Density and Surface Tension of Cu_xO Bearing Slags

T. Takasu*, H. Itou* and T.Nakamura**

**Department Materials Science and Engineering, Kyushu Institute of Technology,Sensui-cho 1-1, Tobata, Kitakyushu, Japan 804-8550*
***Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2 Chome, Aoba. Sendai, Japan 980-8577*

Received April 25,2003; final form May 16 2003

ABSTRACT

Although Cu_xO bearing slags are applied 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- SiO_2 and Cu_xO-CaO were measured in air atmosphere at 1573K by maximum bubble pressure method.

The density and surface tension of Cu_XO melt in airare $5.5Mg/m^3$ and 480mN/m 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.

Density values decreased with an increase of CaO content in the melt and surface tension values increased with an increase of CaO. Data are also discussed with other binary slags containing CaO.

Key Words: Density, Surface Tension, Cu_xO-SiO_2 slag and Cu_xO-CaO slag, Maximum bubble pressure method

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 impure elements such as Fe, Sn, Pb and so on. It is expected that a slag bearing Cu_XO is formed under oxidation conditions. The melt characteristics of the slag containing Cu_XO, therefore, 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,Cu_XO-SiO_2 and Cu_XO-CaO slags have been measured under air at 1573K by maximum bubble pressure method.

2. EXPERIMENTAL

2.1 Sample

In the present study, measurements were carried out using seven types of SiO_2 compositions from pure Cu_xO to 25mol% SiO_2 in the Cu_XO-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/. Since no phase diagram of the 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 melting, 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);

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

where γ 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, ρ is the density of the melt and g is gravitational constant.

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

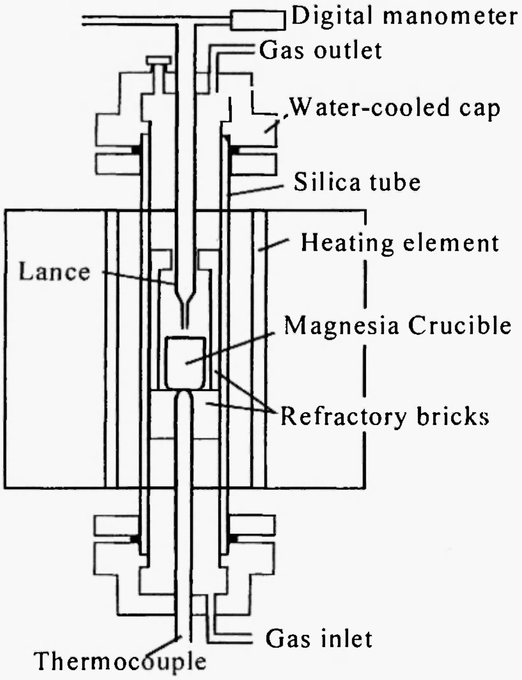

Fig. 1: Schematic diagram of furnace arrangement for maximum bubble pressure method.

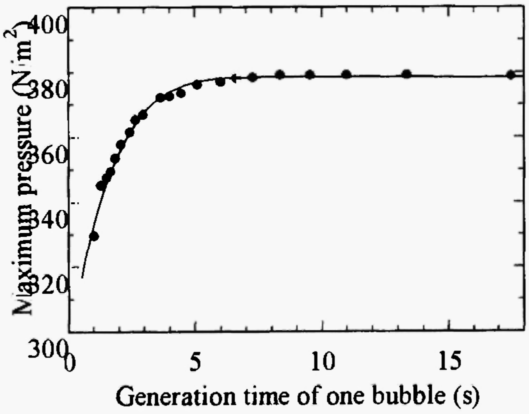

Fig. 2: Relation between maximum bubble pressure and generation time of one bubble.

3. RESULTS AND DISCUSSION

3.1 Cu_XO-SiO_2 slag system

3.1.1 Slag Composition before and after Measurement

Although we used the term "Cu_2O slag" in the present study, it is well known that Cu_2O is partly oxidized to CuO in air atmosphere. The slag samples were analyzed for Cu_2O,CuO, SiO_2 and these chemical compositions are shown in Table 1.The ratios of Cu_2O and CuO were determined by calculation from the total amount of Cu. The 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). This is a so-called "R" type redox reaction /3/.

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

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

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/4/. Fig.3 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.

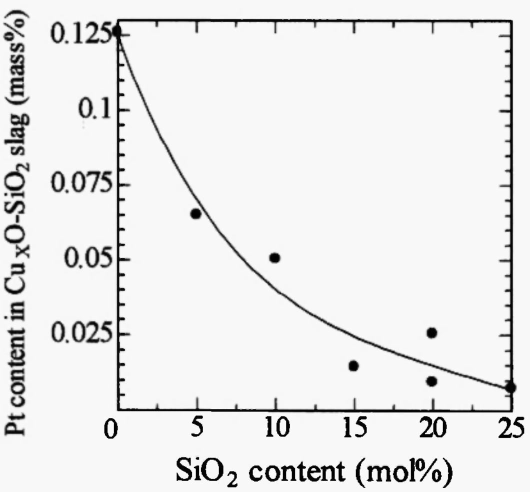

Fig. 3: Platinum dissolution into the slag

3.1.2 Relationship between immersion depth and maximum bubble pressure

An example of the relationship between immersion depth and maximum bubble pressure is shown in Fig. 4. This shows results of measurements for Cu_XO-SiO_2 slag samples 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.

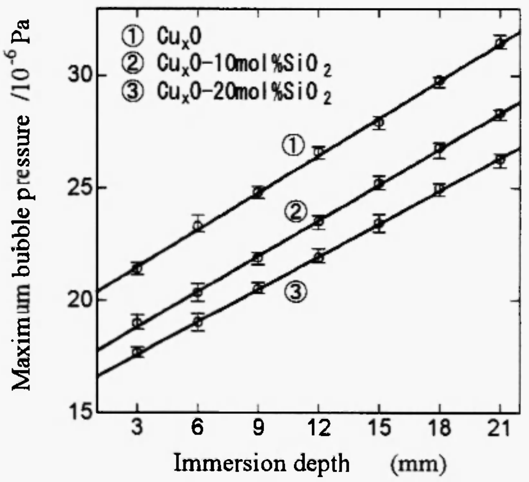

Fig. 4: Relationship between the immersion depth

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.

3.1.3 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 5 shows the relationship between density and amount of SiO_2 addition. It was observed that for initial density of 5.5Mg/m^3 of the Cu_xO melt, the density tends to decrease almost linearly with an increase in SiO_2 addition. Although the density decreases with an addition of SiO_2, its value is relatively high compared with other binary silicates melts.

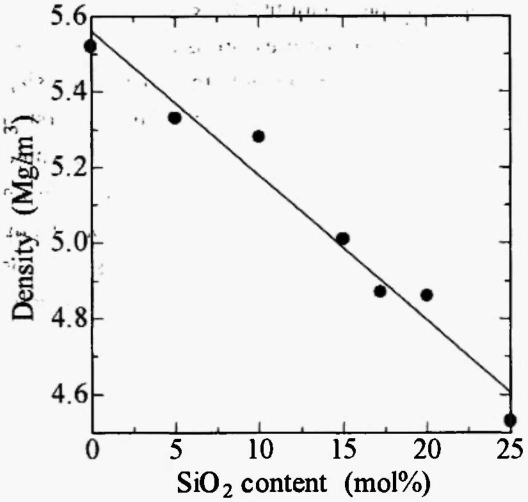

Fig. 5: Density of Cu_xO-SiO_2 slag at 1573K in air

Fig.6 shows the relationship between surface tension and amount of SiO_2 addition. For initial surface tension of 480mN/m 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 Figs. 7 and 8.

Fig. 7 shows the composition dependence of the density of binary silicates melts. Although the plotted data in Fig. 7 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.

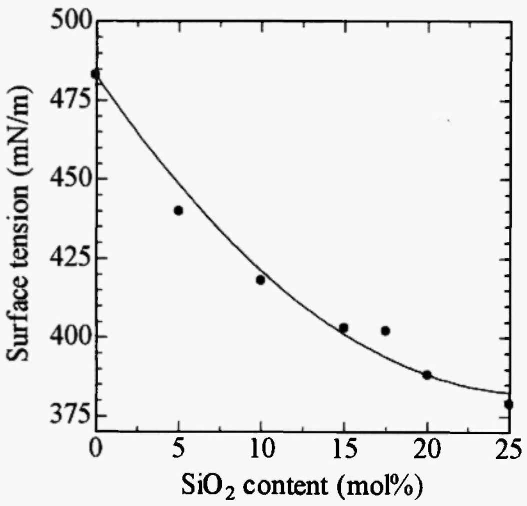

Fig. 6: Surface tension Cu_xO-SiO_2 slag at 1573K in air

The same plots of the surface tension as Fig. 7 are shown in Fig. 8. The hypothetical surface tension value of SiO_2 is estimated about 3mN/m.

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_2content. On the other hand, if the surface tension of

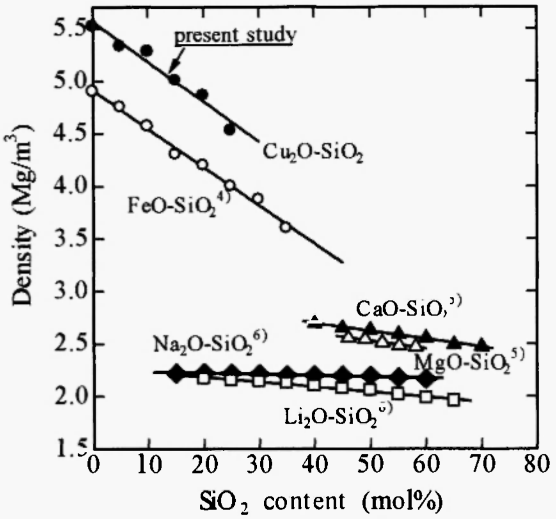

Fig. 7: Composition dependence of density in various binary silicates melts

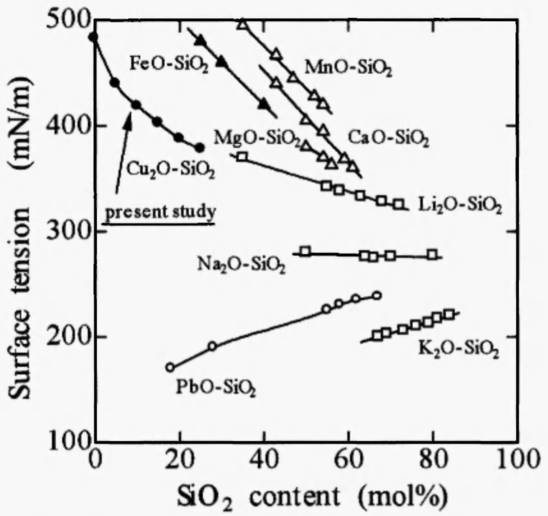

Fig. 8: Composition dependence of surface tension in various binary silicates melts /7/

pure oxides 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. 7 and 8, the density and surface tension data in the present study might be correct.

In practical meaning, the relatively large density of Cu_xO-SiO_2 slag causes 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, in the interfacial tension between the Cu_xO slag and molten copper it is important to clarify the phase separation from an interfacial chemistry point of view /9/. The next step will be that these data will be measured in the recycling project.

3-2 Cu_xO-CaO slag system

3.1.1Slag Composition before and after Measurement

Since magnesia crucibles were used in the experiments, a few amount of magnesia was dissolved into the slag after experiments. Fig. 9 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.

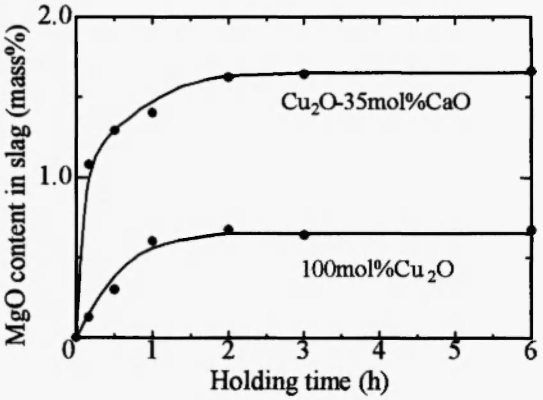

Fig. 9: Dissolved MgO content in Cu_xO-CaO slag.

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 2. The ratios of Cu_2O and CuO were determined in the same manner as before. CuO content in the slag was not greatly changed but Cu_2O decreased with increasing CaO content in the slag. This means that 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. It is quite different in the case of the Cu_xO-SiO_2 system. This behavior might be explained by a Cu^+/Cu^{2+} redox reaction in a Cu_xO-CaO melt shown in equation (3).

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

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

$$\therefore$$

$$\log\frac{(Cu^+)}{(Cu^{2+})}=-\frac{n-1}{2}\log a_{O^{2-}}-\frac{1}{4}\log P_{O_2}-\log K \qquad (3)$$

Equation (3) is a "O" type redox reaction /3/. In a Cu_xO-SiO_2 melt "O" type redox reaction was observed.

Table 2

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	65	35	82.58	17.43	64.55	17.21	16.60	1.64

This means that Cu_XO plays a role of basic oxide in a Cu_XO-SiO_2 melt, on the other hand it plays a role of acidic oxide in a Cu_XO-CaO melt.

3.2.2 Density and Surface Tension

Fig.10 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(30mol%) melt almost linearly with an increase in CaO content. This trend is the same as the Cu_xO-SiO_2 system. 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 hard to confirm the accuracy of the data. Therefore 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 Fig. 11.

Although data of this figure were obtained at various temperatures, the 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.

Fig.12 shows the relationship between the surface tension and the amount of CaO addition. For initial

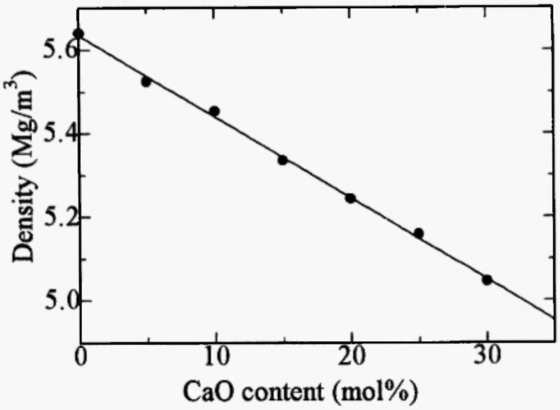

Fig. 10: Relation between density and CaO content in Cu_xO-CaO slag

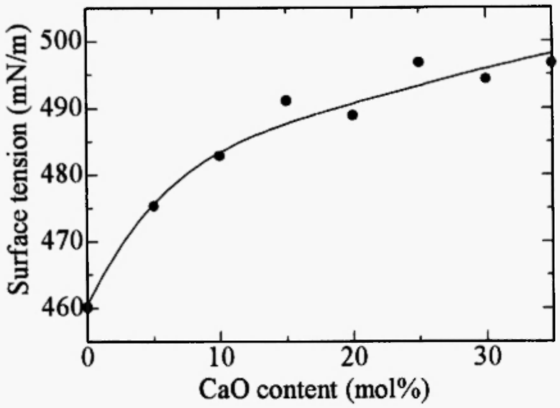

Fig. 11: Relation between surface tension and CaO content in Cu_xO-CaO slag.

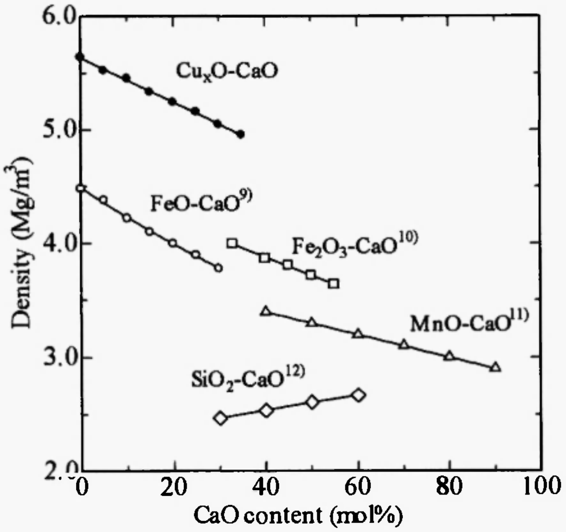

Fig. 12: Relation between density and CaO content.

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 linear but a small positive deviation with CaO content. No theoretical explanation for the data is now available.

Since there have been no data comparable with the present results of the surface tension, the values are summarized with the data of other binary CaO slags in Fig. 13. The hypothetical surface tension value of CaO is estimated at about 600mN/m. This value is almost the highest and about the same as Fe_xO in the oxides, as shown in Fig. 13. Therefore, the following tendency is observed. If the surface tension of pure oxide is almost the same as CaO, surface tension does not change to any great extent 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 linear as the changes of the density. This suggests that the surface tension of melts is more complicated for physical properties than density.

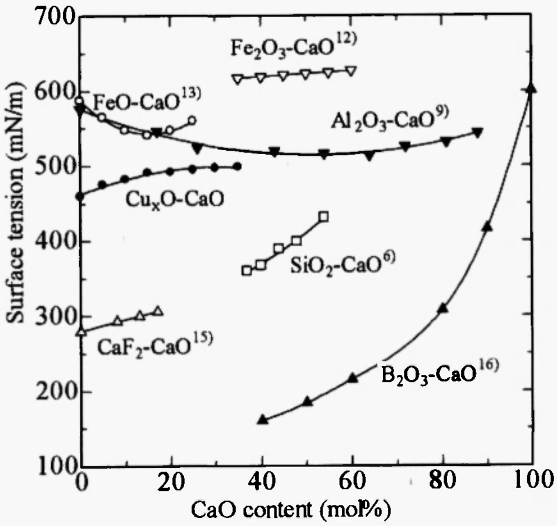

Fig. 13: Relation between surface tension and CaO content.

4. CONCLUSIONS

In the present study, measurements were carried out for density and surface tension of Cu_xO-SiO_2 slag and Cu_xO-CaO 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 both Cu_xO -SiO_2 slag and Cu_xO-CaO slag.

(2) The density and surface tension of Cu_xO melt is 460mN/m , 5.65Mg/m³ respectively at 1573K in air.

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

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

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

ACKNOWLEDGMENTS

One of the authors (T. Nakamura) gives many thanks to the late Professor K. Morinaga for his advice in the slag study.

This research was carried out in the Super Metaland Dust Project supported by New Energy Development Organization (NEDO) and Eco-Mining Center (EMC) in Japan. We would like to thank NEDO and EMC for their financial support.

REFERENCES

1. Ernest M. Levin, Carl R. Robbins and Haward F. McMurdie, The American Ceramic Society, Inc., 86 (1964).
2. J. Hino, K. Itagaki and A. Yazawa, *Journal of the Mining and Materials Processing Institute of Japan*, **105** (4), 315 (1989).
3. N. Masuko, *Journal of Electrochemistry of Japan*, **35**, 508 (1967) in Japanese.
4. A. Paul and R.W. Douglas, *Phys. Chem. Glasses.* **6** (6), 207 (1965).
5. D.R. Gaskell and R.G. Ward, **239**, 249 (1967).
6. J.O'M. Bockris, J.W. Tomlison and J.L. White, *Transactions of the Faraday Society*, **52**, 299, (1956).
7. J.W. Tomlison, M.S.R. Heynes and J.O'M. Bockris, *Transactions of the Faraday Society*, **54** 1822 (1958).
8. R.E. Boni and G. Derge, *Transactions of the Metallurgical Society of AIME.* **206**, 53 (1956).
9. T. Nakamura and J.M. Toguri, *Copper 90 - Pyrometallurgy of Copper*, Pergamon Press, 1990; p. 537.
10. Y.E. Lee and D.R. Gaskell, *Proc. ICSTIS,* 564, (1971).
11. S. Sumita, K. Morinaga and T. Yanagase, *Journal of the Chemical Society of Japan*, 6, 983 (1982).
12. L. Segers, A. Fontana and R. Winand, *Electrochimica Acta,* **23**,1275 (1978).
13. S. Sumita, K. Morinaga and T. Yanagase, *The Journal of the Japan Institute of Metals*, **47**, 127 (1983).
14. Y. Kawai, K. Mori, H. Shiraishi and N. Yamada, *The Journal of the Iron and Steel Institute of Japan*, **62**, 53 (1976).
15. T.B. King, *J. Soc. Glass Technol.*, **35**, 240 (1951).
16. K. Ogino and S. Hara, *The Journal of the Iron and Steel Institute of Japan*, **63**, 2141(1977).
17. B.P. Burylev and A.P. Misov, *Fiz. Khim. Grants Razdela Kontaktruyushchikh Faz.*, (**1976**), 147.