Characteristics of Particle Size Distribution of Deoxidation Products with Mg, Zr, Al, Ca, Si/Mn and Mg/Al in Fe–10mass%Ni Alloy

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1. Introduction

The particle size distribution of primary deoxidation product has been previously measured in a cross sectional area1–3) and on a film filter after electrolytic extraction4,5) with respect to the particles above 0.5 and 0.1 μm, respectively. Effective utilization of fine oxides as the heterogeneous nucleation sites of transformation and precipitation6,7) and the inhibition of austenite grain growth8,9) has been paid much attention. For these purposes, the control of particle size distribution is of crucial importance for the understanding of particle growth mechanism of coarsening and/or coalescence. It is to be noted that the transformation and precipitation, and the grain growth inhibition by pinning are strongly influenced by the size distribution and dispersion of fine particles.

The information on the mean values of size and chemical composition of particles is not sufficiently enough for the discussion on the improvement of steel properties. For the exact control of microstructure of steel, a knowledge on the distribution of size and chemical composition of particles is required along with that on the particle dispersion in the matrix. The control of solute segregation during solidification and grain boundary segregation and precipitation is also important for the microstructure control. Since the microstructure control by work hardening and subsequent heat treatment cannot be expected in the case of near-net shape casting, positive utilization of fine inclusion particles will be one of the most effective tools for the control of material properties.

Ueshima et al.10) studied the deoxidation of a low carbon steel with Ti, Al, Zr, Y, Hf and Ce and found that the number of oxide particles increases and the particle size decreases with an increase in deoxidation potency. They measured the oxide particles in a cross section with the size of greater than a few μm. There are no reports so far dealing with the size distribution including smaller particles below 1 μm obtained by using different deoxidants.

The present investigation has aimed at establishing the measurement of size distribution and its characteristics of deoxidation particles. For this purpose, an Fe–10mass%Ni alloy was deoxidized with Mg, Zr, Al, Ca, Mn/Si and Mg/Al at 1 873 K, the characteristics of particle size distributions have been studied as a function of holding time, amount of deoxidant and order of deoxidant addition. The peak height in particle size distribution decreases and the modal value increases with increasing holding time. The width of the distribution curve is larger for Al₂O₃ particles and smaller for liquid CaO–Al₂O₃ and MnO–SiO₂ particles. The number of particles increases with an increase of deoxidant for a given initial oxygen content and holding time. In the case of Al followed by Mg deoxidation, the particle size distribution is almost the same as that obtained by only Al. The size distribution in case of Mg followed by Al deoxidation is almost the same as that by only Mg.

KEY WORDS: deoxidation; Mg; Zr; Al; Ca; Si/Mn; Mg/Al; particle size distribution; inclusion.

2. Experimental

2.1. Procedure

Induction furnace (100 kHz) was used for melting experiments. A graphite susceptor with 20 mm thickness was employed around the crucible to aid in melting and to eliminate the melt stirring. A mother alloy was prepared by mixing high purity electrolytic iron (99.99 mass%: % represents mass%, hereinafter) and globular Ni (99.97 %) to obtain an overall composition of Fe–10mass%Ni alloy. The Ni–10%Mg, Fe–10%Zr, Fe–10%Al, Ni–7%Ca and Fe–30%Si–60%Mn alloys prepared by an arc furnace were used as a deoxidant.
An Fe–10%Ni alloy (70 g) in an alumina crucible was first melted at 1 873 K in order to control the initial oxygen content of 100 to 120 mass ppm (ppm represents mass ppm, hereinafter) by keeping the holding time for 30 min and the size of the electrolytic Fe constant. Then, a deoxidant was added by the amount of the initial deoxidant [%Mg]i = 0.1, [%Zr]i = 0.05, [%Al]i = 0.05, [%Ca]i = 0.05, [%Si]i = 0.5 and [%Mn]i = 1, and immediately stirred by an alumina rod for 10 s in order to disperse the primary inclusion particles uniformly. Thereafter, a melt was held for 60, 180, 600 and 1 800 s at 1 873 K and then withdrawn from the furnace, followed by rapid quenching in water. In addition to these experiments the experiments with the initial addition of deoxidants of [%Mg]i = 0.05, [%Zr]i = 0.1 and [%Al]i = 0.1 were also carried out.

2.2. Chemical Analysis

Soluble and Insoluble M: The concentration of solute M dissolved in an Fe–10%Ni alloy ([sol. M]) and that of M as an oxide present in an alloy which is insoluble ([insol. M]) are analyzed by the potentiometric electrolytic extraction method. The electrolyte solution was 10% AA for Zr, Al and Si/Mn deoxidations and 2% TEA for Mg and Ca deoxidations. For the preparation of 10% AA solution, tetramethylammonium chloride (10 g) was dissolved in acetylacetone solution (100 ml), followed by addition of methanol so that total volume becomes 1 L. For the preparation of 2% TEA, tetramethylammonium chloride (10 g) was dissolved in triethanolamine (20 mL), followed by addition of methanol so that total volume becomes 1 L. The extraction of a sample (2 g) was made until total charge reached 1200 coulomb by using potentiostatic electrolytic extraction method (150 mV and 45 to 55 mA). Electrolyte solution was filtered using a membrane filter (open pore size: 0.05 μm). The dissolved amount of a metal sample was about 0.4 g. The solute concentration in solution which corresponds to soluble solute content ([sol. M]) and the residue on a membrane filter which corresponds to insoluble solute content ([insol. M]) as an oxide were analyzed by using inductively coupled plasma (ICP) emission spectrometry. More detail is given elsewhere.\cite{5} The total oxygen content in metal ([T.O]) was analyzed by inert gas fusion–infrared absorptiometry.\cite{11}

2.3. Measurement of Particle Size Distribution

The particle size distribution was measured for the particles obtained as residue on a filter after the electrolytic extraction by the following method: The extraction of a metal sample was made by using a potentiometric electrolytic extraction technique (150 mV and 50 mA) so that the total amount of charge reached 150 coulomb. The amount of dissolved metal was about 0.05 g. The electrolyte solution was filtered by using polycarbonate membrane filter of an open pore size of 0.05 μm (10 mm in diameter). The oxide particles on some part of a film filter were measured by SEM at a magnification of 10 000. The observed area was about 10^4 μm^2, which corresponds to the area of about 0.01% of a film filter. The size and number of particles were analyzed by using an image analyzer for the photomicrograph obtained by SEM, which was enlarged by 2 to 2.5 times. The chemical composition of particles was analyzed for the particles on a film filter by EPMA.

The number of particles per unit volume, N_v, was determined as follows: The metal volume, V_metal, which corresponds to the region measured on a film filter by SEM is given by

\[ V_{metal} = \frac{\Delta W}{\rho_{Fe}} \left( S_{obs} / S_i \right) \]  \( (1) \)

where \( \Delta W \) is the weight of a dissolved sample during electrolytic extraction, \( \rho_{Fe} \) is the metal density (7.8 g·cm\(^{-3}\)), \( S_i \) is the area of a film filter with particles (78.5 mm\(^2\)) and \( S_{obs} \) is the area of a film filter analyzed by SEM.

The \( N_v \) value is expressed by using total number of particles observed by SEM, \( n \), as

\[ N_v = n V_{metal} \]  \( (2) \)

If the number of particles, \( n \), is less than 500, the additional electrolytic extraction was made so that \( n \) becomes greater than 500. The size distributions of particles at center and edge parts as well as the parts between center and edge on a film filter were measured in order to confirm uniformity of dispersed particles on a film filter. As a result, it was found that the particle size distribution was independent of the regions on a film filter. More detailed description is given elsewhere.\cite{1–3}

The planar size distribution of particles in a polished cross section of each sample was also observed in this study. Total observed area of each sample was 0.25 mm\(^2\) which corresponds to the 24 observation areas consisting of the continuous 6 observation areas to the horizontal direction and the continuous 4 observation areas to the vertical direction by using a SEM at the magnification of 1000. More detailed description is given elsewhere.\cite{1–3}

3. Results and Discussion

3.1. Time Dependence of Inclusion Quantity and Chemical Composition

The chemical compositions of metal phases in the deoxidation experiments in which an Fe–10%Ni alloy containing initial oxygen of 100 to 120 ppm was deoxidized with Mg (initial Mg content: [%Mg]i = 0.1), Zr ( [%Zr]i = 0.05), Al ( [%Al]i = 0.05), Ca ( [%Ca]i = 0.05) and Si/Mn (%[Si]i = 0.5 and [%Mn]i = 1) are summarized in Tables 1 and 2.

It was confirmed from X-ray microprobe analysis that the chemical compositions of deoxidation products with Mg, Zr and Al were pure MgO, ZrO\(_2\) and Al\(_2\)O\(_3\), respectively, but those with Ca and Si/Mn deoxidations were 37%CaO–63%Al\(_2\)O\(_3\) and 51%MnO–49%SiO\(_2\), respectively. In the case of Ca deoxidation the chemical composition of 45%CaO–55%Al\(_2\)O\(_3\) was obtained at 1 min holding time at 1 873 K. Morphologies of CaO–Al\(_2\)O\(_3\) and MnO–SiO\(_2\) phases were spherical, which can be understood from the phase diagram in which the compositions of these oxides lie in liquid region. It is interesting to note that a constant composition of CaO–Al\(_2\)O\(_3\) particles was obtained soon after the addition of Ca when an alumina crucible was used.

The relationship between total oxygen content and holding time at 1 873 K is shown in the upper diagram of Fig. 1, indicating that total oxygen contents except for those of Al deoxidation are independent of holding time.

The volume fraction of M\(_2\)O\(_3\) oxide, f(\( V_{chem} \)) can be esti-
mated from the value of insoluble M content, [insol. M], by using the following relationship:

\[ f_{V(chem.)} = \rho_{Fe} \cdot \frac{M_{M,O}}{x_{M}} \cdot \frac{[ppm \text{ insol. M}]}{10^{-6}} \]  (3)

where \( \rho_{Fe} \) is the density of Fe and \( \rho_{M,O} \) is the density of oxide \((\rho_{MgO} = 3.65, \rho_{Al_2O_3} = 3.97, \rho_{ZrO_2} = 6.10, \rho_{CaO} = 3.40, \rho_{MnO} = 5.18 \text{ and } \rho_{SiO_2} = 2.65 \text{ g cm}^{-3})). \( P_{CaO-Al_2O_3} \) and \( P_{MnO-SiO_2} \) are calculated from the relations: \( P_{CaO-Al_2O_3} = X_{CaO} \cdot P_{CaO} + X_{Al_2O_3} \cdot P_{Al_2O_3} \) and \( P_{MnO-SiO_2} = X_{MnO} \cdot P_{MnO} + X_{SiO_2} \cdot P_{SiO_2} \). \( M_{M,O} \) and \( X_{M,O} \) are the molecular weight of \( M_{O} \) and the molar fraction of \( M_{O} \).

The \( f_{V(chem.)} \) values plotted against holding time are shown in the lower diagram of Fig. 1. The \( f_{V(chem.)} \) values for MgO, ZrO_2 and CaO–Al_2O_3 particles are constant, but those for Al_2O_3 and MnO–SiO_2 particles decrease with holding time. These experimental observations demonstrate that Al_2O_3 and MnO–SiO_2 particles are removed by flotation and/or adherence to the crucible wall under the present experimental condition and the detailed discussion on separation mechanism is given in a separate publication.

Dissolved oxygen contents are plotted as a function of dissolved M content in the upper diagram of Fig. 2, in which the equilibria for Mg, Zr and Al deoxidations in an Fe–10mass%Ni alloy are calculated from the respective thermodynamic data.\(^{12-14}\) The chemically analyzed values for M obtained at different holding times are plotted on these calculated lines. It follows from the respective lines that the dissolved oxygen contents for Mg, Zr and Al deoxidations are 0.4 to 1.1, 4.1 and 5.7 ppm at [\%M]_i \leq 0.05, respectively.

The composition of CaO–Al_2O_3 particles is nearly equal to the liquidus composition saturated with CaO–Al_2O_3 at which the activity of Al_2O_3 has been determined as 0.33\(^{16}\) and the thermodynamics on the Al deoxidation in Fe–10%Ni system has been studied by the present authors.\(^{13}\) The activity of SiO_2 at the composition of MnO–SiO_2 particles is determined as 0.8.\(^{16}\) The plot of Al and O contents

**Table 1.** Chemical compositions of metal phases in Mg, Zr and Al deoxidation experiments for Fe–10mass%Ni alloy.

<table>
<thead>
<tr>
<th>Deoxidant</th>
<th>Holding time at 1873 K (s)</th>
<th>[T. O] (Mass ppm)</th>
<th>[M] (Mass ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>0.1% Mg</td>
<td>60</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>75</td>
</tr>
<tr>
<td>ZrO_2</td>
<td>0.05% Zr</td>
<td>60</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>78</td>
</tr>
<tr>
<td>Al_2O_3</td>
<td>0.05% Al</td>
<td>60</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1800</td>
<td>25</td>
</tr>
<tr>
<td>MnO</td>
<td>0.05% Mn</td>
<td>60</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>99</td>
</tr>
<tr>
<td>CaO–Al_2O_3</td>
<td>0.05% Ca</td>
<td>60</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>105</td>
</tr>
<tr>
<td>MnO–SiO_2</td>
<td>0.5% Si</td>
<td>60</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>105</td>
</tr>
<tr>
<td>MgO–Al_2O_3</td>
<td>0.05% Mg</td>
<td>180</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>0.1% Al</td>
<td>180</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>110</td>
</tr>
</tbody>
</table>

**Table 2.** Chemical compositions of metal phases in Ca, Si/Mn and Mg/Al deoxidation experiments for Fe–10mass%Ni alloy.

<table>
<thead>
<tr>
<th>Deoxidant</th>
<th>Holding time at 1873 K (s)</th>
<th>[T. O] (Mass ppm)</th>
<th>CaO–Al_2O_3 (Mass ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO–Al_2O_3</td>
<td>0.05% Ca</td>
<td>60</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>105</td>
</tr>
<tr>
<td>MnO–SiO_2</td>
<td>0.5% Si</td>
<td>60</td>
<td>105</td>
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<td></td>
<td></td>
<td>600</td>
<td>105</td>
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</table>

**Fig. 1.** Effect of holding time at 1873 K on total oxygen content and volume fraction of particles.
and that of Si and O contents are calculated by using the above mentioned activities of Al2O3 and SiO2 together with the respective thermodynamic data. Based on the chemically analyzed values of dissolved Al and Si, the dissolved oxygen contents for Ca and Mn/Si deoxidations are estimated as 7.8 and 70 ppm, respectively.

3.2. Number and Size of Two- and Three-dimensional Particles

Fullman derives the following relationship with respect to the two- and three-dimensional particle diameters.

\[ \bar{d}(\text{art.}) = \frac{\pi}{2} \cdot \bar{d}(\text{har.}) = \frac{\pi}{2} \sum_{i=1}^{n} \left( \frac{1}{d_{i}} \right) \] ..........................(4)

where \( \bar{d}(\text{art.}) \) is the arithmetic mean three-dimensional particle diameter, \( \bar{d}(\text{har.}) \) is the harmonic mean two-dimensional particle diameter, \( d_{i} \) is the diameter of a particle, \( i \), in a cross section and \( n \) is the total number of measured particles. This equation is derived for spherical particles. A similar relation to Eq. (4) for other shapes of particles except for sphere is reported.

The arithmetic mean three-dimensional particle diameter can be obtained from the measured diameter of particles in a cross section by using Eq. (4).

The following relationship between number of particles per unit volume, \( N_{\text{V}} \), and that per unit area, \( N_{\text{A}} \), is given by

\[ N_{\text{V}} = N_{\text{A}}/A_{\text{obs}} \] ..........................(5)

From Eqs. (4) and (5) we obtain

\[ N_{\text{V}} = 2/\pi \cdot N_{\text{A}}/\bar{d}(\text{har.}) \] ..........................(6)

The number of particles per unit volume can be obtained from the measured values for \( \bar{d}(\text{har.}) \) and \( N_{\text{A}} \) by using Eq. (6) and the obtained \( N_{\text{V}} \) value denotes \( N_{\text{V(\text{cal.})}} \).

The values for \( \bar{d}(\text{art.}) \) and \( \bar{d}(\text{har.}) \) can be experimentally obtained from the cross section and filtered methods, respectively. The \( \bar{d}(\text{har.}) \) and \( \bar{d}(\text{har.})/\bar{d}(\text{art.}) \) ratio are plotted against \( \bar{d}(\text{art.}) \) in the upper and lower diagrams of Fig. 3, respectively, which corresponds to the relationship given by Eq. (4). It is clear from the results in the lower diagram that the \( \bar{d}(\text{har.})/\bar{d}(\text{art.}) \) ratio deviates from the theoretical value of 2/\( \pi \) with decreasing \( \bar{d}(\text{art.}) \), in particular, in the range of \( \bar{d}(\text{art.}) < 0.5 \mu m \).

The fact that two-dimensional particle diameter in a cross section is overestimated in the range of \( \bar{d}(\text{art.}) < 0.5 \mu m \) is due to the underestimation of the number of particles in a cross section which is explained below.

The particle numbers obtained from the cross section and filtered methods are denoted by \( N_{\text{V}} \) and \( N_{\text{A}} \), respectively. The number of particles per unit volume can be obtained from the measured values for \( \bar{d}(\text{art.}) \) and \( N_{\text{A}} \) by using Eq. (6) and the obtained \( N_{\text{V}} \) value denotes \( N_{\text{V(\text{cal.})}} \).

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As mentioned in Sec. 2.3., the observed area on a film filter is 10^4 mm^2. For the accurate determination of number and size of particles on a film filter, the following measurement should be carried out: Larger size particles are measured at a lower magnification, while smaller size ones are...
measured at a larger magnification in a larger observation area. It should be pointed out, however, that to increase the observed area in the case of high magnification is practically limited. In the present study, the \( \frac{d}{H} \) values obtained on a film filter is used for the following discussion on the size distribution of deoxidation product.

3.3. Particle Size Distribution

3.3.1. Time Dependence

Size distributions of MgO, ZrO\(_2\) and Al\(_2\)O\(_3\) particles and those of CaO–Al\(_2\)O\(_3\) and MnO–SiO\(_2\) particles are shown in Figs. 6 and 7, respectively, as a function of holding time at 1 873 K. In these figures, \( X \) axis denotes particle radius (\( r \)). It can be seen that the peak height diminishes regularly and the modal values increase with holding time. These results imply that the number of smaller size particles decreases, while the number of larger size particles increases. It can be said for the measurement of MgO particles at the holding time of 60 s that the number of smaller particles of \( r < 0.03 \mu \text{m} \) is underestimated due to the limit in the measurement of \( r < 0.05 \mu \text{m} \). The bi-modal distributions observed for MnO–SiO\(_2\) particles are considered to be due to the crystallization and/or precipitation during solidification and cooling. It was found that the mean particle size for stronger deoxidant tend to be smaller in comparison with that for weaker deoxidant. It can be seen that the width of the size distributions of solid MgO, ZrO\(_2\) and Al\(_2\)O\(_3\) particles for a given holding time is broader than that of liquid CaO–Al\(_2\)O\(_3\) and MnO–SiO\(_2\) particles. The nucleation rate for deoxidation liquid particles becomes higher, since the interfacial energy for liquid oxide is smaller than that for MgO, ZrO\(_2\), and Al\(_2\)O\(_3\) particles.
solid oxide. This leads to the difference in the width of initial particle size distribution. More detail for this is discussed in a separate publication.

Particle size distribution are usually found to be well modeled as a log-normal function. Consequently, the size distribution of particles shown in Figs. 6 and 7 are replotted by normalizing with the geometric mean radius, \( r_{\text{geo}} \) in Figs. 8 and 9. The growth of particles under the present experimental condition in which the particle growth by collision can be excluded in the absence of melt stirring is attributed solely to Ostwald ripening effect.

Normalized particle size distribution calculated by the LSW (Lifshitz,20) Slyozov and Wagner21) theory, which is independent of holding time, is also shown in Figs. 8 and 9 for comparison. The modal value of the theoretical curve is located at the mean particle size and the particles with greater than 1.5 times of the mean particle size are not present in the theoretical curve20,21). That is, the experimental particle size distributions are much broader and skewed to the right. The size distributions for solid MgO, ZrO2 and Al2O3 particles tend to approach the theoretical curve with holding time, but those for liquid CaO–Al2O3 and MnO–SiO2 particles are close to the theoretical curve except for the greater particle size and furthermore do not change with holding time. It can be concluded that the particle size distribution obtained in deoxidation approaches the line of the LSW theory with holding time, although its speed is slow.

Comparison of the volume fraction of particles evaluated from chemical analysis by Eq. (3) and that obtained from the size distribution on a film filter has been made in the following: The volume fraction of particles on a film filter, \( f_{V\,(\text{obs.})} \), can be estimated by the following expression:

\[
f_{V\,(\text{obs.})} = \frac{4\pi}{3} \left( \sum_{i=1}^{n} r_{i}^{3} \right) / V_{\text{metal}} \quad (7)
\]

where \( r_{i} \) is the measured radius of a particle \( i \) and \( V_{\text{metal}} \) is the volume of metal corresponding to the dissolved metal on the measured area of a film filter, which is already explained in Sec. 2.3.

The relationship between \( f_{V\,(\text{obs.})} \) from Eq. (7) and \( f_{V\,(\text{chem.})} \) from Eq. (3) is shown in Fig. 10, indicating a relatively good correspondence. This finding suggests that the measurement of size distribution on a film filter by SEM is well established.

The volume fractions of MgO, ZrO2 and CaO–Al2O3 particles \( \left( f_{V\,(\text{chem.})} = 4 \times 10^{-4} \right) \) are higher than that of MnO–SiO2 particles \( \left( f_{V\,(\text{chem.})} = 1 \times 10^{-4} \right) \).

### 3.3.2. Amount of Deoxidant

The effect of deoxidant amount on particle size distribution has been studied in the Mg, Zr and Al deoxidation experiments where the initial deoxidant amount of [%M] =
0.05 or 0.1 was chosen at constant initial oxygen level of 100 to 120 ppm. Figure 11 is the results obtained at holding time of 180 s at 1873 K. It is clear that the number of particles increases and the mean particle size decreases particularly in the Mg and Zr deoxidations with an increase in the amount of deoxidant. The reason for this may be attributed to the increase in the supersaturation degree for oxide nucleation with deoxidant addition. Although the supersaturation degree can be increased by increasing the initial oxygen content for a given deoxidant content, the metastable phase such as FeO·MₓOᵧ appears and causes the coalescence of particles with particles. On the basis of above observation it can be concluded that a large amount of deoxidant should be added to the melt containing an appropriate amount of initial oxygen in order to produce a large amount of fine particles as a primary deoxidation product.

3.3.3. Order of Deoxidant Addition

The effect of the order of deoxidant addition on particle size distribution has been investigated in the following experiments: An Fe–10%Ni alloy containing the initial oxygen of 100 to 120 ppm was deoxidized with Mg followed by Al or vice versa and then held for 3 min at 1873 K followed by rapid quenching. The size distributions of particles in a cross section and on a film filter after electrolytic extraction are shown in Figs. 12 and 13, respectively. It is apparent from the upper diagrams indicating the results obtained by Mg followed by Al that the two- and three-dimensional particle size distributions are in good agreement with those obtained by only Mg. Similarly, it is seen in the lower diagrams that two- and three-dimensional particle size distributions observed in Al followed by Mg are also in good accordance with those by only Al. These results demonstrate that the deoxidation product of MgO (or Al₂O₃) particles reacts with dissolved Al (or Mg), resulting in the MgO–Al₂O₃ particles. It can be concluded that the deoxidation with Mg followed by Al is preferable to the production of a large amount of fine MgO–Al₂O₃ particles. On the basis of these results, it is said in the complex deoxidation that the choice of the first added element is of importance in order to have fine particles.

The effect of the order of deoxidant addition on inclusion composition has been studied and the results obtained by a microprobe analysis of particles in a cross section are shown in Fig. 14. In the case of the deoxidations with Mg followed by Al shown in the upper diagram, most of MgO particles remain without reduction with Al at 3 min, but at 10 min the inclusion particles have a broad composition distribution having the maximum around spinel composition. In the case of the deoxidations with the Al followed by
Mg shown in the lower diagram, the inclusions observed at 3 min have a broad composition distribution, but that at 10 min becomes narrower and has the maximum at spinel composition. These results suggest that the inclusion particles with the spinel composition can be produced more easily by deoxidizing with Al followed by Mg which is a stronger deoxidant than Al. However, in view of producing fine particles, this order of addition is not appropriate as mentioned above.

4. Conclusion

In the experiments of an Fe–10%Ni alloy deoxidized with Mg, Zr, Al, Ca, Mn/Si and Al/Mg at 1 873 K, the characteristics of particle size distributions have been examined as a function of holding time, amount of deoxidant and order of deoxidant addition. The results are summarized as follows:

1) The volume fractions of $\text{Al}_2\text{O}_3$ and MnO–SiO$_2$ particles decrease with holding time at 1 873 K. This can be explained by the separation of particles by flotation and/or adherence to the crucible wall.

2) The peak height in particle size distribution decreases and the modal value increases with increasing holding time; namely, the number of smaller particles decreases and the number of larger particles increases. The width of the distribution curve is larger for Al$_2$O$_3$ particles and smaller for liquid CaO–Al$_2$O$_3$ and MnO–SiO$_2$ particles.

3) The number of particles increases with an increase in deoxidant for a given initial oxygen content and holding time.

4) In the case of Al followed by Mg deoxidation, the particle size distribution is almost the same as that obtained by only Al. In the case of Mg followed by Al deoxidation, the particle size distribution is almost the same as that obtained by only Mg.

REFERENCES