Ab Initio Molecular Dynamics Study of Fe Adsorption on TiN (001) Surface

Chao Wang¹, Yongbing Dai¹, Haiyan Gao¹, Xiaoming Ruan², Jun Wang¹ and Baode Sun^{1,*}

¹The State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

²Baoshan Iron and Steel Corporation, Shanghai 201900, P. R. China

The adsorption energy of atomic Fe on TiN (001) surface was examined by first-principles calculations. The inter-atomic interaction mechanism between TiN crystal and Fe atom was investigated using *ab initio* molecular dynamics simulation. It was found that the N site is more preferable than Ti and bridge sites for Fe atom. These results may be of importance for further understanding heterogeneous nucleation mechanism. [doi:10.2320/matertrans.M2010244]

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1. Introduction

Non-metal inclusions such as TiN particles in steel are of importance for acting as preferential heterogeneous nucleation sites.¹⁻⁴ The steels can solidify with a well-refined equiaxed structure with sufficient additions of TiN particles. There are important technological and fundamental physical reasons for an increased understanding of heterogeneous nucleation mechanism of delta iron on the TiN substrate. Computer simulations are well-suited for unraveling details of reaction dynamics at surfaces which are difficult to explain by means of experiments. In recent years, the interfaces between bcc Fe and transition metal nitrides have been examined by a number of researchers.⁵⁻⁸ Mizuno *et al.* calculated the chemical bonding at the interface between bcc Fe and TiN and it was found that the Fe on N site geometry is more preferable than the Fe on Ti site geometry. Furthermore, they found that the contribution of the chemical bonding for the ferrite nucleation seems to be larger than that of the mismatch strain.⁵ A first-principles study was carried out on the misfit strain energies at coherent interfaces between bcc Fe and nitrides by Jung *et al.* and they found that the difference of interface energy among different types of transition nitrides was closely related to the changes of the bond energies between Fe, transition element and N atoms before and after the formation of the interface.⁶ Hartford⁷ calculated the Fe/VN interface energy. Johansson *et al.*⁸ developed and applied an *ab initio* based approach to determine energies and structures for semi-coherent interface between Fe (001) and VN (001). Cantor and Kim^{9,10} have proposed that, it seems more reasonable to regard heterogeneous nucleation as an adsorption process. Solid nuclei are formed by adsorption of the solidifying atoms on the efficient catalyst surface, rather than by the formation of a bulk spherical cap. Accordingly, as the early stage of the delta Fe nucleation on heterogeneous nucleation site during solidification, the Fe atoms will precipitate on to the TiN surface. However, no theoretical calculations concerning the adsorption of Fe atoms on the surface of heterogeneous nucleation site have previously been reported in the literature.

In this paper, the adsorption energies, geometry optimizations and dynamic information of Fe atom adsorbed on TiN (001) surface at different adsorption sites have been investigated using first-principles calculations and *ab initio* molecular dynamics (AIMD) simulations.

2. Method

Firstly, structure relaxations were performed using first-principles simulations. The generalized gradient approximation (GGA) by Perdew and Wang¹¹ was adopted to evaluate the exchange and correlation energy. The ultra-soft pseudo-potential¹² was used and the cut-off energy set for the plane wave basis was chosen at 370 eV. The periodic boundary condition was applied to all directions. We used a lattice constant of 4.267 m^{-10} which corresponds to the calculated TiN bulk equilibrium lattice constant. A super-cell approach was used for modeling the surface of TiN (001), consisting of five atomic layers. In order to prevent interactions occurring between periodic images under the application of periodic boundary conditions, a vacuum space of 10 m^{-10} has been inserted in the Z-direction. During the simulation, the bottom two TiN layers were fixed while the rest of the layers, as well as Fe atom, were allowed to relax. The system size is limited to tens of atoms because of the computing cost. In the simulation, a (1×1) cell with five layers was used, with one Fe atom adsorbed on one side of the slab in either atop, or bridge (Fig. 1). The Fe atom was located 2 m^{-10} above the TiN (001) surface. Then, in order to achieve more dynamic information and comprehensive understanding of the Fe atom adsorption on TiN (001) surface, *ab initio* molecular dynamics (AIMD) calculations were performed at 1808 K, using a time step of 0.5 s^{-15} for up to 1 s^{-12} . The algorithm of Nose¹³ has been used to control the temperature and the algorithm of Verlet¹⁴ has been used to integrate the equations of motion. The NPT ensemble was used in the calculation.

A comparison of the adsorption energies of Fe atom on different TiN (001) surface sites could possibly give information about preferred surface sites during thin Fe film growth and consequently a clue to evolving delta Fe crystal structures. First principle single point energy calculations were carried out for three initial adsorption configurations

*Corresponding author, E-mail: bdsun@sjtu.edu.cn

Fig. 1 The schematic diagram of the super-cell used for the adsorption of Fe atom on TiN (001) surface, with the Fe atom being over the Ti (a); N (b); and bridge (c) sites. Dark spheres: N atoms, larger gray spheres: Ti atoms, and smaller gray spheres: Fe atoms.

Fig. 2 Geometric structures of the Fe adsorption on the Ti (a); N (b); and bridge (c) sites on the TiN (001) surface after relaxation. Top views are shown. Dark spheres: N atoms, larger gray spheres: Ti atoms, and smaller gray spheres: Fe atoms.

and the adsorption energy^{15,16)} of the Fe atom has been calculated by

$$E_{\text{ad}} = E_{(\text{Fe}+\text{TiN})} - E_{\text{TiN}} - E_{\text{Fe}} \quad (1)$$

where $E_{(\text{Fe}+\text{TiN})}$, E_{TiN} , E_{Fe} represent the total energies of Fe/TiN(001) system, TiN (001) surface and the isolated Fe atom, respectively. A more negative binding energy indicates a more favorable structure.

3. Results and Discussion

The adsorption energies of Fe on the bridge, N and Ti sites of TiN (001) surface are -5.02 eV, -5.81 eV, and -4.12 eV, respectively. The difference in magnitude of the adsorption energy indicates that Fe atom is more strongly bound to the N site.

Figure 2 shows the relaxed geometric structures of the Fe-adsorbed TiN (001) surface after first-principles calculations. It was found that the relaxed geometry of Fe atom adsorbed on the bridge site was almost the same as the relaxed geometry of Fe atom adsorbed on the N site. However, the Fe atom adsorbed on the Ti site did not migrate to the N site after

geometry relaxation. A discrepancy has been found between the geometry relaxation results and the forecast based on the adsorption energy calculation. The reason could be that the default temperature in the first-principles calculations was set at 0 K. However, it is well known that the initial heterogeneous nucleation of Fe on TiN (001) surface is happened just below the melting point of Fe and the temperature can have large effects on the dynamics of the atom adsorption process. The effects of temperature could be studied by *ab initio* molecular dynamics simulations. Therefore, *ab initio* molecular dynamics simulations were performed to monitor the mobility and geometric changes of the surface and it can help to explain the heterogeneous nucleation mechanism of delta Fe.

Figure 3 shows the snapshots of the Fe adsorbed on TiN (001) surface at three different initial sites. During the simulation at 1808 K, the Fe atom starts to approach and then adsorbs onto the TiN (001) surface, accompanied by a decrease in the potential energy. The geometry optimizations of the structures have resulted in nearly the same final location for three different initial adsorptions. The simulation results indicate that the N site on TiN (001) surface is

Fig. 3 Snapshots of the Fe adsorption on the Ti (a); N (b); and bridge (c) sites on the TiN (001) surface after relaxation. Top views are shown. Dark spheres: N atoms, larger gray spheres: Ti atoms, and smaller gray spheres: Fe atoms.

preferred for Fe atom adsorption and the Fe on the bridge and Ti sites have been found to migrate to the N site after the simulation. The simulation results are in agreement with the forecast based on the adsorption energy calculation.

Through comparison between Fig. 2(a) and Fig. 3(a), it is found that the Fe atom in the relaxed configurations stay at different positions. This is because the mobility of adsorbed Fe atoms on TiN (001) surface is governed by the activation energy barrier required for the Fe atom to move from one site to another site. It must be noted that the optimized geometry shown in Fig. 2(a) was determined from calculation at 0 K. However, the adsorption of Fe atom on TiN (001) surface occurs early in the very beginning of iron solidification. Hence, the calculation results of *ab initio* molecular dynamic simulations at high temperatures are more reasonable.

Further details of the adsorption process can be obtained by examining the distance between the Fe atom and the top layer of TiN (001) surface, denoted here as $d_{\text{Fe-TiN}}$, as a function of time (see Fig. 4). The starting value of $d_{\text{Fe-TiN}}$ in all adsorption sites is 2 m^{-10} . It should be noted that $d_{\text{Fe-TiN}}$ on the Ti site increases at the very beginning of the simulation. Once the Fe atom reaches above the N site, there

Fig. 4 Changes in the perpendicular positions between the Fe atom and average top layer TiN atoms during *ab initio* molecular dynamics simulations.

Fig. 5 Trajectory projection of the Fe atom onto the TiN(001) surface during the AIMD calculations at 1808 K. (a) Bridge; (b) N; (c) Ti sites.

is a small oscillation of the Fe atom in the direction perpendicular to the TiN (001) surface. After simulation for 1 ps, all $d_{\text{Fe-TiN}}$ were close to 1.7 m^{-10} .

The trajectory projection of the Fe atom onto the TiN (001) surface was shown in Fig. 5. From Fig. 5, it can be seen that the displacements of the Fe atom in x- and y-directions are more localized on the N site than that on the Ti and bridge sites.

Table 1 Effective atomic charges for the Fe adsorbed on bridge site of the TiN (001) surface.

Layer number	Species	Charge(electron)			
		Unrelaxed	0.25 s ⁻¹²	0.5 s ⁻¹²	1 s ⁻¹²
1	Fe	-0.04	-0.21	-0.13	-0.12
2	Ti	0.75	0.91	0.83	0.74
	N	-0.73	-0.75	-0.75	-0.70
3	Ti	0.74	0.79	0.77	0.80
	N	-0.74	-0.73	-0.72	-0.72
4	Ti	0.73	0.71	0.69	0.71
	N	-0.74	-0.74	-0.74	-0.72

Table 2 Effective atomic charges for the Fe adsorbed over N site of the TiN (001) surface.

Layer number	Species	Charge(electron)			
		Unrelaxed	0.25 s ⁻¹²	0.5 s ⁻¹²	1 s ⁻¹²
1	Fe	0.01	-0.06	-0.01	-0.04
2	Ti	0.72	0.76	0.77	0.77
	N	-0.74	-0.72	-0.73	-0.71
3	Ti	0.74	0.76	0.71	0.73
	N	-0.74	-0.74	-0.72	-0.73
4	Ti	0.74	0.76	0.67	0.74
	N	-0.74	-0.73	-0.73	-0.74

Table 3 Effective atomic charges for the Fe adsorbed over Ti site of the TiN (001) surface.

Layer number	Species	Charge(electron)			
		Unrelaxed	0.25 s ⁻¹²	0.5 s ⁻¹²	1 s ⁻¹²
1	Fe	-0.16	-0.02	-0.10	-0.18
2	Ti	0.84	0.72	0.77	0.87
	N	-0.71	-0.72	-0.70	-0.77
3	Ti	0.76	0.72	0.71	0.79
	N	-0.74	-0.73	-0.70	-0.73
4	Ti	0.73	0.68	0.70	0.76
	N	-0.74	-0.73	-0.72	-0.73

The effective atomic charges of the Fe atom adsorbed on TiN (001) surfaces were obtained by the Mulliken population analysis¹⁷⁾ and are listed in Tables 1–3. The phenomenon of electron redistribution has been observed in the outmost layers after *ab initio* molecular dynamics simulation and these electrons move among the Fe, Ti and N atoms. The charge transfer is accompanied by the changing of the electrostatic repulsion between the atoms in the outmost layers, which results in vertical and horizontal direction displacement and bond length change in all three kinds of

geometric structures. The amount of the transferred charges varies with the initial adsorption sites.

4. Conclusion

In conclusion, the adsorption of Fe atom on TiN (001) surface has been examined using first-principles calculation and *ab initio* molecular dynamics simulations. It was found that the Fe atom adsorbed on the Ti site did not migrate to the N site after static calculation at 0 K. However, the optimized adsorption position for the Fe atom is on the N site at 1808 K. The Fe atom shows more localized on N site than other two sites. The fundamental phenomena discussed in this paper may be an important clue to explore more complicated problems for the heterogeneous nucleation of delta Fe on TiN (001) surface. In order to obtain a detailed mechanism for the complexity of the heterogeneous nucleation of iron on TiN surfaces, further theoretical works are expected.

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REFERENCES

- 1) Ø. Grong, L. Kolbernsen, C. V. D. Eijk and G. Tranell: ISIJ **46** (2006) 824–831.
- 2) C. V. D. Eijk, Ø. Grong, F. Haakonsen, L. Kolbernsen and G. Tranell: ISIJ **49** (2009) 1046–1050.
- 3) E. F. Nordstrand, Ø. Grong, C. V. D. Eijk and S. Gaal: ISIJ **49** (2009) 1051–1058.
- 4) C. Wang, H. Y. Gao, Y. B. Dai, X. M. Ruan, J. G. Shen, J. Wang and B. D. Sun: Metall. Mater. Trans. A **41A** (2010) 1616–1620.
- 5) M. Mizuno, I. Tanaka and H. Adachi: Acta. Mater. **46** (1998) 1637–1645.
- 6) W. S. Jung, S. H. Chung, H. P. Ha and J. Y. Byun: Modell. Simul. Mater. Sci. Eng. **14** (2006) 479–495.
- 7) J. Hartford: Phys. Rev. B **61** (2000) 2221–2229.
- 8) S. A. E. Johansson, M. Christensen and G. Wahnstrom: Phys. Rev. Lett. **95** (2005) 226108.
- 9) B. Cantor: Phil. Trans. R. Soc. Lond. A **361** (2003) 409–417.
- 10) W. T. Kim and B. Cantor: Acta Metall. Mater. **42** (1994) 3115–3127.
- 11) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson and D. J. Singh: Phys. Rev. B **46** (1992) 6671–6687.
- 12) D. Vanderbilt: Phys. Rev. B **41** (1990) 7892–7895.
- 13) S. Nose: J. Phys. Chem. **81** (1984) 511–519.
- 14) L. Verlet: Phys. Rev. **159** (1967) 98–103.
- 15) M. A. S. Miguel, J. Oviedo and J. F. Sanz: Phys. Rev. Lett. **99** (2007) 066102.
- 16) N. Todorova, M. J. S. Spencer and I. Yarovsky: Surf. Sci. **601** (2007) 665–671.
- 17) M. D. Segall, C. J. Pickard, R. Shah and M. C. Payne: Molec. Phys. **89** (1996) 571–577.