

## MEASUREMENT OF CaO-SiO<sub>2</sub>-CaCl<sub>2</sub> SLAG DENSITY BY AN IMPROVED ARCHIMEDEAN METHOD

Y. Wang<sup>a\*</sup>, K. Morita<sup>b</sup>

<sup>a</sup> Sichuan University, School of Chemical Engineering, Department of Metallurgical Engineering

<sup>b</sup> The University of Tokyo, Department of Materials Engineering, Hongo, Bunkyo-ku

(Received 05 September 2014; accepted 06 May 2015)

### Abstract

In order to optimize the removal of boron during the refining of slag to obtain solar grade silicon, the density of molten slag was measured by an improved Archimedean method within a temperature range from 1073 to 1373 K. It was found that the density of molten slag at 1723 K can be deduced by linear fitting, and that the slag density decreases with increasing temperature. However, a reduction in slag density occurs with decreasing CaO concentration. An increase in the molar volume of slag was also observed with increasing temperature.

Keywords: Molten slag; Density; Molar volume; Improved Archimedean method

### 1. Introduction

The widespread use of solar cells is dependent upon the availability of abundant and low-cost solar grade silicon (SOG-Si) feedstock; and although great progress has been made in reducing the energy consumption of modified Siemens and fluidized bed reactor processes, there is still a need for a more cost and energy efficient process. This would not only ensure the sustainability of SOG-Si production, but also offer benefits in terms of productivity and operating costs. To this end, metallurgical methods such as directional solidification [1-3], alloy refining [4-6], oxidation with plasma melting [7-8] and vacuum melting [9-10] have all been investigated, but each has its own inherent limitations. Moreover, none of these processes allow for all impurities to be removed. In the molten Si, some metal impurities, such as Al and Ti, their segregation coefficients are  $2.8 \times 10^{-3}$  and  $2 \times 10^{-6}$ , respectively. They are easier to be removed due to segregation coefficients are far from 1. But the segregation coefficient of B is 0.8 and that of P is 0.35, both of them are hard to be removed due to segregation coefficients are close to 1.

The removal of B and P by slag treatment [11-12] has therefore received considerable attention, as it has the potential for both low cost and mass productivity. Indeed, it has already been confirmed that a ternary slag of CaO-SiO<sub>2</sub>-CaCl<sub>2</sub> is effective in removing B from molten Si at 1723 K. In this, the concentration of B was reduced from 150 to around 30 ppmw, with a B-removal efficiency of as much as 86 % [13]. Further research into the relationship between time

and removal efficiency is therefore warranted to quantify the mass transfer between the slag and molten Si.

The density of molten slag is one of the most important physical properties for determining the mass transfer coefficient, molar volume and structure of the molten slag. However, although the densities of metallurgical slag systems such as MnO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> [14], CaF<sub>2</sub>-CaO-SiO<sub>2</sub> [15] and FeO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [16] have been previously measured, much less is known about the CaO-SiO<sub>2</sub>-CaCl<sub>2</sub> slag system. In the present study, the density of CaO-SiO<sub>2</sub>-CaCl<sub>2</sub> slag was therefore measured by an improved Archimedean method [17] at 1073 K, 1173 K, 1273 K and 1373 K.

### 2. Experimental

#### 2.1 Theoretical fundamentals of the experiments

The Archimedean method for determination of the density of a liquid slag is based on the buoyancy of a bob dipped in the liquid. It is difficult to estimate in reality though, as the effect of surface tension tends to add to the weight of the bob [18]. In order to minimize the influence of surface tension, a two-sphere method [19] has been used, as shown in Fig. 1. So, when only the lower bob is dipped into the molten slag, the weight  $W_1$  measured by the balance is given by:

$$W_1 = W_0 + V_1 \rho_l + \pi d \gamma \cos \theta \quad (1)$$

where  $W_0$  is the weight of the whole probe measured above the liquid surface;  $V_1$  is the volume of the lower bob, including the submerged part of the

\* Corresponding author: wangye@iis.u-tokyo.ac.jp

string;  $\rho_l$  is the density of the liquid;  $d$  is the diameter of the string;  $\gamma$  is the surface tension of the liquid; and  $\theta$  is the contact angle between the liquid and the string. When both bobs are dipped into the liquid, then the weight  $W_2$  is given by:

$$W_2 = W_0 + (V_1 + V_2)V_l\rho_l + \pi d\gamma \cos\theta \quad (2)$$

where  $V_2$  is the volume of the upper bob, which includes the submerged portion of the string.

By subtracting Eq. (1) from Eq. (2), the surface tension term is cancelled and the density  $\rho_l$  can be obtained as:

$$\rho_l = (W_1 - W_2) / V_2 \quad (3)$$

In this instance, the parameter  $V_2$  can be determined by an Archimedean volume measurement at room temperature using a liquid for which an accurate density is known, provided that the thermal expansion coefficient of the bob material is taken into account.

## 2.2 Experimental procedure

In order to apply the method (described in Section 2.1) to the measurement of slag density, the bob material needs to meet certain key requirements. Graphite was therefore selected, because it is significantly less reactive, non wettable and easier to prepare, comparing with SiC, Si<sub>3</sub>N<sub>4</sub> and metal materials [19]. All experiments were carried out using a high speed heating furnace (RMF-1, Hirochiku Co., Ltd.), which had a cylindrical chamber measuring 40 mm in O.D., 220 mm in I.D., and 78 mm in length. The heating element was a Kanthal Super (MoSi<sub>2</sub>) with an Al<sub>2</sub>O<sub>3</sub> refractory material. The maximum temperature was controlled at  $1473 \pm 2$  K using a proportional integral differential (PID) controller with a Pt-6% Rh/Pt-30% Rh thermocouple. A Pt crucible was used to hold the slag, which was kept under an Ar atmosphere during testing. An electronic balance (Shimadzu-UX8205) was used to measure any change in the weight of the bob. An illustration of the furnace, showing its various components and dimensions, is given in Fig. 2.

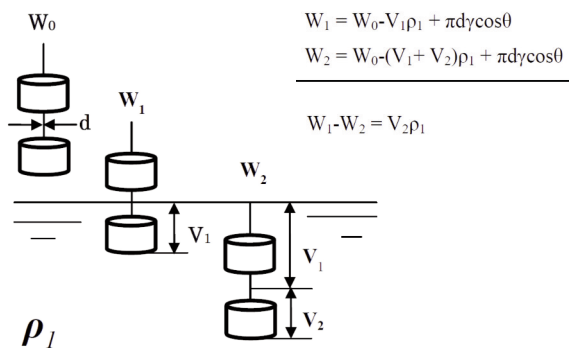


Figure 1. Concept of the double-bob method

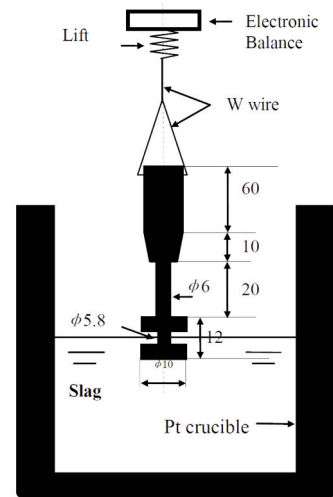


Figure 2. Schematic diagram of experimental set-up (mm)

The mole fraction of the slag used was  $x_{\text{CaO}} / x_{\text{SiO}_2} / x_{\text{CaCl}_2} = 0.47 / 0.23 / 0.3$  [11], giving a total sample mass of 15 grams. After experimentation, the concentration of Ca was measured by ICP-AES, and the SiO<sub>2</sub> and Cl<sup>-</sup> concentrations were measured using a gravimetric [20] and ion-selective electrode method [21], respectively. The weight of the bob was measured at temperature intervals of 1073 K, 1173 K, 1273 K and 1373 K. According to the fact that the furnace was limited to 1473 K, and that weight loss of the graphite bob increases above 1373 K, the density of slag at 1723 K was extrapolated by linear prediction.

## 3. Results and discussion

During measurement of the molten slag height, the bob was first lowered to the bottom of the crucible, with subsequent lifting of the bob causing the balance reading to change accordingly. The height at which the balance reading ceased to change was considered to represent the top of the molten slag. With the height of the molten slag estimated, the bob was lowered by 6 mm to find the balance reading equating to  $W_1$ , and then by a further 6 mm again to find  $W_2$ . The difference in the weight of the bob in argon and inside the slag, gave the weight loss as a result of the buoyant force applied by the molten slag bath. The volume of the slag displaced by the bob was considered equal to the volume of the bob immersed multiplied by a factor containing the volumetric expansion ratio for the linear expansion of graphite ( $\alpha_T$ ) [22] at any given temperature  $T$  (K):  $\alpha_{273} = 2.67\text{E-}5/T$ ,  $\alpha_{1073} = 2.90\text{E-}5/T$ ,  $\alpha_{1173} = 2.91\text{E-}5/T$ ,  $\alpha_{1273} = 2.92\text{E-}5/T$ ,  $\alpha_{1373} = 2.93\text{E-}5/T$  [23] and  $V_2 = 0.367\text{cm}^3$ . Thus, according to Eq. (3), the density at any temperature can be expressed as follows [24]:

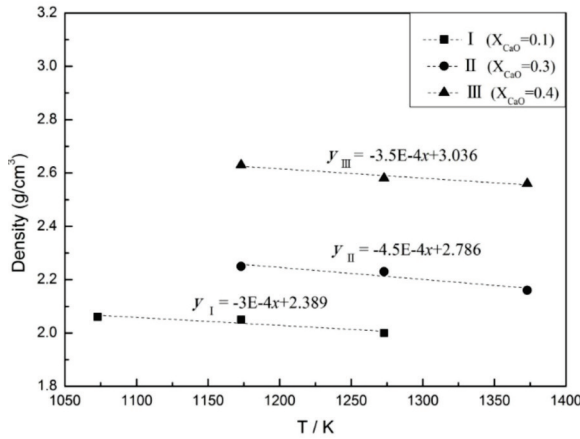
$$\rho_T = (W_1 - W_2) / V_2 (1 + 3\alpha_T \Delta T) \quad (4)$$

**Table 1.** Density of slag with different compositions and temperature

	$x_{CaO}:x_{CaCl_2}:x_{SiO_2}$ ( $x_{CaCl_2}/x_{SiO_2}=2/1$ )	NO.	T (K)	$\Delta W$ (g)	$\alpha$ (T)	V (cm <sup>3</sup> )	$\rho$ (g/cm <sup>3</sup> )
I	Initial: 0.1:0.6:0.3	1	1073	0.81	2.90E-05	0.367	2.06
		2	1173	0.81	2.91E-05	0.367	2.05
	Final: 0.18:0.51:0.31	3	1273	0.8	2.92E-05	0.367	2
II	Initial: 0.3:0.47:0.23	4	1173	0.89	2.91E-05	0.367	2.25
		5	1273	0.89	2.92E-05	0.367	2.23
	Final: 0.36:0.40:0.24	6	1373	0.87	2.93E-05	0.367	2.16
III	Initial: 0.4:0.4:0.2	7	1173	1.04	2.91E-05	0.367	2.63
		8	1273	1.03	2.92E-05	0.367	2.58
	Final: 0.44:0.33:0.23	9	1373	1.03	2.93E-05	0.367	2.56

Based on the calculated results given in Table 1, the relationship between CaO-CaCl<sub>2</sub>-SiO<sub>2</sub> slag density and temperature for different slag compositions is shown in Fig. 3. From this, the linear fitted relationship between density and temperature is found to be as follows:

$$\begin{aligned}
 \text{Slag I} &= 2.389-3 \times 10^{-4}T; \\
 \text{Slag II} &= 2.786-4.5 \times 10^{-4}T; \\
 \text{Slag III} &= 3.036-3.5 \times 10^{-4}T
 \end{aligned}
 \tag{5}$$



**Figure 3.** Temperature dependence of slag density

The first thing of note in Fig. 3 is that as the mole fraction of CaO increases from 0.1 (Slag I) to 0.4 (Slag III), the density of the slag increases from 2.00 to 2.63 g/cm<sup>3</sup>, which is due to the density of CaO (3.35 g/cm<sup>3</sup>) being greater than that of CaCl<sub>2</sub> (2.15 g/cm<sup>3</sup>) and SiO<sub>2</sub> (2.65 g/cm<sup>3</sup>). Secondly, the density of all the slags decreased slightly when the temperature increased, as this causes both the thermal motion of molecules and the volume to increase. Thirdly, using a linear fitting of the points between 1073 and 1373 K, the density of Slag I (2.43 g/cm<sup>3</sup>), Slag II (2.01 g/cm<sup>3</sup>) and Slag II (1.87 g/cm<sup>3</sup>) at 1273 K was determined. Thus, if Slag II is used to remove boron from silicon at 1273 K, its density would be 2.01 g/cm<sup>3</sup>.

The molar volume of a molten slag can be

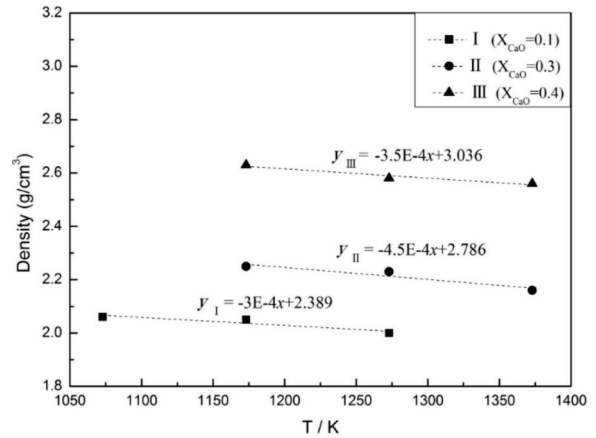
calculated from its molar mass and density by the following equation:

$$V_m = M/\rho \tag{6}$$

where  $V_m$  and  $M$  are the molar volume and molar mass of the slag, respectively. By inserting the values for  $M$  and  $\rho$  for the three slags into Eqn. (6), their molar volume can be expressed as follows:

$$\begin{aligned}
 \text{Slag I} &: 88.6/(2.389-3 \times 10^{-4}T) \\
 \text{Slag II} &: 77.97/(2.786-4.5 \times 10^{-4}T) \\
 \text{Slag III} &: 72.4/(3.036-3.5 \times 10^{-4}T)
 \end{aligned}
 \tag{7}$$

The temperature dependence of the molar volume of the slags is shown in Fig. 4, which clearly shows an increase in molar volume with increasing temperature.



**Figure 4.** Temperature dependence of molar volume for different slags

#### 4. Conclusions

In order to facilitate investigation into the kinetics of boron mass transfer from molten silicon to slag, the density of three different molten slags was measured by an improved Archimedean method at 1073K-1373K. From the results obtained, the following conclusions were made:

(1) The density of a CaO-SiO<sub>2</sub>-CaCl<sub>2</sub> slag decreases slightly with increasing temperature, but increases with increasing mole fraction of CaO increases.

(2) The molar volume of CaO-SiO<sub>2</sub>-CaCl<sub>2</sub> slags increases with temperature.

### References

- [1] X. Ma, T. Yoshikawa, K. Morita, *Metall. Mater. Trans. B*, 44 (2013) 528-533.
- [2] X. Ma, T. Yoshikawa, K. Morita, *J. Cryst. Growth.*, 377 (2013) 192-196.
- [3] N. Yuge, K. Hanazawa, Y. Kato, *Metall. Mater. Trans. B*, 45 (2004) 850-857.
- [4] M.A. Martorano, J.B. Ferreura Beto, T.S. Oliverira, T.O. Tsubaki, *Metall. Mater. Trans. A*, 42 (2011) 1870-1886.
- [5] X. Ma, T. Yoshikawa, K. Morita, *J. Alloys. Compd.*, 529 (2012) 12-16.
- [6] Y. Li, Y. Tan, J. Li, Q. Xu, Y. Liu, *J. Alloys. Compd.*, 583 (2014) 85-90.
- [7] K. Suzuki, T. Kumagai, N. Sano, *ISIJ International*, 32 (1992) 630-634.
- [8] N. Nakakura, H. Baba, Y. Sakaguchi, Y. Kato, *Metall. Mater. Trans. B*, 45 (2004) 844-849.
- [9] T. Ikeda, M. Maeda, *ISIJ International*, 32 (1992) 635-642.
- [10] S. Zheng, T. Abel Engh, M. Tangstad, X. Luo, *Metall. Mater. Trans. A*, 42A (2011) 2214-2215.
- [11] J.J. Wu, K. Liu, M. Xu, W.H. Ma, B. Yang, Y.N. Dai, *J. Min. Metall. Sect. B-Metall.*, 50(1) B (2014) 83-86
- [12] B.J. Jia, J.J. Wu, W.H. Ma, B. Yang, D.C. Liu, Y.N. Dai, *J. Min. Metall. Sect. B-Metall.*, 49(3) B (2013) 257-261
- [13] Y. Wang, X. Ma, K. Morita, *Metall. Mater. Trans. B*, 45B (2014) 334-337.
- [14] K. Mukai, H. Sakao, K. Sano, *J. Japan Inst. Metals*, 31 (1967) 928-933.
- [15] S. Hara, K. Ogino, *Tetsu-to-Hagane*, 75 (1989) 439-445 (in Japanese).
- [16] Z. Yu, K. Mukai, *J. Japan Inst. Metals*, 59 (1995) 806-813.
- [17] H. Sasaki, E. Tokizaki, K. Terashima, S. Kimura, *J. Cryst. Growth*, 139 (1994) 225-230.
- [18] S.C. Hardy, *J. Cryst. Growth*, 69 (1984) 456.
- [19] J.D. Mackenzie, *J. Chem. Phys.*, 29 (1958) 605.
- [20] X. D. Ma, Doctoral Thesis, 2013, U-Tokyo, pp. 100.
- [21] F. M. Najib, S. Othman, *Talanta*, 39 (1992) 1259-1267.
- [22] L. Muhmood, S. Seethataman, *Metall. Mater. Trans. B*, 41B (2010) 833-840.
- [23] B. T. Kelly, P. L. Walker, *Carbon*, 8 (1970) 211-226.
- [24] China Metallurgical Encyclopedia-Carbon Material, Metallurgical Industry Press, 2004, p. 125.