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First-principles study of the effect of Ni segregation on the interface of bcc-Fe/Cu-precipitation

HAIYAN WANG[a,c], XUEYUN GAO[a,b,*], HUIPING REN[c], BAOWEI LI[c], ZONGCHANG LIU[a]
[a] *School of material and metallurgy, Inner Mongolia University of Science and Technology, Baotou 014010, P.R. China*
[b] *Beris Engineering and Research Corporation, Baotou 014010, P.R. China*
[c] *Key Laboratory of Integrated Exploitation of Bayan Obo Multi-Metal Resources, Inner Mongolia University of Science and Technology, Baotou 014010, P.R. China*

The effect of Ni on the interface of ε-Cu precipitates in bcc-Fe matrix was investigated by first principles calculations, and the followed interfacial binding was discussed as well. The result indicate that, when Ni segregate at the bcc-Fe/ε-Cu interface, the electrons around Ni increase, and the interfacial bonding is mixed with ionic nature; at the meanwhile, the charges around the Ni distorted directions toward its neighboring atoms are enhanced. Due to the changes of the electronic structure in the system, the ideal work of adhesion of the interface increases, which means the interface with Ni segregation is more stable than the Ni free one. The calculations of the quasistatic ideal tensile strength show that the tensile strength of the interface is somewhat lower, but the plastic is enhanced, which means that the toughness of the interface is improved significantly due to the Ni segregation.

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1. Introduction

Copper containing high strength low alloy (HSLA) steels, typically HSLA-80 and HSLA-100, are of particular interest for large submarine and offshore structures, pipelines, hull of ships, etc. These applications often demand a combination of strength, toughness and weld ability. In order to attain the desired properties, several alloying elements, such as Mn, Cu, Ni, Cr, Mo, Nb etc., are added to exploit the benefits from the alloy chemistry. For the high strength level, copper precipitation plays an important role, as it contributes to strength through the precipitation hardening process. The amount of copper precipitating as well as its size and morphology govern the properties of the copper bearing steel[1-5].

It is generally accepted that, in the early stages of ageing, Cu-precipitates undergo a multi-stage transformation from body centred cubic (bcc) to face centred cubic (fcc) structure[6-8].However, while the nanometer sized Cu-rich precipitates act as strength contributors, the negative effect on toughness was observed, i.e., leading to hardening but embrittlement. Previous experimental results of thermal-aged high Cu HSLA show that, Ni helps to accelerate the precipitation of copper, and tends to segregate at the interfaces of copper precipitate in ferritic steels[9]. As a potential element in improving strength and toughness properties of this alloy system, Ni was introduced in this alloy designing [10].

As an alternative approach, first-principles method can provide understanding of the segregation of alloying element to phase interface from the point of view of chemical property and energetic explanation. Y.P. Xie [11,12] et al. studied the segregation tendency of Al, Ni, Mn, and Si on the α-Fe/Cu interface, and the effects of these elements on the interfacial embrittlement by comparing the Griffith work. A.S. Murthy [13] et al. investigated the effect of Co on Cu precipitate formation mechanism in Fe-Cu alloy by employing three-dimensional atom probe tomography in conjunction with first-principles.

In the present work, first-principles investigation have been employed to study the effect of Ni on the electronic structure of the α-Fe/Cu interface, as well as the ideal work of adhesion, and then we performed the first-principles tensile test calculations to understand the influence of Ni on the interface strength.

2. Model and theoretical methods

First-principles calculations was carried out by using the Vienna ab-initio simulation package(VASP) in projector augmented waves pseudopotentials, the

generalized gradient approximation (GGA) is used for the exchange and correlation effects [14,15]. The plane-wave cut-off energy is 350eV. The equilibrium structures were determined, up to a precision of 10^{-4}eV in total-energy difference and with a criterion that required the force on each atom to be less than 0.01eV/Å in atomic forces. The k-points samples for these super cells are Monkhorst–Pack grids (6×6×1).

Fig. 1 shows the interfacial model for ε-Cu/ bcc-Fe, there are 64 atoms in this supercell. The orientation relationship between Cu particle with fcc structure and bcc-Fe is K-S orientation relationship: $(111)_{\varepsilon\text{-Cu}}//(110)_{\text{bcc-Fe}}$, $[1\bar{1}0]_{\varepsilon\text{-Cu}}//[1\bar{1}1]_{\text{bcc-Fe}}$ [16]. As for the case of the interface with Ni segregation, we replaced the atom at site Cu1 with Ni. For all the calculations mentioned in the following are based on the optimization of the structure.

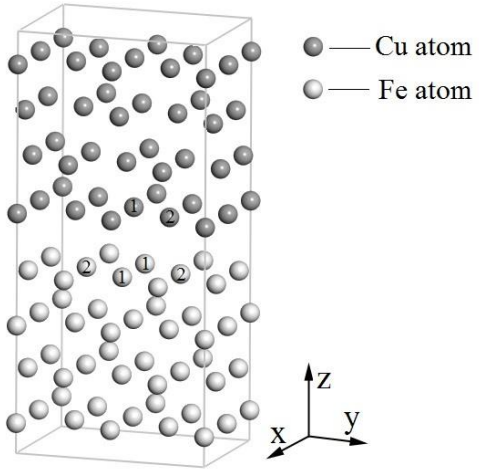

Fig. 1. The atomic structure of the interface between fcc Cu precipitated phases and bcc Fe

3. Results and discussions

3.1 Electronic structure

To reveal the nature of the interfacial bonding between the bcc-Fe and Cu precipitate with and without Ni segregation, the densities of states of the two system were investigated, as depicted in Fig. 2. Fe1, Fe2, Cu1 and Cu2 in Fig. 2 indicate the corresponding atoms in Fig. 1. As for the Ni segregation system, Fig. 2 (b), Cu1 is replaced by Ni in bcc-Fe/Cu interface.

As can be seen in Fig. 2, that the combine bonding of the two interfaces mainly come from the *d* orbital electrons contribution of various alloy atom of Fe, Cu and Ni, plus somewhat weaker mixing of *s* and *p* electrons. Fig. 2 (a) exhibits that the PDOS of Fe1 and Fe2 have substantially the same shape, and Cu1 and Cu2 also has the same tendency too. The PDOS of Fe-*d* and Cu-*d* orbit electrons are overlapping in energy interval 0–-5eV, and the energy peak of -5–-8eV range of the total DOS is mainly contributed by electron interaction of *s* orbit of Fe and Cu atoms.

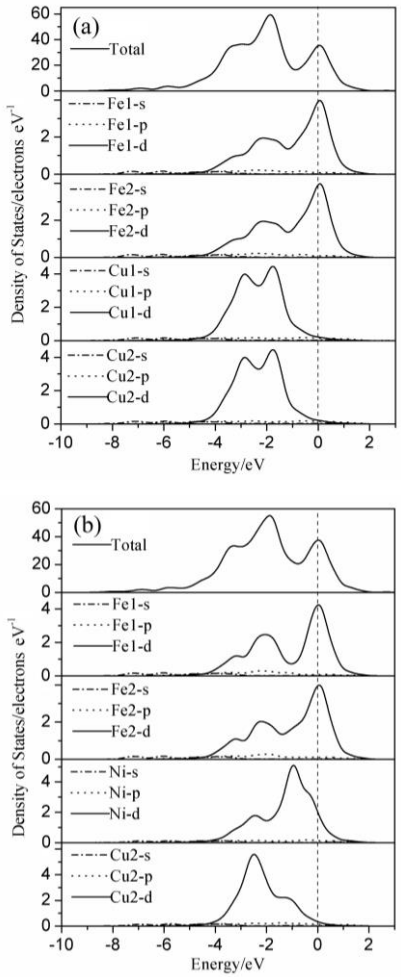

Fig. 2. Total densities of state and partial densities of state of bcc-Fe/ε-Cu (a) and bcc-Fe/ε-Cu-Ni segregation (b) interface

Fig. 2 (b) shows the DOS plots of the interface with Ni segregation. The interaction between Fe-*d* and Cu-*d* orbit electrons has undergone significant changes. The *d* orbit electrons of Cu, Fe and Ni have hybridization effect in -2–-3eV range. Meanwhile, in the same range, Fe1-*d* peak increases from 1.94eV (Fig. 2(a)) to 2.46eV (Fig. 2(b)), and this peak moves to left, which indicate a stronger covalent bond. Moreover, Ni-*d*, Fe2-*d* and Cu2-*d* orbit electrons hybridize with each other. There are two peaks of Cu2-*d* at the left side of the Fermi level, among them the left one in -2.2–-3.2eV increase while the right one decreases with Ni segregation, this bonding state will contribute to the stabilization of bcc-Fe/Cu-Ni interface. Additionally, the states of Fe1-*p* and Fe2-*p* in energy interval -1–-3eV became slightly higher, which also promote the hybridization of interface atoms in the mentioned energy range.

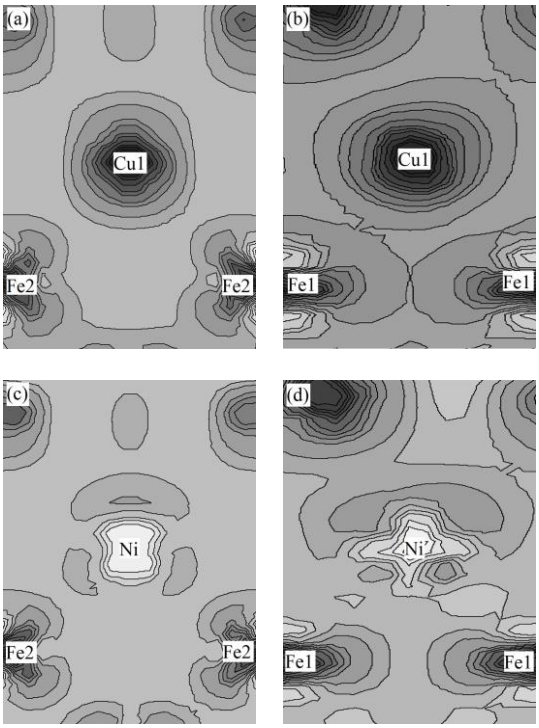

Fig. 3. The valence charge density differences of the two bcc-Fe/ε-Cu interface systems (a) (100) plane for bcc-Fe/ε-Cu (b) (010) plane for bcc-Fe/ε-Cu (c) (100) plane for bcc-Fe/ε-Cu-Ni segregation (d) (010) plane for bcc-Fe/ε-Cu-Ni segregation

For further analysis of the effect of Ni on the α-Fe/ε-Cu interfacial bonding, we calculated the differential charge density distribution $\Delta\rho$ in the (100) and (010) plane of the α-Fe/ε-Cu interface and the Ni-containing α-Fe/ε-Cu interface model, as shown in the Fig. 3. $\Delta\rho$ obtained by subtracting the superimposed charge density from the self-consistent charge density of the relaxed structure [11]. The dark colors denote the charge depletion while the light colors indicate charge accumulation. The planes are chosen purposely in Fig. 3 so that the slice passes through the central atoms, especially the interfacial atoms, thereby allowing us to identify clearly the majority of bonding interactions between them. Fig. 3 (a) and Fig. 3 (b) indicate that the electrons around the Fe and Cu atoms reduced, while public areas have more electrons accumulated. As shown in Fig. 3(c) and Fig. 3 (d), the charge around the Ni accumulates apparently in the interface region when the Ni segregation at interface, which suggesting that the interfacial bonding is mixed with ionic nature. And meanwhile the charges around the Ni atom distorted directions toward its neighboring atoms are enhanced. In summary, the change of the differential charge density distribution of the interface after Ni segregation indicate that the interfacial bonding of the Ni-doped α-Fe/ε-Cu interface is enhanced due to the Ni segregation.

3.2 Interface adhesion

The ideal work of adhesion is one of the keys to predicting the mechanical properties of an interface, which is the reversible work to separate the interface into two free surfaces, neglecting the elastic properties, the size of flaws, and the diffusion, etc. [17]. The ideal work of adhesion is given by the follow equation:

$$W_{ad}= (E_{bcc\text{-}Fe} +E_{\varepsilon\text{-}Cu}\text{-}E_{tot})/A$$

Here, $E_{bcc\text{-}Fe}$ is the total energy of bcc-Fe slab and $E_{\varepsilon\text{-}Cu}$ is the total energy of ε-Cu precipitate slab, E_{tot} is the total energy of the interface system, A is the total interface area.

We calculated the ideal work of adhesion of the two interface systems: bcc-Fe/ε-Cu and Ni segregated bcc-Fe/Cu structure respectively, obtained the W_{ad} of the bcc-Fe/ε-Cu is 279.8mJ/m^2, and the W_{ad} of the Ni contained bcc-Fe/ε-Cu interface structure is 286.7mJ/m^2. The former W_{ad} is close to 276mJ/m^2, which has been reported by N. I. Medvedeva, etc. [14], indicating that the computational model of this paper is reasonable. The results show that the W_{ad} of the Ni segregation system is higher than the bcc-Fe/ε-Cu system, this indicates that the Ni segregation interface structure will be more stable [18] .

3.3 Uniaxial tension experimental

In order to investigate the effect of Ni segregation on the interface of bcc-Fe/ε-Cu, the quasistatic ideal tensile strength in the [001] direction was calculated by using of VASP [19,20]. Specifically, the lattice vectors were incrementally increased along the [001] direction of the interface model, to produce a certain amount of strain. At each step the atomic basis vectors and all the atoms inside the supercell were fully relaxed on the [100] and [010] directions. Fig. 4 depicts the tensile stress-strain curves of the two interface model.

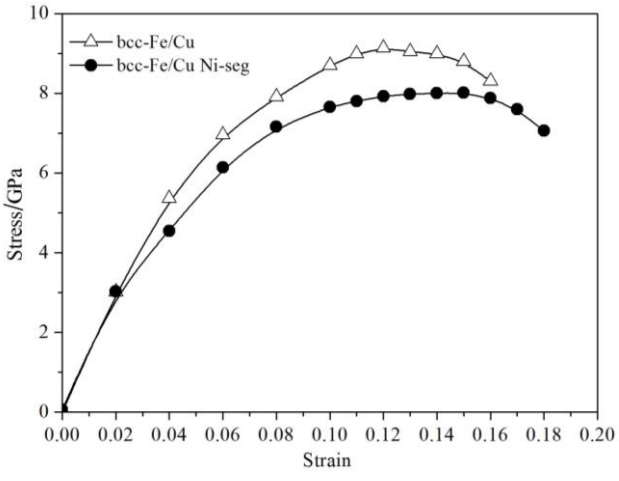

Fig. 4. Calculated stress-strain curves along [001] direction for bcc-Fe/ε-Cu with and without Ni segregation

As shown in Fig. 4, the stress of the [001] direction of the two models increase with increasing strain. The stress of the bcc-Fe/ε-Cu interface model reaches a maximum 9.14GPa when strain ε=0.12, and for the stress of the bcc-Fe/ε-Cu with Ni segregation, reaches its maximum value 8.01GPa when strain ε=0.15. It is noteworthy that, before reaching the maximum 8.01GPa, the stress-strain curve of the bcc-Fe/ε-Cu with Ni segregation is relatively flat in the range of ε=0.1~0.15, compare with the bcc-Fe/ε-Cu interface, the stress increasing trend of the interface with Ni segregation is more gentle before reach the maximum. After Ni segregated at the bcc-Fe/ε-Cu interface, the ideal tensile strength of the interface becomes somewhat lower, about 12% decline, but the plastic is improved, e.g. the strain of the peak tensile stress point has increased about 20%.

4. Conclusions

The interface model of ε-Cu precipitates with bcc-Fe matrix was established, and first-principles calculations based on density functional theory (DFT) was employed to study the effect of Ni segregation on the interface of bcc-Fe/ε-Cu. The electronic structure calculations show that, the interactions between Ni atom and Cu, Fe atoms neighboring significantly increased when Ni segregate at the interface, and the interfacial bonding is mixed with ionic nature. Due to the changes in the electronic structure, the ideal work of adhesion of the Ni segregated bcc-Fe/ε-Cu elevated, which means that the interface become more stable. The calculated results of the quasistatic ideal tensile strength along the [001] direction show that, although the tensile strength of the interface somewhat decreases, the plastic of the interface is significantly improved when the Ni segregate at bcc-Fe/ε-Cu interface.

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*Corresponding author:gaoxueyun126@163.com