First-principles Study of Hydrogen-induced Embrittlement in Fe Grain Boundary with Cr Segregation

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First-principles tensile tests were performed to investigate the effect of Cr segregation on the hydrogen-induced embrittlement in Fe grain boundaries. The Fe grain boundary with H and Cr segregation exhibited the higher maximum stress and strain to failure than those of the Fe grain boundary with only H segregation. Cr segregation suppressed the extension of the Fe-Fe bond weakened by H segregation. In the Fe grain boundary with H and Cr segregation, the decrease in the charge density in the bond with straining was suppressed because of charge transfer from the Cr atom to its neighboring Fe atoms. This charge accumulation in the grain boundary region is responsible for the reinforcement of bonds in the Fe grain boundary with H segregation, contributing to the suppression the hydrogen-induced embrittlement of Fe grain boundaries.

KEY WORDS: first-principles calculations; grain boundary; segregation; hydrogen embrittlement.

1. Introduction

Grain boundary (GB) embrittlement induced by impurity segregation is one of the most fundamental problems in metals and alloys, particularly in high-strength steels, because it remarkably degrades the mechanical properties, and impairs the reliability of structural materials. Hydrogen (H) is one of the most common impurities, which induces GB embrittlement in steels.[1–3] This is well known as H-induced GB embrittlement.

Recent rapid progress of computational materials science has been elucidating mechanisms of GB embrittlement including H-induced GB embrittlement from the electronic viewpoint.[4–8] Using Rice-Wang thermodynamic model,[9] the effects of impurities on GB embrittlement can be estimated from the difference between the segregation energy of the impurity at the GB (ΔE_{GB}) and at the free surface (ΔE_{FS}). These days, first-principles mechanical testing such as first-principles tensile and shear tests, have been carried out to investigate the variation in bonding distance, charge density distribution, stress, and so on, in relation to deformation.[10–15] For example, Lu *et al.*[12] demonstrated by first-principles tensile tests that the Na and Ca segregation in the Al GB changed the interfacial bonding states, and facilitated GB fracture. In particular, related to H-induced GB embrittlement, Zhong *et al.*[16] showed that H segregation reduced Fe GB cohesion because of charge transfer from Fe atoms to an H atom. Yuasa *et al.*[17] performed first-principles tensile test in an Fe GB with H segregation, and suggested that

the charge density in the Fe GB with H segregation reduced more during straining compared to Fe GB without H segregation, as well as the initial charge of Fe atoms transferred to the H atom. Thus, the charge transfer from Fe atoms to H atom is crucial for the H-induced GB embrittlement in steels.

Chromium (Cr) is now one of the candidates for suppressing H-induced GB embrittlement from computational studies. For example, He *et al.*[18] investigated the effect of Cr segregation on H segregation in Fe GB using first-principles calculations. They demonstrated the Cr suppressed the segregation tendency of H atoms at the GB because of charge accumulation in the Fe GB due to Cr segregation. However, Cr segregation cannot remove all H atoms in the GB, and it is essential to investigate the effects of co-segregation of H and Cr on the cohesion of Fe GB. In the present work, first-principles tensile tests were performed on the Fe GB with H and Cr segregation to investigate the effect of Cr segregation on H-induced GB embrittlement of Fe.

2. Calculation Details

First-principles calculations were performed using the Cambridge Serial Total Energy Package (CASTEP),[19] in which a plane wave basis set is used to calculate the electronic properties based on density functional theory (DFT).[20,21] The cutoff energy was set to 300 eV with a Gaussian smearing of 0.1 eV in width in all calculations. The exchange–correlation interactions were treated using the spin-polarized version of the generalized gradient approximation within the scheme due to Perdew–Burke–

Ernzerhof.[22] Ultrasoft pseudopotentials[23] were used for the all elements in the calculations. The Brillouin zone was sampled using Monkhost-Pack $6 \times 4 \times 2$ k-point mech. In geometry optimization calculations, all atomic positions were relaxed until all the Hellman-Feynman forces were less than 0.03 eV/Å.

We have modeled four body-centered cubic (bcc) Σ3 (111)[1$\bar{1}$0] Fe GB: the clean GB model (without segregation), H-segregated GB model (with H segregation), H-Cr-segregated GB model (with H and Cr co-segregation), and Cr-segregated GB model (with Cr segregation). For initial relaxation, geometry optimization including relaxing cell parameter was conducted. The first two models were same models as shown in our previous work.[17] In the H-Cr-segregated GB model, it is necessary to determine the position of H and Cr atoms. The total energies were calculated in the case with substition of a Cr atom for Fe1 (and Fe1') atom and for Fe4 (and Fe4') atom (the H atom was fixed to the position in the H-segregated GB model). The total energy of the former case is 0.2 eV lower than that of the latter case. Thus, the H-Cr segregated GB model was modeled by substituting the Fe1 (and Fe1') atom for a Cr atom in the H-segregated GB model. The H-Cr-segregated GB model in the present work corresponds to the model by He *et al.*[18] The Cr-segregated GB model was obtained from removing the H atoms in the H-Cr-segregated GB model.

First-principles tensile tests were performed applying a uniaxial tensile strain with an increment of 2% in the [111] direction, to the cells. The lattice dimensions in the GB plane were fixed, neglecting Poisson's ratio to simplify the calculation.[10,12,14] This step was repeated until GB fracture occurred. In the present work, a bond breaking was determined from a rapid decrease in stress.

3. Results and Discussion

Figure 2 shows stress-strain curves obtained from first-principles tensile tests for clean, H-segregated, H-Cr-
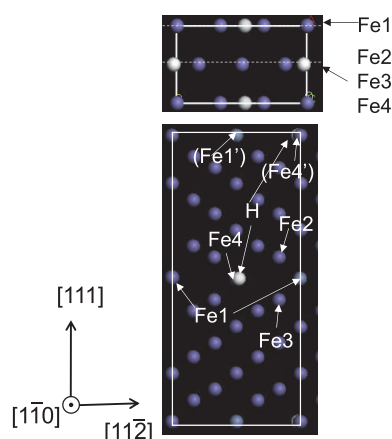

Fig. 1. Top and side views of the Fe Σ3(111)[1$\bar{1}$0] grain boundary (GB) model. Four models are used in the present study: clean GB model with no segregation, H-segregated GB model with H segregation at GB (white circles indicate H atoms), H-Cr-segregated GB model where the Fe1 (and Fe1') atom was substituted by a Cr atom, and Cr-segregated GB model obtained from removing H atoms in H-Cr-segregated GB model. Purple circles indicate Fe atoms. (Online version in color.)

segregated, and Cr-segregated GB models. The maximum stress and the strain when first bond breaking occurred were 24.9 GPa and 30% for the clean GB model, and 23.7 GPa and 22% for the H-segregated GB model, indicating the H segregation induced the GB embrittlement.[18] In the H-Cr segregated GB model, the stress increased up to about 24.4 GPa, and it rapidly decreased at 22% strain. Thus, both the flow stress and the strain for first bond breaking were higher than those in H-segregated GB model, and thus Cr segregation suppressed the H-induced GB embrittlement of Fe. In the Cr-segregated GB model, the stress of 25.2 GPa was the highest of all models although the first bond breaking occurs at the lower strain of 26% than in the clean GB model.

According to the Rice-Wang thermodynamics model,[9] the segregated impurity enhances the GB cohesion if the value of $\Delta E_{GB} - \Delta E_{FS}$ is negative, and vice versa. The calculated values of $\Delta E_{GB} - \Delta E_{FS}$ was 0.39 eV/atom for the H-segregated GB model, −0.01 eV/atom for the H-Cr-segregated GB model, and −0.10 eV/atom for the Cr-segregated GB model. Thus, this indicates that Cr is a GB cohesion enhancer in Fe GB regardless of H segregation based on the Rice-Wang model.

In the previous work,[17] H segregation weakened the Fe2-Fe4 bond in the Fe GB, and facilitated breaking of the Fe2-Fe4 bond. The atomic configuration in the H-segregated and H-Cr-segregated GB models with strain are shown in **Fig. 3**. Figure 3 illustrates the first bond breaking occurred at the Fe2-Fe4 bond in the H-Cr-segregated GB model as with the H-segregated GB model. **Figure 4** shows the variation in the length of the Fe2-Fe4 bond as a function of strain. The length of the Fe2-Fe4 bond in the H-segregated GB model was a slightly larger than that in clean GB model prior to straining, and the variation with increasing strain in the H-segregated GB model was also larger. In contrast, the length in the H-Cr-segregated GB was larger than that in the clean GB model until the strain of 10%, but is almost same from 10% to 18%. This suggested that the Cr segregation reinforced the Fe2-Fe4 bond weakened by H segregation. In addition, the Fe2-Fe4 bond in the Cr-segregated GB model remained almost unchanged until the strain of 20%. The Cr segregation therefore strengthened the Fe2-Fe4 bond regardless of H segregation.

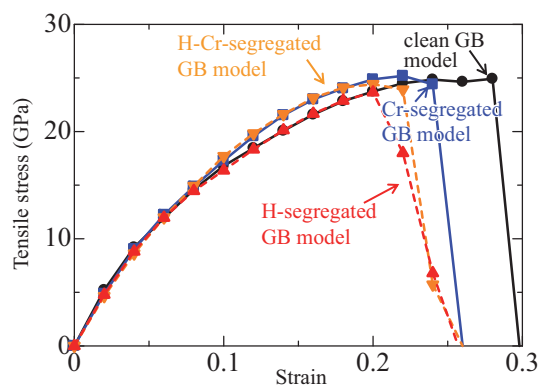The variations in charge-density distribution with increas-

Fig. 2. Stress-strain curves in the clean, H-segregated, H-Cr-segregated, and Cr-segregated GB models obtained by first-principles tensile tests. (Online version in color.)
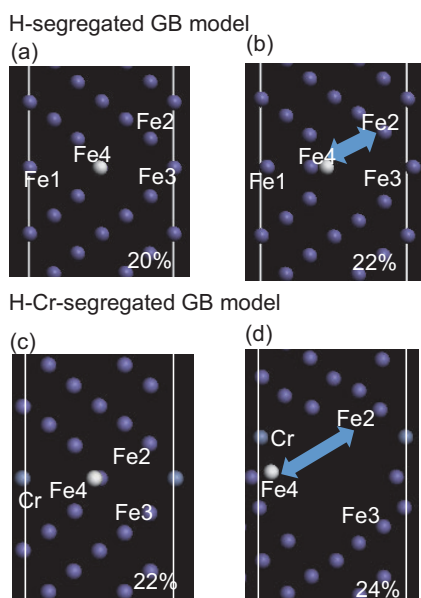
H-segregated GB model

Fig. 3. Atomic configurations of (1̄10): (a) 20% and (b) 22% strain in the H-segregated GB model, and (c) 22% and (d) 24% strain in the H-Cr-segregated GB model. The first bond-breaking site is Fe2-Fe4 bond in both models. (Online version in color.)
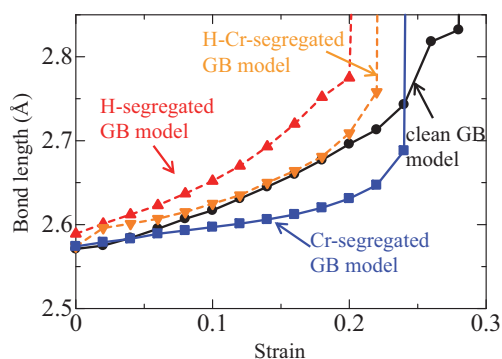

Fig. 4. Variation in length of the Fe2-Fe4 bond as function of strain in the clean, H-segregated, H-Cr-segregated and Cr-segregated GB models. (Online version in color.)

Fig. 5. Charge-density distributions of (1̄10) plane: (a), (b), and (c) are the distributions at strain of 0%, 20%, and 22%, respectively, in the H-segregated GB model, and (d), (e), and (f) are the distributions at strain of 0%, 20%, and 22%, respectively, in the H-Cr-segregated GB model. (Online version in color.)

Fig. 6. Variations in valence numbers of (a) Fe2 and (b) Fe4 atoms as a function of strain in the clean, H-segregated, H-Cr-segregated, and Cr-segregated GB models. (Online version in color.)

ing strain in the H-segregated and H-Cr-segregated GB models are shown in **Fig. 5**. The charge-density distribution in the both models at the strain of 0% is almost same. At the strain of 20%, the charge density between Fe2 (Fe3) and Fe4 in the H-Cr-segregated GB model was higher than that in the H-segregated GB model as shown by the arrows (Figs. 5(b) and 5(e)). The charge density in the H-Cr-segregated GB model sustained at the strain of 22% where the breaking of the Fe2-Fe4 bond occurred in the H-segregated GB model. The increased charge density between Fe2 (Fe3) and Fe4 by Cr segregation is responsible for the reinforced Fe2-Fe4 bond as shown in Fig. 4.

The GB embrittlement mechanism induced by H segregation is due to the charge transfer from neighboring Fe atoms to the H atoms.[16,24] Actually, the occupation numbers of Fe atoms around H atom in the Fe GB decreased with increasing strain.[17] The occupation numbers of the Fe2 and Fe4 atoms were investigated to estimate the charge transfer. **Figure 6** shows the occupation number of the Fe2 and Fe4 atoms with increased strain obtained by the Hirshfeld pop-
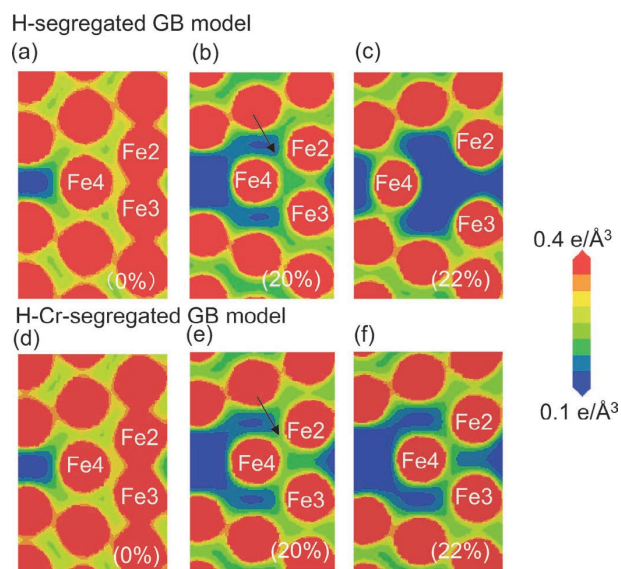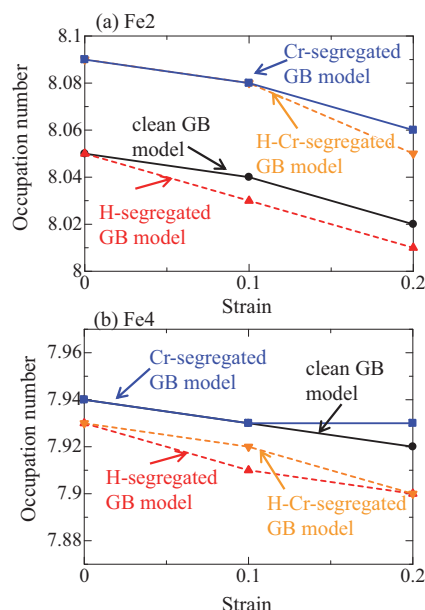
ulation analysis.[25] It was found that charge transfer from Fe atoms occurred induced by H segregation. The occupation numbers of Fe2 atom at 0% strain in the clean and H-segregated GB models were same, but it was more reduced in the H-segregated GB model than in the clean GB model. On the other hand, the occupation number of Fe4 in the H-segregated GB model was less than in the clean GB model at 0% strain and during straining. This is because the distance between the Fe4 atom and the H atom is shorter than that in the case of the Fe2 atom. Namely, the effect of charge transfer induced by H atom is significant in the Fe4 atom.
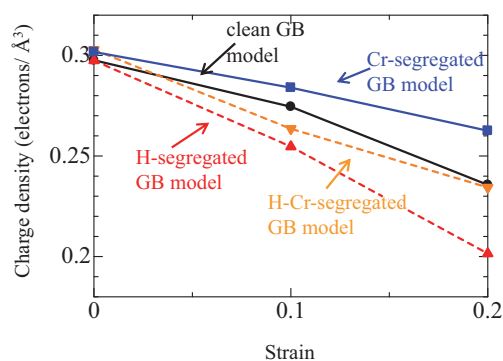
Fig. 7. Variations in Charge density at the bond critical point of Fe2-Fe4 bond, where the first bond breaking occurs in the H-segregated GB and H-Cr-segregated GB models, with strain, in the clean, H-segregated, H-Cr-segregated, and Cr-segregated GB models. (Online version in color.)

The occupation numbers of the Fe2 atom in the H-Cr-segregated and Cr-segregated GB models were higher than those in the clean and H-segregated GB models at 0% strain and during straining. In the case of the Fe4 atom, Cr did not affect the occupation number at 0% strain, but inhibited the charge reduction during straining. Thus, Cr can give its charge to neighboring Fe atoms, and compensates for the charge transfer induced by H segregation and during straining. This behavior agrees with their electronegativity (Fe: 1.88, H: 2.20, and Cr: 1.66.[26]).

The charge density at the bond critical point (BCP) is known to be crucial for bond breaking and bond strength.[27–29] The variation in charge density at the BCP of Fe2-Fe4 bond was investigated with increasing strain. **Figure 7** shows the results. At the strain of 0%, the charge density at the BCP was almost same in all the models. However, the charge density in the H-segregated GB model was rapidly reduced with strain, indicating the weakened Fe2-Fe4 bond by H segregation. In the Cr-segregated GB model, the reduction of the charge density with increasing strain was suppressed and the reduction rate was lower than that in the clean GB model. Hence, Cr segregation can limit the reduction of charge density in the neighboring Fe-Fe bond with straining.

This effect of Cr segregation is also effective in the H-Cr-segregated GB model. As the result, the reduction of the charge density with straining in the H-Cr-segregated GB model was suppressed, and the charge density is almost same at the strain of 20% as in the clean GB model. Thus, Cr segregation in Fe GBs increases the charge density of neighboring Fe atoms and strengthens Fe-Fe bond, resulting in the suppression of H-induced GB embrittlement. Shang et al.[30] also showed the charge accumulation in the Fe GB region induced by Cr segregation, and the most of charge accumulate the vicinities between Fe atoms to enhance their bonding (Their study did not apply the GB to strain). The present work suggests that the effect of Cr segregation on the reinforcement of bonding is attributed to the suppression of the charge-density reduction with strain rather than increasing initial charge density in bonding.

He et al.[18] shows that Cr segregation disturbs H segregation in Fe GBs, but it cannot remove all the H atoms. In the present work, Cr segregation can suppress the H-induced embrittlement of Fe GBs even if the H atoms remain in the GBs. Consequently, Cr can not only suppress the H segregation, but also strengthen the Fe-Fe bond in the GB region weakened by H segregation, suggesting that the Cr is a useful element to suppress the H-induced GB embrittlement in steels.

4. Conclusions

We carried out first-principles tensile tests to investigate the effect of Cr segregation on the H-induced embrittlement in the Fe GB. The stress-strain curves obtained from the first-principles tensile tests showed that maximum stress and the strain to failure in the H-Cr-segregated GB model were higher than those in the H-segregated GB model. The Fe-Fe bond, where the first bond breaking occurs in the H-segregated GB model, was strengthened by Cr segregation. This is due to the charge transfer from the Cr atom to its neighboring Fe atoms. The charge transfer suppressed the reduction of the charge density in the Fe-Fe bond with straining, and strengthened the Fe-Fe bond, resulting in the suppression of H-induced embrittlement of the Fe GB.

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