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Helium effect at grain boundaries in Fe-Cr alloys: A first-principles study.

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Abstract

Helium is produced in the structural materials of nuclear power plants by the nuclear transmutation following neutron irradiation. Since the solubility of helium in all the metals is extremely low, helium tends to be trapped at defects such as vacancies, dislocations and grain boundaries, which cause materials embrittlement. Density functional theory (DFT) calculations were performed in order to investigate the helium effect at grain boundaries (GBs) in iron-chromium alloy. Both cohesive energy and magnetic properties at symmetric Σ3(111) and Σ5(210) tilt Fe GBs are studied in presence of Cr and He atoms. It is found that the presence of Cr atom increases cohesive energy, at different He concentration, and has a strong influence on strongly magnetic properties at GBs. The dependence of segregation energy of helium atom as a function of different position of Cr atoms located inside/outside GB has been considered. Results of the present first-principle study enable us to clarify the role of Cr in understanding of helium effect in Fe-Cr-based alloys.

Keywords: First-principles calculations; Iron-chromium; Grain boundary; Helium segregation; Magnetic properties

1. Introduction

Ferritic and austenitic steels are considered as important materials for nuclear industry applications. In particular ferritic/martensitic steels are promising structural materials for first wall and blankets components in future fusion power plants [1]. Materials in a fusion environment are exposed to the irradiation of high-energy of 14 MeV neutrons that comes from D+T reaction [2], which leads to the (n,α) transmutation. Helium and hydrogen are important products of this reaction for iron-based alloys [3]. He impurities can be trapped by crystallographic defects as vacancies [4-5] or grain boundaries (GBs) [6] because of their very low solubility in iron (Fe) [7]. Experiments show that helium segregation to GBs affects their integrity [8-10]. This segregation leads to the nucleation and growth of He clusters in the form of He bubbles which causes the swelling and embrittlement of material. The previous experimental evidence also shows that Fe alloys with low Cr concentration are resistant to swelling under irradiation [11]. In this work we investigated two low coincident site lattice (CLS) GBs (Σ3 and Σ5) with He impurities in α-Fe and Fe-Cr from the

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first-principles calculations.

2. Computational methods

In the present study all total-energy calculations were performed within the density functional theory (DFT) implemented in Vienna Ab-initio Simulation Package (VASP) code [12]. Interactions of the electron-ionic core were described by the projector augmented waves (PAW) potential without semi-core p electrons [13]. We employed spin-polarized generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) functional [14] for the exchange-correlation interaction which is necessary to describe the ground state of iron [15]. In our calculations we used the Fermi smearing of 0.2 eV and the cut-off energy for the plane-wave basis was equal to 400 eV. The predicted equilibrium lattice constant was 2.829 Å for bcc Fe in ferromagnetic state with magnetic moment of 2.199 μ_B per atom, which are in a good agreement with the previous theoretical [16] and experimental values [17-20]. The Brillouin zones of grain boundary structures were sampled by Monkhorst-Pack scheme [21] with (10x10x2) k-points for normal Σ3(111) and (7x14x2) k-points for Σ5(210) cells. DFT simulations of GBs were performed by full relaxation of the atomic positions as well as the cell shape and size. The free surfaces (FSs) calculations were performed within constant cell volume which was obtained from the relaxed GB structure. The convergence for forces was set to 0.005 eV/Å. Our predictions of energy difference between interstitial tetrahedral and octahedral configuration for helium in 4x4x4 supercell bcc-iron is -0.195 eV compared with -0.23 eV obtained from VASP calculations using PW91 exchange-correlation potential [22]. Convergence studies have been performed for Σ3 GB in α-Fe as function of the three different sizes of cell with 30, 36 and 42 atoms and the corresponding binding energy (see definition from Eq. (3)) differences between them are not significant (<1%). For the Σ5 GB in α-Fe two configurations were considered: shifted and symmetric GBs. It is found that the shifted configuration has lower total energy than symmetric-one by 0.41 eV in a supercell with 42 Fe atoms.

The GB energy γ_{GB} was calculated according to following expression [23]:

$$\gamma_{GB} = (E_{GB} - n * E_{bulk})/2A \qquad (1)$$

where E_{GB} is total energy of GB structure with n atoms; E_{bulk} is total energy per atom of bulk structure; A- is area of GB.

Analogically the free surface (FS) energy E_{FS} was defined according to the equation:

$$\gamma_{FS} = (E_{FS} - m * E_{bulk})/2A \qquad (2)$$

where E_{FS} is total energy free surface structure with m atoms. In present study for both Σ3 and Σ5, m=n/2.

The GB binding energy γ_{bind} was defined by the following expression [24]:

$$\gamma_{bind} = 2\gamma_{FS} - \gamma_{GB} \qquad (3)$$

The strengthening (S) or weakening (W) effect, based on a thermodynamic Rice and Wang approach [25], of helium atoms in Fe GB can be defined as [20]:

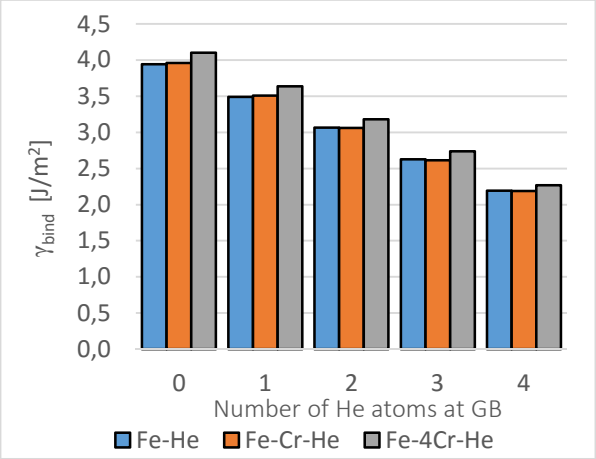
$$\Delta E_{SW} = [E_{GB}^{SA} - E_{GB} - (E_{FS}^{SA} - E_{FS})]/A \qquad (4)$$

where E_{GB}^{SA} is total energy of GB within solute atom (SA) inside of the GB, E_{FS}^{SA} is total energy of FS with solute atom. The negative/positive value of ΔE_{SW} means that solute atom causes strengthening/weakening the GB.

The segregation effect of solute atoms in Fe GB can be defined as [26]:

$$E_{seg} = E_{GB}^{SA} - E_{Bulk}^{SA} \qquad (5)$$

where E_{Bulk}^{SA} is total energy of GB structure with solute atom in the bulk. The negative/positive value of E_{seg} means that GBs uptake/outtake solute atoms. In present study as solute atom we defined helium atom in bcc-Fe and Fe-Cr structures.



3. Results and discussion

3.1. Configurations with Cr at GB.

Table 1 shows the calculated binding, GB, strengthening/weakening and segregation energies for a solute atom of He in both Σ3 with 30 atoms/cell and shifted Σ5 with 42 atoms/cell GB in bcc-iron. Our benchmarking calculations are in good agreement with the previously available DFT data. The presence of He increase relaxation volume for both Σ3 and Σ5 GBs.

Table 1. DFT values of GB energy, binding energy, strengthening/weakening energy, segregation energy, calculated in present work and compared with previous calculations are tabulated in the first four columns, respectively. Last column shows relaxation relative volume [5] of GBs without He and Cr (I) with 1 atom He (II) with respect to V_0, which is volume per atom in the bulk(11.323 Å^3).

	γ_{GB} [J/m^2]	γ_{bind} [J/m^2]	ΔE_{SW} [J/m^2]	E_{seg} [eV]	Relaxation volume [V_0]
Σ3	**1.609 (1.61)[23]**	**3.833 (3.86)[27]**	**3.563**	**-1.393 (-1.37)[28]**	**0.6835 (I) 1.1815 (II)**
Σ5	**2.047 (2.00)[20]**	**3.350 (3.19)[20]**	**2.481**	**-1.667**	**0.9837 (I) 1.8559 (II)**

Figure 1 shows the binding energy for the three configurations with different number of Cr atoms at the Σ3 GB as a function of number of He atoms also located in the GB. The dependence of binding energies as a function of He concentration in pure Fe (blue values) shows a decreasing trend in an agreement with previous calculations [29]. Importantly, it is predicted from our calculations that at fixed number of He atoms at GB, the presence of Cr atoms enhanced the binding energies in comparison with those GB structures without Cr. Accordingly, using Eq. (4) the difference of

Fig. 1. Binding energy dependence as a function of the number of helium atoms for Σ3(111) supercell. (120 Fe+Cr atoms). Blue colour denotes 120 Fe atoms, Orange: 119 Fe atoms + 1 Cr atom, Grey: 116 Fe atoms + 4 Cr. Cr atoms are located in GB.

strengthening/weakening energy (ΔE_{SW}) with and without Cr atoms as a function of He atoms increases linearly. For example, it was found that the weakening energy ($\Delta E_{SW}>0$) of Σ3 GB in presence of 4 Cr and 4 He atoms is 3.658 J/m^2 in comparison with 3.549 J/m^2 in the structure without Cr atom.

Figure 2 shows the dependence of DFT calculated relaxation volume as a function of number of He atoms at Σ3 supercell GB with or without presence of Cr atoms. It is found that almost linear dependence for three different GB configurations (blue – without Cr; orange –1 Cr; grey –4 Cr) has been obtained, but with different slopes. The higher

slope is seen for the GB with the highest Cr concentration that is consistent with the larger atomic size of Cr atom in comparison with those of Fe atom.

3.2. He segregation in presence of solute Cr.

Using Eq. (5) the segregation energies of one He atom to the Σ3 and Σ5 GB in α-Fe have been calculated for different positions of substitutional Cr atom. For the case of Σ3 GB the three configurations are considered: a Cr atom inside GB denoted by Cr(GB), Cr inside grain- Cr(G), and with 2 Cr – one inside the GB and second one in the grain - 2Cr(GB_G). It is found that in the presence of Cr atom the segregation of He atom to GB is decreasing by 0.063, 0.179 and 0.371 eV for the first, second and third case, respectively, in comparison with those without Cr atom. The same trend has been found for Σ5 GB case: the segregation energy of He atom in the presence of Cr atom inside GB is lower by 0.370 eV in comparison with those in pure iron GB case.

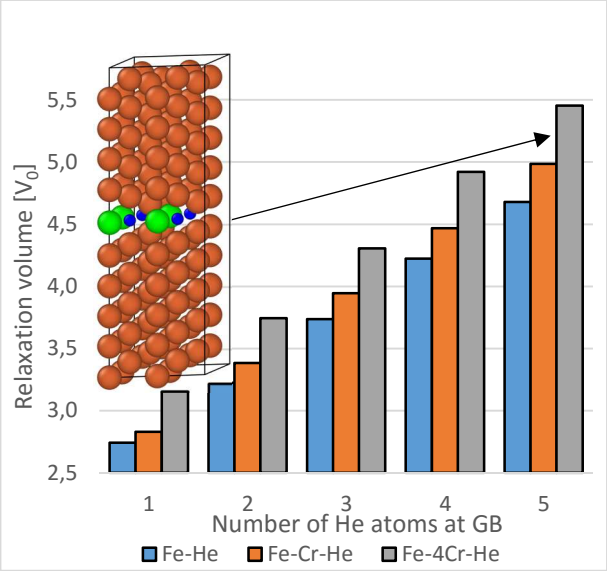


Fig. 2. Relaxation volume (in unit of V_0) as a function of the number of helium atoms for Σ3(111) supercell with the same colour code as in Fig.1. The insert figure shows supercell Σ3 GB with 4 Cr atoms (green) and 4 He atoms (blue) inside GB.

3.3. Magnetic effect at GB in presence of Cr atoms.

In contrast to the GB properties in α-Fe, the presence of Cr atom plays important role in the magnetic properties in GBs. Figure 4 shows DFT predictions of average value of magnetic moment per atomic layers for the four configurations in Σ3 supercell GB with: (a) 120 Fe atoms; (b) 120 Fe atoms +4He inside GB; (c) 119 Fe and 1 Cr atoms +4He atoms inside GB; (d) 116 Fe and 4 Cr atoms +4He atoms inside GB. The average magnetic moment at GB layers (zero layers) decreases from 2.674 μ_B in case (a) to 2.572 μ_B in case (b) to 1.497 μ_B in case (c) and -2.822 μ_B in case (d). It is clear that the presence of Cr atom decreases dramatically the average value of magnetic moment. Interestingly, at the first layer to the GB the average magnetic moment for the three later cases (b, c, d) is significantly higher than those in the first case. At layer 11 located far away from GB the average magnetic moment convergences to the bulk value of 2.2 μ_B.

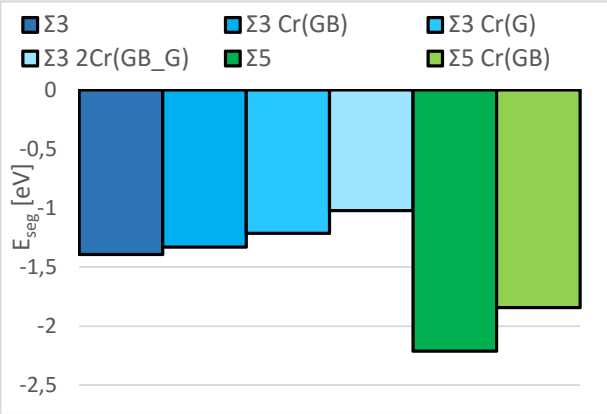


Fig. 3. Segregation energy of 1 He atom to Σ3 without Cr (dark blue), with Cr atom (blue – inside GB; medium blue – in the bulk; light blue – one inside GB and one in a bulk), and Σ5 without Cr (dark green) and with Cr atom inside GB (green).

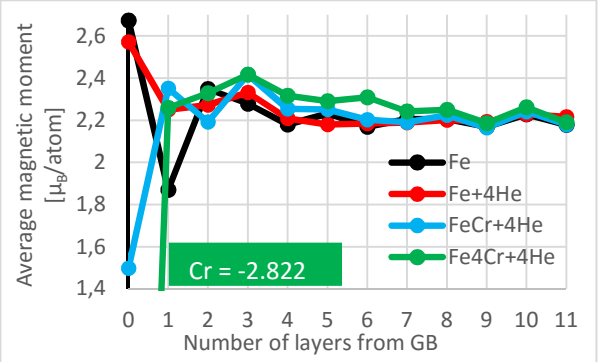


Fig.4. The dependence of average magnetic moment as function of layer number from Σ3 GB.

4. Conclusions

The main conclusions of this work are the following:

- Presence of Cr atom increases binding energy at GB for all considered He concentrations.
- Relaxation volume increases linearly as function of He concentration and the higher concentration of Cr atom corresponds to larger slope of the linear dependence.
- The segregation energy for He atom is sensitive to the position of Cr atoms for both Σ3 and Σ5 GB.
- The magnetic properties at GB with He atoms strongly depends on the presence of Cr atom.

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