Corrosion related properties of iron (100) surface in liquid lead and bismuth environments: A first-principles study*

Song Chi(宋 驰)[a], Li Dong-Dong(李冬冬)[b], Xu Yi-Chun(许依春)[a],
Pan Bi-Cai(潘必才)[b], Liu Chang-Song(刘长松)[a]†, and Wang Zhi-Guang(王志光)[c]

[a] *Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei* 230031, *China*
[b] *National Laboratory for Physical Sciences at Microscale and Department of Physics, University of Science and Technology of China, Hefei* 230026, *China*
[c] *Institute of Modern Physics, Chinese Academy of Sciences, Lanzhou* 730000, *China*

(Received 5 September 2013; revised manuscript received 23 October 2013; published online 25 March 2014)

The corrosion of steels in liquid metal lead (Pb) and bismuth (Bi) is a critical challenge in the development of accelerator driven systems (ADS). Using a first-principles method with a slab model, we theoretically investigate the interaction between the Pb (Bi) atom and the iron (Fe) (100) surface to assess the fundamental corrosion properties. Our investigation demonstrates that both Pb and Bi atoms favorably adsorb on the (100) surface. Such an adsorption decreases the energy required for the dissociation of an Fe atom from the surface, enhancing the dissolution tendency significantly. The segregation of six common alloying elements (Cr, Al, Mn, Ni, Nb, and Si) to the surface and their impacts on the corrosion properties are also considered. The present results reveal that Si seems to have a relatively good performance to stabilize the surface and alleviate the dissolving trend caused by Pb and Bi.

Keywords: corrosion property, interface interaction, alloying atom, first-principles method

PACS: 68.43.Bc, 73.20.Hb, 28.52.Fa **DOI:** 10.1088/1674-1056/23/5/056801

1. Introduction

The ferritic/martensitic steels will be widely used in the next generation of nuclear reactors due to their high thermal conductivities, high resistance to swelling, low expansion coefficients, and so on.[1–3] In accelerator driven systems (ADS), they are chosen as the structural materials and the containers for liquid heavy metals and alloys, such as lead and lead bismuth eutectic (LBE) which are selected as the spallation target and the coolant.[4–6] However, steels can be severely corroded if they are exposed to liquid metals and alloys directly at high temperatures. The so called liquid metal corrosion problem has been recognized as one of the most critical issues in the development of ADS.

So far, many experiments have been carried out to evaluate the corrosion behavior of different kinds of steels in liquid Pb, Bi, and LBE,[7–12] which provide valuable data for the design of ADS. However, compared to the amount of studies on the corrosion in experiments, very few theoretical researches have been carried out on this problem. Also, we still lack detailed knowledge of the atomic processes during the corrosion and a theoretical explanation of the corrosion behavior. As we know, the corrosion of structural materials is essentially related to the chemical and physical processes that happen at the interface of the corrosive environment and the vessel. To gain a deep insight into the corrosion phenomena, it is necessary to explore the interaction details of atoms at the interface. Specifically, how the liquid atoms deposit onto the surface, and how the deposited liquid atoms affect the escape of Fe atoms from the steel surface.

Normally, the steel surface is covered by native oxide films which are mainly composed of Fe–Cr spinel and the magnetite.[12–14] Such films just separate the steel from the corrosive environment and protect the steel to some extent.[12] However, this protective oxide layer is not steady or compact enough to protect the inner matrix. With high temperature and low oxygen concentration, the passive film could be damaged or even removed, exposing the active substrate surface to the liquid metal and alloy.[13,14] Therefore, there might be two kinds of interfaces between the corrosive environment and the steel, depending on whether the oxide films are broken.

In this paper, we focus our attention on the interaction between liquid Pb or Bi atoms and the ideal native surface. The body-center cubic (bcc) Fe (100) surface is chosen since it is found to be the most stable.[15] Using a first-principles method, the adsorption of liquid atoms onto the surface and the dissociation of Fe atoms from the surface are studied, which are both related directly to the corrosion properties. The impact of six common alloying elements in steels on the interaction are also considered. Such a computational method has been applied successfully in the interpretation of experimental results, property predictions, and even the designs of materials,[16–19] and it has also been used in the corrosion

*Project supported by the Strategic Priority Research Program of Chinese Academy of Sciences (Grant Nos. KJCX2-YW-N35 and XDA03010303), the National Natural Science Foundation of China (Grant Nos. 91026002 and 91126002), and the National Magnetic Confinement Fusion Program, China (Grant No. 2011GB108004).

†Corresponding author. E-mail: csliu@issp.ac.cn

© 2014 Chinese Physical Society and IOP Publishing Ltd

studies.[20–24] By performing this atomic study, we try to extend the understanding of the liquid metal corrosion behavior towards the atomic scale.

2. Model and method

Our calculations are performed within the density functional theory (DFT) using the spin polarized version of the Vienna *ab initio* simulation package (VASP) under the generalized gradient approximation (GGA).[25–27] The projector augmented wave (PAW) potentials are employed to describe the electron–ionic core interaction,[28] and the Perdew–Burke–Ernzerhof (PBE) functional has been chosen as the exchange–correlation potential.[29] A cut-off energy of 400 eV is used to expand the electronic wave functions, which yields well converged results. The Brillouin-zone integrations are performed using an 8×8×1 *k*-point mesh generated by the Monkhorst–Pack scheme. To accelerate the convergence, the first order methfessel-paxton method with a Fermi surface smearing of 0.2 eV is adopted.

The (100) surface is modeled by a slab consisting of nine Fe layers separated by a vacuum layer of 15 Å, and a 2×2 surface unit cell is employed as in Ref. [30]. The supercell thus contains 36 Fe atoms. Based on the considerations above, our optimal lattice constant of ferromagnetic Fe is predicted to be 2.831 Å, which is in good agreement with the experimental value 2.866 Å.[15] In order to study the interaction of liquid atoms with the metal surface, a Pb or Bi atom is put on one side of the slab. Three possible adsorption sites on the surface are tested, including the hollow, bridge, and top sites, as displayed in Fig. 1(a). Considering the asymmetry of the slab, an *a posteriori* dipole correction to the total energy is included (the magnitude of the correction is less than 0.01 eV/cell). During the optimization, the Fe atoms in the top five layers together with the adsorbed Pb or Bi atom are allowed to relax until the forces converged to less than 0.01 eV/Å, while the bottom four Fe layers are fixed to represent the semi-infinite bulk crystal beneath the surface.

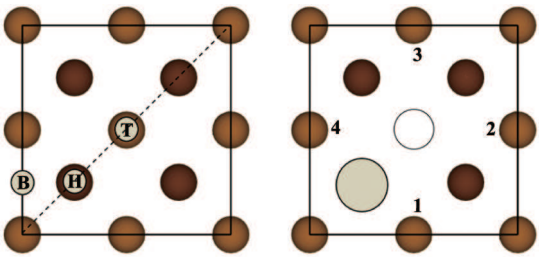


Fig. 1. (color online) Top view of the Fe(100) surface showing (a) the on-surface adsorption sites: hollow (H), bridge (B), and top (T), and (b) the surface configuration with an Fe atom removed. The colors are darker for deeper lying layers. The dashed line on the surface in panel (a) represents the [110] direction. The smaller open circle in panel (b) represents the removed Fe atom, and the bigger one shows the adsorbed liquid atom at the hollow site. Four neighbor atoms of the removed Fe atom on the surface are marked.

The adsorption energy ($E_{\rm ads}$) of the liquid atom is calculated using the formula[30]

$$E_{\rm ads} = E_{\rm slab}^{\rm ads} - E_{\rm slab} - \mu_{\rm ads}, \tag{1}$$

where $E_{\rm slab}^{\rm ads}$ and $E_{\rm slab}$ are the total energies of the Fe slab with and without the liquid atom adsorbed on, respectively, and $\mu_{\rm ads}$ is the chemical potential of the adsorbed atom. Here $\mu_{\rm ads}$ is approximatively taken as the energy per atom of the most stable condensed phase of the adsorbed element. It is close to the value of the chemical potential of the liquid metal if the temperature dependence of the free energy and the latent heat of fusion are, to a good approximation, neglected.[30] According to this definition, a negative $E_{\rm ads}$ indicates that the adsorption is favorable, while a positive value indicates that the adsorption is unfavorable.

To estimate the corrosion property, a dissociation energy ($E_{\rm dis}$) is defined as in Ref. [24], which equals to the energy required to remove an Fe atom from the surface of the material. One Fe atom on the surface is selected and removed, producing a new slab with a surface vacancy. The resulting difference in energy yields the dissociation energy

$$E_{\rm dis} = E_{\rm slab'} + E_{\rm Fe} - E_{\rm slab}, \tag{2}$$

where $E_{\rm slab}$ and $E_{\rm slab'}$ represent the total energies of the optimized original and new slabs, respectively, and $E_{\rm Fe}$ refers to the energy of the isolated Fe atom. It should be pointed out that, as a reference energy, different choices of $E_{\rm Fe}$ do not change the important conclusion that emerges from our calculations, since we are more interested in the relative value of the dissociation energy. Thus, $E_{\rm dis}$ is taken as a measurement of the surface stability and the thermodynamic dissolution tendency of the material.[24] According to this definition, a decrease of $E_{\rm dis}$ indicates that the surface stability is decreased, and consequently, leads to a higher thermodynamic predisposition to dissolution.

3. Result and discussion

3.1. Interaction of liquid atom with pure Fe surface

As the first step of interaction, the adsorption of liquid atoms on the surface is examined. The calculated adsorption energies of liquid Pb and Bi at three different positions and their distances to the surface are listed in Table 1. As one can see, the adsorption energies are all negative, except for the Pb atom at the top site. The result indicates that the adsorption of a liquid atom is energetically favorable. For both atoms, the adsorption energies at the hollow site are the smallest, then followed by the bridge and top sites, which makes the hollow site the most favorable position for liquid atoms. It can also be proved from the distances of the adatoms to the surface after relaxation, where both atoms are closest to the surface (1.75 Å and 1.68 Å, respectively) at the hollow site. Perhaps,

this is attributed to the larger atomic radii of Pb and Bi relative to Fe. Thus, in the following discussion, we will consider only the situation that Pb and Bi atoms are adsorbed at the hollow site. It is noted that our calculated adsorption energies are in good agreement with those obtained by Legris,[30] which gives us confidence in the reliability of our computational method. Comparing the adsorption of Pb with Bi, one can find that the adsorption energy of Bi is smaller than that of Pb by 0.6 eV, and the distance of Bi to the surface is closer than that of Pb. Such a result confirms that the pure Fe substrate surface prefers the Bi adsorption in the liquid environment.[31] In the alloy systems, the preferential adsorption can lead to an enrichment of Bi close to the steel surface, which may change the composition near the surface and affect the corrosion behavior. Unfortunately, this Bi-enriched area close to the steel surface has not been reported by experiments until now. However, there are indeed some interesting results in the liquid lead bismuth eutectic alloy. The surface segregation in LBE has been investigated, and the enrichment of Bi near the surface of this liquid alloy has been observed.[32]

Table 1. The adsorption energies (E_{ads}) of Pb and Bi atoms on the Fe (100) surface at the hollow, bridge, and top sites, and the distances (d) to the surface.

	Pb		Bi	
	E_{ads}/eV	d/Å	E_{ads}/eV	d/Å
Hollow	–0.75 (–0.72[a])	1.75	–1.35 (–1.31[a])	1.68
Bridge	–0.13	2.06	–0.51	1.98
Top	0.10	2.41	–0.12	2.29

[a] Ref. [30]

When a liquid atom is adsorbed on the surface, it can make the electrons around the surface atoms re-distribute. This may change the surface stability and modify the possibility of the Fe atom to escape from the surface. As described in Section 2, we use the dissociation energy to evaluate the surface stability and the dissolution tendency of the material. The changes induced by the deposited liquid atom will be reflected in the estimated E_{dis}. Before the adsorption of the liquid atom, E_{dis} of an Fe atom on the clean surface is calculated by Eq. (2), which yields an energy of 5.62 eV. Such a high energy may block the Fe atom from escaping from the surface under the normal condition. When the Pb or Bi atom is adsorbed on, the dissociation energy is then denoted as E^{ad}_{dis}. According to Eq. (2), it can be calculated by

$$E^{ad}_{dis} = E^{ad}_{slab'} + E_{Fe} - E^{ad}_{slab}, \tag{3}$$

where E^{ad}_{slab} and $E^{ad}_{slab'}$ represent the total energies of the optimized original and new adsorbed slabs, respectively. The dissociation energies of the Fe atom with Pb and Bi adsorbed are then obtained to be 4.53 eV and 4.80 eV, respectively. Compared to the case of a clean surface, we can easily find that E_{dis} is decreased by 1.09 eV in the case of Pb adsorption and by 0.82 eV in the case of Bi adsorption. Apparently, the adsorption of liquid atoms on the surface decreases the energy barrier for the Fe atoms to escape, increasing their possibility to move away. This, together with the thermal effect, causes an increased tendency of surface dissolution. Furthermore, after the structural relaxation, the adsorbed Pb or Bi atom is found to move to the surface vacancy, taking the place of the removed Fe atom. This adsorption–replacement process may be a possible atomic picture of the liquid metal attack. By repeating this atomic process continually, the Fe atom will be depleted and the surface will be damaged.

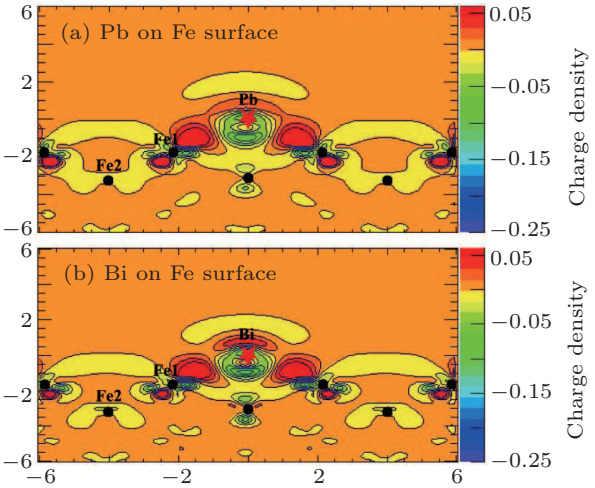


Fig. 2. (color online) Side views of the charge density difference along the [110] direction (see Fig. 1) of the slab. The red stars are the adsorbed Pb (a) and Bi (b) atoms. The Fe atoms are represented by black circles, only the Fe atoms on the topmost layer (Fe1) and the second layer (Fe2) are shown.

The electronic charge density differences caused by the adsorption of Pb and Bi are calculated and plotted along the [110] direction in Fig. 2. In this figure, a negative value indicates the loss of charge density, while a positive one corresponds to the accumulation of it. As one can see, a substantial rearrangement of electrons is observed around the interface. In both Pb and Bi cases, there is an accumulation of charge density between the adsorbed atom and the Fe1 atom on the surface. At the same time, a depletion of charge density between the Fe1 atom and the Fe2 atom on the subsurface is also observed. Such a depletion of charge density indicates a decrease in the bond strength between the Fe atom on the surface and that on the subsurface. This observation clearly demonstrates that the deposited Pb (Bi) atom on the surface significantly weakens the local Fe–Fe bonds nearby. Moreover, one can see that the depletion of charge density is more serious in the case of Pb adsorption. This is in accordance with that obtained from the energetic landscape, where the dissociation energy of the Fe atom under Pb adsorption is smaller than that under Bi adsorption by 0.27 eV. Such a result hints that Pb

might be more aggressive than Bi in such a single adsorption event. However this is not expected, since experiments have confirmed that liquid Bi is more corrosive than liquid Pb.[11] To understand the discrepancy, we note that the corrosion phenomena actually involve a large number of such single adsorption events. Since the Bi adsorption is significantly more favorable than the Pb adsorption, it may have a larger probability of happening during the corrosion process, and the surface would provide more corrosion sites for Bi, which could make it more corrosive from the macroscopic view.

3.2. Effect of alloying elements on the corrosion property

Adding alloying elements is a typical approach to upgrade the materials of construction. However, it is known that these alloying elements may segregate to the surface, and the surface property can be considerably modified, which may have positive or negative effects on the corrosion behaviors. Thus, in the following discussion, we consider the effect of alloying elements.

The segregation properties of six common alloying elements (Cr, Al, Mn, Ni, Nb, and Si) to the Fe (100) surface are examined first. The surface segregation energy is calculated by the formula[33]

$$E_{\text{seg}} = E^{i}_{\text{layer}}(A) - E_{\text{bulk}}(A), \tag{4}$$

where $E^{i}_{\text{layer}}(A)$ and $E_{\text{bulk}}(A)$ represent the total energies of the slabs containing one alloying atom in the i-th layer and at the bulk site (in our case in the fifth layer of the slab), respectively. According to this definition, a negative E_{seg} means that the alloying atom tends to segregate to the surface. The calculated segregation energies are displayed in Fig. 3 as a function of the layer depth. It can be seen that all alloying elements considered have the tendency to segregate to the surface except for Cr. The segregation energy to the topmost layer for Cr is 0.10 eV, which means that Cr prefers to stay in the bulk. However, it has been pointed out that the segregation of Cr depends strongly on its concentration.[34] As the concentration increases, the segregation will be possible. We have confirmed this conclusion by performing another calculation with a smaller supercell of $2\times2\times7$, which yields a segregation energy of -0.04 eV. The segregation energies of Cr are in good agreement with those obtained by Kiejna.[33] Our calculated results also reproduce the anomalous segregation behavior of Cr, that is, the 2nd layer offers a large barrier for segregation.[15] However, for the other alloy elements, there are no available experimental or theoretical results about the surface segregation. Based on the segregation result, we will only consider alloying atoms in the top most layer in the following.

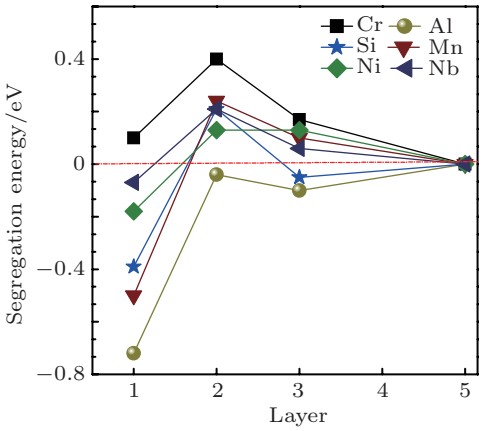


Fig. 3. (color online) Segregation energies calculated for six alloying elements (Cr, Al, Mn, Ni, Nb, and Si) at different layers of the Fe (100) surface.

Considering that these alloying atoms on the surface can either enhance or reduce the adsorption of liquid atoms, we calculate the shift of the adsorption energy. In the slab model, an Fe atom on the surface is replaced by an alloying atom, while the Pb or Bi atom will be adsorbed at the hollow site. Taking into account that the Pb and Bi atoms are much bigger than the Fe atom and all other alloying atoms, it is very likely that the hollow site is still the preferential adsorption site.[30] According to Eq. (1), the adsorption energy shift (ΔE_{ads}) is then calculated as

$$\Delta E_{\text{ads}} = E^{\text{alloy}}_{\text{ads}} - E_{\text{ads}}, \tag{5}$$

where $E^{\text{alloy}}_{\text{ads}}$ and E_{ads} represent the adsorption energies of the liquid atom with and without an alloying atom on the surface, respectively. A positive value means that the adsorption is reduced due to the segregation of alloying atoms, while a negative one indicates that the adsorption is enhanced. The ΔE_{ads} in Pb and Bi adsorption cases are plotted in Fig. 4. According to this figure, the following orders of ΔE_{ads} are obtained: (i) in the case of Pb adsorption, Mn > Al > Si > Cr > Nb >Ni; (ii) in the case of Bi adsorption, Si > Al > Mn > Cr > Ni > Nb. In both cases, ΔE_{ads} for Mn, Al, Si, and Cr are positive, which means that they tend to reduce the adsorption, while the values for Nb and Ni are negative, indicating a tendency to enhance the adsorption. As mentioned above, the adsorption of liquid Pb or Bi breaks the surface stability and makes the surface Fe atom more prone to leave. So the suppression of adsorption may provide a positive effect to the corrosion resistance property of Fe-based alloys.

On the other hand, the impact of alloying atoms on the escaping capability of the Fe atom is also examined when the Pb or Bi atom has deposited. Similarly, the dissociation energy shift ($\Delta E^{\text{ad}}_{\text{dis}}$) of the Fe atom caused by a neighbor alloying atom is calculated. As seen in Fig. 1(b), the liquid atom is adsorbed at the hollow site, while an Fe atom is removed with one of its neighbor atoms on the surface (denoted as 1, 2, 3, and 4)

replaced by an alloying atom. The $\Delta E_{\rm dis}^{\rm ad}$, according to Eq. (2), is then calculated using the formula

$$\Delta E_{\rm dis}^{\rm ad} = E_{\rm dis}^{\rm alloy,ad} - E_{\rm dis}^{\rm ad}, \tag{6}$$

where $E_{\rm dis}^{\rm alloy,ad}$ and $E_{\rm dis}^{\rm ad}$ represent the dissociation energies of the Fe atom with and without an alloying atom in the adsorbed slab, respectively. We plot $\Delta E_{\rm dis}^{\rm ad}$ in Pb and Bi adsorbed cases in Fig. 5. It can be found that the values of $\Delta E_{\rm dis}^{\rm ad}$ are positive for all those alloying elements in both Pb and Bi adsorbed cases. This means that the escape of the Fe atom is delayed to higher energies relative to the clean surface. The local dissolution of the surface caused by the liquid atom adsorption is to some extent alleviated by the alloying atom on the surface. As shown in Fig. 5, $\Delta E_{\rm dis}^{\rm ad}$ under Pb adsorption follows the order Al > Nb > Si > Mn > Cr > Ni, while under Bi adsorption, it follows the order Si > Nb > Al > Mn > Cr > Ni. Combined with the previous effect on the adsorption of liquid atoms, it can be seen that both Al and Si are suitable alloying elements to improve the corrosion resistance of steel for both liquid Pb and Bi. Specifically, Al is the most efficient element to alleviate the surface dissolution under the Pb adsorption, while Si performs the best when Bi is deposited. However, as we have pointed out previously, the pure Fe substrate surface prefers the Bi adsorption in the liquid environment, which makes the Bi adsorption the dominant event in the corrosion process. Therefore, we suggest that Si might be the relatively more suitable alloying element to improve the corrosion resistance of steel.

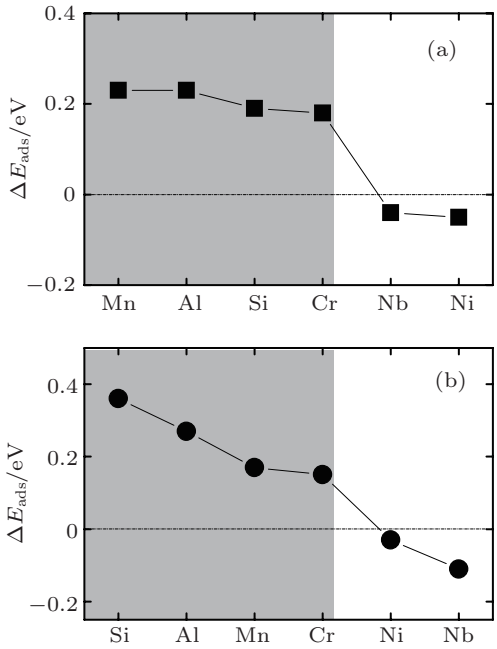


Fig. 4. The adsorption energy shift ($\Delta E_{\rm dis}$) in (a) Pb and (b) Bi cases due to the presence of alloying atoms on the surface.

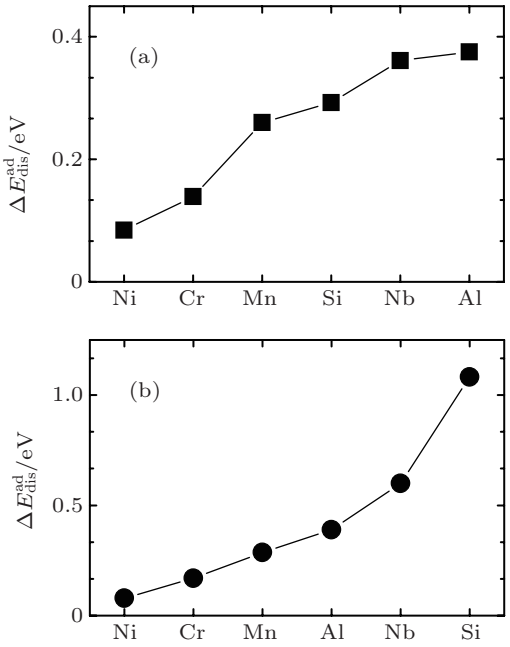


Fig. 5. The dissociation energy shift ($\Delta E_{\rm dis}^{\rm ad}$) of Fe atom due to the presence of alloying atoms on the surface when (a) Pb or (b) Bi atom has been adsorbed.

4. Conclusion

In the present work, we theoretically investigate the interaction between Pb (Bi) atom and the Fe (100) surface using a computational method. By examining the adsorption of the liquid atoms onto the surface and the escape of the Fe atom from the surface, we hope to shed some light on the corrosion phenomena from the microscopic perspective. According to our calculation, both Pb and Bi atoms favorably adsorb at the hollow site on the (100) surface. Such an adsorption decreases the energy barrier for the Fe atom to escape from the surface, which becomes an important factor to induce the corrosion. Basically, the corrosion related adsorption and escaping events take place at each local site between the steel surface and the liquid environment, however, the real systems may be further complicated by the presence of edges and defect sites. Here we only examine the single event and confine our study to the thermodynamic assessments on the ideal native surface. Despite its preliminary character, our results reflect the important role of the interaction between the liquid atom and the metal surface in the liquid metal corrosion process, and provide a possible atomic picture related to the initial stage of the liquid metal attack. Based on this, the impacts of six common alloying elements on the corrosion properties are examined by calculating the shifts of $E_{\rm ads}$ and $E_{\rm dis}$ relative to the case without the alloying atoms. An overall consideration suggests that Si might be a relatively suitable alloying element to improve the corrosion resistance of steel for both liquid Pb and Bi. We note that the good performance of Si on the corrosion resistance property of steels has also been reported by experimental studies.[35,36] It is expected that this atomic study can provide

some useful information for those interested in having a better understanding of corrosion behavior, and give some advice for designing a suitable structural material.

Acknowledgment

Calculations were carried out at the Center for Computation Science, Hefei Institute of Physical Sciences.

References

[1] Mansur L K, Rowcliffe A F, Nanstad R K, Zinkle S J, Corwin W R and Stoller R E 2004 *J. Nucl. Mater.* **329–333** 166
[2] Klueh R L and Nelson A T 2007 *J. Nucl. Mater.* **371** 37
[3] Fazio C, Alamo A, Almazouzi A, De Grandis S, Gomez-Briceno D, Henry J, Malerba L and Rieth M 2009 *J. Nucl. Mater.* **392** 316
[4] Gromov B F, Belomitcev Y S, Yefimov E I, LeonchukMP, Martinov P N, Orlov Y I, Pankratov D V, Pashkin Y G, Toshinsky G I, Chekunov V V, Shmatko B A and Stepanov V S 1997 *Nucl. Eng. Des.* **173** 207
[5] Groeschel F, Fazio C, Knebel J, Perret C, Janett A, Laffont G, Cachon L, Kirchner T, Cadiou A, Guertin A and Agostini P 2004 *J. Nucl. Mater.* **335** 156
[6] Bauer G S 2010 *J. Nucl. Mater.* **398** 19
[7] Zhang J and Li N 2008 *J. Nucl. Mater.* **373** 351
[8] Barbier F and Rusanov A 2001 *J. Nucl. Mater.* **296** 231
[9] Kurata Y, Futakawa M and Saito S 2005 *J. Nucl. Mater.* **343** 333
[10] Glasbrenner H, Konys J and Rusanov A 2001 *J. Nucl. Mater.* **296** 237
[11] Zhang J 2009 *Corros. Sci.* **51** 1207
[12] Ilincêv G, Kárník D, Paulovič M and Doubková A 2006 *Nucl. Eng. Des.* **236** 1909
[13] Zhang J and Li N 2005 *Oxid. Met.* **63** 353
[14] Martinelli L, Balbaud-Célérier F, Terlain A, Delpech S, Santarini G, Favergeon J, Moulin G, Tabarant M and Picard G 2008 *Corros. Sci.* **50** 2523
[15] Levesque M, Gupta M and Gupta R P 2012 *Phys. Rev. B* **85** 064111
[16] Greeley J and Mavrikakis M 2004 *Nat. Mater.* **3** 810
[17] Olsson P 2009 *J. Nucl. Mater.* **386–388** 86
[18] Ren D H and Cheng X L 2012 *Chin. Phys. B* **21** 127103
[19] Koc H, Yildirim A and Deligoz E 2012 *Chin. Phys. B* **21** 097102
[20] Greeley J and Nørskov J K 2007 *Electrochim. Acta* **52** 5829
[21] Lü B L, Chen G Q, Zhou W L and Su H 2013 *Comput. Mater. Sci.* **68** 206
[22] Lü B L, Chen G Q, Zhou W L, Su H and Liu R 2011 *J. Nucl. Mater.* **418** 286
[23] Ma Y G and Balbuena P B 2008 *J. Phys. Chem. C* **112** 14520
[24] Taylor C D, Neurock M and Scully J R 2008 *J. Electrochem. Soc.* **155** C407
[25] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** 558
[26] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
[27] Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758
[28] Blöchl P E 1994 *Phys. Rev. B* **50** 17953
[29] Perdew J P, Burke K and Ernzerhof M 1998 *Phys. Rev. Lett* **80** 891
[30] Legris A, Nicaise G, Vogt J B and Foct J 2002 *J. Nucl. Mater.* **301** 70
[31] Hadjem-Hamouche Z, Auger T and Guillot I 2009 *Corros. Sci.* **51** 2580
[32] Novakovic R, Ricci E, Giuranno D and Gnecco F 2002 *Surf. Sci.* **515** 377
[33] Kiejna A and Wachowicz E 2008 *Phys. Rev. B* **78** 113403
[34] Ponomareva A V, Isaev E I, Skorodumova N V, Vekilov Y K and Abrikosov I A 1981 *Phys. Rev. B* **23** 6265
[35] Johnson A L, Loewen E P, Ho T T, Koury D, Hosterman B, Younas U, Welch J and Farley J W 2006 *J. Nucl. Mater.* **350** 221
[36] Ilincêv G, Kárník D, Paulovič M and Doubková A 2004 *J. Nucl. Mater.* **335** 210