Ab initio study of Fe adsorption on the (001) surface of transition metal carbides and nitrides

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ABSTRACT

Understanding the iron adsorption on the surface of particles is important to predict their nucleation activity and find efficient precipitates. Ab initio calculations of adsorption energy for Fe on the (001)MX surface (M = Ti, V, Nb, Zr, Hf or Ta and X = C or N) were performed to study the initialization of Fe nucleation. We find that the trends in Fe adsorption as dependent on the M and X atoms do not follow the lattice parameter or surface energy of MX, but are closely related to the number of the M and X valence electrons. The strongest binding was predicted for Fe on (001)NbC, and this carbide should have the high nucleation potential at early stage that is consistent with the observed grain refinement of ferritic and austenitic steels with NbC. In order to establish the alloying effect, we studied the adsorption of 3d atoms (M = Ti, V, Cr, Mn, Co, and Ni) on (001)NbC and concluded that Cr and Mn may compete with Fe in adsorption. The calculations of Fe adsorption on the NbC surface covered with 3d atoms demonstrated that the initial layer of the Cr or Mn atoms enhances the subsequent Fe adsorption.

1. Introduction

High strength of many modern steels is achieved by the dispersed precipitates, which significantly increase the yield strength and resistance to brittle fracture. Strength and ductility of these steels depend on composition, stability, and distribution of particles, as well as their interaction with iron matrix. The improved mechanical properties may be also achieved by the grain refinement of solidification structure. The transition metal (TM) carbides and nitrides were suggested as the possible effective sites for promoting the heterogeneous nucleation in iron melt \[1–7\]. To describe the nucleation in solidified alloys, the several models were developed, in which surface energies, lattice misfit or wetting angle between particle and matrix are applied as a criterion for nucleation activity \[8,9\]. The effective nucleation is believed to occur with the low interfacial energy between precipitate and matrix. The interfacial atomic structures and energies have been intensively studied for Fe/TiN \[10\], Fe/TiC \[10,11\], Fe/VN \[12–14\], Fe/NbC \[15\], Co/TiC(TiN) \[16\]. The trends in interfacial energies for transition metals M were predicted for both coherent and semi-coherent interfaces between bcc Fe and MX \[17,18\], as well as between fcc Fe and MX \[19\], where M = Ti, V, Nb, Zr, Hf or Ta and X = C or N. According to these calculations, VC and NbC demonstrate the lowest interfacial energies.

The beginning of nucleation during solidification was suggested as an easily controllable process \[20,21\], where the activity of precipitate is related to the adsorption capability of Fe atoms. Ab initio calculations of the Fe adsorption on the (001)TiN surface were performed to understand the nucleation mechanism of Fe on the TiN particles \[22\]. These calculations demonstrated that adsorption energy is a reliable parameter to describe a first stage of nucleation and the knowledge of adsorption properties of carbides and nitrides is important to predict the efficient precipitates in steel. However, no systematic calculations have been carried out to study the Fe adsorption on the MX surface as dependent on the type of transition metal M and non-metal element X.

In this article we present the theoretical study of possible particles – transition metal (TM) carbides and nitrides MX (M = Ti, V, Zr, Nb, Hf or Ta and X = C or N) through the simulation of Fe adsorption on the (001)MX surface. The goal was to find how the Fe adsorption varies from MC to MN and how it depends on transition metal as well as the Fe concentration on surface. The alloying impurities added for improving properties of steel may also influence the Fe adsorption. Here we investigate the adsorption of 3d-atoms (Ti, V, Cr, Mn, Co, and Ni) on the MX surface and establish if they compete with Fe at the initial stage. Segregation of

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impurities on surface may favor nucleation, as occurs in the Al alloys with TiB_2 particles [23]. In order to find how the segregated impurities may affect the subsequent Fe adsorption, we study the iron adsorption on the $MX_{2}\textsuperscript{d}$ surface covered with 3$d$ TMs.

### 2. Computational details

We employed the Vienna ab initio simulation package (VASP) with projector augmented waves (PAW) for pseudopotentials [24,25] and generalized gradient approximation (GGA) [26] for the exchange–correlation functional. All TMs carbides and nitrides were considered with a rocksalt structure and a 16\slash C2\textsuperscript{16}/C2\textsuperscript{16} k-point mesh was used to find the equilibrium lattice parameter of $MX$ bulk. The plane-wave cutoff energy was set to 500 eV for all configurations. The surface calculations were performed for the (001) face, which has the lowest surface energy ($c\textsubscript{100} < c\textsubscript{110} < c\textsubscript{111}$) and is the most stable in many rocksalt-type carbides and nitrides [27]. The (001)MX surface was simulated by a 24-atom slab consisting of 12 atomic planes separated by 10 Å in vacuum. For these calculations, a 10 \times 10 \times 4 k-point mesh was used. The surface energy was calculated as $\gamma_s = (E_{\text{slab}} - n \times E_{\text{bulk}})/2$, where $E_{\text{slab}}$ and $E_{\text{bulk}}$ are the n-layer slab and bulk total energies. As shown [28], this approach provides $\gamma_s$ with a good accuracy if $n \geq 8$. For simulation of Fe adsorption on (001)MX, we used the 16-atom and 32-atom MX slabs consisting of eight atomic planes with two and four atoms in every plane that corresponds to the Fe monolayer (ML) covering of 1ML Fe and 0.5ML (per carbon atom in plane). These configurations were studied on a mesh of 10\slash C2\textsuperscript{10}/C2\textsuperscript{4} and 6\slash C2\textsuperscript{6}/C2\textsuperscript{4} irreducible k-points, respectively. The calculated lattice parameter of MX was chosen as a lateral size and all atoms were allowed to relax until the atomic forces were smaller than 0.01 eV/Å. The adsorption energy $W_{\text{ad}}$ which describes the interaction between adsorbed atoms and MX surface was estimated from a dependence of total energy on the separation distance between the (001)MX surface and the Fe layer. The calculations of $W_{\text{ad}}$ for Fe on C-top of (001)NbC showed that a distance of 4 Å is enough to consider the surface and Fe atoms to be non-interacting and this separation was used for all configurations. For NbC, which demonstrates the strongest binding with adsorbed Fe, the effect of 3$d$ alloying impurities (Ti, V, Cr, Mn, Co, Ni) was studied with the 16-, 32- and 64-atom supercells to reveal the $W_{\text{ad}}$ dependence on impurity concentration on (001)NbC. Finally, $W_{\text{ad}}$ was calculated for the NbC surface covered with the 3$d$ TM

### Table 1

<table>
<thead>
<tr>
<th>TMS</th>
<th>$a$ (Å)</th>
<th>$\gamma_s$ (m²)</th>
<th>$\delta_{M/X}$ (Å)</th>
<th>1ML Fe</th>
<th>0.5ML Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>4.3376</td>
<td>1.60</td>
<td>0.074/0.032</td>
<td>3.25</td>
<td>2.81/1.76</td>
</tr>
<tr>
<td>TiN</td>
<td>4.2557</td>
<td>1.29</td>
<td>0.108/0.072</td>
<td>2.95</td>
<td>2.73/1.77</td>
</tr>
<tr>
<td>VC</td>
<td>4.1533</td>
<td>1.38</td>
<td>0.077/0.038</td>
<td>3.64</td>
<td>2.87/1.75</td>
</tr>
<tr>
<td>VN</td>
<td>4.1184</td>
<td>1.07</td>
<td>0.110/0.072</td>
<td>2.87</td>
<td>2.79/1.78</td>
</tr>
<tr>
<td>ZrC</td>
<td>4.7238</td>
<td>1.58</td>
<td>0.082/0.031</td>
<td>3.60</td>
<td>2.91/1.75</td>
</tr>
<tr>
<td>ZrN</td>
<td>4.6083</td>
<td>1.39</td>
<td>0.125/0.073</td>
<td>3.51</td>
<td>2.82/1.80</td>
</tr>
<tr>
<td>NbC</td>
<td>4.5099</td>
<td>1.42</td>
<td>0.109/0.068</td>
<td>3.72</td>
<td>2.86/1.76</td>
</tr>
<tr>
<td>NbN</td>
<td>4.4537</td>
<td>1.55</td>
<td>0.117/0.172</td>
<td>2.97</td>
<td>2.79/1.77</td>
</tr>
<tr>
<td>HfC</td>
<td>4.6471</td>
<td>1.74</td>
<td>0.115/0.074</td>
<td>3.39</td>
<td>2.87/1.75</td>
</tr>
<tr>
<td>HfN</td>
<td>4.5331</td>
<td>1.60</td>
<td>0.118/0.219</td>
<td>3.44</td>
<td>2.80/1.76</td>
</tr>
<tr>
<td>TaC</td>
<td>4.4748</td>
<td>1.60</td>
<td>0.129/0.072</td>
<td>3.58</td>
<td>2.94/1.81</td>
</tr>
<tr>
<td>TaN</td>
<td>4.4145</td>
<td>1.24</td>
<td>0.146/0.270</td>
<td>2.92</td>
<td>2.75/1.86</td>
</tr>
</tbody>
</table>

a Theoretical values from [29].
b Experimental values from [30].
c Theoretical values from [28].
layer and the possible influence of these alloying elements on the following Fe adsorption is discussed. Here we present the nonmagnetic results, which simulate the initial process in melt.

3. Results

3.1. Surface properties of (001)MX

To demonstrate a reliability of our calculations, we present the equilibrium lattice parameters of TMs carbides and nitrides as well as their surface energies for the (001) face (Table 1). All TMs carbides have a larger lattice parameter than the corresponding nitrides. For all 3d, 4d, and 5d TMs carbides and nitrides, the lattice parameter decreases from Group IV to Group V and demonstrates a pyramid-shaped trend along each period with the largest values for ZrC and ZrN. These trends follow the atomic radius of TM across the periods. The calculated lattice parameters in agreement with the results of previous calculations and experimental data (Table 1). The difference between the optimized and experimental values is less than 0.2% for all MX compounds except of TaC and TaN, which are 0.4% and 0.7%, respectively. The overestimated lattice parameters of TaC and TaN were also predicted earlier [18,29].

The rocksalt-type carbides and nitrides have a tendency to be sub-stoichiometric MXy due to vacancies on the nonmetal sublattice (y is typically between 0.6 and 1.0 [30,31]) and should exhibit the reduced lattice parameters. The low homogeneity bound may reach 0.48 for TiC, whereas VC has an upper homogeneity bound of 0.88 [32]. However, the experimental dependence of lattice parameter on the stoichiometry of MXy is nonlinear and very small of 4.40 eV (3.72 eV) for the MX carbides and nitrides, respectively, compared to its surface position. The large energy gain predicts a strong preference for carbon vacancies to be away from the topmost surface layer. In order to establish how vacancies are distributed near surface, we performed calculations with a carbon vacancy in the first, second, and third surface layer. For carbon vacancy in the second surface layers, we performed calculations with a 151 atoms (31-atom supercell) and four (63-atom supercell) carbon atoms in defect-free layer. For carbon vacancy in the second layer and the possible influence of these alloying elements on the following Fe adsorption is discussed. Here we present the nonmagnetic results, which simulate the initial process in melt.

3.2. Fe adsorption on the (001)MX surface

First, we testify that the Fe atom prefers to be in the C-top position, but not above the M atom or bridge site, as was also obtained in [22] for Fe on (001)TiN. For example, our calculations for 0.5ML (1ML) of Fe on (001)NbC predict Wad of 4.40 eV (3.72 eV) for the C-top position, compared to 3.26 eV (2.38 eV) above the M atom and 3.97 eV (3.21 eV) for the bridge site. The adsorption energies calculated for the 1ML and 0.5ML of Fe in the X-top site on the (001)MX surface are shown in Table 1. The Fe atom is getting far from surface (both distances dFe-M and dFe-X increase) and adsorption is weaker with increasing Fe concentration in layer. Nevertheless, the main trends in Wad as dependent on M and X are similar for both 1ML and 0.5ML of Fe. For the Group IV TMs carbides, Wad increases from TiC to ZrC and decreases from ZrC to HfC. A similar trend exists for the Group V TMs carbides, where the maximum adsorption energy was obtained for NbC/NbN. The Group V TMs carbides show a stronger Fe adsorption than those of the Group IV TMs, while the opposite trend was obtained for nitrides. The adsorption energy may be compared with the work of separation of pure MX phases, which is equal to twice the surface energy. As seen (Table 1), our calculations predict the adhesion strength of Fe on (001)MX to be stronger than the intrinsic adhesion between the (001) planes in MX bulk as well as in bcc Fe (2.7 eV). Upon relaxation, we considered how adsorbed Fe affects the geometry of surface atoms (Table 1). For carbides and nitrides, the distance between the Fe and nearest M atoms (dFe-M) shows the pyramidal dependence with a maximum for ZrX and NbX within the Groups. The Fe–X distance (dFe-X) is less dependent on the transition metal and it is larger for nitrides. Comparing the interatomic distances for the pure and Fe covered MX surfaces, we find that the adsorbed Fe reduces the rippling and contraction of surface layers.

As seen in Table 1, a correlation between Wad and γs is absent. The surface energy depends on the hybridization of the Md and X2p orbitals, which correlates with the occupation of the bonding and antibonding states. The Group IV TMs carbides show the optimal filling and, as a result, have the largest cohesive strength. Adsorption properties are determined by the interactions between
Fe and the surface $M$ and $X$ atoms and related to the formation of both covalent $\text{Fe}3d$-$X2p$ and metallic $\text{Fe}$-$M$ bonds [18]. To understand why the iron adsorption is stronger when the number of valence electrons of TMs increases for carbides, but the opposite trend exists for nitrides, we considered the density of states (DOS) for $\text{Fe}3d$-orbitals ($\text{dxz}$, $\text{dyz}$, $\text{dz}^2$–$r^2$), which participate in bonding along $z$-direction (perpendicular to surface). The larger occupation and overlapping of these $d$-orbitals provide the stronger $\text{Fe}$–$M$ bonds.
interaction. When going from the Group IV TMs to the Group V TMs carbides (Fig. 2), the Fe3d occupation increases (by 0.17 e from TiC to NbC) resulting in a stronger Fe–M bonding. The increase in the number of valence electrons from carbide to nitride in the Group V TMs (from NbC to NbN) weakens the Fe adsorption due to the occupation of antibonding M–d–Np states. The Group IV TMs carbides and nitrides have close Wad, because the Fermi level remains in a pseudogap between the bonding and antibonding M–d–Np states (Fig. 2), despite the increased number of electrons from C to N. The previous ab initio calculations for bcc Fe/MX [17,18] and fcc Fe/MX interfaces [19] also predicted the larger negative interfacial energies for the Group V TMs carbides and nitrides, which is consistent with the Wad trends for Fe adsorbed on the (001)MX surface. Negative \( \gamma_{\text{M}} \) were obtained for the cohesive Fe/V, Fe/NbC and Fe/TaC interfaces with the lowest values for bcc Fe/NbC [17,18] and fcc Fe/VC [19]. In our calculations, Wad for Fe on (001)NbC has also an extreme value when compared to other (001)MC.

3.3. Transition metal adsorption on (001)NbC

Below, we choose NbC to study the possible effects of 3d-imipurities (M = Ti, V, Cr, Mn, Co and Ni) on the Fe adsorption during the initial stage of nucleation. First, we examine if the 3d-adatoms may compete with Fe in adsorption on (001)NbC. The covalent bonding between the Co3d and C(N)-2p orbitals was considered as a dominate mechanism in the Co/Ti(CN) interface interaction [41]. One would expect that the strong carbide-forming elements in steel such as Ti or V have a better adsorption at the C-top site as compared with other TMs. Nevertheless, our calculations predict a parabolic dependence of Wad with the lowest values for the beginning and end elements in 3d-series (Fig. 3a). Among 3d alloying additions, only Cr and Mn have a strong bonding with (001)NbC and may compete with Fe in adsorption. The dependence of Wad on transition element M correlates with the M–C distance in M/NbC (Fig. 3b), where the early and late elements in 3d-series have the largest height above surface than Fe adatom. The decrease in coverage from 1ML to 0.5ML shifts Wad rigidly by ~0.5 eV for all M atoms, whereas a further decrease to 0.25ML almost does not affect Wad. The height of adsorbed M atoms above the (001)NbC shows a similar behavior – it increases from 1ML to 0.5ML and remains almost unchanged for the lower covering (Fig. 3b). Thus, the TMs adsorption on the (001)NbC surface is not expected to depend strongly on coverage for the TMs concentration less 0.5ML.

Then we considered the Fe adsorption on the (001)NbC surface covered with 3d TMs (M = Ti, V, Cr, Mn, Co and Ni) and calculated Wad between the Fe and M monolayers (this 16-atom configuration was denoted as Fe/M/NbC). In this case, the M atom adsorbs at the C-site, while the Fe atom in the second monolayer are above the Nb site. The subsequent Fe layer shifts the initial layer of M atoms far from the surface due to the Fe–M interaction, nevertheless, the M–C distances in Fe/M/NbC show the similar parabolic trend as in M/NbC (Fig. 3b). The Fe–Nb distances strongly depend on the M type (2.65–3.00 Å) and are less than the M–Nb distances (2.92–3.11 Å), whereas the Fe atoms in the second monolayer are at equal distances (~2.40 Å) from M atoms covered surface. The M layer strongly reduces the rippling of carbide surface: the rippling amplitude (\( \alpha_{\text{MM}} + \alpha_{\text{MN}} \)) for the 1ML and 2ML Fe coverage of (001)NbC decreases to 0.037 Å and 0.009 Å, respectively.

The value of Wad in Fe/M/NbC is higher compared with Fe/NbC (Fig. 3a) due to the increase of coordination number for adsorbed Fe atom by involving the formation of the Nb–Fe–M–Fe bonds. The coverage with 1ML of Cr and Mn provides large Wad for the subsequent Fe layer that even exceeds the value of the two Fe layers. The high adsorption ability of Cr and Mn suggests that the initial layer on the (001) surface may contain these atoms. A total energy gain of 0.44 eV (0.12 eV) was obtained when the Fe and Cr (Mn) monolayers were exchanged that demonstrates a preference for Fe/M/NbC over M/Fe/NbC. This indicates that the presence of thin films or islands of the Cr or Mn atoms on the (001)NbC surface is highly probable. The large values of Wad obtained for the Fe layer on the Cr or Mn monolayer covering (001)NbC demonstrate that these impurities may provide a stronger bonding for the adsorbed Fe atoms and make the following Fe adsorption more efficient. Alloying additions segregated in the interfacial region between Fe and carbide may serve also as a barrier to dislocation motion through the interface resulting in additional hardening [49].

4. Conclusions

First-principles simulation of Fe adsorption on the (001)MX surface (M = Ti, V, Nb, Zr, Hf, Ta and X = C or N) was carried out to predict the nucleant capacity of MX at the initial stage of nucleation. First, the lattice parameters and surface energies for (001)MX were calculated and found in good agreement with available theoretical and experimental data. It was then established that the X-vacancies are located far from the topmost surface layers and the nonstoichiometry observed for many transition metal carbides and nitrides should not affect the Fe adsorption. The dependence of Wad on transition metal M is determined by the both Fe–M and Fe–X interactions and is closely related to the number of valence electrons in the M and X atoms. The maximum absorption was found for Fe on (001)NbC, indicating this carbide precipitate should demonstrate a high nucleation ability at early stage, which agrees with the experimentally observed effective grain refinement of ferritic and austenitic steels with NbC. The competition of 3d transition metals in adsorption strength was analyzed for (001)NbC, and we demonstrate that Cr and Mn may strongly affect the initial stage of nucleation.

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References