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Effects of Co and Cr on bcc Fe grain boundaries cohesion from first-principles study

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Abstract

The segregation effects of Co and Cr on the bcc Fe $\sum 3[1\bar{1}0](1\,1\,1)$ grain boundary cohesion are investigated based on the Rice–Wang thermodynamics model by the first-principles DMol method within the framework of density functional theory. The electronic properties are studied for Co/Fe and Cr/Fe systems. The calculated segregation energy difference between the grain boundary and the corresponding free surface is 0.25 eV for solute Co and −0.43 eV for solute Cr, which indicates that Co could weaken and Cr enhance the grain boundary cohesion in bcc Fe. In these systems the chemical effect induced by Co and Cr play crucial effects, but the geometry effect can be neglected. In addition, an anti-parallel spin island is formed around the central of GB.

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1. Introduction

Because of its low price and excellent mechanical properties, steel is one of the most important and widely used metallic materials. Although modern technology has various effective methods to get good mechanical properties, strength is often contradictory to toughness in the same steel. It is known that the intergranular segregation effects of alloying elements such as Si, Mn, Nb, Mo, V, Ti, Co and Cr play important roles in determining the cohesion properties of Fe grain boundary (GB), and which will further affect the two key mechanical properties: strength and toughness in structure steels. The different alloying elements may have different effects on the intergranular fracture. So the study on intergranular segregation effect of alloying element has great significance for understanding the mechanical properties of steel materials.

On the basis of Griffith fracture theory [1], Rice and Wang [2] have presented a thermodynamic model to describe the mechanism of impurity-induced intergranular embrittlement through the competition between plastic crack blunting by dislocation emission and brittle boundary separation. In their model, the relationship between the cleavage works with ($2\gamma_{\text{int}}$) or without ($2\gamma^0_{\text{int}}$) solute atom is expressed approximately as

$$2\gamma_{\text{int}} = 2\gamma^0_{\text{int}} - (\Delta E_{\text{GB}} - \Delta E_{\text{FS}})\Gamma$$

where Γ is the solute coverage of impurity, ΔE_{GB} and ΔE_{FS} are the impurity segregation energies at GB and at free surface (FS), respectively. One can predict whether the solute atom enhances or weakens the GB cohesion by the sign of $\Delta E_{\text{GB}} - \Delta E_{\text{FS}}$. That is that a solute with positive energy difference $\Delta E_{\text{GB}} - \Delta E_{\text{FS}}$ will be a more potent embrittler, while a solute with a negative difference can enhance grain

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boundary cohesion. The experimental investigation on the iron containing H, B, Sn, Sb and S has provided support on the above descriptions [2].

In the past decade, on the basis of Rice–Wang model, some researchers have made theoretical efforts to understand the segregation effect of light impurity such as B, C, P and S, etc. on Fe GB cohesion by first-principles calculations [3–10]. They obtained some exciting results those are in good agreement with experiment and have been used in materials design. The effects of alloying elements Nb, Ti, V, Mo, Pd, Mn, etc. on bcc GB and Cr and Mn on fcc Fe GB have been studies [11–17]. These studies showed that it may be beneficial to consider the electronic effect in the study of iron materials to give out much insight into the mechanical properties of such materials.

From Rice–Wang model mentioned above, we know that ΔE_{GB} and ΔE_{FS} are the two dominated quantities in the brittle–ductile judgment for solute atom and can be determined accurately by first-principles calculation. In the present work, we have adopted first-principles DMol method [18,19] to investigate the segregation effects of two important alloying elements Co and Cr on bcc Fe $\sum 3[1\bar{1}0](111)$ GB cohesion. We present computational method and cluster model in Section 2, and give results and discussions in Section 3.

2. Computational method and cluster model

The DMol is a first-principles numerical method within the framework of density functional theory [20,21], which can perform accurate quantum mechanical calculations on a wide range of compounds, including metal, biological compounds. One of its merits is that it includes an energy gradient calculation, from which one can obtain the desired optimized atomic structure. The cluster models used in the present DMol calculation are shown in Fig. 1. Fig. 1(a) and (b) presents the atomic structures of Fe $\sum 3[1\bar{1}0] \times (111)$ GB containing 71 atoms and Fe(111) FS containing 58 atoms, respectively. The squares and circles represent different Fe layers along [110] direction. Some atoms in cluster are labeled with numbers for discussing the results clearly. Because of almost the same atomic size, Co and Cr will occupy most possibly the substitution site rather than the interstitial site on the GB or FS. In this work, we just consider the substitution case. Co and Cr atoms are assigned to substitute for Fe1 atom. There are 15 atoms (including Fe1, Fe2, Fe3, Fe8, Fe9, Fe10, Fe11, Fe32, Fe33, Fe34, Fe35, Fe36, Fe37, Fe38, Fe39) in the GB model and 8 atoms (including Fe1, Fe2, Fe8, Fe10, Fe32, Fe33, Fe36 and Fe37) in free surface model labeled in Fig. 1 are to be relaxed.

The DMol method provides various types of basis set, the double numerical basis with polarization functions (DNP) were proved to be able to yield the most reliable result. In this work, we adopted the DNP as the basis set. The orbitals beyond 3s were taken as the self-consistent valence orbitals and those below 3s were taken as the core orbitals for Fe and Co(Cr) atoms. The valence orbitals were

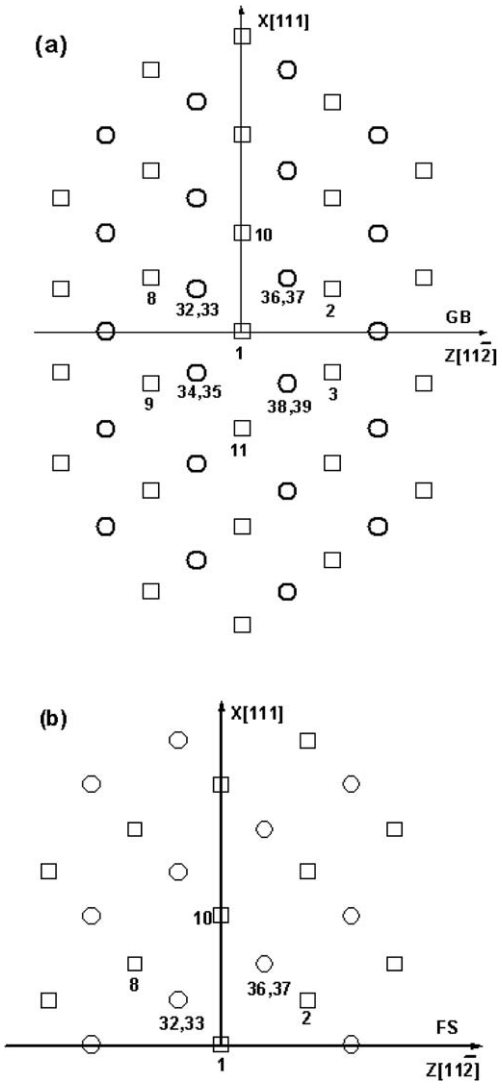

Fig. 1. The atomic structure of cluster models for (a) bcc Fe $\sum 3[1\bar{1}0](111)$ GB, $X=0$ plane is GB plane; (b) bcc Fe(111) FS. The square and circle represent Fe atoms in different Fe layers along [110] direction, respectively. The labeled atom with number is the relaxed atom in DMol calculation. The square labeled by number 1 is the substitution site for Co(Cr) in GB and FS.

further refined by the usual valence-core orbital orthogonalization technique. The Vosko–Wilk–Nisair local spin exchange correlation potential [22] including without and with GGA correction was employed. The binding energy of the cluster system is defined as the difference of the total energy of the interacting atom system with that of the free atom system. We obtained the optimized atomic structure and the binding energy of the system from the energy gradient on the relaxed atom converged to 0.001 eV Å^{-1}.

3. Results and discussion

3.1. The effects of Co(Cr) on atomic structure of GB and FS

In this study, the original atomic configurations of bcc Fe $\sum 3[1\bar{1}0](111)$ GB was constructed by use of the