Investigation of Compositional Change of Inclusions in Martensitic Stainless Steel during Heat Treatment by Newly Developed Analysis Method

Toru TANIGUCHI,¹ Naoya SATOH,¹ Yoichiro SAITO,² Kunichika KUBOTA,¹ Atsushi KUMAGAI,¹ Yasushi TAMURA¹ and Takahiro MIKI³

¹) Hitachi Metals, Ltd., Yasugi Works, Yasugi-cho, Yasugi, Shimane, 692-8601 Japan. ²) HMY, Ltd., Quality Assurance Center, Hashima-cho, Yasugi, Shimane, 692-0014 Japan. ³) Department of Metallurgy, Graduate School of Engineering, Tohoku University, 6-6-11, Aoba-yama, Aobaku, Sendai, 980-8579 Japan.

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The most important subject in the steelmaking process is the control of non-metallic inclusions. Non-metallic inclusions with a high melting point do not deform during a hot working process because they are relatively hard. Hence, the inclusion composition should be controlled in order to achieve a low melting point to prevent product defects. Therefore, an MnO–SiO₂-based inclusion is considered to be one of the preferred systems.

Moreover, the heat treatment of austenitic stainless steel has been reported to influence the composition of MnO–SiO₂-type inclusions; these inclusions change into MnO–Cr₂O₃-type, MnO–Nb₂O₅-type, and MnO–V₂O₃-type inclusions.

In this study, we investigated the influence of heat treatment on the composition of the inclusions in the martensitic stainless steel.

In general, a scanning electron microscope–energy dispersive x-ray spectrometer (SEM–EDS) is used for the quantitative analysis of inclusions; however, SEM–EDS cannot simultaneously analyze a large number of inclusions. Therefore, a new technique using the SEM–EDS along with the image analysis software “Particle Analysis” was used for the chemical analysis and the size measurement of a large number of inclusions (hereafter abbreviated as the PA method). The heat-treatment-induced compositional change of the inclusions in martensitic stainless steel was evaluated by using both the analysis methods.

KEY WORDS: analysis method; inclusion; composition; change; heat treatment; martensitic stainless; alumina; silica; magnesia; manganese oxide; calcia; glass; crystallization.

1. Introduction

Elements such as Al and Si¹ have been generally used in the martensitic stainless steelmaking process because of their deoxidation ability and productive efficiency. Inclusions formed during the deoxidation process may cause product defects. Therefore, the removal of inclusions and the control of inclusions in order to ensure that they are harmless are the most important conditions required to guarantee the product quality and the material properties of the formed martensitic stainless steel. One of the methods to meet these conditions is to control the inclusion composition in order to achieve a low melting point.² It is known that deformation-induced inclusions formed during hot rolling are harmless and are finally dispersed into the steel matrix. Recently, there has been considerable demand for martensitic stainless steel with relatively fine defects. Therefore, hot and cold working processes are used for easily controlling the defects caused by inclusions. Further, a precise control of the inclusion composition is important. The metal composition calculated by the thermodynamic equilibrium between the inclusions and the metal²–⁹ is widely used for controlling the inclusion composition in an actual steelmaking operation. Using this technique, one can ensure that the inclusions formed in ingots and billets during ingot casting and continuous casting have the desired composition.

Recently, Shibata et al.¹⁰–¹² reported the changes in the inclusion composition of austenitic stainless steel deoxidized by Si–Mn at 1 273–1 473 K; this temperature is lower than the solidification temperature of the steel. The composition of MnO–SiO₂-type inclusions in Si–Mn deoxidized austenitic stainless steel was reported to change because of the reaction between the inclusions and the metal during the 1 273–1 473 K heat treatment. From this result, it can be concluded that the composition of inclusions in ingots and billets may change because of the heat treatment even if this composition is controlled to reach a desired value. Therefore, the influence of the heat treatment at 1 273 K and 1 473 K on the inclusion composition in martensite stainless steel was investigated in the present study.

A quantitative analysis of the inclusion composition in steel is usually and conventionally carried out using a scan-
ning electron microscope–energy dispersive x-ray spectrometer (hereafter abbreviated as SEM–EDS). However, the analysis of many inclusions and the calculation of the mean composition of each inclusion by SEM–EDS is time consuming. Therefore, the influence of the heat treatment may not be evaluated precisely. In addition, the spark electric discharge emission during a light spectrum analysis is reported as a quick method for measuring the particle size and the composition of inclusions. Both the diameter and the composition of the inclusions can be analyzed simultaneously by using this method. However, the measurable size is restricted to a diameter range of 1 μm to 10 μm; hence, inclusions having a diameter of more than 10 μm that cause product defects and those having a diameter of less than 1 μm that may be influenced easily by the heat–treatment cannot be analyzed.

A newly developed analysis method (hereafter abbreviated as the PA method) using the SEM–EDS along with the image analysis software “Particle Analysis” was also used for the chemical analysis and size measurement of a large number of inclusions. The PA method was used for measuring the diameter and the composition of inclusions (size: 0.4 μm or more) in the observation field in the present work. First, the change in the inclusion size distribution brought about by the heat treatment was investigated. Next, the average composition of the inclusions was classified on the basis of the size of the inclusions, which was determined before and after the heat treatment; further, the influence of the heat treatment on the inclusion composition was investigated. It was confirmed that the compositional change of each inclusion phase brought about by the heat treatment could be evaluated more accurately by analyzing this change concurrently with the composition and the size distribution.

2. Experimental

SUS410J1 and SUS440B as martensitic stainless steel were examined in this study. Table 1 shows the chemical compositions of these steels, and Fig. 1 shows the steelmaking process. First, these stainless steels were melted in an electric arc furnace. Then, secondary refining was carried out in the ladle furnace, and whose steels were casted to the mold by the means of bottom pouring. The casting temperature was 1 823 K. The samples were collected from the runner after the casting. The runner samples (40 mm (φ) × 20 mm (h)) were cut into four sections. Then, the sample surfaces were polished. Pt–Pd deposition at a rate of 7.5 nm/min was carried out for 5 min on the sample surfaces in order to inhibit the reaction between the inclusion and to the gas phase. A vacuum heating furnace was used for the heat treatment. The schematic representation of this experiment is shown in Fig. 2. The iron jig was set in a graphite crucible. In order to prevent the samples from reacting directly with the crucible, we hung the samples from the jig using a wire. The crucible was set in the furnace. The temperature in the furnace was raised at the rate of 5 K/min at a pressure of 100 Pa. After the temperature reached 1 273 K or 1 473 K, the condition was kept constant for 1 h. Finally, the specimens were cooled to the room temperature in the furnace.

Two methods, a conventional method using SEM–EDS and the PA method, were used for the quantitative analysis of the inclusion composition before and after the heat treatment.

In the conventional method using SEM–EDS, the samples were marked using the Vickers Hardness equipment before the heat treatment in order to identify the inclusions to be observed. The same inclusions were observed after the heat treatment, and the changes in the shape and the composition were investigated using SEM–EDS. The sample surface after the heat treatment was not polished in order to prevent inclusions from detaching. Here, the acceleration voltage was 15 kV, and the working distance was 15 mm. For the quantitative analysis of the inclusion composition, a spot analysis was carried out. When two or more phases were observed in one inclusion, each phase was analyzed.

On the other hand, the acceleration voltage was 15 kV, and the working distance was 10 mm in the case of the PA method. In the device of the PA method, after the image analysis was carried out using the contrast of a back-scattered electron image (BSE image) on the basis of the atomic number, the number of inclusions in the prescribed view was automatically measured, and both the size and the composition of the inclusions could be measured. In this study, bearing in mind the quantitative analysis accuracy and the measurement time, we set the measuring area in the sample to 5.0 mm × 5.0 mm (at 300-fold magnification, the pixel size was 0.208 μm/pix); the inclusion diameter was analyzed in the range starting from 0.4 μm. The inclusion composition was analyzed in the center of the inclusions by...
the spot analysis. The measurement time for one sample was approximately 7–15 h. The size distribution of the observed inclusion was obtained; the average composition of each inclusion was calculated; and the changes in the inclusion composition before and after the heat treatment were investigated. After the heat treatment, the sample surface was polished to a mirror finish in order to observe the internal inclusions that did not react in the gas phase during the heat treatment in the PA method.

3. Result and Discussion

3.1. Observation of Inclusions and Quantitative Analysis of Inclusion Composition by Conventional Method

Figures 3 and 4 show the SEM images of inclusions before and after the 1 273 K heat treatment in SUS410J1 and SUS440B. Figures 5 and 6 show the compositions of these inclusions. The inclusion composition shown by the arrow in Figs. 3 and 4 corresponds to the measurement point shown in Figs. 5 and 6. Here, the concentration of FeO and Cr2O3 in the inclusions was disregarded in Figs. 5 and 6 because the concentration of FeO and Cr2O3 may contain Fe and Cr from the steel matrix. This is described later. Therefore, the changes in only the concentration of MgO, Al2O3, SiO2, CaO, and MnO were verified in Figs. 5 and 6.

From the SEM images shown in Figs. 3 and 4, we confirmed that there was no change in the shape of the inclusions. In addition, a hole was observed in the inclusions. The reaction between the inclusions and the gas phase was believed to be one of the reasons for this hole formation. This will be discussed later. Moreover, gaps were observed at the interface between the inclusions and the metal after the heat treatment. This is described in the next section.

Figures 3 and 5 show that most of the inclusions in SUS410J1 are composed of two phases: the MgO–Al2O3(−MnO) system in the center and the CaO–MgO–MnO–Al2O3–SiO2 system at the boundary. In a small inclusion

![Fig. 3. SEM images of inclusions in SUS410J1 after the 1273 K heat treatment.](image)
shows the compositions of these inclusions. In the case of the 1473 K heat treatment, the inclusions often disappeared after the heat treatment. Moreover, in the case of the inclusions that remained after the heat treatment, as shown in Fig. 7, a large part of these inclusions disappeared. In addition, the inclusions after the heat treatment were composed of the Al₂O₃–CaO systems, disregarding the FeO or Cr₂O₃ concentration.

In the case of SUS440B, all inclusions disappeared after the 1473 K heat treatment. There was a possibility that not only the reaction between the inclusions and the metal but also the reaction between the inclusions and the gas phases took place. Then, by the following thermodynamic consideration, we verified whether the reactions interacted with the gas phases during the heat treatment, under the experimental conditions.

The inclusions considered in this study were composed of the MgO–Al₂O₃(–MnO) system and the CaO–MgO–MnO–Al₂O₃–SiO₂ system. Among these components, MgO(s) and SiO₂(s) are well known to decompose in a CO gas atmosphere at almost 1873 K (i.e., the steelmaking temperature). In this experimental condition, the components in the inclusions may decompose because of the equilibrium relation among the inclusion, the CO gas, and the CO₂ gas.

The decomposition reaction of the inclusion component MOₓ(s) under the condition that the component MOₓ(s) in the inclusion and the CO gas coexist is expressed in Eq. (1).

$$MO_x(s) + xCO(g) = M(s, l, g) + xCO_2(g)$$  \hspace{1cm} (1)

The free energy change $\Delta G^{\text{f}}$ in this reaction is calculated as shown in Eqs. (2) and (3).

$$\Delta G^{\text{f}}(s) = -RT \ln \frac{a_{MO_x} \cdot P_{CO(g)}}{a_{MO_x(s)} \cdot P_{CO_2(g)}}$$ \hspace{1cm} (2)

$$\frac{P_{CO(g)}}{P_{CO_2(g)}} = \left( \frac{a_s}{a_{MO_x(s)}} \right) \exp \left( \frac{\Delta G^{\text{f}}(s)}{RT} \right)$$ \hspace{1cm} (3)

where $a$ represents the activity, and the subscript denotes the component. $P$ is the partial pressure, and the subscript indicates the gas component. $a_M$ and $a_{MO_x(s)}$ were assumed to be unity in the first approximation. Mg and Ca were in the gas phase in this experimental condition. Partial pressure $P_M$ and $P_Ca$ was assumed to be the atmospheric pressure. All standard free energy changes of the formation of each component were taken from the JANAF Tables. The relation between the equilibrium $P_{CO}/P_{CO_2}$ ratio and the temperature of each component was calculated by using Eq. (3). Figure 8 shows the results.

Moreover, SiO₂(β-cr) is known to decompose because of the reaction as shown in Eq. (4). Then, the equilibrium $P_{CO}/P_{CO_2}$ ratio is calculated by using Eq. (5).

$$SiO_2(\beta-cr) + CO(g) = SiO_2(g) + CO_2(g)$$ \hspace{1cm} (4)

$$\frac{P_{CO(g)}}{P_{CO_2(g)}} = \frac{a_{SiO_2(g)}}{a_{SiO_2(\beta-cr)}} \exp \left( \frac{\Delta G^{\text{f}}(s)}{RT} \right)$$ \hspace{1cm} (5)

The relation between the equilibrium $P_{CO}/P_{CO_2}$ ratio and the temperature was calculated by using Eq. (5). Figure 8 shows
the results. The equilibrium $P_{CO}/P_{CO_2}$ ratio used in this experiment was calculated in a similar manner.

Figure 8 shows that $SiO_2$, $MgO$, and $MnO$ decomposed at 1473 K under the abovementioned experimental condition because the equilibrium $P_{CO}/P_{CO_2}$ ratio was lower than the $P_{CO}/P_{CO_2}$ ratio in the experimental environment. There was a correlation between the calculation results shown in Fig. 8 and the results of the changes to the $Al_2O_3$--$CaO$ systems in the inclusions after the 1473 K heat treatment, given in Table 2. The equilibrium $P_{CO}/P_{CO_2}$ ratio of each component shown in Fig. 8 was calculated when the activity of each component was unity. However, because the inclusions confirmed in this study were multi-component oxides, the actual activity of each component was less than unity. However, from the reported value$^{16,17}$ of the component activity in the two- and three-component oxide systems, it was considered that the activities of each component were more than at least $10^{-4}$. Therefore, by referring Eq. (3), we conclude that the equilibrium $P_{CO}/P_{CO_2}$ ratios of each inclusion component shown in Fig. 8 did not change with a large reversal in the magnitude relation under the experimental condition. In addition, Fig. 8 shows that $MnO$ decomposed under this experimental condition. There was a correlation between the calculation results shown in Fig. 8 and the decrease in the $MnO$ concentration after the 1273 K heat treatment shown in Figs. 5 and 6. In this experiment, Pt--Pd was deposited on the sample surface, and the suppression of the reaction
between the inclusions and the gas phase was planned as far as possible. However, we believe that such an effect was insufficient. As shown in Fig. 7, the reaction was remarkably observed on the inclusions in the sample heat treated at 1473 K. Moreover, there is a possibility that the holes and the gaps in the inclusions after the 1273 K heat treatment, shown in Figs. 3 and 4, were formed because of the reaction between the inclusions and the gas phase.

The inclusion composition before and after the 1273 K heat treatment is plotted in the phase diagram of the CaO–Al₂O₃–SiO₂ system and the MgO–Al₂O₃–SiO₂ system in Figs. 9 and 10 in order to confirm the existence of a deviation in the component phase. The numerals in the plots denote the sequential turn of the measured data shown in Figs. 5 and 6. The open and solid symbols indicate the values before and after the heat treatment, respectively. As the change in the MnO concentration in the MgO–Al₂O₃(–MnO) phase in the inclusions was

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**Table 2. Composition of inclusion in SUS410J1 (mass%, Heat treatment: 1473 K).**

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<td>12.2</td>
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**Fig. 7.** SEM Images of inclusions in SUS410J1 after the 1473 K heat treatment.

**Fig. 8.** Relation between $P_{CO}/P_{CO_2}$ and Temperature.

**Fig. 9.** Inclusion composition in SUS410J1 after the 1273 K heat treatment on SiO₂–CaO–Al₂O₃–MgO phase diagram (Quantitative analysis of the inclusion composition by conventional method).

**Fig. 10.** Inclusion composition in SUS440B after the 1273 K heat treatment on SiO₂–CaO–Al₂O₃–MgO phase diagram (Quantitative analysis of the inclusion composition by conventional method).
already confirmed by Fig. 5, the compositions excluding MnO are indicated on the phase diagram of MgO–Al2O3–SiO2, and the changes in the MgO and Al2O3 concentrations were confirmed. The compositions of the CaO–MgO–MnO–Al2O3–SiO2 phase in the inclusions were plotted on the phase diagram of the CaO–Al2O3–SiO2 system. The MgO and MnO concentrations in the CaO–MgO–MnO–Al2O3–SiO2 phase were plotted as the sum of the CaO + MgO + MnO concentrations. The MgO and MnO concentrations were comparatively low and had little effect even if the CaO concentration was added to their sum. In addition, some overlapped plots are not shown in the figures in order to clearly show the results.

From Figs. 9 and 10, we observed that the composition of the MgO–Al2O3–(MnO) phase changed little before and after the heat treatment. Moreover, in the case of the composition of the CaO–Al2O3–SiO2 (CAS2) and were distributed on the area of coexistence of CaO–Al2O3 (CA), 2CaO·Al2O3·SiO2 (C2AS) and CAS2, or coexistence of CaO·6Al2O3 (CA6), C2AS, and CAS2. A little change in the composition was brought about by the heat treatment was not clear.

The same phase diagram of SUS440B is shown in Fig. 10. Most of the inclusion compositions were positioned around CAS2 as in the case of SUS410J1. However, they were mostly distributed in the region of the coexistence composition of CA, C2AS, and CAS2, and in the composition brought about by the heat treatment was scarcely observed.

The tendency of the compositional change of the CaO–Al2O3–SiO2 (MgO–MnO) phase was not clarified by the conventional method. As mentioned before, the reaction between the inclusions and the gas phase might influence the changes in the inclusion composition.

### 3.2. Observation of Inclusion and Quantitative Analysis of Inclusion Composition by PA Method

The distributions of inclusion sizes before and after the heat treatment are shown in Fig. 11. Here, the inclusion size was classified into six ranges. The first range was 0.4–1 μm; it has been reported that this range is impossible to measure by using the spark electric discharge emission of a light spectrum analysis. The next range was under 2 μm; this range could not be measured by the conventional method, as shown in Figs. 3–6. Moreover, the inclusions with sizes in the ranges of 2–5 μm and 5–10 μm, which were confirmed as single- or two-phase inclusions by the conventional method, as shown in Figs. 3 and 5. Finally, the range including the maximum size, shown in Figs. 3–6, was classified as under 20 μm.

As mentioned in the preceding section, the measured area was 5 × 5 mm. Two areas of the specimen were measured before the heat treatment in order to confirm the dispersion of the data. The distribution of the inclusion sizes of each measured area was almost the same for both grades of steels; thus, it was confirmed that this measurement was reasonable. In the PA method, approximately 1 000 inclusions could be measured by in a single measurement. Therefore, the evaluation of the average composition and that of the distribution of inclusion size were accurate even if different measurement areas were observed. Hence, the internal inclusions that did not come in contact with the gas phase during the heat treatment were evaluated by the PA method. As shown in Fig. 11, we confirmed that the number of inclusions having a size of 0.4–5 μm was high in each steel grade and at each temperature of the heat treatment, and the number of inclusions larger than 5 μm decreased sharply during heat-treatment. Moreover, the decrease in the number of inclusions (size: 0.4–10 μm) during the heat treatment was confirmed for both the steel grades and the considered heat-treatment temperatures. Because there were few inclusions larger than 10 μm, the overall tendency could not be confirmed.

Figure 12 shows the results of the quantitative analysis of the distributions of each steel grade in SUS440B before the heat treatment. The analysis result of all the components is shown in Fig. 12-a). Because the measured concentrations of FeO and Cr2O3 also include the influence from the steel matrix, the result is dispersed remarkably. On the other hand, the analysis result of the components excluding FeO and Cr2O3 is shown in Fig. 12-b); the composition became more stable in this case. The generation region of the characteristic X-rays induced by the electron beam in the inclusions could be calculated by using the Castaing equation:

\[
Z_m = 0.033 + \left( E_0^{1.7} - E_c^{1.7} \right)/\rho Z
\]

where \( Z_m \) is the generation region of the characteristic X-rays (μm); \( E_0 \), the accelerating voltage (kV); \( E_c \), the critical excitation voltage (kV); \( A \), the average atomic weight; \( \rho \), the average density (g/cm³); and \( Z \), the average atomic number.

According to this equation, the generation regions of the characteristic X-rays of Al, Ca, Cr, Fe, Mn, and Si in the Al2O3–SiO2–CaO phase was 1.0–1.3 μm. Therefore, we concluded that inclusions that were approximately 2 μm in size were influenced by the matrix. Therefore, FeO and Cr2O3 were excluded from the evaluation in this study.

Figure 13 shows the average compositions of each size distribution of the inclusions before and after the heat treatment; the compositions were calculated using the PA method. In addition, Figs. 14–17 show the diagrams of a ternary CaO–Al2O3–SiO2 system; the compositions of the inclusions before and after the heat treatment are plotted in the
The numerals in the plots denote the maximum diameter within a particular range of the inclusion size. The solid symbols indicate the inclusion composition before the heat treatment, and the open symbols denote the composition after the heat treatment. The average compositions of only the inclusions that were 10 μm or less in size are shown in the figures because inclusions that were larger than 10 μm were seldom observed and it was not possible to investigate the changes in their compositions before and after the heat treatment.

In Figs. 13–15, we observed that the relatively large inclusions in SUS410J1 exhibited a tendency to have relatively high concentrations of Al2O3 and MgO and low concentrations of MnO, CaO, and SiO2. As shown in Figs. 3 and 5, inclusions larger than 5 μm in SUS410J1 were composed of two phases: an MgO-Al2O3-MnO system in the center and a CaO-MgO-MnO-Al2O3-SiO2 system at the boundary. Because the inclusion composition was analyzed at the center of the inclusion by the spot analysis, the relatively large inclusions seemed to have high concentrations of Al2O3 and MgO. Moreover, as shown in Figs. 13–15, the concentration of Al2O3 in inclusions, particularly the large inclusions, increased after the heat treatment.
From Figs. 13, 16, and 17, we could not confirm a large change in the composition of the inclusions in SUS440B during the heat treatment unlike that in the case of SUS410J1.

### 3.3. Results of Two Analysis Methods

The following were confirmed by comparing each phase in the inclusions before and after the heat treatment in the conventional method. Figures 3 and 5 show that the inclusions in SUS410J1 consist of two phases: an MgO–Al2O3(–MnO) system in the center and a CaO–MgO–MnO–Al2O3–SiO2 system at the boundary. Moreover, the small inclusions of the single-phase CaO–MgO–MnO–Al2O3–SiO2 system were observed. We confirmed that the concentration ratio of MgO and Al2O3 in the MgO–Al2O3(–MnO) phase was not changed by the heat treatment. In SUS440B, most of the inclusions were the single-phase CaO–MgO–MnO–Al2O3–SiO2 system. On the basis of thermodynamic calculation, it was predicted that the inclusion reacted with the gas phase under the experimental condition. Therefore, we confirmed that the reaction between the inclusions and the metal or between the oxide phases in the inclusions could not be evaluated by using the conventional method.

On the other hand, the PA method could evaluate that the reaction between the inclusions and the metal because a considerable number of inclusion compositions were averaged in a sufficiently large measuring area. By using the PA method, we confirmed that the composition of the CaO–MgO–MnO–Al2O3–SiO2-type inclusions did not change by the heat treatment. However, the PA method could not evaluate the composition of inclusions that contained multiple phases because the quantitative analysis of each inclusion could be executed only once by the PA method. Therefore, the investigation using the conventional method was necessary as well.

We confirmed that the changes in the distribution of the inclusion sizes before and after the heat treatment could be measured by using the PA method. Hence, we could confirm that the number of inclusions decreased upon the heat treatment of the samples. The inclusions may have shrunk or have detached from the sample during polishing after the heat treatment, as shown in Fig. 18. The gaps were observed at the interface of the inclusions and the metal in Figs. 3 and 4, as described in the preceding section. The shrinkage of the inclusions seemed to have caused these gaps. According to the heat-transfer calculation, the cooling rate was 10 K/s or more when the samples were cooled at the runner; this was comparatively fast. In the case when the inclusions were glassy, they were crystallized by the heat treatment, and a large shrinkage in volume occurred. For example, the crystallization shrinkage in volume of the SiO2 single phase was 4.3%. The glassy composition range is shown in gray in Figs. 14–17. The compositions of inclusions of all the considered sizes were positioned within the glassy composition area for each steel grade. Therefore, we assumed that the inclusions had a glassy structure before the heat treatment. We believed that every type of inclusion was shrunk by the heat treatment, as confirmed in this study and shown in Fig. 19. In particular, as shown in Figs. 19-a) and 19-c), the single-phase inclusions shrunk considerably. This result correlated with the result that revealed that the number of inclusions (0.4–1 μm) in SUS410J1 and that of all types of inclusions in SUS440B decreased drastically. Additional examinations such as a crystal structural analysis of the inclusions after the heat treatment might be necessary to discuss the crystallization in further detail in the future.

Moreover, the shrinkage may influence the analysis results of the inclusion composition after the heat treatment in the PA method.

As shown in Figs. 13–15, the concentration of Al2O3 in the inclusions in SUS410J1 increased after the heat treatment. On the other hand, a significant change in the inclusion composition in SUS440B was not confirmed during the heat-treatment, unlike the change in the inclusion composition of SUS410J1. A significant change in the inclusion composition in SUS440B can be considered as follows:

As shown in Fig. 20, in case of the boundary of the inclusions that contained two phases, the composition was a CaO–MgO–MnO–Al2O3–SiO2 system. The CaO–MgO–MnO–Al2O3–SiO2 phase was crystallized by the heat treatment; further, shrinkage in this phase was observed. Then, the composition of the boundary was influenced by the MgO–Al2O3(–MnO) phase, which had a high Al2O3 concentration. Therefore, the concentration of Al2O3 in the inclusions increased after the heat treatment. In addition, as shown in Figs. 14 and 15, we considered that the reason the composition of a small inclusion did not change considerably was that the small influence of MgO–Al2O3(–MnO)
phase due to the existence of the CaO–MgO–MnO–Al₂O₃–SiO₂ single-phase inclusions.

As mentioned above, we confirmed that the compositional change of each inclusion phase, brought about by the heat treatment, could be evaluated more accurately by concurrently analyzing this change with the composition and the size distribution. In addition, the composition of the CaO–MgO–MnO–Al₂O₃–SiO₂ phase in each steel grade seemed to remain unchanged during the heat treatment in this study. Shibata et al. 10–12) reported the compositional change of the MnO–SiO₂ phase in the inclusions in austenitic stainless steel during the heat treatment. The differences between this study and their study are the type of metal considered and the inclusion composition. In this study, there is a possibility that the equilibrium composition of the inclusions hardly changes at the heat-treatment temperature and the refinement temperature.

4. Conclusions

The influence of the heat treatment on the composition of the inclusions in SUS410J1 and SUS440B was investigated. Most of the inclusions in SUS410J1 were composed of two phases: an MgO–Al₂O₃(–MnO) system in the center and a CaO–MgO–MnO–Al₂O₃–SiO₂ system at the boundary. The main inclusions in SUS440B had a single-phase CaO–MgO–MnO–Al₂O₃–SiO₂ system. The heat treatment was performed at two temperatures (1 273 K and 1 473 K). Two methods were used for the quantitative analysis of the inclusion composition, and the following knowledge was obtained:

(1) In the conventional method, we confirmed that the concentration ratio of MgO and Al₂O₃ in the MgO–Al₂O₃(–MnO) system did not change during the heat treatment carried out at 1 273 K.

(2) The compositional change of the CaO–MgO–MnO–Al₂O₃–SiO₂ phase could not be evaluated accurately by using the conventional method.

(3) The size distribution of the inclusions could be determined by the PA method. Using this method, we confirmed that the measured number of inclusions decreased because of the heat treatment.

(4) The compositional change of the multiple-phase inclusions could not be evaluated accurately because the quantitative analysis could be carried out only for one inclusion at a time by using the PA method. In addition, we confirmed that the composition of the CaO–MgO–MnO–Al₂O₃–SiO₂-type inclusions did not change at both temperatures of the heat treatment and for all the considered inclusion sizes in SUS440B.

(5) We confirmed that the compositional change of each inclusion phase brought about by the heat treatment could be evaluated more accurately by concurrently analyzing this change with the composition and the size distribution using a combination of the conventional method and the PA method.

REFERENCES

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