Density of the Blast Furnace Slag Bearing TiO$_2$ at 1 673 K

Yanhui LIU, Xuewei LV,* Chenguang BAI and Xi ZHANG

School of Materials Science and Engineering, Chongqing University, Chongqing, China.

(Received on July 21, 2013; accepted on November 11, 2013)

The density of blast furnace slag bearing TiO$_2$ has been investigated using the dispensed drop method at 1 673 K under the Argon atmosphere (Pressure $\approx$ 1.2 atm). The influence of slag basicity and the TiO$_2$ content on the density was analyzed according to the measurements. It was found that the density of the slag increases with increasing the TiO$_2$ content from 0% to 23%, once the TiO$_2$ content exceed of 23%, the density decreases. The reason of this transition can be attributed to the reduce of the coordination numbers of Ti–O, Ca–O and Mg–O by means of the molecular dynamics simulation. For the influence of the increase of basicity from 0.9 to 1.2, the density slightly rises from 2.83 g/cm$^3$ to 2.92 g/cm$^3$. The empirical formulas for the density which relates TiO$_2$ content and basicity are developed. The prediction model for the density by the partial molar volume method was also discussed, indicating that the calculated values can reach a good quantitative agreement with the measured values without the apparent change of the coordination numbers of the cations with O.

KEY WORDS: density; dispensed drop method; molecular dynamics simulation; slag bearing TiO$_2$.

1. Introduction

The density of the molten slag is a key property of thermo-physical in the metallurgical industrial. The density difference between the slag and the metal has a great effect on their separation process, especially in the extractive process of the metal like iron making.

Usually, density of slag provided relies on some developed models$^{1-4}$, most of which employ empirical constants and equations derived from actual experimental data. However, the experimental data are scarce due to the high reactivity of molten slag and the technical difficulty of taking precise measurements at elevated temperature. Therefore, it is inevitable that the calculation models cannot perfectly fit well with the measured results or the true values. The limited availability of these data is partly due to the complexity of the oxides involved and the difficulties encountered in performing experiments at elevated temperatures.

Particularly, in the process of iron making with blast furnace with full Vanadic Titanomagnetite, the mass percent of TiO$_2$ can reach as high as 30%, causing several critical problems, such as foaming slag$^{5-8}$, viscous slag and high metal loss. There have been a large number studies aimed at the foaming slag. Fruehan et al.$^7$ adopted the foam index, in terms of the slag viscosity, density and surface tension, to describe the stability of the slag foams, which the density is a very important parameter.

In this study, the density of the molten TiO$_2$–CaO–SiO$_2$–Al$_2$O$_3$–MgO blast furnace slag was determined by adopting the improved sessile drop method. Besides, the change of structure in the TiO$_2$–CaO–SiO$_2$–Al$_2$O$_3$–MgO system with the variation of both the TiO$_2$ content and the basicity was investigated by means of molecular dynamics simulation.

2. Experimental

2.1. Experimental Apparatus

The modified sessile drop technique improved by the traditional sessile drop method, which was proposed by Fujii et al.$^9$ was adopted as the method for measuring the density. An optical camera (Nikon D90) was used to record the image of the liquid drop. An advanced computer software, ADSA (Axisymmetric Drop Shape Analysis) software, was used to facilitate the calculation of the density. The flowchart$^{10}$ presented in Fig. 1 shows the general procedure of ADSA for the determination of the density from the sessile drops. The drop profile coordinates are obtained from the image of the drop using an image analysis process. The drop profile and physical properties, i.e. density and gravity, are the input to numerical schemes which are used to fit a series of Laplacian curves with known surface tension values to the experimental profile. The best fit identifies liquid-fluid interfacial tension, contact angle (in the case of sessile drops), drop volume, surface area, radius of curvature at the apex, and the radius of the contact circle between the liquid and solid (in the case of sessile drops). However, the outputs of the ADSA method are the density, surface tension and contact angle because of a firm fixed package of the software.

The apparatus (shown in Fig. 2) includes the following six parts: the furnace, image-forming system, the vacuum-mad system, the heating-control system, the cooling system and data processing system. To isolate the heating element from the sample, a reaction tube made from quartz was used. The tube was inserted into the furnace through an...
opening on the top furnace plate.

2.2. Sample Preparation

Samples for density measurement were prepared from the pure chemical reagents, SiO2, Al2O3, MgO, TiO2 and CaO powders. These reagents were precisely weighed according to the given compositions (shown in Table 1), and mixed in an alumina mortar homogeneously. The samples were pre-melted in the alumina crucible with a resistance furnace for one hour and then cooled in the air. The chemical composition analysis of slag were conducted by XRF (X-ray fluorescence), indicating that the Al2O3 mass fraction will increase by 0.6–1.5%, resulting in the slight reduce of the other oxides, such as CaO, SiO2, MgO and TiO2. Then, the cube samples with 3×3×3 mm³ for the measurements were prepared by cutting the bulk slag carefully.

2.3. Substrate Preparation

For the accurate measurement of the density, and the pyrolytic graphite (99.9% purity) was used to obtain the non-wetting drop shape necessary for accurate sessile drop measurement because of its non-wettability with the molten slag and chemical inertness. The graphite was in plate shape with the surface dimensions of 20 mm × 20 mm and the height of 4 mm. Its surface was mechanically ground and carefully polished using different sizes of diamond pastes to get an average roughness (Ra) of < 400 nm.

2.4. Density Measurement

Both the slag and the substrate were cleaned in acetone with ultrasonic for three times before measurement, and the

Table 1. Chemical composition of the samples (in mass%).

<table>
<thead>
<tr>
<th>Samples</th>
<th>TiO2</th>
<th>Al2O3</th>
<th>MgO</th>
<th>CaO</th>
<th>SiO2</th>
<th>Basicity (CaO/SiO2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.00</td>
<td>14.00</td>
<td>8.00</td>
<td>36.67</td>
<td>33.33</td>
<td>1.10</td>
</tr>
<tr>
<td>2</td>
<td>13.00</td>
<td>14.00</td>
<td>8.00</td>
<td>34.05</td>
<td>30.95</td>
<td>1.10</td>
</tr>
<tr>
<td>3</td>
<td>18.00</td>
<td>14.00</td>
<td>8.00</td>
<td>31.43</td>
<td>28.57</td>
<td>1.10</td>
</tr>
<tr>
<td>4</td>
<td>23.00</td>
<td>14.00</td>
<td>8.00</td>
<td>28.81</td>
<td>26.19</td>
<td>1.10</td>
</tr>
<tr>
<td>5</td>
<td>28.00</td>
<td>14.00</td>
<td>8.00</td>
<td>26.19</td>
<td>23.81</td>
<td>1.10</td>
</tr>
<tr>
<td>6</td>
<td>33.00</td>
<td>14.00</td>
<td>8.00</td>
<td>23.57</td>
<td>21.43</td>
<td>1.10</td>
</tr>
<tr>
<td>7</td>
<td>23.00</td>
<td>14.00</td>
<td>8.00</td>
<td>26.05</td>
<td>28.95</td>
<td>0.90</td>
</tr>
<tr>
<td>8</td>
<td>23.00</td>
<td>14.00</td>
<td>8.00</td>
<td>27.50</td>
<td>27.50</td>
<td>1.00</td>
</tr>
<tr>
<td>9</td>
<td>23.00</td>
<td>14.00</td>
<td>8.00</td>
<td>30.00</td>
<td>25.00</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Fig. 1. The general procedure of ADSA for the determination of the density.

Fig. 2. Schematic of the density measurement apparatus.
Where, \( f_0 \) is the unit constant \((=6.9511*10^{-11}\text{N})\), \( a_i \) and \( a_j \) the parameters which reflect the repulsive radius, and the \( b_i, b_j \) are the softness parameters. The last two terms which represent the dipole-dipole and dipole-quadruple interactions could be omitted due to the minuteness values compared with the first and the second terms. Therefore, the potential function is simplified as,

\[
U_{ij} = \frac{Z_iZ_j e^2}{4\pi\epsilon_0 r_{ij}} + B_{ij} \exp\left(-\frac{R_{ij}}{b_i} - \frac{R_{ij}}{b_j}\right) \quad \text{............... (3)}
\]

where, \( U_{ij} \) is the interatomic potential, \( Z_i, Z_j \) the charge of the atoms corresponding to the valence of every element, \( e \) the electron charge, and \( r_{ij} \) denotes the interatomic distance between a pair of atoms. The potential function consists of two parts. The first term on the right hand of the Eq. (3) represents the Coulombic interaction which was calculated by the Ewald method and the cutoff of the potential is always equal to the half of the box in which the ions were inserted. It was set to 10 Å in this work to simplify the computation. \( B_{ij} \) and \( R_{ij} \) are the parameters to describe the short-range repulsion interaction between two atoms corresponding to the second term in Eq. (3). The adopted values are listed in Table 3. The number of atoms within the molecular dynamics simulation is shown in Table 4. The total atomic numbers were determined according to the chemical compositions shown in Table 1. Taking No. 1 sample as an example, the mass of slag is set to be 100 g, then the mole numbers of oxides can be got by the mole mass. Then the mole numbers multiply by 1000/\( N_A \), where \( N_A \) is the Avogadro’s constant, so the atomic numbers of \( \text{Ca}^{2+}, \text{Si}^{4+}, \text{Mg}^{2+}, \text{Al}^{3+}, \text{Ti}^{4+} \) are obtained. The atomic number of \( \text{O}^{2-} \) can be acquired by the chemical formula. Finally, the total atomic number of No. 1 sample is obtained by adding all the atomic numbers of ions.

The three-dimensional periodic boundary conditions were applied on the model box, in which all of the atoms were inserted randomly and the Gear integration of motion equations was used. The atoms were equilibrated at 5 000 K for 3 000 time steps with a time step \( \Delta t = 1 \times 10^{-15} \text{s} \). Subsequently, it was cooled down to 1 673 K within 2 000 steps and equilibrated at 1 673 K for 15 000 time steps in order to acquire the information of the structure by statistics.

The pair distribution function (PDF), \( g_x(r) \) is generally used to describe the feature of short-range order of the slag melt, which gives the probability to find an ion within \( \Delta r \) at a distance \( r \) from a specified ion. This function can be calculated by the following equation,

\[
g_x(r) = \frac{1}{\rho} \frac{n(r)}{V} = \frac{V}{N_iN_j} \sum_{i,j} \frac{n(r)}{4\pi r^2 \Delta r} \quad \text{............... (4)}
\]

Where, \( N_i \) and \( N_j \) are the total number of ions \( i \) and \( j \), respec-
tively, $V$ is the volume of the system, and the $n(r)$ denotes the average number of the ions $j$ surrounding the ion $i$ in a spherical shell within $r \pm \Delta r/2$. The mean coordination number (CN) can be obtained from the pair distribution function $g(r)$. The CN is calculated by integrating the $g(r)$ curve to the first valley of it, and the formula is presented as,

$$N_i(r) = \frac{4\pi N_i}{V} \int_0^r r^2 g_i(r) dr$$  \hspace{1cm} (5)

### Table 3. Potential parameters used in this study.

<table>
<thead>
<tr>
<th>Atom $i$</th>
<th>Atom $j$</th>
<th>$B_{ij}$ (eV)</th>
<th>$R_{ij}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>Ca</td>
<td>329.605</td>
<td>6.2500</td>
</tr>
<tr>
<td>Ca</td>
<td>Si</td>
<td>26.720</td>
<td>6.2500</td>
</tr>
<tr>
<td>Ca</td>
<td>Ti</td>
<td>107.675</td>
<td>6.2500</td>
</tr>
<tr>
<td>Ca</td>
<td>Al</td>
<td>36.981</td>
<td>6.2500</td>
</tr>
<tr>
<td>Ca</td>
<td>Mg</td>
<td>67.806</td>
<td>6.2500</td>
</tr>
<tr>
<td>Ca</td>
<td>O</td>
<td>719.034</td>
<td>6.0606</td>
</tr>
<tr>
<td>Si</td>
<td>Si</td>
<td>2.166</td>
<td>6.2500</td>
</tr>
<tr>
<td>Si</td>
<td>Ti</td>
<td>8.729</td>
<td>6.2500</td>
</tr>
<tr>
<td>Si</td>
<td>Al</td>
<td>2.998</td>
<td>6.2500</td>
</tr>
<tr>
<td>Si</td>
<td>Mg</td>
<td>5.497</td>
<td>6.2500</td>
</tr>
<tr>
<td>Si</td>
<td>O</td>
<td>62.900</td>
<td>6.0606</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti</td>
<td>35.177</td>
<td>6.2500</td>
</tr>
<tr>
<td>Ti</td>
<td>Al</td>
<td>12.081</td>
<td>6.2500</td>
</tr>
<tr>
<td>Ti</td>
<td>Mg</td>
<td>2215.126</td>
<td>6.2500</td>
</tr>
<tr>
<td>Ti</td>
<td>O</td>
<td>243.000</td>
<td>6.0606</td>
</tr>
<tr>
<td>Mg</td>
<td>Mg</td>
<td>13.949</td>
<td>6.2500</td>
</tr>
<tr>
<td>Mg</td>
<td>Al</td>
<td>7.608</td>
<td>6.2500</td>
</tr>
<tr>
<td>Mg</td>
<td>O</td>
<td>155.178</td>
<td>6.0606</td>
</tr>
<tr>
<td>Al</td>
<td>Al</td>
<td>4.149</td>
<td>6.2500</td>
</tr>
<tr>
<td>Al</td>
<td>O</td>
<td>86.202</td>
<td>6.0606</td>
</tr>
<tr>
<td>O</td>
<td>O</td>
<td>1499.563</td>
<td>5.8824</td>
</tr>
</tbody>
</table>

### Table 4. The number of atoms within the molecular dynamics simulation.

<table>
<thead>
<tr>
<th>Samples</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total atomic number</td>
<td>4088</td>
<td>4000</td>
<td>3913</td>
<td>3825</td>
<td>3738</td>
<td>3650</td>
<td>3865</td>
<td>3844</td>
<td>3808</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Influence of TiO$_2$ Content on the Density

Figure 3 shows the images used to calculate the density, indicating that the slag does not wet the graphite and the contact angle is above 90°. The density data affected by the TiO$_2$ content obtained from the study at 1673 K are shown in Fig. 4.

With the increase of TiO$_2$ content in the slag, the density gradually rises and then slightly decreases, meaning that there is the presence of density maximum against TiO$_2$ content as shown in Fig. 4. In addition, the calculated results by the molecular dynamics simulation shown in Figs. 6 and 7 also indicates that there is a maximum CNs when the TiO$_2$ content is 23.00% and the interatomic distance, $r$, exceeds 3.0Å.

It is well known that densities of the oxide melts are related to the densities of oxides in the melt and the structure of the melt.\(^{17}\) Table 5 shows the densities\(^{18}\) of some oxides. Easy to find that the density of TiO$_2$ is higher than that of both CaO and SiO$_2$. The density of the slag will increase

![Fig. 3. Images used to calculate the density indicating the effect of TiO$_2$ content.](image-url)

![Fig. 4. The variation of density as a function of TiO$_2$ content in the slag.](image-url)
because of the addition of the dense component, TiO$_2$, when TiO$_2$ content is below 23.00% (in mass). On the contrary, the density slightly decreases along with the continuing rise of the TiO$_2$ content.

The continuing increase of TiO$_2$ may lead to the dramatic variation of the structure within the slag. The interesting information concerning the structure of the slag obtained by the molecular dynamics simulation includes the PDFs, CNs and the bond length. Furthermore, it is well known that the CN is closely related to the space utilization rate, affecting the drop volume. Figure 5 shows an example of CNs of sample No. 4 in Table 1 calculated by the molecular dynamics simulation, indicating that the CNs of ions, i.e., Ca–O, Si–O, Mg–O, Al–O and Ti–O. More specially, the increase of TiO$_2$ reduces the CNs of some cations with O, such as Ti–O, Ca–O and Mg–O shown in Fig. 7, which can be explained for the subtle decrease of the density.

As can be easily seen from the Figs. 6 and 7, the TiO$_2$ content (0–33%) has little effect on the CNs of Si–O and Al–

**Table 5.** The densities of some oxides (g/cm$^3$).

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>MgO</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>2.32</td>
<td>3.32</td>
<td>3.50</td>
<td>4.20</td>
<td>3.97</td>
</tr>
</tbody>
</table>

![Fig. 5. The coordation number of sample NO. 4.](image)

![Fig. 6. The effect of TiO$_2$ content on the variation of CNs of Si–O and Al–O.](image)

![Fig. 7. The effect of TiO$_2$ content on the variation of CNs of Ti–O, Ca–O and Mg–O.](image)
O, but leads to the decrease of the CNs of Ti–O, Ca–O and Mg–O. When the TiO₂ content is below 23.00%, the CNs of Mg–O and Ca–O hardly change, and that of Ti–O slightly goes from 5.8 to 5.6, which is not enough to attenuate the function of the addition of the dense TiO₂. However, the continuing rise of TiO₂ content, all the CNs of Ti–O, Ca–O and Mg–O violently decreases. The reduce of the space utilization rate results in the increase of the volume of droplet, attenuating the function of the addition of the dense TiO₂. Consequently, the density does not linearly increase with the rise of TiO₂ content.

Furthermore, an empirical formula for the density was also developed considering the change of the CNs in order to achieve the more accurate results. The formula is as follows, For TiO₂,

\[
\rho = 2.3964 + 0.0379\omega_{(TiO_2)} - 7.58 \times 10^{-4} \omega_{(TiO_2)}^2
\]  

(6)

Where \(\omega_{(TiO_2)}\) indicates the mass fraction of TiO₂ content, i.e. 8.00, 13.00, 18.00.

\[\delta = \rho_{\text{meas}} - \rho_{\text{calc}} \]  

(7)

Where \(\delta\) is the residual errors, g/cm³. \(\epsilon\) is the error calculated according to Eq. (8).

\[\epsilon = \frac{\left|\rho_{\text{meas}} - \rho_{\text{calc}}\right|}{\rho_{\text{meas}}} \times 100\%\]  

(8)

The residual errors are shown in Fig. 8. The maximum error between measurements and predicted values for TiO₂ is 2.01%, meaning that the calculated values can reach a good quantitative agreement with the measured values.

3.2. Influence of Basicity on the Density

Figure 9 shows the images used to calculate the density the contact angle is also above 90°, indicating that the slag does not wet the graphite. The density data concerning the CaO/SiO₂ mass ratio obtained from the experiments at 1673 K are shown in Fig. 10.

As the increase of basicity within the slag, the density gradually rises from 2.83 g/cm³ to 2.92 g/cm³ because of the addition of dense TiO₂ without no appearance of a break.
point. When the CaO/SiO\(_2\) varies from 0.90 to 1.10, Fig. 11 shows that the CNs of Mg–O, Al–O, Ca–O and Si–O hardly change, but that of Ti–O slightly rises from 5.5 up to 5.65 shown in Fig. 12, both meaning that the faint effect of CNs on the density can be neglected. Therefore, the density linearly increases along with the rise of the CaO/SiO\(_2\) mass ratio.

What’s more, an empirical formula for the density was also developed considering the change of the CNs in order to achieve the more accurate results. The formula is as follows, For basicity,

\[
\rho = 2.5348 + 0.3329R - 0.0001R^2, \quad R = \frac{\omega_{\text{CaO}}}{\omega_{\text{SiO}_2}}
\]  

... (9)

The residual errors are shown in Fig. 13. The maximum error between measurements and predicted values for basicity is 0.85%, meaning that the calculated values can reach a good quantitative agreement with the measured values.

### 3.3. Validity of the Measurement

As mentioned above, the density of the slag is related to both the densities of oxides and the structure of the melt. As for the calculation model of the density of the oxide melts, the method by the partial molar volumes is widely used to provide the density data. The relation for one gram slag is given in Eq. (10). Next the applicability of the method is discussed based on the measurement of the densities.

\[
\frac{1}{\rho} = \sum_{i=1}^{n} V_i M_i
\]  

Where \(M_i\) is the mole of a given component and \(V_i\) is the partial molar volume of a given component, shown in Table 6.\(^{17,19}\) According to partial molar volumes of oxides, the densities are calculated and shown in Fig. 14.

It is easy to find that the calculated density values are in

---

**Fig. 11.** The effect of basicity on the variation of CNs of Al–O, Si–O, Mg–O and Ca–O.

**Fig. 12.** The effect of basicity on the variation of CNs of Ti–O.

**Fig. 13.** The residual error between measurements and predicted values as a function of basicity.
good quantitative agreement with the measured data in the condition that there is no apparent change of the structure of the slag. More specially, a deviation from the measured density appears in view of the apparent effect caused by the change of the CNs of some cations with O.

4. Conclusions

The density of the molten TiO$_2$–CaO–SiO$_2$–Al$_2$O$_3$–MgO blast furnace slag was determined by adopting the improved sessile drop method, and the pyrolytic graphite was attempted for accurate sessile-drop measurement. Analysis of the experimental data indicates the following:

(1) When TiO$_2$ content is below 23.00%, the addition of the dense TiO$_2$ results in the increase of the density. Then, the density goes down very slowly along with the continuing rise of TiO$_2$ because of the reduce of CNs of Ti–O, Ca–O and Mg–O, meaning that there is the presence of density maximum against TiO$_2$ content. The formula is as follows:

$$\rho = 2.3964 + 0.0379\omega_{(TiO_2)} - 7.58 \times 10^{-4} \omega^2_{(TiO_2)}$$

(2) As the increase of the CaO/SiO$_2$ ratio, the density slightly rises from 2.83 g/cm$^3$ to 2.92 g/cm$^3$. The formula is as follows:

$$\rho = 2.5348 + 0.3329 R \cdots \cdots R = \omega_{(CaO)} / \omega_{(SiO_2)}$$

(3) The calculated densities by the partial molar volume method for the melts without the apparent variation of the CNs of the cations with O can reach a good quantitative agreement with the measured values. More studies should be considered by modifying the partial molar volume method for a better agreement in a wide range.

Acknowledgements

The authors are especially grateful to the National Natural Science Foundation (NSFC) (Grant No. 51090383).

REFERENCES