

Ab initio simulation of alloying effect on stacking fault energy in fcc Fe



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ABSTRACT

The effect of 3d and 4d transition metal (TM) additions on the intrinsic stacking fault energy (SFE) in fcc Fe is studied to elucidate the role of alloying in the deformation mechanisms in austenitic steels. The results of ab initio calculations reveal that only Mn reduces the SFE, stabilizing the local hcp structure, whereas all other *d*-additions are expected to decrease the hcp → fcc transformation temperature and restrain the ϵ -martensite formation. We predict a parabolic dependence of SFE on the atomic number of *d*-element across the series, with the largest increase in SFE obtained for the early and late elements in the *d*-series that follow the difference in the valence electrons between the TM and Fe atoms. To understand the SFE behavior in fcc Fe alloys, the driving forces for the fcc to hcp phase transformations of transition metal X and solid solution Fe–X were considered with an ab initio approach. It is found that the solution model explains the SFE trends for all TM additions except the late TMs with fully occupied *d*-shells (Cu and Ag).

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1. Introduction

The active deformation mechanism in austenitic steels is controlled by the stacking fault energy (SFE). The intrinsic stacking fault energy plays an important role in the formation of deformation twins and ϵ -martensite allowing either twinning induced plasticity (TWIP) or transformation induced plasticity (TRIP) to respectively occur. TRIP was shown to be the dominant mechanism in steels with a low SFE, less than 20 mJ/m², whereas TWIP is associated with a medium SFE of about 15–35 mJ/m² [1]. To enable the TRIP mechanism, the intrinsic stacking fault should be stabilized with respect to austenite through a decrease in SFE, which may be achieved by altering alloy chemistry, temperature, and strain.

The effect of transition metal elements on SFE – either as alloying additions or residual elements – is of concern for alloy development since these additions may significantly alter SFE and therefore affect the active deformation mechanism [2–4]. The SFE values of multicomponent systems are often considered to be proportional to the Gibbs free energies of the fcc to hcp transformation within a regular solution model with estimated parameters from experimental thermodynamic data. These estimations have been made for the Fe–Mn–C and Fe–Mn–Al–Si–C alloys [1,5–7]. For

Mn additions, a parabolic behavior was calculated with an SFE minimum at 12 at.% [8], 15 at.% [9], or 22 at.% Mn [10].

Ab initio methods have been employed to determine the stacking fault energies following both explicit and implicit approaches. The SFE may be explicitly calculated as a total energy difference between the ideal and faulted lattices. This explicit approach has been used to predict the SFE in nonmagnetic Fe [11,12], as well as Fe–N [13], Fe–C [12,14], Fe–Mn and Fe–Al [12] alloys. An implicit ab initio approach to calculate SFE has also been used recently following the axial next-nearest-neighbor Ising (ANNNI) model, where the energies of the fcc, hcp and double hcp phases are calculated to determine SFE of the fcc phases in the Fe–Mn system [15–17]. The implicit approach allows for a more homogeneous description of the bulk environment whereas the explicit calculations provide a more complete understanding of segregation effects as well as the electronic structure changes at the stacking fault [14].

In this study, a first-principles approach was employed to describe the effects of 3d and 4d transition metal alloying additions on the stacking fault energy in fcc Fe. The objective of this work was to contribute towards a systematic understanding of the correlation between composition and stacking fault energy in austenitic steels. Our strategy was to obtain the SFE from the explicit ab initio simulation of stacking fault defect and to predict how additions can affect stabilization of austenite or ϵ -martensite. Furthermore, we applied ab initio estimations within a regular solution model in order to find the correlations with the phase transformations. To analyze the calculated trends in SFE, we estimated the

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driving forces for the fcc to hcp transformations of the 3d or 4d transition metal X and solid solution Fe–X.

2. Method

The total-energy calculations were performed with the Vienna ab initio Simulation Package (VASP) [18], using projector augmented waves (PAW) [19,20] and the generalized gradient approximation (GGA) for exchange correlation functional [21]. Calculations were performed on a 24-atom supercell consisting of six (111) layers, where one of four Fe atoms in the stacking fault plane was substituted for alloying addition. This supercell has been shown sufficiently large to remove interference effects across the layers [12,13]. The supercell configuration corresponds to the impurity concentration of 25% in layer and 4% in bulk. A $6 \times 6 \times 4$ Monkhorst–Pack mesh was used for 24-atom supercell to generate k -points with convergence in the total energy within 0.02 eV/atom.

Stacking fault energy was calculated via the total energy difference between undistorted lattice and sheared lattice. The latter was simulated by a rigid shift along the $\langle 112 \rangle$ direction in the (111) slip plane that corresponds to the partial Burgers vector in fcc structure, $b_p = 1/6 \langle 112 \rangle \{111\}$. Atomic positions were relaxed in the direction normal to the stacking fault plane until the atomic forces were less than 0.02 eV/Å. In this work, we restricted the explicit calculations of SFE to the nonmagnetic Fe state, following previous investigations [11,12] where similar SFE values were obtained for the ferromagnetic and nonmagnetic states in Fe and Fe–Mn. The stacking fault energy for fcc Fe–X was calculated for the substitutional X addition which was placed at the stacking fault plane. Recent works have shown that SFE decreases linearly as the substitutional point defect is moved from the stacking fault region into the bulk, with the effects absolved upon reaching a depth of two layers from the stacking fault [12,14].

In order to analyze the trends in SFE, a regular solution model was employed, where the driving forces for the fcc to hcp phase transformations of transition metal X and solid solution Fe–X were calculated ab initio.

3. Results & discussion

For pure fcc Fe in nonmagnetic state, we predict the SFE value to be -390 mJ/m^2 which is in agreement with the values obtained from previous explicit ab initio calculations [11–14]. For fcc Fe–X, the calculated stacking fault energies demonstrate a parabolic dependence on the atomic number of d -impurity across the series (Fig. 1a). The calculated SFE values do not follow the atomic size misfit between the impurity and Fe atoms, but rather appear to have an electronic origin correlated with the difference in the number of valence electrons of Fe and the substitutional addition. The 3d- and 4d-additions which have the same number of valence

electrons (e.g., Ru) or 1–2 fewer (e.g., Cr, Mn, or Tc) as compared to that of Fe, slightly affect the SFE, Fig. 1a. In contrast, the additions with a larger or much smaller number of valence electrons than that of Fe increase the SFE strongly. Only Mn addition is found to lower the SFE to $\sim 20 \text{ mJ/m}^2$, indicating a stabilization of hcp over fcc structure for the considered concentration of 4 at.%Mn in the fcc Fe–Mn alloy.

The crystal structure of alloying elements (hcp for Ti, Zr, Co, Tc, and Ru; bcc for V, Cr, Nb, and Mo; or fcc for Ni, Cu, Pd, and Ag) does not correlate with the obtained SFE trends. Moreover, the calculated energy difference between fcc and hcp structures, $\Delta E^{\text{hcp} \rightarrow \text{fcc}}$, for the 3d and 4d transition metals, Fig. 1b, is also a poor predictor of the trends in the SFE obtained in the explicit calculations. Based on the nonmagnetic values of $\Delta E^{\text{hcp} \rightarrow \text{fcc}}$, which are in agreement with previous nonmagnetic results obtained by the tight-binding method [22], the fcc structure is more stable for the transition metals with a larger number of valence electrons than Fe as well as for V, Cr, Nb, Mo, while the hcp structure is preferred by Ti, Zr, Mn, Fe, Tc, Ru. Thus, the beginning elements in the d -series (Ti and Zr) demonstrate a strong preference to have hcp structure, Fig. 1b, however, they provide the largest increase in the SFE (Fig. 1a).

The trends obtained within the explicit SFE calculations were further analyzed using the proportionality of the SFE and the Gibbs energy. The Gibbs free energy associated with the phase transformation from fcc to hcp (ΔG) is an indicator of the thermodynamic driving force for stacking fault creation [23]. In this study we estimate the driving force within the framework of a regular solution model as shown in the following equation:

$$\Delta G^{\text{hcp} \rightarrow \text{fcc}} = c_{\text{Fe}} \Delta E^{\text{hcp} \rightarrow \text{fcc}}(\text{Fe}) + c_{\text{X}} \Delta E^{\text{hcp} \rightarrow \text{fcc}}(\text{X}) + c_{\text{Fe}} \cdot c_{\text{X}} \Delta E^{\text{hcp} \rightarrow \text{fcc}}(\text{Fe}_{c_{\text{Fe}}} \text{X}_{c_{\text{X}}}) \quad (1)$$

where c_{Fe} and c_{X} are the concentrations of Fe and X in the Fe–X alloy, respectively.

The value of $\Delta E^{\text{hcp} \rightarrow \text{fcc}}$ for solid solution Fe–X (Fig. 2a) was estimated as a total energy difference between the hcp and fcc structures of $\text{Fe}_{0.75}\text{X}_{0.25}$ with volumes equal to fcc Fe. The concentration of X in this configuration exactly corresponds to those at the stacking fault plane in our explicit calculations. We find that the $\Delta E^{\text{hcp} \rightarrow \text{fcc}}$ values are positive and largest for the elements in the beginning of each period with the maximum values corresponding to Ti and Zr that have hcp structure. The elements with the same or greater number of the valence electrons as Fe (Co, Ni in 3d-series, and Rh, Pd in 4d-series) as well as Mn provide almost equal $\Delta E^{\text{hcp} \rightarrow \text{fcc}}$. The strongest preference to have hcp structure is obtained for $\text{Fe}_{0.75}\text{X}_{0.25}$ where X is TM with the filled d -states (Cu, Ag) Fig. 2a.

The total $\Delta G^{\text{hcp} \rightarrow \text{fcc}}$ values calculated according to Eq. (1) are shown in Fig. 2b. We find that the $\Delta G^{\text{hcp} \rightarrow \text{fcc}}$ curves correlate with the parabolic dependences of SFE (Fig. 1a) for all additions except for the end elements in the 3d and 4d series (Ni, Cu, Pd, and Ag). Based on the results of $\Delta E^{\text{hcp} \rightarrow \text{fcc}}$ for transition metals (Fig. 1b)

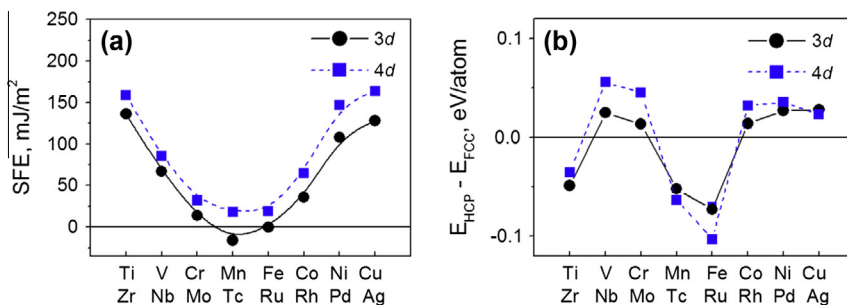


Fig. 1. (a) The calculated stacking fault energies for fcc Fe–4 at.%X with respect to fcc Fe and (b) the energy difference between the hcp and fcc structures for transition metals X.

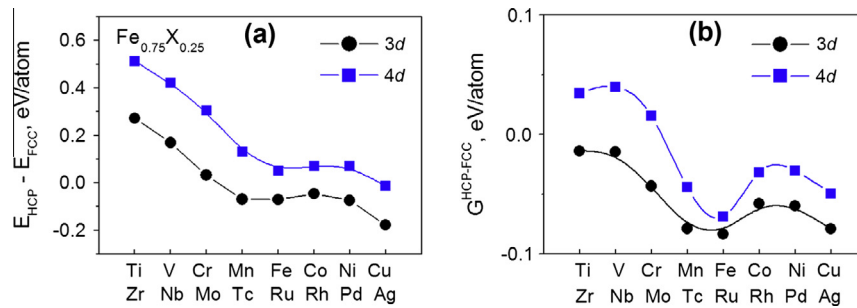


Fig. 2. The energy difference between the hcp and fcc structures for (a) solid solution $\text{Fe}_{0.75}\text{X}_{0.25}$ and (b) total $G^{\text{hcp-fcc}}$ (c.f., Eq. (1)).

and solid solutions (Fig. 2a), we conclude that the energy difference between the hcp and fcc structures of solid solution determines the SFE for the early elements (Ti, Zr), whereas the structural stability of transition metal is important for Fe alloys with the late additions. Thus, the dependence of stacking fault energy in fcc Fe alloys on the atomic number of d -alloying impurity can be explained using simple model calculations. An exception is additions X with the filled d -states for which the Fe–X alloy demonstrates a strong preference to hcp structure. Furthermore, the calculations of $\Delta E^{\text{hcp} \rightarrow \text{fcc}}$ for $\text{Fe}_{1-x}\text{Cu}_x$, where $x = 0.25, 0.5, 0.75, 1.0$ showed that fcc structure is favorable over hcp only for $x = 1.0$.

4. Conclusions

In summary, first-principles method was employed to examine the effects of alloying elements on stacking fault energy of fcc iron. A parabolic behavior of the SFE across the periods for 3d and 4d alloying elements was obtained. We predict that all transition metal additions except manganese increase SFE and the increasing effect correlates with the difference in the number of valence electrons of TM and Fe atoms. Thus, all TM additions except Mn should decrease the hcp \rightarrow fcc transformation temperature and restrain the ε -martensite formation. The driving forces for the fcc to hcp phase transformations of transition metal X (X = 3d and 4d elements) and solid solution Fe–X were analyzed using a regular solution model. The stacking fault energies calculated explicitly for fcc Fe–X are in accord with the trends in solution model, with the exception for transition metal additions with the filled d -states.

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