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First-principles study of the segregation effects on the cohesion of F.C.C. grain boundary

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Abstract

A scheme to evaluate the Griffith work of interfacial separation, $2\gamma_{\text{int}}$, is proposed based on first principles to investigate the segregation effects on a $\Sigma 11[1\bar{1}0]/(11\bar{3})$ γ -iron grain boundary. The chemical interaction of substitutional segregants Cr and Mn is able to enhance the cohesion of the grain boundary by anisotropic bonding, which weakens the bondings in the grain boundary plane and strengthens those in the vertical plane. However, their structural relaxation contributions are both detrimental to the cohesion of the grain boundary. After combining these two contributions, Cr acts as a cohesion enhancer but Mn as an embrittler. The interstitial segregants carbon and nitrogen can strengthen the cohesion of the grain boundary by forming strong bonding with their neighbour Fe atoms and restraining their surrounding Fe atom relaxation. The ability of carbon and nitrogen to improve the property of the grain boundary is relative to the environment of their segregation sites. The consistency between the present work and the previous reports gives evidence for the correctness of the scheme.

1. Introduction

It is well known that the intergranular embrittlement strongly affects mechanical properties of structural steels. The segregation of alloying elements or metalloid impurities to grain boundaries will often improve or deteriorate the cohesion of the grain boundaries. The beneficial elements include B, C, N, Mo, W etc and the detrimental segregants include P, S, Sn etc [1]. Extensive research has been done on the segregation effects due to their importance. Among them, the simulation works within the thermodynamic framework based on the quantum mechanics are of high importance to study the mechanism of effects of segregants on grain boundaries.

Rice and Wang [2] developed a thermodynamic theory to describe the mechanism of interfacial embrittlement due to solute segregation. The fracture would be brittle if the work of dislocation emission at a crack tip, G_{dis} , were larger than the Griffith work $2\gamma_{\text{int}}$

of interfacial cleavage, but the fracture would be ductile if $G_{dis} < 2\gamma_{int}$. The segregation-induced embrittlement (or ductilization) can be explained in terms of the effects of segregant on $2\gamma_{int}$. According to the segregation thermodynamics, $2\gamma_{int}$ may be described as

$$2\gamma_{int} \cong (2\gamma_{int})_0 - (\Delta g_b - \Delta g_s)\Gamma \quad (1)$$

where $(2\gamma_{int})_0$ is the separation work of a clean interface, and Γ is the concentration of segregants per unit area on an interface. Δg_b and Δg_s are the Gibbs free energies of a grain boundary and a free surface respectively due to the solute segregation. Ignoring the entropy terms, Δg_b and Δg_s can be given by the segregation energies, ΔE_{GB}^0 and ΔE_{FS}^0 , of the solute atoms towards the grain boundary and the free surface, respectively. ΔE_{GB}^0 and ΔE_{FS}^0 are defined as

$$\Delta E_{GB}^0 = \frac{1}{M}(E_{GB+M}^b - E_{GB}^b) \quad (2)$$

and

$$\Delta E_{FS}^0 = \frac{1}{M}(E_{FS+M}^b - E_{FS}^b) \quad (3)$$

where E_{GB+M}^b and E_{GB}^b represent the binding energies of the grain boundary with or without segregants respectively and E_{FS+M}^b and E_{FS}^b represent those of the free surface with or without segregants respectively. M is the segregant content in the model. If the solute atoms tend to segregate to the grain boundary but not the surface, i.e. $\Delta g_b - \Delta g_s < 0$, the brittle potency of the interface separation will be reduced.

As one important type of structural steel, the austenite stainless steels have been widely applied to chemical, nuclear and building industries owing to their excellent corrosion resistance, high ductility and fine weldability or non-magnetism. Crystal defects of grain boundaries in γ -iron usually cause serious problems for deterioration of its mechanical properties. Many efforts have been made to strengthen grain boundaries of the γ -iron base alloys, but the situation has not been improved over that in the ferrite base alloys [3]. It was reported that the addition of C, N and B to austenitic alloys could improve their yield strength without significant reduction of their toughness [4–7]. Cr and Mn are the common additive elements for a γ -iron alloy, acting as enhancing the corrosion resistance of the steel and stabilizing the austenite structure. The segregation of the alloying elements on the grain boundary has been observed in iron [8], but their effects on the cohesion of grain boundaries are ambiguous.

The purpose of the present paper is to provide a scheme to estimate $2\gamma_{int}$ of a grain boundary with or without segregants. We employ a discrete variational method (DVM) within the framework of the local density approximation (LDA) [9–13] to investigate the effects of the substitutional segregants Cr and Mn on the cohesion of the γ -iron $\Sigma 11[1\bar{1}0]/(11\bar{1})$ grain boundary. In order to examine the validity of the scheme, we also study the effects of interstitial segregants C and N on the grain boundary.

2. Model and computation method

A cluster model containing 67 Fe atoms is used to simulate the γ -iron $\Sigma 11[1\bar{1}0]/(11\bar{1})$ tilt grain boundary as shown in figure 1. The grain boundary cluster is separated into two single surface clusters A1 and A2 along the grain boundary plane to simulate the crack procession. To consider sufficiently the influence of the environment, the grain boundary and the surface clusters are embedded into 908 and 463 circumstance Fe atoms in the calculation respectively.

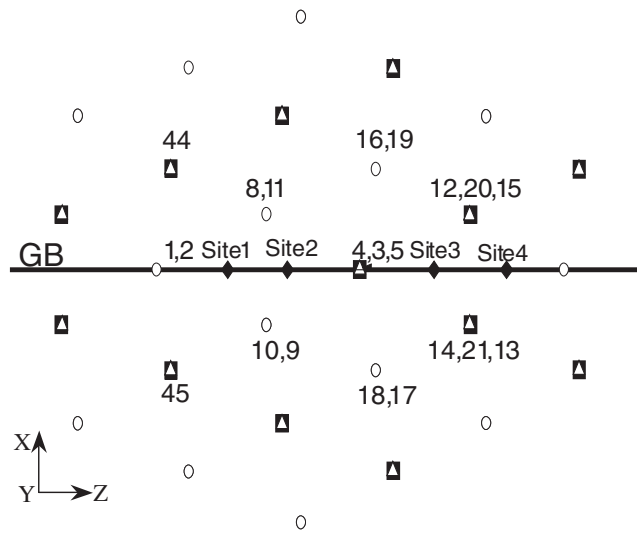


Figure 1. Atomic cluster for γ -iron $\Sigma 11[1\bar{1}0]/(11\bar{3})$ tilt grain boundary. The different symbols (O, ■, Δ) represent different atomic layers in the X - Z plane. The Y axis is denoted by the symbol Y which points from the inner to the outer. The possible doping sites are signed by the diamond symbol and labelled by the words.

The initial clean Fe grain boundary is created by using the coincidence site lattice (CSL) model and then its stable configuration is determined by using molecular dynamical (MD) method. Cr or Mn atoms substitute for the Fe3 atom in the clean boundary to construct a segregated boundary.

In order to determine the segregation sites of C or N on the segregated grain boundary, four possible interstitial sites for them are shown in figure 1. According to the elastic theory in the rigid-sphere model, it is difficult for an impurity to enter the interstitial hole if the misfit degree δ between the impurity atomic radius and interstitial hole radius exceeds 15% [14]. It means that site 3 and site 4 could be excluded from consideration because δ for C or N to occupy them is much larger than 15% but site 1 and site 2 are possible sites as their δ for them is less than 15%. Site 1 is the central of a trigonal prism and site 2 is located within a pyramid.

The relaxed grain boundary and free surface structure of Cr/Fe, Mn/Fe, C/Fe and N/Fe binary systems are determined by using total energy minimization method [15]. The equilibrium configuration for the cluster system can be obtained when its minimum of the binding energy is achieved. The results after relaxation show that Cr or Mn atoms push Fe4 and Fe5 atoms away along the y -axis but Fe16–Fe19 atoms are shifted towards the Cr or Mn atom.

The Rice–Wang thermodynamic model has been successfully applied to much research about the segregation effects of different systems up to now [16–23]. In this research, $\Delta g_b - \Delta g_s$ was calculated based on the first principles method to give the embrittle potential of segregants and there exist satisfactory agreements with the experimental results. Unfortunately, $2\gamma_{\text{int}}$ has not been considered in all the research we know. In order to evaluate the degree to which the segregants change the cohesion of the grain boundary, we estimate the value of $2\gamma_{\text{int}}$ in the present work.

$2\gamma_{\text{int}}$ represents the work needed to break the bonding between the atoms in the grain boundary region during fracture. On the one hand, it can be defined as the following equation:

$$2\gamma_{\text{int}} = f_s^{A1} + f_s^{A2} - f_b^{A1/A2} \quad (4)$$

where A1 and A2 denote the two solids that join along the interface and f denotes excess free energy per unit area on a surface (f_s) or on a grain boundary interface (f_b).

On the other hand, $2\gamma_{\text{int}}$ can be physically understood as the energy needed to separate the grain boundary into two free surfaces, i.e. the separation energy E_{sep} , which can be expressed as

$$E_{\text{sep}} = E_b^{A1} + E_b^{A2} - E_b^{A1/A2} \quad (5)$$

where E_b^{A1} and E_b^{A2} are the binding energies of the single surface atomic clusters A1 and A2 created by the crack; $E_b^{A1/A2}$ is the binding energy of the grain boundary joined by solids A1 and A2. The right-hand part of equation (5) reflects the lost cohesive (or needed) energy of the grain boundary system after being separated into two surfaces.

In order to deeply interpret the essence of the energy change, the bond order between atoms A and B, BO_{A-B} , is introduced according to the Mulliken population analysis [24]. It is defined as

$$\text{BO}_{A-B} = \sum_l n_l \sum_{m' \in B} \sum_{m \in A} \alpha_{lm'} \alpha_{lm} S_{m'm} \quad (6)$$

where α_{lm} or $\alpha_{lm'}$; are the coefficients of the atomic orbital m or m' in the molecular orbital l ; $S_{mm'}$ is a overlap matrix element between atomic orbital m' and m . n_l is the occupied charge of the molecular orbital l . BO_{A-B} can be used to evaluate the strength of the covalent bonding between atom A and B, which will be discussed in section 3.3.

3. Results and discussion

3.1. The separation energy of the grain boundary with substitutional segregants

In this paper, we assumed that the separation procedure of a grain boundary could be divided into two steps. In the first step, the grain boundary (GB) splits into two separate surfaces (SS) and then in the second step, each separate surface relaxes into a free surface (FS). The E_{sep} values for the two systems are calculated and listed in table 1 with and without the segregation atoms. $E_{\text{sep}}^{\text{un}}$ is obtained from the binding energy difference between SS and GB and it could be considered as the chemical contribution to E_{sep} of GB. $E_{\text{sep}}^{\text{re}}$ is given by the binding energy difference between FS and GB, which could be considered as a synthetic effect after the structural relaxation contribution to be combined.

Table 1. The separation energy, of the clean grain boundary (GB) and the grain boundary with the substitutional segregants. $E_{\text{sep}}^{\text{un}}$ means the separation energy of the grain boundary cracked without considering the structural relaxation effect and $E_{\text{sep}}^{\text{re}}$ means the separation energy of the grain boundary after considering the structural relaxation effect. $\Delta E_{\text{sep}}^{\text{un}}$ or $\Delta E_{\text{sep}}^{\text{re}}$ means the change of E_{sep} due to the substitution of Cr or Mn for Fe3 in GB for the unrelaxed or relaxed case, respectively; $E_{\text{sep}}^{\text{un}}$ (clean) or $E_{\text{sep}}^{\text{re}}$ (clean) means the $E_{\text{sep}}^{\text{un}}$ or the $E_{\text{sep}}^{\text{re}}$ of the clean Fe GB respectively.

Model	$E_{\text{sep}}^{\text{un}}$ (eV)	$\Delta E_{\text{sep}}^{\text{un}}/E_{\text{sep}}^{\text{un}}$ (clean)	$E_{\text{sep}}^{\text{re}}$ (eV)	$\Delta E_{\text{sep}}^{\text{re}}/E_{\text{sep}}^{\text{re}}$ (clean)
Clean Fe GB	22.82		17.95	
Mn/Fe GB	23.35	2.34%	15.91	-11.39%
Cr/Fe GB	25.07	9.90%	19.09	4.77%

In the unrelaxed system, the $E_{\text{sep}}^{\text{un}}$ of the clean Fe grain boundary is 22.82 eV. It goes up to 23.35 eV for the Mn/Fe GB after substituting Mn for Fe3 and it goes up further to 25.07 eV after substituting Cr for Fe3 in Cr/Fe system. The rise of $E_{\text{sep}}^{\text{un}}$ makes sense in that the cohesion of the grain boundary is enhanced, leading to that the intergranular fracture would be difficult

to occur. It can be concluded from above analysis that the chemical contribution, E_{sep}^{un} , of Cr and Mn to GB are both in favour of enhancing the cohesion of the grain boundary. The ratio of $\Delta E_{sep}^{un}/E_{sep}^{un}$ (clean) is 9.90% for Cr but 2.34% for Mn, where ΔE_{sep}^{un} is the variant of E_{sep} due to the substitution of Cr or Mn for Fe3 in GB without considering the structural relaxation and E_{sep}^{un} (clean) is the E_{sep}^{un} of the clean Fe GB. The obvious increase in the ratio means that the effect of Cr on chemically enhancing cohesion of GB is much stronger than that of Mn.

The structural relaxation contribution is added to the E_{sep}^{un} after each separate surface has relaxed into a free surface. The energy released during the structural relaxation will generally facilitate the fracture of the grain boundary because it decreases the energy needed for a GB to be separated. It can be easily found from table 1 that E_{sep}^{re} is less about 4–7 eV than E_{sep}^{un} for the clean Fe, Mn/Fe and Cr/Fe GBs. The decrease of E_{sep}^{un} for the clean Fe GB is to $E_{sep}^{re} = 17.95$ eV and that for Mn/Fe GB is to $E_{sep}^{re} = 15.91$ eV. The ratio of $\Delta E_{sep}^{re}/E_{sep}^{re}$ (clean) is -11.39% , where ΔE_{sep}^{re} is the variation of E_{sep} due to the substitution of Cr or Mn for Fe3 in GB after considering the relaxation and E_{sep}^{re} (clean) is the E_{sep}^{re} of the clean Fe GB. In contrast, the decrease of E_{sep}^{un} for the Cr/Fe GB is to $E_{sep}^{re} = 19.09$ eV and the ratio of $\Delta E_{sep}^{re}/E_{sep}^{re}$ (clean) is 4.77% . It follows that although the structural relaxation effect for all the systems is detrimental to the cohesion of the grain boundary, the detrimental effect on GB is stronger for Mn than that for Cr. The synthetical effect of Mn may facilitate the brittle fracture of the grain boundary as compared with the clean Fe GB. In comparison with Mn, the synthetical effect of Cr is to enhance the cohesion of the grain boundary more than the clean Fe GB, because the detrimental structural relaxation effect of Cr on the Cr/Fe GB is not strong enough to counteract its beneficial chemical effect.

Weng and McMahon [8] studied an α -Fe–Mn alloy and found that Mn is a powerful embrittling element. Mega *et al* [25] studied the grain boundary segregation of Mn in a high tensile strength steel sheet and concluded that Mn reduces the cohesion of the grain boundary. The studies from Zhong *et al* [26] demonstrated that the effect of Mn added to the α -Fe grain boundary is similar to our results, although they used a full-potential linearized augmented plane wave (FLAPW) method based on the Rice-Wang thermodynamic model. In their reports, the calculated segregation energy difference between grain boundary and free surface for Mn is +0.2 eV. It follows that Mn is a direct embrittler for the α -Fe grain boundary. Our present results coincide with above experimental and computational reports in α -Fe and it may be concluded that the effects of Mn on the cohesion of iron grain boundary are insensitive to the matrix structure (f.c.c. or b.c.c.).

3.2. The separation energy of the grain boundary with interstitial segregants

The separation energies of the grain boundary with the interstitial C or N are listed in table 2, in which the abbreviations have the same meaning as in table 1. For unrelaxed systems, C and N are to enhance the cohesion of the grain boundary, no matter where the interstitial site is. Table 2 shows that the separation energy of carbon at each site is larger than nitrogen. For example, E_{sep}^{un} for C at site 1 is 25.45 eV; it is larger than that for N at site 1, which is 24.25 eV. In the case of site 2, E_{sep}^{un} for the C/Fe GB is 28.36 eV and that for the N/Fe GB is 27.37 eV. It seems to indicate that carbon has stronger affinity to the grain boundary than nitrogen, as reported by the general experimental papers [5, 27, 28]. Moreover, this effect of the segregants is sensitive to their segregation sites. It is seen from table 2 that the interstitial C or N doped at site 2 have stronger effects on enhancing the cohesion of the grain boundary than those at site 1, which will be explained in more detail by the bond order analysis in section 3.3.

The structural relaxation contribution can be incorporated after the separate surface has relaxed into the free surface. Although the values of E_{sep}^{re} of the grain boundary with either the

Table 2. The separation energy, of the grain boundary (GB) with the interstitial segregants. The abbreviations in this table have the same meaning as in table 1.

Model	E_{sep}^{un} (eV)	$\Delta E_{sep}^{un}/E_{sep}^{un}$ (clean)	E_{sep}^{re} (eV)	$\Delta E_{sep}^{re}/E_{sep}^{re}$ (clean)
C/Fe GB site 1	25.45	11.63%	20.52	14.32%
N/Fe GB site 1	24.25	5.90%	21.60	20.31%
C/Fe GB site 2	28.36	24.30%	25.85	43.99%
N/Fe GB site 2	27.37	19.96%	24.93	38.89%

Table 3. The bond order between atoms in the grain boundary (GB) with the substitutional segregants Cr and Mn.

Direction	Atomic pairs	Clean Fe GB	Mn/Fe GB	Cr/Fe GB
Vertical to GB plane	Fe 9–Fe 11	0.424	0.431	0.423
	Fe 21–Fe 20	0.347	0.350	0.347
	Fe 13–Fe 15	0.519	0.517	0.520
	Fe 3 (Mn, Cr)–Fe 16	0.267	0.279	0.294
In GB plane	Fe 9–Fe 10	0.260	0.255	0.280
	Fe3 (Mn, Cr)–Fe 4	0.276	0.274	0.201

interstitial C or N all decrease, their values are still larger than E_{sep}^{re} (clean) = 17.95 eV. For example, E_{sep}^{re} of the grain boundary with the interstitial C at site 1 decreases to 20.52 eV from $E_{sep}^{un} = 25.45$ eV but $\Delta E_{sep}^{re}/E_{sep}^{re}$ (clean) increases to 14.32% from $\Delta E_{sep}^{un}/E_{sep}^{un}$ (clean) = 11.63%. As for N at site 1, the change of $\Delta E_{sep}^{un}/E_{sep}^{un}$ (clean) is much more obvious from 5.90% to 20.31%. It follows that the energy released from the separate surface with interstitial carbon or nitrogen during relaxation is less than that from the clean Fe separate surface. The relaxation of the separate surface Fe atoms becomes more difficult due to the interstitial C or N to be added; they will increase the separation work of the grain boundary. It can be concluded that the structural relaxation of the GB with the interstitial C or N is beneficial to its cohesion and not detrimental to it, unlike the case for the GB with the substitutional Cr or Mn. It is also noted that the structural relaxation contribution is relative to the interstitial sites and the combined effects of carbon on enhancing cohesion are stronger than nitrogen at site 1 but are weaker at site 2.

3.3. Bond order

To understand the essence of the effects of Cr and Mn on the cohesion of the grain boundary, the bond orders (BOs) between atoms in different systems are given in table 3. In the clean Fe grain boundary, Fe3 forms bonds with its neighbouring Fe atoms almost in equal strength, such as Fe3–Fe4, Fe3–Fe5 and Fe3–Fe16(–19) bonds, indicating that these bonds are isotropic. If the Fe3 atom is replaced by an Mn atom, a slight anisotropic bonding is caused. The Mn–Fe4 and Mn–Fe5 bonds in the grain boundary plane become weaker while the Mn–Fe16(–19) bonds, that are almost vertical to the grain boundary plane, become stronger than the corresponding Fe–Fe bonds in the clean Fe grain boundary. The ratio of $BO_{Mn-Fe16}$ to BO_{Mn-Fe4} is 1.04, which is larger than the ratio 0.96 for $BO_{Fe3-Fe16}$ to $BO_{Fe3-Fe4}$ in the clean Fe grain boundary. Except these, the BO of other atomic pairs changes not very much. As for the Cr/Fe GB, the bonding anisotropy induced by Cr in the Cr/Fe GB is more obvious than that induced by Mn in the Mn/Fe GB and the ratio of $BO_{Cr-Fe16}$ to BO_{Cr-Fe4} goes up to 1.45. This anisotropy in bonding is in favour of strengthening the cohesion of the grain boundary as reported by

the relevant papers [22, 23]. Those papers pointed out that the impurities, which induce the stronger vertical and weaker lateral bonding with the neighbouring Fe atoms, are favourable to enhancing the cohesion of the grain boundary, like boron. Because the bondings between host Fe atoms may not be changed too much from one system to another as shown in table 2, it seems to be evident that the chemical effects of Mn or Cr on strengthening the grain boundary come from the bonding anisotropy induced by them. The larger strengthening effects of Cr come from its more obvious bonding anisotropy than Mn.

Table 4. The bond order between atoms in the grain boundary (GB) with the interstitial segregants C and N.

Atomic pairs	Clean Fe GB	Site 1		Site 2	
		C/Fe GB	N/Fe GB	C/Fe GB	N/Fe GB
C, N–Fe 1, 2		0.350	0.325		
C, N–Fe 3				0.560	0.515
C, N–Fe 8–11		0.366	0.329	0.376	0.331
Fe 1–Fe 2	0.263	0.140	0.133	0.263	0.271
Fe 1–Fe 8	0.302	0.190	0.168	0.279	0.278
Fe 1–Fe 44, 45	0.260	0.201	0.201	0.265	0.270
Fe 3–Fe 4, 5	0.276	0.296	0.303	0.299	0.300
Fe 3–Fe 8–11	0.233	0.212	0.207	0.003	–0.007
Fe 3–Fe 16–19	0.267	0.256	0.251	0.255	0.248
Fe 8–Fe 10	0.424	0.263	0.249	0.199	0.195
Fe 8–Fe 11	0.260	0.156	0.144	0.069	0.054

The bond orders between atoms in the grain boundary with interstitial segregants C or N are listed in table 4. In the case of site 1, carbon and nitrogen atoms form stronger bonding with the neighbouring Fe atoms, such as Fe1, 2 and Fe8–11. The BO values of these bonds exceed 0.30, which are larger than those between Fe atoms. The bonds between their neighbouring Fe atoms except for Fe3–5 in the C/Fe or N/Fe GB become weak compared with those in clean Fe GB. At site 2, the effects of the interstitial C or N are also obvious and they form strong bondings with its five neighbouring Fe atoms, Fe3 and Fe8–11 and some of the Fe–Fe bonds are stronger compared with those at site 1, as shown in table 4. To compensate the stronger bonding formed by C or N with their neighbouring Fe atoms, the values of $BO_{Fe3-Fe8(-Fe11)}$ decrease greatly relative to those at site 1. However, the values of $BO_{Fe3-Fe4}$, $BO_{Fe3-Fe5}$ and $BO_{Fe3-Fe16(-Fe19)}$ change not very much.

Those strong bonds between C or N and its neighbouring Fe atoms play a key role in the enhancing effects of C or N on the cohesion of the grain boundary no matter which sites, site 1 or site 2, the segregants occupy. However, there exists the difference in bonding between the two sites owing to their structural diversity. As will be readily seen, the segregants weaken those Fe bonds surrounding them vertical to the grain boundary plane such as Fe1–Fe44, 45 at site 1. Thus, the cohesion of the grain boundary will be weakened. At site 2, the effects of the segregants are only restrained within a local region constructed by Fe3 and Fe8–11. The Fe bonds surrounding them such as Fe3–Fe4, 5 and Fe3–Fe16–19 suffer less from them. Those differences determine that the cohesion of the grain boundary due to segregants is stronger at site 2 than at site 1.

3.4. Structural relaxation effect

The detrimental effect of structural relaxation depends generally on the atomic volume difference between a doping atom and a host metal atom. Messmer *et al* [29, 30] proposed that the larger atom is a more potent embrittler than a smaller one owing to the strains produced by the doping atom into a matrix. It stands to reason that Mn causes larger strains than Fe due to its larger atomic radius (1.35 Å for Mn and 1.26 Å for Fe). Furthermore, in comparing with Fe, Mn does not form stronger bonds with its neighbour Fe atoms, leading to that the Fe atoms surrounding it can move easily. As a result, Mn/Fe grain boundary will release the more energy during the structural relaxation than clean Fe grain boundary. Although Cr also has a larger atomic radius (1.30 Å) than the Fe atom and the energy released during the relaxation is larger than that in the clean Fe GB, the obvious bonding anisotropy of Cr limits the motion of the atoms surrounding it compared with Mn. The energy released from the relaxation of Cr/Fe system is less than that from the Mn/Fe system.

C or N atoms form very strong bonds with their neighbour Fe atoms as mentioned above; these bonds limit the motion of the Fe atoms surrounding them. It will decrease the released energy during the relaxation as compared with the clean Fe GB. Combining with their chemical contribution, the synthetic effect of C or N is beneficial to enhance the cohesion of the grain boundary (from $E_{sep}^{re} = 17.95$ eV for the clean Fe GB to those larger than $E_{sep}^{re} = 20.52$ eV for the C/Fe or N/Fe GB).

4. Conclusions

A scheme to evaluate the work of interfacial separation, $2\gamma_{int}$, is proposed to investigate the effects of the substitutional segregants Cr and Mn and the interstitial segregants C and N on the property for the γ -iron $\Sigma 11[110]/(11\bar{3})$ grain boundary. The chemical interaction of Cr or Mn is both in favour of strengthening the cohesion of grain boundary by anisotropic bonding, which weakens the bonds in the GB plane and strengthens those vertical to the GB plane. However, their structural relaxation contributions are both detrimental to the cohesion of the grain boundary. Cr serves as a cohesion enhancer and Mn is an embrittler after the synthetic consideration of the two contributions. Carbon and nitrogen both can strengthen the cohesion of the grain boundary by forming the strong bonding with their neighbour Fe atoms. These strong bonds limit the relaxation of the host Fe atoms. The consistency between the present work and the previous reports raise valid support for this scheme.

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