Density Measurements of Mould Flux Slags by Electrostatic Levitation Method

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In the present work, the densities of a mould flux slag were measured as a function of temperature by electrostatic levitation (ESL) method. The density of a mould flux, as measured by ESL method decreased linearly with increasing temperature. The results obtained are compared with the value measured by the sessile drop method just above the melting point of the slag. The discrepancies are explained on the basis of the inherent merits and demerits of the two types of measurements. The experimental values of present work were also compared with the density data for other mould flux slags from Swedish plant practice, obtained by the sessile drop method as part of the present work as well as literature data. A thermodynamic model of molar volume, developed in the present group was used to predict the density of slags. The molar volume was described as a function of integral molar enthalpies of mixing. In the case of ternary systems corresponding to the mould flux slag, the calculated values are in reasonable agreement with the experimental values.

KEY WORDS: density; mould flux; sessile drop; electrostatic levitation; thermodynamic model.

1. Introduction

Reliable thermophysical data are of utmost importance to metals processing industries as revealed by a survey by the European Space Agency (ESA).1) Various experimental methods, for example, the sessile drop method (at 1 G) as well as by levitation method under parabolic flights (microgravity conditions, μG) are currently in use. In the case of metallic materials, serious discrepancies between 1 G and μG measurements have been observed as reported in the project,1) financed by ESA. It would be interesting to see if similar discrepancies are observed with respect to molten oxide systems. The present work has been sponsored by Swedish Space Board. The aim is to compare the results of terrestrial and microgravity experiments in the measurements of densities of oxide melts. In the first stage of the measurements, the Electrostatic Levitation (ESL) facility available at Japanese Aerospace Exploration Agency, Tokyo, Japan was adopted for microgravity experiments and the results are compared with those obtained using the X-ray sessile drop method.

In conventional experimental technique like sessile drop method, the measurements of physical properties at the terrestrial level are likely to be somewhat affected by gravitational forces. Furthermore, the container reactions affect the chemistry of the silicate melts seriously. It is recognized that the contamination of the liquid from a container or substrate is one of the most serious problem in density measurement. In this respect, the advantages of the reliable containerless methods are numerous. A comparison of terrestrial measurements with those under microgravity could be invaluable.

Among the levitation methods, the ESL method is very appropriate in the case of oxidic systems. The ESL method allows to levitate liquid sample spherically whereas the liquid oxide or silicate sample is distorted by electromagnetic force and aerodynamic force for the Electro Magnetic Levitation (EML), aerodynamic and aero-acoustic levitation case. The ESL technique, has thus less inherent experimental measurement errors of density and thus is more suitable for silicate melts. Ishikawa et al. have investigated the density of refractory metal by the ESL method.2)–7) To the knowledge of the present authors, very little work has been reported on ESL measurements of oxide materials8)–9) and levitation of multicomponent oxide systems has never been reported yet. In the present study, the measurements of the density a complex slag by the ESL method and similar measurements by the sessile drop method have been carried out and the results are compared.

Molar volume is an important thermodynamic property. It is reflective of the structure of the melt. Silicate melts are highly polymeric at high silica concentrations, while the silicate network is broken into smaller units as basic oxides
Table 1. Chemical composition and properties of mould fluxes.

<table>
<thead>
<tr>
<th>mass %</th>
<th>Flux A</th>
<th>Flux B</th>
<th>Flux C</th>
<th>Flux D</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>34.2</td>
<td>28.8</td>
<td>25.5</td>
<td>32.7</td>
</tr>
<tr>
<td>CaO</td>
<td>29.4</td>
<td>36.5</td>
<td>22.7</td>
<td>28.8</td>
</tr>
<tr>
<td>MgO</td>
<td>1.01</td>
<td>1.3</td>
<td>0.97</td>
<td>1.77</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.92</td>
<td>6.5</td>
<td>12</td>
<td>4.7</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.1</td>
<td>0.3</td>
<td>0.46</td>
<td>0.11</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.09</td>
<td>0.8</td>
<td>2.86</td>
<td>1.24</td>
</tr>
<tr>
<td>MnO</td>
<td>0.05</td>
<td>3.3</td>
<td>0.04</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Na₂O</td>
<td>12.8</td>
<td>7.20</td>
<td>2.62</td>
<td>11.3</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.37</td>
<td>0.1</td>
<td>1.43</td>
<td>0.31</td>
</tr>
<tr>
<td>F⁻¹</td>
<td>7.95</td>
<td>5.9</td>
<td>4.42</td>
<td>9.4</td>
</tr>
<tr>
<td>CF₆ hostage</td>
<td>3.6</td>
<td>1.5</td>
<td>17.7</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>7.9</td>
<td>8.8</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>C total</td>
<td>5.74</td>
<td>20.3</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>10.9</td>
<td>14.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>0.69</td>
<td>0.86</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Basicity (CaO/SiO₂)</td>
<td>0.89</td>
<td>1.27</td>
<td>0.93</td>
<td>0.88</td>
</tr>
<tr>
<td>Basicity (CaO+MgO/SiO₂+Al₂O₃)</td>
<td>0.8</td>
<td>1.07</td>
<td>0.63</td>
<td>0.82</td>
</tr>
</tbody>
</table>

*1: Content of fluorine in the form of fluorides

are added. The present results are part of the efforts in the present laboratory to understand the structure of oxide melts by a closer look at the thermodynamic properties.

Density of slags is also very important in the metals processing. The density of the slag resulting from the melting of mould flux is one of the most important properties in modeling of the mould flux flow during the continuous casting of steel. Some researchers proposed models for the density of silicate melts. A project on characterization of commercial mould fluxes used in Swedish steel industries is currently being carried out in the Division of Materials Process Science, Royal Institute of Technology, Stockholm, Sweden. Among the properties investigated, priority is given to surface- and interfacial tensions, densities, viscosities and thermal conductivities. The present results would be of great importance even in this context. The choice of the silicate system in the present work is thus expected to be of importance to the fundamental understanding as well as industrial applications.

2. Experimental

2.1. Materials

In this experiment, four different commercial mould fluxes were used. These are designated as Flux A, B, C and D and are used in the Swedish plant practice. The chemical compositions and physical properties of the mold fluxes are presented in Table 1. The mould fluxes were decarburized in air at 1073 K for 48 h and melted in a graphite crucible at 1423 K using an induction furnace, and the molten slags were pored on a steel plate. The quenched glassy sample was then crushed and a piece of crashed sample was fitted into the ESL chamber. The sample was levitated aerodynamically and heated up by a laser and made spherical for electrostatic levitation.

2.2. Apparatus and Procedure

2.2.1. ESL method

The measurements by the ESL method reported in this paper have been carried out using an electrostatic levitation furnace constructed by Japan Aerospace Exploration Agency (JAXA). As shown in Fig. 1, the apparatus consists of four side electrodes to control horizontal position of sample, top and bottom electrodes to control vertical position of sample, two CCD cameras (one camera offers general view of both the electrode assembly and the sample, and the other camera offers a magnified image of sample), position detectors and pyrometers. The apparatus consists of a stainless steel chamber, which was pressurized to 350 kPa air before processing was initiated. After the pressurizations, the flow rate through the diffuser was slowly increased to achieve stable aerodynamic levitation. After the sample was launched aerodynamically, the gas flow for aerodynamic levitation was shut off as quickly as possible and the sample was levitated by the sole action of the electrostatic forces. The laser power then was increased slowly and the sample was heated to the experimental temperature. Sample heating was performed using a 100 W CO₂ laser (Synrad, Evolution 100). Figure 2 shows temperature–time curve at the density measurements of Flux C by the ESL method. The sample was heated to 1436 K and was then radiatively and conductively cooled. The measurements of
density by ESL method were carried out over a wide temperature range including the super-cooled range, viz, between 1148 K and 1436 K. Temperature was measured using an optical pyrometer. The levitated sample of mould flux slag was observed using a CCD camera and was recorded on videotape. The densities of molten mould flux slag (Flux C) were calculated from the image of levitated mould flux by using an image analysis software developed by JAXA. Levitation experiments with other mould fluxes failed despite repeated efforts as the samples could not be levitated.

After the experiments, the video images recorded on videotape were transferred to a hard disk of a computer using a video grabber, digitized, and the sample volume was calculated from each image based on a spherically symmetric shape. The recorded images were calibrated by levitating an Al2O3 sphere with a precisely known radius. After the experiments, the video images recorded on videotape were transferred to a hard disk of a computer using a video grabber, digitized, and the sample volume was calculated from each image based on a spherically symmetric shape. The recorded images were calibrated by levitating an Al2O3 sphere with a precisely known radius under identical experimental conditions. The sample density \( \rho(T) \), was calculated from the known mass of the sample \( m \), and the calculated volume \( V(T) \) using the following equation.

\[
\rho(T) = \frac{m}{V(T)} \quad (1)
\]

2.2.2. Sessile Drop Method

**Figure 3** shows the experimental apparatus for density measurements by sessile drop method, which consists of a furnace with graphite elements and an X-ray radiographic apparatus. The experiments were carried out in Ar atmosphere. The Ar gas was purified by gas cleaning system as follows. To remove the moisture in the gas, the gas was passed through silica gel columns and Mg(ClO4)2. CO2 was absorbed by ascarite and traces of oxygen were removed by passing the gas through copper and magnesium turnings at 823 K and 773 K, respectively. The flow rate was 150 mL/min. The heating and cooling rates were 4 K/min. A platinum plate was used as a substrate in this experiment. The mould flux powder was pressed into cylinders and the sample (approx. 0.4 g) was set on the substrate. The substrate was kept in a horizontal position by a water level.

After reaching the experimental temperature, the X-ray photographs of the molten mould flux slag drop were taken every 0.6 ks and recorded on PC. The measurement time was 1.8 ks for every temperature. The density, surface tension and contact angle were measured from the image recorded on the PC. The density of molten mould flux slags were calculated from the image contour of droplet by determining the curve with best fit between the numerical solution to the classical Laplace’s equation and experimentally measured points using an image analysis software developed by Carnegie Mellon University, USA and Royal Institute of Technology, Stockholm. The digitization was performed several times for every picture.

3. Results and Discussion

3.1. ESL Method Measurements

To the knowledge of the authors, the only work reported was the thermophysical properties measurements of Y3Al5O128) and Al2O39) by ESL method by Paradis et al. The levitation of multicomponent oxide like slag or mould flux has never been successful.

In theory, the sample is positively charged by electron emission (thermionic emission) and levitated by repulsion from the positively charged lower electrode. However, in the case of mould flux slag, the sample was not levitated under this condition. Although the exact charging mechanism is not fully understood, the sample was negatively charged. Therefore, in this experiment, the lower electrode was negatively charged. However, the levitation of sample was not always attained even under this condition. In the case of fluxes A, B and D, the experiments totally failed as mentioned earlier. The reasons might be related to not only composition of mould flux but also the structure of the slag sample.

**Figure 4** shows a typical photograph of a levitated sample. As seen in this figure, after the sample was melted, it took a spherical shape due to the surface tension. The volume of the spherical sample was calculated at each temperature from the photograph of the levitated sample.

The density of Flux C was determined at various temperatures immediately after the heating laser was blocked, and plotted against temperature as shown in **Fig. 5**. It is found experimentally that the temperature dependence of density for Flux C is slightly curve-linear. In this paper, however, the temperature dependence of density was represented by the following equation13) over the experimental temperature range, even though this equation is usually applied to density of liquid metals.

\[
\rho = \rho_m + K(T - T_m) \quad (2)
\]

where \( \rho \) is density, \( \rho_m \) is density at melting point \( T_m \) and \( K \) is temperature coefficient at constant pressure. The temperature dependence of the density of mould fluxes can be de-
scribed as follows:

\[ p = 2.638 + 0.2978(T-1373) \ [\text{kg/m}^3] \] ............(3)

3.2. Sessile Drop Method Measurement and Comparison of the Density Value

The density measurements of mould fluxes by sessile drop method were carried out at 1473 K. The results of measurement by sessile drop method are presented in Fig. 6 along with literature values. The densities of molten mould flux slags measured by sessile drop method in the present work were found to decrease with increasing Na\(_2\)O content. The density of a synthetic slag with CaO=40.9 mass%, SiO\(_2\)=48.5 mass%, Al\(_2\)O\(_3\)=10.6 mass% investigated by Takayanagi et al.\(^{14}\) was also reported to decrease with increasing the Na\(_2\)O content. The density of Flux B (7.20 mass% Na\(_2\)O), Flux C (2.62 mass% Na\(_2\)O) and Flux D (11.3 mass% Na\(_2\)O) are in reasonable agreement with Line 3 (6.13 mass% Na\(_2\)O), Line 1 (0 mass% Na\(_2\)O) and Line 4 (12.49 mass% Na\(_2\)O), respectively. Thus, the densities of mould flux slags are strongly influenced by the Na\(_2\)O content. One anomaly was observed in the case of flux A with 12.8 mass% Na\(_2\)O, which was expected to show agreement with Line 4 (12.49 mass%). This is attributed to possible experimental uncertainties associated with the measurements with this flux.

The density of Flux C obtained by ESL method is also shown in Fig. 6. The density value obtained by ESL method is lower than that obtained by sessile drop method and the literature data. The noticeable difference between the ESL method and sessile drop method in density is being traced to the experimental uncertainties due to the evaporation of some of the slag components in the latter case.

3.3. Experimental Uncertainties in the ESL Method

As shown in Fig. 2, sample temperature change is fast in the ESL experiments. Hence, it is likely that the temperature change was not followed by the corresponding structure change of mould flux due to fast cooling rate. Hence, the volume of sample tends to be higher than that of equilibrium state. As a result of calculation of density using increased apparent volume, the volume for density calculations tends to be lower.

As shown in Fig. 5, the ESL method allows a continuous measurement of density over a wide temperature range including the super cooled range. Furthermore, in the ESL method, the temperature reaches the experimental temperature in a few minutes because laser is used for heating. Therefore, the measurement error due to evaporation of components is less than that of sessile drop method. However, due to the high cooling rate, there would be possible temperature gradients between the surface of sample and interior. The effect of temperature gradient can be negligible in the case of metal sample. However it is not certain if this would be the situation in the case of oxide systems. The uncertainty of the measurements due to the resolution of the video grabbing capabilities (640×480 pixels) and the uncertainty in mass measurement (±0.0001 g) are estimated to be less than 2 percent.\(^{2}\)

3.4. A Thermodynamic Model

An attempt was made in this study to estimate molar volume of silicate melts investigated in the present work using a semi-empirical relationship between the enthalpies of mixing and the integral molar volume. According to earlier work presented by our group,\(^{15}\) the molar volume is shown as following equation.

\[ V_m = \sum x_i V_{m,i} + V^M \]

\[ = \sum x_i V_{m,i} + \lambda \frac{H^M}{RT} \sum x_i V_{m,i} \] ............(4)

where \(V^M\) represents the relative integral molar volume of...
where \( H^M \) is the relative integral molar enthalpies of mixing, \( \sum x_i V_i \) the average molar volume, \( R \) the gas constant, \( T \) the temperature and \( \lambda \) is an empirical constant determined by comparison with experimental data. The relative integral molar enthalpies were computed from the relative partial molar Gibbs energies estimated from a model proposed by Björkvall.16)

The \( V_m \) can be obtained from the experimental density by using following equation.

\[
V_m = \frac{\sum x_i M_i}{\rho} \tag{5}
\]

where \( \rho \) is the density, \( x_i \) and \( M_i \) the mole fraction and the mass per mole for the component \( i \), respectively.

In the case of multicomponent slags, the \( \lambda \) values in Eq. (4) could be affected by the mutual interactions between different cations. In the present work, the density was predicted as a first approximation, with \( \lambda = 0.035 \) for the 40.9\%CaO–48.5\%SiO\(_2\)–10.6\%Al\(_2\)O\(_3\) slag (Line 1) in Fig. 6 by the model mentioned above. The value of \( \lambda \) is likely to be a function of composition and the value seems to be lower than that of binary systems because in the case of ternary systems the interaction between cations can have a stabilizing effect compared to binary systems. The predicted value (Curve 6) for the slag is shown in Fig. 6.

The calculated density was in good agreement with that of literature data by Takayanagi et al. As shown in Table 2, the calculated temperature coefficient, \( dp/dT \), of Curve 6 (−0.44 to −0.40) in the range of temperature from 1500 to 1800 K is in good agreement with the literature data (−0.48).

An attempt is made to predict the density of mould flux also by the model calculation. It is difficult to investigate all the interactions in the case of multicomponents. Therefore the density of mould flux was predicted with the three major components of Flux C as a first approximation, viz, 37.7\%CaO–42.4\%SiO\(_2\)–19.9\%Al\(_2\)O\(_3\) with \( \lambda = 0.035 \). The calculated density value of this component is shown as Curve 5 in Fig. 6. The calculated density value is higher than that of measured value by ESL and sessile drop method. It is to be noted that, apart from the uncertainty in the estimation of \( \lambda \), the influence of Na\(_2\)O etc. on density is also ignored in this calculation.

The temperature coefficients of Curve 5 are −0.50 to −0.45 in the range of temperature from 1600 to 2000 K as shown in Table 2. On the other hand, the absolute value of temperature coefficient obtained by ESL experiment (−0.29) is lower than that of model calculation though the temperature range is not identical. According to the results measured by Takayanagi et al., it is presumed that the absolute value of temperature coefficient is slightly decreased with increasing Na\(_2\)O content. Therefore the discrepancy of temperature coefficient between the calculated value and the experimentally obtained value is believed to be due to the fact that some components (Na\(_2\)O etc.) were excluded in the model calculations.

### 4. Conclusions

In the present work, the density of mould flux has been measured by two methods, i.e., the sessile drop method and the electrostatic levitation method (ESL). Experimental results indicate that the density of mould flux (multicomponent oxide) can be measured by using ESL method. This method allows a contactless and continuous measurement of density in a single experiment.

Thermodynamic model for molar volume developed in the present laboratory was considered in the present work. The density as well as molar volume can be calculated by using this model with interaction between cations. In the case of mould flux slag, the comparison is made difficult due to uncertainties in the estimation of model parameters.

### Acknowledgment

The financial support to the present project as well as the support for Dr. Matsushita in carrying out the measurements at JAXA are gratefully acknowledged. The authors are also thankful to JAXA for making the ESL facilities available for the present work. Dr. Jianding Yu of JAXA is thanked for his useful suggestions and supports.

### REFERENCES


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Table 2. Temperature coefficients of mould flux slags and synthetic slags.

<table>
<thead>
<tr>
<th>Denote in Fig. 6</th>
<th>( dp/dT[Kg m^{-3} K^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.48</td>
</tr>
<tr>
<td>2</td>
<td>0.57</td>
</tr>
<tr>
<td>3</td>
<td>0.40</td>
</tr>
<tr>
<td>4</td>
<td>0.39</td>
</tr>
<tr>
<td>5</td>
<td>−0.50 to −0.45 (1600–2000K)</td>
</tr>
<tr>
<td>6</td>
<td>−0.44 to −0.40 (1500–1800K)</td>
</tr>
<tr>
<td>(Flux C, ESL)</td>
<td>−0.29</td>
</tr>
</tbody>
</table>