First-Principles Study on Enhanced Grain Boundary Embrittlement of Iron by Phosphorus Segregation

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It is known that segregation of P atoms at grain boundaries (GB) enhances the intergranular embrittlement in Fe. In the present work, first-principles tensile tests have been performed on two bcc Fe cell models with a $\Sigma 3$ (111)\/[110] tilt GB: the cell model without P segregation at the GB (clean GB model) and the cell model with P segregation at the GB (P-segregated GB model). The tensile strength and the strain to failure in the P-segregated GB model were 6% and 13% lower than those in the clean GB model. The first bond breaking occurred at the Fe-P bond due to the covalent-like characteristics, although the charge densities were high at the Fe-P bonds. This premature bond breaking of Fe-P was independent of the location of the P atom.

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1. Introduction

Grain boundary (GB) embrittlement in metals is often enhanced by impurity segregation at the GB. It is known that segregation of P atoms at GBs enhances the intergranular embrittlement in Fe.1–6) Freeman and colleagues3,4) showed by first-principles calculations that the enhanced intergranular embrittlement by P segregation is related to the embedded-like electrostatic characteristics. Also, Yamaguchi et al.7,8) explained the enhanced GB embrittlement by P and S segregation on the base of the Rice-Wang model.9) However, there are still some unsolved problems on mechanisms of the GB embrittlement enhanced by impurity segregation, for example, the first site for bond breaking.

Recently, first-principles tensile tests have been performed to investigate the GB embrittlement mechanisms because GB fracture is related not only to the initial electronic states, but also to the variation in electronic states with increasing strain.10–16) Kohyama and coworkers10,12–14) studied various effects of impurities on the GB embrittlement in Al through the first-principles tensile tests. Yuasa et al.16) investigated the bond mobility mechanism in Fe with a P-segregated GB and they showed that the first bond breaking occurred at the Fe-P bond.

The energy of GB segregated by impurities depends on the location of impurity atoms. Yamaguchi7,8) showed that the most stable site for a P atom in a Fe GB is the second site from the GB, not just at the GB. Thus, the GB embrittlement behavior may be affected by the location of the impurity atoms. In the present work, enhanced GB embrittlement of Fe by P segregation, where a P atom is located at the most stable site, is investigated by the first-principles tensile tests.

2. Experimental

Two bcc Fe cells with a $\Sigma 3$ (111)\/[110] tilt GB were used: one was the cell without P segregation at the GB (clean GB model) and the other was the cell with P segregation at the P-segregated GB model, in which the Fe3 (Fe3*) atom was substituted by a P atom, as shown in Fig. 1. In the P-segregated GB model, the segregation energy was $-1.1$ eV/atom.7,8) In the previous work,6) the Fe2 atom was substituted by a P atom. In this case, the segregation energy was $-0.1$ eV/atom.7,8) The previous works17,18) suggested that P atoms segregate to interstitial positions in the GBs. In the segregation to interstitial position, however, the segregation energy was $-0.8$ eV/atom.7,8) Therefore, the substitution of the Fe3 atom by a P atom is energetically the most favorable in the $\Sigma 3$ (111)\/[110] Fe GB segregated by a P atom. The initial cell size was 4.05 $\times$ 7.02 $\times$ 14.89 Å. Geometry optimization calculations were performed using the Cambridge Serial Total Energy Package (CASTEP),19) in which the density functional theory20,21) was used with a plane wave basis set to calculate the electronic properties of solids from first principles. The exchange-correlation interactions were treated using the spin-polarized version of the
generalized gradient approximation within the scheme due to Perdew-Burke-Ernzerhof. The ultrasoft pseudopotentials represented in reciprocal space were used for all elements in the calculations. The Kohn-Sham wave functions of valence electrons were expanded to the plane wave basis set within a specified cutoff energy (\(\approx 300 \text{ eV}\)). The Brillouin zone was sampled using a Monkhorst-Pack \(6 \times 4 \times 2\) k-point mesh and the Gaussian smearing with 0.1 eV width.

After the geometry optimization calculation including cell optimization, an uniaxial tensile strain with an increment of 2\% in the [111] direction, which was normal to the GB plane, was applied to the cells for the first-principles full-relaxed tensile tests. The lattice dimensions in the GB plane were fixed, neglecting Poisson’s ratio to simplify the calculation. This step was repeated until GB fracture occurred. In each step, all atomic positions were optimized in accordance with Hellman-Feynman forces until all the forces were less than 0.03 eV/Å. In the present work, the bond breaking was determined from a rapid increase in bond length.

3. Results and Discussion

The stress-strain curves are shown in Fig. 2 for the clean GB and P-segregated GB models. In the clean GB model, the stress increased up to about 25 GPa with increasing strain until the strain reached 24\%, and then it was nearly constant in the strain range of 24–28\%. The stress rapidly decreased at 28–30\%, and finally GB fracture occurred at 30\%. In the P-segregated GB model, the stress increased up to about 23 GPa until the strain reached 16\% and the stress rapidly decreased at 16–18\%. After the abrupt decrease of the stress, the stress slightly increased at 18–24\%, and it decreased rapidly after 24\% and GB fracture occurred. Thus, the tensile strength and the strain to failure in the P-segregated model were 6\% and 13\% lower than those in the clean GB model. The similar trend of reduced strength and strain to failure was obtained for the substitution of the Fe2 atom by a P atom, which was energetically less favorable than the substitution of the Fe3 atom by a P atom in the present work. In the case of the substitution of the Fe2 atom by a P atom, the tensile strength and the strain to failure in the P-segregated model were 27\% and 47\% lower than those in the clean GB model.

It is of interest to note that the strain and strain to failure are more reduced for the substitution of the Fe2 atom by a P atom than for the substitution of the Fe3 atom by a P atom. Therefore, it is suggested that the P segregation located at the energetically unfavorable site more enhances the GB embrittlement.

Another important result in Fig. 2 is that the flow stress up to 16\% in the P-segregated GB model was higher than that in the clean GB model although P was an embrittler of the Fe GB. The higher flow stress in the P-segregated GB model was not found in the case of the substitution of the Fe3 atom by a P atom.

The atomic configurations of (110) at 28 and 30\% in the clean GB model and at 16 and 18\% in the P-segregated GB model are shown in Fig. 3. In the clean GB model, no bond breaking occurred until 28\%, and the Fe-Fe bonds were broken at 28–30\%. In the P-segregated GB model, the Fe1-P bond was broken at 16–18\%. This bond breaking of Fe1-P corresponds to an abrupt decrease of stress at 16–18\% in Fig. 2. Note that the first bond breaking occurred at the Fe1-P bond in the P-segregated GB model. The Fe1-Fe2 bond was broken after the bond breaking of Fe1-P, but the Fe4 and Fe5 atoms moved to the region where the Fe1-P and Fe1-Fe2 bonds were broken. This atomic rearrangement prevented the GB fracture at 18\%, as shown in Fig. 2.

The variations in the charge density distributions of (110) with strain are shown in Fig. 4. Although the number of valence electrons of a P atom is less than that of a Fe atom, the charge densities of the Fe-P bonds (Fe1-P, Fe6-P and Fe7-P) at 0\% in the P-segregated GB model were higher than those of the Fe-Fe bonds (Fe1-Fe3, Fe6-Fe3 and Fe7-Fe3) at 0\% in the clean GB model. Note that the higher charge densities of the Fe-P bonds were found even at the strain of 16\%, which was just before the bond breaking of Fe1-P.

Figure 5 shows the variations in bond length of Fe1-Fe3/Fe1-P as a function of strain. The length of the Fe1-P bond was shorter than the Fe1-Fe3 bond up to the strain of 16\%. However, the length of the Fe1-P bond suddenly increased at 18\%, showing that the Fe1-P bond breaking occurred at 16–18\%. Thus, the strong Fe1-P bond provided the preferential bond-breaking site. This trend was obtained for the substitution of the Fe2 atom by a P atom as well. As shown in Fig. 4, the charge densities of Fe-P bonds were high. Note that the first bond breaking occurred at the strong bond of Fe-P, not the weak bonds of Fe-Fe.

Figure 6 shows the partial density of states (PDOS) for the Fe1 atom in the clean GB model and for the Fe1 and P atoms in the P-segregated GB model. The d-electrons in the Fe1 atom in the P-segregated GB model were more localized than those in the clean GB model. Also, in the s- and p-electrons, hybridization peaks were observed at \(-13\) and \(-8\) eV in the Fe1 and P atoms in the P-segregated GB model. Such hybridization peaks have been reported in Fe with B- and O-segregated GBs. Thus, the Fe1 atom in the P-segregated GB model exhibited covalent-like characteristics, compared with that in the clean GB model. The covalent-like bonding corresponds to the strong bond of Fe1-P (Fig. 5). As shown in Fig. 3, the first bond breaking site
was the Fe1-P bond although the Fe1-P bond was strong. The same result was obtained for the substitution of the Fe2 atoms by a P atom.\textsuperscript{16} Therefore, it is suggested that the bond breaking of Fe-P preferentially occurs owing to its covalent-like bonding, which is independent of the location of the P atom, in the bond mobility mechanism of GB embrittlement.

Figure 7 shows the PDOS at the strains of 16\% for the Fe1 atom in the clean GB and P-segregated GB models. In the clean GB model, the states of $d$-electrons of the PDOS at 16\% were different from those at 0\% shown in Fig. 6(a). In the P-segregated GB model, however, the states of $d$-electrons of the PDOS were not changed, compared with those at 0\% shown in Fig. 6(b). In the previous work,\textsuperscript{16} the states of $d$-electrons of the PDOS for the Fe1 atom in the P-segregated GB model varied with the strain. The unchanged states of $d$-electrons suggest that the covalent-like characteristics of Fe-P bonds in the present work are stronger than that in the previous work, which may be due to the segregation of the P atom at energetically the most favorable site. Besides, the Fe1-P bond in the present work was parallel to the tensile direction, but the Fe1-P bond was not in the previous work. These are probably responsible for the enhanced flow stress for the P-segregated GB model in the present work.

To date, two mechanisms for the enhanced GB embrittlement by impurity segregation have been proposed: one is the bond mobility mechanism,\textsuperscript{25–27} where the mobility of electrons is limited due to the covalent-like bonding, and the other is the decohesion mechanism,\textsuperscript{28,29} where the metal-metal bond is weakened owing to the charge transfer. In the Fe GB segregated by Cu,\textsuperscript{30} the decohesion mechanism is responsible for the enhanced GB embrittlement. In this case, the flow stress in the Cu-segregated GB model was the same as that in the clean GB model until the GB fracture occurred, although the Cu atom was located at the most stable site. However, as shown in Fig. 2, the flow stress in the P-segregated GB model was higher than that in the clean GB model until the bond breaking of Fe1-P occurred. Thus, the...
enhanced flow stress is attributed to the covalent-like characteristics of Fe-P bond where the P atom is located at energetically the most favorable site.  

In the present work, GB embrittlement by P segregation was investigated in the case of substitution of a Fe atom by a P atom. However, Hashimoto et al.17) showed from the molecular dynamics that a P atom segregates to interstitial positions in Fe GBs. This is supported by the thermodynamics analyses based on the experimental results.18) In the interstitial segregation of a P atom as well as the substitutional segregation, the covalent-like characteristics of Fe-P bond may play an important role in the GB embrittlement. Further research is needed to understand the GB embrittlement by the interstitial segregation of a P atom.

4. Conclusions

We have performed first-principles tensile tests on Fe with a P-segregated GB, where the P atom is located at the energetically the most favorable site. The tensile strength and the strain to failure in the P-segregated GB model were 6% and 13% lower than those in the clean GB model. However, the strength and strain to failure were less reduced in this case, compared with the case where the P atom was located at the energetically the unfavorable site. Although the charge densities were high at the Fe-P bonds, the first bond breaking occurred at the Fe-P bond. This premature bond breaking of Fe-P was independent of the location of the P atom.

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REFERENCES