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# First-principles Calculation of Interaction between Boron Atom and Transition Metal Elements in *α*-Fe —Effect of Boron on Recrystallization Behavior in Ti Added Ultra-low Carbon Cold-rolled Steel Sheets—

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## Abstract

The attractive interaction between B and Ti atoms is assumed to strongly suppress the recrystallization by the B addition in the Ti added interstitial atom free steel sheets. In this study the suppression mechanism of recrystallization by the B addition was evaluated by the interaction energies between B and Ti atoms at the  $(111)\Sigma 3[1\bar{1}0]$  symmetrical tilt grain boundary in  $\alpha$ -Fe estimated by the first-principles calculation. The attractive interaction between B and Ti atoms was obtained for most of the examined atomic sites in the grain boundary. The solute drag effect of Ti was concluded to suppress the growth of recrystallized grain because of the co-segregation of B and Ti at the interface between recrystallized and unrecrystallized grain due to the attractive interaction between B and Ti atoms. The interaction metal elements and the spin alignment, which can lead to the retardation of recrystallization for the Mn, Cu, and Nb addition.

#### 1. Introduction

Interstitial atom free (IF) steel sheets with excellent deep drawability are mainly used for inner and outer panels of automobiles. To improve the deep drawability, ND//<111> recrystallization texture needs to be formed, where ND denotes the normal direction to sheet surface. To enhance the ND//<111> texture, reducing interstitial type elements in solid solution, that is to say, reducing solute C and solute N is effective. Therefore, for IF steel sheets, Ti and/or Nb are added to scavenge C and N as precipitates such as TiC, TiN, and NbC. Interstitial type elements such as C and N tend to segregate at grain boundaries, so they work to strengthen the grain boundaries and prevent grain boundary embrittlement. However, on IF steel sheets, since no segregated C and N exist at grain boundaries, grain boundary embrittlement called secondary-cold-work embrittlement (SCWE) tends to occur as a harmful effect. B is added as a common measure to prevent SCWE. The grain boundary segregation enthalpies of various elements correlate with their solid solubility. The solid solubility of B is smaller by approximately one magnitude of order than that of C and N, so it is understood that B is an element that easily segregates at grain boundaries.<sup>1)</sup> It has been succeeded to suppress SCWE by B addition: B segregates at grain boundaries; and the B atoms themselves strengthen the grain boundaries or they segregate competitively with P that is considered to cause grain boundary embrittlement. Meanwhile, B addition conversely deteriorates the deep drawability. This is considered to be caused by the fact that B addition increases the recrystallization temperature and the formation of ND//<111> recrystallization texture is hindered. Therefore, to improve deep drawability while preventing SCWE, the mechanism of recrystallization suppression by the B addition needs to be clarified.

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Haga et al. provided ultra-low carbon cold-rolled steel sheets with the amount of B added changing from 1 to 14 mass ppm (hereinafter, ppm) for two levels of Ti added. The sheets were subjected to isothermal annealing at 650 °C after cold-rolling. Recrystallization behavior during the annealing was studied using an optical microscope.<sup>2)</sup> Figure 1 shows the effect of B on the recrystallization behavior of the IF steel sheets by the addition of B (the change in the maximum recrystallized grain diameter with the annealing time when Ti contents were 0.025 mass% [amount of solute Ti: 0.005 mass%] and 0.051 mass% [amount of solute Ti: 0.030 mass%]). When the amount of solute Ti is 0.005 mass%, the maximum recrystallized grain diameter does not depend on the amount of B and thereby B does not suppress the growth of recrystallized nuclei. On the other hand, when the amount of solute Ti is 0.030 mass%, the maximum recrystallized grain diameter is smaller with the increase in the amount of B. This shows that B considerably suppresses the growth of recrystallized nuclei.

As the mechanism of this phenomenon, the hypothesis below is proposed. The boundary mobility (*M*) of pure iron can be expressed by Eq.(1) using the grain boundary diffusion coefficient ( $D_{\rm Fe}^{\rm gb}$ ) of Fe,<sup>3)</sup>

$$M = D_{\rm Fe}^{\rm gb} / \lambda RT \tag{1}$$

where  $\lambda$  is the thickness of the grain boundary, *R* is the gas constant, and *T* is the absolute temperature. When solute elements segregate at an interface, the boundary mobility possibly decreases due to their solute drag effect.<sup>4)</sup> The decrease limit of the mobility is equivalent to the case where the segregation sites in the interface are saturated with solute elements and their bulk diffusion determines the rate of the boundary migration. The mobility (*M*') in such case can be expressed as Eq. (2) by replacing  $D_{\rm Fe}^{\rm gb}$  in Eq. (1) with the bulk diffusion coefficient ( $D_s^{\rm l}$ ) of the solute element.<sup>4</sup>

$$M' = D_s^1 / \lambda R T \tag{2}$$

B is an element that segregates at grain boundaries very easily. In Ti-IF steel, B has already segregated at grain boundaries of hot bands.<sup>5)</sup>

In addition, the diffusion coefficient of B is large. Therefore, B possibly segregates at the interface between recrystallized nuclei and deformed matrices. However, the bulk diffusion coefficient of B<sup>6)</sup> at 650 °C, at which recrystallized nuclei form and grow, is much larger than the grain boundary diffusion coefficient of Fe<sup>7</sup> as shown in Fig. 2. Therefore, even if a B atom segregates at an interface, the mobility possibly does not decrease due to B segregation. To rationally explain the suppression of the growth of recrystallized nuclei by B addition, the effect of Ti on the mobility needs to be taken into account. Because the bulk diffusion coefficient of Ti<sup>8)</sup> at 650 °C is much smaller by approximately four magnitude of order than the grain boundary diffusion coefficient of Fe, Ti segregating at the interface significantly reduces the boundary mobility, which possibly suppresses the growth of recrystallized nuclei. Although the diffusion of Ti is slow, the solute Ti within the grain possibly builds up at the B segregated interface (sweep effect) when the attractive interaction works between B and Ti atoms. In other words, the attractive interaction between them possibly causes the Ti to segregate at the interface, and thereby when the amount of B is larger, the growth of recrystallized nuclei is more suppressed.

However, this hypothesis in terms of atomic interaction between B and Ti in the interface has not been verified. Therefore, we studied the interaction between B and Ti atoms, which is the key of the hypothesis, using the first-principles calculation. The first principle calculation was widely applied to the atomic interaction between B







Fig. 2 Bulk diffusion constant of B and Ti and grain boundary diffusion constant of Fe in  $\alpha$ -Fe

and other transition metal elements in a bulk  $\alpha$ -Fe.

#### 2. Calculation Method

A specific grain boundary needs to be selected for calculation regarding grain boundaries. In this study, the (111) $\Sigma$ 3[110] grain boundary was used for calculation. According to the calculation result for the [110] symmetrical tilt grain boundary in which a classic molecular dynamics method was used to calculate the dependence of grain boundary energy on misorientation angles based on the Johnson potential,<sup>9)</sup> the energy of the (111) $\Sigma$ 3 grain boundary is 1.23 J/m<sup>2</sup> indicating that its energy is highly equivalent to that of other high angle grain boundaries. In addition, the energy of the grain boundary is close to that of the (552) $\Sigma$ 27 grain boundary (1.48 J/m<sup>2</sup>) that has a high index and is thought to be close to a random grain boundary, so the (111) $\Sigma$ 3 grain boundary can be regarded as a general grain boundary in steel.

A unit cell using the periodic boundary condition needs to be made for the first-principles calculation. The  $(111)\Sigma 3[1\bar{1}0]$  grain boundary can be made up of 76 atoms.<sup>10)</sup> The maximum number of atoms that the first-principles calculation can handle is approximately a few hundred as of now when a large super computer (e.g., K computer) is not used. Therefore, the  $(111)\Sigma 3[1\bar{1}0]$  grain boundary is calculable. **Figure 3** illustrates the structure of the  $(111)\Sigma 3[1\bar{1}0]$ grain boundary. The grain boundary consists of mono-structural units shown with the red lines. The high energy of this grain boundary shows that the structural unit has high energy. There is one more layer of these units in the  $[1\bar{1}0]$  direction in Fig. 3, so the number of



Fig. 3 Atomic structure model of (111)Σ3[110] symmetrical tilt grain boundary for the first-principles calculation White and black circles denote different coordinates in [110].



Fig. 4 Voronoi volume of Fe atoms in relation to the distance from the  $(111)\Sigma 3[1\bar{1}0]$  symmetrical tilt grain boundary

atoms in the unit cell is 76. In addition, vacuum areas are provided at both ends in the [111] direction to make expansion and contraction near the grain boundary possible.

In order to consider how many layers from right above the grain boundary can be regarded as a grain boundary layer, the voronoi volume of each atom in the unit cell of the  $(111)\Sigma 3[1\overline{1}0]$  grain boundary is shown in Fig. 4. Voronoi volume refers to the volume of the area divided by perpendicular bisectors drawn between atoms and can be regarded as the volume that each atom occupies in the crystal. Figure 4 shows that the voronoi volume of the atom rows in the third to sixth layers from right above the grain boundary is almost equivalent to that in the bulk. In other words, the unit cell including this grain boundary can express changes in the volume of the atoms near the grain boundary and is well reproducing the state within the grain. As a characteristic of this grain boundary, the voronoi volume of the atoms right above the grain boundary and those in the second layer from right above the grain boundary is larger than that of the atoms in the bulk, but the voronoi volume of the atoms in the first layer from right above the grain boundary is equivalent to that of the atoms in the bulk. In this study, the atom layers within the three layers from right above the grain boundary are called the grain boundary layer and segregation at the grain boundary layer is called grain boundary segregation.

For the first-principles calculation, the Vienna ab initio simulation package (VASP)<sup>11, 12</sup>) that adopted the projector augmentedwave (PAW) method<sup>13, 14</sup>) based on the density functional theory was used. As the exchange correlation energy, generalized gradient approximation by Perdew-Burke-Ernzerhof (PBE) was used.<sup>15</sup>) The cutoff energy of the wave function was 320 eV. The Monkhorst Pack<sup>16</sup>  $1 \times 4 \times 4$  reciprocal lattice point mesh and Methfessel-Paxton smearing<sup>17</sup>) with 0.2 eV width were used to sum up the occupied states. For the convergence of electronic states, the threshold for both the total energy change and the band structure energy change between two continuous steps was  $1 \times 10^{-4}$  eV in iterative calculation for obtaining a self-consistent solution of the electronic structure. The threshold of the force acting on each atom in structure optimization was 0.02 eV/Å.

#### 3. Results and Discussion

#### 3.1 Grain boundary segregation energy of Ti and B atoms

**Figure 5** illustrates the arrangement of B and Ti atoms examined in this study. The B atoms locate at the three sites of site 1 (Fig. 5a)), site 2' (Fig. 5b)), and site 3 (Fig. 5c)) in the grain boundary layer. The Ti atoms locate near the B atoms in the grain boundary layer. The sites shown with the same symbol in the same figure are equivalent. Regarding the site in solid solution of B in  $\alpha$ -Fe, some experimental results of studies reported that it is interstitial<sup>18</sup>) and others reported that it is substitutional.<sup>19</sup> As an example examination by the first-principles calculation, Bialon et al.<sup>20</sup> carried out  $\alpha$ -Fe (bulk) energy calculation and reported that substitutional sites are more stable by 0.81 eV than interstitial tetrahedral sites, and by 0.07 eV than interstitial octahedral sites. In this study, we assumed that B would occupy the substitutional site both in the matrix and at the grain boundary in accordance with the result by Bialon et al.

The grain boundary segregation energy of a Ti atom  $(\Delta E_{Ti}^0)$  when it was arranged alone in a unit cell was calculated using Eq. (3). The grain boundary segregation energy of a B atom  $(\Delta E_B^0)$  when it was arranged alone in a unit cell was calculated using Eq. (4),

 $\Delta E_{\text{Ti}}^{0} = E^{\text{gb}}[\text{Fe}_{75}\text{Ti}] + E^{1}[\text{Fe}_{76}] - E^{\text{gb}}[\text{Fe}_{76}] - E^{1}[\text{Fe}_{75}\text{Ti}]$ (3)  $\Delta E_{\text{B}}^{0} = E^{\text{gb}}[\text{Fe}_{75}\text{B}] + E^{1}[\text{Fe}_{76}] - E^{\text{gb}}[\text{Fe}_{76}] - E^{1}[\text{Fe}_{75}\text{B}]$ (4)

 $\Delta E_{\rm B}^{\rm g} = E^{\rm gb}[{\rm Fe}_{75}{\rm B}] + E^{\rm i}[{\rm Fe}_{76}] - E^{\rm gb}[{\rm Fe}_{76}] - E^{\rm i}[{\rm Fe}_{75}{\rm B}] \qquad (4)$ where  $E^{\rm gb}$  is the total energy of the unit cell with grain boundary

consisting of the atoms in the square brackets.  $E^1$  is the total energy of the unit cell without the grain boundary consisting of the atoms in the square brackets. Fe<sub>76</sub> means that the unit cell consists of 76 Fe atoms. Fe<sub>75</sub>Ti means that one Fe atom has been replaced with a Ti atom. Fe<sub>75</sub>B means that one Fe atom has been replaced with a B atom. In addition, the grain boundary segregation energy of the Ti



Fig. 5 Sites of B and Ti atoms in the (111)Σ3[110] symmetrical tilt grain boundary region examined in the first-principles calculation Site of B atom: a) Site 1, b) Site 2', c) Site 3

atom ( $\Delta E_{Ti}^{B}$ ) when a Ti atom was arranged in a unit cell containing a B atom in the grain boundary layer was calculated using Eq. (5). The grain boundary segregation energy of the B atom ( $\Delta E_{B}^{Ti}$ ) when a B atom was arranged in a unit cell containing a Ti atom in the grain boundary layer was calculated using Eq. (6).

 $\Delta E_{\text{Ti}}^{\text{B}} = E_{\text{gb}}^{\text{gb}}[\text{Fe}_{74}\text{TiB}] + E^{1}[\text{Fe}_{76}] - E^{\text{gb}}[\text{Fe}_{75}\text{B}] - E^{1}[\text{Fe}_{75}\text{Ti}]$ (5)

 $\Delta E_{\rm B}^{\rm Ti} = E^{\rm gb} [{\rm Fe}_{74}^{'4} {\rm TiB}] + E^{\rm I} [{\rm Fe}_{76}^{'0}] - E^{\rm gb} [{\rm Fe}_{75}^{'7} {\rm Ti}] - E^{\rm I} [{\rm Fe}_{75}^{'8} {\rm B}]$ (6)

 $Fe_{74}$  TiB means that two Fe atoms in the unit cell have been replaced with a Ti atom and a B atom.

**Figure 6** a) shows the relationship between the grain boundary segregation energy of the Ti atoms and their voronoi volume. The indexes in the same figure mean that the Ti atoms were arranged at the sites shown in Fig. 5. When only a Ti atom exists, the grain boundary segregation energy of the Ti atom  $(\Delta E_{Ti}^0)$  is negative except for site 2'. The Ti atoms show a tendency to segregate at the grain boundaries. The minimum  $\Delta E_{Ti}^0$  was -0.48 eV at site 1. The atomic radius of a Ti atom is larger than that of an Fe atom. Therefore, Ti atoms tend to segregate at sites with larger voronoi volume such as sites 1 and 3. The grain boundary segregation energy  $(\Delta E_{Ti}^0)$  correlates well with the Ti atom's voronoi volume  $(V_{Ti})$  and  $\Delta E_{Ti}^0$ 





further decreases as  $V_{\text{Ti}}$  increases.

When Ti and B atoms co-exist in the grain boundary, the grain boundary segregation energy ( $\Delta E_{\text{Ti}}^{\text{B}}$ ) is lower as  $V_{\text{Ti}}$  is larger. The grain boundary segregation energy values of the Ti atoms to  $V_{\text{Ti}}$  are almost the same regardless of whether a B atom exists. Therefore, when  $V_{\text{Ti}}$  becomes larger by placing a B atom near a Ti atom, the grain boundary segregation energy of the Ti atom becomes lower, which accelerates grain boundary segregation of the Ti. When a B atom exists at site 1 and a Ti atom exists at site 2 or site 2',  $\Delta E_{\text{Ti}}^{\text{B}}$  becomes specifically low. However, this is because of the positional relationship where the arrangement of a Ti atom largely changes (reduces) the voronoi volume of the B atom as will be explained later.

When only a B atom exists in the grain boundary, the grain boundary segregation energy of the B atom ( $\Delta E_B^0$ ) is 0.39 eV for site 1, -1.85 eV for site 2', and -1.49 eV for site 3. These values closely match the calculation results by Yamaguchi et al.<sup>10</sup> Although our calculation results are different from the experimental value of -1.04 eV (100 kJ/mol) by Liu et al.,<sup>21</sup> they match the experimental results in the respect that B shows a very strong tendency to segregate at grain boundaries. The calculated segregation energies for elements with low solid solubility are different from the experimental values to some extent,<sup>22</sup> and our calculation results can be interpreted as within such difference.

 $\Delta E_{\rm B}^0$  tends to lower as the B atom's voronoi volume ( $V_{\rm B}$ ) becomes smaller as shown in Fig. 6b). This tendency is also seen when B and Ti atoms coexist. Focusing on the B atom in the same site, the figure shows that  $\Delta E_{\rm B}^{\rm Ti}$  lowers as  $V_{\rm B}$  decreases according to the sites of Ti atoms.

## **3.2** Interaction energy between B and Ti atoms at the grain boundary

Interaction energy between B and Ti atoms ( $\Delta E_{B,Ti}^{int}$ ) in a grain boundary is defined as an energy difference between when a B atom exists near a Ti atom in a grain boundary and when they exist separately. It can be calculated using Eq. (7) below.

 $\Delta E_{B,Ti}^{int} = E^{ab}[Fe_{74}TiB] + E^{ab}[Fe_{76}] - E^{ab}[Fe_{75}B] - E^{ab}[Fe_{75}Ti] (7)$ Meanwhile, the difference between  $\Delta E_{Ti}^{B}$  and  $\Delta E_{Ti}^{0}$  ( $\Delta E_{Ti}^{B} - \Delta E_{Ti}^{0}$ ) calculated using Eqs. (5) and (3) is equal to  $\Delta E_{B,Ti}^{int}$ . Therefore, the difference in the grain boundary segregation energy of Ti between when Ti and B atoms co-exist in a grain boundary and when only a Ti atom exists is equivalent to the interaction energy between the B and Ti atoms.

**Figure 7** shows the relationship between  $\Delta E_{B,T}^{int}$  calculated using Eq. (7) and  $\Delta V_{Ti}$  and  $\Delta V_{B}$ .  $\Delta V_{Ti}$  refers to the variation of the voronoi volume of the Ti atom when Ti and B atoms co-exist in the grain boundary and when only a Ti atom exists.  $\Delta V_{B}$  refers to that of the B atom when Ti and B atoms co-exist in the grain boundary and when only a B atom exists.  $\Delta E_{B,Ti}^{int}$  ranges from -2.44 to 0.08 eV. Attractive interaction acts between the B and Ti atoms in many sites examined in this study. In addition,  $\Delta E_{B,Ti}^{int}$  tends to decrease as  $\Delta V_{Ti}$  increases or  $\Delta V_{B}$  decreases. When  $\Delta E_{B,Ti}^{int}$  is organized using the sum of the increase in the voronoi volume of a Ti atom ( $\Delta V_{Ti}$ ) and the decrease in the voronoi volume of a B atom ( $-\Delta V_{B}$ ),  $\Delta E_{B,Ti}^{int}$  correlates well with  $\Delta V_{Ti} - \Delta V_{B}$  as shown in Fig. 7 c). That is to say, when Ti and B atoms are close to each other in a grain boundary, as  $V_{Ti}$  increases and  $V_{B}$  decreases, the attractive interaction between the B and Ti atoms possibly becomes stronger.

When each atom exists at an unfavorable site, for example, when a B atom exists at site 1 and a Ti atom exists at site 2 or site 2',  $\Delta V_{\text{Ti}}$ and  $-\Delta V_{\text{B}}$  are large and thereby the attractive interaction tends to be stronger. Meanwhile, when each atom locates at a favorable site, for example, when a B atom exists at site 2' and a Ti atom exists at site 1 or site 1',  $\Delta V_{\text{Ti}}$  and  $-\Delta V_{\text{B}}$  are small and thereby the interaction is weak.



Fig. 7 Relationship between interaction energy of B and Ti atoms and the change in voronoi volume by co-segregation a)  $\Delta E_{B,Ti}^{int}$  vs.  $\Delta V_{Ti}$ , b)  $\Delta E_{B,Ti}^{int}$  vs.  $\Delta V_{B}$  and c)  $\Delta E_{B,Ti}^{int}$  vs.  $\Delta V_{Ti}^{-} \Delta V_{B}$  Small numbers denote Ti sites.

The energy difference between when a B atom exists near a Ti atom in a grain boundary and when they exist separately in a matrix is defined as co-segregation energy ( $\Delta E_{B,Ti}^{co}$ ). It can be calculated using Eq. (8) below.

$$\Delta E_{B,Ti}^{co} = E^{ab}[Fe_{74}TiB] + 2 \times E^{1}[Fe_{76}] - E^{1}[Fe_{75}B] - E^{1}[Fe_{75}Ti] - E^{ab}[Fe_{76}]$$
(8)

When a B atom exists at site 2' and a Ti atom exists at site 3, the  $\Delta E_{\rm B,Ti}^{\rm co}$  value is the smallest (-2.33 eV), so this arrangement is the most stable site for the co-segregation of B and Ti atoms. The interaction energy between the B and Ti atoms at the most stable sites is -0.10 eV. This energy value is the same level as the interaction energy between C and Cr atoms in  $\alpha$ -Fe. (-0.11 eV).<sup>23)</sup>

Cr addition to low carbon steel sheets suppresses the development of ND//<111> recrystallization texture. Some researchers think that this is because the attractive interaction between the C and Cr atoms forms a Cr-C dipole (atom pair) and the orientation selectivity of recrystallized nuclei is weakened through the suppression of recovery.<sup>24)</sup> Although our study calculated the interaction in a grain boundary, the interaction energy of -0.10 eV could possibly affect the recrystallization behavior. The most stable sites of the B and Ti atoms are rather favorable segregate sites and interaction energy is not so low among that shown in Fig. 7. Although cases where two or more B and Ti atoms are placed in a grain boundary have not been calculated in this study, when the numbers of B and Ti atoms segregating at a grain boundary increase and when they occupy sites other than the most stable sites, the average interaction energy may be estimated further lower.

From the atomistic consideration above, the mechanism by which B suppresses recrystallization based on the interaction between B and Ti atoms is reasonable. The suppression of the growth of recrystallized nuclei by the B addition is originated from the solute drag effect in the sense that the number of Ti atoms segregating at the interface between the recrystallized nucleus and deformed matrix increases through the attractive interaction between B and Ti atoms, which reduces the boundary mobility of the interface.

# 3.3 Interaction between transition metal elements and B atoms in bulk

The previous section showed the attractive interaction between B and Ti atoms at a grain boundary. Incidentally, attractive interaction acts at the first nearest neighbor position in an  $\alpha$ -Fe bulk.<sup>25)</sup> That is to say, the attractive interaction at a grain boundary could be caused by the interaction at the first nearest neighbor position in the bulk. To study the physical origin of attractive interaction between B and Ti atoms and search other transition metal elements such as Ti atoms, the interaction energy between transition metal elements and a B atom was studied at the first nearest neighbor position. Equation (9) below was used to calculate the interaction energy in a bulk by the first-principles calculation,

 $\Delta E = E^{1}[Fe_{n-2}MB] + E^{1}[Fe_{n}] - E^{1}[Fe_{n-1}B] - E^{1}[Fe_{n-1}M] \qquad (9)$ where  $E^{1}$  is the total energy of the unit cell in the square bracket and M is a transition metal element. We assumed that B would occupy substitutional sites as is the case with the calculation with a grain boundary. *n* is the number of atoms contained in the unit cell used for the calculation. The periodic boundary condition is employed. When *n* is too small in the actual calculation, interaction acts with the substitutional atoms contained in adjacent unit cells and thereby the interaction energy cannot be calculated in an accurate way. In this study, *n* in the calculation was 128. The positional relationship between M and B in  $E^{1}[Fe_{n-2}MB]$  is the first nearest neighbor.

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**Figure 8** shows the interaction energy between each of the transition metal elements (M) and a B atom calculated using Eq. (9). The interaction energy with an Fe atom is zero from the definition of Eq. (9). The figure shows that the 3d transition metal elements that are further away from Fe in the periodic table have more attractive interaction, except Mn atom.

Figure 9 shows the voronoi volume of each element.  $M(Fe_{126}MB)$ is the voronoi volume of the M atom when unit cell Fe126MB was used for calculation.  $M(Fe_{127}M)$  is the voronoi volume of the M atom when unit cell Fe<sub>127</sub>M without B was used for calculation. They are slightly different, but the trend is almost the same and the voronoi volume values of the transition metal elements at the first nearest neighbor position do not vary much by the existence of a B atom. This result differs from the result in the previous section that when B and Ti atoms segregate near a grain boundary, the voronoi volume of the Ti atom significantly varies depending on the arrangement of the B and Ti atoms. However, this is possibly because the structural unit of the  $(111)\Sigma 3[1\overline{1}0]$  grain boundary owns a large space, having high energy. In addition, B(Fe<sub>126</sub>MB) is the voronoi volume of the B atom when unit cell Fe126MB was used for calculation. The values rarely change regarding the 3d transition metal elements, except the Mn and Cu atoms. Regarding 4d transition metal elements such as Nb and Mo atoms, the volume is approximately 1% larger than that of an Fe atom.

Figure 10 shows the interaction energy between the M and B atoms as a function of the voronoi volume ( $M(Fe_{126}MB)$ ) of the transition metal element (M) shown in Fig. 9. In Fig. 10, the 3d transition metal elements with smaller atomic numbers than that of Fe are plotted in red, those with larger atomic numbers than that of Fe are plotted in blue, and 4d transition metal elements are shown in green.

This figure shows that all the red, blue, and green lines showing the interaction energy between the M and B atoms is steadily declining with the voronoi volume of the M atom, except for the Mn atom. Therefore, more attractive interaction acts for the larger voronoi volume of the M atom. This result does not conflict with the description in the previous section (in a grain boundary) that the interaction between the B and Ti atoms in a bulk is more attractive for larger  $V_{\rm Ti}$  and smaller  $V_{\rm B}$ .

In addition, to interpret the difference between the elements with smaller atomic numbers than that of Fe (red) and those with larger atomic numbers than that of Fe (blue), magnetic moments of the M and B atoms are shown in **Fig. 11**. The spin alignment of the 3d transition metal elements (M atoms) with smaller atomic numbers than that of Fe is antiferromagnetic to Fe atoms and that of the elements with larger atomic numbers than that of Fe is ferromagnetic to Fe atoms. This phenomenon has been reported in the past<sup>26)</sup> and is basically similar to the previous one. The B atom's magnetic moment is antiferromagnetic to the Fe atom's magnetic moment and the origin is thought to be as described below.<sup>26)</sup>

In  $\alpha$ -Fe, the potential of up spins is deeper than that of down spins. Thereby the potential that up spins of elements feel without spin polarization is shallower than the potential that down spins feel, so more down spins are occupied. However, the B atom's magnetic moment is rarely affected by the M atom at the first nearest neighbor position. Considering the interaction between the M and B atoms in terms of the spin alignment, interaction between spins in the same alignment is repulsive and that between spins with opposite signs is attractive. That is to say, the interaction between the Ti/V/Cr/Mn/Nb/Mo atoms and B atom is attractive. When seeing the interaction energy in Fig. 10 based on the interaction between spins, among the



Fig. 8 Interaction energy between transition metal element M and B atom





Fig. 10 Relationship between interaction energy of transition metal element M and B atom and voronoi volume of M



Fig. 11 Magnetic moment of transition metal element M and B atom

3d transition metal elements, the interaction energy of the elements with larger atomic numbers than that of Fe (blue) is more attractive than that of the elements with smaller atomic numbers (red) when comparing the same levels of voronoi volume. It is suggested that the origin is the interaction between spins.

From the consideration above, the mechanism to suppress recrystallization by adding both B and Ti can be understood from the voronoi volume and spin alignment of the M atom. Figure 8 shows that Mn, Cu, and Nb may suppress recrystallization strongly when they coexist with B. Regarding Nb, the increase in the recrystallization temperature by the addition of B is larger for the higher Nb content.<sup>27)</sup> It can be inferred that the mechanism described above is responsible for the suppression of recrystallization by the coexistence of Nb and B.

#### 4. Conclusions

The interaction between the B and Ti atoms in  $\alpha$ -Fe was studied by the first-principles calculation. The mechanism of recrystallization suppression by the B addition in Ti-IF steel was examined. The following results are obtained.

- (1) The first-principles calculation using the  $\alpha$ -Fe (111) $\Sigma$ 3[1 $\overline{10}$ ] symmetrical tilt grain boundary showed that attractive interaction tends to occur between B and Ti atoms in a grain boundary. The attractive interaction is stronger for the larger voronoi volume of Ti and smaller voronoi volume of B, when the B and Ti atoms are close to each other in the grain boundary.
- (2) When B and Ti co-exist, the B and Ti co-segregate at the interface between the recrystallized nuclei and deformed matrix due to the attractive interaction, which significantly suppresses the growth of the recrystallized nuclei.
- (3) The first-principles calculation for an α-Fe bulk showed that the interaction between transition metal elements (M atom) and a B atom can be understood by the voronoi volume and spin

alignment of the M atom. It is also suggested that Mn, Cu, and Nb, besides Ti, may strongly suppress recrystallization due to the attractive interaction with B.

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