Density Measurements of CaO–MnO–SiO₂ Slags

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Density measurements of CaO–MnO–SiO₂ slags were carried out using the Archimedean method. The density decreased with increasing temperature, and the negative temperature coefficient (−dρ/dT) was in the range of 1.46–3.10 × 10⁻¹ kg/m³ K. At a fixed CaO content (25 wt%) and at a fixed SiO₂ content (30 wt%), the density of CaO–MnO–SiO₂ slag increased with increasing MnO content. The molar volumes of CaO, MnO and SiO₂ at 1 773 K were estimated 21.0, 17.2, and 28.0 × 10⁻⁶ m³/mol, respectively. The molar excess volume was expressed by V̴X = ΩX⁎X_{SiO₂}(1–X_{SiO₂}), where Ω = –8.97 × 10⁻⁶ m³/mol at 1 773 K. The thermal expansion coefficient decreased with increasing X_{SiO₂} because of the enhanced silicate network structure.

KEY WORDS: Archimedean method; CaO–MnO–SiO₂ slag; density; molar volume; silicate network structure; thermal expansion coefficient.

1. Introduction

Manganese is one of the most cost effective elements to control properties of steels. Manganese is used to increase strength, toughness, and hardness of steels, and it also plays a role of the austenite stabilizer.¹ During the refining process, manganese is used to remove sulfur, and to control the morphology of sulphides. Sometimes, it can be used as deoxidizer.

In order to optimize the extraction, refining, and casting processes of manganese ferroalloys and high manganese steels (ex. TRIP and TWIP steels), many studies have been performed on thermodynamic and thermo-physical properties of manganese alloys and MnO-based slags.²⁻⁷) Density is one of the fundamental physical properties at high temperatures not only for the process optimization but also for the measurements of other physical properties such as surface tension. Several research works have been reported on the density measurements of Fe–Mn alloys,⁶,⁷) but not so many works on MnO-based slag systems.⁸) Moreover, Mills asserted that the reliability of the experimental data for the MnO-based slag system was questionable.⁹)

Slags used in the production of manganese ferroalloys and refining process of high manganese steels are generally composed of CaO, MnO, SiO₂, Al₂O₃ and MgO, and the CaO–MnO–SiO₂ system is considered to be the basic slag system.¹⁻⁸) Density of silicate slag is affected by the structural factors, namely the bonding structure of oxygen ions.⁸) In this study, the density measurements of the CaO–MnO–SiO₂ slags were performed at a fixed CaO content (25 wt%), and at a fixed SiO₂ content (30 wt%) using the Archimedean method. In addition, the excess molar volume due to the modification of the silicate network structure was estimated based on the Mill’s model¹⁰) with the current experimental data.

2. Experimental

Figure 1 shows a schematic illustration of the experimental setup for the density measurements. The maximum operating temperature of 1 873 K was achieved with the MoSi₂ heating elements. The temperature of the furnace was monitored by using a B-type thermocouple contacting on the surface of a mullite reaction tube (O. D.: 0.1 m, I. D.: 0.092 m, L.: 0.9 m, KM, Nikkato). The temperature difference between the position of the sample and the surface of the reaction tube was determined in advance by placing another B-type thermocouple at the sample position. A Pt-20wt%Rh

Fig. 1. Experimental apparatus to measure density of liquid slags.
sinker, wires, and a crucible of the same material were used to prevent any possible chemical attack by molten slag. The CaO–MnO–SiO2 slag was prepared from extra pure grade reagents. CaO was prepared by the calcination of CaCO3 at 1273 K for 10 hours. After the heat treatment of the individual slag components, the materials were mixed thoroughly and then loaded in the Pt-20wt%Rh crucible. Approximately 0.12 kg slag was loaded into the crucible. During the experiments, a purified Ar gas atmosphere (P_{O2} = 4.07 \times 10^{-7} Pa) was maintained to prevent oxidation of the slag. The oxygen partial pressure in the Ar gas was separately investigated by using an oxygen sensor (Australian Oxygen Systems PTY. LTD). The slag mixture was heated to 1873 K and was kept at this temperature for 60 min. After the slag was stabilized at 1873 K, the Pt-20wt%Rh sinker was lowered. When the tip of the sinker touched the surface of molten slag, the digital balance showed a change in the weight, from which it was confirmed that the sinker actually had touched the surface of molten slag. Then the sinker was lowered further to be placed at a pre-determined depth.

The density of slag could be estimated by Eq. (1). \[ \rho = \frac{\Delta W + s}{V + v} \] 
where \( \Delta W \) is the apparent weight change by immersing a sinker, \( V \) is the volume of the sinker, \( v \) is the volume of the immersed suspension wire, and \( s \) is the surface tension correction. The surface tension correction factor can be obtained from Eq. (2).
\[ s = \frac{2\pi r \gamma \cos \theta}{g} \]
where \( g \) is gravitational acceleration, \( r \) is the radius of the suspension wire (0.25 \times 10^{-3} m), \( \gamma \) is the surface tension of slag, and \( \theta \) is the contact angle between the slag and the suspension wire. The thermal expansion of the sinker was corrected by Eq. (3). \[ V_f = V_i(1 + 3\alpha \Delta T) \]

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where \( \alpha \) and \( \Delta T \) are linear expansion coefficient of Pt-20wt%Rh\(^{12}\) and the temperature difference between room and measuring temperatures. The volume of the Pt-20wt%Rh sinker at room temperature was determined by the Archimedean method using distilled water as immersion liquid. The surface tension was obtained from Ref. 13, and the contact angle was assumed to be 15°, an average contact angle value of the slag/Pt systems.\(^{14,15}\) The surface tension correction was corresponding to 1.9–2.3% of the measured density. (If the uncertainty of the contact angle were ±10°, the inaccuracy of the density would be less than 0.1%. If the uncertainty of the surface tension were 10%, the inaccuracy of the density data would be 0.2%).

### 3. Results

In Table 1, experimental data are summarized. The liquidus temperatures of the slags are shown together. In Fig. 2, the temperature dependence of density of the CaO–MnO–SiO2 slags is shown at a fixed SiO2 content (30 wt%). The slag density decreased with increasing temperature at each composition, and the negative temperature coefficient (\(-d\rho/dT\)) was almost constant, in the range of 2.49–3.10 \times 10^{-1} kg/m^3 K. The density increased with increasing MnO content, which suggests that the density of pure MnO is higher than that of pure CaO. Figure 3 shows the temperature dependence of density of the CaO–MnO–SiO2 slags at a fixed CaO content (25 wt%). The density at 1773 K increased from 2.85 to 3.19 \times 10^3 kg/m^3, and the negative temperature coefficient increased from 1.46 to 3.10 \times 10^{-1} kg/m^3 K with increasing MnO content.

| Sample No. | Slag composition (wt%) | Liquidus temp. (K) | Density (10^3 kg/m^3) |
|------------|------------------------|--------------------|------------------------|
|            | CaO  MnO  SiO2         |                    |                        |
| 1          | 25  35  40             | 1563               | 3.45 – 2.38 \times 10^{-3} |
| 2          | 25  45  30             | 1609               | 3.74 – 3.10 \times 10^{-3} |
| 3          | 15  55  30             | 1530               | 3.83 – 2.76 \times 10^{-3} |
| 4          | 5   65  30             | 1591               | 4.05 – 3.14 \times 10^{-3} |
| 5          | 35  35  30             | 1806               | 3.54 – 2.49 \times 10^{-3} |
| 6          | 25  25  50             | 1620               | 3.11 – 1.46 \times 10^{-3} |
4. Discussion

For a better understanding, density is converted to molar volume. The molar volume of slags can be described by Eq. (4).

\[ V = \sum X_i \bar{V}_i = \sum X_i V_i + V_{\text{mix}} \]  

(4)

where \( X_i \) is the mole fraction, \( \bar{V}_i \) the partial molar volume of oxide \( i \), \( V_i \) the molar volume of hypothetical pure liquid oxide \( i \), and \( V_{\text{mix}} \) the molar excess volume. For basic oxides mixture, it is reasonably assumed that \( V_{\text{mix}} \approx 0 \). \(^{8,16}\) On the other hand, when acidic oxides are mixed, the excess volume cannot be neglected due to the complex structures of slags. \(^{8,9,17}\) Mills suggested that the excess volume of ternary slag system could be simply given as a function of \( X_{\text{SiO}_2} \). \(^8\) When the regular solution model is applied, the molar volume of the CaO–MnO–SiO\(_2\) slags can be expressed in the form of Eq. (5).

\[ V = X_{\text{CaO}} V_{\text{CaO}} + X_{\text{MnO}} V_{\text{MnO}} + X_{\text{SiO}_2} V_{\text{SiO}_2} + \Omega X_{\text{SiO}_2}(1 - X_{\text{SiO}_2}) \]  

(5)

The values of \( V_{\text{CaO}}, V_{\text{MnO}}, V_{\text{SiO}_2}, \) and \( \Omega \) are obtained by numerically solving Eq. (5) at 1723, 1773 and 1823 K with the experimental data. The calculated parameters are shown in Table 2. In Fig. 4, a comparison between the calculated values and the experimental results is shown. The calculated molar volumes reasonably accord with the experimental values within ± 0.73%.

In Fig. 5, the molar volumes of pure oxides are shown as a function of temperature. The molar volume of CaO at 1773 K is 21.0 \( \times 10^{-6} \) m\(^3\)/mol, which is close to the reported data by Mills (20.7 \( \times 10^{-6} \) m\(^3\)/mol)\(^8\) but slightly higher than that by Segers \( et \ al. \) (19.2 \( \times 10^{-6} \) m\(^3\)/mol).\(^{17}\) The molar volume of MnO at 1773 K is 17.2 \( \times 10^{-6} \) m\(^3\)/mol, which is slightly higher than the reported data by Mills (15.6 \( \times 10^{-6} \) m\(^3\)/mol)\(^8\), but close to that by Segers \( et \ al. \) (17.3 \( \times 10^{-6} \) m\(^3\)/mol).\(^{17}\) The molar volume of SiO\(_2\) at 1773 K is 28.0 \( \times 10^{-6} \) m\(^3\)/mol, which is close to the value by Mills (27.5 \( \times 10^{-6} \) m\(^3\)/mol),\(^8\) but slightly higher than the extrapolated value from pure liquid SiO\(_2\) by Bacon \( et \ al. \) (25.7 \( \times 10^{-6} \) m\(^3\)/mol).\(^{18}\) The molar volumes are in the order of \( V_{\text{SiO}_2} > V_{\text{CaO}} > V_{\text{MnO}} \).

In Fig. 6, the excess volume of slag is shown with respect to the mole fraction of SiO\(_2\) (\( X_{\text{SiO}_2} \)) at 1773 K. The molar excess volume is negatively deviated from the ideal mixing behavior, and can be expressed by \( V_{\text{mix}} = \Omega X_{\text{SiO}_2}(1 - X_{\text{SiO}_2}) \), where \( \Omega \) is estimated to be \( -8.97 \times 10^{-6} \) m\(^3\)/mol. The maximum molar excess volume is corresponding to approximately 9.2–10.3% of the slag volume, which may be related to the bonding structure of the silicate melts. \(^8\) There is a slight difference between the measured data and the calculated values, which can be caused by difference in the characteristics of CaO and MnO in the silicate structure.\(^{4,19}\) Nevertheless, the maximum difference between the experimental data and the calculated values is less than 0.14 \( \times 10^{-6} \) m\(^3\)/mol (less than 1% of the measured data) and this difference can be ignored. In Fig. 7, the density of the 25 wt%CaO–MnO–SiO\(_2\) slag at 1773 K is plotted with respect to the MnO concentration. The present results and the reported data by Segers \( et \ al. \) show

![Fig. 4. Comparison between the calculated molar volumes and the measurements at 1773 K.](image)

![Fig. 5. Molar volumes of hypothetical pure liquid oxides (CaO, MnO, and SiO\(_2\)) as a function of temperature.](image)

![Fig. 6. Molar excess volume of the CaO–MnO–SiO\(_2\) slag with respect to \( X_{\text{SiO}_2} \) at 1773 K.](image)
reasonable agreement with the calculated ones, while the data reported in Slag Atlas\(^8\) are higher.

Mills reported that thermal expansion coefficient \((\beta = 1/V \times dV/dT)\) is related to the silicate structure, namely, as the bridging oxygen ion increases, \(\beta\) decreases.\(^{20}\) In Fig. 8, \(\beta\) of the CaO–MnO–SiO\(_2\) slag at a fixed CaO content (25 wt\%, \(X_{\text{CaO}} = 0.27\)–0.28) is shown with respect to \(X_{\text{SiO}_2}\). As \(X_{\text{SiO}_2}\) increases, \(\beta\) decreases. In Fig. 9 are shown the oxygen fractions that are calculated with FactSage. As \(X_{\text{SiO}_2}\) increased, the fraction of the bridging oxygen ions \(O^0\) monotonically increases, whereas that of the non-bridging oxygen ions \((O^-, O^{2-})\) decreases. Therefore, it is concluded that thermal expansion coefficient \(\beta\) of the CaO–MnO–SiO\(_2\) slag decreases with increasing \(X_{\text{SiO}_2}\) because of the enhanced rigid silicate network structure.

5. Conclusions

The density of CaO–MnO–SiO\(_2\) slag was investigated using the Archimedean method in the temperature range of 1 719–1 856 K. The density was increased by increasing MnO content or decreasing temperature at a fixed CaO or at a fixed SiO\(_2\) contents. From numerical calculations, the molar volumes of pure CaO, MnO, and SiO\(_2\) at 1 773 K were evaluated 21.0, 17.2, and 28.0 \(\times 10^{-6}\) m\(^3\)/mol, respectively. The molar excess volume could be described by \(V_{\text{Ex}} = \omega \times X_{\text{SiO}_2} (1 - X_{\text{SiO}_2})\), where \(\omega = -8.97 \times 10^{-6}\) m\(^3\)/mol at 1 773 K. The excess volume was negatively deviated from the ideal mixing behavior by 9.2–10.3% of the slag volume. The thermal expansion coefficient \(\beta\) decreased with increasing \(X_{\text{SiO}_2}\) because of the enhanced rigid silicate network structure.

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