Improvement of Anti-aging Property at Low Temperature by Cr Addition in Bake Hardenable Ultra Low Nitrogen Steels

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The effect of Cr, Mn, Mo, V, Nb, and Al on bake hardenability (BH) at 170°C and anti-aging properties, i.e. the inhibition of the appearance of yield point elongation (YPE) after low temperature aging, in ultra low N steels was investigated. It was found that Cr addition of 0.5–1.0 mass% apparently inhibit the appearance of YPE after aging for 3.6 ks at 100°C without much decreasing the amount of 2%BH at 170°C. The reason for the inhibition by Cr addition was discussed on the diffusion trap model, by using the interactions among Cr atom, N atom, and vacancy evaluated by first-principles calculation. The estimation indicates that (i) Cr would not inhibit the diffusion of N atoms as a repulsive interaction was expected for Cr–N complexes, (2) a small amount of vacancies introduced by skinpass rolling, which attracts strongly with N atoms, seems to play a main role on the inhibition of the diffusion of N atoms, (3) Cr could retard the annihiation of vacancies which trap N atoms during aging, since Cr atom attractively interacts with vacancy–N complexes. Moreover, the effect of annealing temperature and coiling temperature on bake hardenability was investigated, and the effect was found to be understood by the change of solute N, owing to the precipitation of CrN which has a precipitation nose at 650–700°C.

KEY WORDS: bake hardenability; first-principles calculation; I-S interaction; vacancy; anti-aging.

1. Introduction

Bake hardenable (BH) steels have been developed in 1980's1–3) and widely used for the manufacture of outer body car parts. Ultra low carbon BH steels are mainly used nowadays because they deliver both excellent formability and in-service dent resistance of the outer panels. As the better dent resistance is obtained by the higher yield stress after paint baking, higher yield strength after forming and subsequent baking process is preferred. However, the amount of yield strength increase during baking at 170°C for 1.2 ks after 2% prestraining, which is a typical measure of BH, is limited to 30–40 MPa. This is because anti-aging property at room temperature deteriorates with increasing the amount of BH.

Anti-aging properties at room temperature is required for the sheets for the outer body parts, because press forming of aged sheets results in the appearance of strain mark. Anti-aging properties of the steels is often evaluated by the appearance of yield point elongation (YPE) after room temperature aging or accelerated aging at elevated temperature,4) because the strain mark is related with the non-uniform yielding within the sheets. The increase of yield stress by strain aging and the appearance of YPE after aging have been known to be due to the diffusion and the subsequent pinning of mobile dislocation by solute C or N atoms5–7) and/or precipitation of iron carbides, 6,7) so that the compatibility of higher BH more than 50 MPa with the anti-aging properties is difficult and has long been a matter of research. Taniguchi et al. showed that the addition of Mo in ULC steels helps to inhibit the appearance of YPE at room temperature in BH steels, and claimed that Mo atoms inhibit the migration of carbon atoms at room temperature by the ambient attractive interaction between Mo and C atoms,9) although no evidence of attractive interaction energy between Mo and C atoms has been reported by internal friction studies9) and first-principles calculation.10)

Concerning the interaction between substitutional and interstitial solutes, Numakura et al. have reported that interaction between Cr–N and Cr–C is dissimilar.11) The interaction of Cr–N appeared to be attractive (\(E_a=-0.18\) eV)12) while that of Cr–C is nil as evidenced by the measurement of solubility of N and C. Previous internal friction studies have also indicated the stronger interaction of Cr–N, Mo–N, V–N than those for C, as observed by the splitting and shift of Snoek peak by the addition of substitutional atom to N-added steels.9,11) Despite that Cr and other substitutional elements may improve the anti-aging property in N added steels, the studies on the aging behaviour of N added steels seems to be limited. Another important requirement for obtaining the BH steels of Fe–X–N system (X: substi-
tional alloying element) is that solute N must remain after annealing process. Previous studies on the solubility product of nitrides in α-Fe have shown that CrN\(^{13}\) gives higher solubility of N in α-Fe at a typical annealing temperature for industrial continuous annealing line, around 800°C, in comparison with VN,\(^{14}\) NbN,\(^{15}\) and AlN.\(^{16}\) Thus, Cr–N system seems to be a candidate for BH steels with anti-aging property at room temperature.

The purpose of the present study is to investigate the effect of substitutional alloying elements (Cr, Mn, Mo, V, Al, Nb) on strain aging at 170°C and the appearance of YPE after accelerated aging at low temperature in ultra low N added steels. Among those elements, Cr was found to inhibit the appearance of YPE at accelerated aging at 100°C without much lowering the bake hardenability at 170°C. Since our atom probe analysis showed the attractive interaction between Cr atoms and N atoms,\(^{17}\) we investigated the atomic interactions by first-principles calculation to seek for the origin of the Cr–N interaction and the compatible mechanism of higher BH with anti-aging property. As the information on the solute N after hot-rolling and annealing process is industrially important to control the bake hardenability, the precipitation behaviour of Cr nitrides in α-Fe with different Cr contents is also investigated in detail.

2. Experimental and Calculation Details

2.1. Aging Behaviour in X–N Steels

The materials used for the investigation of strain aging are shown in Table 1. The base composition of the steels was 0.0015N–0.001C–0.1Si–0.1Mn–0.01P (mass%), and either of Mn, Cr, V, Nb, or Al was added to the base steel. The steels were homogenised at a temperature of 1 250°C and subsequently hot-rolled with a finish-rolling temperature of 800°C to 460°C/s and then reheated for 20 s at 520°C, and cooled to 350°C with a cooling rate of 15°C/s.

The precipitation behaviour of Cr nitride in low N steels with different Cr contents was investigated by using the steels shown in Table 2. The steels were solution treated at 950°C for 300 s to dissolve Cr nitride, and then water quenched to room temperature to avoid N precipitation. The amount of Cr nitrides in the specimen was first filtered by electrochemical method in an electrolyte of methanol with 10% acetylacetone and 1% tetramethylammonium chloride,\(^{20}\) and then the filtered residue was quantified by ICP mass spectrometry. The amount of N as Cr nitrides after the solution treatment was ensured by the analysis as less than 2 ppm for each of the Cr contents. The specimens were then reheated and isothermally held for 3.6 ks at a temperature in a range between 400°C and 800°C. Internal friction analysis was then carried out in the elevation rate of 2°C/min from –20°C to 120°C at a constant frequency of 1.5 Hz (Rigaku IFM1500). Solute N after the holding was estimated by using the Snoek peak at 25°C, which is attributed to solute N,\(^{13}\) since the obvious shifts of the Snoek peak at 25°C by the addition of Cr and by the isothermal holding at various temperatures were not observed. The amount of solute N was calculated by comparing the Snoek peak height after the isothermal holding with the height just after solution treatment at 950°C in each of the Cr contents, under the assumption that the Snoek peak height is linearly related with the amount of solute N. The structure of the precipitates was observed by FEG-TEM (Hitachi HF2000).

2.3. First-principles Calculation

To assess the interaction of N atoms and substitutional atoms in α-Fe, we carried out first-principles calculation based on density functional theory\(^{21,22}\) employing the projector augmented wave (PAW) method\(^{23}\) within the Vienna Ab-initio Simulation Package (VASP).\(^{24–27}\) The 3p, 3d and

<table>
<thead>
<tr>
<th>Table 1. Amount of alloying elements added to the base steels (mass%).</th>
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<tbody>
<tr>
<td>Mn</td>
</tr>
<tr>
<td>0.5, 1.0, or 1.5</td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td>0.01, 0.02, or 0.04</td>
</tr>
<tr>
<td>Base composition: 0.0015N–0.001C–0.1Si–0.1Mn–0.01P</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. Chemical composition of steels (mass%).</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
</tr>
<tr>
<td>0.0041</td>
</tr>
<tr>
<td>0.0042</td>
</tr>
<tr>
<td>0.0042</td>
</tr>
<tr>
<td>Base composition: 0.6Mn–0.04P–0.008Nb</td>
</tr>
</tbody>
</table>

room temperature takes a long time, accelerated aging condition of 100°C×3.6 ks, which almost corresponds to that of 20°C×3 month in terms of diffusion distance of N atoms in α-Fe,\(^{13,15}\) was chosen.

2.2. Aging and Precipitation Behaviour in Cr–N Steels

The effect of annealing temperature was investigated by using the steels shown in Table 2. The steels were reheated to 1 250°C for 3.6 ks, and hot-rolled at a finish rolling temperature of 940°C and quenched and held at 700°C or 500°C for 3.6 ks to simulate coiling process, and air-cooled to room temperature. The plates were then cold-rolled by 80%, and annealed in the heat cycle of typical continuous galvannealing line, where the specimens were annealed for 90 s at 750°C, 800°C, or 850°C, and subsequently cooled to 460°C with a cooling rate of 5°C/s and then reheated for 20 s at 520°C, and cooled to 350°C with a cooling rate of 15°C/s.

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4s states of 3d transition metals, 4p, 4d and 5s states of 4d transition metals, and 2s and 2p states of N were treated as valence states. The cutoff energy for the plane wave expansion of the wave functions was set to 400 eV for all calculations. For the exchange-correlation energy, the generalised gradient approximation with the parameterisation proposed by Perdew, Burke and Ernzerhof was used. The Monkhorst-Pack 5×5×5 k-point mesh and Methfessel-Paxton smearing with a width of 0.2 eV are used to sum up the occupied states. The electronic relaxation was performed until the total energy change between two successive steps was less than 1×10⁻⁴ eV. Structural optimisation was performed until the forces acting on each atom became less than 0.02 eV/Å under the condition of constant supercell volume, but also under the condition of constant supercell volume. The interaction energies were inspected by placing Cr atom or vacancy in substitutional position, D, E, or F, as presented in Fig. 1(b). The interaction energies of Cr–Cr and Cr–vacancy interactions were estimated by placing N atom in each octahedral position within the 3rd nearest neighbour distance from substitutional solute X as presented in Fig. 1(a). In the calculations, attractive X–N interaction gives a negative value. In order to estimate the effect of volume relaxation of supercell on the interaction energies, the interaction energies between Cr and N were calculated not only under the condition of constant supercell volume, but also under the condition of volume relaxation. The effect of the volume relaxation on the interaction energies of Cr–N was less than 0.02 eV.

We also investigated the interaction energies of Cr–Cr, Cr–vacancy, and further the effect of vacancy (denoted by Vac in Fig. 1) on the Cr–Cr and Cr–Vac interactions by the first-principles calculation. The Cr–Cr and Cr–vacancy interactions were inspected by placing Cr atom or vacancy in substitutional position, D, E, or F, as presented in Fig. 1(b).

$$\Delta E_b = E[\text{Fe}_{n-1}\text{Fe}_n] + E[\text{Fe}_n] - 2E[\text{Fe}_{n-1}\text{Cr}] \quad \text{(2)}$$

$$\Delta E_b = E[\text{Fe}_{n-2}\text{CrVac}] + E[\text{Fe}_n] - E[\text{Fe}_{n-1}\text{Cr}] - E[\text{Fe}_{n-1}\text{Vac}] \quad \text{(3)}$$

The Cr–vacancy–Cr interaction was also estimated by placing Cr atom in substitutional position, G, H, or I, as presented in Fig. 1(c).

$$\Delta E_b = E[\text{Fe}_{n-1}\text{CrVac}] + E[\text{Fe}_n] - E[\text{Fe}_{n-1}\text{Cr}] - E[\text{Fe}_{n-1}\text{CrVac}] \quad \text{(4)}$$

The interaction energies of Cr–vacancy–N and Cr–vacancy–Cr–N were estimated in the atomic configuration presented in Figs. 1(d) and 1(e), where N atom was placed at interstitial octahedral site, A, B or C.

$$\Delta E_b = E[\text{Fe}_{n-2}\text{CrVacN}] + E[\text{Fe}_n] - E[\text{Fe}_{n-1}\text{CrVac}] \quad \text{(5)}$$

$$\Delta E_b = E[\text{Fe}_{n-1}\text{CrVac}] + E[\text{Fe}_n] - E[\text{Fe}_{n-1}\text{CrVac}] \quad \text{(6)}$$

3. Results

3.1. Balance between Bake Hardenability and Anti-aging Property

Figure 2 shows the effect of Mn, Cr, Mo, V, Nb and Al on BH170 and YPE after accelerated aging of 100°C×3.6 ks (YPE100) after annealing at 800°C. BH170 and YPE100 of the base steel with 0.0015N–0.001C–0.1Si–0.1Mn–0.01P were 62 MPa and 1.2%, respectively. The addition of Cr and Mo suppressed the appearance of YPE after aging for 3.6 ks at 100°C without decreasing the amount of BH170, with the suppression effect much larger for Cr when compared at the same amount of addition. Among the steels without YPE after aging for 3.6 ks at 100°C, the steel containing 0.9%-Cr showed the largest BH170, 66 MPa. No effect of Mo on the BH170 and YPE100 was observed at least up to the addition of 0.1 mass%.

On the other hand, the addition of V, Nb or Al suppressed both BH170 and YPE100. For instance, BH170 and YPE100 decreased to 38 MPa and 0% by the V addition of 0.02 mass%. The larger decrease of BH170 was observed by Nb addition, where BH170 and YPE100 decreased to 2 MPa and 0% by the addition of 0.02 mass%. BH170 also decreased to approximately 25 MPa by Al addition of 0.02 mass%, but kept almost the same value by the further addition. The decrease of BH170 and YPE100 by the addition of V, Nb, or Al could be attributed to the decrease of solute N owing to the formation of VN, NbN, and AlN during the annealing at 800°C. The amount of solute N after annealing and the effect of solute C will be discussed in Section 4.1. Figure 3 summarises the balance between BH170 and YPE100 in the investigated steels. It is apparent that the addition of Cr improves anti-aging properties at lower
3.2. Effect of Annealing Temperature and Hot-rolling Condition in Cr–N Steels

As the good balance between BH and anti-aging properties was suggested in Cr steels, we further investigated the effect of Cr contents, holding temperature (HT) at hot-rolling process, and annealing temperature in a heat cycle of a typical continuous annealing line, to clarify that the idea of Cr–N system is industrially applicable.

Figure 4 shows the effect of annealing temperature on BH170 in a different Cr content. BH170 apparently decreased with increasing Cr content, especially at the annealing temperature of 750°C. Furthermore, BH170 after annealing was affected by HT which simulates a heat cycle of coiling process. HT at 500°C gave larger BH170 than HT at 700°C. Figure 5 summarises the balance between BH170 and YPE100 after the annealing from 750 to 850°C in 0%, 0.6% or 1.0%-Cr steel. Thus, BH170 of 55–65 MPa with anti-aging properties at low temperature was confirmed to be obtained at a wide range of annealing condition in both 0.6%-Cr and 1.0%-Cr steels. The anti-aging property of the steels is mainly attributed to the effect of Cr, since the effect of Mn, containing by 0.6% in the steels, on YPE100 was much smaller than the effect of Cr, as shown in Fig. 1.

3.3. Precipitation Kinetics of Cr Nitride

Figure 6 shows a typical precipitate observed after annealing at 800°C in Cr steel.31) The precipitate was found to be γ-CrN with a cubic structure of a=0.414 nm, as was previously reported by Massardier et al.32) Our internal friction measurement has shown that, as presented in Fig. 7, the precipitation nose of CrN was around 650–700°C, and the amount of CrN increased with increasing Cr content. The amount of solute N after the annealing of 700°C and 800°C in 1.0%-Cr steel was 8.8 ppm and 33.1 ppm, respectively. This agreed well with the value in 1.0%-Cr steel calculated...
from the solubility product of CrN reported by Baliktay et al.,\(^{13}\) which is 5.4 ppm at 700°C and 32.1 ppm at 800°C. Thus, the smaller BH170 in the higher Cr content, and the smaller BH170 in the annealing at 750°C in 1%-Cr steel, shown in Fig. 4, is probably due to the decrease of the amount of solute N by the precipitation of CrN during annealing. Similarly, the effect of holding temperature after hot-rolling on BH 170 can be explained by the precipitation of CrN during the holding. When the specimen is hot-rolled and subsequently held at 700°C, the amount of solute N is expected to be smaller than that in case when HT is 500°C owing to the precipitation of CrN. As the period of annealing after cold rolling was 90 s, it is probable that CrN formed in the holding process after hot-rolling could not dissolve in a limited period of annealing, and results in a smaller amount of solute N in ferrite.

3.4. Interactions among Cr, N and Vacancy

Atom probe analysis of Cr added ultra low N steel has indicated the attractive interaction between Cr atom and N atom.\(^ {17}\) Since the diffusion trap\(^ {33}\) of N atoms by the attractive Cr–N interaction could be the possible reason for antiaging property at room temperature, the atomic interaction was evaluated by first-principles calculation to validate the diffusion trap mechanism.

3.4.1. Substitutional Solute–N Interaction

The interaction energy of X–N (X: Cr, V, Mo) at the 1st to the 3rd nearest neighbour (nn) octahedral positions is presented in Fig. 8. All the considered substitutional solute exhibited repulsive interaction with N atom up to the 3rd nn. The interaction energy for Cr–N agreed well with the previous first-principles calculation.\(^ {34}\)

3.4.2. Cr–Cr and Cr–vacancy Interaction

Before inspecting the Cr–vacancy–N interaction, we first calculated the Cr–Cr and Cr–vacancy interaction to seek for the energetically stable configuration between Cr atoms and vacancy. As presented in Fig. 9, Cr-vacancy exhibited attractive interaction and it became maximum at the 1st nn substitutional site ($\Delta E_b = -0.05$ eV). The Cr–Cr interaction was repulsive and the interaction became weaker as the distance became larger. The Cr–vacancy and Cr–Cr interaction energies were almost the same as the previous first-principles calculation.\(^ {35,36}\) The Cr–Cr interaction became attractive by the existence of vacancy when Cr was placed at H site or I site in Fig. 1(c).

3.4.3. Cr–vacancy–N Interaction

Since the Cr–vacancy attractive interaction was strongest in the 1st nn configuration (Fig. 9), Cr–vacancy–N interaction was calculated in the configurations shown in Fig. 1(d). As presented in Fig. 10, the stronger attractive interaction

![Fig. 5. BH170-YPE10% balance in 0%-Cr, 0.6%-Cr, and 1.0%-Cr steels annealed at various temperatures.](image)

![Fig. 6. TEM image of CrN.](image)

![Fig. 7. Precipitation-temperature diagram of CrN in 0%-Cr, 0.6%-Cr, and 1.0%-Cr steels held for 3.6 ks.](image)

![Fig. 8. Interaction energy for Cr–N, V–N, and Mo–N calculated in the configuration shown in Fig. 1(a).](image)
than the case for Cr–vacancy complexes was obtained in all the configurations containing N atom. This implies that N atoms can be attractively trapped by Cr–vacancy complexes. The attractive interaction energy became largest ($E_b = -0.91 \text{ eV}$) when N atom was placed at B site, the nearest octahedral site from vacancy. The major source of the strong attractive interaction at the nearest site B is probably due to the attractive interaction between N atom and vacancy. Our calculation also showed that the N atom moves slightly toward vacancy by 0.04 nm from the original octahedral site after the energy optimisation. It is noted here that N atoms at A or C site, the 2nd nn octahedral site from vacancy, exhibits moderate attractive interaction of $E_b = -0.25 \text{ eV}$ and $-0.28 \text{ eV}$, which looks close to the Cr–N interaction of $-0.18 \text{ eV}$ obtained by internal friction measurement. Similar tendency was also obtained for Cr–Cr–vacancy–N configuration.

4. Discussion

4.1. Solute N and C after Annealing

One important requirement for obtaining higher BH is that solute N should be retained after annealing and subsequent cooling. Table 3 shows the amount of soluble N and C at 800°C calculated from the solubility limit of CrN, VN, NbN, AlN, Mo2C, VC, and NbC.

<table>
<thead>
<tr>
<th>Amount of addition (mass%)</th>
<th>Soluble N (mass ppm)</th>
<th>Soluble C (mass ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr (CrN)</td>
<td>0.2</td>
<td>161</td>
</tr>
<tr>
<td>Mo (Mo2C)</td>
<td>0.02</td>
<td>–</td>
</tr>
<tr>
<td>V (VN, VC)</td>
<td>0.01</td>
<td>14</td>
</tr>
<tr>
<td>Nb (NbN, NbC)</td>
<td>0.02</td>
<td>0.2</td>
</tr>
<tr>
<td>Al (AlN)</td>
<td>0.05</td>
<td>0.2</td>
</tr>
</tbody>
</table>

CrN, VN, NbN, AlN, Mo2C, VC, and NbC at a various amount of alloying addition. In the range of alloying investigation in this study, the soluble N is largest for Cr, and then V, and smallest for Nb and Al. The expected amount of solute N is less than 1 ppm for 0.04% Nb and 0.04% Al. Thus, the smaller BH170 and YPE100 in Nb, Al and V steels than in Mn, Mo and Cr added steels can be explained by the decrease of solute N owing to the precipitation of alloy nitrides.

It is important to note here that, in Al-added steel, BH170 has not changed with increasing Al content of more than 0.02%, and ~30 MPa of BH170 was observed even in 0.11%-Al steels (Fig. 2), where solute N is almost not expected due to the formation of AlN at present annealing conditions. Since the formation of Al carbide at around 800°C has not been reported, the BH170 of approximately 30 MPa in the steels with higher Al content is probably attributed to 10 ppm of solute C containing in the steels. Similarly, as the carbides containing Cr were rarely observed by TEM in the Cr-added steels, the effect of solute C on bake hardenability cannot be ignored in the annealed and quenched Cr-added steels. In the V added steels, both of solute N and solute C could contribute to BH170 in the present conditions, because the amount of C in the steels is well within the solubility of C for V carbide. The smaller BH170 in Nb added steel can be explained by the decrease of the amount of both solute C and solute N by the formation of Nb carbide and nitride or carbonitride during annealing.

4.2. The Balance between Anti-aging Properties at Low Temperature and BH at 170°C

4.2.1. Diffusion Trap Model

The aggregation of Cr and N atoms during room temperature aging has been actually found by our atom probe.
Therefore, diffusion trap of N atoms by Cr atoms or Cr–vacancy complexes seems to be a candidate for the anti-aging property in Cr containing low N steels.

When N atoms attract with trap site Tr, the diffusion coefficients \( D_N \) under the interaction can be expressed in the following:\(^{33} \)

\[
D_N = \frac{D_0^N}{1 - X_T + X_T \exp(-B / kT)} \quad \text{(7)}
\]

where, \( X_T \) is the atomic fraction of trap site, \( B \) is the Tr–N interaction energy, and \( D_0^N \) is the diffusion coefficient of N in \( \alpha \)-Fe. Here, the value of \( D_0^N \) was taken from Ref. 18).

**Figure 11** shows the diffusion distance of N atoms, \( \sqrt{D_{\text{ex}}t} \), during aging of 100°C×3.6 ks and 170°C×1.2 ks, which corresponds to aging conditions used as the evaluation of anti-aging property and bake hardenability, as a function of the trap fraction and Tr–N interaction. The diffusion distance decreases with increasing the fraction of trap site, and the diffusion can be more strongly inhibited as the attractive interaction energy becomes larger. The dotted lines presented in Figs. 11(a) and 11(b) show the average dislocation distances in the specimens used for the evaluation of YP100 and BH170, respectively. The former \( d_{\text{SR}} \) represents the average dislocation distance after skinpass rolling by 1.0%, and the latter \( d_{2\%PS} \) represents that after tensile prestraining by 2%. Here, the average dislocation distances were roughly calculated as the inverse of square root of dislocation density, where dislocation densities of 5.7×10^{13} m/m² and 8.0×10^{13} m/m² measured by transmission electron microscopy was used.

The increase of YPE and yield stress during aging has often been understood as the pinning of mobile dislocations by solute C or N. We thus compare the average dislocation distance and the diffusion distance during each aging in the following, under the assumption that the increase of YPE or yield stress is inhibited when the diffusion distance of N is smaller than the average dislocation distances. For instance, in the case of a trap energy of \( B = -0.2 \) eV, the diffusion distance of N during 100°C×3.6 ks becomes smaller than \( d_{\text{SR}} \) when the concentration of trap site is larger than \( 1 \times 10^{-3} \). Similarly, the diffusion distance becomes smaller than \( d_{\text{SR}} \) when the fraction of trap site is larger than \( 3 \times 10^{-6} \) in the case of \( B = -0.4 \) eV. In contrast, the diffusion distance of N is always larger than \( d_{\text{SR}} \) at \( B = -0.1 \) eV even containing trap site \( X_T \) of \( 1 \times 10^{-5} \). The above estimation implies that the appearance of YPE during low temperature aging could be more effectively inhibited when a larger amount of trap site with larger trap energy is distributed.

We then investigate the condition which satisfies both \( D_N \) at 100°C×3.6 ks < \( d_{\text{SR}} \), and \( D_N \) at 170°C×1.2 ks > \( d_{2\%PS} \), in order to make sure that the condition of larger BH170 with anti-aging property at 100°C×3.6 ks exists. The comparison of Figs. 11(a) and 11(b) has indicated that both of the conditions can be satisfied when \( X_T \) is around \( 1 \times 10^{-2} \) at \( B = -0.2 \) eV, \( X_T \sim 1 \times 10^{-3} \) at \( B = -0.4 \) eV, and \( X_T \sim 1 \times 10^{-10} \) at \( B = -0.9 \) eV. Since the interaction energy between Cr and N has been reported to be \( -0.18 \) eV by internal friction study,\(^{12} \) it seems to be reasonable to understand that the inhibition of YPE appearance by the Cr addition of 0.5–1.0 at% during the 100°C aging with keeping BH at 170°C is attributable to the N trapping by Cr atoms. However, the present first-principles calculation has indicated the inhibition effect of Cr cannot be explained by the Cr–N interaction because repulsive interaction is predicted between Cr atom and N atom.

**4.2.2. Effect of Vacancies on the Diffusion of N Atoms**

The first-principles calculation has shown that the attractive interaction between Cr and N atom is expected under the existence with vacancies, as presented in Fig. 10. Thus, it is important to estimate the concentration of vacancies in the specimens in order to discuss the effect of vacancies or vacancy–Cr complexes on N diffusion.

In thermal equilibrium, the vacancy fraction \( X_V^\delta \) in a pure metal is given by statistical thermodynamics,

\[
X_V^\delta = \exp \left( \frac{\Delta S_V}{kT} \right) \cdot \exp \left( \frac{-\Delta H_V}{kT} \right) \quad \text{(8)}
\]

where \( k \) is the Boltzmann constant, \( T \) the absolute temperature, and \( \Delta S_V \) and \( \Delta H_V \) are the vacancy formation entropy and enthalpy, respectively. First term on right hand side of...
Eq. (8) is a constant ~3 independent of \( T \). By substituting vacancy formation enthalpy of \( \alpha\Fe \) of 2.0 eV\(^{40,41}\) in Eq. (8), the vacancy fraction in thermal equilibrium at 800°C is calculated to be in the order of 10\(^{-5}\). The vacancy fraction is negligibly small when compared with the amount of Cr addition in the order of 10\(^{-2}\), even assuming that all the vacancies at 800°C are quenched-in after the cooling.

Since the specimen used in this study is rolled by 1% or tensile prestraining by 2%, it should contain vacancies associated with the plastic deformation. From an electric resistivity measurement, a fraction of point defects of 4\(^{-10}\) was reported in \( \alpha\Fe \) deformed by 20% at room temperature.\(^{42}\) The positron annihilation measurement of rolled \( \alpha\Fe \) has shown that the vacancy clusters are formed by the rolling with a strain of 2% and the density is levelled off over the rolling of more than the strain of 10%.\(^{43}\) Although the fraction of vacancies and its clustering behaviour after 1% rolling are uncertain, the fraction of vacancies should be less than the order of 10\(^{-5}\) according to Takamura \textit{et al.}\(^{42}\)

According to the first-principles calculation, N atoms attract with Cr–vacancy complexes with strong interaction energy of −0.91 eV and also with moderate interaction energy of around −0.25 eV. Even taking into account the maximum vacancy fraction of the order of 10\(^{-5}\) introduced by 1% rolling, the fraction of Cr–vacancy trap site with moderate interaction of −0.25 eV is too small to inhibit the arrival of N atoms to dislocations, as was described in Section 4.2.1. On the other hand, the strong interaction for Cr–vacancy with N atom is the probable candidate for the trap site of N diffusion because only the trap site of the order of 10\(^{-10}\) is enough for the inhibition of the arrival of N atoms to dislocation in 100°C×3.6 ks. However, it should be noted that the strong trap site has been reported to be originated from the interaction between vacancy and N atom,\(^{40}\) and thus the addition of Cr is not necessary for the strong interaction. Therefore, it is hard to conclude that the strong interaction energy of −0.9 eV for Cr–vacancy–N complexes is the main reason for the inhibition effect of N diffusion by the addition of Cr.

4.2.3. Effect of Cr on the Diffusion of Vacancy-N Complexes

If the annihilation of the vacancies during low temperature aging is inhibited by the addition of substitutional elements such as Cr, the strong trap effect of N diffusion by vacancies continues longer, and may thus result in the improvement of anti-aging behaviour at low temperature. Vehanen \textit{et al.}\(^{44}\) have reported from positron-lifetime measurements that monovacancies formed by the irradiation in high purity \( \alpha\Fe \) are mobile even at around 220 K, and the diffusion causes vacancy clusters. Toji \textit{et al.}\(^{45}\) have indicated that vacancies introduced by rolling in interstitial-free steels decrease with the thermal aging less than 100°C, by the measurement of the diffusesible hydrogen which interacts with vacancies and dislocations. These reports suggest that vacancies could move at around room temperature in \( \alpha\Fe \).

In general, the migration of vacancies is inhibited when alloying elements attractively interact with vacancies. Table 4 summarises the binding energy of vacancy with Cr, Mn, Mo and V atoms from this study and from Refs. 36) and 46). The experimental result on the balance between BH170 and YPE100, represented in Fig. 2, has shown that the inhibition effect on aging at 100°C×3.6 ks is larger for Cr than for Mn, while the attractive interaction for Cr–vacancy is smaller than Mn–vacancy. Thus, the larger inhibition effect of Cr than Mn on YPE appearance cannot be explained only by the diffusion trap of vacancies.

We then discuss the effect of Cr on the vacancy diffusion under vacancy-N interaction. Our first-principles calculation showed that the largest Cr–vacancy–N binding energy is −0.91 eV, and it is slightly larger than the vacancy–N binding energy of −0.86 eV obtained by first-principles calculation.\(^{36}\) Furthermore, as presented in Fig. 10, Cr–Cr vacancy–N complex gave a binding energy of −0.99 eV, which is larger than vacancy–N binding energy by −0.13 eV. Atom probe measurement in Cr added ultra low N steels has clearly shown that aggregates of Cr and N are formed during aging of 25°C and 100°C.\(^{17}\) This implies that Cr–vacancy–N complexes are certainly formed during low temperature aging, probably by the diffusion of vacancies and N atoms to Cr atoms, because the formation of Cr–N complexes seems to be difficult due to the repulsive interaction between Cr atoms and N atoms. Therefore, it is possible to understand that Cr atoms trap vacancy–N complexes, so that retarding the annihilation of vacancies which trap N atoms. However, it should be mentioned here that vacancy clusters, rather than monovacancy, could be actually formed after cold rolling.\(^{43}\) and the vacancy could combine with not only one N atom but two or three N atoms.\(^{36}\) Thus, in order to understand the effect of Cr on aging behaviour in N steels, further study is necessary on the binding energy for high order vacancy clusters with N complexes, and on its effect of substitutional elements such as Cr, Mn and so on.

Finally, we comment on the reliability of the present first-principles calculation, where periodic boundary conditions were applied in the limited number of atoms in a supercell \( (n=128) \). It is likely that the calculated interaction energies contain artefact, since the larger spurious interaction energy arising from the periodic boundary conditions has been reported in the smaller number of atoms in a supercell.\(^{47}\) The estimation of the artefact in the present cases will also be needed for further quantitative discussion on the diffusion trapping mechanism.

5. Conclusions

The effect of Cr, Mo, V, Nb, and Al on bake hardenability at 170°C and the inhibition of the appearance of yield point elongation (YPE) after low temperature aging in ultra low N steels was investigated. We also studied the interactions among a vacancy, substitutional solute, and interstitial N atoms by using first-principles calculation in order to under-
stand the inhibition mechanism of Cr addition on aging. The results can be summarised as follows:

(1) Cr addition of 0.5–1.0 mass% inhibited the appearance of YPE after aging for 3.6 ks at 100°C without much decreasing the amount of 2%BH at 170°C (BH170), with the inhibition effect much stronger than Mn. Small addition of V, Nb, and Al suppressed not only the appearance of YPE at accelerated aging at 100°C but also the amount of BH170 probably due to the decrease of solute N by the formation of alloy nitrides during annealing.

(2) Maximum decrease of the amount of solute N during isothermal holding in Cr containing ultra low N steels was obtained at around 650–700°C, owing to the precipitation of CrN. The dependence of annealing temperature, amount of Cr addition, and holding temperature after hot-rolling on BH170 can be well understood by the change of the amount of Cr addition, and holding temperature after hot-rolling on BH170 can be well understood by the change of solute N due to the precipitation of CrN.

(3) Our first-principle calculation has indicated that the interaction between Cr atom and N atom was repulsive for the 1st to the 3rd nn octahedral positions from the substitutional atom. Similarly, the atomic interaction for Mo–N and V–N was shown to be repulsive.

(4) Concerning Cr–vacancy–N complexes, the attractive interaction became strongest ($\Delta E_b = -0.91$ eV) when N atom is placed at the nearest octahedral distance from the vacancy. N atoms in the 2nd nn and 3rd nn octahedral sites from the vacancy exhibited moderate attractive interaction of $-0.25$ eV and $-0.28$ eV. The interaction of Cr atom with vacancy was attractive ($\Delta E_b = -0.05$ eV).

(5) The reason for high BH with superior anti-aging property in Cr added steels was discussed by using trap model for N diffusion. If the interaction energy between Cr and N atoms is attractive by $-0.18$ eV, the experimentally obtained value reported by Numakura et al., the high BH with the anti-aging property at low temperature can be reasonably understood by the diffusion trap by Cr atoms. On the other hand, if we assume the interaction energies among Cr atom, N atom, and vacancy estimated by the first-principles calculation, it is possible to understand that the trap site of N diffusion is small amount of vacancies introduced by pretraining or skinpass rolling. In this case, the effect of Cr on the improvement of the anti-aging property can be understood by the retardation of the annihilation of vacancies-N complexes during low temperature aging.

REFERENCES