that HEAs have almost vanishing local magnetic moments at equilibrium volume and closely resemble to the non-magnetic state. Experimentally, para-magnetism was identified for FeCrNiCo and CrNiCo. In all, it's safe to treat HEAs as non-magnetism here.

3. Results and discussion

In Table 1, the lattice parameters are tabulated for CrNiCo and FeCrNiCo with FCC and/or HCP structures, together with the comparison of other theoretical work and experimental measurements. The lattice constants of FCC CrNiCo and FeCrNiCo are predicted to be 3.515 Å and 3.498 Å, respectively. They agree very well with other theoretical studies (3.516 Å for CrNiCo [16] and 3.51 Å for FeCrNiCo [17]), and experimental results (3.579 Å for CrNiCo [18] and 3.575 Å for FeCrNiCo [4]). Besides, the lattice constant of CrNiCo alloy is 0.5% smaller than that of the quaternary FeCrNiCo alloy. Experimental results also show the same trend, which verifies the reliability of our calculations. For HEA alloys with HCP structure, no structural information is available in experiments. The lattice constants of HCP FeCrNiCo are firstly reported here as 2.491 Å (a) and 3.981 Å (c). For HCP CrNiCo, the lattice constants are predicted to be 2.492 Å (a) and 4.031 Å (c), which also agree very well with the calculation results of Zhang et al. (2.499 Å (a) and 4.013 Å (c)) [16].

Thereafter, we constructed the intrinsic stacking faults for FCC CrNiCo and FeCrNiCo, as well as HCP FeCrNiCo based on the optimized structural parameters. First, the pristine supercells with 192 atoms were built up with a bulk slab and a vacuum slab of 16 Å. The lattice vectors of the supercells were defined as $a = [2\,0\,\bar{2}]_{fcc}$, $b = [0\,2\,\bar{2}]_{fcc}$, $c = [4\,4\,4]_{fcc}$ for the FCC structures, and $a = [4\,0\,0\,0]_{hcp}$, $b = [0\,4\,0\,0]_{hcp}$, $c = [0\,0\,0\,6]_{hcp}$ for the HCP phases. The vacuum slab was added to screen the pseudo-interactions between periodically repeated slabs. To create the stacking faults, the upper half part of the supercells were rigidly sheared along the Shockley partial dislocations, i.e., $b_p = 1/6[11\bar{2}]a_0$ in FCC structures and $b_p = 1/3[10\bar{1}0]a_0$ in HCP structures (where a_0 is the lattice constant). Thereafter, the origin c vector was distorted as $c' = (c + b_p)$. Finally, a relaxation scheme of pure alias shear (a full relaxation of the supercell and atomic coordinates with the only constraint of shearing angle fixed) [6,19,20] was utilized for the faulted supercells. The stacking fault energy was then derived as

$\gamma_{isf} = (E_{isf} - E_0) / S_0$, where E_{isf} and E_0 are the total energies of faulted and pristine supercells, respectively, and S_0 is the area of the stacking fault. The corresponding configurations of intrinsic stacking faults (ISFs) are illustrated in Fig. 1. Following the notation by Liu [21], the change of the stacking sequence in FCC materials can be expressed as

…cccccccccccc… → …ccccchhccccc…

and while, in HCP structures, the local atomic stacking change can be expressed as

…hhhhhhhhhhhh… → …hhhhhcchhhhh…

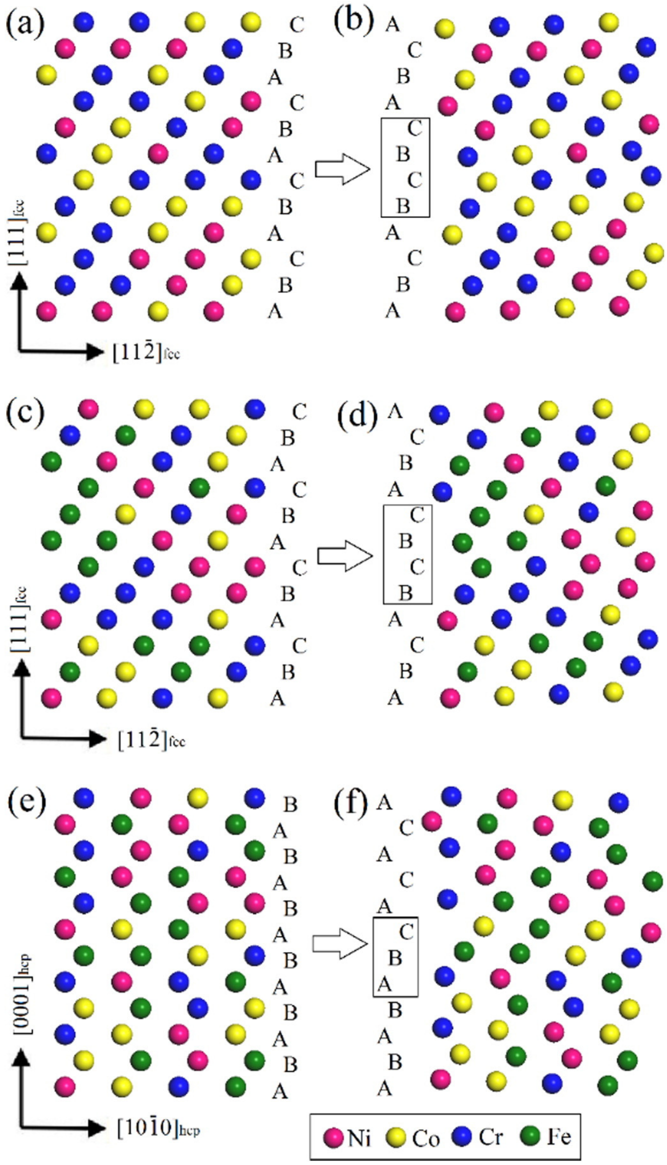

Fig. 1. Configurations of (a) FCC CrNiCo, (b) FCC CrNiCo with ISFs, (c) FCC FeCrNiCo, (d) FCC FeCrNiCo with ISFs, (e) HCP FeCrNiCo, and (f) HCP FeCrNiCo with ISFs.

The stacking fault energies for different configurations are summarized in Table 2.

Interestingly, the stacking fault energies in FCC phases are extremely negative at 0 K and spread in a wide range when the local atomic environments are different. In FCC CrNiCo, the ISF configurations of FCC1, FCC2, and FCC3 have negative SFEs at −18 mJ/m^2, −49 mJ/m^2, and −77 mJ/m^2, respectively. The SFEs decrease with decreasing valence electron counts (VECs) and *d*-electron density near ISFs. Surprisingly, the SFEs change more than three times depending on the local

Table 1
Structural parameters and local lattice distortion in CrNiCo and FeCrNiCo (FCC and HCP) alloys.

Systems		CrNiCo		FeCrNiCo	
		FCC	HCP	FCC	HCP
Lattice parameter (Å)	This work	$a = 3.515$	$a = 2.492$, $c = 4.031$	$a = 3.498$	$a = 2.491$, $c = 3.981$
	Others	$a = 3.516$ [16]	$a = 2.499$ [16] $c = 4.013$ [16]	$a = 3.51$[17]	
	Exp.	$a = 3.579$ [18]		$a = 3.575$ [18]	