DENSITY AND SURFACE TENSION OF CU_XO SLAG

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ABSTRACT

The density and surface tension of molten slag are very important physical properties on the smelting process. In the case of recycling of copper scraps in oxidation refining, it is expected that Cu_xO slag are formed. However the physical properties of Cu_xO slag have hardly been reported because of experimental difficulties.

In the present work, density and surface tension of Cu_xO-SiO_2 melts have been measured in air at 1573 K by maximum bubble pressure method using Pt crucible.

The density and surface tension of Cu_xO melt in air are 5.5×10^3 $kg\cdot m^{-3}$ and 480×10^{-3} $N\cdot m^{-1}$ respectively at 1573K. The density and surface tension of Cu_xO-SiO_2 slag decreased gradually with an increase in SiO_2 addition. It was found that these results showed the same trend when compared with previously reported data of density and surface tension for other binary silicate melts.

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 scraps in pyrometallurgy, oxidation refining could be applied since copper is more noble than impurity elements such as Fe, Sn, Pb and so on. As it is expected that under oxidation conditions, Cu_xO slag are formed as a main slag component. Therefore, the melt characteristics of Cu_xO slag will be required for the design of the process vessel and slag separation from copper melt.

In the present work, density and surface tension of the molten Cu_xO and Cu_xO-SiO_2 slag have been measured under air at 1573K by maximum bubble pressure method.

2. EXPERIMENTAL

2.1 Samples

In the present study, measurements were carried out using seven types of SiO_2 compositions from pure Cu_xO to 25 mol% SiO_2. These compositions are determined from the phase diagram for the system Cu_2O-SiO_2 reported by A. S. Berezhnoi et al [1]. The slag used were prepared from the respective reagents and weighed in order to obtain specific compositions. These were then mixed with a postle, placed in a Pt crucible and melted at 1573K in air. After melted , the slag were quenched onto a water-cooled copper vessel.

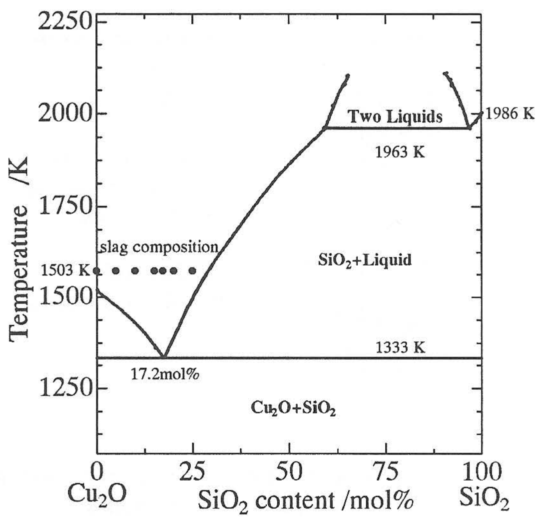


Fig. 1 - Phase diagram for the system Cu_2O-SiO_2

2.2 Experimental Method

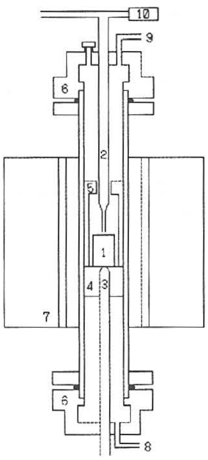
The density and surface tension were determined using the maximum bubble pressure method. In this method gas were passed from the upper part of the capillary tube which was immersed into the melts. When bubbles were formed at this end of the tube, the maximum bubble pressure were measured and the density 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. 2.

For the measurement, a small amount of gas were passed through a platinum tube of inner diameter 1mm, which were gradually immersed in the melt. The gas flow volume were adjusted such that one bubble is formed every 20 seconds. The maximum bubble pressure obtained when the bubble breaks away were measured by a digital manometer and measurement were also carried out at several immersion depths.

The densities were calculated by a slope of the immersion depth against the maximum bubble pressure. The surface tensions were calculated by Schrödinger equation (1).

$$\gamma = \frac{r \cdot P \cdot g}{2}\left\{1-\frac{2}{3}\left(\frac{r \cdot \rho}{P}\right)-\frac{1}{6}\left(\frac{r \cdot \rho}{P}\right)^2\right\} \quad (1)$$

where γ is the surface tension, P 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 linear expansivity, ρ is the density of the melt and g is gravitational constant.



1. Platinum crucible
2. Lance
3. Thermocouple
4. Supporter
5. Refractory brick
6. Water-cooled cap
7. Heating element
8. Gas inlet
9. Gas outlet
10. Digital manometer

Fig. 2 - Schematic diagram of furnace arrangement for maximum bubble pressure method.

Since the maximum bubble pressure method is a static measurement method, the static conditions must be satisfied at the time the bubble breaks away. Hence the relationship between maximum bubble pressure and discharge flow volume of micro tube pump were measured at a fixed immersion depth. It was found that if the discharge flow volume of the pump was carried out at more than 5 ml/min, the static condition could be satisfied. In this study , a flow rate of 6 ml/min was employed.

3. RESULTS AND DISCUSSIONS

3.1 Slag composition before and after measurement

Although we used a term of "Cu_2O slag" in the present study, it is well known that Cu_2O is partly oxidized to CuO in air atmosphere. DTA·TG analysis of Cu_2O reagent were carried out to clarify the oxidation behaviors of Cu_2O. Fig.3 and 4 show the results of DTA · TG measurement of Cu_2O reagent under air and Ar atmosphere respectively. From these results, oxidation of Cu_2O started from 673K and decomposition of CuO to Cu_2O occurred at 1373K. Over 1450K Cu_2O was partly oxidized to CuO and melted in air. On the other hand, Cu_2O is stable under Ar atmosphere. It was clear that melting point of Cu_2O-CuO melt is lower than the Cu_2O melt.

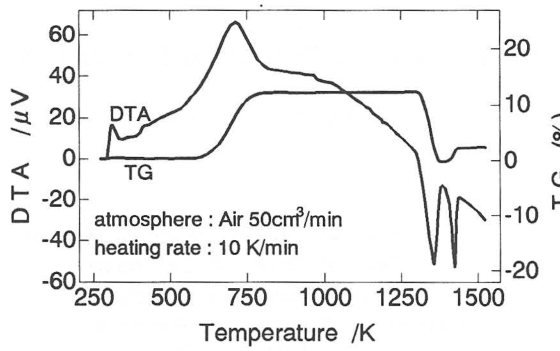


Fig. 3 - Result of DTA·TG measurement of Cu_2O in air.

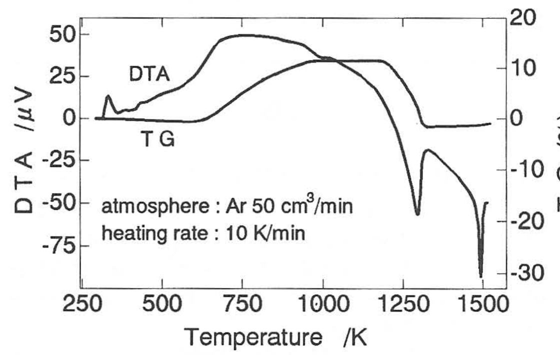


Fig. 4 - Result of DTA·TG measurement of Cu_2O under Ar atmosphere.

Therefore the slag samples were analyzed for Cu_2O, CuO, SiO_2 and these chemical compositions are shown Table 1. The ratio of Cu_2O and CuO were determined by calculation from the total amount of Cu. Amount of CuO increased with increasing SiO_2 content in the slag. This behavior might be explained by a Cu^+/Cu^{2+} redox reaction in the Cu_XO-SiO_2 melt shown in equation (2).

$$Cu^{+} + \frac{1}{4}O_2(g) = Cu^{2+} + \frac{1}{2}O^{2-} \quad (2)$$

Table 1 Chemical composition of Cu_XO-SiO_2 slags.

Sample No.	composition before melting (mol%)		composition after melting (mol%)		
	Cu_2O	SiO_2	Cu_2O	CuO	SiO_2
1	100	0	73.1	26.9	0.0
2	95	5	61.1	33.4	5.5
3	90	10	52.9	36.7	10.4
4	85	15	47.7	37.0	15.3
5	82.8	17.2	40.8	41.7	17.6
6	80	20	36.4	43.6	20.1
7	75	25	28.9	46.0	25.0

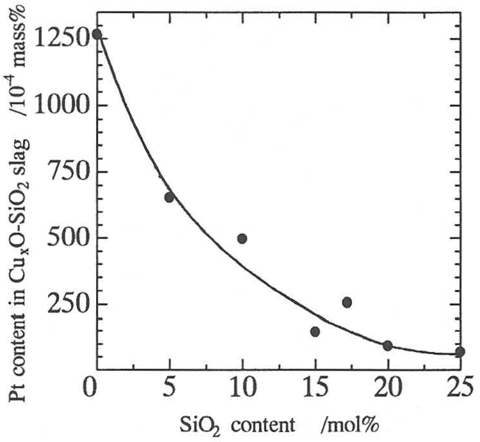


Fig. 5 - Platinum dissolution into the slag

When Cu_xO-SiO_2 slags were melted in a platinum crucible, the slag reacted with platinum and made a hole at the lower wall of the platinum crucible. It is expected that a small amount of platinum dissolved into the slag[(2)]. Fig.5 shows results of platinum solubility into the slag. Since dissolution of platinum is very small, it is considered that platinum dissolution has no influence on the density and surface tension.

3.2 Relationship between immersion depth and maximum bubble pressure

An example of the relationship between immersion depth and maximum bubble pressure is shown in Figure 6. This shows results of measurements for Cu_xO-SiO_2 slag sample No. 1, 3 and 6 carried out in air. The immersion depth was varied between 3 - 21 mm and maximum bubble pressure was measured at various depths. From these results, density was obtained from the slope using the least square method. The surface tension was obtained from density and maximum bubble pressure at immersion depth of zero.

From these experiments, a linear relationship was obtained for immersion depth and maximum bubble pressure. However, due to various factors such as fluctuations of temperature and gas flow rate, differences in results were known to occur in same instances and therefore precautions were necessary.

3.3 Density and Surface Tension

The results of determination of density and surface tension of Cu_xO-SiO_2 slag using the maximum bubble pressure method in air at 1573K are shown in the following figures. Fig. 7 shows the relationship between density and amount of SiO_2 addition. It was observed that for initial density of 5.5 $\times 10^3$ $kg{\cdot}m^{-3}$ of the Cu_xO melt, the density tends to decrease almost linearly with an increase in SiO_2 addition. Although the

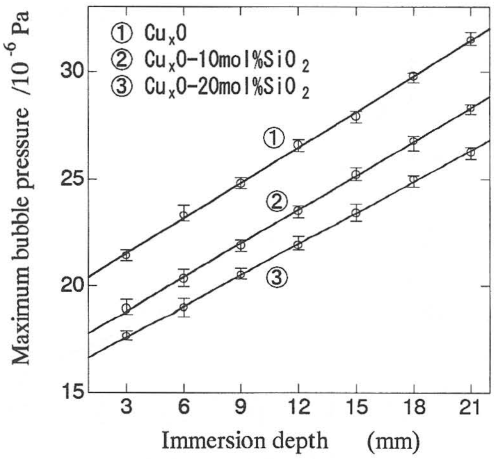


Fig. 6 - Relationship between the immersion depth and the maximum bubble pressure.

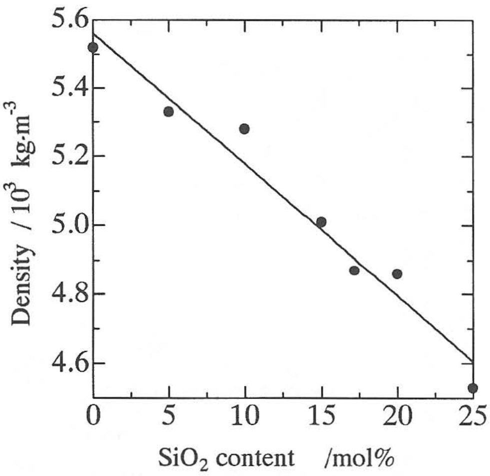


Fig. 7 - Density of Cu_xO-SiO_2 slag at 1573K in air.

density decreases with an addition of SiO_2 , it's value is relatively high compared with other binary silicates melts.

Figure 8 shows the relationship between surface tension and amount of SiO_2 addition. For initial surface tension of 480×10^{-3} $N{\cdot}m^{-1}$ of Cu_xO melt , the surface tension also tends to decrease with an increase in SiO_2 addition.

Since there have been no data comparing with the present results of the density and surface tension, the values of density and surface tension obtained in the present study were summarized with the data of other binary silicates in Fig.9 and 10.

Fig. 9 shows the composition dependence of the density of binary silicates melts. Although the plotted data in Fig. 9 were measured at different temperatures using various techniques , densities of binary silicate melts tend to decrease with increasing SiO_2 content due to a large molar volume of SiO_2 .

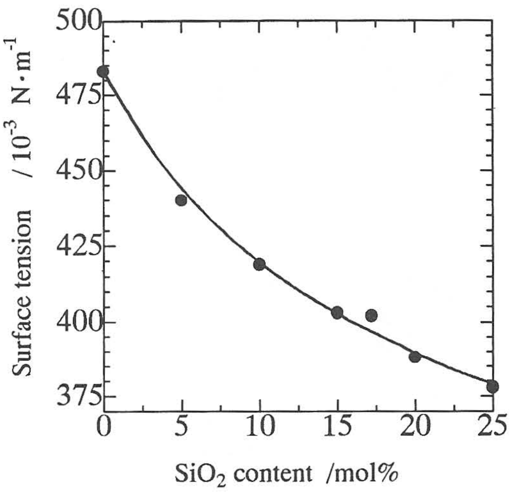


Fig. 8 - Surface tension Cu_xO-SiO_2 slag at 1573K in air.

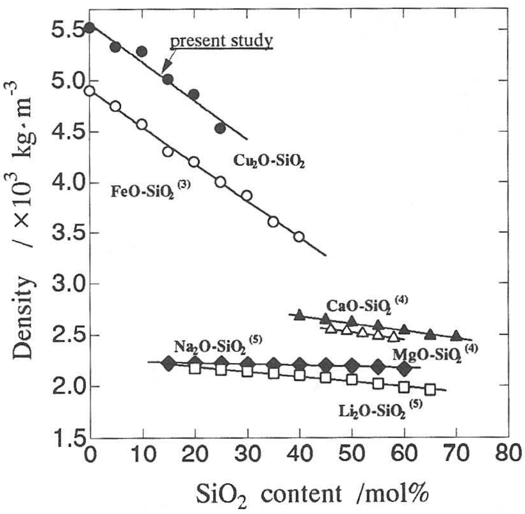


Fig. 9 - composition dependence of density in various binary silicates melts.

The same plots of the surface tension as Fig.9 are shown in Fig.10. The hypothetical surface tension value of SiO_2 is estimated about 3×10^{-3} N·m^{-1}. Therefore, the following tendency is observed. If the surface tension of pure oxide is higher than SiO_2, surface tension decreases with an increase of SiO_2 content. On the other hand, if the surface tension of pure oxide is lower than SiO_2, for example, PbO, the surface tension of the binary silicates increases with an increase of SiO_2 content.

It was found that these results showed the same trend when compared with previously reported data of density and surface tension for other binary silicate melts. It can be concluded from these observations that both density and surface tension of Cu_xO-SiO_2 slag decreases with an increase in amount of SiO_2. From both plots of Fig. 9 and 10 , the density and surface tension data in the present study might be correct.

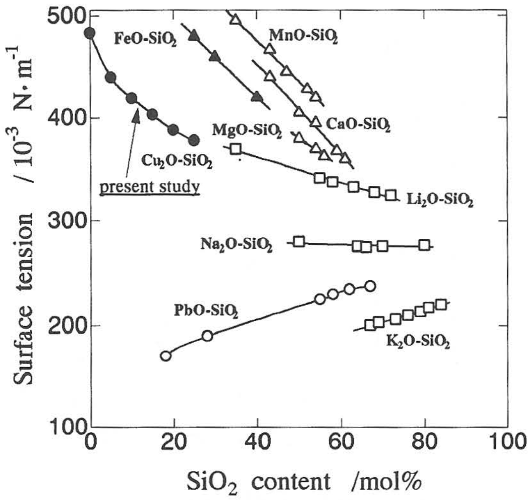


Fig. 10 - composition dependence of surface tension in various binary silicates melts[6].

In practical meaning, relatively large density of Cu_xO-SiO_2 slag causes to a difficulty of the phase separation between the slag and copper melt. Only the surface tension of the Cu_xO slag has been measured in the present study. However, the interfacial tension between the Cu_xO slag and molten copper must be important to clarify the phase separation from a interfacial chemistry point of view[7]. The next step these data will be measured in the recycling project.

4. CONCLUSIONS

In the present study, measurements were carried out for density and surface tension of Cu_xO-SiO_2 slag using the maximum bubble pressure method at 1573K in air.
The following conclusions were obtained.

(1) A fairly good linear relationship was obtained between immersion depth and maximum bubble pressure for Cu_xO -SiO_2 slag used in this experiment.

(2) The density and surface tension of Cu_xO melt is 5.5×10^3 kg·m^{-3} , 480×10^{-3} N·m^{-1} at respectively 1573K in air.

(3) The density of Cu_xO-SiO_2 slag tends to decrease gradually with an increase in SiO_2 addition.

(4) The surface tension of Cu_xO-SiO_2 slag also tends to decrease gradually with an increase in SiO_2 addition.

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