Application of Laser Ablation ICP Mass Spectrometry for Analysis of Oxide Particles on Cross Section of Alloys and Steels

Andrey Vladimirovich KARASEV,¹⁾ Hideaki SUIITO²⁾ and Ryo INOUE³⁾

1) Formerly Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, 980-8577 Japan. Now at Department of Materials Science and Engineering, KTH Royal Institute of Technology, 100 44 Stockholm, Sweden.

2) Professor Emeritus, Tohoku University, Sendai, 980-8577 Japan.

3) Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, 980-8577 Japan.

(Received on June 2, 2011; accepted on July 22, 2011)

Some aspects for the application of Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) are considered and discussed from the viewpoint of the rapid analysis of oxide inclusions in metal samples. The inclusion characteristics in Fe–10% Ni alloy samples such as number, size and particle size distribution obtained by LA-ICP-MS method are compared with those from three-dimensional observation of particles on a film filter after electrolytic extraction. Though some limits had to be considered regarding to the content of soluble elements, the number and dispersion of analyzed inclusions in metal matrix, it was found that the LA-ICP-MS technique can be successfully applied for the rapid analysis of oxide inclusions containing Al_2O_3 , MgO and others.

KEY WORDS: LA-ICP-MS; steel; nonmetallic inclusions; particle size distribution; soluble elements.

1. Introduction

In a recent steelmaking process, an online analysis of inclusion characteristics in steel such as size, number and composition takes on special significance for the rapid control of ladle treatment. Therefore, the development and improvement of rapid analytical methods and techniques, by which the accurate information on inclusion characteristics in steel sample can be obtained within short time (3–7 min), have been required. One of the potential methods is the Optical Emission Spectroscopy with Pulse Discrimination Analysis (OES-PDA),^{1–4)} which is based on a spectral analysis of inclusions by spark ablation of steel sample surface. However, this method has some serious limitations because of a large diameter and a small depth of spark-ablated zone on metal surface.

Other candidates for the rapid analysis of inclusion particles on a surface of steel sample are a Laser Ablation-Inductively Coupled Plasma-Atomic Emission Spectrometry (LA-ICP-AES) and a Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). In recent years, the LA-ICP-MS was applied for the direct analysis of steels and alloys concerning to the determination of the bulk composition,^{5–8)} the content of soluble and insoluble elements^{7,8)} the spatial and surface distribution of elements in steels and alloys,^{8,9)} and the mapping analysis of inclusions.^{10–14)}

In this study, the LA-ICP-MS method is applied for the estimation of oxide particles containing Al_2O_3 , MgO and other oxides on the cross section of Fe–10 mass% Ni alloy. Some limit factors for the analysis of particles by the LA-ICP-MS are discussed regarding to the content of soluble elements and the number of inclusions in metal. The inclu-

sion characteristics such as number and size distribution obtained using LA-ICP-MS method are compared with those from three-dimensional SEM observation of particles on a film filter after an electrolytic extraction from metal specimens.

2. Experimental

2.1. Preparation of Metal Samples

An application of LA-ICP-MS for the quantitative analysis of inclusions characteristics in metal is carried out by using Fe–10 mass% Ni alloy samples deoxidized with Mg and Al. The metal sample was prepared as follows: A mixture of high-purity electrolytic iron plate (99.99 mass%) and globular nickel (99.97 mass%) was melted at 1 600°C under an deoxidized Ar-gas flow (200 mL/min) using a high frequency induction furnace (100 kHz, 20 kW) with graphite heating element. A high purity Al_2O_3 crucible was used for melting. A total weight of metal sample was 70 g. After holding for 30 min at 1 600°C for the homogenization of metal composition, the melt was deoxidized by the addition of appropriate amount of Ni–10 mass% Mg and Fe–10 mass% Al alloys. The charged contents of Mg and Al in metal are given in **Table 1**. The melt after deoxidation was stirred for 10–20 s using an Al_2O_3 rod and held for 3–10 min at 1 600°C for homogenization, followed by quenching in water.

An effect of soluble Al and Ti contents in metal matrix on the minimum size of oxide inclusions, which was determined by LA-ICP-MS analysis, was investigated experimentally using standard metal samples LSt-1 to LSt-6, whose compositions are listed in **Table 2**. These standard

Table 1. Chemical composition of metal samples.

Exp. No.	Charged amount of deoxidant	Content of elements (mass%)				
		Mg _{sol}	Mg _{insol}	Al _{sol}	Al _{insol}	T.O
1	0.05 mass% Mg	0	0.0101	0.0010	0.0022	0.0126
2	0.10 mass% Mg	0.0008	0.0117	0.0079	0.0013	0.0082
3	0.10 mass% Mg	0.0137	0.0113	0.0102	0.0008	0.0072
4	0.05 mass% Mg + 0.10 mass% Al	0.0005	0.0107	0.0365	0.0051	0.0084
5	0.05 mass% Mg + 0.10 mass% Al	0.0002	0.0102	0.0732	0.0101	0.0132
6	0.10 mass% Al + 0.05 mass% Mg	0	0.0122	0.0513	0.0066	0.0110
7	0.10 mass% Al + 0.05 mass% Mg	0.0001	0.0084	0.0772	0.0113	0.0097
8	0.015 mass% Al	0	0	0.0001	0.0042	0.0041

Table 2. Chemical compositions of standard metal samples prepared in laboratory.

Sample No.	Content of elements (mass%)			
	Ti _{sol}	Ti _{insol}	Al _{sol}	Al _{insol}
LSt-1	0.0096	0.0003	0.0057	0.0000
LSt-2	0.0511	0.0000	0.0474	0.0000
LSt-3	0.0964	0.0009	0.0933	0.0001
LSt-4	0.148	0.0001	0.133	0.0029
LSt-5	0.201	0.0001	0.181	0.0026
LSt-6	0.233	0.0003	0.211	0.0005

samples were prepared by melting an Fe–10 mass% Ni alloy with different amount of Fe–50 mass% Ti and Fe–50 mass% Al alloys in a hermetic arc furnace under Ar atmosphere. For decreasing an initial oxygen amount in furnace atmosphere, a piece of pure Ti (10 g) was previously melted during 5 minutes. The weight of standard samples was 8–10 g. After arc melting, each standard sample was quenched on the water cooled copper plate and overturned without opening the arc furnace. Before the next melting of standard samples, the piece of Ti was melted again during 5 minutes for decreasing the oxygen amount in furnace atmosphere. These procedures were repeated 5 times for the homogenization of standard sample composition.

Six standard glass samples SBL-0 to SBL-5 were used for drawing the calibration lines of elements contained in inclusions. The preparation procedure and composition of those glass samples were noted in previous paper.⁷⁾

2.2. LA-ICP-MS Measurement

The inclusion characteristics in metal such as composition, size and number were analyzed on polished cross section of samples by LA-ICP-MS. A schematic illustration of LA-ICP-MS system, general instrumental conditions and analytical procedures were described in previous articles.^{7,10,14)}

The samples (Exp. 1–8 in Table 1), standard metal samples (LSt-1 to LSt-6 in Table 2) and glass standard samples (SBL-0 to SBL-5) were measured using LA-ICP-MS at the

same operating parameters: laser scan speed = 0.01 mm/s, laser energy = 2.0 mJ/shot, laser shot frequency = 20 Hz and defocus of laser beam = 0 mm. The stable melting zone and the continuous laser track with almost same ablated profile were observed during the laser ablation of metal surface under these parameters. The ion intensity of one isotope was measured with the length step of 0.1 μm at the integration time of 0.01 s. A pattern of laser ablation during LA-ICP-MS analysis was rectilinear in horizontal direction by keeping the focus on sample surface. The total horizontal length of laser tracks in the analysis of inclusion size distribution was 9–15 mm for each sample.

The standard glass samples (SBL-0 to SBL-5) with different contents of elements⁷⁾ were used for quantitatively analyze of inclusion composition. In this case, the ion intensity of one isotope was measured every 1.0 μm at the integration time of 0.1 s. The length of laser track in the analysis of standard glass samples was 1 mm. The measurement of glass standard samples was carried out every one hour for the correction of calibration lines. Detailed description on the time-correction method were given in previous articles.^{7,10)}

2.3. SEM Investigation of Inclusions

The inclusion particles were extracted from each metal sample by a potentiostatic electrolysis using 10%AA (10 v/v% acetylacetone-1 w/v% tetramethylammonium chloride-methanol) electrolyte. The dissolved sample weight during electrolysis was in the range of 0.2 to 0.3 g. The inclusion particles extracted were separated using a polycarbonate film filter with an open pore size of 0.05 μm , and were estimated three- dimensionally (3-D) by using a scanning electron microscope (SEM) and an electron probe micro analyzer (EPMA) at magnifications of 1 000, 2 000 and 5 000. The total observed area on film filter was varied from 0.02 to 0.05 mm² depending on the number of particles on SEM images. The total number of analyzed inclusions was 180 to 380. The size of each inclusion was evaluated as the equivalent spherical diameter, d_v , which was measured on the SEM photographs using a semi-automatic image analyzer.

2.4. Chemical Analysis

The soluble and insoluble Mg, Al and Ti contents in metal samples (Exp. 1 to 8) and standard metal samples (LSt-1 to LSt-6) were determined by ICP-AES after the electrolysis with 10% AA in the same manner as described in the previous.¹¹⁾

The total oxygen content in metal samples (Exp. 1–8) was measured by an inert gas fusion-infrared absorptiometry.¹⁵⁾

3. Results and Discussion

The chemical composition and total oxygen content in metal samples are given in Table 1.

3.1. Analysis of Particle Size Distribution in Metal Sample by LA-ICP-MS

The inclusion size distribution in Fe–10% Ni alloy deoxidized with different amount of Mg and Al (Exp. 1–8) was estimated by using LA-ICP-MS.

Typical time charts of ion intensity obtained by laser abla-

tion (Exp. 5 and 7) are shown in **Fig. 1**. The ion intensity peaks for ^{24}Mg and ^{27}Al isotopes correspond to the contents of these elements in ablated inclusions. The time chart of metal sample Exp. 5 in Fig. 1(a) indicates Mg, Al and Mg and Al peaks, which correspond to MgO , Al_2O_3 and $\text{MgO-Al}_2\text{O}_3$ inclusions, respectively. Metal sample Exp. 7 contains mostly typical small inclusions ($< 2\ \mu\text{m}$) of pure MgO , as shown in Fig. 1(b). However, large size inclusions and/or clusters, whose number on the surface of metal sample is drastically lower, contain both MgO and Al_2O_3 . It is confirmed by significant content of insoluble Al_2O_3 in this sample (Table 1). The number of ion intensity peaks on time chart corresponds to that of inclusions detected during laser ablation of metal sample. Moreover, the peaks of ion intensity in Fig. 1(a) are sufficiently greater than those in Fig. 1(b). Since the ion intensity of isotope is directly proportional to the mass of this element in ablated inclusion,^{7,14)} it can be concluded that the maximum size of inclusions in sample Exp. 5 is larger than that in Exp. 7. According to the obtained results (Fig. 1), it is apparent that on average 4–5 non-metallic inclusions per minute can be detected on the time charts of these samples. Therefore, it can be expected that almost 40–100 inclusions in steel samples can be analyzed by LA-ICP-MS during 10–20 minutes. However, the number of detected inclusions on time charts critically depends on the total number and distribution of inclusions in steel samples. Thus, LA-ICP-MS can be applied for rapid and simple qualitative estimation of the composition, number and size of inclusions in metal samples.

Based on the calibration lines for respective elements in inclusion, the composition and size of ablated inclusions can be estimated quantitatively using the area of each ion intensity peak, A_M^p , on time chart. The detailed description for the determination of peak area, inclusion composition and size were given in previous articles.^{7,14)} The following size cali-

bration lines for MgO and Al_2O_3 particles are used for the calculation of d_V :

$$A_{\text{Mg}}^p = 67040 \cdot (d_{V,\text{MgO}})^{3.04} \quad r = 0.972 \dots \dots \dots (1)$$

$$A_{\text{Al}}^p = 66620 \cdot (d_{V,\text{Al}_2\text{O}_3})^{3.04} \quad r = 0.985 \dots \dots \dots (2)$$

The size of multi-component oxide particles containing MgO and Al_2O_3 , $d_{V,\text{MgO-Al}_2\text{O}_3}$, is estimated as follows:

$$d_{V,\text{MgO-Al}_2\text{O}_3} = \left(\frac{6}{\pi} \cdot V_{\text{MgO-Al}_2\text{O}_3}^p \right)^{1/3} = (d_{V,\text{MgO}}^3 + d_{V,\text{Al}_2\text{O}_3}^3)^{1/3} \dots (3)$$

where $V_{\text{MgO-Al}_2\text{O}_3}^p$ is the volume of $\text{MgO-Al}_2\text{O}_3$ particle.

The number of inclusions per unit volume of metal, $N_{V,\text{LA-ICP-MS}}$, can be estimated as follows:

$$N_{V,\text{LA-ICP-MS}} = n/V_{\text{anal}} = n/(V_{\text{abl}}/k_{\text{abl}}) \dots \dots \dots (4)$$

where n is the inclusion number determined from the number of peaks on time chart during laser ablation of metal sample. V_{anal} is the analyzed metal volume, which is swept from melt surface during laser ablation and delivered directly to the ICP-MS by Ar carrier gas. V_{abl} is the volume of ablated metal by laser irradiation on sample surface. k_{abl} is the ablation coefficient which is related to the profile of laser track as well as the ablated and analyzed volume of metal.

The V_{abl} can be estimated based on the mean values of width, W_{tr} ($= 25\ \mu\text{m}$), depth, D_{tr} ($= 45\ \mu\text{m}$), and total length, L_{tr} , of laser track formed by ablation of metal. The typical image for vertically cross-sectional profile of laser track after ablation of metal sample is shown in **Fig. 2(a)**. A schematic illustration for ablated zone of metal with an inclusion and the width, depth and length of laser track is shown in Fig. 2(b). For this shape of track profile, V_{abl} can be estimated by Eq. (5).

$$V_{\text{abl}} = L_{\text{tr}} \cdot (W_{\text{tr}} \cdot D_{\text{tr}})/2 \dots \dots \dots (5)$$

The k_{abl} value is proportional to the $V_{\text{abl}}/V_{\text{anal}}$ ratio, and depends on some parameters of operating procedure (laser energy, frequency of laser shot, defocus of laser beam, laser scan speed) and laser ablation system (volume of ablation

Fig. 1. Ion intensity charts obtained by laser ablation of Fe-10% Ni alloy deoxidized with Mg and Al. (a) - Exp. 5, (b) - Exp. 7.

Fig. 2. Typical profile of laser track on metal surface (a) and schematic diagram of laser ablation of particle in metal (b).

chamber, flow rate of Ar carrier gas, distance from ablation zone to ICP torch and so on). The k_{abl} value is estimated by Eq. (6).

$$k_{abl} = N_{V,SEM}/N_{V,LA-ICP-MS} \dots \dots \dots (6)$$

where $N_{V,SEM}$ is the number of inclusions per unit volume determined by SEM observation on film filter after electrolytic extraction. In previous study,¹¹⁾ k_{abl} was experimentally determined as 11.8 based on the ablation of hot-pressed iron samples with various standard Al_2O_3 powders (white fused alumina, JIS Z8901, No.3 and No.4 with the mean particle size of $6.77 \pm 0.54 \mu m$ and $13.14 \pm 2.9 \mu m$, respectively). Since the k_{abl} value depends on the many factors as mentioned above, the measurements of particle size and number in metal samples by LA-ICP-MS were carried out at the same operating parameters.

The size distributions of whole inclusions in metal samples obtained from SEM observation and LA-ICP-MS analysis are shown in Figs. 3(a) and 3(b) for Exp. 3 and 7, respectively. The number of inclusions per unit volume, N_V , is plotted against d_V with the size step of $0.2 \mu m$. It can be seen that the inclusion size distributions at $d_V \geq 1 \mu m$ obtained from LA-ICP-MS measurement of metal surface are in good agreement with those from SEM observation of inclusions on film filter after electrolytic extraction. However, the number of small size inclusions with $d_V < 1 \mu m$ obtained by laser ablation of metal surface is evidently underestimated by comparison with that from SEM investigation. The similar tendencies were found in the particle size distribution of other metal samples.

The comparison of N_V values for small ($d_V < 1 \mu m$) and large ($d_V \geq 1 \mu m$) inclusions determined by LA-ICP-MS and SEM analysis is shown in Fig. 4 for Exp. 1 to 7. It can be seen that all data points for small particles are located under 1/1 line because $N_{V(SEM)}$ values are significantly larger than $N_{V(LA-ICP-MS)}$ values. The deviation of data points from 1/1 line in most experiments increases with an increased number of small size particles in metal. The reason for this

trend is explained by the simultaneous ablation of some small inclusions at a same moment. In this case, the decrease of number of detected small inclusions corresponds to that of ion intensity peaks on time chart in LA-ICP-MS analysis.

The number of large size inclusions in the range of $d_V \geq 1 \mu m$ obtained from LA-ICP-MS measurement agree satisfactorily well with those from SEM observation in most experiments, as shown in Fig. 4. The deviation of data points from 1/1 line in some experiments also might be explained by the simultaneous ablation of two or more inclusions at same moment. The reasons for underestimation of $N_{V(LA-ICP-MS)}$ values in LA-ICP-MS analysis, particularly for small size inclusions in the range of $d_V < 1 \mu m$, will be discussed in Section 3.2.

3.2. Limit for Determination of Inclusion Characteristics on Metal Surface by LA-ICP-MS

It was suggested in previous study¹¹⁾ that the accuracy for LA-ICP-MS measurement of inclusion in the size range of $d_V < 1 \mu m$ is limited by some characteristics of analyzed metal such as the content of soluble elements and the number of inclusions per unit volume. In this study, those suggestions are examined in detail.

3.2.1. Effect of Content of Soluble Elements in Metal Matrix

The effect of soluble element content in metal sample on the minimal size of inclusions identified by LA-ICP-MS analysis is investigated by ablating the standard metal samples (LSt-1 to LSt-6). It can be seen from Table 2 that the contents of insoluble elements included in inclusion particles are very low in all samples. The homogeneity for the dispersion of soluble elements on the vertical cross-section of these samples is examined using LA-ICP-MS. The representative ion intensity charts for ^{27}Al isotope of standard metal samples LSt-1, LSt-3 and LSt-5 are shown in Fig. 5. Some deviations of ion intensity values from the mean value of matrix are explained by the laser pulsation during ablation of metal surface. The absence of significant peaks in the

Fig. 3. Comparison of spatial size distributions of inclusions obtained from SEM observation and LA-ICP-MS analysis. (a) – Exp. 3, (b) – Exp. 7.

Fig. 4. Comparison of particle number per unit volume, N_V , in different size ranges for various experiments obtained from SEM observation and LA-ICP-MS analysis.

Fig. 5. Ion intensity chart observed by laser ablation of metal standard samples with different concentration of soluble Al.

ion intensity charts proves the small number of inclusions in metal matrix. Based on the obtained results, it is suggested that these samples are sufficiently homogeneous and can be used as the standard metal samples. It should be pointed out that the average levels of ^{27}Al ion intensity on Figs. 1 and 5 are different though operating parameters of laser ablation for samples were mostly same. This can be explained by different conditions of LA-ICP-MS equipment during ablations of these metal samples. The reasons and method for avoiding of this difference described in previous article.¹⁰⁾

It can be seen in Fig. 5 that the deviation of ion intensity values from the mean ion intensity of ^{27}Al isotope in metal matrix, $\bar{I}_{\text{Me}}$, increases with increasing the soluble Al content in samples. In the case of the metal sample with low soluble Al content (0.006 mass%), the ion intensity peaks caused by small size inclusions could be distinguished easily. However, in the cases of the metals with high soluble Al contents (0.093 and 0.182%), the peaks of small size inclusions could be hardly identified from the deviation of ion intensity peaks of soluble Al in metal matrix. The similar trends were observed for Ti. It follows from these results that the LA-ICP-MS method has the serious limitation for the analysis of small size inclusions on a surface of metal sample with high soluble element content. Moreover, the minimum size of inclusions detected by LA-ICP-MS increases with increasing the soluble element contents in metal matrix.

For exact verification of small size inclusions, the signal of ion intensity for ablated particle, I_{p} , must be visually larger than that maximum metal matrix signal, $I_{\text{Me,max}}$. It is assumed that $I_{\text{Me,max}}$ value is estimated by Eq. (7).

$$I_{\text{Me,max}} = \bar{I}_{\text{Me}} + 2\sigma \quad (7)$$

where σ is the value of standard deviation of ion intensity signals from the average ion intensity of metal matrix without inclusions.

A coefficient k_{crit} , which is calculated as the ratio $I_{\text{Me,max}} / \bar{I}_{\text{Me}}$ ($= 1 + 2\sigma / \bar{I}_{\text{Me}}$), can be used for the evaluation of minimum inclusion size detected by LA-ICP-MS analysis in

Fig. 6. Relationship between the critical coefficient, k_{crit} , of ion intensity signal for ^{27}Al and ^{48}Ti isotopes obtained by LA-ICP-MS analysis of metal standard samples (LSt-1 to 6) with different content of soluble Al and Ti in metal matrix.

metal matrix with different content of soluble elements. The value of $I_{(\text{Me}+\text{P})}$ denotes the ion intensity signal of the sum of metal matrix and inclusion particle. When the $I_{(\text{Me}+\text{P})} / \bar{I}_{\text{Me}}$ ratio on time chart exceeds a critical value of k_{crit} , this peak can be considered to correspond to an ablated inclusion particle in metal matrix.

The k_{crit} values for ^{27}Al and ^{48}Ti isotopes are determined experimentally using the results obtained by the ablation of standard metal samples (LSt-1 to LSt-6) with different concentration of soluble Al (0.006–0.211%) and Ti (0.010–0.233%). Figure 6 shows the relations between k_{crit} value and soluble Al (Ti) content. It can be seen in Fig. 6 that the most values of k_{crit} for Al and Ti are almost constant regardless of the contents of these soluble elements, and varies in the ranges of 1.4–1.5 and 1.3–1.4, respectively. It should be pointed out that the effect of inclusions on the k_{crit} value is negligibly small in these standard metal samples due to the very small amount of Al_{insol} and Ti_{insol} as is seen in Table 2.

The mass of Al ablated from the metal with Al_2O_3 particle, $m_{\text{Al}(\text{Me}+\text{P})}$, and that from the metal without Al_2O_3 particle, $m_{\text{Al}(\text{Me})}$, can be expressed by Eqs. (8) and (9), respectively.

$$m_{\text{Al}(\text{Me}+\text{P})} = \frac{\Delta l \cdot (S_{\text{p}} \cdot k_{\text{p/Me}} \cdot \rho_{\text{p}} \cdot [\% \text{Al}]_{\text{p}} + (S_{\text{Me}} - S_{\text{p}}) \cdot \rho_{\text{Me}} \cdot [\% \text{Al}]_{\text{Me}})}{100\%} \quad (8)$$

$$m_{\text{Al}(\text{Me})} = \frac{\Delta l \cdot S_{\text{Me}} \cdot \rho_{\text{Me}} \cdot [\% \text{Al}]_{\text{Me}}}{100\%} \quad (9)$$

where Δl is the thickness of metal layer ablated during a sampling time step. S_{p} and S_{Me} are the areas of Al_2O_3 particle and metal matrix in ablated metal layer, respectively. $k_{\text{p/Me}}$ is the coefficient of difference between material vaporization of oxide particle and that of steel. $k_{\text{p/Me}}$ is assumed as 1 for most small inclusions in this study, when $S_{\text{p}} \ll S_{\text{Me}}$. ρ_{p} and ρ_{Me} are the density of ablated Al_2O_3 particle (0.00397 g/mm³) and metal matrix (~0.00785 g/mm³ for Fe–10% Ni alloy), respectively. $[\% \text{Al}]_{\text{p}}$ and $[\% \text{Al}]_{\text{Me}}$ are the mass% of Al in Al_2O_3 particle (52.94 mass%) and that in metal matrix, respectively.

In this study, by assuming that Δl value ($= 0.1 \mu\text{m}$) is very

small in comparison with ablated particle size, the slice of spherical particle ablated during short sampling time ($= 0.01$ s) can be expressed as a disc with constant diameter.

Since the ion intensity signal is directly proportional to the mass of element in ablated metal, the $I_{\text{Al(Me+P)}}/I_{\text{Al(Me)}}$ ratio can be evaluated from Eqs. (8) and (9) as follows:

$$\frac{I_{\text{Al(Me+P)}}}{I_{\text{Al(Me)}}} \approx \frac{m_{\text{Al(Me+P)}}}{m_{\text{Al(Me)}}} = \frac{S_p \cdot \rho_p \cdot [\% \text{Al}]_p}{S_{\text{Me}} \cdot \rho_{\text{Me}} \cdot [\% \text{Al}]_{\text{Me}}} + \frac{(S_{\text{Me}} - S_p)}{S_{\text{Me}}} \quad \dots (10)$$

The maximum value of S_p for the spherical inclusions with diameter of d_v and the value of S_{Me} are calculated by Eqs. (11) and (12), respectively.

$$S_p = \frac{\pi}{4} \cdot d_v^2 \quad \dots (11)$$

$$S_{\text{Me}} = (W_{\text{tr}} \cdot D_{\text{tr}})/2 \quad \dots (12)$$

The relationships between the calculated $I_{\text{(Me+P)}}/I_{\text{(Me)}}$ values and the size of ablated Al_2O_3 and Ti_2O_3 inclusions, d_v , in metal matrix are shown in **Fig. 7(a)** and **7(b)**, respectively. The $I_{\text{(Me+P)}}/I_{\text{(Me)}}$ value increases rapidly with increasing the inclusion size. From these figures, it is understood that the large inclusions can be easily distinguished by LA-ICP-MS analysis of metal sample. In both diagrams of Fig. 7, $I_{\text{(Me+P)}}/I_{\text{(Me)}}$ value decreases drastically with increasing the soluble element content in metal matrix, M_{sol} at a constant d_v . When the k_{crit} value for Al ($= 1.4$ – 1.5) obtained experimentally in Fig. 6 is used as the minimum $I_{\text{(Me+P)}}/I_{\text{(Me)}}$ value for distinguished Al_2O_3 inclusions, the minimal size of detected Al_2O_3 inclusions, $d_{v,\text{min}}$, becomes around $0.8 \mu\text{m}$ in the metal matrix containing 0.05% Al_{sol} as illustrated in Fig. 7(a). Therefore, the Al_2O_3 inclusions with $d_v < 0.8 \mu\text{m}$ cannot be exactly distinguished on time chart by the ablation of metal with $0.05 \text{ mass}\% \text{ Al}_{\text{sol}}$. In the case of Ti, the minimal size of detected Ti_2O_3 inclusions is around $0.35 \mu\text{m}$ in the metal containing 0.02% Ti_{sol} from Fig. 7(b) by using the k_{crit} value for Ti ($= 1.3$ – 1.4) in Fig. 6. These results explain well the difference between the particle size distributions

Fig. 7. Ratio between ion intensity signals obtained by ablation of metal matrix with particle, $I_{\text{(Me+P)}}$, and pure metal matrix, $I_{\text{(Me)}}$, for samples with different particle size and content of soluble Al (a) and Ti (b) in metal.

obtained by LA-ICP-MS analysis and those by SEM observation in Fig. 3.

The relationships between the minimum size, $d_{v,\text{min}}$, for some pure oxide inclusions, which might be distinguished by LA-ICP-MS analysis of metal samples, and the content of soluble M ($M = \text{Si, Mn, Ti, Al, Mg}$ and Ca) element can be calculated from Eqs. (10), (11) and (12) by using the parameters given in **Table 3**. The results are shown in **Fig. 8**, where the $I_{\text{(Me+P)}}/I_{\text{(Me)}}$ value is assumed to be 1.5 in the approximate estimation of minimum size for all inclusions. The relationships between $\log d_{v,\text{min}}$ and $\log [\% M]_{\text{sol}}$ for various oxide inclusions have a linear character in Fig. 8. These relationships are expected to be used for the prediction of minimum size for spherical inclusions, which can be detected by LA-ICP-MS analysis of metal samples. Based on the obtained experimental and calculated results, it is concluded for LA-ICP-MS analysis of metal samples that the detectable minimum size of MO_x inclusions increases with increasing the content of soluble M element in metal.

3.2.2. Effect of Inclusion Number per Unit Volume of Metal Matrix

The number of inclusions per unit volume of metal sample, N_v , is another important factor, which considerably influences on the analytical accuracy of inclusion characteristics estimated by LA-ICP-MS. As mentioned in Section 3.1, the number of ion intensity peaks on time chart, which

Table 3. Parameters for calculation of minimum size of detected inclusions by LA-ICP-MS.

Inclusion	Content of M element in MO_x inclusion (mass%)	ρ_{MO_x} (g/mm^3)
Al_2O_3	52.94	0.00397
MgO	60.00	0.00365
CaO	71.43	0.00337
Ti_2O_3	66.67	0.00456
MnO	77.46	0.00518
SiO_2	46.67	0.00265

Fig. 8. Minimum size of oxide inclusions, $d_{v,\text{min}}$, detected by LA-ICP-MS analysis of metal samples with different content of soluble elements, M_{sol} , for $I_{\text{(Me+P)}}/I_{\text{(Me)}} = 1.5$.

can be identified as inclusion peaks, decreases because of the simultaneous ablation of two or more inclusions. As a result, the number of detected inclusions is underestimated by LA-ICP-MS analysis, while the size of some inclusions determined from the areas of ion intensity peaks is overestimated. Those trends become appear when the N_V value is larger than a critical value, $N_{V,crit}$, or the inclusions disperse heterogeneously in metal sample. In this study, the uniform dispersion of inclusions in metal sample is assumed.

The calculated critical value of inclusion number per unit volume of ablated metal, $N_{V,crit-cal}$, is estimated by Eq. (13) by assuming that one sampling step corresponds to ablation of pure metal matrix without inclusion at least.

$$N_{V,crit-cal} = 1/V_{anal} = 1/[(W_{tr} \cdot D_{tr}/2) \cdot (d_v + 2\Delta l)/k_{abl}] \dots (13)$$

The thickness of ablated zone after one sampling time, Δl , can be expressed by Eq. (14).

$$\Delta l = v_s \cdot \tau_{samp} = v_s \cdot (\tau_{int} \cdot n_{is}) \dots (14)$$

where v_s is the scan speed of laser beam on metal surface ($= 0.01$ mm/s). τ_{samp} and τ_{int} are the total sampling time for all isotopes and the integration time only for one isotope ($= 0.01$ s), respectively. n_{is} is the total number of analyzed isotopes during total sampling time in the ablation of metal sample.

The relation between the calculated $N_{V,crit-cal}$ value in LA-ICP-MS analysis of metal samples and the size of ablated inclusions are shown in Fig. 9 as a function of the number of analyzed isotopes, n_{is} . It can be seen that the $N_{V,crit-cal}$ values for large inclusions ($\geq 1 \mu\text{m}$) in metal samples are varied in the range of $0.2\text{--}2.0 \times 10^7 \text{ mm}^{-3}$ depending on the number of analyzed isotopes, while those for small inclusions ($< 1 \mu\text{m}$) are ranged in $0.9\text{--}7.0 \times 10^7 \text{ mm}^{-3}$. These $N_{V,crit-cal}$ values are much higher than the real number of large and small inclusions in metal samples obtained by SEM observation, $N_{V(SEM)}$, given in Fig. 4.

Based on the assumption mentioned above, the theoretical ablation time required for the analysis of one pure Al_2O_3 inclusion, τ_{cal} , can be evaluated as $(d_v + 2\Delta l)/v_s$. For example, the τ_{cal} value for analysis of one Al_2O_3 particle with $d_v = 1 \mu\text{m}$ is 0.12 s at $v_s = 0.01$ mm/s and $\tau_{samp} = 0.01$ s. The rep-

resentative ion intensity peaks on time chart obtained by the ablation of single pure Al_2O_3 inclusion with three different diameters are shown in Fig. 10 after LA-ICP-MS analysis of metal sample Exp. 8, where the diameter of ablated particle estimated by Eq. (2) is given in parentheses. The ion intensity peaks are drawn not by steep curves but by smooth curves without spike of I_{Al} signal. The time width of ion intensity peak on time chart at the ablation of single inclusion on metal surface, τ_{exp} , is significantly longer than τ_{cal} at a given scan speed of laser beam. The difference between τ_{cal} and τ_{exp} can be explained as follows: Fine aerosol, which is produced by laser ablation of metal surface, disperses in the ablation chamber. Detailed description of LA-ICP-MS apparatus and processes are given in previous paper.⁷⁾ But the ablated oxide in chamber atmosphere diluted gradually by continual Ar carrier gas in the chamber. The time for complete replacement of chamber atmosphere depends on the chamber volume, the chamber shape, the consumption of Ar carrier gas, the volume of ablated inclusion and other factors. Therefore, the time width of ion intensity peak on time chart cannot be used for the accurate estimation of the real size of ablated inclusions.

The relation between the length of laser beam track at the ablation of single inclusion on metal surface, $L_p (= v_s \cdot \tau_{exp})$, and the size of this Al_2O_3 particle in Fe-10%Ni alloy is shown in Fig. 11 for the metal sample No. 8 deoxidized by Al. The Al_2O_3 inclusions in different zones (top, middle and bottom of vertically sliced metal plate) were analyzed by LA-ICP-MS. The size of ablated Al_2O_3 inclusion, d_v , was calculated from Eq. (2) using the area of appropriate ion intensity peak on time chart, A_{Al}^p . It can be seen from Fig. 11 that the L_p value increases with increasing inclusion size. The L_p/d_v ratio for inclusions with the size range from 1 to $5 \mu\text{m}$ was 23.5 on the average. The approximate d_v value can be simply calculate using this mean L_p/d_v ratio, v_s and τ_{exp} .

The experimental critical number of inclusions in LA-ICP-MS analysis, $N_{V,crit-exp}$, which was estimated by Eq. (13) using L_p value ($= 23.5 d_v$) instead of d_v , is shown in Fig. 12 for different Al_2O_3 inclusion size. The numbers of small ($< 1 \mu\text{m}$, open marks) and large ($\geq 1 \mu\text{m}$, filled marks) inclu-

Fig. 9. Relationship between the calculated critical number of inclusions per unit volume in metal sample, $N_{V,crit}$, and inclusion size, d_v , by LA-ICP-MS analysis.

Fig. 10. Typical ion intensity peaks for Al_2O_3 inclusions with different size obtained by laser ablation of metal sample (Fe-10%Ni alloy, Exp. 8).

Fig. 11. Relationship between the length of ion intensity peak on time chart, L_p , and size of Al_2O_3 inclusions, d_v , in metal samples of Fe-10%Ni alloy (Exp. 8) by analysis using LA-ICP-MS method.

Fig. 12. Comparison of number for oxide inclusions in different deoxidation experiments with limit number of particles, $N_{v,\text{crit-exp}}$, determined experimentally by LA-ICP-MS analysis of inclusions on metal surface without overlapping of ion intensity peaks.

sions obtained by LA-ICP-MS and SEM analysis are shown in this figure for different deoxidation experiments. It is found that the N_v values for most experiments are present below $N_{v,\text{crit-exp}}$ -line. Therefore, almost of all inclusions were ablated and analyzed by LA-ICP-MS without overlapping the ion intensity peaks if all inclusions in metal matrix were dispersed homogeneously. In this case, the major factor, which determines a limit for application of LA-ICP-MS for analysis of Al_2O_3 inclusions in given metal samples, is only the content of soluble Al in metal matrix discussed in Section 3.2.1.

It is expected that the LA-ICP-MS technique can be suc-

cessfully applied for rapid analysis of oxide inclusions in steel samples, though some limits regarding to soluble element content, number and dispersion of analyzed inclusions in metal matrix have to be considered.

4. Conclusions

Some application aspects of Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) for rapid analysis of oxide inclusions in Fe-10% Ni alloy samples were discussed. The inclusion characteristics such as number and particle size distribution obtained by LA-ICP-MS method were compared with those by three-dimensional observation of particles on film filter after the electrolytic extraction from metal samples using SEM and EPMA. The following conclusions were summarized:

(1) For metal samples with total content of $\text{Mg} \leq 0.025\%$ and $\text{Al} \leq 0.09\%$, the particle size distributions obtained by LA-ICP-MS method are in good agreement with those from three dimensional SEM investigations of particles for the oxide inclusions in the range of $d_v \geq 1 \mu\text{m}$.

(2) The minimum size of various oxide inclusions in metal, which could be detected by LA-ICP-MS analysis, increased with increasing the contents of soluble elements in metal. The lower limit of oxide inclusion size in LA-ICP-MS method was estimated for the various steel grades with different content of soluble elements.

(3) The ratio between the experimental length of ion intensity peak on time chart and the estimated size of Al_2O_3 inclusion ablated from metal surface by LA-ICP-MS analysis varied from 20 to 25 for the particles in the size range of 1 to $5 \mu\text{m}$.

(4) For accurate LA-ICP-MS analysis of Al_2O_3 inclusions without overlapping the ion intensity peaks, the maximum critical number of inclusions per unit volume of metal sample was estimated.

REFERENCES

- 1) F. Reinholdsson, A. Lind, R. Nilsson, P. Sjödin and P. Jönsson: *ISIJ Int.*, **37** (1997), 637.
- 2) M. Göransson and P. Jönsson: *ISIJ Int.*, **41** (2001), S42.
- 3) V. Tusset, Ch. Marique, H. Mathy, B. Gommers and N. Van Poeck: *Ironmaking Steelmaking*, **30** (2003), 142.
- 4) T. Muroi, W. Nagasawa, H. Narai and M. Ohori: *Journal of ASTM International*, Vol.3, Issue 9 (2006), DOI:10.1520/JAI14036.
- 5) Y. Ishibashi: *ISIJ Int.*, **42** (2002), S137.
- 6) A. G. Coedo, I. Padilla and M. T. Dorado: *Appl. Spectrosc.*, **58** (2004), 1481.
- 7) A. V. Karasev, R. Inoue and H. Suito: *ISIJ Int.*, **41** (2001), 757.
- 8) G. Müller, F. Stahnke and D. Bleiner: *Talanta*, **70** (2006), 991.
- 9) A. G. Coedo, T. Dorado, I. Padilla and J. C. Fariñas: *Talanta*, **71** (2007), 2108.
- 10) A. V. Karasev and H. Suito: *ISIJ Int.*, **44** (2004), 356.
- 11) A. V. Karasev and H. Suito: *ISIJ Int.*, **44** (2004), 364.
- 12) C. Dubuisson, A. G. Cox, C. W. Mcleod, I. Whiteside, R. Jowitt and H. Falk: *ISIJ Int.*, **44** (2004), 1859.
- 13) A. G. Coedo, T. Dorado, I. Padilla and R. Usero: *ISIJ Int.*, **48** (2008), 194.
- 14) A. V. Karasev and R. Inoue: *Mater. Trans.*, **50** (2009), 341.
- 15) R. Inoue and H. Suito: *Mater. Trans., JIM*, **31** (1992), 1164.