Density and Surface Tension of a Cu_xO-CaO-MgO Slag System

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ABSTRACT

Although Cu_xO bearing slags are considered to be used in a pyrometallurgical copper recycling process from industrial waste, there are few physical property data on them. Therefore, densities and surface tensions of the melts in the system of Cu_xO-CaO were measured in air atmosphere at 1573K by maximum bubble pressure method using MgO crucible. Although MgO content increased with increasing CaO content in the melts, maximum MgO content in this experiment after measurement was 1.6 mass%. There is a very small effect of MgO on this work. Density values decreased with an increase of CaO content in the melt and surface tension values increased with an increase of CaO. Data are discussed with other binary slags containg CaO.

1. INTRODUCTION

Copper is ranked next to Iron and Aluminum as a mass produced metal and these minerals are well known as primary resources. Due to the uneven distribution and exhaustion of these minerals, the recycling of copper will be important.

In the case of recycling of copper scrap using a pyrometallurgical process, an oxidation refining technique could be applied since copper is more noble than impurity elements such as Fe, Sn, Pb and so on. It is expected that a slag bearing Cu_XO is formed under oxidation conditions. Therefore, the melt characteristics of the slag containing Cu_XO will be required for the design of the process vessel and slag separation from copper melt. We have already presented density and surface tension of a Cu_xO-SiO_2 slag system at last slag symposium in Sydney [1)].

In the present work, density and surface tension of the Cu_XO-CaO slag have been measured under air at 1573K by maximum bubble pressure method.

2. EXPERIMENTAL

2.1 Sample

Since no phase diagram of Cu_xO-CaO system is available, 8 compositions of the slag were chosen from pure Cu_xO to 65mol% Cu_xO-35mol% CaO slag considering the melting points of the slags [2)]. The slag used for the measurement was prepared from the respective reagents and weighed in order to obtain specific compositions. These were then mixed with a mortar, placed in a magnesia crucible and melted at 1573K in air. After melted, the slag was quenched onto a water-cooled copper vessel.

2.2 Experimental Method

The density and surface tension were determined using the maximum bubble pressure method. In this method, gas was passed from the upper part of the capillary tube which was immersed into the melts. When bubbles were formed at this end of the tube, the maximum bubble pressure was measured and the density and surface tension were determined. The advantage of this method is that both density and surface tension can be determined simultaneously in spite of a very simple apparatus. The schematic diagram of the electric furnace is shown in Fig. 1.

The density was calculated from a slope of the maximum bubble pressure against the immersion depth. The surface tension was calculated by the Schrödinger equation (1);

$$g = \frac{rP_0}{2}\left\{1-\frac{2}{3}\left(\frac{rrg}{P_0}\right)-\frac{1}{6}\left(\frac{rrg}{P_0}\right)^2\right\} \qquad (1)$$

where g is the surface tension, P_0 is the maximum bubble pressure at the melt surface, r is the corrected inner radius of capillary tube calculated from that measured at room temperature and the expansion coefficient, r is the density of the melt and g is gravitational constant.

For the measurement, a small amount of gas was passed through a magnesia tube with inner diameter of 1mm, which was gradually immersed into the melt. A wettability between a nozzle material and slag is very important in this method. Since the magnesia tube showed a good wettability to the slag, inner diameter of the magnesia tube was used for the calculation of surface tension.

Since the maximum bubble pressure method is a static measurement method, the static conditions must be satisfied at the time when the bubble has a minimum radius. Hence the relationship between maximum bubble pressure and discharge volume flow rate controlled by a micro tube pump was measured at a fixed immersion depth. Figure 2 shows the relationship between the maximum bubble pressure and generation time of one bubble. From the results, the gas flow rate was adjusted such that one bubble is formed every 20 seconds. The maximum bubble pressure obtained when the bubble has minimum radius was measured by using a digital manometer and measurements were also carried out at several immersion depths.

3. RESULTS AND DISCUSSION

3.1 Slag Composition before and after Measurement

It is well known that Cu_2O is partly oxidized to CuO at a high temperature in air atmosphere. Then we used "Cu_xO" as the copper oxide form in this study.

Since magnesia crucibles were used in the experiments, a few amount of magnesia was dissolved into the slag after experiments. Figure 3 shows measured transition of MgO content. MgO content in the slag was saturated after 2hours. It normally took more than 5 hours to finish the measurements. Then the experiments were done under MgO saturation. Magnesia dissolution into the Cu_xO-CaO slag is, however, less than 1.7 mass% and it is not significant for the data of the density and surface tension.

The slag samples were analyzed for Cu_2O, CuO, CaO and MgO after experiments. The chemical compositions before and after experiments are shown in Table 1. The ratio of Cu_2O and CuO were determined by calculation from the total amount of Cu and total Oxygen. CuO content in the slag was not changed so much but Cu_2O decreased with increasing CaO content in the slag. This means the ratio of Cu^+/Cu^{2+} slightly decreased with an increase of basicity of the slag if basicity of CaO is stronger than Cu_xO. This behavior might be explained by a Cu^+/Cu^{2+} redox reaction in the Cu_XO-CaO melt shown in equation (2).

$$\left(Cu^{+}\right)+\frac{1}{4}O_2(g)+\frac{n-1}{2}\left(O^{2-}\right)=\left(CuO_{n/2}^{2-n}\right)$$

$$K=\frac{a_{CuO_{n/2}^{2-n}}}{a_{Cu^+}\cdot P_{O_2}^{1/4}\cdot a_{O^{2-}}^{(n-1)/2}}$$

$$\log\frac{\left(Cu^{+}\right)}{\left(Cu^{2+}\right)}=-\frac{n-1}{2}\log a_{O^{2-}}-\frac{1}{4}\log P_{O_2}-\log K \qquad (2)$$

3.2 Relationship between Immersion Depth and Maximum Bubble Pressure

An example of the relationship between immersion depth and the maximum bubble pressure is shown in Figure 4. There is a good liner relationship between them. Density was obtained from the slope using the least square method and the surface tension was obtained from the density and the maximum bubble pressure at the immersion depth of zero.

However, due to various factors such as fluctuations of temperature and gas flow rate, differences in results were known to occur in the same instances and therefore precautions were necessary.

3.3 Density and Surface Tension

Figure 5 shows the relationship between density and CaO content in the slag. It was observed that the density tends to decrease from 5.65Mg/m^3 of the Cu_XO melt to 5.05Mg/m^3 of the Cu_XO-CaO(30 mol%) melt almost linearly with an increase in CaO content.

This trend is same as Cu_xO-SiO_2 system reported in last slag symposium (2). It is reasonable because mole volume of hypothesis CaO at 1573K is smaller than that of Cu_xO. Since there have been no data about the density of the Cu_xO-CaO system, it is hardly to confirm the accuracy of the data. Then the present data were compared with the data of other binary CaO systems. Density variations against CaO content in several binary MO-CaO slag systems are shown in Figure 6.

Although data of this figure were obtained at various temperatures, a trend shows that the densities of CaO focus to around 3.0Mg/m^3. It suggests that data of the present study are reasonable and an additional rule is adapted to the densities or mole volumes in MO-CaO binary systems.

Figure 7 shows the relationship between the surface tension and the amount of CaO addition. For initial surface tension of 460mN/m of Cu_XO melt, the surface tension tends to increase with an increase in CaO content and change of the surface tension is not liner but a little positive deviation with CaO content. No theoretical explanation on the data is now available.

Since there have been no data comparable with the present results of the surface tension, the values of surface tension obtained in the present study were summarized with the data of other binary CaO slags in Fig.8. The hypothetical surface tension value of CaO is estimated about 600 mN/m. This value is almost the highest and about the same as Fe_xO in the oxides as shown in Figure 8. Therefore, the following tendency is observed. If the surface tension of pure oxide is almost same as CaO, surface tension does not change so much with increase of CaO content. On the other hand, if the surface tension of pure oxides is lower than CaO, for example, B_2O_3, the surface tension of the binary CaO slags increases with an increase of CaO content. The changes of the surface tension with CaO content are not linearly as the changes of the density. It suggests that the surface tension of melts is more complicate physical properties than density.

4. CONCLUSIONS

In the present study, measurements were carried out for the density and the surface tension of Cu_XO-CaO slag by using the maximum bubble pressure method at 1573K in air. The following conclusions were obtained.

(1) The density and the surface tension of Cu_XO melt is 5.65Mg/m^3, 460mN/m respectively at 1573K in air.

(2) The density of Cu_XO-CaO slag tends to decrease gradually with an increase in CaO content.

(3) The surface tension of Cu_XO-CaO slag tends to increase gradually with an increase in CaO content.

(4) Magnesia dissolution into the Cu_xO-CaO slag is less than 1.7 mass% and it is not significant for the data of the density and surface tension.

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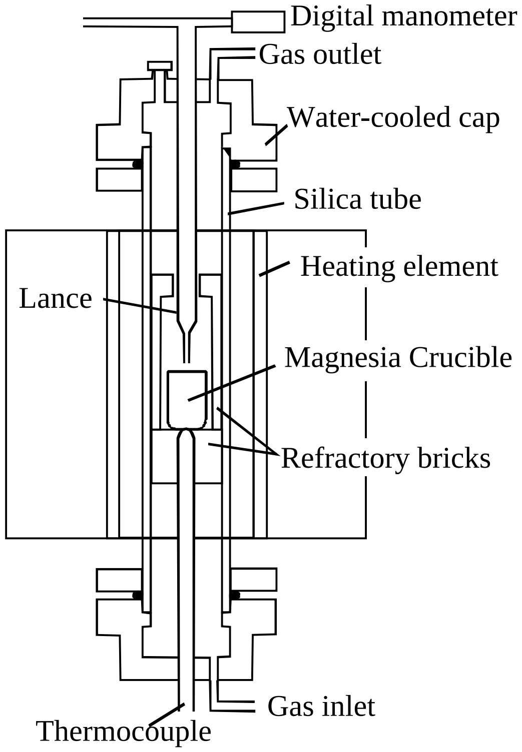

Fig. 1 - Schematic diagram of furnace arrangement for maximum bubble pressure method.

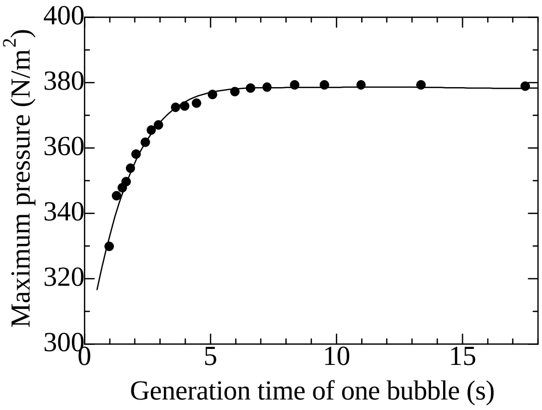

Figure 2 - Relation between maximum bubble pressure and generation time of one bubble.

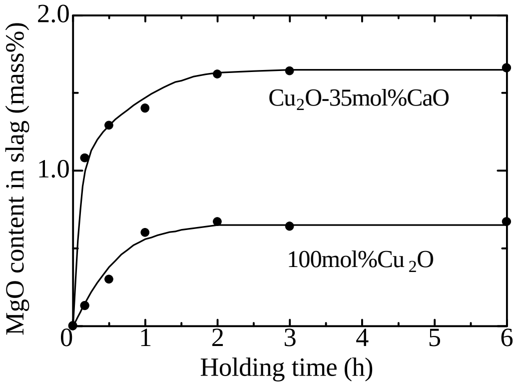

Figure 3 - Dissolved MgO content in Cu_xO-CaO slag.

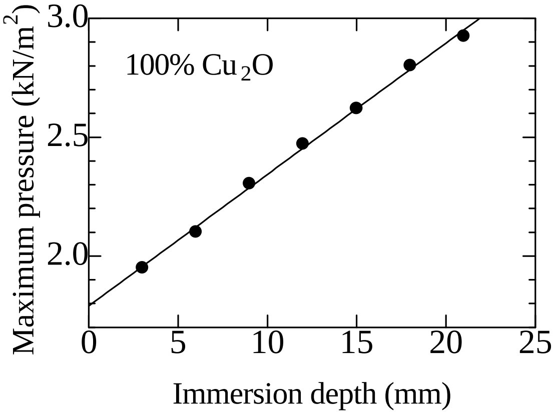

Figure 4- Relation between maximum bubble pressure and immersion depth.

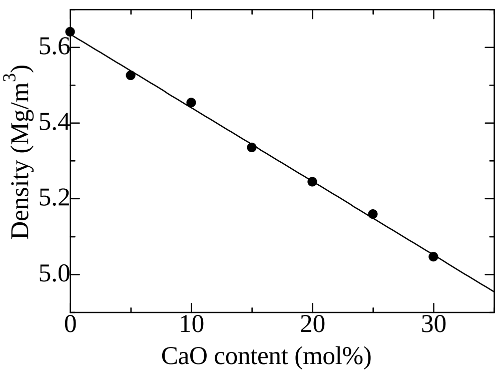

Figure 5 - Relation between density and CaO content in Cu_xO-CaO slag.

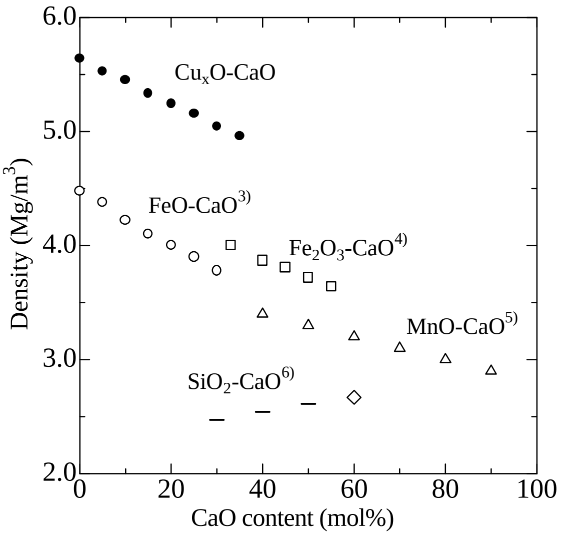

Figure 6 - Relation between density and CaO content.

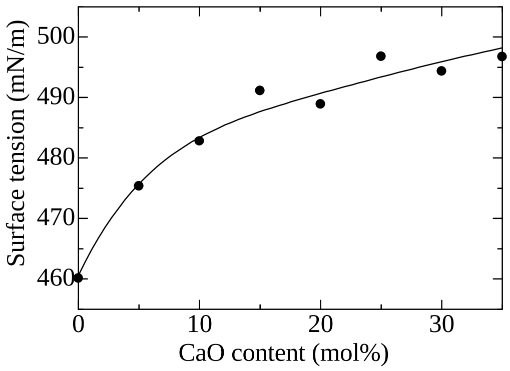

Figure 7 - Relation between surface tension and CaO content in Cu_xO-CaO slag.

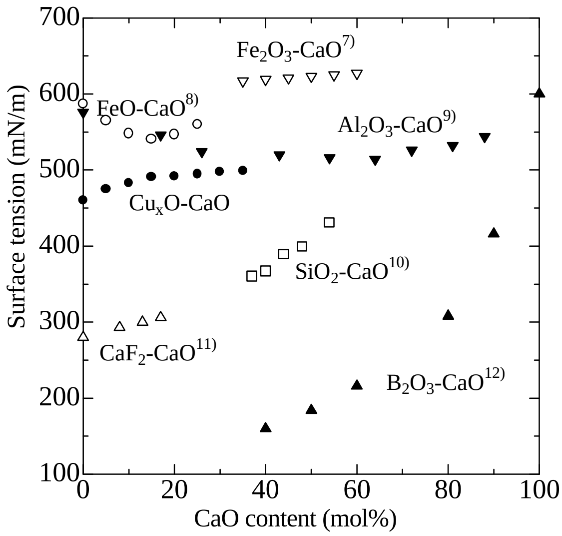

Figure 8 - Relation between surface tension and CaO content.

Table 1 Slag compositions before and after experiments

Sample No.	Composition before melting				Composition after melting			
	mol%		mass%		mass%			
	Cu_2O	CaO	Cu_2O	CaO	Cu_2O	CuO	CaO	MgO
1	100	0	100.00	0.00	80.29	19.10	0.00	0.61
2	95	5	97.98	2.02	77.87	19.40	1.97	0.76
3	90	10	95.83	4.17	75.42	19.67	4.13	0.78
4	85	15	93.53	6.47	73.74	18.76	6.45	1.05
5	80	20	91.08	8.92	71.80	18.45	8.86	0.89
6	75	25	88.45	11.55	69.43	17.98	11.44	1.15
7	70	30	85.62	14.38	66.47	18.33	13.93	1.27
8	75	35	82.58	17.43	64.55	17.21	16.60	1.64