Full length article

Direct observation of niobium segregation to dislocations in steel

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Abstract

It is well known that niobium in solute solution retards the recovery of dislocations in steel. Segregation of niobium atoms to dislocations was observed for the first time by atom probe tomography in niobium added ferritic stainless steels for high temperature use. The observation results suggest that solute niobium atoms solely have strong attractive interaction with dislocations. We name it niobium-Cottrell atmosphere, and discuss the trapping site and interaction energy through a comparison with segregation to the grain boundary in the same steel.

1. Introduction

Niobium is important alloying element in steels, because it is used for grain refinement by the retardation of recrystallization in the hot-rolling process [1–3]. The solute drag effect by solute niobium atoms and the pinning effect by niobium carbonitride precipitates have been proposed for the mechanism of recrystallization retardation [4,5]. Based on calculations, the former is reported to be more effective in ferrite, while in austenite phase, depending on the exact recrystallization temperature, either the former or the latter may be more effective [6].

Niobium in solid solution also significantly retards the recovery of dislocations in steel [3,7]. Recently, Shrestha et al. reported by in situ heating transmission electron microscopy (TEM) that niobium addition impeded the dislocation movement during aging at 575 °C [8]. However, it is unclear why solute niobium impeded the dislocation movement and retarded recovery strongly. Niobium atoms have been reported to attractively interact with vacancies in steel, and thus impede the dislocation movement (climbing) by decreasing the self-diffusion of iron through decrease in the density of mobile vacancies [7]. Furthermore, niobium atoms are also reported to make dipole or clusters with solute carbon and nitrogen atoms, and consequently suppress the dislocation migration because carbon and nitrogen atoms have strong attractive interactions with dislocations [8,9]. In contrast, the direct interaction between dislocations and lattice distortion by solute niobium atoms was proposed [3]. Dang and Wang reported the strong interaction between the dislocation core and niobium atoms by the calculation based on the first-principles discrete variational method [10]. Kirchheim reported that solute segregation to dislocations reduces the line energy of the dislocations, and consequently, reduces the driving force for recrystallization [11,12]. To elucidate the mechanism, direct observation of the attractive interaction between niobium atoms and dislocations is required.

Atom probe tomography (APT) is widely used for the atomic-scale observation of alloying elements in steel. Wilde et al. reported that the Cottrell atmosphere of carbon atoms around dislocations was observed in low-carbon martensite steels, wherein the dislocation was identified by spiral steps on field ion microscopic (FIM) images [13,14]. Furthermore, some simulations of the Cottrell atmosphere of carbon have been reported, wherein the difference in carbon distribution between edge and screw dislocations was predicted by the static energy calculation [15,16].

Recently, the analysis region of the atom probe was enlarged using new technologies, namely, wide-angle reflector and short flight length [17]. Many studies have reported on solute segregation and precipitation to the dislocation were reported [18–20]. However, most of the reports were conducted in neutron-irradiated
materials because the high density of point defects introduced by neutron radiation increased bulk diffusion and produced radiation-induced segregation. There have been few reports on the segregation of substitutional atoms to dislocations in commercial steels, even though the phenomena are very important to directly discuss the interaction between solute atoms and dislocations.

This paper investigated the state of solute niobium atoms in niobium added ferritic steels by APT. The segregations of niobium atoms to single dislocations and the dislocation wall were observed in the steel. From the quantitative estimation of segregating atoms, their trapping sites and interaction energies were discussed.

2. Experimental

2.1. Materials

Niobium added ferritic stainless steel was used in this study. The steel is actually applied for exhaust manifold in the automotive industry because of its high performance against thermal fatigue, where the proof strength is sufficiently maintained under repeated heating cycles. The improvement of proof strength at the high temperature was considered attributable to solid solution strengthening including the effect of niobium in solid solution on the retardation of recovery and recrystallization [21]. The chemical composition of the steel is shown in Table 1. Sufficient amounts of niobium and titanium were added to scavenge solute carbon and nitrogen for the improvement of ductility, high temperature strength, high thermal fatigue and corrosion resistance. A small amount of molybdenum and copper was added for further improvement of the heat-resistance property [22]. Moreover, a very small amount of boron was added for the suppression of secondary work cracking by grain boundary segregation [23]. This stainless steel did not undergo austenite transformation, and hot-rolling was conducted in the ferrite phase. The slab was homogenized at 1250 °C for 3.6 ks and then hot-rolled to a thickness of 4 mm. The final temperature of hot-rolling was about 860 °C, and the hot-rolled sheet was immediately cooled by water spray and coiled at about 520 °C. The yield stress and tensile stress of the hot-rolled sheet were 515 MPa and 571 MPa at room temperature.

2.2. Analysis methods

A transmission electron microscope (H8000, Hitachi) operated at 200 kV was used to investigate the distribution and number density of dislocations in the steel sheet. Thin film with a thickness of about 50 μm was fabricated from the steel sheet by mechanical and chemical polishing. Thin foil specimens for TEM observation were thinned by electropolishing in an electrolyte containing 10% perchloric acid in acetic acid held at 286 K with an applied potential of DC 30 V.

An energy-compensated three-dimensional atom probe (3DAP, Oxford NanoScience Ltd.) with a large-angle reflector was used to investigate the distribution of alloying elements in the steel. The two-stage electropolishing method was applied for the needle tip fabrication, since gallium radiation of focused ion beam (FIB) milling may influence solute segregation to dislocation through the formation of point defects [24]. Small square rods (0.3 mm × 0.3 mm × 10 mm) cut from the steel sheet were directly electropolished using the standard electrolyte of 25% perchloric acid in acetic acid for the first stage and 2% perchloric acid in 1-butoxyethanol for the second stage [25].

APT measurements of five million atoms were performed at a specimen temperature of 40–60 K, total probe voltage of 8–15 kV, pulse fraction of 20%, and pulse frequency of 20 kHz. FIM images were observed at 90 K using neon as the imaging gas. The crystallographic direction of dislocations and grain boundaries in three-dimensional (3D) elemental maps was determined by the FIM polefitting method [26]. Atomic data sets were analyzed using IVAS software (version 3.6.4). Peaks of 27, 28, 28.5 and 29 Da were assigned to Fe2+, a peak of 27.5 Da to Mn2+, peaks of 31 and 46.5 Da to Nb5+ and Nb6+, respectively, peaks of 5 and 5.5 Da to B2+, peaks of 10 and 11 Da to B+, peaks of 25, 26 and 26.5 Da to Cr2+, peaks of 10.3 and 15.5 to P3+ and P5+, peaks of 31.5 and 32.5 Da to Cu2+, Peaks of 63 and 65 to Cu+, peaks of 14, 14.5 and 15 Da to Si2+, peaks of 30.7, 31.3, 31.7, 32, 32.7, 33.3 Da to Mo3+, and peaks of 46, 47.5, 48.5, 49, 50 Da to Mo5+ in the mass-to-charge spectrum. Carbon is normally assigned as peaks at 6 Da (C2+) and 12 Da (C+), but such peaks were not observed in the steel, indicating that most solute carbon was scavenged by carbide precipitation with niobium and titanium. Nitrogen is assigned as a peak at 14 Da (N+), which overlaps with the main isotopic peak of Si2+. But locally enriched nitrogen can be identified by the peak.

3. Experimental result

Fig. 1 shows TEM bright field images of the niobium added stainless steel. Grain size was in the range of several micrometers, and a slightly high number density of dislocations was observed in each grain. Fine particles locking the dislocations were not observed with TEM although submicron-sized particles of chromium intermetallic compounds were occasionally observed in the grains and at the grain boundaries. The dislocations were almost homogeneously distributed within the grains although the dislocation cell like structures were occasionally observed. The dislocation density in the region with homogeneous distribution of dislocations was estimated to be about 1.8 × 1010 cm-2 with TEM. The density means that the analyzed volume of 5 million atoms (168000 nm3; e.g., ~40 nm × 40 nm × 105 nm) has a dislocation line of about 30 nm on average, where the ion detection efficiency is 0.35 in 3DAP. This suggests that the dislocation included in the analyzed volume may be about 50% in the dataset of 5 million atoms.

Fig. 2a shows 3D elemental maps within a grain in the steel, obtained by APT measurement in a random direction. Niobium atoms were homogeneously in solid solution. The niobium concentration (~0.28 at.%) in the analyzed volume was nearly coincident with the excess niobium estimated by subtracting the content of (Nb,Ti)(C,N) precipitates from the total content (Table 1). Niobium-enriched regions were observed as curved lines, which are indicated by the arrow heads. To visualize the enriched regions clearly, the isoconcentration surface of 1.2 at.% is represented in Fig. 2b. Neither carbon nor nitrogen was observed in the niobium-enriched regions, indicating that the niobium-enriched regions correspond not to precipitation such as carbide and nitride, but to

| Table 1 Chemical comparison of the niobium ferritic stainless steel. |
|------------------------|------|------|------|------|------|------|------|------|------|------|
|                        | C    | Si   | Mn   | P    | Cr   | Mo   | Cu   | Ti   | Nb   | N    |
| mass%                  | 0.008| 0.21 | 1.02 | 0.025| 16.95| 0.31 | 1.25 | 0.12 | 0.53 | 0.013|
| at.%                   | 0.037| 0.42 | 1.04 | 0.045| 18.20| 0.18 | 1.10 | 0.14 | 0.32 | 0.052|
|                        |      |      |      |      |      |      |      |      |      | B    |
|                        |      |      |      |      |      |      |      |      |      | 0.0041|
the segregation of solute niobium atoms to dislocation. The niobium maps show the small denuded zones outside the enriched regions around the dislocation. The niobium maps rotated by about 70° around the horizontal axis are shown on the right-hand side. The views from two different directions indicate that the dislocation exists on two or more different slip plains. Slight segregations of boron and phosphor atoms were observed in the same region, while segregations of other elements except niobium, boron and phosphor were not observed. No segregations of molybdenum, manganese, titanium and chromium suggest that the attractive interactions between these atoms and dislocations are smaller than that between niobium atoms and dislocations.

Fig. 3 shows 3D elemental maps of a grain boundary in the steel, obtained by APT measurement in a random direction, where the views from three different directions are presented. The maps in the left column indicate that niobium atoms were segregated at the grain boundary. The maps in the center and right columns show that the niobium enriched regions correspond to the parallel straight lines at intervals of about 12 nm. Therefore, the grain boundary is a small angle grain boundary composed of multiple parallel screw dislocations with \( \mathbf{b} = 1/3[111] \). The crystallographic directions are inserted in the right column (Fig. 3).

The tilt angle \( \theta \) of the small tilt angle grain boundary is as follows:

\[
\theta = 2 \sin^{-1}\left( \frac{\mathbf{b}}{2\mathbf{h}} \right),
\]

where \( \mathbf{b} \) is the magnitude of Burgers vector \( \mathbf{b} \), and \( \mathbf{h} \) is the distance between dislocations [27]. From the equation, the tilt angle was estimated to be about 1.1°. The boundary was generated by restructuring of the dislocations in the coiling at 520 °C, and thus the segregation of substitutional atoms is considered to be generated mainly during the coiling.

Fig. 4 shows 3D elemental maps of a large angle grain boundary in the steel. The misorientation angle was estimated to be about 18° by the FIM pole-fitting method [26]. Different from the small angle grain boundary (Fig. 3), the dislocation structure was not identified. Planer like heavy segregation of niobium is observed at the grain boundary, where the maximum concentration reaches as much as 8 at.% in the concentration profile. The segregations of boron and phosphor are also observed at the boundary. Slight segregations of molybdenum and manganese are observed, but no segregation of chromium is observed. Table 2 shows the estimated...
interfacial excesses of elements segregating at the grain boundary [25]. The result indicates that there is a similar tendency in the order of segregation degree between the grain boundary (Fig. 5) and the dislocations (Figs. 3 and 4) although no segregation to dislocations was observed in molybdenum and manganese.

4. Discussion

4.1. Interaction between niobium and dislocation

The niobium added stainless steel has excellent performance at high temperatures. The recovery of dislocations was retarded by the solute niobium in addition to solid solution strengthening of the solute niobium. In the steel, the atomic content of niobium (~0.32 at.%) and titanium (~0.14 at.%) was sufficiently higher than the total content of carbon and nitrogen (~0.09 at.%), indicating that there was a sufficient amount of solute niobium. Actually, the APT results showed that the concentration of solute niobium in grains was about ~0.28 at.%. In contrast, the density of dislocations decorated by niobium atoms, observed with APT, was mostly coincident with the dislocation density estimated with TEM, indicating that all of the dislocations have the niobium segregation. Neither carbon nor nitrogen was observed at the dislocations, and only a small enrichment of phosphor and boron was observed except niobium. Therefore, there is a strong attractive interaction between niobium atoms and dislocations in the steel. This fact suggests that mobile dislocations are dragged by niobium atoms in the high temperature region where niobium atoms can diffuse moderately. In contrast, other substitutional elements with sufficient content, namely, molybdenum, manganese, and chromium did not show such segregation to dislocation. The results indicate that the interaction energy between niobium atoms and dislocation is significantly larger than those between other substitutional elements and dislocations.

Here, the dislocation excess of solute per unit length of the dislocation was estimated by the method reported by Miller [18], which is obtained by subtracting the solute atoms in the matrix region of the same volume from the enriched solute atoms in the cylindrical region around the dislocation. The selected cylindrical volume 10 nm in diameter was cut out along the dislocation. Table 3 shows the estimated values of the dislocation excess per unit length of the dislocation line. The dislocation excess of niobium in the edge dislocations forming the small tilt angle grain boundary was estimated to be 21.9 ± 0.8 atoms/nm on average, where the detection efficiency was assumed to be 0.35 in 3DAP. However, the dislocation excess of niobium in the single dislocations, whose characteristics were not identified, was estimated to be in the range of 7.2–16.8 atoms/nm. The dislocations probably have edge and screw components. These results imply that the edge dislocations have larger dislocation excess than screw or mixed dislocations [15,20].

The value of dislocation excess of 21.9 ± 0.8 atoms/nm for niobium indicates 2.55 ± 0.10 atoms per the (112) lattice plane of the dislocation. Taketomi et al. reported that the number of substitutional sites in the \{112\}<111> edge dislocation core in ferritic iron was estimated to be 8 per the (112) lattice plane normal to the dislocation line, and that the number of sites with expansive strain was estimated to be 4 per the plane [28]. The small value of the dislocation excess and the small expanse of niobium enriched regions (Fig. 4b) suggest that almost all of the segregating niobium atoms occupy the dislocation core sites with expansive strain.
Based on the Langmuir–Mclean model [29], the grain boundary concentration of segregating atoms ($X_b$) in the equilibrium state is expressed as follows:

$$\frac{X_b}{X_{b0} - X_b} = \frac{X}{1 - X} \exp\left(\frac{-\Delta G_b}{RT}\right).$$

(2)

where $R$ is the gas factor, $T$ is temperature, $X_{b0}$ is the saturated value of $X_b$, $X$ is the atomic fraction of the element in the matrix, and $\Delta G_b$ is the Gibbs free energy of segregation. The equation is applied to the segregation to dislocation. Assuming that the site number (saturated value) for niobium atoms in the dislocation core is 4 per the (112) lattice plane and that the segregating state is formed during coiling at 520 °C, the interaction energy between niobium atoms and the edge dislocation is estimated to be $42.4 \pm 0.7$ kJ/mol in average. However, from the interfacial excess of the large angle grain boundary in Table 2, the Gibbs free energy of segregation at the grain boundary was estimated to be about $37.1 \pm 0.4$ kJ/mol using the monolayer model [30], where the saturated value is assumed to be 21.2 atoms/nm$^2$ from the site number in the boundary with the width $b$ in ferritic iron. The two interaction energies of the niobium atoms with dislocation and grain boundary show almost the same values.

According to the assumption of the site number of 4 per the (112) plane in the edge dislocation core, the saturated value per unit length of the dislocation is 34.3 atoms/nm. The tilt angle of the small angle grain boundary, which has the same saturated value for niobium as that of the large angle grain boundary (21.2 atoms/nm$^2$), is estimated to be about 9° by Eq. (1). This angle is the border between small and large angle grain boundaries and mostly agrees

Fig. 3. 3D elemental maps of the small tilt angle grain boundary corresponding to the screw dislocation wall. Views from three different directions are presented. The arrows indicate the measurement direction.
Fig. 4. (a) 3D niobium maps in the selected box (44 nm × 10 nm × 60 nm) containing the small tilt angle grain boundary. Views from two different directions are presented. (b) Magnified 3D elemental maps of enriched atoms in the selected box (8 nm × 8 nm × 10 nm) along the edge dislocation.

Fig. 5. 3D elemental maps of the large angle grain boundary and concentration profiles along the direction perpendicular to the boundary (the inserted box). The arrowhead in the concentration profile represents the boundary position.

Table 2
Interfacial excess of segregating elements in the large angle grain boundary (Fig. 5).

<table>
<thead>
<tr>
<th>Element</th>
<th>Nb (atoms/nm²)</th>
<th>B (at.%)</th>
<th>P (at.%)</th>
<th>Mo (at.%)</th>
<th>Mn (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interfacial excess</td>
<td>9.3 ± 0.30</td>
<td>1.2 ± 0.11</td>
<td>2.9 ± 0.17</td>
<td>0.6 ± 0.08</td>
<td>0.4 ± 0.06</td>
</tr>
</tbody>
</table>
with that reported by Watanabe about tin segregation in ferritic iron [31], where the concentration of tin segregation increased with the misorientation angle in the small angle boundaries and saturated in the large angle boundaries. Therefore, it is suggested that the two interactions of niobium atoms with dislocation and grain boundary arise from a similar mechanism, probably the difference in atomic size between elements and iron in the region with distorted crystal structure.

Taketomi et al. reported that the expansive strain region in the dislocation core was 4b × b (−0.99 nm × 0.25 nm), and that the distance between expansive and compressive strain regions in the core was about b (−0.25 nm). However, the excess niobium atoms were distributed within the small circle 2–3 nm in diameter. Normally, it may be difficult to separate the expansive strain region from the compressive strain region in the core even with APT analysis, because APT has some aberrations associated with field evaporation, resulting in degradation in special resolution [17,25].

### 4.2. Interaction between other elements and dislocation

The order of the size of substitutional solute element is B < P < Fe – Mn < Cr < Ti < Mo < Nb according to the first-principle calculation results [32,33], where boron occasionally occupies the interstitial sites in ferritic iron [34]. Thus, boron and phosphor can be segregated in the compressive strain region because their atomic sizes are smaller than iron. However, no distinct difference in the center position of atomic distribution among these elements was identified.

Boron atoms were dispersedly observed around the niobium enriched region in Fig. 4. It is reported that boron atoms were observed behind the boundary due to the preferential retention with APT [35]. Actually, the phenomenon was observed at the grain boundary in Fig. 5. Therefore, the determination of the precise position of boron atoms is difficult using these data alone. Boron is considered to be trapped in compressive strain fields around the core, reproduced by niobium atoms segregated at dislocation core sites. In contrary, we have to consider the possibility that boron segregates in the expansive strain region as interstitial atoms.

The distribution area of phosphor atoms was smaller than that of boron atoms and was almost the same as that of niobium atoms in Fig. 4, although phosphor is larger than boron. This implies that there is an attractive interaction between phosphor and niobium, or phosphor prefers a disordered structure chemically.

Manganese and molybdenum did not segregate to dislocation probably because of the small interactions between these elements and dislocations. Actually, the elements showed a very slight segregation at the large angle grain boundary in comparison with niobium (Fig. 5). These results are derived from the difference in atomic size between the elements and iron. Thus, these elements are considered to have a small effect on the impediment of the dislocation movement, in comparison with niobium.

This is the first report to directly observe the niobium-Cottrell atmosphere around dislocations in commercial steel without irradiation. Such a distinct segregation has not been observed in other substitutional elements such as molybdenum and manganese. This indicates that the attractive interaction between niobium atoms and dislocations is significantly larger than those between other elements and dislocations because of its large atomic size, implying that solute niobium effectively retards the recovery in high temperatures [2,3,7]. Dynamic strain aging, caused by the segregation of niobium atoms to dislocations, was reported in iron-niobium alloy [36]. Furthermore, the niobium-Cottrell atmosphere might influence the high temperature yield point phenomenon that was observed in niobium added ferritic stainless steels [37,38].

The segregation of niobium atoms to dislocations was considered due to size effect. In addition, the presence of Nb–Nb attractive interaction, which was proposed by Pesold et al. for hydrogen, might stabilize niobium segregation [39]. Further experimental and theoretical researches on the formation mechanism of the niobium-Cottrell atmosphere and the effect of the atmosphere on the steel properties are required.

### 5. Conclusion

Segregation of niobium atoms to dislocations was directly observed in the niobium added ferritic stainless steel by APT analysis. Such segregation of niobium atoms to dislocation is called the niobium-Cottrell atmosphere. The segregation energy was estimated to be about 42.4 ± 0.7 kJ/mol in the (112) edge dislocation, which was almost the same as the grain boundary segregation energy. This implies that the large attractive interaction between niobium atoms and dislocations caused the retardation of the recovery of dislocations at high temperature.

### Acknowledgment

We would like to thank Prof. K. Ushioda for the fruitful discussions.

### References
