Analysis of Size Distribution of Inclusions in Metal by Using Single-particle Optical Sensing Method

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The spatial size distributions of oxide and/or nitride inclusions on a film filter after chemical or electrolytic extraction have been measured using single-particle optical sensing (SPOS) method in an Fe–10mass%Ni–0.2mass%M (M=Ti and Al) and an Fe–10mass%Ni–0.025mass%Al–0.1mass%Ti–0.02mass%N alloys. The size distributions obtained from the SPOS method are compared with those obtained from the three-dimensional observation of particles on a film filter using scanning electron microscope (SEM) with electron probe microanalysis. The volume fractions of particles calculated from the size distributions by the SPOS method and SEM observation have been compared with those calculated from chemical analysis. It is found that in the size distribution measurement the SPOS method is superior to the SEM observation, particularly, in the range of $d_V>5\mu m$.

KEY WORDS: inclusion; particle size distribution; volume fraction; single-particle optical sensing; scanning electron microscope.

1. Introduction

The size of particles in metal strongly influences many of the material properties. Size distribution, therefore, ranks as one of the most important parameters representing the basic characteristics of inclusions in metal. The method of single-particle optical sensing (SPOS), which is also called by the optical particle counting (OPC), is used for a quantitative analysis of particle size distribution in gases, aerosols, emulsions, and suspensions. This method is characterized by the quick measurement for the number and size of a large number of particles, one at a time, thus leading to the true particle size distribution. The SPOS method determines the size distribution of particles with high resolution and accuracy, comparable to that produced by the classical electrical sensing zone (Coulter Counter) method.

Up to now, the application field of SPOS technique included the particle analysis of pharmaceutical powders and solutions, food and drug, pigments, polymers, abrasives, and some other. In this article, the SPOS method is used for the investigation of size distribution of oxide and/or nitride inclusions on a film filter after chemical or electrolytic extraction in an Fe–10mass%Ni–0.2mass%M (M=Ti and Al) and an Fe–10mass%Ni–0.025mass%Al–0.1mass%Ti–0.02mass%N alloys. The particle characteristics such as the size distribution and volume fraction obtained from the SPOS method are compared with those obtained from the three-dimensional observation of particles on a film filter by using scanning electron microscope with the electron probe microanalysis.

2. Experimental

2.1. Procedure

An Fe–10mass%Ni alloy was melted and deoxidized by the addition of an appropriate amount of an Fe–50mass%M (M=Ti and Al) alloy at 1 600°C under an Ar–7vol%H2 atmosphere in a LaCrO3 resistance furnace. The melt with 0.2mass%M was held for 1 to 5, and 10 min at 1600°C and then quenched in water. The experimental conditions of Exp. Nos. 1 through 5 are given in Table 1 and more detailed description is given in previous article.

An Fe–10mass%Ni–0.025mass%Al–0.1mass%Ti–0.02mass%N (Exp. No. 6 in Table 1) alloy was melted by using an induction furnace. A charge containing high-purity electrolytic iron (60 g) and pure globular nickel (10 g) was heated to 1 600°C under an 50vol%N2–46.5vol%Ar–3.5vol%H2 atmosphere. The melt was held for 20 min at 1 600°C and deoxidized by an Fe–50mass%Al (0.0259 g) alloy. And it was immediately stirred for 10 sec using an Al2O3 rod. Then, an Fe–20mass%Ti alloy (0.353 g) was added and the melt was stirred again for 10 sec for homoge-

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>Alloy</th>
<th>Deoxidant</th>
<th>Holding time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe-10% Ni-0.2% M</td>
<td>Ti</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Ti</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Al</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>Al</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>Al</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>Fe-10% Ni-0.1% Ti-0.02% N-M</td>
<td>Al</td>
<td>0</td>
</tr>
</tbody>
</table>
nization. The melt was cooled from 1 600 to 1 400°C at a rate of 0.70°C/sec, followed by quenching in water.

High purity alumina crucible was used for all experiments.

2.2. Chemical Analysis

For the determination of total \( M \), a metal sample (0.2 g) was dissolved with HCl–HNO₃–H₂SO₄ and HCl–HNO₃ acids in Exp. Nos. 1 and 2 and in Exp. Nos. 3 through 5, respectively. For the chemical analysis of insoluble \( M \) in all experiments and soluble \( M \) in Exp. No. 6, a metal sample (0.2 to 0.4 g) was dissolved with 4 % MS (4 % methyl salicylate–1% salicylic acid–1% tetramethylammonium chloride–methanol) using an electrolytic extraction method. After filtration the solution and residue on a PTFE film filter with 47 mm in diameter and an open pore size of 0.1 \( \mu \)m were analyzed for the contents of soluble and insoluble \( M \), respectively, by using inductively coupled plasma (ICP) emission spectrometry. The details of the electrolytic extraction and chemical analysis are given elsewhere.

The total oxygen content in metal sample was analyzed by inert gas fusion-infrared absorptiometry. The newly developed method of ion chromatography was used for an analysis of total nitrogen after extracting as ammonia from a sample solution by Kjeldahl method.

2.3. Estimation of \( f_{V} \) from Chemical Analysis

In Exp. Nos. 1 and 2, both Ti₂O₃ and Al₂O₃ particles were observed in metal, since an alumina crucible was used for the Ti deoxidation experiments. The volume fraction of oxide particles, \( f_{V} \), was calculated from the analyzed contents of insoluble Ti and Al by the following equation:

\[
f_V = f_{V}(Ti_2O_3) + f_{V}(Al_2O_3) \]  \hspace{1cm} (1)

where \( f_{V}(Ti_2O_3) \) and \( f_{V}(Al_2O_3) \) are the volume fractions of Ti₂O₃ and Al₂O₃ particles, respectively.

The values of \( f_{V}(Ti_2O_3) \) can be evaluated from the following relation by assuming that \( f_{V}(Ti_2O_3) \) is much smaller than unity:

\[
f_{V}(Ti_2O_3) = \frac{\rho_{Fe-10\%Ni}}{\rho(Ti_2O_3)} \cdot \frac{M_w(Ti_2O_3)}{n \cdot A_w(Ti)} \cdot \frac{[Ti_{insol}]}{10^6} .... (2)
\]

where \( \rho_{Fe-10\%Ni} \) is the density of an Fe–10mass%Ni alloy (7.97 g/cm³) and \( \rho(Ti_2O_3) \) is the density of Ti₂O₃ particle (4.56 g/cm³). \( M_w(Ti_2O_3) \) and \( A_w(Ti) \) are the molecular weight of Ti₂O₃ and the atomic weight of Ti, respectively. \( n \) (=2) is the number of atoms of Ti in Ti₂O₃, and \( [Ti_{insol}] \) is the analyzed content of insoluble Ti in mass ppm.

The value of \( f_{V}(Al_2O_3) \) was estimated in a manner similar to Eq. (2) using \( \rho(Al_2O_3) \) (=3.97 g/cm³).

The total volume fraction of particles, \( f_{V} \), in Exp. No. 6 was calculated as the sum of volume fractions of oxides and nitride:

\[
f_V = f_{V}(Al_2O_3) + f_{V}(Ti_2O_3) + f_{V}(TiN) .... (3)
\]

The \( f_{V}(Ti_2O_3) \) value in Eq. (3) was evaluated from Eq. (2) using the analyzed content of insoluble Ti as oxide, [Ti_{insol-o}], which can be estimated as follows:

\[
[Ti_{insol-o}] = 96 \left( \frac{[T.O]}{48} - 48 \left[Al_{insol} - [O_{eq}] \right] \right) .... (4)
\]

where \([T.O]\) and \([O_{eq}]\) are the total and equilibrium oxygen contents in mass ppm, respectively. \([Al_{insol}]\) is the analyzed content of insoluble Al in mass ppm. The \([O_{eq}]\) values were calculated for Ti and Al deoxidants at 1 600°C.

The volume fraction of TiN was evaluated from the following relation:

\[
f_{V}(TiN) = \frac{\rho_{Fe-10\%Ni}}{\rho(TiN)} \cdot \frac{[Ti_{insol}]}{48} \cdot \left( 10^6 \right) .... (5)
\]

where \( \rho(TiN) \) is the density of TiN particle (5.40 g/cm³).

2.4. Observation of Inclusions

A metal sample (0.2 to 0.4 g) was dissolved by using the chemical extraction method with 14 wt/vol% iodine–methanol (14 % IM) under ultrasonic vibration (Exp. Nos. 1 through 5) and the electrolytic extraction method with 4 % MS (Exp. Nos. 1 through 6). After extraction the particles on a membrane film filter (PTFE with an open pore size of 0.1 \( \mu \)m) were observed by using the scanning electron microscope (SEM) with the electron probe microanalysis (EPMA) at a magnification of 1000 to 10 000 and by the single-particle optical sensing (SPOS) method. Figure 1 shows the extracted particles on a PTFE film filter for (a) an Fe–10mass%Ni–0.2mass%Ti alloy and (b) an Fe–10mass%Ni–0.025mass%Al–0.1mass%Ti–0.02mass%N alloy. Detailed description of the SEM observation of particles on a film filter are already given elsewhere.

3.1. Apparatus and Principle of SPOS Measurement

The single-particle optical sensing apparatus is schematically shown in Fig. 2.

The liquid suspension of methanol (3 ml) with particles, which is sufficiently diluted in measuring cell by filtered methanol, is analyzed in a thin stream (1×1 mm). The dispersed particles flow one by one through a small “photozone” consisting of a narrow, slab-like region of uniform illumination. The passage of a particle through the sensing zone causes a detected pulse. The magnitude of this pulse depends on the mean diameter of a particle. The light scattering of small size particles (d<1.5 μm) plus the light blockage from the larger particles is combined to provide a wide size range. A particle size distribution is obtained from the detected pulse heights by using a standard calibration curve, which is obtained from a set of latex standard particles with known size.

The range of particle size (0.5 to 400 μm) can be classified logarithmically into the 512 size class. The resulting size distribution of particles in liquid suspension can be obtained in histogram form.

3.2. Measurement of Particle Size Distribution by SPOS Method

Methanol, which was filtered three times by using a PTFE filter with an open pore size of 0.1 μm, was used as a diluent for a particle suspension and for dilution in measuring cell. The limited number of particles in a SPOS measurement must be chosen in order to avoid the particle coincidence in “photozone”. Therefore, 1/16 of a film filter with extracted inclusions was used for the dispersion of particles in 3 ml of diluent in a beaker. After ultrasonic dispersion for 3 min, 3 ml of the concentrated particle suspension was injected into the measuring cell, which contained 50 ml of fresh diluent. The particle suspension in the cell was stirred continuously for homogenization during measurement.

3.2.1. Measurement of Particles Injected in SPOS Cell

Forty milliliters from 53 ml of suspension was measured immediately in a flow rate of 1 ml/s. This is because, with an increase of the measured volume of suspension more than 40 ml, air from the measuring cell is introduced into the channel of optical particle sizer, which results in the error in the size distribution.

It was observed that the size distribution was significantly influenced by the particles remained in the cell. Therefore, 40 ml of fresh diluent was added again into the measuring cell, which contained the suspension remained in the previous analysis. Then, 40 ml from 53 ml of obtained suspension was measured again. Such a measurement cycle was repeated 4 to 7 times until the amount of measured inclusions in suspension was nearly equal to the particle number in the fresh diluent. The total size distribution of particles injected into the SPOS cell was obtained by subtracting the particles in the fresh diluent from the sum of measured particles in cycle Nos. 1 through 8 (Series I).

3.2.2. Measurement of Particles on Film Filter (Series II–VIII)

It was observed after the first ultrasonic dispersion and the measurement of Series I that some particles remained on the film filter and at the bottom of beaker. Therefore, 3 ml of the fresh diluent was added again into the beaker with the film filter containing remained particles. After ultrasonic dispersion for 3 min, 3 ml of this suspension was injected into the clean measuring cell in the SPOS system, together with 50 ml of fresh diluent. Then, this dilute sample suspension with particles was measured (Series II) by the aforementioned method in Sec. 3.2.1. Such a measurement of the particles, which were remained on the film filter and at the bottom of beaker, was repeated 4 to 6 times (Series III through VIII) until the number of measured particles in suspension decreased to less than 1 % of the particle number of the first measurement. The total particle size distribution on a film filter was obtained by subtracting the particles in a fresh diluent from the sum of all measured particles in Series Nos. I through VIII.

The analyzed area of a film filter for one sample measurement was 60 to 160 mm² which corresponded to 6.3 to 12.5 % of the total area of a film filter. This was 1000 to 10,000 times larger than the analyzed area by using the SEM observation. Total number of inclusions measured by the SPOS method was in the range of 10⁹ to 10²¹.

3.3. Estimation of Nₜ and fₜ by SPOS and SEM

In the SPOS measurement, the range of particle size can be divided automatically into the 512 size class on logarithmic scale. The number of particles per unit volume for each j-th size class of particles, Nₜ(j), can be calculated by using the following relationship

\[
Nₜ(j) = \sum_{i=1}^{j} n_i (j) \frac{A_{l,i}}{A_{l,\text{anal}}} \frac{P_{Fe,10\%Ni}}{W_{\text{dis}}} \tag{6}
\]

where n_i (j) is the number of particles in the j-th size class from the i-th SPOS measurement series. l is the total num-
As

\[
A_{\text{fil}} \text{ and } A_{\text{anal}} \text{ are the total area of a film filter with particles and the area of a film filter analyzed by using the SPOS method, respectively.}
\]

\[
W_{\text{dis}} \text{ is the weight of dissolved sample during electrolytic extraction.}
\]

The volume fraction of particles in the \( j \)-th size class, \( f_{V}(j) \), is expressed as:

\[
f_{V}(j) = \frac{4}{3} \pi \left( \frac{d_{V}(j)}{2} \right)^{3} N_{V}(j)
\]

where \( d_{V}(j) \) is the average diameter of particles in the \( j \)-th size class of size distribution obtained by the SPOS method.

The total number of particles per unit volume, \( N_{V} \), and the total volume fraction of particles, \( f_{V} \), can be obtained from the summation of \( N_{V}(j) \) and that of \( f_{V}(j) \), respectively.

The values of \( N_{V}(j) \), \( f_{V}(j) \), and total \( f_{V} \) from the size distribution obtained by the SEM observation were calculated with the step width of 0.2 \( \mu \)m in a manner similar to that for the SPOS method.

4. Results and Discussion

4.1. Size Distribution of Particles from SPOS Method

The results for the particle size distribution in the sample suspension (Exp. No. 1 in Table 1) are shown in Figs. 3 and 4. The numbers of analyzed particles are shown as a function of the number of measurement cycle and series in the upper and lower diagrams of Fig. 3, respectively. It can be seen in the upper diagram that 98 to 99% of particles injected into the SPOS cell are measured in cycle Nos. 1 through 5. As shown in the lower diagram, 97 to 98% of particles on an analyzed part of film filter can be measured in Series Nos. I, II, and III.

The cumulative frequencies of particles are plotted against the spatial diameter of particles in Fig. 4 as a function of measurement cycle in Series I (upper diagram) and measurement series (lower diagram). Most of large size particles \((d_{V}>1 \mu m)\) are measured in cycle Nos. 1 and 2 and in Series Nos. I and II, as shown in the upper and lower diagrams of Fig. 4, respectively. The proportion of large size particles in size distribution decreases with an increase of the number of measurement cycle and series. As shown in Fig. 4, the cumulative frequency curves approach the constant curve with increasing the number of measurement cycle and series, and the curves for cycle Nos. 4 through 8 and Series Nos. IV through VIII are almost the same.

It follows from these results that 97 to 99% of particles on a part of film filter can be analyzed by the SPOS method from Series I, II, and III with five measurement cycles in each Series.

4.2. Analysis of Particle Size Distribution of Sample

A film filter after extraction contains both the particles from a metal sample (deoxidation products and/or precipitated nitrides) and the extraneous particles which arise from a solvent or electrolyte, PTFE film filter, dust in air, undisolved metal pieces, and reaction products of solvent with iron such as FeI3. The amount of the extraneous particles was evaluated by using a film filter obtained after extraction of the solution without a metal sample. This was carried out under the same extraction conditions as those used for a metal sample. The extraction methods with and without a metal sample denote “Sample” and “Blank”, respectively, in this article.

The typical size distributions and cumulative volume fractions of particles in “Sample” and “Blank” after chemical extraction using 14 %IM are shown in Figs. 5 and 6 for Exp. Nos. 1 and 2, respectively. The size distribution of “Sample—Blank” represented by plus marks is obtained as the difference between “Sample” and “Blank”. It can be seen from the upper diagrams of Figs. 5 and 6 that in the
range of \( d_V < 8 \mu m \) the \( N_V \) values for “Sample” are significantly larger than those for “Blank”. In the range of \( d_V > 8 \mu m \) the \( N_V \) values for the “Sample” and “Blank” are approximately the same.

The cumulative \( f_V \) values for “Sample—Blank” are compared with the \( f_V \) values obtained from the chemical analysis of insoluble Ti. The chemical composition of metal phase and the \( f_V \) values calculated from the contents of insoluble \( M \), and those of total and equilibrium oxygen and nitrogen are summarized in Table 2 for different experiments. As shown in the lower diagrams of Figs. 5 and 6, the cumulative \( f_V \) values for “Sample—Blank” are significantly overestimated in comparison with those from chemical analysis in the ranges of \( d_V > 50 \mu m \) (Exp. No. 1) and >20 \( \mu m \) (Exp. No. 2). The reason for this discrepancy will be explained later.

The number, size, and composition of extraneous particles with large size are analyzed by SEM with EPMA on a nuclepore polycarbonate (PC) film filter (with an open pore size of 5 \( \mu m \)) after ultrasonic dispersion in methanol and filtration of all particles from a 1/8 part of “Sample” film filter. The results for the analysis of inclusions in a metal sample and extraneous particles from SPOS and SEM measurements are given in Table 3. It follows from Table 3 that the \( N_V \) and \( f_V \) values of particles from SPOS diluent, and beaker and injector are very small compared with those from “Sample”. Some pieces of a metal sample, which are not dissolved during extraction, can be completely removed by using a magnet. Therefore, they do not affect the \( N_V \) and \( f_V \) values of “Sample”. The extraneous particles from a PTFE film filter and solvent significantly increase the \( N_V \) and \( f_V \) values of inclusions on a film filter, as shown in Table 3. The typical particles of FeI$_3$ and dust on a PC film filter are shown in Fig. 7. Although the \( N_V \) value of reaction products of solvent with iron is small, the \( f_V \) value of these particles (2.87%), whose size is in the range of 10 to 50 \( \mu m \), is nearly the same as that (3.09%) for the inclusions in a metal sample (\( d_V < 20 \mu m \)). The \( N_V \) value of accidental dust particles is negligible compared with total \( N_V \) of particles on “Sample” film filter. However, these particles lead to a large discrepancy between the volume frac-

### Table 2. Chemical composition of metal and \( f_V \) values obtained from chemical analysis.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>( T.M )</th>
<th>( M_{\text{insol}} )</th>
<th>( T.A.I )</th>
<th>( M_{\text{insol}} )</th>
<th>( T.V. )</th>
<th>( T.O. )</th>
<th>( T.N. )</th>
<th>( f_V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti</td>
<td>1900</td>
<td>208</td>
<td>46</td>
<td>111</td>
<td>6</td>
<td>0.57</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>Ti</td>
<td>1640</td>
<td>80</td>
<td>79</td>
<td>57</td>
<td>48</td>
<td>0.19</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>Al</td>
<td>1200</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>0.90</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>Al</td>
<td>1530</td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>0.52</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>Al</td>
<td>1500</td>
<td>34</td>
<td>34</td>
<td>34</td>
<td>34</td>
<td>0.34</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>( M )</th>
<th>( f_V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1500</td>
<td>52</td>
</tr>
<tr>
<td>2</td>
<td>1500</td>
<td>34</td>
</tr>
</tbody>
</table>

### Table 3. Analysis of inclusions from metal sample and extraneous particles by SPOS measurement.

<table>
<thead>
<tr>
<th>Source of particles</th>
<th>( d_V )</th>
<th>( N_V )</th>
<th>( f_V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Sample&quot; (Exp. No. 2)</td>
<td>&lt; 310</td>
<td>730660</td>
<td>100</td>
</tr>
<tr>
<td>1. Inclusions in metal sample</td>
<td>≤ 20</td>
<td>622486</td>
<td>85.19</td>
</tr>
<tr>
<td>2. Extraneous particles:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Diluent for SPOS</td>
<td>≤ 5</td>
<td>54</td>
<td>0.01</td>
</tr>
<tr>
<td>- Beaker and injector</td>
<td>&lt; 25</td>
<td>760</td>
<td>0.10</td>
</tr>
<tr>
<td>- Undissolved metal pieces</td>
<td>20--100</td>
<td>6</td>
<td>0.001</td>
</tr>
<tr>
<td>- PTFE film filter</td>
<td>&lt; 40</td>
<td>30602</td>
<td>4.19</td>
</tr>
<tr>
<td>- Solvent (14% I$_3$M)</td>
<td>&lt; 40</td>
<td>76620</td>
<td>10.49</td>
</tr>
<tr>
<td>- Reaction products of solvent with iron</td>
<td>10--50</td>
<td>126</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.87</td>
</tr>
<tr>
<td>- Solvent with iron</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Dust or accidental particles</td>
<td>20--310</td>
<td>6</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Fig. 5. Spatial size distribution and cumulative volume fraction of particles observed on film filter in SPOS measurement.

Fig. 6. Spatial size distribution and cumulative volume fraction of particles observed on film filter in SPOS measurement.
tion calculated from observed size distribution and that from chemical analysis. This is due to the fact that the size of most dust particles is found to be located in the range of $d_V < 40 \mu m$. Therefore, it is said that the dust has no influence on the measurement of inclusions with $d_V \geq 20 \mu m$.

The $N_V$ and $f_V$ values for inclusions in a metal sample and extraneous particles are plotted against various ranges of $d_V$ in Fig. 8. It can be seen in the upper diagram that the number of inclusions in a metal sample represented by open circles decreases with increasing the size range of particles and their ratio (85.2%) to total $N_V$ in the range of $d_V < 10 \mu m$ decreases to that (27.5%) in the range of $10 \leq d_V < 20 \mu m$. The inclusions in the range of $d_V \geq 20 \mu m$ were not observed on a PS film filter by SEM observation. The size of most particles from solvent (open triangles) and PTFE film filter (open squares) was observed to be in the range of $d_V < 20 \mu m$. The total number of these particles in this range corresponds to 14.7% of total number of particles. The $N_V$ values of other extraneous particles (undissolved metal pieces, FeI₃, and dust) are considerably small compared with those of inclusions in metal.

As shown in the Table 3 and lower diagram of Fig. 8, the volume fraction of inclusions (3.09%) in a metal sample is significantly overestimated because the $f_V$ values of the dust (90.61%) and all other extraneous particles are very large. The proportion of $f_V$ value for extraneous particles increases with an increase of size range. The $f_V$ value of dust particles increases from 3.8% of total volume fraction in the range of $40 \leq d_V < 100 \mu m$ to 86.7% in the range of $d_V \geq 100 \mu m$. This is due to the fact that the $f_V$ value is proportional to the cube power of $d_V$. The volume fraction of other extraneous particles from solvent (14% IM), PTFE film filter, FeI₃, and undissolved metal pieces is roughly the same as that for inclusions in metal.

The undissolved metal pieces can be completely removed by using a magnet. Therefore, the effect of chemical solvent (14% IM), FeI₃, and PTFE film filter on the $N_V$ and $f_V$ values must be reduced in order to obtain true size distribution of inclusion in metal. For this reason, an electrolytic extraction with 4% MS using a PTFE film filter, which was cleaned by filtered methanol, was carried out. The spatial size distribution and cumulative volume fraction of particles observed in “Blank” using 14% IM and those using 4% MS in SPOS measurement are shown in Fig. 9. It can be seen in Fig. 9 that the $N_V$ and $f_V$ values using 4% MS electrolyte in the range of $d_V < 20 \mu m$ are 5 to 10 times smaller than those using 14% IM solvent. Furthermore, the extra-
neous particles from electrolyte and PTFE film filter in the range of $d_V>50\,\mu m$ are not observed in 4% MS “Blank”. The total $N_V$ and $f_V$ values using 4% MS are 5 and 15 times smaller than those using 14% IM.

The spatial size distribution and cumulative volume fraction of particles in “Sample” and “Blank” after electrolytic extraction with 4% MS are shown in Fig. 10. It can be seen from the upper diagram that in the range of $d_V<20\,\mu m$ the $N_V$ value for “Sample” are 5 to 15 times larger than that for “Blank”. In the range of $d_V\geq20\,\mu m$ the $N_V$ values for the “Sample” and “Blank” are approximately the same. The total $f_V$ value for “Sample—Blank” is in good agreement with that obtained from the chemical analysis, as shown in the lower diagram of Fig. 10.

It follows from these results that the size distribution and total $N_V$ value of inclusions on a film filter after electrolytic extraction of a metal sample can be estimated reasonably well from “Sample—Blank” by SPOS measurement. However, it should be pointed out that the volume fraction of inclusions calculated from the size distribution for “Sample—Blank” leads to a large discrepancy in comparison with that from chemical analysis in the range of large size. This is due to the fact that the dust particles, which have the size in the range of $d_V>20\,\mu m$, are contained accidentally on a “Sample” film filter and cannot be eliminated during the electrolytic extraction and SPOS measurement without special technique.

4.3. Comparison of Spatial Size Distributions from SPOS and SEM

The size distribution of inclusions on a PTFE film filter after electrolytic extraction of a metal sample using 4% MS was obtained by SPOS measurement as the difference between “Sample” and “Blank”. For the comparison of the size distribution obtained from the SEM observation with that from the SPOS method, the data for the SPOS measurement were classified into the size class with the step width of 0.2 $\mu m$, which was the same step for the size distribution from the SEM observation.

The spatial size distributions obtained from the SPOS method and SEM observation are shown in Figs. 11 through 13 on logarithmic scale. It can be seen that the size distribution of particles obtained by the SPOS method in most cases agrees reasonably well with those from the SEM observation in the range of $d_V<2\,\mu m$. In the range of $d_V>2\,\mu m$, however, the particle size distribution from the SEM observation is overestimated compared with that from the
SPOS measurement in all experiments. This discrepancy of size distributions can be explained by 1000 to 10000 times larger observation area in the SPOS measurement in comparison with that in the SEM measurement.

The cumulative volume fractions of inclusions, which are calculated from the size distribution of particles on a film filter by the SEM observation and the SPOS method, are plotted against the spatial diameter of particles in Figs. 14 through 16 on logarithmic scale. It can be seen that the cumulative volume fraction calculated from the size distribution by the SPOS measurement in most cases is below or equal to that obtained from chemical analysis in the range of $d_V < 40 \mu m$. In the range of $d_V > 40 \mu m$, however, the cumulative $f_V$ values calculated from SPOS are larger in some cases than those from chemical analysis. This is due to the fact that the observed size distribution in the range of $d_V > 40 \mu m$ includes the accidental dust particles.

4.4. Comparison of SEM Observation and SPOS Method

The measurement of particle size distribution by SEM observation is compared with that by the SPOS method and the characteristics in both methods are summarized in Table 4. The SEM observation has the following advantages: The particles less than 0.5 \( \mu m \) can be measured and the particle composition can be analyzed simultaneously by using EPMA. The problems related to the extraneous particles are not involved in this case. Therefore, the effect of extraneous particles on size distribution can be eliminated. However, the SEM observation is time-consuming and total number of measured particles by using a magnification of 1000 to 10000 is limited usually from 500 to 5000 particles. Furthermore, if the particle distribution on a film filter is not uniform, the true size distribution cannot be obtained.

In the SPOS method, large number of particles (10^5–10^8) can be measured quickly for a large observation area of a
film filter (60–160 mm²). The effect of nonuniformity of particle distribution on a film filter can be reduced by increasing the observation area in the SPOS measurement. The size distribution and total \( N_v \) value of inclusions on a film filter after electrolytic extraction of a metal sample can be estimated reasonably well as “Sample Blank” by SPOS measurement. However, the particle composition cannot be analyzed by SPOS method. Therefore, the volume fraction of inclusions calculated from the size distribution of “Sample Blank” leads to a large discrepancy in comparison with that from chemical analysis. This is due to the fact that the dust particles, which have on the average the size of \( d_v \geq 40 \mu m \), appear accidentally on a “Sample” film filter during the electrolytic extraction and SPOS measurement without special technique.

It can be concluded that the SPOS method is an useful technique to the quantitative analysis of a size distribution of inclusions on a film filter after chemical or electrolytic extraction of metal sample, particularly, in the range of \( d_v \geq 40 \mu m \), in which the \( N_v \) value for “Sample” is higher than that for “Blank”. The \( f_v \) value can be estimated reasonably well by the size distribution obtained by SPOS method, coupled with the analysis of extraneous particles with large size using SEM with EPMA.

5. Conclusions

The spatial size distributions of oxide and/or nitride inclusions on a film filter after chemical or electrolytic extraction have been measured by using the method of single-particle optical sensing (SPOS) in an Fe–10mass%Ni–0.2mass%M (M=Ti and Al) and an Fe–10mass%Ni–0.025mass%Al–0.1mass%Ti–0.02mass%N alloys. The size distributions obtained from the SPOS method are compared with those from the three-dimensional observation of the particles on a film filter by using the SEM with EPMA. The volume fractions of particles calculated from the data by the SPOS method and SEM observation are compared with those calculated from chemical analysis. The following conclusions were obtained:

(1) The size distributions of particles obtained by using the SPOS method are in good agreement with those obtained by the SEM observation in the range of \( d_v < 2 \mu m \). In the range of \( d_v > 2 \mu m \) the size distribution obtained by the SEM observation is overestimated compared with the SPOS method. This is due to the limit of the observation area in the SEM observation.

(2) In the size distribution measurement the SPOS method is superior to the SEM observation, particularly, in the range of \( d_v \geq 40 \mu m \). This is because larger number of particles \((10^3–10^6)\) can be measured on a larger observation area of a film filter. The effect of nonuniformity of particle distribution on a film filter can be eliminated by increasing the observation area in the SPOS method.

(3) The volume fraction calculated from the size distribution obtained by the SPOS method agrees well with that calculated from chemical analysis in the range of \( d_v \leq 40 \mu m \).

(4) In the range of \( d_v > 40 \mu m \), the volume fraction calculated from the size distribution obtained by the SPOS method leads to a large discrepancy in comparison with that from chemical analysis. This is due to the dust particles with large size contained accidentally on a “Sample” film filter during the electrolytic extraction and SPOS measurement.

REFERENCES