Simultaneous Determination of the Composition and Size of Oxide Particles in Solid Materials by Laser Ablation-Inductively Coupled Plasma Mass Spectrometry

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Laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) has been used for the determination of the composition and size of oxide particles consisting of SiO₂, MnO, Al₂O₃, MgO and CaO on the surface of a glass or metal sample. The composition and size of multicomponent oxide particles such as MnO-SiO₂, CaO-Al₂O₃ and CaO-Al₂O₃-MgO evaluated by LA-ICP-MS are compared with those obtained by chemical analysis and by SEM observation. It is confirmed that LA-ICP-MS method has prospects to be applied for quick and simultaneous measurement of the composition and size of particles on the surface of metals in steelmaking industry. The difference between the particle size determined by LA-ICP-MS and that by SEM ranges from 6 to 13% on an average in the range of $d_v = 7\sim 40\mu\text{m}$.

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1. Introduction

It is well known that the particles, which present as inclusion in high quality materials such as steels and alloys, influence considerably their mechanical properties. Therefore, the development of a rapid and accurate method for simultaneous determination of composition, size and number of particles is necessary for the quality control of these materials, especially during those continuous productions.

The laser ablation-inductively coupled plasma-atomic emission spectrometry (LA-ICP-AES) and the laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) are known as the well-accepted analytical techniques in view of the quick analysis of solid samples with high precision,¹⁻¹⁶⁾ which was reported as approximately 5 to 10% for most of elements.^{5,11)} The utilization of these methods has been reported often for direct analysis of total composition of steels,^{1-5,11,14)} ceramics and rocks^{7,9,10,16)} and for determination of element segregation in minerals and rocks.^{6,8,12,13,15,16)} Mochizuki *et al.*,³⁾ Akiyoshi *et al.*⁴⁾ and Ishibashi^{5,11,14)} investigated the favorable condition of the laser ablation in detail, and applied LA-ICP-AES to the *in-situ* analysis of steel matrix in steelmaking plant.

In previous reports,¹⁷⁻¹⁹⁾ it was concluded that LA-ICP-MS can be successfully applied to the composition and size determination of oxide particles containing Al₂O₃, MgO and CaO in metals and alloys deoxidized with Al, Mg and Ca. However, the other elements such as Si, Mn and Ti are used also often in steelmaking processes for deoxidation and alloying. In this study, the results of previous investigations¹⁷⁻¹⁹⁾ are summarized, and then supplemented with respect to the application of LA-ICP-MS method to the analysis of composition and size of one component and multicomponent particles consisting of Al, Mg, Ca, Mn and Si oxides. For this purpose, the calibration lines for Si and Mn have been obtained. The results of particle composition and size measured by using LA-ICP-MS are compared with those by chemical analysis and SEM. An error of particle size measurement by LA-ICP-MS is estimated for particles in the range of $d_v = 7\sim 40\mu\text{m}$.

2. Experimental

2.1 Instrumentation

An inductively coupled plasma mass spectrometer (Hewlett-Packard HP-4500) combined with a laser ablation system (CETAC LSX-100) is used. In laser ablation system, the Nd:YAG laser is operated in Q-switched mode. A sample in a chamber is irradiated by a laser under Ar carrier gas. The laser beam melts the surface of analyzed sample, ablates and forms fine aerosols. The sample aerosols are swept on a stream of Ar carrier gas directly to the ICP and are ionized by plasma. Then, number of ions for each element is determined by mass spectrometry. The CCD camera system with magnification from 20 to 200 make possible to observe the process of melting and ablation of material on a sample surface in chamber of LA-ICP-MS. The basic instrumental conditions and operating parameters are listed in Table 1. Detailed description of the LA-ICP-MS system was given elsewhere.¹⁷⁾

2.2 Standard sample for determination of particle composition

Mochizuki *et al.*²⁰⁾ developed a new method in the utilization of aqueous standard solutions to the calibration of alloying element contents in low alloy steels, which was determined by LA-ICP-AES, but solid standard samples such as glasses and metals have been used usually in LA-ICP-AES and LA-ICP-MS. Because the heterogeneity of commercial glass and metal standard samples was observed in our preliminary experiment, standard glass samples were synthesized as follows: The glass samples of 13% NiO-72% B₂O₃-15% Li₂O and 60% SiO₂-21% B₂O₃-19% Li₂O (in mass%) with different contents of M_xO_y (M = Mn, Si, Al, Mg, Ca, Ti and Fe), which used for the analysis of particle composition, were prepared as follows: A mixture (10 g) of pure B₂O₃, Li₂CO₃ and NiO or SiO₂ powders was melted in a Pt dish at 950°C and held for 30 minutes at this temperature. This melt was stirred by a pure iron rod at interval of 10 minutes for homogenization. Then, an appropriate amount of M_xO_y powders was added to the melt, followed by stirring for 10

Table 1 Instrumental conditions and operating parameters.

ICP-MS	
RF power/W	1100
Ar-gas flow rates/L·min ⁻¹	
plasma	15.0–16.0
auxiliary	1.0–1.1
carrier	1.4
Integration time/s	0.1
Laser Ablation	
Type of laser	Nd:YAG
Wavelength/nm	266 (UV light)
Laser scan rate/mm·s ⁻¹	0.01
Frequency of the laser shot/Hz	20
Laser energy/mJ·shot ⁻¹	2.0–3.0
Defocus of laser beam/mm	0

seconds. After cooling, this sample was crushed, melted again and held for 30 minutes at 950°C. This procedure was repeated 5 times for homogenization. Homogeneity of glass composition for each sample was examined by LA-ICP-MS. These samples are used as the laboratory standards for the quantitative analysis of particle composition.

2.3 Standard sample for measurement of particle size

In order to obtain the relationship between the particle size and the Al intensity peak²¹⁾ during optical emission spectrometry, the standard sample for the measurement of particle size was prepared by sintering the mixture of classified Al₂O₃ particles with pure iron powder using a hot isostatic pressure (HIP) method. In present work, the samples containing synthetic particles on a surface were prepared as follows: Synthetic material of MnO·SiO₂ and 2MnO·SiO₂ were obtained by melting a pressed mixture of appropriate amount of MnO and SiO₂ powders at 1520°C for 5 minutes under an Ar atmosphere in a Mo crucible, followed by quenching on a water cooled copper plate. After crushing and sieving, the synthetic particles with the size of 7 to 40 µm were pasted with a double-coated carbon adhesive tape on a pure copper holder (99.999% Cu).

Synthetic particles such as CaO·2Al₂O₃ (CA₂), CaO·Al₂O₃ (CA), 12CaO·7Al₂O₃ (C₁₂A₇), 3CaO·Al₂O₃ (C₃A), and MgO·Al₂O₃ (MA) were obtained by sintering a pressed mixture of appropriate amount of CaCO₃ or MgO and Al₂O₃ powders at 1300°C for 72 h in a Pt crucible. Particles of 35% CaO·57% Al₂O₃·8% MgO (CAM) were obtained by melting a mixture of CaCO₃, Al₂O₃ and MgO powders at 1580°C for 10 minutes in an induction furnace by using a MgO crucible, followed by quenching on water cooled copper plate. After crushing and sieving, the particles in the range of $d_v = 7\sim 40\mu\text{m}$ were placed on one end of a copper cylindrical rod and then pressed on the glass (60% SiO₂·21% B₂O₃·19% Li₂O), which was previously melted at 950°C. The photomicrographs of synthetic particles on a surface of glass sample are shown in Fig. 1.

The glass samples with pure Al₂O₃ and MgO particles on a surface were prepared in the same procedure. The standard powders of white fused alumina (JIS Z 8901-No. 3, 4 and 5, Al₂O₃ ≥ 99%) with the size of 7 ± 2 , 13 ± 3 and $27 \pm 6\mu\text{m}$

Fig. 1 Synthetic particles on surface of glass sample and position of intended track during laser ablation.

were used as pure Al₂O₃ particles. The pure MgO particles in the size range of 10 to 40 µm were obtained by crushing and sieving of high purity MgO crucible (MgO ≥ 99%).

Unfortunately, the particles with $d_v < 5\mu\text{m}$ on a surface of sample are usually difficult to detect and identify by using the present optical system of LA-ICP-MS. Therefore, the synthetic glass sample with Al₂O₃ or MgO particles, whose diameters are smaller than 5 µm, was not used to obtain the calibration lines for particle size analysis in this study. For the individual ablation of each particle and to obtain the clear isolate peak on an ion intensity chart, the particles on a sample surface were dispersed more than 0.2 mm apart. Moreover, the particles must be strongly fixed on the sample surface during laser ablation in order to obtain the reliable calibration lines for particle size analysis by LA-ICP-MS.

The samples with pure Al₂O₃ and MgO particles on surface of copper holder and glass were used to obtain the size calibration lines.

2.4 Analytical procedure

The laboratory standard glass samples and particles on glass or metal surface are ablated in horizontal direction only along the X axis. In this case, the laser beam is moved at a constant speed of 0.01 mm/s by keeping the focus on sample

surface. For the generation of a continuous and stable melting of material during ablation, the samples were ablated by using the laser energy of 2.0 to 3.0 mJ/shot and frequency of the laser shot of 20 Hz. The length of laser tracks by ablation of each glass standard sample was 1 mm.

In order to obtain a clear relationship between the particle size and ion intensity of isotopes by LA-ICP-MS analysis, the width and depth of laser track must be larger than the ablated particle, as shown in Fig. 1(a). For the ablation of whole particle, the depth and width of laser track can be changed in the ranges of 15 to 105 μm and of 10 to 45 μm , respectively, by the variation of energy and the defocus of laser beam.¹⁷⁾ In present investigation, the laser energy was 2.0 mJ/shot for the particles with $d_v < 20 \mu\text{m}$ and 3.0 mJ/shot for that with $d_v = 20 \sim 40 \mu\text{m}$. In these cases, the width of laser track after ablation is 25 and 45 μm , respectively. The length of laser tracks was fixed as 0.5 and 1.0 mm for particles smaller and larger than 20 μm , respectively.

Marking of $2 \times 2 \text{ mm}$ squares was made on surface of a sample in order to identify easily the location of particles. Prior to laser ablation, each particle was observed by optical (OM) or scanning electron (SEM) microscopy at a magnification of 1000. The size of particles on photomicrograph was estimated by using an image analyzer as a diameter of circle having the same area as a measured particle (Heywood diameter). Then, the sample was set up into the laser ablation chamber. By using the optical system of LA-ICP-MS, the particles on a sample surface, whose sizes were estimated previously by SEM or OM, are detected and identified. The sample in the chamber is moved horizontally along the X or Y axis so that the analyzed particle is placed through the center of the intended laser track, as shown in Fig. 1. The initial point of laser track was positioned at a distance of 150 to 200 μm from the particle (Fig. 1(b)). The operating parameters of laser ablation were selected so that the width of laser track was more than the size of this particle. Moreover, only one particle was ablated in each laser track to provide a clear ion intensity peak of isotopes for size calibration line. In the LA-ICP-MS measurement, the size of analyzed particle was estimated as spatial diameter of hypothetical sphere having the same volume as an ablated particle.

2.5 Chemical analysis

The total contents of elements in laboratory standard glass samples and those in synthetic materials of $\text{MnO} \cdot \text{SiO}_2$ and $2\text{MnO} \cdot \text{SiO}_2$ were analyzed by using the inductively coupled plasma-atomic emission spectrometer (ICP-AES) after fusion of 0.1 g of sample with 1 g of ultrapure-grade Na_2CO_3 , followed by dissolution in the mixture of 10 cm^3 of hot HCl (1+1) and 5 cm^3 of HNO_3 (1+1).

3. Results and Discussion

3.1 Determination of particle composition

The chemical compositions of the laboratory standard glass samples with different concentration of added oxides are given in Table 2. The samples (St-0 to St-5), whose matrix glass contains 13% NiO -72% B_2O_3 -15% Li_2O , were used for the analysis of complex particles containing SiO_2 . The other standard samples (St-6 to St-11), whose matrix

Table 2 Chemical composition of laboratory standard samples.

Sample No.	Content of elements/mass%						
	Mn	Si	Al	Mg	Ca	Ti	Fe
St-0*	0.001	0.010	0.003	<0.001	0.010	<0.001	0.012
St-1*	0.034	0.022	0.042	0.035	0.047	0.034	0.085
St-2*	0.072	0.065	0.086	0.069	0.086	0.065	0.161
St-3*	0.156	0.136	0.162	0.132	0.148	0.166	0.172
St-4*	0.315	0.298	0.354	0.289	0.315	0.342	0.367
St-5*	0.441	—	0.532	0.456	0.402	0.547	0.570
St-6**	—	—	0.016	0.008	0.027	0.003	0.002
St-7**	0.009	—	0.025	0.010	0.031	0.011	0.022
St-8**	—	—	0.024	0.022	0.031	0.028	0.016
St-9**	0.058	—	0.096	0.051	0.081	0.043	0.067
St-10**	0.074	—	0.084	0.083	0.103	0.077	0.052
St-11**	0.101	—	0.121	0.111	0.136	0.105	0.070

Composition of glass: * 13% NiO -72% B_2O_3 -15% Li_2O , ** 60% SiO_2 -21% B_2O_3 -19% Li_2O .

Fig. 2 Ion intensity chart by laser ablation of laboratory standard glass sample (a) and $\text{MnO} \cdot \text{SiO}_2$ particle (b).

glass contains 60% SiO_2 -21% B_2O_3 -19% Li_2O , were used for the analysis of particles not containing SiO_2 . The homogeneity of the element content in each glass sample was examined previously by LA-ICP-MS. The typical ion intensity chart by laser ablation of sample St-2 is plotted in Fig. 2(a). It is seen that the ion intensity levels of ^{27}Al , ^{28}Si and ^{55}Mn isotopes are higher in initial 20 seconds. This is because the melting zone of laser track is not stable in the initial period of ablation. The ion intensity level becomes almost constant after 30 seconds. The finding that the ion intensity peaks, which correspond to the ablated particles, are not present suggests that the analyzed elements in a glass sample are dissolved homogeneously. The same results were obtained for other elements by the examination of each sample. Therefore, it is concluded that the present glass samples can be used as the laboratory standards for the quantitative analysis of the composition of oxide particles.

Fig. 3 Schematic diagram of ion intensity peaks by ablation of complex MnO-SiO₂ particle.

More detail is given elsewhere.¹⁷⁾ The mean ion intensity for each isotope ($\bar{I}_M$) corresponds to total content of element M in an ablated zone of sample. The $\bar{I}_M$ value is calculated as the average ion intensity in the period of ablation time from 30 to 100 s.

The representative ion intensity chart for ²⁸Si and ⁵⁵Mn isotopes at the ablation of MnO-SiO₂ particle is shown in Fig. 2(b). A schematic diagram of ion intensity peak obtained by ablation of one complex particle consisting of MnO and SiO₂ is shown in Fig. 3. The gray-colored area of the peak for each element, A_M^p , is proportional to the amount of M element in an ablated particle and calculated as eq. (1).

$$A_M^p = \sum_{i=1}^n I_{M,i}^p - \bar{I}_{M,blank} \cdot n \quad (1)$$

where $I_{M,i}^p$ is the ion intensity value of i -th segment in a peak for M isotope, n is the total number of the ion intensity segments in a peak, and $\bar{I}_{M,blank}$ is the average ion intensity of M element for the matrix. The high level of $\bar{I}_{Si,blank}$ for ²⁸Si isotope in Fig. 2(b) can be explained by the additional effect of CO, N₂ and some other ions which have the same mass number of 28.

The composition and size of oxide particle can be determined by using the respective calibration lines and A_M^p values for all elements. The detailed description for the calculation of intensity peak area is described elsewhere.^{17,18)}

The calibration lines for the analysis of particle composition are obtained by the ablation of samples St-0 to St-5 using the same parameters. The correlation between mean ion intensity levels of ²⁴Mg, ²⁷Al, ²⁸Si, ⁵⁵Mn, ⁴³Ca, ⁴⁷Ti and ⁵⁷Fe isotopes and total contents of these elements in glass samples is shown in Fig. 4. It is seen that the mean ion intensity of each isotope increases linearly with increasing the element content. The data points fall reasonably well on the appropriate lines. It can be said from these results that the mean ion intensity signal for M isotope is in direct proportion to the content of M element in matrix or oxide particles.

Fig. 4 Correlation between mean ion intensity of isotope and content of elements in laboratory standard glass samples.

The calibration line for M element, which is obtained by ablation of the laboratory standard glass samples, can be expressed by

$$\bar{I}_M^{st} = \alpha_M^{st} + \beta_M^{st} \cdot [\% M]^{st} \quad (2)$$

where $\bar{I}_M^{st}$ and $[\% M]^{st}$ are the mean ion intensity of isotope and the total content of M element in the standard glass sample, respectively, and the values for α_M^{st} and β_M^{st} are constant for the calibration line of M element. As shown in Fig. 4, the calibration lines for ²⁴Mg, ²⁷Al, ⁵⁵Mn, ⁴⁷Ti and ⁵⁷Fe start from origin. In this case, the value for α_M^{st} equals to 0 or has an insignificant value. However, the value for α_M^{st} for ²⁸Si and ⁴³Ca calibration lines has considerable value due to the additional effect of other isotopes with the same mass number of ion. In this study, the calibration lines for Si and Mn are obtained as follows:

$$\bar{I}_{Si}^{st} = 1.989 \times 10^6 + 8.154 \times 10^6 [\% Si]^{st} \quad r = 0.995 \quad (3)$$

$$\bar{I}_{Mn}^{st} = 0.136 \times 10^6 + 13.85 \times 10^6 [\% Mn]^{st} \quad r = 0.996 \quad (4)$$

The lines given by eqs. (3) and (4) in which r represents the correlation coefficient were used as the calibration lines for the analysis of MnO-SiO₂ particles. Similar relationships with reasonably large correlation coefficients (0.925 to 0.995) were obtained for the calibration lines of the others elements.

It should be noted that the relationship between mean ion intensity and total content of element is dependent on the factors such as the condition of LA-ICP-MS system and the operating parameters by ablation. The change of ion intensity signal during long operation time can be eliminated by using the following time correction factor. The corrected ion intensity of isotope for M element, $I_{M,t}$, can be estimated by the following equation assuming the linear decrease of ion intensity signal with time:

$$I_{M,t} = I_{M,tj} \cdot ft_{M,tj} = I_{M,tj} \cdot I_{M,t1}^{st} / \{ \bar{I}_{M,t1}^{st} - (\bar{I}_{M,t1}^{st} - \bar{I}_{M,t2}^{st}) \cdot (t_j - t_1) / (t_2 - t_1) \} \quad (5)$$

where $I_{M,tj}$ and $f_{tM,tj}$ are the ion intensity of isotope in an analyzed sample and the time correction factor, respectively, at a given time t_j , and $\bar{I}_{M,t1}^{\text{st}}$ and $\bar{I}_{M,t2}^{\text{st}}$ are the mean ion intensities in a laboratory glass standard at time t_1 and t_2 , respectively. The analysis of the same laboratory glass standard was repeated at the same operating parameters every 60 minutes for the correction of the sample data.

In order to ablate whole synthetic particle large than $20\mu\text{m}$, the laser energy was increased to 3.0 mJ/shot . In this case, the width and depth of laser track were about 45 and $90\mu\text{m}$, respectively. Since the volume of ablated material (matrix and particle) increases, the ion intensity of analyzed isotope also increases. The data obtained at different laser energy are corrected by using the following parameter correction factor:

$$I_{M,p} = I_{M,p2} \cdot f_{pM,p2} = I_{M,p2} \cdot \bar{I}_{M,p1}^{\text{st}} / \bar{I}_{M,p2}^{\text{st}} \quad (6)$$

where the values for $I_{M,p2}$ and $f_{pM,p2}$ are the ion intensity of isotope and the parameter correction factor, respectively, for M element at a given set of operating parameters $p2$. The values for $\bar{I}_{M,p1}^{\text{st}}$ and $\bar{I}_{M,p2}^{\text{st}}$ are the mean ion intensities of isotope in the same laboratory glass standard obtained at different sets of operating parameters $p1$ and $p2$, respectively.

The content of each element M in a homogeneous or heterogeneous multicomponent particle, $[\%M]^p$, is in direct proportion to the area of ion intensity peak and can be evaluated from eq. (1) and eq. (2) as follows:

$$[\%M]^p = A_M^p / \beta_M^{\text{st}} \quad (7)$$

The content of M_xO_y oxide in a particle can be calculated from $[\%M]^p$ value by using the molecular weight of M_xO_y and the atomic weight of M element. The final composition of ablated particle is obtained by recalculating the sum of all oxide components to 100 percentages. More detailed description of calculation of particle composition by LA-ICP-MS analysis is given elsewhere.^{17,18)}

The final contents of SiO_2 and MnO in synthetic MnO-SiO_2 particles measured by LA-ICP-MS are compared with those from chemical analysis in Fig. 5(a). The Al_2O_3 and MgO contents in synthetic particles such as $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and $35\% \text{ CaO} \cdot 57\% \text{ Al}_2\text{O}_3 \cdot 8\% \text{ MgO}$ on surface of a glass sample are measured by LA-ICP-MS. These values are plotted against those from chemical analysis in Fig. 5(b). The error bar in Figs. 5(a) and 5(b) represents the arithmetic standard deviation of oxide content in several particles of the same synthetic material measured by LA-ICP-MS analysis. It can be seen in Fig. 5 that the concentrations of oxides in particles determined by LA-ICP-MS agree reasonably well with those by the chemical analysis. However, it should be pointed out that the arithmetic standard deviation for MnO-SiO_2 particles ($\pm 8\%$) is not so small as for most other synthetic materials. This can be explained by the slight heterogeneity of composition among the synthetic MnO-SiO_2 particles.

3.2 Determination of particle size

The size of one component oxide particle (M_xO_y) can be estimated from the area of the ion intensity peak for M element, A_M^p , in ablated particle (see Fig. 2(b)) by using a size calibration line for M element. This calibration line is

Fig. 5 Comparison of oxide content in synthetic particles obtained from LA-ICP-MS with that from chemical analysis. (a) MnO-SiO_2 and (b) $\text{CaO-Al}_2\text{O}_3$, $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ and $\text{MgO-Al}_2\text{O}_3$ particles.

obtained by the individual ablation of more than 10 M_xO_y particles with known size. It was found in a previous study¹⁸⁾ that A_M^p value is proportional to the amount of this element in an ablated oxide particle, m_M^p , and expressed as eq. (8).

$$A_M^p = k_M^{\text{st}} \cdot m_M^p \quad (8)$$

where k_M^{st} is a constant estimated from the slope of size calibration line for M element.

By assuming that an ablated particle is spherical, the mass of one component in M_xO_y particle, $m_{M_xO_y}^p$, can be estimated as follows:

$$m_{M_xO_y}^p = v_{M_xO_y}^p \cdot \rho_{M_xO_y} = \pi/6 \cdot d_{V,M_xO_y}^3 \cdot \rho_{M_xO_y} \quad (9)$$

where $v_{M_xO_y}^p$, $\rho_{M_xO_y}$ and d_{V,M_xO_y} are the volume, density and spatial diameter of a M_xO_y particle, respectively. Moreover, the $m_{M_xO_y}^p$ value of an analyzed particle can be expressed by eq. (10).

$$\begin{aligned} m_{M_xO_y}^p &= m_M^p \cdot \text{MW}_{M_xO_y} / (x \cdot \text{AW}_M) \\ &= A_M^p / k_M^{\text{st}} \cdot \text{MW}_{M_xO_y} / (x \cdot \text{AW}_M) \end{aligned} \quad (10)$$

where $\text{MW}_{M_xO_y}$ and AW_M are the molecular mass of M_xO_y and the atomic mass of M element, respectively. x is the number of atoms of M element in M_xO_y molecule.

The relationship between the A_M^p value and size of one component oxide particle can be evaluated from eqs. (9) and (10) as follows:

$$\begin{aligned} A_M^p &= (\pi/6 \cdot x \cdot \text{AW}_M \cdot k_M^{\text{st}} \cdot \rho_{M_xO_y} / \text{MW}_{M_xO_y}) \cdot d_{V,M_xO_y}^3 \\ &= c_M \cdot d_{V,M_xO_y}^3 \end{aligned} \quad (11)$$

where c_M is a constant which can be estimated from the slope of size calibration line for M element.

The correlation between the A_M^p and d_{V,M_xO_y} values for the ^{28}Si and ^{55}Mn isotopes in MnO-SiO_2 and 2MnO-SiO_2 particles and for ^{27}Al isotope in Al_2O_3 , $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ and $35\% \text{ CaO} \cdot 57\% \text{ Al}_2\text{O}_3 \cdot 8\% \text{ MgO}$ particles are shown in Fig. 6. The obtained relationships for Si, Mn and Al are expressed by

Fig. 6 Correlation between area of ion intensity peak and size of SiO_2 , MnO and Al_2O_3 particles.

$$A_{\text{Si}}^{\text{P}} = 20470 (d_{\text{V},\text{SiO}_2})^{2.58} \quad r = 0.927 \quad (12)$$

$$A_{\text{Mn}}^{\text{P}} = 56840 (d_{\text{V},\text{MnO}})^{2.99} \quad r = 0.965 \quad (13)$$

$$A_{\text{Al}}^{\text{P}} = 66620 (d_{\text{V},\text{Al}_2\text{O}_3})^{3.04} \quad r = 0.985 \quad (14)$$

The relationship for Al expressed by eq. (14) was obtained with consideration for results of previous reports^{18,19} and new data of present study. Some scattering of the data points from the lines in Fig. 6 is due to the error arising from the estimation of size for irregular particles from the equivalent-area diameter. The correlation between the A_{Mg}^{P} and $d_{\text{V},\text{MgO}}$ values for the ^{24}Mg isotope by LA-ICP-MS analysis of pure MgO particles are obtained in previous study¹⁸ and can be written in similar form

$$A_{\text{Mg}}^{\text{P}} = 67040 (d_{\text{V},\text{MgO}})^{3.04} \quad r = 0.972 \quad (15)$$

It can be seen that the correlation between the A_{M}^{P} and $d_{\text{V},\text{M}_x\text{O}_y}$ values obtained experimentally with reasonably large correlation coefficients (0.927 to 0.985) and expressed by eqs. (12) to (15) have a similar shape with eq. (11). These relationships for Si, Mn, Al and Mg were used in present study as calibration lines for the size determination of oxide particles containing SiO_2 , MnO, Al_2O_3 and MgO.

The total mass of a homogeneous multicomponent oxide particle, $m_{\text{V},\text{hom}}^{\text{P}}$, such as $\text{MnO} \cdot \text{SiO}_2$ or $2\text{MnO} \cdot \text{SiO}_2$, can be calculated by using the values of mass, $m_{\text{M}_x\text{O}_y}^{\text{P}}$, and concentration, $[\% \text{M}_x\text{O}_y]^{\text{P}}$, for one oxide component of this particle

$$m_{\text{V},\text{hom}}^{\text{P}} = m_{\text{M}_x\text{O}_y}^{\text{P}} / [\% \text{M}_x\text{O}_y]^{\text{P}} \times 100\% \quad (16)$$

In this case, the diameter of this particle in 3-D, $d_{\text{V},\text{hom}}$, can be evaluated from eqs. (10), (11) and (16) as follows:

$$d_{\text{V},\text{hom}} = (6/\pi \cdot m_{\text{V},\text{hom}}^{\text{P}} / \rho_{\text{hom}})^{1/3} \\ = (100/[\% \text{M}_x\text{O}_y]^{\text{P}} \cdot \rho_{\text{M}_x\text{O}_y} / \rho_{\text{hom}} \cdot A_{\text{M}}^{\text{P}} / c_{\text{M}})^{1/3} \quad (17)$$

where ρ_{hom} is the density of a homogeneous particle ($= 3.77 \times 10^{-3} \text{ g/mm}^3$ for $\text{MnO} \cdot \text{SiO}_2$ and $4.12 \times 10^{-3} \text{ g/mm}^3$ for $2\text{MnO} \cdot \text{SiO}_2$). In accordance with eq. (17), the sizes of any homogeneous complex oxide particles with known density, ρ_{hom} , can be estimated from LA-ICP-MA analysis by using values of $[\% \text{M}_x\text{O}_y]^{\text{P}}$, A_{M}^{P} and c_{M} , which can be obtained from composition and size calibration lines for one of oxide component in this particle.

In the case of LA-ICP-MS analysis for a heterogeneous multiphase particle or homogeneous complex particle with unknown density such as $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{MgO}$, it is assumed that total volume of particle, $V_{\text{het}}^{\text{P}}$, is equal to the sum of volumes for all oxide components ($V_{\text{het}}^{\text{P}} = V_{\text{CaO}}^{\text{P}} + V_{\text{Al}_2\text{O}_3}^{\text{P}} + V_{\text{MgO}}^{\text{P}}$). The size of this particle, $d_{\text{V},\text{het}}$, is estimated by eq. (18).

$$d_{\text{V},\text{het}} = (6/\pi \cdot V_{\text{het}}^{\text{P}})^{1/3} = \{6/\pi (m_{\text{CaO}}^{\text{P}} / \rho_{\text{CaO}} + m_{\text{Al}_2\text{O}_3}^{\text{P}} / \rho_{\text{Al}_2\text{O}_3} + m_{\text{MgO}}^{\text{P}} / \rho_{\text{MgO}})\}^{1/3} \quad (18)$$

where $m_{\text{CaO}}^{\text{P}}$, $m_{\text{Al}_2\text{O}_3}^{\text{P}}$ and $m_{\text{MgO}}^{\text{P}}$ are the mass of CaO, Al_2O_3 and MgO oxides in an ablated heterogeneous particle, respectively, and ρ_{CaO} , $\rho_{\text{Al}_2\text{O}_3}$ and ρ_{MgO} are the density of CaO ($= 3.37 \times 10^{-3} \text{ g/mm}^3$), Al_2O_3 ($= 3.97 \times 10^{-3} \text{ g/mm}^3$) and MgO ($= 3.65 \times 10^{-3} \text{ g/mm}^3$), respectively. The comparison of results obtained from eq. (17) and eq. (18) for complex particles such as $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, $3\text{CaO} \cdot \text{MgO} \cdot 2\text{Al}_2\text{O}_3$, $\text{MgO} \cdot \text{SiO}_2$, $\text{MnO} \cdot \text{SiO}_2$, $2\text{MnO} \cdot \text{SiO}_2$ and some others, whose densities are known, showed that the difference between the d_{V} values calculated from these equations is not greater than 10%. Therefore, eq. (18) can be used with sufficient accuracy for estimation of size not only for heterogeneous multiphase particles, but also for homogeneous complex particles with unknown density.

When the particle composition is already determined by using appropriate calibration lines, the $m_{\text{CaO}}^{\text{P}}$ and $m_{\text{MgO}}^{\text{P}}$ values can be expressed by using $m_{\text{Al}_2\text{O}_3}^{\text{P}}$ value as follows:

$$m_{\text{CaO}}^{\text{P}} = [\% \text{CaO}]^{\text{P}} / [\% \text{Al}_2\text{O}_3]^{\text{P}} \cdot m_{\text{Al}_2\text{O}_3}^{\text{P}} \quad (19)$$

$$m_{\text{MgO}}^{\text{P}} = [\% \text{MgO}]^{\text{P}} / [\% \text{Al}_2\text{O}_3]^{\text{P}} \cdot m_{\text{Al}_2\text{O}_3}^{\text{P}} \quad (20)$$

where $[\% \text{CaO}]^{\text{P}}$, $[\% \text{Al}_2\text{O}_3]^{\text{P}}$ and $[\% \text{MgO}]^{\text{P}}$ are the content of CaO, Al_2O_3 and MgO oxides in the analyzed particle, respectively.

By substituting eqs. (10), (11), (19) and (20) into eq. (18), the size of heterogeneous particle, $d_{\text{V},\text{het}}$, can be written as follows:

$$d_{\text{V},\text{het}} = (A_{\text{Ca}}^{\text{P}} / c_{\text{Ca}} + A_{\text{Al}}^{\text{P}} / c_{\text{Al}} + A_{\text{Mg}}^{\text{P}} / c_{\text{Mg}})^{1/3} \\ = \{([\% \text{CaO}]^{\text{P}} / [\% \text{Al}_2\text{O}_3]^{\text{P}} \cdot \rho_{\text{Al}_2\text{O}_3} / \rho_{\text{CaO}} + 1 + [\% \text{MgO}]^{\text{P}} / [\% \text{Al}_2\text{O}_3]^{\text{P}} \cdot \rho_{\text{Al}_2\text{O}_3} / \rho_{\text{MgO}}) \cdot A_{\text{Al}}^{\text{P}} / c_{\text{Al}}\}^{1/3} \quad (21)$$

In accordance with eq. (21), the size of any heterogeneous multiphase particles or homogeneous complex particles with unknown density can be estimated from LA-ICP-MA analysis by using the content of all oxides in ablated particle and A_{M}^{P} and c_{M} values which can be obtained from size calibration lines for one of oxide component of this particle.

The comparison of particle size determined by LA-ICP-MS with that by SEM observation is shown in Fig. 7. In Fig. 7(a), the diameters, d_{V} , of $\text{MnO} \cdot \text{SiO}_2$ and $2\text{MnO} \cdot \text{SiO}_2$ particles are calculated by using the calibration lines for Si

Table 3 Deviation of particle size measured by LA-ICP-MS from that by SEM.

Composition of particles	Size range of particles (μm)	Calibration line for isotope	Content of MO_x in particles (%)	Average deviation of size measurement	
				(μm)	(%)
2MnO-SiO ₂	8–30	⁵⁵ Mn	70% MnO	1.32 ± 1.03	7.7
MnO-SiO ₂	7–24	⁵⁵ Mn	54% MnO	2.34 ± 1.35	12.5
MnO-SiO ₂	7–24	²⁸ Si	46% SiO ₂	1.52 ± 1.10	8.9
2MnO-SiO ₂	8–30	²⁸ Si	30% SiO ₂	1.62 ± 0.95	8.7
Al ₂ O ₃	9–24	²⁷ Al	100% Al ₂ O ₃	1.34 ± 0.81	8.5
CAM	7–34	²⁷ Al	57% Al ₂ O ₃	1.45 ± 0.95	6.3
12CaO·7Al ₂ O ₃	10–35	²⁷ Al	52% Al ₂ O ₃	1.50 ± 1.04	9.1
MgO	14–37	²⁴ Mg	100% MgO	1.20 ± 0.87	5.8
CAM	7–34	²⁴ Mg	8% MgO	2.25 ± 1.85	9.9

Fig. 7 Comparison of particle size obtained by LA-ICP-MS and that by SEM. (a) MnO-SiO₂ and (b) CaO-Al₂O₃, CaO-Al₂O₃-MgO and MgO-Al₂O₃ particles.

and Mn which are expressed by eq. (12) and eq. (13), respectively. The d_V values for the CaO-Al₂O₃, 35% CaO-57% Al₂O₃-8% MgO and MgO-Al₂O₃ particles shown in Fig. 7(b) are estimated by using the calibration lines for Al and Mg which are expressed by eq. (14) and eq. (15), respectively. It is clear from Fig. 7 that the diameter of particles determined by LA-ICP-MS agrees reasonably well with that obtained by SEM.

The average deviation of particle size measurement by using LA-ICP-MS and that by SEM ($\Delta d_V = d_{V(\text{SEM})} - d_{V(\text{LA-ICP-MS})}$) is given in Table 3 for different pure and complex oxide particles consisting of SiO₂, MnO, Al₂O₃ and MgO. The spatial diameters, d_V , of analyzed particles are in the range of 7 to 37 μm . It can be seen that the difference between the d_V values obtained by LA-ICP-MS using the size calibration lines for Si and Mn and those by SEM is on average 1.3 to 1.6 μm (8–9%) for 2MnO-SiO₂ and 1.5 to 2.3 μm (9–13%) for MnO-SiO₂ particles. The significant Δd_V values obtained in the size estimation of MnO-SiO₂ particles with non-congruent melting can be explained by the nonuni-

form composition due to the precipitation of SiO₂, MnO-SiO₂ and 2MnO-SiO₂ phases during cooling. The difference between the d_V values obtained by LA-ICP-MS using the size calibration lines for Al and Mg and those by SEM is on average 1.3 to 1.5 μm (8–9%) and 1.2 to 2.3 μm (6–10%), respectively. The significant error caused by using the Mg calibration line for LA-ICP-MS analysis of CaO-Al₂O₃-MgO particles is supposed to be due to the small content of MgO (only 8%) in this synthetic material.

It follows from the results given in Table 3 that the Δd_V value for LA-ICP-MS measurement of particle size increases with decreasing the content of M_xO_y oxide in ablated particle by using the size calibration lines for M isotope. Therefore, when M_xO_y is dominant in this particle, the calibration line of major element M should be chosen for the size determination by LA-ICP-MS.

The quantitative analyses of particle size and composition by LA-ICP-MS are carried out based on the difference between concentrations of elements in matrix or background material and that in particles. It is considered that this difference in the case of steel and alloys deoxidized with Si, Mn, Al, Mg, Ca and others deoxidants is suggested to be the range from 10 to 1000 times or more. In this case, the ion intensity peaks of particles obtained by LA-ICP-MS analysis are distinct clear from background level which corresponds to the content of matrix metal. Therefore, the application of LA-ICP-MS in steelmaking industry is one of perspective direction for simultaneous quantitative analysis of the composition and size of inclusion particles in metals. The results, some problems and limitation of LA-ICP-MS method by analysis of particles in real alloys and steels would be discussed in a separate paper.

4. Conclusions

A new analytical approach by using LA-ICP-MS has been developed for the simultaneous quantitative determination of composition and three-dimensional size of oxide particles consisting of SiO₂, MnO, Al₂O₃, MgO and CaO. The method for the preparation of laboratory glass standard samples has been improved. The procedure for the preparation of samples with the synthetic particles fixed on a surface of glass or copper plate was also developed. These samples are used to obtain the calibration lines for analysis

of particle composition and size. It was found that the area of ion intensity peak for each element is linearly proportional to the amount of this element in an ablated particle. The composition and size of multicomponent oxide particles could be determined by using LA-ICP-MS technique and the obtained calibration lines for Si, Mn, Al and Mg. The composition and size of one component and complex synthetic particles measured by LA-ICP-MS are in good agreement with those by chemical analysis and by SEM observation. The difference between the size of multicomponent oxide particles determined by LA-ICP-MS and that by SEM is from 6 to 13% on average in the range of $d_v = 7\sim 40\ \mu\text{m}$. It was confirmed that LA-ICP-MS method has the perspective to be applied for the quick and simultaneous measurement of composition and size of particles on surface of metal and other materials.

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