



First-principles study of phosphorus embrittlement in austenitic steels with κ -carbide precipitates



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ABSTRACT

Ab initio density functional theory calculations were performed to study the effect of phosphorus on the structural, electronic, and magnetic properties of bulk, surface, and interface of κ -carbide (Fe_3AlC) and fcc Fe. The aim was to shed light on the role of phosphorus in austenitic steels with κ -carbide particles, where its presence promotes both intergranular and transgranular embrittlement. The embrittling potency energy calculated as a difference between phosphorus binding energies at the Fe_3AlC or fcc Fe surfaces and at $\text{Fe}_3\text{AlC}/\text{Fe}$ interface, indicates that phosphorus promotes embrittling behavior. Phosphorus at the interface has negative segregation energy which strongly depends on the phosphorus location as well as its concentration. The calculated cleavage energy decreases sharply for κ -carbide with substituted phosphorus as well as for the interface with segregated phosphorus; both contribute to the embrittlement. These results elucidate the microscopic reasons why phosphorus favors crack nucleation in κ -carbide, and why a crack propagates along the boundary between κ -carbide and austenite.

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1. Introduction

Carbide-strengthened steels are currently of great interest for many applications including automotive, oil and gas line pipe, aerospace, defense, and nuclear industries – owing to a higher strength and lower density as compared to conventional steels. Among nanostructured steels with extraordinary strength, the high aluminum Fe-Al-C and Fe-Mn-Al-C steels (9–12 wt.% Al) are of particular interest because they exhibit a low density, high strength to 1100 MPa, superior ductility (total elongation more than 70%), excellent formability, and a high energy absorption capacity. The ultimate tensile strength and enhanced ductility in these austenitic steels are due to the homogenous precipitation and dispersion of nano-sized Fe_3AlC known as κ -carbide [1–7]. The fine precipitation of κ -carbide was considered as the main reason for strengthening in Fe-Mn-Al-C steels. There is a correlation between toughness decrease and phosphorus content in Fe-Mn-Al-C steels with κ -carbide particles, where the ductile-to-brittle transition occurs above the room temperature for P concentration of $\sim 0.04\%$ [8,9]. Cracks usually start in κ -carbide and propagate along the boundary between κ -carbide and austenite [8–10].

Phosphorus has been known to reduce toughness and ductility in steels due to grain boundary embrittlement which occurs when the resistance to plastic deformation is comparable with the stress required for separation at the boundaries. The mechanism of phosphorus embrittlement is well studied theoretically in bcc Fe [11–14] where phosphorus was shown to have a very low solubility in the bulk and a strong tendency for segregation at grain boundaries. Segregation of an impurity depends on its solubility in bulk as well as its interaction with a surface or a grain boundary [15]. Impurities at grain boundaries may either have a strengthening effect or result in decohesion which promotes intergranular brittleness. The embrittling potency of impurity is described by a difference in its energies at free surface (FS) and a grain boundary (GB). This approach is based on the Rice-Wang model [16] where these energies are used to describe a competition between brittle separation and dislocation blunting at interfacial crack.

In this paper, we present *ab initio* studies of phosphorus in the bulk of κ -carbide and fcc Fe, at (001) Fe_3AlC and (001)Fe surfaces, and at the (001) $\text{Fe}_3\text{AlC}/(001)\text{Fe}$ interface. Based on the results of density functional calculations, we predict the energetically favorable sites of phosphorus in bulk, at surfaces and at the interface, and study the phosphorous effect on the structural, electronic, and magnetic properties of these structures. Since a direct modeling of phosphorus at grain boundaries is beyond the framework of this study, we attempt to elucidate the role of phosphorus in

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fracture by comparing the binding energies for phosphorus at surfaces and interface. This approach is appropriate since κ -carbide is coherent with austenite and crack propagates along the boundary between the carbide and austenite. We calculated the segregation and cleavage energies for different phosphorus concentrations in interfacial region and discussed the phosphorus effect on fracture.

2. Computational details

All calculations were performed within the Vienna *Ab Initio* Simulation Package (VASP) using the projector-augmented wave (PAW) method [17,18] and the Perdew-Burke-Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA) for exchange-correlation functional [19]. We used a kinetic-energy cutoff of 350 eV and the k-point sampling that gets the converged total energies within 0.01 eV/cell. The first-order Methfessel–Paxton scheme [20] with a smearing parameter of 0.2 eV was chosen for integration over k-points. Ternary carbide Fe_3AlC has crystal structure $E2_1$ which is closely related to $L1_2$ (Fe_3Al), where carbon occupies the central octahedral position relative to iron atoms [21,22]. The P substitutions in the Al (P^{Al}), Fe (P^{Fe}) and C (P^{C}) positions of κ -carbide were modeled using a 40-atom ($2 \times 2 \times 2$) supercell ($\text{Fe}_{24}\text{Al}_8\text{C}_8$). The total energies of Al (fcc), Fe (bcc), C (graphite) and P (rhombohedral black phosphorus) were taken as references. The substitutional and interstitial phosphorus in fcc Fe was simulated with a 32-atom supercell. As shown in prior numerous studies of impurities and vacancies in κ -carbide as well as in bcc Fe and fcc Fe [23–27], the size of chosen supercells is sufficient to predict correctly the positions and formation energy of defects.

Fcc Fe is paramagnetic within the temperatures of thermodynamic stability from 1184 to 1665 K, whereas the ground state is non-collinear as demonstrated in the experimental [28,29] and theoretical [30–32] studies. In our calculations, we choose the ferromagnetic high-spin (FM/HS) state which has the largest lattice constant 3.65 Å [26,33] among the collinear magnetic structures of fcc Fe (FM/LS, FM/HS, AFM, AFMD) and, hence, provides a better match between Fe_3AlC and fcc Fe. The FM/HS state was also used to study carbon diffusivity [34] and stacking fault energies in fcc Fe [27] as well as the phase transformations among austenite, ferrite and cementite [35]. In [35], the authors refer to the presence of FM ordering near carbon interstitials [25,26] as well as to the increasing volume and tetragonality in fcc Fe [36] to support the argument. In addition, the FM state provides a good convergence of the electronic self-consistent calculations for austenite/ferrite and austenite/cementite interfaces [35].

The conjugate-gradient method implemented in VASP, was used for structural optimization. Both the lattice parameter and the atomic coordinates were relaxed for the Fe_3AlC and fcc Fe bulk with P until the forces on all atoms were less than 0.02 eV/Å. To estimate the interaction between two P atoms in bulk, we calculated the binding energies as $E_b(\text{P},\text{P}) = E(2\text{P}) - 2 E(\text{P}) + E_{\text{ref}}$, where $E(\text{P})$ and $E(2\text{P})$ are the energies of supercells with one and two P atoms, and E_{ref} is the energy of supercell without P atoms [37]. The negative and positive binding energies correspond to attractive and repulsive interactions between P atoms, respectively.

The (001) Fe_3AlC and (001)Fe surfaces were modeled by the repeated supercells with 12 layers (1×1) separated by 10 Å vacuum in the direction perpendicular to surface (Fig. 1). Our calculations of cleavage in κ -carbide [38] showed that this separation is sufficient to consider the two slabs as non-interacting parts. *Ab initio* modeling of the bcc and fcc Fe surfaces as dependent on the number of layers in the supercell, showed [39] that the surface energy converges properly for slabs with more than 6 atomic layers. The optimized lattice parameters of Fe_3AlC and fcc Fe were used as the lateral dimensions, whereas all atoms were

allowed to relax in perpendicular direction to the surface until all atomic forces were smaller than 0.02 eV/Å. The same supercell was used for simulation of P atom on the surface, where one P atom was located over the Fe, Al or C sites or interstitial surface octa-sites (denoted by Fe-top, Al-top or C-top and octa-site). The binding energy of phosphorus at the different sites on the surface was calculated relative to free (001)Fe and (001) Fe_3AlC with non-interacting P atom; and both Al-terminated (S^{Al}) and carbon-terminated (S^{C}) κ -surfaces were considered.

The high ductility and hardening in Fe–Mn–Al–C alloys are realized when κ -carbide has a cube-on-cube orientation relationship with the austenitic matrix: $\{001\}_{\kappa} \parallel \{001\}_{\gamma}$. The lattice parameters of κ -carbide (fcc-type structure) and fcc Fe (FM/HS state) are very close and, hence, their interface may be considered as coherent. The (001) $\text{Fe}_3\text{AlC}/(001)\text{Fe}$ interface was modeled by a supercell consisting of 8 layers of Fe_3AlC and 8 layers of fcc Fe, where the formation of both $\text{S}^{\text{Al}}/\text{P}/\text{Fe}$ and $\text{S}^{\text{C}}/\text{P}/\text{Fe}$ was taken into account. The lateral lattice parameter and all atomic coordinates were relaxed. For the (001) $\text{Fe}_3\text{AlC}/\text{P}/(001)\text{Fe}$ interface, the binding energies of phosphorus in the interstitial and substitutional sites at the interface were calculated relative to free interface with a non-interacting P atom; again, the formation of both $\text{S}^{\text{Al}}/\text{P}/\text{Fe}$ and $\text{S}^{\text{C}}/\text{P}/\text{Fe}$ was taken into account.

The embrittling potency of phosphorus is described by the difference in the total energies of the structures with phosphorus at grain boundary (GB) and free surface (FS). A negative embrittling potency energy $E_{\text{ep}} = E_{\text{GB}} - E_{\text{FS}}$ indicates the enhancement of the GB cohesion, while a positive value points out embrittlement induced by phosphorus. In addition, the segregation energy of phosphorus at the $\text{Fe}_3\text{AlC}/\text{Fe}$ interface was calculated as an energy gain with respect to the inner bulk positions (we take the lowest solution energy of phosphorus in the bulk as a reference). Finally, to verify our conclusions, we estimated the cleavage energy for P-free interface and the one with different P concentration in the interfacial region, and compared it with the corresponding value for κ -carbide. The cleavage energy was determined as the energy required to split a system into two non-interacting parts. Here, we refer to our previous work [38] for computational details of cleavage characteristics.

3. Results and discussion

3.1. Phosphorus in bulk Fe_3AlC

For Fe_3AlC , we obtained a ferromagnetic ground state with the lattice parameter 3.753 Å, which is close to the experimental value 3.78 Å [22] and previous theoretical results 3.75–3.78 Å [40–42]. The density of states (DOS) shows (Fig. 2) that the $\text{C}2s,2p$, $\text{Al}3s,3p$ and $\text{Fe}3d$ states give the contributions below -4 eV, whereas the $\text{Fe}3d$ states are dominant for higher energies. The iron magnetic moment in Fe_3AlC is reduced to 1.10 μ_{B} compared with those in bcc Fe and Fe_3Al ($\sim 2 \mu_{\text{B}}$ [26,33,41–43]), where the occupation of the $\text{Fe}3d^{\uparrow}$ states is much larger than that of the $\text{Fe}3d^{\downarrow}$ states.

The lowest substitution energy, 0.67 eV, was obtained for phosphorus substituted in the Al position (P^{Al}), whereas the Fe (P^{Fe}) and C (P^{C}) sites are less favorable for phosphorus (2.40 eV and 1.22 eV, respectively). The P^{Al} substitution does not significantly change the occupancies of the $\text{Fe}3d^{\uparrow}$ and $\text{Fe}3d^{\downarrow}$ states (Fig. 3a) and only slightly reduces the magnetic moment of the nearest iron atoms from 1.10 to 0.92 μ_{B} . An increased phosphorus concentration in κ -carbide was modeled by two substitutional P atoms in the nearest (n) and next nearest (nn) Al sites. We find that the two P atoms prefer to be in the n positions with the energy gain of 0.16 eV compared to the nn sites. Thus, the P atoms prefer to occupy positions corresponding to short-range order of $L1_2$ -type and phosphorus

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