Density and Surface Tension of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ ($\text{R}=\text{Li, Na, K}$) Melts

Sohei SUKENAGA, Shinichiro HARUKI, Yoshitaka NOMOTO, Noritaka SAITO and Kunihiro NAKASHIMA

Department of Materials Science and Engineering, Kyushu University, 744, Motoooka, Nishi-ku, Fukuoka, 819-0395 Japan.
E-mail: sukenaga@zaiko.kyushu-u.ac.jp, haruki@melts.zaiko.kyushu-u.ac.jp, nomoto@melts.zaiko.kyushu-u.ac.jp, saito@zaiko.kyushu-u.ac.jp, nakasima@zaiko.kyushu-u.ac.jp

(Received on January 26, 2011; accepted on March 9, 2011)

In the present work, we measured the density and the surface tension of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ ($\text{CaO/SiO}_2=0.67$, $\text{Al}_2\text{O}_3=20$ mass%, $\text{R}_2\text{O}=10.8$ mol%, $\text{R}=\text{Li, Na, K}$) quaternary melts at elevated temperature using the double-bob Archimedean method and the ring method, respectively.

The density of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ melts decreased with temperature due to the thermal expansion of the melts. In addition, the density of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ ternary melt decreased with the addition of the alkali oxides. We converted the density into the molar volume to have a consideration on the microstructure of the melts. The molar volumes of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ melts are proportional to cube of the cationic radius for the alkali ions, which indicates the structural roles of the alkali oxides are mainly charge compensator to AlO_4^{5-} anions.

The surface tension of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ melts changed only slightly with temperature. The surface tension of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ ternary melt increased with the addition of Li_2O . In contrast, the surface tension decreased with the addition of Na_2O or K_2O . As for quaternary system, the surface tension increased with the ionic potential of the additive alkali ions; it is the same tendency with the binary alkali silicate melts. However, the mechanism of the surface tension change with the addition of the alkali oxides has not been clarified in the present study.

KEY WORDS: density; surface tension; structure of aluminosilicate melts and glasses; $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ based slags; physical property; alkali oxides; charge compensating cation.

1. Introduction

It is well known the cohesive zone is a main gas-permeability resistance in the blast furnace. Therefore, decreasing the temperature intervals of the cohesive zone would have a significant effect on the operation efficiency of the blast furnace and productivity of pig iron. Generally, the formation of the cohesive zone involves softening and melting of the ferrous burden, separation of the metal and slag, and finally dripping of the both phases.¹⁾ Higher separation and dripping rate of molten slag from metal phase would result in the shorter intervals of the cohesive zone. Density and surface tension of the molten slags are known to play important roles on the separation and the dripping behavior of molten slag from metal in the cohesive zone. For instance, Hino *et al.*²⁾ reported that dripping behavior of molten slag from metallic iron depends on the surface tension and the density of the slag melts. Additionally, the density and the surface tension of the molten slag are important physical properties to understand the microstructure of the slags at elevated temperature for the fundamental aims of the scientific study on molten slags.

According to these practical and fundamental backgrounds, the density and the surface tension of binary silicate and ternary aluminosilicate slags have been measured

by a large number of researchers.^{3–10)} However, the practical slags formed at the cohesive zone are multi-component systems, which are known to be mainly composed of CaO , SiO_2 and Al_2O_3 with some extent of MgO , FeO and alkali oxides.¹¹⁾ Few studies have been conducted on the multi-component aluminosilicate systems and reliable data of these physical properties for multi-component slags have been strongly desired.

The basicity (CaO/SiO_2) of typical blast furnace type slags is known to be 0.8–1.2.¹²⁾ However, we employed the slags with the basicity of 0.67 because the microstructure of the melts have been clarified in the previous study.^{13,14)} In the present paper, we measured the density and the surface tension of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ ($\text{CaO/SiO}_2=0.67$; $\text{Al}_2\text{O}_3=20$ mass%; $\text{R}=\text{Li, Na, K}$) quaternary melts at elevated temperature using the double-bob Archimedean method and the ring method, respectively. Effect of the alkali oxide addition on the density and the surface tension of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ melt were mainly explored.

2. Experimental

2.1. Sample Preparation

$\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ ($\text{CaO (mass\%)/SiO}_2 \text{ (mass\%)} = 0.67$, $\text{Al}_2\text{O}_3=20\text{mass\%}$)- R_2O ($\text{R}=\text{Li, Na, K}$) slags were employed

for the density and the surface tension measurements. The R_2O additives were replaced with CaO and SiO_2 ; the CaO (mass%)/ SiO_2 (mass%) ratio was fixed as 0.67. Mass percentages of the chemical compositions are converted into molar percentage listed in **Table 1**. To make clear the effect of the kinds of R_2O additives on density and surface tension, the content of R_2O (10.8 mol%) additives in these slags was kept constant; the molar fraction of CaO, SiO_2 and Al_2O_3 changes only slightly with the kinds of the alkali oxides. The samples were prepared from reagent grade SiO_2 , $CaCO_3$, Al_2O_3 , Li_2CO_3 , Na_2CO_3 and K_2CO_3 powders (suppliers: Sigma Aldrich, Inc.). These reagents were precisely weighed to form given compositions and mixed in a mulite mortar thoroughly. The mixtures were placed in a Pt crucible and then melted at 1873 K in a resistance furnace for 30 minutes under air. Finally, the melts were quenched on a copper plate. Then these quenched samples were employed for density and surface tension measurements.

2.2. Density Measurement

Densities of the sample melts were measured by the double-bob Archimedean method.^{5,10)} **Figure 1** represents the schematic illustrations of the apparatus for density measurements. An electric resistance furnace with six U-shape $MoSi_2$ heating elements was employed for heating and melting (Fig. 1(a)). A Pt crucible (inner diameter: 65 mm, height: 27 mm) and two kinds of Pt bobs with different size were used in the experiments. The dimensions of these bobs are given in Figs. 1(b) and 1(c). The density of the sample melts, ρ , was determined by the following equation:

$$\rho = \frac{B_1 - B_2}{V_1 - V_2} \quad \text{..... (1)}$$

where B_1 and B_2 are buoyancies, and V_1 and V_2 are the submerged volume of the large and the small bobs, respectively. The buoyancies were measured by using a commercial electric balance. The thermal expansion of the large and the small bobs are corrected by Eq. (2):

$$V_1 - V_2 = (V_1' - V_2') \cdot (1 + 3\alpha\Delta T) \quad \text{..... (2)}$$

where V_1' and V_2' are the submerged volume of the large and the small bobs at room temperature determined by the Archimedean method using distilled water as immersion liquid. α and ΔT are linear expansion coefficient of Pt and a difference between room and measuring temperature, respectively.

Measurements were conducted at temperature intervals of 50 K on cooling under air (temperature range: 1623–1773 K). We measured the buoyancies 5 times at each of the examined temperature. The scatter of the measured density value was estimated to be within $\pm 1.8\%$; the scatter was due to the repetitive error of the buoyancies measurements.

2.3. Surface Tension Measurements

Surface tension of the sample melts was measured by the ring method.¹⁰⁾ **Figure 2** shows the schematic illustrations of the apparatus for surface tension measurements. A heating system of the apparatus is the same as the apparatus for density measurements (Fig. 2(a)). A Pt crucible (inner diameter: 65 mm, height: 27 mm) and a Pt-10mass%Rh-0.16mass% ZrO_2 ring were used in the experiments. The dimension of the ring is given in Fig. 2(b). Determination of the surface tension, γ , is based on measurements of the maximum force, $W_{\max}$, exerted on a ring body as the ring is withdrawn from the surface of the liquid. γ is expressed by Eq. (3):

$$\gamma = \frac{W_{\max} \cdot g}{4\pi R_0 (1 + \alpha\Delta T)} \cdot S \quad \text{..... (3)}$$

where R_0 is the radius of the ring. S is an empirical correc-

Table 1. Chemical compositions (mol%) of the CaO– SiO_2 – Al_2O_3 – R_2O slags for density and surface tension measurements.

Sample	Components (mol%)					
	CaO	SiO_2	Al_2O_3	Li_2O	Na ₂ O	K_2O
CAS	36.5	51.0	12.5	–	–	–
CAS-Li	32.2	45.1	11.9	10.8	–	–
CAS-Na	31.9	44.7	12.6	–	10.8	–
CAS-K	31.6	44.2	13.4	–	–	10.8

Fig. 1. Schematic illustrations for (a) the apparatus for density measurements, (b) the large Pt bob and (c) the small Pt bob.

Fig. 2. Schematic illustrations for (a) the apparatus for surface tension measurements and (b) the Pt-10mass%Rh-0.16mass% ZrO_2 ring.

tion factor known as Harkins and Jordan's correction factor,¹⁵⁾ which is dependent on $W_{\max}/\rho$. In the present work, an empirical relationship between S and $W_{\max}/\rho$ was determined by using the molten salts (PbCl_2 , KNO_3 , KCl , NaNO_3 , K_2SO_4 and Na_2SO_4) as reference samples; the density and the surface tension of these molten salts are known.¹⁶⁾ The relationship between S and $W_{\max}/\rho$ of these molten salts are shown in Fig. 3. We employ the linear relationship in Fig. 3 to determine the correction factor S that is expressed by the following equation.

$$S = 0.65 + 0.2229 \times 10^6 \cdot \frac{W_{\max}}{\rho} \quad (4)$$

The sample slag was placed in the Pt crucible and heated up to 1 823 K under air. The ring was touched on the surface of the sample melts, and then pulled up slowly. The force exerted on the ring was detected by using a commercial strain gauge as the potential difference; $W_{\max}$ was calculated based on the reference relationship between the exerted force and the potential difference, which was obtained by using various standard weights beforehand. The measurements were made at temperature intervals of 50 K on cooling under air (temperature range: 1 623–1 823 K). We measured the $W_{\max}$ 5 times at each of the examined temperature. The scatter of the measured surface tension value was estimated to be within $\pm 0.9\%$; the scatter was due to the repetitive error of the measured $W_{\max}$ and the density value.

3. Results and Discussion

3.1. Density

Figure 4 shows temperature dependences for the density of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ melts. Density of all the samples decreased with temperature due to the thermal expansion of the melts. The density of the CAS melts decreased with the addition of the alkali oxides. The decrease in density was larger in the order of cationic radius of the alkali ion. Density of the melt is not only dependent on the struc-

ture of the slag but also dependent on the molecular weight of the component oxides. Therefore, we converted the density into the molar volume by Eq. (5) to have a structural consideration.

$$V_m = \frac{\sum n_i \cdot M_i}{\rho} \quad (5)$$

n_i and M_i are the molar fraction and molar weight (10^{-3} kg/mol) of a component i , respectively.

Figure 5 represents the molar volume of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ melts. The molar volume of the CAS melts increased with the addition of the alkali oxides. It should be also noted that the molar volume of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ quaternary melts was in the order of the cationic radius of alkali ion ($\text{CAS-K} > \text{CAS-Na} > \text{CAS-Li}$).

It is well known that Al_2O_3 is an amphoteric oxide and its behavior depends on the basicity of the melts to which it is added. When an AlO_4^{5-} is incorporated into the silicate network, it is necessary that the electrical charge balance is

Fig. 4. Temperature dependences of the density for the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ melts.

Fig. 3. The relationship between $W_{\max}/\rho$ and the empirical correction factor S for the several kinds of molten salts.

Fig. 5. Temperature dependences of the molar volume for the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ melts.

maintained. Namely, an AlO_4^{5-} tetrahedra requires a charge compensating alkali or alkaline earth cation as shown in **Fig. 6**, otherwise Al^{3+} ions behave as network modifying cation. In the previous paper,¹⁴⁾ we performed the ^{27}Al MAS NMR spectra of the glasses in the same composition as the present samples. ^{27}Al MAS NMR spectra indicated that most of Al^{3+} was in four-fold coordination in the glasses. Since the sample was in the percalcic region (CaO (mol%)/ Al_2O_3 (mol%)>1), there are enough calcium or alkali ions to charge-compensate the AlO_4^{5-} tetrahedron. Roy *et al.*¹⁷⁾ reported the stability of aluminosilicate framework is inversely related to the cationic field strength (CFS) of charge compensating cations for AlO_4^{5-} tetrahedrons. CFS is expressed by the following equation (6):

$$\text{CFS} = \frac{Z}{r^2} \dots\dots\dots (6)$$

where Z is the valence number of the cation, r is the cationic radius. Since the CFS of the alkali ions is smaller than that of calcium ion (Li: 1.73, Na: 0.96, K: 0.53, Ca: 2.00)*, the negative charges of AlO_4^{5-} tetrahedrons would be preferentially compensated by the alkali ions in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ system. Lee and Sung¹⁹⁾ examined the effect of the ratio of Na_2O to CaO on the cation distribution in $(18.75\text{-X})\text{CaO-XNa}_2\text{O-6.25Al}_2\text{O}_3\text{-75SiO}_2$ (mol%) quaternary aluminosilicate glasses ($X=18.75\cdot\text{Na}_2\text{O}/(\text{CaO}+\text{Na}_2\text{O})$) by using ^{17}O 3QMAS NMR. They reported that Na ion plays a preferential role of a charge compensator, while Ca ion can act as a network modifier. Additionally, in their study, most of Na ions behave as a charge compensator to AlO_4^{5-} anions in the glass with $\{\text{Na}_2\text{O}/(\text{CaO}+\text{Na}_2\text{O})\}=0.250$; the ratio, $\{\text{Na}_2\text{O}/(\text{CaO}+\text{Na}_2\text{O})\}$, is comparable to that of the CAS-Na ($=0.253$). Therefore, we assumed the structural role of Na ions were charge compensator to AlO_4^{5-} anions in the CAS-Na melt in the present study. If the structural roles of Li and K ions were the same as Na ions (charge compensator), the molar volume of the melts would be linearly related to the cationic volume of the alkali ions. **Figure 7** shows the relationship between the cube of alkali ion radius and the molar volume of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ quaternary melts at 1773 K. The molar volume of the melts increased linearly

Fig. 6. Schematic representation of the local network structure for aluminosilicate anion.

with the cube of the radius for the alkali ions, which indicates that all kinds of the alkali ions would mainly behave as the charge compensator for AlO_4^{5-} tetrahedron in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ quaternary melts. Therefore, the addition of the alkali oxides to the CAS melts means the formation of AlO_4^{5-} tetrahedrons compensated by the alkali ions and the non-bridging oxygen bonded with calcium ions.

The molar volume of CaO-SiO_2 melts has been reported to decrease with the addition of CaO .⁵⁾ However, the molar volume of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ melts increased with formation of Si-O-Ca bonding in the present study. Hence, the formation of AlO_4^{5-} tetrahedrons compensated by alkali ions dominates the change in the molar volume of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ melts with the addition of the alkali oxides. Tomlinson *et al.*⁵⁾ reported that the occupied volume of the two monovalent cations was approximately 3 times a divalent cation which has the same cationic radius as the monovalent cation. Since the charge compensating cation changed from calcium to alkali cation with the addition of the alkali oxide to the CAS melt, the occupied volume of the charge compensating cation increased. Therefore, the molar volume of the CAS melt was thought to increase with the addition of the alkali oxide.

3.2. Surface Tension

Figure 8 shows temperature dependences of the surface tension of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ melts. The surface tension of the CAS ($36.5\text{CaO-51.0SiO}_2\text{-12.5Al}_2\text{O}_3$ (mol%)) melt is consistent with the surface tension of the $35.9\text{CaO-51.2SiO}_2\text{-12.9Al}_2\text{O}_3$ (mol%) melt measured by Mukai *et al.*,⁹⁾ the chemical compositions of these melts are comparable. In addition, the surface tension of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ melts changed only slightly with temperature.

The surface tension of the CAS melt increased with the addition of Li_2O . In contrast, the surface tension of the CAS melt decreased with the addition of Na_2O or K_2O . The mechanisms of the surface tension change for silicate and aluminosilicate melts with addition of the oxides compo-

Fig. 7. Relationship between the cube of cationic radius for the alkali ions and the molar volume of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-R}_2\text{O}$ melts at 1773 K.

*Cationic radii reported by Shanon *et al.*¹⁸⁾ are employed for calculation of the CFS.

Fig. 8. Temperature dependences of the surface tension for the CaO-SiO₂-Al₂O₃-R₂O melts.

Fig. 9. Variation of the surface tension for the CaO-SiO₂-Al₂O₃-R₂O melts at 1773 K is plotted with the ionic potential of the alkali ions. The solid lines represent only guide for eyes.

nents have not been well understood. However, as for binary silicate melts, the surface tension is known to depend on the kinds of network modifier cation. Boni and Derge²⁰⁾ suggested that surface tension of the binary silicate melts increased with an increase in the ionic potential (I_p) of the network modifier cation. I_p is expressed by the following equation (7):

$$I_p = \frac{Z}{r} \quad \text{..... (7)}$$

Figure 9 represents the relationship I_p of the additive alkali ions and the surface tension of the CaO-SiO₂-Al₂O₃-R₂O melts at 1773 K. The surface tension of the CaO-SiO₂-Al₂O₃-R₂O melts increased with the I_p of the alkali ions. The order of Li > Na > K found in Fig. 9 is the same tendency as the surface tension of the binary alkali silicate melts.³⁾ As we have described previously, the alkali ions

would mainly behave as charge compensator to the AlO₄⁵⁻ anions in the CaO-SiO₂-Al₂O₃-R₂O system. Hence, the alkali ions behaving as charge compensator had similar contribution to the surface tension with those ions behaving as a network modifier. However, the mechanism of the surface tension change with the addition of the alkali oxides was not clarified in the present study.

4. Concluding Remarks

In the present study, the effect of the alkali oxide (Li₂O, Na₂O, K₂O) addition on the density and the surface tension of the 36.5mol%CaO-51.0mol%SiO₂-12.5mol%Al₂O₃ (CAS) melt have been explored.

The density of the CAS melt decreased with the addition of the alkali oxides. We could have a consideration on the microstructure of the melts by converting the density into the molar volume. The molar volume of the CaO-SiO₂-Al₂O₃-R₂O melts is proportional to cube of the cationic radius for the alkali ions, which indicates the structural roles of the alkali oxides are mainly charge compensator to AlO₄⁵⁻ anions. The direct observation of the cation distribution in the CaO-SiO₂-Al₂O₃-R₂O quaternary melts by using spectroscopic method is desired for understanding of the microstructure for the melts.

The surface tension of the CAS melt increased with the addition of Li₂O. In contrast, the surface tension decreased with the addition of Na₂O or K₂O. As for quaternary system, the surface tension order Li > Na > K is same as that of binary alkali silicate melts. However, the mechanism of the surface tension change with the addition of the alkali oxides has not been clarified in the present study. More of the measurements for the surface tension of the ternary and quaternary aluminosilicate melts are desired to understand the mechanism of the surface tension change with the addition of the alkali oxides.

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