Vol 15 No 3, March 2006
1009-1963/2006/15(03)/0604-06

Chinese Physics

© 2006 Chin. Phys. Soc.
and IOP Publishing Ltd

Effect of element Re on the grain boundary cohesion of α-Fe*

Chen Zheng-Zheng(陈征征)[a)†] and Wang Chong-Yu(王崇愚)[a)b)]

[a)] *Department of Physics, Tsinghua University, Beijing* 100084, *China*

[b)] *China Center of Advanced Science and Technology (World Laboratory), Beijing* 100080, *China*

(Received 14 July 2005; revised manuscript received 2 December 2005)

The effect of Re segregation on the α-Fe $\Sigma5$ [001] (010) grain boundary (GB) is investigated by using a software called DMol and discrete variational method (DVM). Based on the Rice–Wang model, the calculated segregation energy and defect formation energy show that Re is a strong cohesive enhancer. We also calculated the interatomic energy (IE) and bond order (BO) of several atomic pairs to investigate the mechanism of the cohesive effect of Re microscopically and locally. The results show that IEs of atomic pairs formed by those atoms which cross the plane of GB are strengthened due to the segregation of Re, while the BOs of the corresponding pairs are slightly decreased. This discrepancy demonstrates that IE which contains the Hamiltonian of interaction between atoms is a good quantity to describe the bonding strength. The analysis suggests that the electronic effect between atomic pair which comes directly from Hamiltonian is the key factor. The charge density is also presented, and the result indicates that the bonding strength between the Fe atoms on the GB is enhanced due to the segregation of Re, which is consistent with the analysis of IE.

Keywords: mechanical properties, grain boundary, first-principles electron theory
PACC: 6000, 6170N, 7115M

1. Introduction

In the past two decades, the more and more excellent properties such as high strength, strong resistance to stress-corrosion and long lifetime under temperature and stress fields are required for the structural materials in the development in aero-industry. The key task to material designers and physicists is to improve the room-temperature brittleness and enhance the strength of widely-used structural materials, such as steel and some B2 binary alloys. It has been widely accepted that intergranular embrittlement is often the controlling factor limiting the ductile of high-strength steel and metallic alloys.[1] Intergranular fracture is the main reason for failure of materials.[2] Numerous studies have been done both experimentally and theoretically, aiming at improving the mechanical properties of materials. The theoretical simulation becomes an important aspect in this project with the progress in computational technique and ability. Molecular dynamics (MD) and quantum-mechanical methods are the two powerful tools for physicists and technologists. The former can simulate a large system which includes hundreds of thousand atoms and thus could be regarded as a good approximation of real bulk materials; it also can give a dynamical process of the failure of materials, and structure evolution in the fracture process. But its foundation is classical mechanics, thus it cannot give a basic picture of these processes at electronic level. On the contrary, the quantum mechanical method can be used to study the quantum effects, and give various microscopic information related to the electronic structure of materials. Thus, the quantum mechanical method can provide a deeper understanding on this subject. Because of these advantages, together with the speedy development in computer science, quantum mechanical method, especially first-principles program within the framework of density functional theory (DFT), are recently more demanding in theoretical explorations of material design.

According to previous works,[3–8] it is realized

*Project supported by the State Key Development Program for Basic Research of China (Grant No G2000067102).
†E-mail: chenzz01@mails.tsinghua.edu.cn

that the metalloid impurities and/or alloying additions have significant effect on GB embrittlement: Some impurities such as B, C, Mo, etc. play roles as cohesive enhancers when segregating to the GB, some others such as H, P, Si spoil the ductile of GB. Based on the thermodynamic theory developed by Rice and Wang,[9] Wu and Freeman *et al*[3] the embrittlement potency of impurities can be predicted by using the first-principles method. One can presume two states of a GB: one is the integrated GB (before fracture), the other consists of two separated free surfaces (FSs) (after fracture). If an impurity or alloying addition is segregated to the GB/FS, it will change the binding energy $E_{\rm b}$ of the two subsystems, $\Delta E_{\rm b}^{\rm GB}$ and $\Delta E_{\rm b}^{\rm FS}$, and thus determine the effect of the impurity on the GB embrittlement. Simply put, if $(\Delta E_{\rm b}^{\rm GB}-\Delta E_{\rm b}^{\rm FS})$ is positive, the subsystem consisting of two separated FSs is more favourable in energy, thus the impurity is an embrittler; if it is negative, the impurity will enhance the cohesion of GB.

Several previous papers[10−12] revealed that low concentration addition of Re can obviously strengthen α-Fe; however, the microscopic mechanism of the strengthening effect of Re is still open for discussion. In the present paper, we employ the first-principles method DMol[13] based on the DFT and discrete variational method (DVM) to study the electronic structure of Re-doped α-Fe $\Sigma5$ [001]/ (010) GB, and try to give a quantum-mechanical explanation of the effect of Re based on charge density, density of states (DOS) and binding energy, etc. The rest of the paper is organized as follows: the details of cluster model and computation are described in Section 2, the segregation of energy and interatomic energy are discussed in Section 3, charge density is provided and discussed in Section 4, the density of states (DOS) analysis is given in Section 5, and finally the conclusion is given in Section 6.

2. Atomic model and computation

In a bulk material with local defects such as GB, dislocation, vacancy and dopant etc., the periodic condition is broken down, so it is convenient to use a cluster model to simulate this kind of system. The DMol and DVM methods are good for studying the cluster system at electronic level because of the high accuracy and low computational cost. In the present study, we use DMol to optimize the atomic configuration to the ground state and obtain the binding energy, charge density, and DOS, and then the interatomic energy is calculated by DVM. In the DMol calculation, the double-numerical-polarized (DNP) basis sets and Vosko–Wilk–Nisair local exchange-correlation functional[14] are used in self-consistent calculation, and the convergence criteria for the energy gradient and the atomic displacement are 0.015 eV/Å and 0.002Å, respectively.

The three-dimensional (3D) cluster model of α-Fe $\Sigma5$ [001]/ (010) GB is shown in Fig.1. It consists of 91 atoms in 5 stacking layers along [010] direction, and it is constructed according to the coincidence site

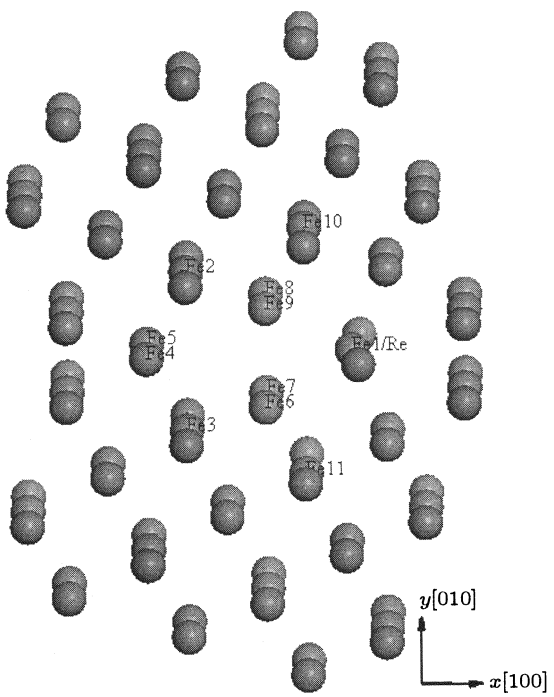


Fig.1. The 3D atomic cluster model and the notation for the structure of α-Fe $\Sigma5$ [001]/ (010) grain boundary. The notations of atoms are used in both GB model and FS model (not shown).

lattice (CSL) model. In a Re-doped cluster, Re replaces Fe1 in the GB core. All the outermost atoms of the cluster are fixed in optimization to simulate real bulk environment and vertical positions of other Fe atoms are adjusted according to the energy gradient at each of these atoms positions.[15] The $C_{2\rm V}$ symmetry of the cluster is kept within the optimization process. The optimization is regarded as completed when the above-mentioned criterion is reached. Utilizing the cluster as a ground-state configuration, we employ the DMol to calculate the binding energy, charge density and DOS of pure-Fe and Re-doped systems, while we use DVM to obtain interatomic energies (IEs) and bond orders (BOs) of the given atom pairs; these two quantities are convenient in the representation of the interaction strength of one atomic

pair. IE is defined as[16]

$$E_{ll'} = \sum_n N_n \sum_{\alpha\alpha'} a^*_{n\alpha l} a_{n\alpha' l'} H_{\alpha' l' \alpha l}, \qquad (1)$$

where N_n is the occupation number for molecular orbital ψ_n, $H_{\alpha' l' \alpha l}$ is the Hamiltonian matrix element connecting the atomic orbital α' of atom l' to the atomic orbital α of atom l. The coefficient $a_{n\alpha l}$ is obtained from

$$a_{n\alpha l} = \langle \phi_{\alpha l}(r) | \, \psi_n(r) \rangle \,, \qquad (2)$$

where ϕ is the atomic orbital α of atom l. $E_{ll'}$ can reveal the interaction between adjacent atoms. Similarly, the BO between two atoms is defined as

$$BO_{ll'} = \sum_n N_n \sum_{\alpha\alpha'} a^*_{n\alpha l} a_{n\alpha' l'} S_{\alpha' l' \alpha l}, \qquad (3)$$

where $S_{\alpha' l' \alpha l}$ is the overlap matrix element between the corresponding atomic orbitals. To minimize the effect of basis sets on the results of DMol and DVM, we use 3d4s4p for Fe atom and 5d6s6p for Re atom in DVM.

3. Segregation energy and interatomic interaction

3.1. Segregation energy

As stated above, based on Rice–Wang model, the embrittlement potency of Re can be qualitatively predicted by the sign of ($\Delta E_{\rm b}^{\rm GB}$–$\Delta E_{\rm b}^{\rm FS}$), so the binding energies of pure GB/FS and Re-doped GB/FS are calculated respectively. The data obtained show that when Re substitutes for Fe1, it enhances the binding energy in the state of integrated GB, with $\Delta E_{\rm b}^{\rm GB}$ being –1.01 eV; while it weakens the $E_{\rm b}$ in the state of separated FS, with $\Delta E_{\rm b}^{\rm FS}$ being 0.97 eV. Thus, ($\Delta E_{\rm b}^{\rm GB}$–$\Delta E_{\rm b}^{\rm FS}$) is –1.98eV, and Re can be regarded as a potent cohesive enhancer in α-Fe GB. Several previous works[17–19] have presented an idea that chemical potential of doping element is a dominant factor of its embrittlement potency. Recently, Geng *et al*[20] gave a preliminary discussion on this idea theoretically based on their first-principles investigation. Now we discuss this theory more deeply. The formation energy of a Re atom replacing a Fe atom is defined as[21]

$$E_{\rm F} = E({\rm Re, Fe}) - E({\rm pure_Fe}) - \mu_{\rm Re} + \mu_{\rm Fe}, \qquad (4)$$

where E (Re, Fe) and E (pure_Fe) are the total energies of Re-doped and pure Fe clusters, respectively, $\mu_{\rm Re}$ is the chemical potential of Re, and $\mu_{\rm Fe}$ is the chemical potential of Fe. The chemical potentials for bulk Re and Fe are –8.06eV and –4.31eV, respectively,[1)] $E_{\rm F}$ of Re is –4.76eV obtained from these data. The negative $E_{\rm F}$ means Re tends to segregate to GB and is beneficial to lower the energy of GB; the contribution from the difference of chemical potentials of the two elements is 75% of $E_{\rm F}$, and thus is the dominant factor. The results show that the element with large chemical potential tends to segregate to GB and is beneficial to the mechanical properties of Fe.

3.2. Interatomic energy

The calculated IEs are listed in Table 1. When Re replaces Fe1, the interactions between Fe atoms lying on the GB are apparently enhanced. For example, the $E_{\rm Fe6-Fe9}$ changes from –2.86eV to –5.56eV, and the $E_{\rm Fe2-Fe4}$ changes from –1.76eV to –3.23eV. Both are almost twice as large as those in pure Fe system. It should be noticed that the $E_{\rm Fe6-Fe7}$ changes from –0.61eV to –2.63eV. The interaction of Re atom with its nearest neighbour atoms is stronger than that of Fe1: the $E_{\rm Re-Fe6(9)}$ is –3.03eV, nearly twice that of $E_{\rm Fe1-Fe6(9)}$, which is –1.50eV in absolute value. It should be noticed that these atomic pairs are all across the GB, and the enhanced interaction is apparently beneficial to strengthen the cohesion of GB.

Table 1. The interatomic energies $E_{\rm A-B}$ (in eV) and bond order (BO) of given atomic pairs in pure Fe and Re/Fe GB.

Atomic Pair	Pure Fe GB		Re/Fe GB	
	IE	BO	IE	BO
Fe1(Re)–Fe6(9)	–1.50	0.14	–3.03	0.11
Fe2–Fe4	–1.76	0.15	–3.23	0.14
Fe2–Fe5	–1.76	0.15	–3.23	0.14
Fe6–Fe7	–0.60	0.06	–2.63	0.12
Fe6–Fe9	–2.86	0.22	–5.56	0.23

In Table 1, the calculated BOs are also listed. It should be noticed that though IEs of several given atomic pairs strengthen, the BOs of the corresponding pairs slightly decrease compared with those in pure Fe GB. The decrease is attributed to the fact that the number of valence electrons of Re is 7, fewer than that of Fe, which is 8. This discrepancy between IE and BO suggests that the change of energy in bonding states due to the doping of Re plays an important

1) The chemical potential is calculated as the energy per atom in bcc structure for Fe, and in hcp structure for Re.

role in the enhancing effect of Re. It also reveals the disadvantage of the traditional BO analysis of clusters and molecules: the energy in bonding states has not been included in BO. Thus it should be pointed out that IE which contains the Hamiltonian of interaction of atoms is a good quantity to describe the bonding strength. The analysis also indicates that the mechanism of Re in enhancement of GB is very different from that of B, in this case the trends of change of IE and BO are consistent with IE, thus the bonds are strengthened by increasing the overlapping of orbitals.[22]

4. Charge density

The charge density difference in (001) plane of pure Fe and Re-doped GB are shown in Fig.2. The charge density difference is obtained by subtracting the electron density of free atoms at the position from that of the cluster system, it can reveal the bonding character of the cluster.[23] Comparing these two figures, we can find out bonds among iron atoms on GB are strengthened due to Re-doping, especially between Fe3 and Fe17, Fe2 and Fe16. Perpendicular to the interface of GB, electrons accumulate between Fe10 and Fe11. Compared with Fe1, Re makes stronger bonds with the two Fe atoms in (001) plane. All these bonding characters indicate the strengthening effect of Re segregating to the GB.

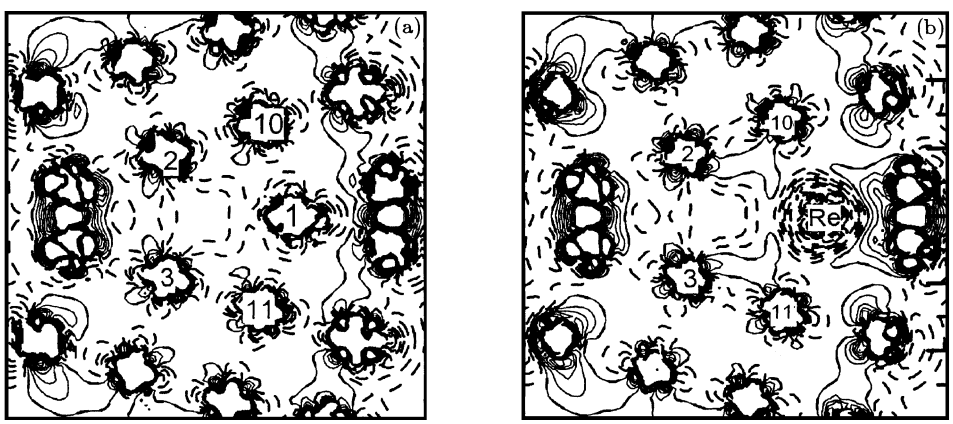


Fig.2. Charge density difference in a) Pure α-Fe $\Sigma5$ [001]/ (010) GB, b) Re-doped GB. Contours plotted from 0.01 e/a.u.^{3} to –0.01e/a.u. at interval of 0.002 e/a.u.^{3}. The solid lines indicate electrons accumulation, and the dashed lines indicate electrons depletion.

5. Density of states

The local DOS (LDOS) are shown in Fig.3 for further understanding of the electronic structure of Re-doped cluster. The Fermi level (E_f) is set as zero. In pure Fe system, the DOSs of Fe2, Fe4 and Fe6, which lie on the GB, all have large peaks beyond E_f, while in Re-doped system, the DOS of each of these atoms shifts towards the low energy region. The aforementioned peaks shift below E_f due to Re doping, which means the electrons in anti-bonding states now transfer into bonding states, and lower the total energy of the GB. This change of LDOS contributes to the beneficial effect of Re. The overlap between DOS of Re and other atoms on the GB does not enhance compared with the pure Fe system. In the DOS of Re, there are only several small hybridized peaks in –4eV∼–3eV region. This character indicates that the cohesive effect of Re is not due to the overlap between orbitals of Re and other atoms on the GB, but due to the change of the distribution of DOS of Fe atoms with respect to the energy due to Re doping. The analysis on LDOS explains the discrepancy between IE and BO, and confirms the conclusion made in Section 3.2: the change of energy in bonding states, not the overlap between the atomic orbitals, is the key factor in the effect of doping element.

The effect of Re is opposite in the FS case. The LDOS of Fe2, Fe4 and Fe6 all move into the higher energy region. There appear anti-bonding peaks beyond E_f. These changes will raise the total energy of the system. Thus the Re-doped GB is not favourable in separated FS state because of the higher energy.

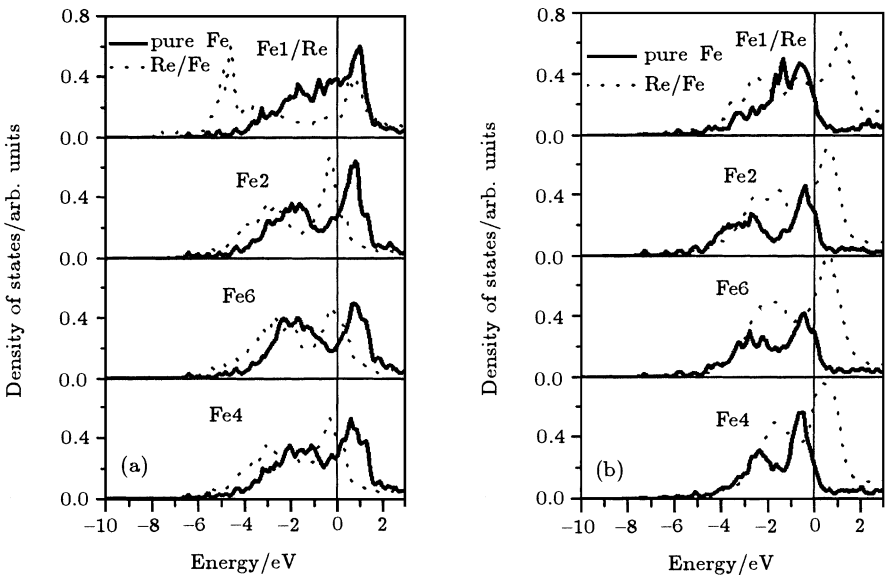


Fig.3. Local densities of states (LDOS) of Fe1/Re, Fe2, Fe20, and Fe24 atoms in a) pure Fe, Re/Fe, GB, b) pure Fe, Re/Fe FS.

6. Summary

The effect of Re on the cohesion of α-Fe Σ5 [001]/(010) GB has been studied by employing DMol and DVM in the framework of DFT. Based on Rice–Wang model, Re is found to be a strong cohesion enhancer (–1.98 eV). The charge density difference reveals that bonds between Fe atoms on the GB are strengthened due to Re doping. We have also studied the effect of Re on the GB cohesion from the standpoint of IE, BO and LDOS. The calculated results indicate that when Re segregates to the GB, the IEs of atomic pairs which cross the GB are apparently strengthened. The enhanced effect of Re indicates that the bonding strength is controlled quantitatively by the interatomic energy of atomic pair, which is presented by local Hamiltonian, but not simply the overlap pattern between electronic states. It can be shown from the distribution of LDOS directly. We also point out the disadvantage of BO, which is only a coefficient of interatomic Hamiltonian between atomic pair in IE. Here we only give a preliminary study on the mechanism of impurity effect locally and microscopically. A deeper study on this topic is necessary.

Acknowledgments

One of the authors, Z Z Chen, is grateful to Dr Yan J A, Dr Liu E Z and Dr Meng T Z for beneficial discussion and suggestion.

References

[1] Olson G B 1990 In *Innovations in Ultrahigh-Strength Steel Technology*, edited by Olson G B, Azrin M, and Wright E S, Sagamore Army Materials Research Conference Proceedings No. 34 (Washington, DC: US GPO), p3

[2] Feng D 1998 in *Metal Physics* Vol.1 *Structure and Defects* edited by Feng D (Beijing: Science Press) p416 (in Chinese)

[3] Wu R, Freeman A J and Olson G B 1994 *Science* **265** 376

[4] Krajnikov A V 1997 *Mater. Sci. Technol.* **4** 956

[5] Daw M S and Baskes M I 1983 *Phys. Rev. Lett.* **50** 1285.

[6] Zhang J M, Wei X M, Xin H and Xu K W 2005 *Chin. Phys.* **14** 1015

[7] Wu R, Freeman A J and Olson G B 1996 *Phys. Rev.* B **53** 7504

[8] Collins A, O'Handley R C and Johnson K H 1988 *Phys. Rev.* B **38** 3665

[9] Rice J R and Wang J S 1989 *Mater. Sci. Eng.* A **107** 23

[10] Geng W T, Freeman A J and Olson G B 2001 *Phys. Rev.* B **63** 165415

[11] Mekhrabov A O and Akdeniz M V 1999 *Acta Mater.* **47** 2067

[12] Harris K, Erickson G L and Schwer R E 1990 *Metals Handbook* **Vol.1** 10th Edition: *Properties and Selection* edited by ASM INTERNATIONAL Handbook Committee (Materials Park, OH: ASM International) p995
[13] Delley B 1990 *J. Chem. Phys.* **92** 508
[14] Vosko S J, Wilk L and Nusair M 1980 *Can. J. Phys.* **58** 1200
[15] Tang S P, Freeman A J and Olson G B 1993 *Phys. Rev.* B **47** 2441
[16] Wang C Y 1995 *Defect Diffusion Forum* **125-126** 79
[17] Stark J P and Marcus H L 1977 *Metall. Trans.* A **8** 1423
[18] Lee D Y, Barrera E V, Stark J P and Marcus H L 1984 *Metall. Trans.* A **15** 1415
[19] Seah M P 1979 *Acta Metall.* **28** 955
[20] Geng W T, Freeman A J, Wu R and Olson G B 2000 *Phys. Rev.* B **62** 6208
[21] Venezuela P, Miwa R H and Fazzio A 2004 *Phys. Rev.* B **69** 115209
[22] Wang F H and Wang C Y 1996 *J. Phys. Condens. Matter* **8** 5527
[23] Shang J X and Wang C Y 2002 *Phys. Rev.* B **66** 184105