Journal of Physics and Chemistry of Solids 116 (2018) 30–36

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Investigation of iron adsorption on composite transition metal carbides in steel by first-principles calculation

Hui-Hui Xiong [a,b,*], Lei Gan [a], Zhi-Fang Tong [a], Heng-Hua Zhang [b], Yang Zhou [a]

[a] School of Metallurgy and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou, 341000, China
[b] School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

ARTICLE INFO

Keywords:
Adsorption energy
Composite transition metal carbides
First-principles calculation
Iron

ABSTRACT

The nucleation potential of transition metal (TM) carbides formed in steel can be predicted by the behavior of iron adsorption on their surface. Therefore, Fe adsorption on the (001) surface of $(A_{1-x}m_x)C$ (A = Nb, Ti, m = Mo, V) was investigated by the first-principles method to reveal the initialization of Fe nucleation. The Mulliken population and partial density of state (PDOS) were also calculated and analyzed in this work. The results show that Fe adsorption depends on the composition and configuration of the composite carbides. The adsorption energy (W_{ads}) of Fe on most of $(A_{1-x}m_x)C$ is larger than that of Fe on pure TiC or NbC. The maximum W_{ads} is found for Fe on $(Nb_{0.5}Mo_{0.5})C$ complex carbide, indicating that this carbide has the high nucleation capacity at early stage. The Fe adsorption could be improved by the segregation of Cr and Mn atoms on the surfaces of $(Nb_{0.5}Mo_{0.5})C$ and $(Ti_{0.5}Mo_{0.5})C$. The PDOS analysis of (Cr, Mn)-doped systems further explains the strong interactions between Fe and Cr or Mn atoms.

1. Introduction

Because of their excellent yield strength and toughness, high-strength low-alloy (HSLA) steels have been widely used in many fields, such as high-pressure vessels, ships, railways, and energy transportation [1–5]. The mechanical properties of HSLA steels can be controlled through dispersion strengthening and grain refinement [6]. Grain refinement can be achieved by the heterogeneous nucleation of ferrite and austenite on the transition metal (TM) carbides [7,8]. Actually, the interfacial energy between carbides and matrix can be used to evaluate the nucleation potential for various carbides [9,10]. For example, Yang et al. [11] investigated the electronic, structural, and interfacial properties of the Fe—TiC interface by first-principles calculations, and found that ferrite heterogeneous nucleation preferably occurred on the C-termination interface. Similarly, the first-principles method was also used to study the Fe—NbC [12,13], Fe–WC [14,15], Fe–VN [16], Fe—ZrC [17], Fe—TiN [18,19] interfaces, and their interfacial properties and bonding characteristics were revealed. In addition, the interfacial energies of coherent and semicoherent fcc Fe/MX and bcc Fe/MX (M = Ti, Zr, Hf, V, Nb, Ta, X = C, N) were explored using the first-principles approach [20–22], which confirmed that NbC has the largest nucleation potential.

It is reported that heterogeneous nucleation during the early stage of solidification is an adsorption process [23,24], and the larger adsorption ability of Fe atoms on the precipitate surface is associated with a higher nucleation potential of particles. At present, first-principles calculations have been considerably applied to research the metal atom adsorption on particle surfaces, which can provide the atomic and electronic structures of the adsorption system. Wang et al. [19] used density functional theory (DFT) simulations to study the adsorption of Fe on the TiN(001) surface, and the heterogeneous nucleation mechanism of Fe on TiN precipitate was revealed. Furthermore, the iron adsorption on the (001) surface of TM carbides and nitrides was calculated using the first-principles method, and the nucleation tendency and potential of these precipitates in steel were confirmed [25]. Besides the pure carbides, the addition of alloying elements also could result in the formation of composite carbides in steel, such as (Ti, Mo)C [26], (Ti, V)C [27], and (Nb, Mo)C [28]. Those particles can lead to grain refinement and thus improve mechanical properties of steel. However, the theoretical research of Fe adsorption on composite carbide surfaces has not been previously reported in the literature.

In this article, first-principles calculations about Fe adsorption on the possible (001) surfaces of composite carbides $(A_{1-x}m_x)C$ (A = Nb or Ti, m = Mo, V) were performed to explore their nucleation behaviors. The electronic structure and bonding characteristics of those adsorption structures were also analyzed. Moreover, the segregation of alloying elements on $(A_{1-x}m_x)C$ surfaces may affect the Fe adsorption, as is the case

* Corresponding author. School of Metallurgy and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou, 341000, China.
E-mail address: xionghui8888@126.com (H.-H. Xiong).

https://doi.org/10.1016/j.jpcs.2018.01.013
Received 11 September 2017; Received in revised form 9 January 2018; Accepted 10 January 2018
Available online 10 January 2018

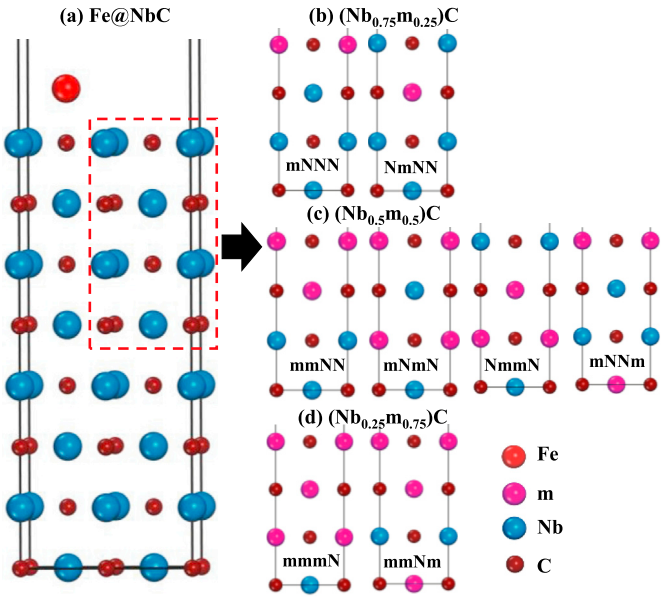

Fig. 1. (a) Supercell model of Fe adsorption on NbC(001) surface. Atomic structures of (b) $(Nb_{0.75}m_{0.25})C$, (c) $(Nb_{0.5}m_{0.5})C$, (d) $(Nb_{0.25}m_{0.75})C$, where N and m represent Nb and alloying elements (e.g., Mo, V, and Ti). The brown, blue, and red spheres are C, Nb, and Fe atoms, respectively. The stacking sequence of $(Nb_{1-x}m_x)C$ is shown from the top to the bottom. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

with Ni alloys with Ni_3Al precipitate [29,30]. Therefore, we also discuss the Fe adsorption on 3d-TM-doped $(Nb_{0.5}Mo_{0.5})C$ and $(Ti_{0.5}Mo_{0.5})C$ (TM = Ti, V, Cr, Mn, Co and Ni) to reveal the influence of these alloying elements on the subsequent Fe nucleation.

2. Calculation method and details

The Cambridge serial total energy package (CASTEP) code [31,32], which is based on density functional theory (DFT), was used for all the calculations in this work. The ultra-soft pseudopotential method [33] was used to describe the interactions between ionic core and valence electrons. The valence electrons of the atoms chosen were Nb $4s^24p^64d^45s^1$, Ti $3s^23p^63d^24s^2$, and C $2s^22p^2$, respectively. Generalized gradient approximation (GGA) of Perdew–Burke–Ernzerh of(PBE) functional [34] was used to treat the exchange–correlation interactions. The Brillouin zone was sampled with the Monkhorst–Pack k-point grid. The cutoff energy was selected as 400 eV and the k-point sampling was set as $8 \times 8 \times 8$ for the bulk and $8 \times 8 \times 1$ for the surfaces, respectively. The geometry optimization was performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [35] to achieve relaxation of atoms fully. The convergence parameters used in the calculations were as follows: total energy tolerance, 1.0×10^{-5} eV/atom; maximum force tolerance, 0.03 eV/Å; and maximal displacement, 1.0×10^{-4} nm.

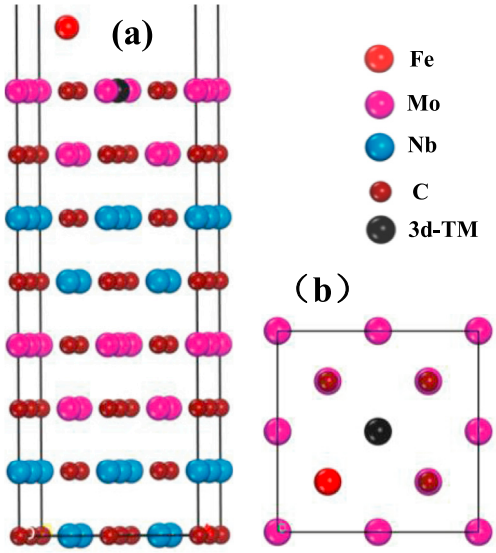

Fig. 2. Supercell structure of Fe adsorption on 3d-TM-doped 2×2 $(Nb_{0.5}Mo_{0.5})C(001)$ surface (a), top view of the adsorption system (b). The black, brown, blue, pink, and red spheres are 3d-TM, C, Nb, Mo, and Fe atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Calculated lattice constants "a," volume "V_0," bulk modulus "B," and surface energy "γ_s" [(001) surface] of NbC and TiC compared with experimental results and other references.

Phases	Method	a = b = c (Å)	V_0 (Å^3)	B (GPa)	γ_s (J/m^2)
TiC	$GGA_{this\ work}$	4.332	81.3	250	1.69
	GGA [36]	4.331	81.2	248	1.60 [25]
	Expt. [37]	4.329	81.1	242	
NbC	$GGA_{this\ work}$	4.480	89.9	301	1.49
	GGA-PBE [38]	4.493		307	1.42 [25]
	Exp. [39]	4.470	89.3	311 [40]	1.55 [41]

Lekakh et al. [25] have demonstrated that the optimal adsorption position for Fe on TMC(001) is the C-top site instead of the TM-top site or bridge site. Therefore, the Fe adsorption on only the C-top site of TMC(001) was considered in this work. First, we established the model of Fe adsorption on complex carbides with different configurations of $(A_{1-x}m_x)C$. Taking the Fe adsorption on the 2×1 $(Nb_{1-x}m_x)C(001)$ surface (Fig. 1) for example, each adsorption model consists of eight atomic layers with four atoms in each layer that corresponds to the Fe monolayer (ML) covering of 0.25ML. The atomic structures of $(Nb_{1-x}m_x)C$ (x = 0, 0.25, 0.50, and 1) with different stacking sequences are shown in Fig. 1 (b)-(d). In Fig. 1 (a), Fe adsorption on the NbC(001) surface is defined as "Fe@NbC" (where A@B means A adsorption on B) and N and m represent Nb and alloying elements (e.g., Mo, V, and Ti), respectively.

It is reported that Fe adsorption can be affected by the segregation of alloying elements on TM carbide surfaces [25]. Therefore, we also studied iron adsorption on the $(A_{1-x}m_x)C(001)$ surface covered with 3d TM(TM = Ti, V, Cr, Mn, Co, and Ni) to understand how these substitutional atoms influence the Fe nucleation. The $(Nb_{0.5}Mo_{0.5})C$ and $(Ti_{0.5}Mo_{0.5})C$ complexes, having the relatively large Fe adsorption ability (see the "Adsorption Energy" section), were chosen to investigate the influences of 3d TM on Fe adsorption. Fig. 2 shows the supercell structure of Fe adsorption on the 3d-TM-doped 2×2 $(Nb_{0.5}Mo_{0.5})C(001)$ surface; each adsorption model is composed of eight atomic layers with one 3d atom substituting an Mo atom in the first layer. Here the nonmagnetic iron was considered due to the simulation of the initial process. The adsorption energy (W_{ads}) of Fe on complex carbide surfaces is derived according to the following equation:

$$W_{ads} = E_{Fe} + E_{surface} - E_{Fe+surface} \quad (1)$$

where $E_{surface}$ and E_{Fe} are the total energy of composite carbide surfaces and a single Fe atom, respectively. $E_{Fe+surface}$ is the total energy of carbide surfaces adsorbing Fe atom.

3. Results and discussion

3.1. Bulk and surface properties of NbC and TiC

To make sure the accuracy of our calculation methods, we carried out a series of calculations on the properties of NbC and TiC, whose crystal