Surface tension of selected CaO-MgO-Al$_2$O$_3$-SiO$_2$ slag with low silica content

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Abstract: The surface tension in CaO-MgO-Al$_2$O$_3$-SiO$_2$ slag with low silica was measured by the Slide method using the RTW-08 type-testing instrument from 1773K to 1873K. The measurements were carried out under reducing atmosphere. Nine different slag compositions were chosen based on three different levels of CaO content and three different levels of SiO$_2$ content. The MgO content was equaled to 7.00 wt%. The CaO content were varied from 40.04 wt% to 50.64 wt%, for SiO$_2$ content between 10.25 wt% and 20.70 wt%. Experimental results showed that, in general, the effect of the temperature on the surface tension of the selected slag system was not obvious. The results also indicted that the surface tension decreasing with the increase of the NBO/T ratio, and following by increasing with further increasing of the NBO/T ratio. Based on the experimental data as the boundary of the homogenous phase region predicated by FACTSAGE software. The mass triangle model was used to calculate the surface tension of selected limited homogenous phase region. The results showed the mass triangle model working well. The overall trend that the effects of component content on the surface tension was found in agreement with the experimental observation.

Keywords: CaO-MgO-Al$_2$O$_3$-SiO$_2$, surface tension, low silica, NBO/T ratio

1. Introduction

The measurement of surface tension of molten slags is of great importance not only to the fundamental research for the melts, which is directly linking to their structure of molten slags, but also to the industrial applications. Many metallurgy phenomena such as inclusion formation in metal bath and its removing, slag foaming, slag-metal reaction kinetics are closely related to surface tension of the molten slag.

The CaO-MgO-Al$_2$O$_3$-SiO$_2$ system is of considerable importance in the technology of a large number of industrial processes, and it is one of fundamental to the understanding of metallurgical slags, refractory, ceramic materials and geological phenomena. Many researchers have reported the surface tension at various compositions [1]. However, few researchers have made measurements in the low-silica region. Al$_2$O$_3$ slags containing silicate are applied in a wide range in metallurgical processes. The structural role of Al$_2$O$_3$ in silicate is also an important subject attracting a lot of interest [2-4]. It is widely accepted that Al^{3+} has a strong preference for tetrahedral coordination in silicate melts [5]. The CaO/SiO$_2$ ratio is an indication of the degree of polymerization, which is sensitive to the physical and chemical properties of slag. Under a low content of Al$_2$O$_3$, the CaO/SiO$_2$ ratio can be characterized to determine the slag metallurgical, physical and chemical properties (including viscosity, desulphurization performance, etc.). However, under a high content of Al$_2$O$_3$, the CaO/SiO$_2$ ratio was not suitable to evaluate the metallurgical and physical and chemical properties of slag. But its effect on the structure of low SiO$_2$ containing slags is less well known and resulting effect on the slag surface tension has not been quantified.

Since the information on the surface tension in CaO-MgO-Al$_2$O$_3$-SiO$_2$ system with low silica content have not yet been reported systematically yet so far, and further work in this direction to meet the demand in the industry is essential.

The aim of the present study is to experimentally investigate the influences of temperature on synthetic slag of the selected CaO-MgO-Al$_2$O$_3$-SiO$_2$ system. The selected compositions in the present study are close to the synthetic-slag used in secondary refining processes. For instance, LF and ESR the slags have typically high basicity with high Al$_2$O$_3$, but low SiO$_2$. The relationship between the surface tension and the NBO/T ratio as a structural parameter to measure the depolymerization of melts was also discussed. However, accurate experimental data of surface tension for slag system required are not available mainly due to the difficulties in high temperature measurements. Based on the experimental data as the boundary of the homogenous phase region, the surface tension of the selected homogenous phase region pre-defined was predicated by the mass triangle model proposed by K. C. Chou[6].

2. Experimental

2.1 Sample preparation

These samples were prepared from chemical powders in C.P. grade purity, i.e. CaO ($\geq$99.0 pct), Al$_2$O$_3$ ($\geq$99.5 pct), MgO ($\geq$99.0 pct) and SiO$_2$ ($\geq$99.0 pct). The powders were ground and weighed to the desired compositions and mixed in a mortar, and then mixtures were melted in a graphite crucible in induction furnace for 30 min at 1773K under air-atmosphere. The fused slag samples were poured onto the surface of a cold steel plate. For further homogenization, these samples were crushed and ground into fine powders. These samples in corundum crucible were dried for decarburize at 1223K for 30h in a muffle furnace. Finally, chemical analysis was carried out to check the composition of the samples. These homogeneous slag powders were ready to be used in surface tension measurement. The slag in the measurements was prepared in the laboratory, and the method of preparation was reported elsewhere [7]. Table 1 also gives the analyzed chemical compositions of the homogeneous samples. Therefore, the composition of the homogeneous samples is more representative than the desired compositions. Summation of the wt. pct is not 100 because of errors in chemical analysis.

Table 1 Nominal and analyzed chemical composition of slag samples

Sample	Weighted-in compositions (mass%)				Analyzed compositions (mass%)					
	CaO	MgO	Al$_2$O$_3$	SiO$_2$	CaO	MgO	Al$_2$O$_3$	SiO$_2$	Total	NBO/T
C1	40.00	43.00	7.00	10.00	40.38	41.73	6.60	10.25	98.96	0.96
C2	40.00	38.00	7.00	15.00	40.04	36.80	6.45	15.24	98.53	1.06
C3	40.00	33.00	7.00	20.00	40.37	32.11	6.63	19.45	98.56	1.20
C4	45.00	38.00	7.00	10.00	45.58	37.70	6.62	10.44	100.34	1.34
C5	45.00	33.00	7.00	15.00	45.38	32.11	6.45	15.87	99.81	1.47
C6	45.00	28.00	7.00	20.00	45.40	27.75	7.12	19.53	99.80	1.65
C7	50.00	33.00	7.00	10.00	50.64	32.51	6.40	10.40	99.95	1.84
C8	50.00	28.00	7.00	15.00	50.30	27.66	6.63	15.53	100.12	1.98
C9	50.00	23.00	7.00	20.00	50.09	22.84	6.70	20.70	100.33	2.11

2.2 Measurement

The surface tension was measured by using a RTW-08 typed testing instrument by the Slide method, which involves measuring the maximum excess force exerted on a cylinder during its withdrawal from immersion in the melt. The furnace has a maximum continuous temperature of 1873K, and its temperature is controlled by a controller unit. The temperature was measured by a B-type thermocouple touching the crucible bottom from outside, its accuracy was 1K between 1073K and 1973K. The experimental temperature range was from 1773K to 1823K. The metal pin for surface

tension measurement was made of molybdenum, which has a melting point of 2896K. The dimension of the pin at high temperature was calculated from those measured at room temperature and coefficient of thermal expansion of molybdenum [8]. Dimension of the pin was presented in Fig. 2. The size of pin has to be carefully designed so that it is applicable in the required measurement range. The crucible was made of graphite. As the graphite crucible, measurement process is carried out under reducing atmosphere. Knowledge of this maximum force and the dimensions of the cylinder allow the surface tension of the melt to be determined as follows:

$$\sigma = \frac{M_{max}g}{4\pi R} f(\frac{R^3}{V}, \frac{R}{r}) = \frac{M_{max}g}{4\pi R} C \qquad (1)$$

where M_{max} is the maximum excess force required for detachment of the pin from the surface of the melt, R is the average of the inner and outer radii of the pin, r is half the wall thickness of the pin, V is the volume of liquid suspended above the free surface of the melt, and f (R^3/V, R/r) is a correction factor to account for the noncylindrical shape of the suspended liquid, which was measured by pure water several times until the measured values are stable measurement at room temperature and coefficient of thermal expansion of molybdenum.
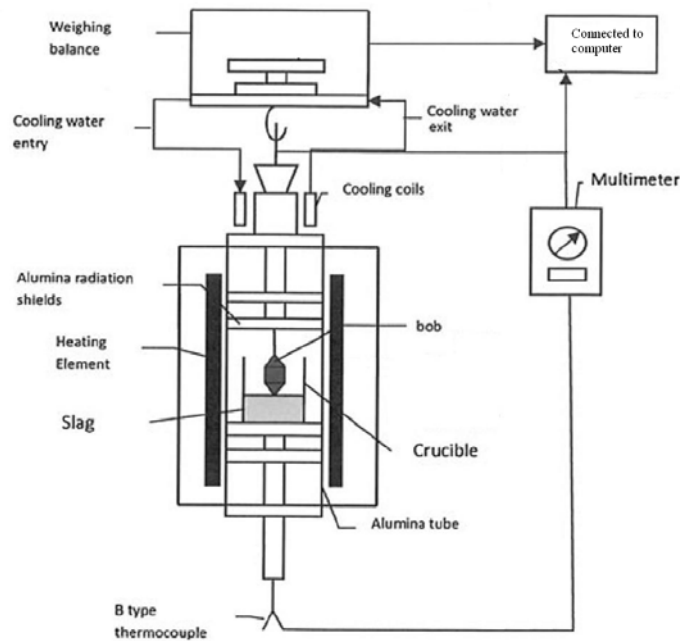

Fig. 1 Schematic diagram of experimental apparatus

The container was 80mm in deep, which may seems too deep. However, when the crucible was filled and treaded with a slag powder, it was almost completely full. After melting, the volume of the slag was only about 50% of the powder's volume. The crucible filled with 120g slag was placed in the furnace, and the furnace was programmed to heat up to 1773K with heating rate of 10K/min. The furnace was kept at the temperature at least for 30min before the first measurement. Then the furnace was heated up to 1823K with heating rate of 2K/min. The surface tension of slags was measured at the predetermined temperature, which was repeated several times until the measured values are stable measurement. After all determined temperature measurement was completely, drained off, the furnace was cooled down

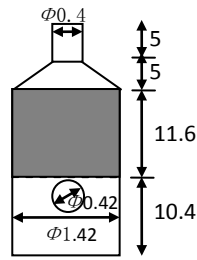to the room temperature.

Fig. 2 Dimension of the pin (mm)

3. Results and Discussion

The surface tension of the selected quaternary $CaO-MgO-Al_2O_3-SiO_2$ slag with low silica content was measured. Nine different slag compositions were chosen in this system based on three different levels of CaO content and three different levels of SiO_2 content. The MgO content was equaled to 7.00wt%. The CaO content was varied from 40.04 wt% to 50.64 wt%, for SiO_2 content between 10.25 wt% and 20.70 wt%. The surface tension measurements were performed in a wide temperature range from 1773K to 1873K. In order to ascertain the reliability of the data, some of the experiments were repeated with the new samples, such as in numbers of C7, C8 and C9. The mean derivations of three slags were about 2.80 %.

3.1 Effect of temperature on surface tension

The surface tension of selected slags, which was determined at various temperatures, is shown in Fig. 3. Experimental results showed that some surface tensions of slag increased with the increase of temperature, while others decreased, such as C6, C7, C8 and C9. As shown in Table 2, the temperature coefficients, dσ/dT, of the selected slags were in wide range from -2.64×10^{-3} to $2.62\times10^{-3}N\bullet m^{-1}\bullet K^{-1}$. In general, the temperature on the surface tension of the slag system has little influence. This could be considered as follows. When the temperature increased, the particle's thermal motion was enhanced and the distance between particles increased, the force between particles was weakened, which led to the decrease of the surface tension of the melt. However the temperature rise would cause the kinetic energy of particles to increase, therefore to promote the complex ions adsorbed on surface of the melt to be desorbed into the melt. This would increase the surface tension [9]. The surface properties may be affected by the structure of molten slag, the positive temperature coefficients may be associated with the presence of bridging oxygen on the surface [10].
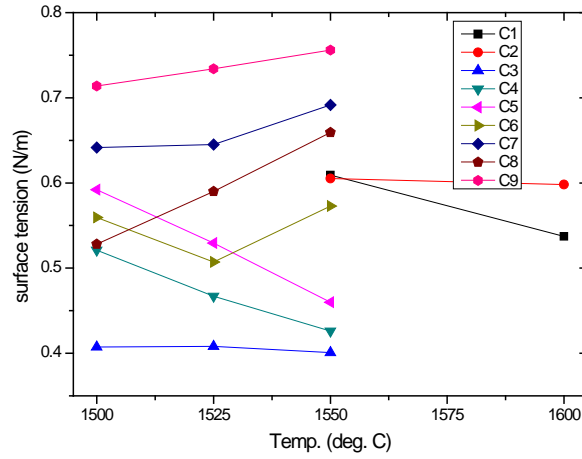
Fig. 3 Temperature dependence of the selected slags surface tension

Table 2 Temperature coefficients of surface tension for selected slags

	C1	C2	C3	C4	C5	C6	C7	C8	C9
$d\sigma/dT \times 10^3$ [$N \cdot m^{-1} \cdot K^{-1}$]	-1.44	-0.14	-0.14	-1.90	-2.64	0.26	1.00	2.62	0.84
$\triangle$T (K)	1823-1873				1773-1823				

3.2 Effect of the NBO/T ratio on the surface tension of the selected slags

Since the surface tension of liquid slags is slightly dependent upon structure, in recent years the (NBO/T) ratio was adopted to indicate the number of non-bridging oxygens per tetrahedrally-coordinated atom, and to represent the degree of depolymerization of the melt by many workers [10]. The NBO/T ratio for multi-component slag can be given as follows:

$$Y_{NB} = \sum 2[x(CaO) + x(MgO) - 2x(Al_2O_3)] \qquad (1)$$

$$x_T = \sum [x(SiO_2) + 2x(Al_2O_3)] \qquad (2)$$

$$NBO/T = Y_{NB}/x_T \qquad (3)$$

where x_i is the mole fraction of pure component i.

The effect of the NBO/T ratio on the surface tension of the selected slags was shown in Figure 4. It is obvious that the NBO/T ratio had obvious influence on the surface tension of the selected slags. As can be seen, while increasing the NBO/T ratio, the surface tension decreasing first to a minimum value, which was 0.401 N/m when the NBO/T ratio was 1.20 at 1773K, then increasing slowly again. Slags mainly are composed by the cations and complex anions, the attraction force between ions directly affect the slag surface tension [11]. The tendency of the surface tension changed with composition could be due to the degree of polymerization, and the NBO/T ratio could be considered to provide an alternative measure of the degree of polymerization. It can be seen from that the NBO/T ratio **does allow for the cations occupation on charge-balancing duties.** The NBO/T ratio is probably the best measure of the degree of polymerization.

In a molten silicate slag system, the gradual addition of CaO and MgO would result in the progressive breaking of these oxygen bonds with the formation of non-bridging oxygen (NBO), with an increasing in basicity, the complex

polymers of silicate complex structures as SiO_4^{4-} and AlO_4^{5-} tetrahedral would break down into smaller units to release O, and even form of free oxygen, O^{2-}, ions. Higher CaO concentration could make the complex polymers of aluminum complicated structures as SiO_4^{4-} and AlO_4^{5-} tetrahedral break down into smaller units, reduce the degree of polymerization and the attraction force between ions increase. The pure components surface tension of CaO, MgO, Al_2O_3 and SiO_2 are as high as 0.621N/m, 0.611N/m, 0.701N/m and 0.300N/m respectively [12]. With constant CaO and MgO contents, using Al_2O_3 to replace SiO_2 in the present slags should reduce the degree of polymerization, and lower surface tension of the slags. With the increasing CaO content, the Al_2O_3 content decrease should also reduce the degree of polymerization, the mole fraction of SiO_2 decreases would slowly increase the surface tension of the slag.
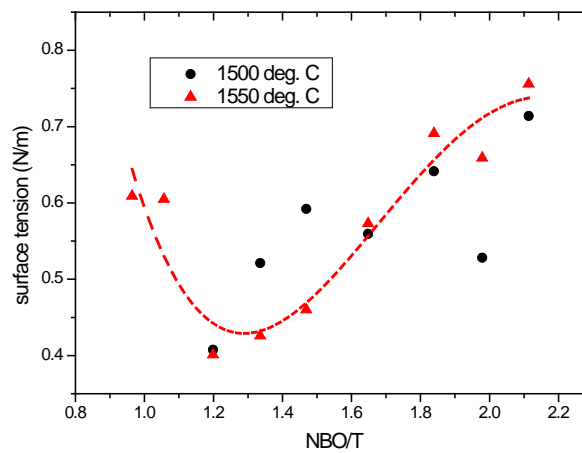

Fig. 4 Relationship between surface tension and the NBO/T ratio at 1823K

4. Estimated surface tension of the selected limited homogenous phase region

It is necessary to have access to reliable models for estimating surface tension of slags, because the inherent problems and difficulties associated with measurements at high temperature. There are many kinds of model [12-20] for estimating surface tension of slag, which are physical model and semi-empirical model. However, it is difficult to use these models in a system with a limited homogenous phase region since information in its subsystems is not available. In order to overcome this problem, Chou et al. [20] proposed a new model, which is presented below. This model is the so-called the mass triangle model which does not have to use subsystem information. Instead, it can use the limited data on the boundary of a homogenous region to calculate the properties within it. The advantage of this model is its flexibility to use limited experimental data within the homogenous phase region to predict the physical chemical properties at any point within the region. It has earlier been proved that the mass triangle model had been successfully used to calculation of properties in the system with a limited solubility area [21-23]. In order to orient the readers, a brief description of the mass triangle method can be found in reference [6].

As shown in Fig.5, the selected area of CaO-7 mass%MgO-Al_2O_3-SiO_2 slag in the present work has a limited homogenous phase region of liquid phase at 1823 K, where the liquidus isotherms was predicated by FACTSAGE

software [24]. Based on the experimental data as mentioned above within this region, the mass triangle model was used to calculate surface tension with surface tension information only on the boundary of the homogenous phase region. Eight experimental data, which are the present experimental data except C5, were picked up for calculation boundary. Three surface tension contour lines were calculated and shown as open points in Fig. 7. The experimental data are also shown in the same figure as markers. It can be seen from this figure that the calculated surface tension agrees with the experimental data of C5. Thus, the overall trend that the effects of component content on the surface tension is in agreement with the experimental observation. Our calculation in the present work clearly indicates that the mass triangle model is working well. Thus, the mass triangle model approach towards the computation of surface tension of CaO-MgO-Al_2O_3-SiO_2 slags with low silica. More applications of this model will be presented elsewhere.
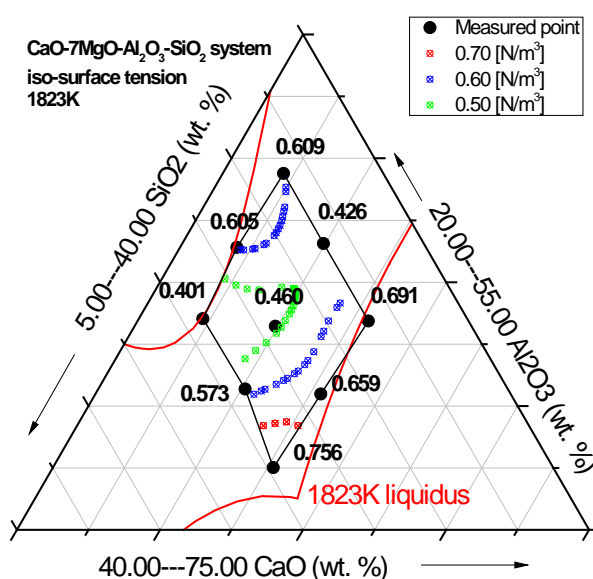

Fig. 5 Predicted liquid iso-surface tension [N/m^3] at 1823K in CaO-7mass%MgO-Al$_2$O$_3$-SiO$_2$ with low silica content

5. Conclusions

(1). The surface tension of the selected quaternary CaO-MgO-Al_2O_3-SiO_2 system with low silica content was measured by the Slide method in a wide temperature range from 1773K to 1873K. Nine different slag compositions were chosen based on three different levels of CaO content and three different levels of SiO$_2$ content. Experimental results showed that some surface tensions of slag increased with the increase of temperature, while others decreased.

(2). Effects of the NBO/T ratio on surface tension at 1823K were investigated. The results also indicted that the surface tension decreased with increasing of the NBO/T ratio, and following by increasing with further increasing of the NBO/T ratio.

(3).The surface tension of the selected limited homogenous phase region of CaO-7 mass%MgO-Al$_2$O$_3$-SiO$_2$ with low silica was calculated. The results showed that the mass triangle model working well. The overall trend of the effects

of component content on the surface tension attained from the model is in agreement with the experimental observation

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