Plastic deformation transition in FeCrCoNiAl\(_x\) high-entropy alloys

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**ABSTRACT**

The competition between plastic deformation mechanisms in FeCrCoNiAl\(_x\) high-entropy alloys is explored as a function of temperature by first-principle theory. Investigating the generalized stacking fault energy, we identify a strong interplay between the magnetic and chemical effects. At cryogenic conditions (ferromagnetic state), full-slip is accompanied by martensitic transformation, whereas increasing temperature towards room-temperature (paramagnetic state) changes the deformation mechanism to full-slip plus twinning. Alloying with Al reduces the susceptibility for stacking fault formation in the ferromagnetic state and promotes twinning in the paramagnetic state. The present advance in magneto-plasticity reveals new opportunities for tailoring the mechanical response in high-entropy alloys.

**IMPACT STATEMENT**

Magnetic state critically affects the \(\gamma\)-surface of FeCrCoNiAl\(_x\) and is responsible for the emergence of the exceptional metastable twinning phenomena at room temperature.

The development of alloys with enhanced strength and ductility represents a continuous challenge in materials design. Over the past years, high-entropy alloys (HEAs) have generated considerable excitement for their unique combinations of mechanical properties [1–3]. For example, the equiatomic FeCrCoNiMn with single face-centered cubic (fcc) solid solution phase displays fracture toughness values at crack initiation well above 200 MPa\(\cdot\)m\(^{1/2}\) associated with increasing tensile strengths from 730 to 1280 MPa as the temperature is lowered from 300 to 77 K [4]. Experimental observations indicated that the key to the unusual temperature-dependent strength and ductility is the presence of twinning as the dominant deformation mechanism at cryogenic conditions [4]. More recently, the Fe\(_{80-x}\)Mn\(_x\)Co\(_{10}\)Cr\(_{10}\) alloys with a decrease of Mn content produce a partial martensitic transformation of the fcc phase to the hexagonal close-packed (hcp) phase at room temperature, i.e. the so-called transformation-induced plasticity (TRIP) assisted dual-phase HEAs, accompanied by a mechanical response similar to that of FeCrCoNiMn [5]. Since the deformation mode transition plays an important part in tuning the strength-ductility trade-off in such alloys, a theoretical understanding is indispensable for optimizing high-performance HEAs.

Generalized stacking fault energy (\(\gamma\)-surface), which represents the energy dependency of the rigidly sheared crystal within the fcc \{111\} plane along the \langle{11\bar{2}}\rangle
magnetic disorders. Using first-principle methods, here we divide γ into three contributions: the chemical part γ_{chem}, the magnetic part γ_{mag}, and the electronic part γ_{el}. It is clear that γ_{chem} follows closely the trend of γ, while γ_{mag} gives opposite contributions. Further analysis shows that γ_{chem} gives the major contribution to the total fault energy (order of 10^2 mJ/m^2, especially for γ_{usf} and γ_{utf}). On the other hand, γ_{mag} plays an important role in establishing the actual values for γ_{usf} and γ_{utf} (where γ_{chem} is relatively small). Finally, γ_{el} is very small (<10^0 mJ/m^2) for the present system and temperatures of interest and thus can safely be ignored.

The magnetic fluctuation contribution is therefore important to identify γ_{mag} of the paramagnetic FeCrCoNi, as shown in Figure 1(b). In perfect fcc lattice, the local magnetic moments per Fe and Co atoms are 2.08 and 3.23 μ_B, respectively, while for Cr and Ni atoms, the static DLM magnetic moments are nearly zero. For all types of planar fault, the main magnetic changes are observed in the layers around the fault plane. For the intrinsic stacking fault, the Fe magnetic moment near the fault plane decrease by ~4% as compared to its bulk value. The Co magnetic moment follows qualitatively the same behavior. The loss of the paramagnetic moment results in lower magnetic entropy, and thus has a positive contribution to γ_{usf}. In the case of the unstable stacking fault, the magnetic entropy is larger than the corresponding bulk values. From the feature of the local magnetic moments, the unstable twinning fault can be treated as a sum of unstable stacking fault and intrinsic stacking fault, and the extrinsic stacking fault as a pair of intrinsic stacking fault located on neighboring planes.

For the considered system, the Curie temperature estimated via the mean-filed method [39] varies from ~155 to ~140 K when x changes from 0 to 0.3 in the fcc phase [40]. Figure 2(a) displays the obtained γ_{usf}, γ_{utf} and γ_{af} of the ferromagnetic and paramagnetic FeCrCoNi in the temperature range of 77–300 K. It is clear that for both magnetic states, γ_{usf} increases, whereas γ_{utf} and γ_{af} decrease with increasing temperature. The values of γ_{usf} at 77 K for the ferromagnetic and paramagnetic states are −12.9 and −12.3 mJ/m^2, respectively, and increase to −11.0 and −0.3 mJ/m^2 when temperature...
Figure 1. Generalized stacking fault energy of the paramagnetic FeCrCoNi at room temperature. In panel (a), \( b = (11\bar{2})/6 \) is the Burgers vector of the partial dislocation (in units of fcc lattice parameter). For comparison, the dash line marks the \( \gamma \)-surface of the ferromagnetic FeCrCoNi at room temperature. Panel (b) shows the magnetic part \( \gamma_{\text{mag}} \) for the paramagnetic FeCrCoNi at room temperature. Insets show the changes of magnetic moments for Fe around the faulted planes as a function of layer index with respected to the corresponding values for the perfect fcc lattice. The stacking fault is formed between the fifth and sixth layers.

Figure 2. Intrinsic stacking fault energy \( \gamma_{\text{isf}} \), unstable stacking fault energy \( \gamma_{\text{usf}} \), and unstable twining fault energy \( \gamma_{\text{utf}} \) of the ferromagnetic and paramagnetic FeCrCoNiAl\(_{x}\), respectively. Panel (a) shows the results for FeCrCoNiAl\(_{0}\) at \( x = 0 \) as a function of temperature. As one can see, removing the magnetic order yields a positive effect on all three parameters within the considered composition range. In the case of the paramagnetic state, \( \gamma_{\text{isf}} \) increases from \(-0.3\) to \(10.3\) mJ/m\(^2\) when \( x \) changes from \(0\) to \(0.3\), whereas \( \gamma_{\text{usf}} \) and \( \gamma_{\text{utf}} \) decrease from \(290.5\) and \(289.5\) mJ/m\(^2\) to \(262.7\) and \(269.4\) mJ/m\(^2\), respectively. Actually, \( \gamma_{\text{isf}} \) can be connected to the stability of the fcc and hcp structures, i.e. \( \gamma_{\text{isf}} \simeq 2(E_{\text{hcp}} - E_{\text{fcc}})/A \), based on the second-order approximation of the axial interaction model [22]. Thus, the negative \( \gamma_{\text{isf}} \) found in low-Al content system at cryogenic temperatures indicates that the fcc structure becomes unstable with respect to the hcp structure.

It is known that in fcc metals, stacking fault (SF), twinning (TW), and full-slip (SL) are important plastic deformation modes [41]. Previous work indicated that the preferred mode is decided by the competition between the corresponding effective energy barriers (EEBs) [42], i.e. \( \tilde{\gamma}_{\text{SF}} = \gamma_{\text{usf}}/\cos \theta \), \( \tilde{\gamma}_{\text{TW}} = (\gamma_{\text{utf}} - \gamma_{\text{isf}})/\cos \theta \), \( \tilde{\gamma}_{\text{SL}} = (\gamma_{\text{usf}} - \gamma_{\text{isf}})/\cos(60^\circ - \theta) \). Here, \( \tilde{\gamma}_{\text{SF}}, \tilde{\gamma}_{\text{TW}} \), and \( \tilde{\gamma}_{\text{SL}} \) denote the EEBs of SF, TW, and SL, respectively, and \( \theta \) measures the angle between the stacking fault easy direction \((11\bar{2})\) and the applied resolved shear stress \((0^\circ \leq \theta \leq 60^\circ)\). The activated deformation mechanism is decided by the lowest EEBs. For example, TW is preferred over SF when \( \tilde{\gamma}_{\text{TW}} < \tilde{\gamma}_{\text{SF}} \), which should be characteristic for metals showing twinning-induced plasticity.
(TWIP) effect. In Figure 3(a), we present the calculated EEBs of the ferromagnetic and paramagnetic FeCrCoNi at 300 K as a function of $\theta$. We notice that the actual value of $\theta$ does not influence the competition between TW and SF, while at high angle SL mode can always be activated. In the following, we show $({\bar{\gamma}}_{SF} - {\bar{\gamma}}_{TW}) \equiv {\bar{\gamma}}_{SF}(0^\circ) - {\bar{\gamma}}_{TW}(0^\circ)$ for the sake of simplicity, and do not always mention SL when discussing the SF and TW modes.

Some typical multi-component alloys with excellent mechanical properties are reported to be thermodynamically unstable at ambient and cryogenic conditions \cite{4,5,31-35}. Since twinning is recognized as an important deformation mode behind the simultaneous increase of strength and ductility in these alloys, Huang et al. introduced a mechanism of metastable twinning (MTW) based on the stacking fault energies and related intrinsic materials parameters \cite{35}. It was shown that the condition of MTW reads $\delta < \gamma_{slf}/2 < \sigma^*$, where $\sigma^*$ is the pseudo-interfacial energy between the hcp embryo and the fcc matrix \cite{43}, and $\delta \equiv \gamma_{slf} - \gamma_{suf} - \gamma_{slf}/2$ expresses the deviation relative to the so-called universal scaling law \cite{44}. Notice that MTW can only be realized when $\delta - \sigma^* < 0$, and alloys with $(\gamma_{slf}/2 - \delta) < 0$ and $(\gamma_{slf}/2 - \sigma^*) > 0$ represent SF and normal TW, respectively.

The deformation mode is sensitive to the shearing condition in some metastable alloys \cite{35}. The beneficial effect of strain on the twinnability is also mentioned in connection with the empirical deformation maps \cite{41}. We notice that two different types of deformations (alias and affine) have been used in the theoretical investigations \cite{6,45}. For the alias shear, only half of the crystal is displaced in the shearing direction, and the corresponding energy-displacement curve is the $\gamma$-surface, as shown in Figure 1. For the affine shear, all atomic planes are shifted parallel to the shearing direction. In order to illustrate the shearing effect, here we combine these two deformations in the following way: affine shear is applied first in elastic deformation regime, and then alias shear occurs when the critical strain is reached. The shear strain is given by $|\vec{x}|/h$, where $\vec{x}$ is the displacement of the end point of the lattice vector $\vec{c}$ along the Burgers vector, and $h$ is the corresponding interlayer spacing.

Figure 3(b) presents the critical MTW parameters $({\gamma}_{slf}/2 - \sigma^*)$ and $(\delta - \sigma^*)$ of the ferromagnetic and paramagnetic FeCrCoNi at 300 K as a function of affine shear strain. It is found that at the ferromagnetic state, SF is the active deformation mode in the low-strain region, and MTW becomes favorable with increasing the affine shear strain. On the other hand, the paramagnetic FeCrCoNi satisfies the MTW condition at all strains from the figure and thus it is prone to MTW. Extending the above study to FeCrCoNiAl$_x$ ($0 \leq x \leq 0.3$), as shown in Figure 4(a), indicates that SF or MTW can appear at 300 K within the certain composition and magnetic state.

Figure 4(b) presents the composition, temperature, and strain-dependent $({\bar{\gamma}}_{SF} - {\bar{\gamma}}_{TW})$ of the ferromagnetic and paramagnetic FeCrCoNiAl$_x$, respectively. We recall that $({\gamma}_{slf}/2 - \sigma^*) < 0$ implies a thermodynamically unstable fcc phase. Accordingly, normal TW happens only in a high-Al content system or at high temperature (not shown). Within the considered composition and temperature ranges, the MTW (SF) mode occurs with increasing (decreasing) Al content, temperature, and strain, since $({\bar{\gamma}}_{SF} - {\bar{\gamma}}_{TW})$ is positive (negative) in the right-higher (left-lower) corner of the map. Particularly, magnetism plays an important role in determining the favored deformation mode. For example, the equiatomic FeCrCoNi is predicted to show SF instead of MTW if the alloy remains in the ferromagnetic state at room temperature. The present theoretical results are helpful to explore
alternative ways to tune the plastic flow mechanisms in engineering materials involving HEAs.

The TWIP effect was indeed observed in the considered HEAs at various deformation conditions in experimental, and it was suggested to be the main reason for the measured large work hardenability [10–15]. In addition, smaller twin spacing and larger twin thickness were reported in the as-cast alloy compared with the recrystallized one, i.e. large grain size results in a high twinning activity [13]. Here, we would like to highlight this interesting experimental fact which now gains theoretical support in the mirror of the present data. For example, MTW is predicted in the paramagnetic FeCrCoNiAl$_x$ ($0 \leq x \leq 0.3$) at 300 K, which has a Curie point far below room temperature. The good agreement between theory and experiment demonstrates the validity of evaluating the deformation mechanism based on the above criteria.

The combined increase in strength and ductility observed in the recently developed HEAs broadened the palette of advanced metallic materials. A theoretical understanding of the underlying plasticity mechanisms is therefore important for the optimal design and use of these new alloys. In this study, we have investigated the composition and temperature dependence of the generalized stacking fault energy for the ferromagnetic and paramagnetic FeCrCoNiAl$_x$ ($0 \leq x \leq 0.3$) HEAs using quantum mechanical first-principle methods. The activation of plastic deformation mechanisms is analyzed by the effective energy barriers in connection with a transparent atomic-level theory of the metastable twinning mechanism. The observed TWIP effect is discussed, and the strain condition exhibits a positive effect on the twinnability. Theory predicts that the TRIP phenomena become the favored deformation mode in low-Al content system and at cryogenic conditions. The disclosed behavior of the present HEAs demonstrates that a proper control of the magnetic state offers a way to identify alloys with a change in the main activated plastic deformation modes, which can facilitate the design and optimization of alternative HEAs with desired strength-ductility combinations.

Disclosure statement

No potential conflict of interest was reported by the authors.

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