Characterization of the Inhomogeneous Distribution of Light Elements in Ferritic Heat-Resistant Steels by Secondary Ion Mass Spectrometry

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The addition of a small amount of boron and nitrogen is known to improve the creep strength and life of ferritic heat-resistant steels. These light elements are thought to be distributed in the microstructures in a complicated manner during the heat treatment and creep of these steels. In order to understand the influence of the light elements on the mechanical properties of ferritic heat-resistant steels, a microscopic distribution analysis of the light elements is of importance. In this study, two types of secondary ion mass spectrometry (SIMS) methods were used to investigate the measurement conditions for analyzing secondary ions derived from boron and nitrogen in steels. In dynamic SIMS with a quadrupole analyzer, boron in the samples was effectively detected as BO2– ions under irradiation with primary O2+ ions. From the time-of-flight (ToF) SIMS using a focused primary Bi32+ ion beam coupled with the exposure of the sample to a low partial pressure of oxygen, it was suggested that boron is enriched in M23C6 carbides in the steels and it may be, more or less, segregated at prior austenite grain boundaries with a moderate amount of nitrogen during normalizing. It was also demonstrated that nitrogen is precipitated as boron nitride in steels containing an excess amount of boron and nitrogen. The characteristics of the distribution of boron and nitrogen in the steels are discussed on the basis of the thermodynamic properties of these elements in the steels.

KEY WORDS: secondary ion mass spectrometry; boron; segregation; precipitation; grain boundary.

1. Introduction

Light elements, such as boron (B), carbon (C), and nitrogen (N), strongly influence the mechanical properties of steel products. Boron is typically known to enhance the hardenability of steel,1,2) and it has been shown that the addition of a small amount of boron and nitrogen improves the creep strength and life of ferritic heat-resistant steels that are used under severe steam conditions at approximately 950 K.3–9) These heat-resistant steels are 9 to 12% Cr martensitic steels, which may be replaced with nickel-based superalloys. In these 9% Cr steels, fine nano-sized MX carbonitrides (M: Nb, V, Cr and X: C, N) are known to be very effective for creep strengthening of the steels.3,10,11) Boron is a strong nitride-forming element and boron nitrides (BN) may be formed in 9 to 12% Cr steels during heat treatment at high temperatures, thereby decreasing the amount of dissolved B and N. By considering these effects of boron and MX carbonitrides on creep-strengthening, tempered martensitic 9% Cr steels based on 9Cr-3W-3Co-VNb steels were developed.3–9) Thus, boron and nitrogen are thought to be distributed in the microstructures in a complicated manner during the creep as well as heat treatment of the steels, and these elements play an important role in improving the mechanical properties of the steel products.

In order to understand the influence of the light elements on the mechanical properties of the steel products, the microscopic distribution of the light elements must be characterized. The total amount of light elements can be determined from a chemical analysis. However, the distribution of boron and nitrogen must be analyzed using microscopic analytical methods. For instance, a technique based on the detection of 10B(n,α)7Li reaction products using track etch detectors has been utilized to analyze the microscopic distribution of boron in iron-, nickel-, and aluminum-based alloys.12) The results indicated boron enrichment at the grain boundaries in recrystallized samples, and that boron is rearranged after rolling.13) This technique was also used to observe the boron distribution in stainless steels and carbon steels,1,13) demonstrating that the boron distribution was affected by the heat treatment of steels. Thus, the method based on the 10B(n,α)7Li reaction is utilized to analyze the distribution of boron in steel, although this method is applicable only to the detection of boron, and a comparison of the results with microscopic results acquired by other methods.

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is difficult.

By using atom probe field ion microscopy, it was also shown that boron is distributed in an austenitic stainless steel\(^1\) and medium carbon steels.\(^2\) In the medium carbon steels, boron was found to be segregated in retained austenite for 100 ppm B-added steels, whereas boron was randomly distributed in 20 ppm B-added steels. Electron energy loss spectroscopy was also applied to detect the elements in steels, although little significant trend in the distribution of boron was observed.\(^3\) Electron energy loss spectroscopy (EELS), in conjunction with aberration corrected scanning transmission electron microscopy, has also been used to detect boron segregated into grain boundaries.\(^4\) In the STEM-EELS analysis, the boron concentration profiles obtained near prior austenite grain boundaries were treated using a principle component analysis to obtain the real boron distribution around the boundaries. The results suggested that the non-equilibrium segregation of boron occurred in that case.

Secondary ion mass spectrometry (SIMS) is another technique that can be applied to the analysis of light elements, though there are a number of measurement conditions such as detection of species of primary ions and secondary ions. In order to detect boron (B), carbon (C), and nitrogen (N) in BCN coatings using SIMS, complex MC\(^{3+}\) ions (M: metallic element, Cs: cesium) were analyzed.\(^5\) The SIMS technique is effective for a qualitative analysis of the light elements in a specific matrix. Furthermore, SIMS has been utilized to analyze the N in N-doped SiC,\(^6\) and the concentration of N was determined from the intensities of CN ions. The SIMS analysis offers many advantages because of the micro-focusing techniques and selection of primary ion beams. SIMS has a relatively high sensitivity, although it strongly depends on the positive or negative ion species. So far, several studies on analysis of inhomogeneous distribution of boron, such as grain boundary segregation of boron, in low carbon steels were carried out by using dynamic SIMS (D-SIMS).\(^7\) In these studies, B\(^+\) and BO\(_2^-\) secondary ions were analyzed for observing the inhomogeneous distribution of boron. It is particularly found that BO\(_2^-\) ions are detected in the enough sensitivity when O\(_2^-\) primary ions were used.\(^8\) Thus, although SIMS is one of the potential techniques for detecting light elements such boron and nitrogen, a procedure for the analysis of light elements in steels has not yet been established for a new type SIMS like time-of-flight SIMS (ToF-SIMS). Therefore, the establishment of analytical techniques for characterizing the microscopic distribution of light elements such as boron and nitrogen in steels remains an important task given that these elements significantly influence the properties of steels.

On the basis of the above analytical procedures, the objective of the present study is to analyze the relevant ions of boron and nitrogen using two types of SIMS techniques, those are D-SIMS and ToF-SIMS. In particular, the measurement conditions for analyzing the distribution of B and N in steels are investigated in order to improve the quality of the microscopic data for light elements obtained using SIMS.

The samples used in this study are 9Cr-3W-3Co-0.2V-0.05Nb-0.08C steels, which were developed as heat-resistant steels.\(^9\) These steels are utilized under severe steam conditions at approximately 950 K to achieve high efficiency in power plants, and it has been demonstrated that the addition of boron and nitrogen improves the creep strength of 9% Cr steel at approximately 920 K. Boron may interact strongly with nitrogen in iron-based alloys thereby affecting the microstructure of steels.\(^10\) The interaction between boron and nitrogen is considered in the analysis of light elements in the steels in this study.

2. Experimental Procedure

2.1. Sample Preparation

The fundamental composition of the present heat-resistant steel is 9%Cr-3%W-3%Co, in addition to small amounts of boron and nitrogen. In this study, the 9Cr-3W-3Co-0.2V-0.05Nb steels with 47, 130, and 150 ppm boron were prepared by vacuum induction melting of 50 kg ingots. Different concentrations of nitrogen were added to investigate the effect of nitrogen on boron nitride (BN) formation and on the microstructure of the present steels. The steels were hot forged and hot rolled to produce 20 mm thick plates. The distribution of boron and the formation of boron nitride were the points of focus in the SIMS analysis and microstructural evaluation of these steels. The samples were normalized at approximately 1370 K for 1 h, followed by air cooling. The heating rate and cooling rates are considered to be the order of magnitude of plus and minus 10\(^3\) K/min, respectively. Then they were tempered at approximately 950 K for 1 h, followed by air cooling. The chemical compositions of the three samples are listed in Table 1, which shows analysis values of elements of interest in the heat-resistant steels. The samples with different amounts of nitrogen are hereafter referred to as Sample A, Sample B, and Sample C.

The microstructure of these samples was observed as inverse pole figure maps observed by an electron backscatter diffraction (EBSD) analysis, as shown in Fig. 1. Good contrast is observed in these maps because the high-density dislocations produced by martensitic transformation after normalizing may be reduced during tempering. The microstructures indicate that the size of the prior austenite grains is approximately 100 \(\mu\)m, and that lath and block-like martensite microstructures of approximately 10 \(\mu\)m order of magnitude were formed in the large prior austenite grains. However, no significant difference was observed in the microstructures for the different samples.

2.2. SIMS Measurements

Two different types of SIMS equipment were used for analyzing the ion species emitted from the sample surfaces. The first is the PHI-6600 with a quadrupole-type mass analyzer (Q-SIMS), which is one of the D-SIMS, It offers rel-

<p>| Table 1. Chemical composition of Sample A, Sample B, and Sample C used in this study (in mass%) |
|------------------|---|---|---|---|---|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>W</th>
<th>Co</th>
<th>V</th>
<th>Nb</th>
<th>N</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>0.079</td>
<td>0.30</td>
<td>0.30</td>
<td>8.77</td>
<td>2.93</td>
<td>2.91</td>
<td>0.18</td>
<td>0.046</td>
<td>0.0017</td>
<td>0.0047</td>
</tr>
<tr>
<td>Sample B</td>
<td>0.080</td>
<td>0.33</td>
<td>0.33</td>
<td>9.03</td>
<td>2.79</td>
<td>3.01</td>
<td>0.19</td>
<td>0.056</td>
<td>0.0071</td>
<td>0.0130</td>
</tr>
<tr>
<td>Sample C</td>
<td>0.078</td>
<td>0.30</td>
<td>0.51</td>
<td>9.08</td>
<td>3.05</td>
<td>3.03</td>
<td>0.20</td>
<td>0.055</td>
<td>0.030</td>
<td>0.0150</td>
</tr>
</tbody>
</table>
atively low mass resolution compared to the other types of analyzers, but facilitates the analysis of a number of ion species over a wide mass range. In Q-SIMS measurements, the samples were irradiated with an incident beam of 5.0 keV Cs\(^+\) ions or 5 keV O\(_2^+\) ions, and positive and negative secondary ions were detected from the sample surfaces.

The second technique involves the use of time-of-flight type SIMS (ToF-SIMS) employing a micro-focused ion beam to analyze the microscopic distribution of boron and nitrogen in the steels. The ToF-SIMS instrument (TOF-SIMS V (ION-TOF GmbH)) with primary Bi\(^{32+}\) ion beams of 25 keV can be operated in different modes. In the operation of the ToF-SIMS, positive and negative ions were carefully analyzed. Because the exposure of the samples to a low partial pressure of oxygen enhances the intensity of the secondary ions, the sample surfaces were exposed to oxygen gas with a partial pressure of 2 \times 10^{-4} \text{ Pa O}_2. Secondary ions of high mass resolution (typically, \(m/\Delta m = 11\,000\) at \(^{29}\text{Si}\)) were measured in the high-current bunched mode with a beam diameter of approximately 5 \(\mu\text{m}\). In contrast, different secondary ions were imaged in the burst alignment mode using a beam diameter of approximately 0.2 \(\mu\text{m}\); the images were obtained at a resolution of 256 \times 256 square pixels in area of 200 \times 200 square \(\mu\text{m}\). As the beam diameter is smaller than the pixel size, the secondary ion count from the one pixel is considered as a representative value. Because the whole secondary ion mass spectra are stored for an analyzed area in the ToF-SIMS analysis, line scans of specific ions can be plotted using the spectral data. Such line scans are useful to investigate the inhomogeneous distribution of elements in a sample.

3. Results and Discussion

3.1. Mass Spectra of Secondary Ions by Q-SIMS

The positive and negative secondary ions generated by irradiation with Cs\(^+\) and O\(_2^+\) as primary ions were measured using Q-SIMS and compared. Figures 2 and 3, respectively, show the positive and negative secondary ion spectra obtained from Sample A upon irradiation with primary Cs\(^+\) ions. Secondary ions derived from adsorbed oxygen and carbon were observed in the negative ion mass spectra with relatively high sensitivity, whereas several secondary ions arising from metallic elements were detected in the positive ion mass spectra.

Figures 4 and 5, respectively, show the positive and negative secondary ion spectra obtained from Sample A on irradiation with O\(_2^+\) primary ions. Influences of oxygen on the mass spectra of the samples are observed. The negative secondary ion mass spectrum is considerably different from the positive ion mass spectrum. It should be noted that BO\(_2^–\) (\(^{10}\text{B}^{16}\text{O}_2^–\) and \(^{11}\text{B}^{16}\text{O}_2^–\)) ions are clearly detected in the negative ion mass spectrum, whereas B\(^+\) (\(^{10}\text{B}^+\) and \(^{11}\text{B}^+\)) ions are scarcely detected in the positive ion mass spectrum. These results are fundamentally consistent with those obtained by different types of D-SIMS,\(^{20–22}\) although the sample compositions in the present study are different from those used in the previous works. The negative ion mass spectrum shows that the ion-count ratio of \(^{10}\text{B}^{16}\text{O}_2^–\) to \(^{11}\text{B}^{16}\text{O}_2^–\) is comparable to the abundance ratio of boron. The negative ion mass spectrum indicates that complex BO\(_2^–\) ions are formed from sputtered boron species and incident oxygen ions. Here, it is noted that the abundance ratio of \(^{16}\text{B}^{16}\text{O}^–\) to \(^{11}\text{B}^{16}\text{O}^–\) ions is apparently different from that \(^{10}\text{B}^{16}\text{O}_2^–\) to \(^{11}\text{B}^{16}\text{O}_2^–\) ions. This is because a peak of \(^{10}\text{B}^{16}\text{O}^–\) ions is overlapped with that of different ions such as \(^{13}\text{C}^{14}\text{N}^–\) with similar mass in the low mass resolution mode. Although such peak overlapping is observed in SIMS measurements of the low mass resolution, this implies that the exposure of the sample surface to a low partial pressure of oxygen gas may

Fig. 1. Inverse pole figure maps of Sample A (a), Sample B (b) and Sample C (c), in which the [001], [011], and [111] orientations are displayed in red, green, and blue, respectively.
be effective to detect boron in steels by SIMS.

### 3.2. Mass Spectra of Secondary Ions by ToF-SIMS

Because the exposure of the sample surface to oxygen was demonstrated to enhance the intensities of complex ions containing oxygen in the negative secondary ion mass spectra, the samples were also exposed to a low partial pressure of oxygen gas during the analysis of the secondary ions by ToF-SIMS. In order to detect the secondary ions of interest with sufficient sensitivity, secondary ion mass spectra should be identified in the high mass resolution mode. Then, images of secondary ions of high special resolution should be obtained in the low mass resolution mode. The microscopic distribution of light elements such as boron and nitrogen can be investigated taking into account the quality of secondary ion mass spectra. A number of secondary ions were detected in the ToF-SIMS mass spectra of the positive secondary ions of the present samples; these secondary ions included B⁺ (11.008 amu), Si⁺ (27.976), V⁺ (50.943), Cr⁺ (51.939), Mn⁺ (54.937), Fe⁺ (55.933), Co⁺ (58.931), and Nb⁺ (92.900). On the other hand, in the negative secondary ion mass spectra, ¹²C²⁻ (24.000 amu), ¹²C¹⁴N⁻ (26.003 amu), ¹¹B¹⁶O₂⁻ (43.000), ³¹P¹⁶O₃⁻ (78.963), ³²S¹⁶O₃⁻ (79.957), ⁵⁶Fe¹⁶O₂⁻ (87.924), ⁵⁵Cr¹⁶O₂⁻ (99.927), and ¹⁸⁴W¹⁶O₂⁻ (215.939) were detected. The sensitivity of several negative ion species analyzed under specific conditions is listed in Table 2. These results show that the negative ions of CN⁻, BO₂⁻, FeO₂⁻, and CrO₃⁻ can be detected with sufficient sensitivity under the present measurement conditions.

**Figure 6** shows the CN⁻ ion mass spectrum of Sample A acquired in the high mass-resolution mode using ToF-SIMS. The CN⁻ secondary ions are formed from the carbon and nitrogen atoms of the sample during bombardment with primary ions. In a study related to the detection of CN⁻ secondary ions, secondary ion species derived from nitrogen were detected in silicon carbide (SiC), in which nitrogen is the most popular donor impurity. In general, the determination of nitrogen by using SIMS is difficult because the direct monitoring of N⁺ ions is limited by the small ion yield. Nevertheless, it was shown that the complex nitrogen-matrix ions, CNN⁺ and SiₙN⁺ (n = 1, 2, 3), were emitted from the silicon carbide by using the oxygen primary beam to determine the positive ion yield and the cesium primary beam for the negative ions. Thus, the ion yield of CN⁻ ions from carbon- and nitrogen-containing steels is sufficiently high for the detection of nitrogen. Carbon in CN⁻ ions is originated from dissolved carbon and fine carbides precipi-
tated in the matrix, although it is difficult to distinguish them. On the other hand, nitrogen in CN\(^-\) ions is primarily coming from dissolved nitrogen in the matrix, and it is also originating from boron nitride formed in a sample containing boron nitride precipitates. In spite of such complicated formation processes of secondary ions, it is considered that the inhomogeneous distribution of nitrogen is detected using CN\(^-\) secondary ions.

In Fig. 7, a BO\(_2^-\) peak is apparent in the negative secondary ion mass spectrum of Sample A acquired by ToF-SIMS, the peak intensity of which was higher than that of B\(^+\) in the positive secondary ion mass spectrum. This observation indicates that a small amount of boron emitted from the sample is combined with oxygen to form the complex BO\(_2^-\) ions, which are relatively stable negative ions. This ion species can be used to observe the microscopic distribution of boron in the samples given that there are no interference secondary ions. Here, it should be remarked that BO\(_2^-\) ion counts depend on several factors, such as the boron composition in a sample, pressure of oxygen, ion formation probability and so on. In addition, the effect of the sputtered matrix, such as iron matrix boron nitride, on the BO\(_2^-\) secondary ion counts is also considered to influence the formation yields of secondary ions.

Figures 8 and 9 show the mass spectra of FeO\(_2^-\) and CrO\(_3^-\) emitted from the matrix of Sample A, acquired by ToF-SIMS, measured under the same conditions as in Figs. 6 and 7. These negative secondary ions may also be formed by the combination of iron and chromium with oxygen gas. The intensities of these ions were sufficiently high for imaging the ions relevant to constituent elements, and the images were used to investigate the correlative distribution of different elements.

### Table 2. Comparison of analytical sensitivity of ToF-SIMS for complex ion species derived from several elements under the present conditions. For elemental imaging, negative secondary ion species with high and medium sensitivity are recommended.

<table>
<thead>
<tr>
<th>Element</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>Cr</th>
<th>Fe</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion species</td>
<td>(^{11})B(^{16})O(_2^-), (^{12})C(^2^-), (^{12})C(^{14})N, (^{52})Cr(^{16})O(_3^-), (^{56})Fe(^{16})O(_2^-), (^{186})W(^{18})O(_2^-)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sensitivity</td>
<td>medium, low, medium, high, high, low</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.3. Imaging of Secondary Ions by ToF-SIMS

The distribution of ions derived from light elements such as boron and nitrogen was investigated on the basis of the intensities in the negative mass spectra acquired by ToF-SIMS in order to compare the elemental information with the microstructure of the steels given in Fig. 1. In particular, the formation of boron nitride particles in the matrix of the high nitrogen steel was focused because the formation of boron nitride is known to degrade the creep properties of the...
In order to observe the two-dimensional distribution of secondary ions from the samples, images of several secondary ions were obtained by using ToF-SIMS in burst alignment mode that is the low mass resolution mode. Although positive and negative secondary ions can be imaged by ToF-SIMS, no significant contrast was observed in the images of the positive secondary ions. On the other hand, microstructural contrasts were obtained for the secondary negative ions of BO$_2^–$ from Sample A, Sample B, and Sample C, as shown in Fig. 10. As the size of the primary ion is smaller than one pixel in the images, an ion count acquired at one pixel is considered as a representative value in the area. Because BO$_2^–$ ions are formed by boron sputtered from the samples upon exposure to oxygen gas, these contrasts observed in Fig. 10 are attributed to the inhomogeneous distribution of boron in these samples. The inhomogeneous distribution of boron is likely to correspond to precipitation or segregation of boron, although atomic segregation of boron at grain boundaries should be carefully discussed. A comparison of the images of the BO$_2^–$ ions in Sample A and Sample B with the microstructure shown in Fig. 1 reveals that the fine precipitation or segregation of boron occurs along prior austenite boundaries. In contrast, the image of Sample C shows that boron is precipitated as relatively large particles in the matrix, which are presumably nitride particles, as discussed later.

Because the samples contain different amounts of nitrogen, the state or distribution of boron and nitrogen must be discussed on the basis of the solubility product of boron and nitrogen in the matrix. The formation of boron nitride particles is expected from the solubility product of boron nitride, which was estimated for the present steels in the normalizing temperature range of 1320 to 1420 K. The relationship between the boron and nitrogen amounts in the present steels is given as follows:

\[
\log [\%B] = -2.45 \log [\%N] - 6.81, \quad \text{(1)}
\]

where [\%B] and [\%N] are the amounts of dissolved boron and nitrogen in mass%, respectively. This equation indicates that approximately 0.01 mass% nitrogen is dissolved in the matrix containing approximately 0.01 mass% boron without the formation of boron nitride during normalizing. This is consistent with the images of the BO$_2^–$ ions shown in Figs. 10(a) and 10(b). On the other hand, the formation of boron nitride is expected in Sample C (0.015 mass% boron and 0.030 mass% nitrogen), which is in good agreement with the results shown in Fig. 10(c).

3.4 Inhomogeneous Distribution of Different Elements

Because the ion images obtained by ToF-SIMS are less quantitative, line scans of the secondary ion counts were plotted to observe the heterogeneous distribution of elements in each sample. In particular, in order to analyze the correlative distribution of boron and other elements, the counts of different ions were plotted in the line scan. Figures 11, 12, and 13 show the line scans of the ion counts of BO$_2^–$, CN$^–$, CrO$_3^–$, and FeO$_2^–$ for Sample A, Sample B, and Sample C, respectively. The results show that boron is fundamentally dissolved in the matrix in Samples A and B, although boron atoms trapped by lattice defects such as lath or block martensite boundaries cannot be distinguished from dissolved boron. In addition, a portion of the boron seems to be segregated or precipitated at prior austenite grain boundaries. The lateral resolution may not be enough high
to distinguish precipitated boron with segregated boron in the present ToF-SIMS data, although boron is known to be easily segregated at grain boundaries. However, since a new SIMS apparatus using focused ion beam SIMS (FIB-SIMS), which enables us to investigate the grain boundary segregation in steels, has been developed recently, it may be effective to study the inhomogeneous distribution of elements in the complicated microstructure.

No significant inhomogeneous distribution of CN⁻ ions was observed for Samples A and B, implying that no boron nitride particles were precipitated in these samples. However, partial boron enrichment seemed to occur in M23C6 (M: Cr, Fe) carbides along prior austenite grain boundaries, because boron is known to be contained in M23C6 carbides. A correlation between the distribution of boron and that of chromium is apparent from Figs. 11 and 12. This correlative distribution is considered to result from the enrichment of boron in the M23C6 carbides. In addition, it is worth noting that boron is known to be enriched at grain boundaries in steels. Therefore, a part of the boron seems to be roughly segregated at prior austenite grain boundaries.

In contrast, the distribution of CN⁻ ions was characteristically correlated with that of the BO₂⁻ ions in Sample C, as shown in Fig. 13. This also indicates that boron is precipitated as boron nitrides in Sample C, consistent with the BO₂⁻ ion image shown in Fig. 10(b). Moreover, it should be noted that the level of BO₂⁻ ions in the matrix together with prior austenite grain boundaries is very low in Sample C because of a considerable decrease in the amount of boron as a result of boron nitride formation in this sample. In addition, it should be remarked that the level of CN⁻ ions in the matrix is influenced by fine MX precipitates in Samples A and B, because nitrogen can be precipitated as fine MX (X: C, N) in the matrix. The lath or block martensite boundaries in the prior austenite grains were formed during cooling after normalizing; these boundaries are not random but have specific crystallographic orientations due to martensitic transformation. During tempering, fine MX carbonitrides as well

Fig. 11. Line scans of BO₂⁻, CN⁻, and FeO₂⁻ ions in Sample A using ToF-SIMS.

Fig. 12. Line scans of BO₂⁻, CN⁻, and FeO₂⁻ ions in Sample B using ToF-SIMS.

Fig. 13. Line scans of BO₂⁻, CN⁻, and FeO₂⁻ ions in Sample C using ToF-SIMS.
as $M_23C_6$ (M: Cr, Fe) carbides can be precipitated at interfaces such as martensite boundaries and prior austenite grain boundaries, depending on the concentration and temperature.

On the basis of the discussion on compositional distribution presented above, the inhomogeneous distribution of elements can be considered, although the quantification of the main constituent elements is limited because of the complexity of the secondary ion formation. Figure 14 illustrates the schematics of several kinds of precipitates formed in the microstructure of the present steels containing different amounts of nitrogen after normalizing and tempering. In the schematics of the microstructure, only prior austenite grain boundaries are drawn, whereas the lath, block, and packet boundaries are omitted for simplicity. In the steel containing a moderate amount of nitrogen, boron-enriched $M_23C_6$ carbides are precipitated at prior austenite grain boundaries during tempering after normalization. Boron is considered to be already segregated at prior austenite grain boundaries during normalization because boron is easily segregated even in the austenite phase at high temperatures. On the other hand, fine MX carbonitrides are formed along the lath, block, and packet boundaries. At such interfaces, the segregation of boron is not significant because the lath, block, and packet boundaries are formed by martensitic transformation after normalization.

4. Summary

Two SIMS techniques were used to investigate the measurement conditions for analyzing ions derived from boron and nitrogen in steels. The secondary ions from 9Cr-3W-3Co-VNb steel with added boron and nitrogen were analyzed by using Q-SIMS and ToF-SIMS. The main results of this study are as follows:

(1) Q-SIMS data demonstrated that boron in the steel samples can be effectively analyzed by detecting $BO_2^-$ ions formed by irradiation with primary $O^{2-}$ ions. These results are fundamentally consistent with those obtained by the previous works. In the case of ToF-SIMS using a primary $Bi^{2+}$ ion beam, secondary $BO_2^-$ ions could be effectively detected by the exposure of the sample to a low partial pressure of oxygen.

(2) The ion images measured by ToF-SIMS showed that boron is precipitated or segregated at prior austenite grain boundaries in the steels containing moderate amounts of boron, although clear atomic segregation of boron at grain boundaries should be further investigated. It is postulated that boron enrichment of $M_23C_6$ carbides occurs in the steels containing adequate amounts of boron. In contrast, it is demonstrated that boron is precipitated as boron nitrides in steels containing an excess amount of nitrogen. The characteristic distribution of boron and nitrogen in this steel is interpreted in terms of the solubility product of boron and nitrogen in the present heat-resistant steels during normalizing.

(3) The present results show that the yield of secondary $BO_2^-$ ions is sufficiently high to analyze the correlative distribution of boron and other elements in steels, although the relationship between elemental composition in a sample and counts of secondary ions should be carefully analyzed. Therefore, the ToF-SIMS technique is useful for the analysis of the microscopic composition by comparing the microstructures, although the influence of matrix effects on the intensities of the secondary ions must be considered.

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REFERENCES