Quantitative Analysis of Total and Insoluble Elements and Inclusion Composition in Metal by Laser Ablation ICP-MS Method

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Total (M_total) and insoluble (M_insol) contents of element, and inclusion composition in metal samples have been analyzed quantitatively by using the laser ablation ICP-MS (LA-ICP-MS). The contents of M_total and M_insol in Fe-M, Fe-10mass%Ni-M, and Fe-0.2mass%C-M (M=Ti, Al, and Ce) alloys obtained by LA-ICP-MS are compared with those from chemical analysis. The compositions of synthetic particles (CA, CaO, Al2O3, and MgO) and complex inclusions (Al2O3–TiN and Ce2O3–TiN) on a surface of glass or metal sample are analyzed by LA-ICP-MS, and these values are compared with those from EPMA and chemical analysis. It is found that LA-ICP-MS is an useful technique to the quantitative analysis of total and insoluble contents of elements and composition of inclusions in the range of particle diameter from 1 to 100 μm.

KEY WORDS: quantitative analysis; steel; total and insoluble elements; inclusion composition; laser ablation ICP-MS.

1. Introduction

The development of a rapid and accurate method for determining soluble and insoluble contents of elements and inclusion composition is indispensable to the quality control of steels. The laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) has been successfully applied to the direct analysis of steel composition1–6) and to the determination of trace element concentrations in geological minerals and rocks.7–12) The LA-ICP-MS technique is characterized by the quick analysis with high precision (approximately 5 to 15% for most of elements).1,4,5,8–12) Up to now, only total concentration of elements in a metal sample has been determined by this technique, but the application to the analysis of inclusion composition has not been made despite of the fact that the accurate control of inclusion composition is of considerable importance to the high quality steel production.

This study is concerned with the application of the LA-ICP-MS technique to the quantitative analysis of total (M_total) and insoluble (M_insol) contents of elements, and the composition of inclusions in Fe-M, Fe-10mass% Ni-M, and Fe-0.2mass%C-M (M=Ti, Al, and Ce) alloys. The contents of M_total and M_insol obtained from the LA-ICP-MS method are compared with those from chemical analysis. The compositions of synthetic particles (CA2, CA, C12A7, C3A, CAM, and MA; C=CaO, A=Al2O3, and M=MgO) and complex inclusions (Al2O3–TiN and Ce2O3–TiN) obtained by LA-ICP-MS are compared with those from EPMA and chemical analysis.

2. Apparatus and Operating Conditions

The Hewlett-Packard HP 4500 inductively coupled plasma mass spectrometer with the LSX-100 laser ablation system was used for the analysis of metal samples.

A schematic diagram of the LA-ICP-MS system is shown in Fig. 1. A sample is sealed in an ablation chamber where it is irradiated by a laser under flowing Ar carrier gas. The Nd:YAG laser is operated in Q-switched mode, producing a highly collimated beam (<0.8 mrad divergence) and near-Gaussian beam energy profile. The laser beam focuses onto the sample surface via the objective...
lens, ablates the sample in chamber, and forms a fine sample aerosol (typically 20 to 100 μm particle diameter). The sample aerosol is swept on a stream of Ar carrier gas directly to the ICP torch and is ionized by Ar plasma. The number of ions is determined by mass spectrometer. The sample is viewed through the same objective lens used to focus the laser. The image is captured by a color CCD camera. A motorized zoom lens adjusts the image magnification from 20 to 200 and the ablation process of a metal sample is monitored on a computer monitor.

In this study, the sample analysis is made by controlling line (raster) pattern. The basic operating parameters of the LA-ICP-MS system for the quantitative analysis of total and insoluble elements and inclusion composition in metal samples are given in Table 1. During ablation, the laser beam is moved horizontally at a speed of 0.01 mm/s by keeping the focus on sample surface. By using this laser scan rate and the integration time of 0.01 or 0.1 s, the ion intensity of one isotope is measured every step with length of 0.1 or 1.0 mm, respectively.

Since the mass and volume of analyzed metal by LA-ICP-MS are dependent on the parameters of laser ablation, the cross-sectional profile of laser track is observed after ablation of pure iron at different energy (1.5 to 4.0 mJ/shot) and defocus (0 to 5 mm) of laser beam. The laser track after ablation of a metal sample is shown in Fig. 2, as one of the representative results.

The effects of the energy and defocus of laser beam on the width and depth of laser track, which are measured by optical microscopy at a magnification of 500 or 1000, are shown for pure iron in Figs. 3 and 4, respectively. It can be seen in Fig. 3 that the width and depth change with laser energy in the ranges from 10 to 45 μm and from 15 to 105 μm, respectively. The depth of laser track increases more rapidly in comparison with its width in the range of laser energy from 1.5 to 3.0 mJ/shot, as shown in Fig. 3. However, the width and depth do not increase to a significant degree with increasing the laser energy above 3.0 mJ/shot. With increasing the defocus of laser beam, the width increases from 40 to 170 μm, and the depth decreases from 90 to 20 μm, as shown in Fig. 4. The cross-sectional profile of laser track changes with defocus of laser beam from type I to type III, as shown schematically in the upper diagram of Fig. 4.

In order to determine the total composition of inclusion particles by using LA-ICP-MS, the width and depth of laser track must be larger than inclusion size. Therefore, the type

| Table 1. Operating parameters in LA-ICP-MS system. |
|---------------------------------------------------|
| **ICP-MS**                                       |
| RF power: 1100 W                                 |
| Integration time: 0.01 - 0.1 s                    |
| **Laser Ablation System**                         |
| Type of laser: Nd:YAG pulsed with Q-switch        |
| Wavelength: 266 nm (UV light)                     |
| Laser scan rate: 0.01 mm/s                        |
| Frequency of the laser shot: 20 Hz                |
| Laser energy: 1.5 - 4.0 mJ/shot                   |
| Defocus of laser beam: 0 - 5 mm                   |

![Fig. 2. Track of laser beam after ablation of metal sample by LA-ICP-MS.](image)

![Fig. 3. Effect of laser energy on width and depth of laser track in metal.](image)

![Fig. 4. Effect of laser beam defocus on width (W), depth (D), and profile of laser track in metal.](image)
II in which the width is close to the depth is generally preferable to the analysis of whole inclusion.

The analysis of standard samples was made every one hour since the slopes of calibration lines change with ablation time.

3. Sample Preparation

3.1. Metal Sample

The experimental conditions for the preparation of metal samples are given in Table 2. In Exp. Nos. 1 to 6, an Fe–M or Fe–10mass%Ni–M (M=Ti and Al) alloy with different contents of Ti and Al was prepared in an arc furnace under an Ar atmosphere. A charge containing high-purity electrolytic iron, Fe–50mass%M alloys, and pure globular nickel (in Exp. Nos. 4 to 6) was melted for 5 minutes and immediately quenched onto a water-cooled copper plate. Then, a sample (10 and 20 g in Exp. Nos. 1 to 3 and Exp. Nos. 4 to 6, respectively) was overturned and melted again. This process was repeated 5 times for homogenization.

In Exp. Nos. 7 to 12, an Fe–10mass%Ni alloy (100 g) was melted and deoxidized by an appropriate amount of Fe–50mass%M (M=Ti and Al) alloy at 1600°C under an Ar–7vol%H2 atmosphere in a LaCrO3 resistance furnace. The melt with 0.2 mass% M was held for 1 to 5, and 10 min at 1600°C and then quenched in water. More detailed description is given in previous article.13

In Exp. Nos. 13 to 17, an Fe–10mass%Ni–0.02mass%N–0.01 or 0.1mass%Ti–M (M=Al and Ce) alloy was prepared by using an induction furnace as follows: A charge (70 g) containing high-purity electrolytic iron and pure globular nickel was heated to 1600°C under 50vol%N2–46.5vol%Ar–3.5vol%H2 atmosphere. The melt was held for 20 min at 1600°C and deoxidized by an Fe–50mass%Al (0.03 mass% Al in Exp. Nos. 13, 15, and 16 and 0.015 mass% Al in Exp. No. 14) alloy or an Fe–10mass%Ce (0.08 mass% Ce in Exp. No. 17) alloy and immediately stirred for 10 s using an Al2O3 rod. Then, an Fe–20mass%Ti (Exp. Nos. 13 to 16) or Fe–50mass%Ti (Exp. No. 17) alloy was added and the melt was stirred for 10 s for homogenization. In Exp. No. 13, the melt was held for 60 min at 1600°C. Then, it was cooled to 1400°C at a rate of 0.70°C/s and kept for 60 min (Exp. Nos. 14 and 17), followed by quenching in water.

In Exp. No. 18, a charge (70 g) containing high-purity electrolytic iron, an Fe–5mass%C alloy, and an Fe–26mass%P alloy was heated to 1600°C and held for 30 min under an Ar–7vol%H2 atmosphere in an induction furnace. The Fe–0.2mass%C–0.02mass%P melt was deoxidized by an Fe–10mass%Ti alloy (0.35 g) and immediately stirred for 30 s using an Al2O3 rod. Then, the melt was cooled to 1400°C at a rate of 0.80°C/s and quenched in water. High purity alumina crucible was used for Exp. Nos. 7 to 18.

3.2. Standard Sample

The standard steel samples (JSS 168-6 to 175-6 and BCS 321) were used for the quantitative analysis of total Ti and Al contents in metal samples. The total contents of Ti and Al in these standard samples are given in Table 3.

The standard steel samples for Ti and Al were found to contain large size inclusions (>5 mm) which lead to the errors in obtaining the calibration lines by LA-ICP-MS analysis. This will be described in Sec. 6.1.

The glass samples (60 mass% SiO2, 21 mass% B2O3, and 19 mass% Li2O) with different contents of elements were prepared for the estimation of the composition of synthetic particles and inclusions in metal samples. A mixture (10 g) of pure SiO2, B2O3, and Li2CO3 powders was melted in a Pt dish at 950°C and held for 30 min. Then, an appropriate amount of MgO, Al2O3, CaCO3, TiO2, MnO, FeO, ZrO2, and CeO2 powders was added and the melt was immediately stirred for 10 s using an quartz tube. After cooling, this glass sample was crashed and melted again for 30 min. This procedure was repeated 5 times for homogenization. These glass samples were used as the standard for the quantitative analysis of inclusion composition.

3.3. Glass Sample with Synthetic Particles

The synthetic particles such as CaO·2Al2O3 (CA2), CaO·Al2O3 (CA), 12CaO·7Al2O3 (C12A7), 3CaO·Al2O3 (C3A), and MgO·Al2O3 (MA) were obtained by sintering

| Table 2. Experimental conditions for metal preparation. |
|----------------|----------------|----------------|
| Exp. No. | Deoxidant M (mass%) | Holding time (min) |
|----------------|----------------|----------------|
| Fe–M | | |
| 1 | 0.005 | 0.005 | – | – |
| 2 | 0.02 | 0.02 | – | – |
| 3 | 0.1 | 0.1 | – | – |
| Fe–10% Ni–M | | |
| 4 | 0.01 | 0.01 | – | – |
| 5 | 0.05 | 0.05 | – | – |
| 6 | 0.1 | 0.1 | – | – |
| 7 | 0.2 | – | 1 | – |
| 8 | 0.2 | – | 2 | – |
| 9 | 0.2 | – | 10 | – |
| 10 | – | 0.2 | 5 | – |
| 11 | – | 0.2 | 10 | – |
| Fe–10% Ni–0.02% N–M | | |
| 13 | 0.01 | 0.01 | 60 | 0 |
| 14 | 0.01 | 0.015 | 0 | 60 |
| 15 | 0.01 | 0.03 | 0 | 0 |
| 16 | 0.1 | 0.03 | 0 | 0 |
| 17 | 0.1 | Ce 0.08 | 0 | 60 |
| Fe–0.2% C–0.02% P–M | | |
| 18 | 0.05 | – | 0 | 0 |

* Exp. Nos. 1–6: Arc furnace; Exp. Nos. 7–12: Resistance furnace; Exp. Nos. 13–18: Induction furnace.

| Table 3. Total contents of Ti and Al in standard steel samples. |
|----------------|----------------|
| Standard | T. Ti | T. Al |
| JSS 168-6 | 0.078 | 0.044 |
| JSS 169-6 | 0.012 | 0.046 |
| JSS 170-6 | 0.103 | 0.045 |
| JSS 171-6 | 0.046 | 0.050 |
| JSS 172-6 | – | 0.019 |
| JSS 173-6 | – | 0.031 |
| JSS 174-6 | – | 0.047 |
| JSS 175-6 | – | 0.073 |
| BCS 321 | 0.13 | – |
the pressed mixture of CaCO₃ or MgO and Al₂O₃ powders at 1300°C for 72 h, followed by crushing and sieving. The particles of a mixture of CaO–Al₂O₃–MgO (CA2, CA, C12A7, C3A, CAM, and MA) were obtained by melting the mixture of CaCO₃, Al₂O₃, and MgO powders at 1580°C for 10 min in an induction furnace by using MgO crucible, followed by quenching in water and crushing. The synthetic particles with the diameter (dₜ) of 10 to 50 μm were used for the quantitative analysis of particle composition by LA-ICP-MS.

The glass samples containing aforementioned synthetic particles were prepared by first melting pure glass sample (60 mass% SiO₂, 21 mass% B₂O₃, and 19 mass% Li₂O) in a Pt dish at 950°C. Then, the Pt dish was withdrawn from the furnace, and the synthetic particles were placed on the surface of one end of a copper cylindrical rod distributed on a glass surface by pressing before a glass sample solidified.

4. Analysis of Composition

4.1. Chemical Analysis

For the determination of total Ti and total Al contents as the sum of acid-soluble and acid-insoluble, a metal sample (0.2 g) obtained in Exp. Nos. 1 to 9 and in Exp. Nos. 10 to 12 was dissolved with HCl–HNO₃–H₂SO₄ and HCl–HNO₃ acids, respectively. Detailed description of the chemical analyses for acid-soluble and acid-insoluble Ti and Al is given in previous articles.14,15)

For the chemical analysis of insoluble M (Exp. Nos. 4 to 18) and soluble M (Exp. Nos. 13 to 18), a metal sample (0.3 to 0.5 g) was dissolved with 2% TEA (2v/v% triethanol amine–1w/v% tetramethylammonium chloride–methanol–0.1 to 0.2w/v%Ba) in Exp. Nos. 4 to 6, and 17, with 4% MS (4v/v% methyl salicylate–1v/v% salicylic acid–1w/v% tetramethylammonium chloride–methanol) in Exp. Nos. 7 to 16, and with 10% AA (10v/v% acetylacetone–1w/v% tetramethylammonium chloride–methanol) in Exp. No. 18 using a potentiostatic electrolytic extraction method. After filtration the solution and residue on a film filter were analyzed and the chemical analysis are given elsewhere.13)

The total M contents in standard glass samples and in synthetic materials were analyzed by the ICP emission spectrometry after fusion of sample (0.1 g) with Na₂CO₃, and dissolution with HCl and HNO₃, and with HCl acids, respectively. The compositions of synthetic materials (CA₂, CA, C₁₂A₇, C₃A, CAM, and MA) were also confirmed by the X-ray diffraction analysis (XRD).

4.2. LA-ICP-MS and EPMA Analysis

The standard steel samples and metal samples were ablated and analyzed by LA-ICP-MS using the following parameters: laser scan rate of 0.01 mm/s, laser energy of 2.0 mJ/shot, frequency of laser shots of 20 Hz, defocus of laser beam of 0.5 mm, and integration time of 0.1 s.

In the present study, the compositions of the synthetic particles (CA₂, CA, C₁₂A₇, C₃A, CAM, and MA) or complex inclusions (Al₂O₃–TiN and Ce₂O₃–TiN) are analyzed quantitatively by using LA-ICP-MS and EPMA. The synthetic particles in the range of 10≤dₜ≤50 μm were measured on a surface of glass sample. The complex inclusions in the range of dₜ≥5 μm were analyzed on a polished cross section of metal specimen in an Fe–10mass%Ni–0.02mass%N–0.1mass%Ti–M (M=Al and Ce in Exp. Nos. 16 and 17, respectively) alloy. Each inclusion was analyzed by EPMA, and then by LA-ICP-MS. A surface of glass or metal sample was marked by scratching as 1×1 mm squares in order to identify the location of each inclusion for the studies by EPMA and LA-ICP-MS.

The standard glass samples, the synthetic particles on a surface of glass, and the complex inclusions on a polished surface of metal were ablated by LA-ICP-MS under the parameters such as the laser scan rate of 0.01 mm/s, frequency of laser shots of 20 Hz, and integration time of 0.01 s. In order to analyze whole volume of a particle, the laser energy and defocus of laser beam were increased from 2.0 to 4.0 mJ/shot and 0 to 2.5 mm, respectively, depending on particle size.

The compositions of complex inclusions (dₜ≥1 μm) in an Fe–10mass%Ni–0.02mass%N–0.1mass%Ti–Ce alloy (Exp. Nos. 17) were analyzed by using LA-ICP-MS. In this case, the standard glass samples and metal specimen were ablated under the laser energy of 2.0 mJ/shot and laser beam defocus of 0.5 mm.

5. Estimation of Element Content and Inclusion Composition in Metal by LA-ICP-MS

5.1. Total and Insoluble Contents of Element

The ion intensity chart for a metal sample is shown schematically in Fig. 5. The peaks of ion intensity on a chart correspond to the ablated inclusions in a metal sample. The mean ion intensity of element M, Iₓ, is estimated from the value using the calibration line for M element.

Total area of all intensity peaks on a chart, Aₓ, which corresponds to insoluble M content in metal, can be obtained from the sum of the area of each intensity peak as follows:
Fig. 6. Schematic diagram of intensity peak by ablation of inclusion in metal.

where $A_{M,j}$ is the area of the $i$-th intensity peak on a chart, and $n$ is the total number of intensity peaks.

A schematic diagram of one intensity peak of an inclusion is shown in Fig. 6. The area of this intensity peak, $A_{M,j}$, is correlated to the amount of $M$ element in an ablated inclusion and is calculated as

$$A_M = \sum_{j=1}^{n} I_{M,j} - \bar{I}_{M,\text{sol}} \cdot m$$

where $I_{M,j}$ is the $j$-th ion intensity value of $M$ element at the time of $\tau_j$ in a peak, $m$ is the total number of the ion intensity values in a peak, $\bar{I}_{M,\text{sol}}$ is the ion intensity which corresponds to the soluble metal content in metal. This value is calculated as the average ion intensity which corresponds to the ablation of metal matrix without inclusions.

The insoluble $M$ content, $M_{\text{insol}}$, in an ablated metal can be estimated under the assumption that the ion intensity is proportional to the amount of element in an ablated inclusion by using the following equation:

$$M_{\text{insol}} = \frac{A_{M,\text{insol}}}{A_{M,\text{total}}} \cdot M_{\text{total}}$$

where $A_{M,\text{total}}$ is total area of ion intensity which is calculated as the sum of all ion intensity values for $M$ element on a chart.

5.2. Inclusion Composition

The area of the intensity peak for each element in one particle, $A_{M,p}$, can be calculated from Eq. (2). The calibration line for each element, which is obtained by ablation of the standard glass sample, is obtained as follows:

$$\bar{I}_M^u_{\text{total}} = a_M + b_M \cdot M_{\text{total}}^u$$

where $\bar{I}_M^u_{\text{total}}$ and $M_{\text{total}}^u$ are the mean ion intensity of isotope and the total $M$ content in the standard glass sample, respectively. $a_M$ and $b_M$ are the constant for the calibration line of $M$ element.

The $\text{Al}_2\text{O}_3$ content in mass% for each synthetic particle consisting of oxide only is evaluated from the following equation:

$$[\% \text{ Al}_2\text{O}_3] = 100 \cdot \frac{(\text{Al}_2\text{O}_3)}{\alpha \cdot (\text{CaO}) + (\text{Al}_2\text{O}_3) + (\text{MgO})} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 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contents of Ti and Al obtained by LA-ICP-MS agree reasonably well with those from chemical analysis. The deviation of some points from the 1:1 line in Figs. 8 and 9 can be explained by the presence and heterogeneous distribution of inclusions in an ablated zone of metal. In addition the limit of total weight of analyzed metal by LA-ICP-MS, which varies from $10^{-2}$ to $10^{-3}$ g in comparison with 0.1 to 0.5 g for chemical analysis, is also one of the reasons for this deviation. It should be noted that one large size inclusion ($d_V > 5$ mm) of Ti$_2$O$_3$ in $10^{-2}$ g of an ablated metal corresponds to the 30 to 240 ppm of the Ti$_{insol}$ content.

The effect of the length of laser track on the Ti total content determined by LA-ICP-MS is shown for the standard steel sample (JSS 170-6) in Fig. 10. It can be seen that the Ti total contents from LA-ICP-MS approach the values from chemical analysis indicated by the solid line with increasing the length of laser track, which is proportional to the weight of ablated metal. Although LA-ICP-MS is an useful technique to the rapid quantitative analysis of total and insoluble contents of elements in metal samples, the weight of an ablated metal should be larger than $5 \times 10^{-3}$ g if a metal sample contains the inclusions in the range of $d_V \geq 5$ μm.

7. Quantitative Analysis of Inclusion Composition in Metal by LA-ICP-MS

The chemical composition of the standard glass samples

Table 4. Chemical composition of metal samples.

| Exp. No. | Ti (mass ppm) | Ti$_{insol}$ | Al (mass ppm) | Al$_{insol}$ |
|----------|---------------|--------------|---------------|-------------|
| 1        | 35            | NA           | 57            | NA          |
| 2        | NA            | 219          | NA            | 4           |
| 3        | 1185          | NA           | 889           | NA          |
| 4        | 98            | 1            | 57            | 0           |
| 5        | 511           | NA           | 474           | NA          |
| 6        | 973           | 15           | 934           | 0           |
| 7.1      | 1990          | 208          | 46            | 4           |
| 7.2      | 1970          | 198          | 31            | 4           |
| 8.1      | 2030          | 112          | 64            | 5           |
| 8.2      | 1970          | 120          | 72            | 5           |
| 9.1      | 1530          | 151          | 69            | 6           |
| 9.2      | 1590          | 180          | 14           | 7           |
| 9.3      | 1590          | 120          | 6            | 2           |
| 10.1     | -             | -            | 1840          | 80          |
| 10.2     | -             | -            | 1800          | 78          |
| 10.3     | -             | -            | 1820          | 77          |
| 11.1     | -             | -            | 2070          | 52          |
| 11.2     | -             | -            | 2000          | 50          |
| 11.3     | -             | -            | 2000          | 55          |
| 12.1     | -             | -            | 1530          | 46          |
| 12.2     | -             | -            | 1490          | 54          |
| 12.3     | -             | -            | 1520          | 60          |
| 13       | 70            | 6            | 160           | 9           |
| 14       | 107           | 77           | 72            | 46          |
| 15       | 136           | 67           | 297           | 34          |
| 16       | 813           | 902          | 210           | 53          |
| 17*      | 705           | 690          | 46            | 19          |
| 18       | 327           | 115          | 24            | 19          |

*, Ti: Ce = 288 ppm, Ce$_{insol}$ = 286 ppm.
NA - not analyzed.

Fig. 7. Correlation between mean ion intensity and contents of Ti and Al in standard steel samples.

Fig. 8. Comparison of total M content obtained from LA-ICP-MS and that from chemical analysis.

Fig. 9. Comparison of insoluble M content obtained from LA-ICP-MS and that from chemical analysis.
The representative ion intensity charts for $^{24}$Mg, $^{27}$Al, $^{43}$Ca, $^{47}$Ti, $^{90}$Zr, and $^{140}$Ce isotopes are shown in Fig. 11, indicating that the present standard glass samples are homogeneous.

The correlation between mean ion intensity of isotopes, $I_{\text{st}}$, obtained by LA-ICP-MS and total $M$ content from chemical analysis is shown in Fig. 12 for the standard glass samples. It can be seen that the mean ion intensity increases linearly with an increase of total $M$ content. These lines were used as the calibration lines for the quantitative analysis of inclusion composition.

The synthetic particles (CA, CA, C12A7, C3A, CAM, and MA) dispersed on a glass surface were analyzed by LA-ICP-MS. The $Al_2O_3$ contents in synthetic particles obtained from LA-ICP-MS, EPMA, and chemical analysis are plotted against those for the synthetic compounds in Fig. 13. The error bar represents the arithmetic standard deviation for analyzed $Al_2O_3$ concentration. The $Al_2O_3$ contents evaluated without correction factor $\alpha$ by LA-ICP-MS are represented by filled circles. It is clear that the filled circles fall on the broken line which is parallel to the 1:1 line. This systematic deviation can be corrected by using the factor $\alpha$ (0.683) in Eq. (5), which is the average ratio of CaO content obtained from LA-ICP-MS without correction to that from chemical analysis for all synthetic particles. The corrected $Al_2O_3$ contents are represented by open circles in Fig. 13. The $Al_2O_3$ contents in the synthetic particles obtained by LA-ICP-MS, EPMA, and chemical analysis agree well with each other, as shown in Fig. 13, and agree with those for the corresponding synthetic compounds, which were confirmed by X-ray diffraction analysis.
The complex inclusions of the Al$_2$O$_3$–TiN and Ce$_2$O$_3$–TiN systems in the range of $d<5\mu$m were analyzed in an Fe–10mass%Ni–0.02mass%N–0.1mass%Ti–M (M=Al and Ce) alloy. Comparison of the Al$_2$O$_3$ and Ce$_2$O$_3$ contents in complex inclusions, which were estimated in a manner similar to that of [% TiN] given in Eq. (7), obtained by LA-ICP-MS and those from EPMA is shown in Fig. 14. Some Ce$_2$O$_3$–TiN inclusions contain a small amount of Al$_2$O$_3$, since an alumina crucible was used in this experiment. It can be seen that the $M_{O_y}$ content in complex inclusions obtained from LA-ICP-MS is in disagreement with that from EPMA. This is due to the fact that only thin surface layer (about 1μm) of inclusion can be analyzed by EPMA. The surface composition determined by EPMA is dependent on the cross section of complex inclusions and does not correspond to the composition of whole inclusion. Therefore, it may be concluded that the LA-ICP-MS technique is superior to EPMA in the quantitative analysis of the compositions of complex inclusions, particularly, in the range of $d<5\mu$m.

The compositions of complex inclusions in the range of $d<1\mu$m were analyzed in an Fe–10mass%Ni–0.02mass%N–0.1mass%Ti–M alloy by using LA-ICP-MS. The ablated area of metal surface was 0.48 mm$^2$ and total number of analyzed inclusions was 74. All analyzed inclusions were classified into three groups depending on different values of total ion intensity in inclusion ($I_{incl}$, 10$^6$, 10$^7$, and 10$^8$ cps) which corresponds to inclusion size. The TiN content in the analyzed Ce$_2$O$_3$(+Al$_2$O$_3$)–TiN inclusions, [% TiN], was evaluated from Eq. (7). The [% TiN] values are divided into 10 classes, namely, the step width of 10 mass%. The number of complex inclusions in pet is plotted against the TiN content as a function of three different total inclusion intensities in Fig. 15. It can be seen that the mean TiN content indicated by an arrow increases in each $I_{incl}$ group and the number of complex inclusions, $n_T$, decrease with increasing the total intensity, which is related to inclusion size. The group of small size inclusions with $I_{incl}<10^6$ cps contains mostly Ce$_2$O$_3$(+Al$_2$O$_3$)–TiN particles, and a small amount of Ce$_2$O$_3$(+Al$_2$O$_3$) and TiN particles. Some inclusions contain Al$_2$O$_3$ ranging from 0 to 10mass%. The middle group of inclusions in the range of $10^6< I_{incl}<10^7$ cps contains the TiN rich-Ce$_2$O$_3$(+Al$_2$O$_3$) and less amount of TiN particles. The Al$_2$O$_3$ content is varied from 0 to 4mass%. The group of large size inclusions with the $I_{incl}>10^7$ cps has the TiN rich-Ce$_2$O$_3$(+Al$_2$O$_3$) particles. In this group the inclusions contain Al$_2$O$_3$ ranging from 0 to 0.8 mass%.

The application of the LA-ICP-MS technique to the quantitative analysis of the composition of complex inclusions, which have different size, is useful to the understanding of the mechanism of inclusion formation. The measurement of the size distribution of inclusions by LA-ICP-MS will be presented in proceeding article.

8. Conclusions

Total ($M_{total}$) and insoluble ($M_{insol}$) contents of Ti and Al in Fe–M, Fe–10mass%Ni–M, and Fe–0.2mass%C–M (M=Ti, Al, and Ce) alloys obtained by LA-ICP-MS are compared with those from chemical analysis. The compositions of synthetic particles and complex inclusions analyzed by LA-ICP-MS are compared with those from EPMA and chemical analysis. The following conclusions were obtained:

1. Total and insoluble contents of elements in metal obtained by LA-ICP-MS agree reasonably well with those from chemical analysis. Total and insoluble contents of elements in metal from the LA-ICP-MS analysis approach the values from chemical analysis with increasing the weight of ablated metal.

2. The compositions of homogeneous particles ob-
tained by LA-ICP-MS agree well with those from EPMA and chemical analysis. The LA-ICP-MS analysis of inclusion composition is considered to be superior to EPMA for heterogeneous complex inclusions.

REFERENCES

1) Y. Ishibashi: ISIJ Int., 37 (1997), 885.
2) T. Mochizuki, A. Sakashita, T. Tsuji, H. Iwata, Y. Ishibashi and N. Gunji: Anal. Sci., 7 (1991), 479.
3) J. W. Hager: Anal. Chem., 61 (1989), 1243.
4) T. Mochizuki, A. Sakashita, H. Iwata, T. Tagaya, T. Shimamura and P. Blair: Anal. Sci., 4 (1988), 403.
5) P. Arrowsmith: Anal. Chem., 59 (1987), 1437.
6) T. Akiyoshi, A. Sakashita, Y. Ishibashi and T. Mochizuki: CAMP-ISIJ, 10 (1997), 706.
7) J. S. Becker and H. J. Dietze: Fresenius’ J. Anal. Chem., 365 (1999), 429.
8) F. Vanhaecke and L. Moens: Fresenius’ J. Anal. Chem., 364 (1999), 440.
9) D. Güntner, S. E. Jackson and H. P. Longerich: Spectrochim. Acta, 54B (1999), 381.
10) K. Simon, U. Wiechert, J. Hoefs and B. Grote: Fresenius’ J. Anal. Chem., 359 (1997), 458.
11) M. D. Norman, N. J. Pearson, A. Sharma and W. L. Griffin: Geostand. Newsl., 20 (1996), 247.
12) F. E. Lichte: Anal. Chem., 67 (1995), 2479.
13) A. V. Karasev and H. Suito: Metall. Mater. Trans. B, 30B (1999), 249.
14) M. Kishi, R. Inoue and H. Suito: ISIJ Int., 34 (1994), 859.
15) Y. Kawashita and H. Suito: ISIJ Int., 35 (1995), 1468.