

Density of molten CaO-MnO-SiO₂ slag

Joonho LEE^{1,*}, Le Thu HOAI¹, Joongkil CHOE¹, Joo-Hyun PARK²

1) Department of Material Science and Engineering, Korea University, Seoul, 136-713, Korea

2) School of Materials Science and Engineering, University of Ulsan, Ulsan 680-749, Korea

Abstract: Archimedean method is a general method to measure molten slag density. For accurate measurements, the information of thermal expansion of the sinker is essential. In the previous studies, a linear thermal expansion of the sinker had been simply assumed, which might give us wrong information of slag density at high temperatures. In the present study, the thermal expansion of a Pt-10 pct Rh sinker was directly investigated by investigating the volume as a function of temperature, and a non-linear thermal expansion relation was obtained. This information was used to determine the molten slag density. CaO-MnO-SiO₂ slag system was chosen for this study. The slag densities obtained in the present study were lower than the reported values. The density decreased with increasing temperature, and the temperature coefficient was in the range of $-3.10 \sim -7.65 \times 10^{-4} \text{ g/cm}^3\text{K}$. At a fixed CaO content (25 wt%) and at a fixed SiO₂ content (30 wt%), the slag density increased with increasing MnO content.

Key words: Archimedean method, CaO-MnO-SiO₂ slag, Density, Molar volume, Thermal expansion.

1. Introduction

Manganese is the most cost effective elements to control properties of steels. Manganese is added to steel to increase strength, toughness, and hardness. Manganese is also used to remove sulfur and control the morphology of sulphides. Sometimes, it can be used as deoxidizer. During the heat treatments, manganese also plays a role of the austenite stabilizer¹⁾.

Recently, many attentions have been paid to high manganese steels (ex. TRIP and TWIP steels), and many studies on thermodynamic and thermo-physical properties of manganese alloys and MnO-based slags have been carried out to optimize the extraction, refining and casting processes²⁻⁷⁾. Density is one of the fundamental thermo-physical properties not only for the process optimization but also for the measurements of other physical properties such as surface tension. There are several reports on the density measurements of Fe-Mn alloys^{6, 7)}, but not so many works have been reported on slag systems⁸⁾.

The major components of slags in the production of manganese ferroalloys and refining process of high manganese steels are CaO, MnO, SiO₂, Al₂O₃ and MgO, and the CaO-MnO-SiO₂ system is the basic slag system¹⁾. Segers *et al.* measured the density of CaO-MnO-SiO₂ slags using the Archimedean method⁹⁾. They used a Pt-20%Rh sinker, but the volume of the sinker at the experimental temperatures was extrapolated from 273K with a linear thermal expansion coefficient⁹⁾. They only checked the thermal expansion in the temperature range between 1273 and 1373K by measuring the density of pure molten NaF, but did not extend the measurements to much higher temperatures. In this study, the density measurements of CaO-MnO-SiO₂ slags were carried out at a fixed CaO content (25 wt%), and at a fixed SiO₂ content (30 wt%) with a Pt-10%Rh sinker, of which thermal expansion was calibrated by a direct observation at high

temperatures. In **Table 1**, the experimental compositions are summarized. In addition, estimation of the excess molar volume was carried out based on the current experimental data.

Table 1 Experimental results of the density measurements of CaO-MnO-SiO₂ slag.

Sample No.	Slag composition			Density (10 ³ kg/m ³)
	wt% CaO	Wt% MnO	Wt% SiO ₂	
1	25	35	40	3.58-4.07×10 ⁻⁴ T
2	25	45	30	3.87-4.85×10 ⁻⁴ T
3	15	55	30	3.96-4.61×10 ⁻⁴ T
4	5	65	30	4.19-5.06×10 ⁻⁴ T
5	35	35	30	3.67-4.21×10 ⁻⁴ T
6	25	25	50	3.24-3.10×10 ⁻⁴ T

2. Experimental

Density measurements were carried out using the Archimedean method. **Figure 1** shows the experimental setup for the density measurements. The furnace was capable of attaining temperatures up to 1873K with MoSi₂ heating elements. A B-type thermocouple was employed to monitor the temperature. The temperature difference between the position of experiments and the monitoring thermocouple contacting the reaction tube was determined in advance by placing another B-type thermocouple at the experimental position. A mullite reaction tube (O.D.: 100 mm, I.D.: 92 mm, L.: 900 mm, KM, Nikkato) was used. The same material (Pt-10 wt% Rh) was used as a sinker, wires, and a crucible to prevent any possible chemical attack by molten slag. The CaO-MnO-SiO₂ slag was prepared from extra pure grade reagents. CaO was prepared in advance by the calcination of CaCO₃ at 1273K for 10 hours. After the heat treatment of the individual slag components, the materials were mixed thoroughly and then loaded in the Pt-10 wt% Rh crucible. Approximately 120 g slag was loaded into the crucible. During the experiments, a purified Ar gas atmosphere was maintained to prevent oxidation of the slag. The slag mixture was heated to 1873 K and was maintained at this temperature for 60 minutes. After the slag was stabilized at this temperature, the Pt-10 wt% Rh sinker was lowered. When the lower tip of the sinker touched the surface of molten slag, the digital balance showed a change in the weight to confirm that the sinker actually had touched the surface of molten slag. Then the sinker was lowered further to a pre-determined depth to maintain a constant depth of the sinker at each experiment.

The density of slag could be estimated by Eq. (1)¹⁰.

$$\rho = \frac{\Delta W + s}{V + v} \quad (1)$$

where 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 can be obtained from Eq. (2).

$$s = \frac{2\pi r\gamma \cos \theta}{g} \quad (2)$$

where g is gravitational acceleration, r is the radius of the suspension wire, γ is the surface tension of slag, and θ is the contact angle between the slag and the suspension wire.

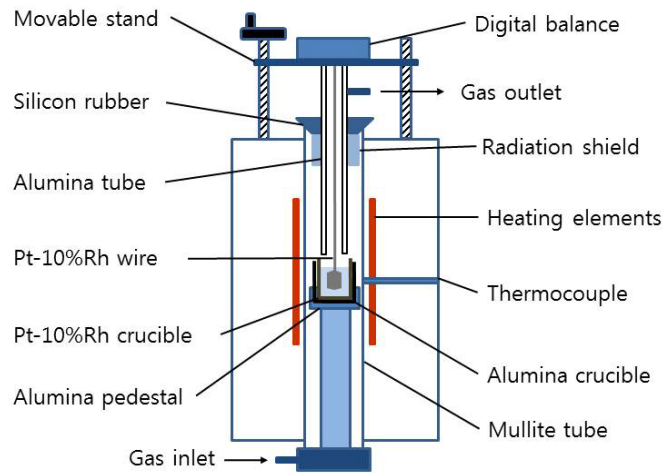


Fig. 1 Experimental apparatus to measure density of liquid slags.

The volume expansion of the Pt-10 wt% Rh sinker was measured by direct observation in advance. **Figure 2** shows a schematic diagram of the experimental apparatus to measure the thermal expansion of the Pt-10 wt% Rh sinker. The volume expansion of the sinker is shown with respect to temperature in **Fig. 3**, and described as a function of temperature in Eq. (3).

$$V_T = V_0(0.98 + 3.42 \times 10^{-5}T + 2.37 \times 10^{-8}T^2) \quad (943\sim 1698\text{K}) \quad (3)$$

Since the maximum operating temperature limit of the machine, the thermal expansion of the sinker was measured below 1700K. Although the density measurements were carried out in the temperature range between 1719 and 1856K, the extrapolation of Eq. (3) to the experimental temperature region was acceptable rather than the extrapolation from the room temperature with a constant temperature coefficient. The surface tension was obtained from ref. 11, and the contact angle was assumed to be 15° , an average contact angle value of the slag/Pt systems^{12), 13)}.

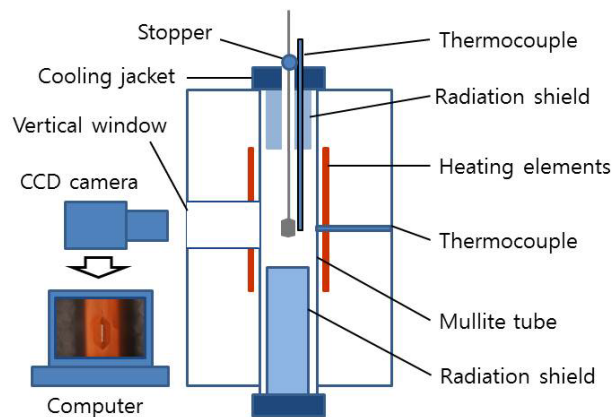


Fig. 2 Experimental apparatus to measure the thermal expansion of the Pt-10wt% Rh sinker.

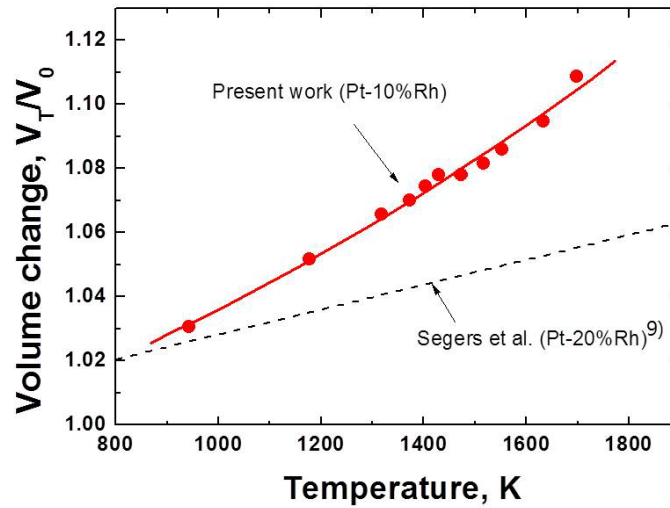


Fig. 3 Thermal expansion of the Pt-10 wt% Rh sinker.

3. Results

Experimental data are summarized in **Table 1**. **Figure 4** shows the temperature dependence of density of the CaO-MnO-SiO₂ slags at a fixed SiO₂ content (30 wt%). The density decreased with increasing temperature at each composition, and the temperature coefficient ($d\rho/dT$) was almost constant, in the range of $-4.21 \sim -5.06 \times 10^{-4} \text{ g/cm}^3\text{K}$. Some parts of CaO-35 wt% MnO-30 wt% SiO₂ slag might be solidified at lower temperatures, but did not affect the temperature coefficient. The density increased with increasing MnO content, which suggests that the density of pure MnO is higher than that of pure CaO. **Figure 5** shows the temperature dependence of density of the CaO-MnO-SiO₂ slags at a fixed CaO content (25 wt%). The density increased with increasing MnO content, but the temperature coefficient slightly changed in the range of $-3.10 \sim -4.85 \times 10^{-4} \text{ g/cm}^3\text{K}$.

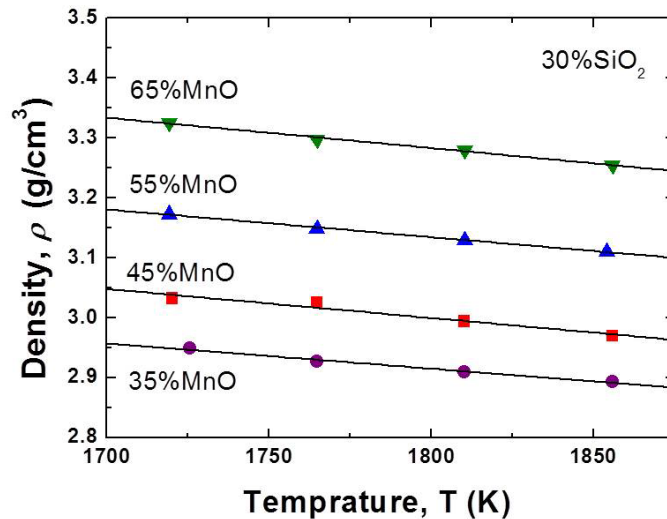


Fig. 4 Temperature dependence of density of the CaO-MnO-30 wt% SiO₂ slags.

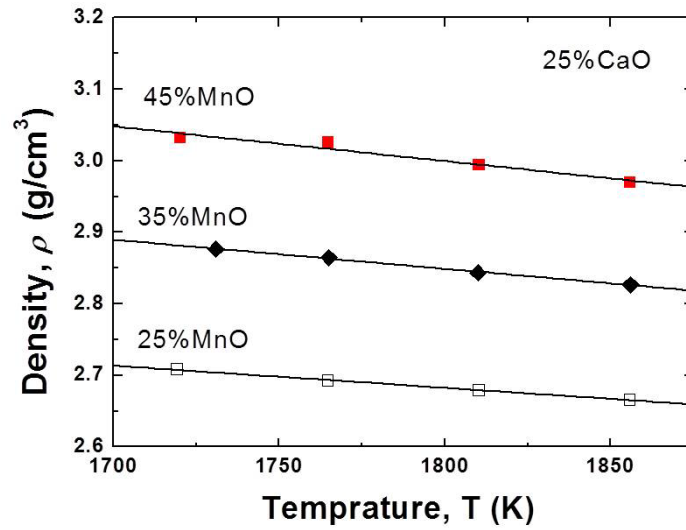


Fig. 5 Temperature dependence of density of the 25 wt% CaO-MnO-SiO₂ slags.

4. Discussion

For a better understanding, density was converted to molar volume. The molar volume of slags can be described by Eq. (4)⁸⁾.

$$V = \sum X_i \bar{V}_i = \sum X_i V_i + V^{Ex} \quad (4)$$

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^{Ex} the molar excess volume. For basic oxides mixture, it is reasonably assumed that $V^{Ex} \approx 0$ ⁸⁾.¹⁴⁾ On the other hand, when acidic oxides are mixed, the excess volume cannot be neglected due to the complex structures of slags^{8), 9), 15)}. Mills suggested that the excess volume of ternary slag system could be simply given as a function of X_{SiO_2} ⁸⁾. When the regular solution model is applied, the molar volume of the CaO-MnO-SiO₂ slags can be expressed in the form of Eq. (5).

$$V = X_{CaO} V_{CaO} + X_{MnO} V_{MnO} + X_{SiO_2} V_{SiO_2} + \beta X_{SiO_2} (1 - X_{SiO_2}) \quad (5)$$

The values of V_{CaO} , V_{MnO} , β , and V_{SiO_2} were obtained by numerically solving Eq. (5) at 1723, 1773 and 1823K with the experimental data. The calculated parameters are shown in **Table 2**. In **Fig. 6**, a comparison between the calculated values and the experimental results is shown. The calculated molar volumes reasonably accord with the experimental values within $\pm 0.88\%$.

Table 2 Numerical calculation results of molar volume and parameter β .

Temp. (K)	V_{CaO}	V_{MnO}	V_{SiO_2}	β
1823	22.6	18.5	29.6	- 9.48
1773	22.3	18.3	29.7	- 9.73
1723	21.5	17.9	29.9	- 9.57

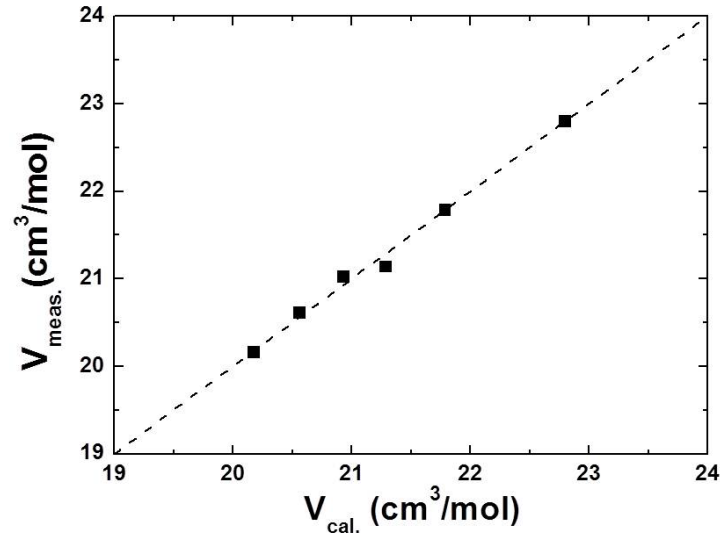


Fig. 6 Comparison between the calculated molar volumes and the measurements at 1773K.

In Fig. 7, the molar volumes of pure oxides are shown as a function of temperature. The molar volume of CaO at 1773K was 22.3 cm³/mol, which was close to the reported data by Mills (20.7 cm³/mol⁸) but slightly higher than that by Segers *et al.* (19.2 cm³/mol¹⁵). The molar volume of MnO at 1773K was 18.3 cm³/mol, which was slightly higher than the reported data by Mills (15.6 cm³/mol⁸), but close to that by Segers *et al.* (17.3 cm³/mol¹⁵). The molar volume of SiO₂ at 1773K was 29.7 cm³/mol, which was close to the value by Mills (27.5 cm³/mol⁸), but slightly higher than the extrapolated value from pure liquid SiO₂ by Bacon *et al.* (25.7 cm³/mol¹⁶). The molar volumes obtained in this study were mostly higher than the reported values, which was caused by the use of the non-linear thermal expansion data of the sinker (Eq. (3)). Nevertheless, the qualitative tendencies of the composition dependence were almost the same. The molar volumes are in the order of $V_{SiO_2} > V_{CaO} > V_{MnO}$. Accordingly, it is concluded that as the mole fraction of MnO increases, the slag volume decreases.

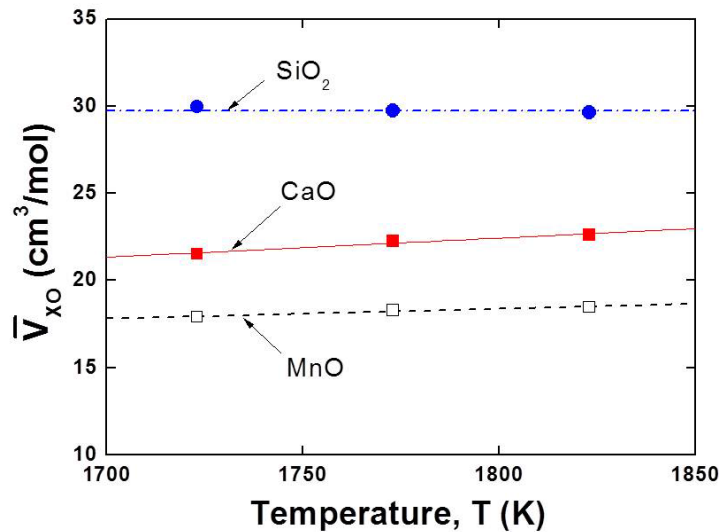


Fig. 7 Molar volumes of hypothetical pure liquid oxides (CaO, MnO, and SiO₂) as a function of temperature.

In **Fig. 8**, the excess volume of slag is shown with respect to the mole fraction of SiO₂ (X_{SiO_2}) at 1773 K. The molar excess volume was negatively deviated from the ideal mixing behavior, and could be expressed by $V^{Ex} = \beta X_{SiO_2} (1 - X_{SiO_2})^8$, where β is estimated to be -9.73. The maximum molar excess volume was corresponding to approximately 9.5~10.6% of the slag volume, which might be related to the bonding structure of the silicate melts. There was a slight difference between the measured data and the calculated values, which might be caused by difference in the characteristics of CaO and MnO in the silicate structure^{4), 17)}. Nevertheless, the maximum difference between the experimental data and the calculated values was less than 0.2 cm³/mol (less than 1% of the measured data) and this difference could be ignored.

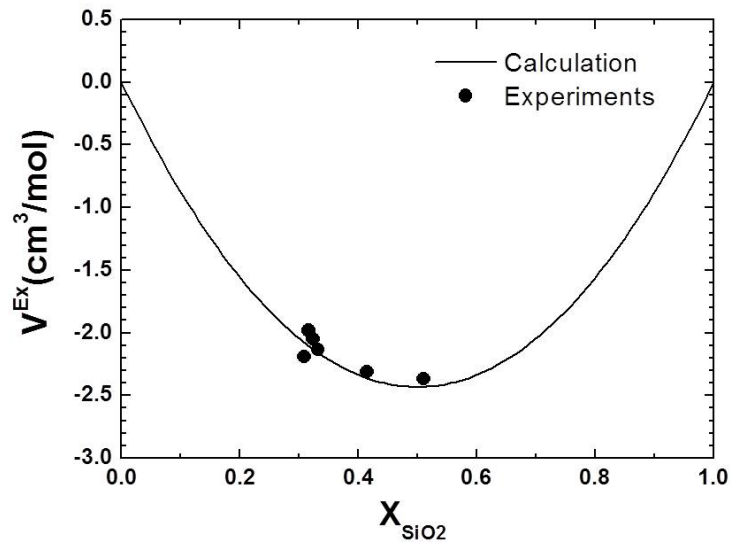


Fig. 8 Molar excess volume of the CaO-MnO-SiO₂ slag with respect to X_{SiO_2} at 1773K.

5. Conclusions

The density of CaO-MnO-SiO₂ slag was measured using the Archimedean method in the temperature range of 1719~1856K. The density was increased by increasing MnO content or decreasing temperature at a fixed CaO or at a fixed SiO₂ contents. From numerical calculations, the molar volumes of pure CaO, MnO, and SiO₂ at 1773K were evaluated 22.3, 18.3, and 29.7 cm³/mol, respectively. The molar excess volume could be described by $V^{Ex} = \beta X_{SiO_2} (1 - X_{SiO_2})^8$, where $\beta = -9.73$. The excess volume was negatively deviated from the ideal mixing behavior by 9~10% of the slag volume.

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