Microscopic Distribution of Minor Elements in Iron-Based Alloys Analyzed by Secondary Ion Mass Spectrometry

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This paper overviews analytical results of the microscopic distribution of minor elements in iron-based alloys, obtained by secondary ion mass spectrometry (SIMS). Since trace amounts of some elements play crucial roles in the properties of steels, it is important to analyze their distribution in the microstructure of iron-based alloys. Time-of-flight SIMS (TOF-SIMS) and conventional dynamic SIMS are powerful methods for detecting minor elements in iron-based alloys and analyzing their distribution in the microstructure of these materials. In this paper, we report several examples of the microscopic distribution of minor elements in iron-based alloys, which provide significant information on complicated phenomena related to the alloy microstructure. The depth profiles obtained by dynamic SIMS showed how a specific trace element penetrates the alloy matrix, indicating that the diffusion of the element is strictly related to the microstructure. On the other hand, high-sensitivity and high-spatial-resolution TOF-SIMS was used to characterize the microscopic distribution of trace elements, such as boron and nitrogen, in iron-based alloys, which is also related to the alloy microstructure. [DOI: 10.1380/ejssnt.2018.150]

Keywords: Secondary ion mass spectrometry; Hydrogen; Carbon; Iron; Steel

I. INTRODUCTION

High-sensitivity secondary ion mass spectrometry (SIMS) is a powerful tool for detecting trace elements in solid surfaces. Since small amounts of an alloying or impurity element strongly influence the mechanical properties of steels, it is important to characterize the distribution of those elements in their microstructure. Dynamic SIMS and static SIMS, specifically time-of-flight SIMS (TOF-SIMS), are utilized to analyze the distribution of elements in the microstructure of metallic materials. They provide important information on iron-based alloys, where SIMS has enough sensitivity for their secondary ions. Here, we report several examples of the microscopic distribution of minor elements in iron-based alloys or steels, which the authors have investigated over the past 15 years. The results obtained by the SIMS methods, where several parameters such as primary and secondary ions must be selected, include information on the enrichment of the elements in the complicated microstructure of iron-based alloys or steels.

Dynamic SIMS is one of the surface analysis methods used to obtain depth profiles of specific trace elements in bulk, from which their penetration curves can be estimated and their diffusion studied. Iron-based alloys or steel sheets are often annealed at high temperatures under low oxygen partial pressure, where reactive alloying elements are oxidized but iron is not. For instance, during the annealing of silicon steels, reactive alloying elements, such as silicon, are selectively oxidized on the surface layer [1-3]. The chemical composition of silicon steel sheets is about Fe-3mass%Si [4], and the selective oxidation of silicon is very important in manufacturing processes. It is accompanied by complicated phenomena, such as the penetration of oxygen into the bulk and the formation of silicon in the surface layer. The microscopic processes associated with selective oxidation have been investigated using dynamic SIMS, for example, the depth distribution of gold in the surface layer [1]. Gold was used as a typical non-reactive tracer element which was deposited on the surface and penetrated the bulk. The effective diffusion coefficients of gold were calculated from its penetration curves, which were also used for comparing the effective diffusion coefficients obtained in a surface layer of silicon steel with those obtained in iron and the previous data obtained at high temperatures [5].

The control of the distribution of light elements in steels is a known method for improving their mechanical properties, for example the creep properties of ferritic heat-resistant steels at high temperatures [6-8]. While dynamic SIMS has been employed to analyze the boron distribution in conventional steels [9], TOF-SIMS has been utilized to analyze the microscopic distribution of minor elements in heat-resistant steels [10]. Track etch detectors have been used for the 10B(n,α)7Li reaction products, to observe the microscopic distribution of B in stainless and carbon steels [11]. The results demonstrated that the boron distribution was affected by the heat treatment of the steels. Observations using atom probe field ion microscopy also revealed how boron is distributed in the microstructure of an austenitic stainless steel [12]. It is also possible to detect the boron distribution in steels by using electron energy loss spectroscopy (EELS) in a transmission electron microscope [13]. EELS in conjunction with aberration-corrected scanning transmission electron microscopy, has been employed to detect boron segregated into grain boundaries [14]. An example of the microscopic distribution of a small amount of trace elements analyzed by TOF-SIMS is their distribution in heat-resistant steels. Boron segregation was also investigated using Auger electron spectroscopy [15]. In a recent investigation, aimed to understand the influence of light elements on the mechanical properties of ferritic heat-resistant steels at high temperatures, a microscopic...
distribution analysis of the light elements was carried out by TOF-SIMS. As it had been shown that boron in iron-based alloys was effectively detected as BO$_2$ ions by dynamic SIMS under O$_2$ exposure, this method was applied in TOF-SIMS to enhance the sensitivity of boron detection analyses [10].

One of the advantages of SIMS is the investigation of isotopes such as $^2$H, $^{13}$C, and $^{18}$O, which are discriminated from the main isotopes by high mass resolution measurements. However, SIMS is sometimes limited in achieving the combination of high-spatial and high-depth resolutions. However, TOF-SIMS can overcome this problem; thus, this technique has been used for analyzing various materials not only inorganic but also organic, such as polymers and biological tissue. In addition, it is also possible to measure a depth profile by using a dual-beam technique, where low energy sputter ions are alternatively bombarded to the sample after the measurement with the primary ions. The secondary ions emitted from the sputter crater are analyzed by TOF-SIMS. In the present study, the distribution of deuterium and other elements from the shallow region of a pure iron-chromium alloy and from duplex stainless steel was measured by using Bi-cluster TOF-SIMS equipped with a liquid metal ion gun [16]. This is important because hydrogen plays a significant role in the mechanical properties of steels and its diffusion strongly depends on the crystal structure and the defects of the steels [17–20].

As mentioned above, dynamic SIMS and TOF-SIMS have been utilized in the analysis of the distribution of minor elements in metallic materials, which were here iron-based alloys, with optimized operation conditions. These minor elements were intentionally added to the iron-based alloys, in order to understand important phenomena in the metallic materials. In this work, analytical examples of the results obtained by these SIMS techniques are reported, together with observations on the microstructural characterization of different iron-based alloys.

**II. PENETRATION OF A SMALL AMOUNT OF GOLD INTO IRON-BASED ALLOYS**

Depth profiles by dynamic SIMS have been measured for characterizing the penetration of gold in pure iron and iron-silicon alloys. First, gold was deposited on the surface of pure Fe and of Fe–3mass% Si, and they were then annealed under low partial pressure of oxygen. The degree of gold penetration was evaluated using the effective diffusion coefficients of gold estimated from the SIMS depth profiles [1]. Figure 1(a, b) shows the count ratio versus $x^2$ (where $x$ is the in-depth distance) for Fe and Fe–3mass% Si annealed at 973 K during 1800 s. The plot for Fe–3mass% Si does not show a simple linear correlation, which may be due to the complicated microstructure formed by the selective oxidation of silicon. Although some linear segments are observed in these plots, they deviate from the linear slopes at deeper profiles, due to the roughness produced by sputtering. The linear slopes can be used to evaluate the penetration of gold and provide its effective diffusion coefficients. These results clearly indicated that the penetration depth of gold in Fe–3mass% Si alloy is larger than in pure Fe.

In order to evaluate the degree of gold penetration, its effective diffusion coefficients in the surface layers of the samples were estimated from the depth profiles. A small quantity of gold, $M$, was deposited as a thin film on the sample surface. When a sample is annealed for time $t$ so that diffusion can occur, the in-depth concentration of gold, $C$, will be given by the equation:

$$C = M/2\sqrt{\pi Dt} \exp(-x^2/4Dt).$$  

(1)

A diffusion coefficient $D$ of gold in the samples is calculated from the slope in a log $C$ versus $x^2$ plot. In this work, the concentration could be approximated by the ratio of gold-ion to iron-ion counts, since the concentration of gold is very small in the surface layer of an annealed sample.

In order to compare the penetration of gold in the Fe–3mass% Si alloy and in Fe, the effective diffusion coefficients of gold obtained in this work are summarized in an Arrhenius plot, shown in Fig. 2. The temperature dependence of the diffusion coefficients of gold in iron measured by Borg and Lai [5], $D = 21.6 \exp(-256 \text{ [kJ/mol]/[K]}) \text{ [m}^2\text{/s]}$, is also plotted in Fig. 2. The effective diffusion coefficients of gold in iron obtained in this work are comparable to the results by Borg and Lai, although in this work SIMS depth profiles were used for the diffusion measurements. On the other hand, the effective diffusion coefficients in Fe–3mass% Si alloy are higher than those in Fe. An apparent activation enthalpy for the diffusion of gold in the Fe–3mass% Si alloy was estimated as ca. 50 kJ/mol.
III. DISTRIBUTION OF BORON AND NITROGEN IN FERRITIC HEAT-RESISTANT STEELS

The distribution of elements such as boron and nitrogen in 9Cr-3W-3Co-0.2V-0.05Nb (mass %) steels was investigated by using TOF-SIMS [10]. Sample A with 0.007% N and 0.013% B (mass %) and Sample B with 0.030% N and 0.015% B were prepared in order to observe the two-dimensional distribution of secondary ions from these samples. Images of several secondary ions were obtained by using TOF-SIMS in burst alignment mode, by which adequate lateral resolution is achieved by reducing mass resolution at moderate primary ion currents [10]. Although positive and negative secondary ions can be imaged by TOF-SIMS using a primary Bi<sup>3+</sup> ion beam, no significant contrast was observed in the images of the positive secondary ions. Therefore, microstructural contrasts were obtained for the secondary negative ions of BO<sub>2</sub><sup>−</sup> from both samples, as shown in Fig. 3. In order to compare the elemental information with the microstructure of the steels, the distribution of ions derived from minor elements was observed on the basis of the intensities in the negative TOF-SIMS mass spectra. Because BO<sub>2</sub><sup>−</sup> ions are formed by boron sputtered from the samples during exposure to oxygen gas, the contrast observed in Fig. 3 is attributed to the inhomogeneous distribution of boron in these samples, which corresponds to the segregation and precipitation of boron. The images of the BO<sub>2</sub><sup>−</sup> ions in the microstructure of Sample A revealed that segregation or fine precipitation of boron took place along prior austenite boundaries. In contrast, the image of Sample B showed that boron was precipitated as relatively large-sized particles in the matrix, arising from nitride particles. In particular, we focused on the formation of boron nitride particles in the matrix of the high-nitrogen steel because it is known to degrade the creep properties of this steel [6-8].

Since these samples contained different amounts of nitrogen, the microscopic distribution of boron and nitrogen should be discussed on the basis of the solubility product of boron and nitrogen in the matrix. The formation of boron nitride particles is predicted from the solubility product of boron nitride, which was estimated for the present samples at the normalizing temperature of about 1400 K based on previous results [8]. The relationship between the boron and nitrogen amounts in ferritic steels is given as follows:

\[
\log[\% B] = -2.45 \log[\% N] - 6.81, \tag{2}
\]

where [% B] and [% N] are the amounts of dissolved boron and nitrogen in mass percent, respectively. This formulation indicates that during normalizing, 0.01 mass % of nitrogen is dissolved in the matrix containing about 0.01 mass % of boron. This is consistent with the BO<sub>2</sub><sup>−</sup> ion image shown in Fig. 3(a). On the other hand, boron nitride is formed in Sample B (0.015 mass % B and 0.030 mass % N), which is in good agreement with the results shown in Fig. 3(b).

Although the ion images obtained by TOF-SIMS are less quantitative, line scans of the secondary ion counts are useful to discuss the heterogeneous distribution of elements in each sample. Figures 4 and 5 show the line scans of the ion counts of BO<sub>2</sub><sup>−</sup>, CN<sup>−</sup>, CrO<sub>3</sub><sup>−</sup>, and FeO<sub>2</sub><sup>−</sup> for

FIG. 2. Arrhenius plot of effective diffusion coefficients, \(D_{\text{eff}}\), of gold in Fe and Fe-3mass% Si. The results by SIMS are given as marks, and the dotted line is an extrapolation based on data by Borg and Lai [5]. (Source: From Suzuki et al. [4], Fig. 4)

FIG. 3. Images of BO<sub>2</sub><sup>−</sup> ions from Sample A (a) and Sample B (b). (Source: From Suzuki et al. [10], Fig. 10)
Sample A and Sample B, respectively. The results show that in Sample A boron was fundamentally dissolved in the matrix, although it must be noted that boron atoms trapped by lattice defects, such as martensite boundaries, cannot be distinguished from dissolved boron. Furthermore, a part of the boron is likely to have been segregated or precipitated at prior austenite grain boundaries. However, little significant inhomogeneous distribution of CN\(^-\) ions was observed in Sample A, indicating that no boron nitride particles were precipitated. However, it has been reported that boron is contained in M\(_{23}\)C\(_6\) (M: Cr, Fe) carbides and that partial boron enrichment occurs along the prior austenite grain boundaries [8]. In addition, it is known that boron is also enriched at grain boundaries in other steels [15].

In contrast, the distribution of CN\(^-\) ions was clearly correlated with that of BO\(_2\)\(^-\) ions in Sample B, that indicated that boron was precipitated as boron nitrides, which is consistent with the BO\(_2\)\(^-\) ion image shown in Fig. 3(b). Moreover, it was noted in this sample, the level of BO\(_2\)\(^-\) ions in the matrix with prior austenite grain boundaries was very low as a result of a considerable decrease in the amount of boron in the matrix, due to boron nitride formation [8].

IV. DISTRIBUTION OF DEUTERIUM IN FE-CR BASED ALLOYS

It is known that hydrogen and deuterium easily penetrate the ferritic phase with body-centered cubic structure, although these elements occupy interstitial sites, like carbon [16-20]. This agrees to the fact that the diffusivity of hydrogen and deuterium in ferrite is higher than in austenite [17].

TOF-SIMS results showed that in the case of the Fe-10% Cr alloy charged with \(^2\)H\(_2\)O, the intensity ratio of \(^2\)H\(^-\) to H\(^-\) was almost equal to the natural isotope ratio. The deuterium was not detected in the Fe-10% Cr alloy when analyzed after charging. Actually, the signal intensity counts of deuterium from the Fe-10% Cr alloy were not enough to study its distribution. The image results from the Fe-10% Cr alloy, obtained in burst alignment mode, are shown in Fig. 6. It was found that the signal intensity counts of C\(^-\) and CN\(^-\) in the grain-boundary were higher than in other areas. It is known that these elements play an important role in the properties of the iron-based alloys, as they are segregated grain boundaries of the alloys which were investigated by Auger electron spectroscopy [21]. Thus, although the distribution of \(^2\)H\(^-\) was not established yet, the present results showed that the distribution of the minor elements is investigated by TOF-SIMS.

TOF-SIMS was also applied to detect the distribution of deuterium in Fe-Cr-based duplex stainless steels. Figure 7 shows high spatial resolution images of duplex stainless steel charged with \(^2\)H\(_2\)O and the subsequently annealed steel. These images were obtained by integrating the images analyzed at each depth. In this measurement, high-current bunched mode was used to evaluate the quantity of deuterium. It was found that the distribution of secondary ion counts of Fe\(^-\) from the total area was almost uniform. The results suggested that it was possible to visualize the deuterium distribution in the microstructure of the duplex stainless steel after charging it with \(^2\)H\(^-\). Moreover, in the measurement of the duplex stainless steel performed one month after charging with \(^2\)H\(^-\), the signal intensity of deuterium was more than one hundred times the natural isotope ratio, even though the deuterium was not detected in the Fe-10% Cr alloy when analyzed after charging. These results suggested that the microscopic distribution of alloying elements in the ferritic phase had the effect of trapping the deuterium in...
the microstructure. As it has been reported that substitutional alloying elements in ferritic iron have the effect of decreasing the diffusion coefficient of hydrogen [18], it is considered that the measurement by TOF-SIMS was an effective method to investigate the distribution of light element including deuterium in the Fe-Cr alloys.

As shown in Fig. 7(a, b), in the high spatial resolution images of the duplex stainless steel, it was noted that the phase enriched with $^2\text{H}^-$ was different from the C$^-$ and CN$^-$ phases. In order compare the enrichment of $^2\text{H}^-$ with the microstructure of the ferritic and austenitic phases, electron micro probe analysis (EPMA) was carried out in the same area as shown in Fig. 8, where compositional images of nickel and molybdenum determined by EPMA are displayed together with a backscattered electron image. The EPMA results showed that the nickel concentration is high in the austenitic phase while the molybdenum concentration is high in the ferritic phase. The comparison of these results with the SIMS images showed that $^2\text{H}^-$ was relatively enriched at the ferrite side near the interface between ferrite and austenite in the duplex stainless steel.

V. CONCLUDING REMARKS

In this review, several results obtained by dynamic SIMS and TOF-SIMS, under different measuring conditions, are reported as applications of these techniques to characterize the distribution of minor elements in iron-based alloys. In the first application, SIMS was used for analyzing the penetration profiles of trace elements into metallic materials. It was shown that gold penetrates Fe and Fe–3mass% Si alloy by annealing under low partial pressure of oxygen. Effective diffusion coefficients of gold in the surface layers of Fe and Fe–3mass% Si were estimated from the penetration of gold in the surface layer. These results suggest that gold penetration is correlated with the selective oxidation of silicon, by which silicon oxides are formed in the surface layer when annealing under low oxygen partial pressure.

As the next application, the microscopic distributions of boron and nitrogen in 9Cr-3W-3Co-based steels analyzed by TOF-SIMS were established. It was shown that in the case of TOF-SIMS using a primary Bi$^{3+}$ ion beam, secondary BO$_2^-$ ions can be effectively detected under the exposure of the alloys to a low partial pressure of oxygen.
EPMA images of nickel (a) and molybdenum (b), and a backscattered electron image (c) in the microstructure of the duplex stainless steel doped with $^2\text{H}_2\text{O}$. (Source: From Shishido et al. [16], Fig. 6)

The $\text{BO}_4^-$ ion images showed that boron is precipitated or segregated at prior austenite grain boundaries in the alloys containing adequate amounts of boron, while it is precipitated as boron nitrides in alloys containing an excess amount of nitrogen.

Finally, TOF-SIMS images of light elements, such as hydrogen, deuterium, carbon, and nitrogen, in the Fe–10% Cr alloy and in duplex stainless steel, were reported. The results indicated that deuterium is more easily introduced into ferrite than austenite. This preferential distribution of deuterium in ferrite is likely to be due to its high diffusion in ferrite compared to that in austenite. It was also suggested that the complicated microstructure in the ferritic phase has an effect of trapping deuterium.

In summary, the depth profiles of minor elements by dynamic SIMS provide information on short-circuit diffusion as well as bulk diffusion in iron-based alloys with complicated microstructure. TOF-SIMS with micro-focused primary ions is effective to analyze the microscopic distribution of minor elements in microstructures, although the influence of matrix effects on the intensities of the secondary ions must be taken into account. Therefore, SIMS techniques are powerful for the microstructural characterization of materials, when selecting an adequate SIMS apparatus and optimized operation conditions.

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