Effects of Dissolved Sulphur, Oxygen, Selenium and Tellurium on the Surface Tension of Liquid Copper*

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The authors are attempting to clarify the fundamental factors relating to cermet making from the view points of surface and interfacial tensions. The authors' previous paper described the surface tensions of pure metals and alloys, and this paper reports experimental results due to effects of dissolved sulphur, oxygen, selenium and tellurium on the surface tension of liquid copper. The results obtained are as follows: The elements of group VI b of the periodic table are highly surface active in liquid copper. The effects of negative elements on the surface tension become more severe with lowering temperature. The degree of adsorption of these negative elements on the liquid copper surface has been calculated, and from the results each adsorption-layer is considered to consist of a monolayer of negative ions attracting copper ions.

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I. Introduction

Surface phenomena are interesting and important both to the metallurgist and ceramist, but at present the phenomena are not completely understood. Even the values of the surface tension of liquid metals—the most elementary phenomena—in the existing data do not agree. For instance the published values of the surface tension of “pure” metals differ by 10 or 20 pct as summarized in our previous paper.⁽¹⁾ On the other hand the effect of dissolved sulphur on the surface tension of liquid copper was investigated by Baes and his co-worker⁽²⁾, and it has been confirmed that sulphur behaved as a surface-active agent in copper. Then it is worthy of consideration that the discrepancy in the values for the surface tension of pure metals may be due to the presence of traces of surface-tension-lowering impurities such as oxygen and sulphur in samples. Similar effects should be expected from dissolved selenium and tellurium. In order to clarify the effects of surface active elements on the surface tension of liquid metals, and to utilize the results for the consideration of mechanisms of cermet-sintering, the effects of dissolved sulphur, oxygen, selenium and tellurium on the surface tension of liquid copper have been measured by the sessile drop method at various temperatures, and the results have been discussed.

II. Experimental Procedure

In the present work the surface tension was measured by the sessile drop method as described in the authors' previous paper.⁽¹⁾

A schematic diagram of the apparatus for the measurement of surface tension of liquid copper containing sulphur is shown in Fig. 1. The weighed electrolytic copper (about 6 grams) was placed on a horizontally

adjusted graphite plaque surface (ash < 0.08 %) which was polished to a mirror finish. The apparatus was assembled and a stream of dry hydrogen introduced in

Fig. 1 Schematic diagram of the apparatus for surface tension-measurement of liquid copper containing sulphur.

the furnace tube. Then the assembly was heated and the temperature was controlled within $\pm 1^\circ\text{C}$ at a given temperature. Then the hydrogen stream was replaced by a H_2 - H_2S mixed gas stream which was prepared by introducing purified hydrogen through heated Bi_2S_3 . The velocity of the stream was 50 cc/min., and the concentration of H_2S in the stream of gas was analyzed. As soon as the H_2S gas was introduced, the shape of the drop of copper flattened while the shape became stable. Then the gas stream was cut off by means of stopcocks at the inlet and outlet, after the drop was kept at a certain temperature for 30 min., the image of the drop was traced on a paper with an Abbe's apparatus. As soon as the tracing was finished, the heating current was turned off and the system cooled rapidly, and the samples were chemically analyzed to determine the

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(1) K. Monma & H. Suto: Trans. J.I.M., 1 (1960), 69.

(2) C. F. Baes & H. H. Kellog: J. Met., 5 (1953), 643.

sulphur content. In some cases, the samples were previously sulphurized with higher sulphur-potential gas, and the surface tension was measured when the sulphur content of the sample reached the desired concentration by depleting the sulphur with lower sulphur-potential gas.

The measuring method of surface tension of the Cu-O system was similar to the case of the Cu-S system except sintered magnesia plaques were used, and the atmosphere was controlled by changing the CO/CO₂ ratio of the mixed gas of CO and CO₂.

The surface tension measurement method for the Cu-Se and the Cu-Te systems were similar to the above methods. However in the last cases, graphite plaques were used and the samples were prepared by alloying 99.99 % Se and Te with the electrolytic copper in an argon atmosphere. Static hydrogen atmosphere was used in order to avoid loss of selenium or tellurium by evaporation.

III. Experimental Results

The results of surface tension measurements of liquid copper containing sulphur up to 17.6 wt.% at 1114°, 1200°, 1300°C and 1340°C are shown in Fig. 2. The

Fig. 2 Effect of sulphur on the surface tension of liquid copper.

data mentioned above was obtained by decreasing the sulphur content (indicated by ↓) and by increasing sulphur content (no indication). The data obtained by both methods agree fairly well. As shown in Fig. 2, the surface tension of liquid copper is lowered by dissolved sulphur, and the value of surface tension at a constant sulphur content increases with increasing temperature. The data obtained at 1114°C in this current work agree with the result reported by Baes and his co-worker⁽²⁾ at 1120°C.

The data of surface tension of liquid copper containing oxygen up to 0.4 wt.% at 1150°, 1230° and 1300°C are shown in Fig. 3. Comparing Fig. 2 with Fig. 3, it is clear that the effect of dissolved oxygen on the surface tension of liquid copper is more remarkable than that of sulphur in the very dilute solution range. However, the values of surface tension of copper saturated with sulphur and oxygen show about 500 dyne.cm⁻¹ and 750 dyne.cm⁻¹ respectively.

Fig. 4 and Fig. 5 show the effects of selenium and

tellurium on the value of surface tension of liquid copper at 1150° and 1200°C. Fig. 6 shows the values of surface tension of liquid copper-tellurium alloys at temperatures which are higher by about 50°C above the

Fig. 3 Effect of oxygen on the surface tension of liquid copper.

melting point of each alloy respectively. The reason why values at a constant temperature were not shown was that the volatilization loss of tellurium in alloy could not be disregarded with increasing temperature, especially when the tellurium content is high. Table 1 shows the values of surface tension of high tellurium-copper alloys. These experimental results show that dissolved selenium and tellurium in liquid copper behave in a similar way with dissolved sulphur and oxygen in copper. That is, the elements of group VIb in the periodic table behave surface-actively in liquid copper, and the value of surface tension of an alloy containing a given amount of a surface-active element increases with rising temperature. However, as shown by the data of Table 1, the temperature-coefficients of surface tension, $d\gamma/dT$, of high tellurium alloys may be considered to be nearly zero or somewhat

negative and that of pure tellurium is clearly negative. On the other hand, the values of surface tension of almost pure metals as well as that of pure copper⁽³⁾ decrease with rising temperature. As a result, it is considered that when the temperature-coefficient of the

Fig. 4 Effect of selenium on the surface tension of liquid copper.

surface tension of a pure metal is observed as positive,

(3) c. f. S. Takeuchi & Y. Kachi: J. Japan Inst. Met., 14A (1950), 19.

the sample should be suspected to contain some surface active impurities such as elements of group VIb.

IV. Discussion of the Results

As pointed out in the authors' previous paper, the value of surface tension of an ionic liquid is in general

Fig. 5 Effect of tellurium on the surface tension of liquid copper.

Fig. 6 Surface tension of Cu-Te alloys and the diagram of the alloy system.

of the liquids. The rate of adsorption, or the excess surface concentration, Γ , can be calculated from a surface tension-concentration curve at a constant temperature with Gibbs' equation;

$$\Gamma = \frac{-1}{RT} \frac{d\gamma}{d \ln a} \quad (1)$$

where a is the activity of the solute. When the systems considered in the present work are assumed quasi-binary systems of Cu-Cu₂X (X denotes O, S, Se and Te), Γ in Eq. 1 represents the excess surface concentration of Cu₂O etc. and a represents the activity of Cu₂O etc. in liquid copper respectively.*

The activity of Cu₂S in copper, $a_{\text{Cu}_2\text{S}}$ is calculated from the following equation.

$$a_{\text{Cu}_2\text{S}} = x \exp \left\{ \frac{ZW_{\text{Cu-Cu}_2\text{S}}}{KT} (1-x)^2 \right\} \quad (2)$$

where x denotes the molar fraction of Cu₂S in copper and $ZW_{\text{Cu-Cu}_2\text{S}}$ denotes the contribution of the mixing energy of copper and Cu₂S. $ZW_{\text{Cu-Cu}_2\text{S}}$ is given by the equilibrium relationship between the activity $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ and x in the system $2\text{Cu} + \text{H}_2\text{S} \rightleftharpoons \text{Cu}_2\text{S} + \text{H}_2$. That is⁽³⁾,

$$\ln \left\{ \frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2}} \frac{(1-x)^2}{x^2} \right\} = - \frac{ZW_{\text{Cu-Cu}_2\text{S}}}{KT} x(2-x) + B(T) \quad (3)$$

On the other hand, $ZW_{\text{Cu-Cu}_2\text{S}}$ can be obtained from the phase diagram of the Cu-Cu₂S system. In the phase diagram of this system there is a monotectic reaction. Then if the conjugate concentrations of the two liquids at a given temperature are assumed x and $(1-x)$ respectively, $ZW_{\text{Cu-Cu}_2\text{S}}$ is given by⁽⁴⁾

$$ZW_{\text{Cu-Cu}_2\text{S}} = KT / (1-2x) \ln \{ (1-x)/x \} \quad (4)$$

The value of $ZW_{\text{Cu-Cu}_2\text{S}}$ which is calculated from Yagihashi's data⁽⁵⁾ with Eq. 3 is 2.5×10^{-12} erg. While, Umezū⁽⁶⁾, K. Sudo⁽⁷⁾ and Tanaka and his co-worker⁽⁸⁾

Table 1 Surface tension of Te-Cu alloys.

100 % Te		88.5 % Te		79.2 % Te		68.5 % Te		60.5 % Te		49.1 % Te	
Temp.	γ	Temp.	γ	Temp.	γ	Temp.	γ	Temp.	γ	Temp.	γ
450	270	400	270	400	280	600	350	700	380	850	450
500	265	500	270	500	280	700	345	800	380	950	450
600	255	550	265	600	275	800	345	900	380	1030	455

Temp.; °C, γ ; dyn/cm

considerably smaller than those of liquid metals which have similar melting points. Now, surface tension is a kind of free energy. Considering the thermodynamical equilibrium between the surface layer of the liquid and the bulk, the solute has to be distributed into both layers as to minimize the total free energy of the system. This phenomenon, as is well known, is called "adsorption". The above mentioned effects of the negative elements on the surface tension of liquid copper may be due to the adsorption of these elements on the surface

reported that the relation between $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ and the

* The reasons why the models of these systems were assumed as mentioned above were described in detail in the authors reports. [J. Japan Inst. Met. 24 (1960), 374; 377; 544.]

(4) R. Becker: Ann. Physik., 32 (1938), 128.

(5) T. Yagihashi: J. Japan Inst. Met., 17 (1953), 483.

(6) Y. Umezū: J. Min. Met. Inst. Japan., 66 (1950), 337.

(7) K. Sudo: Sci. Rep. R.I.T.U., A2 (1950), 519; Sci. Rep. Research Inst. Mineral Dressing & Metallurgy (Japanese) 10 (1954), 45.

(8) K. Hiramori, T. Tanaka & K. Watanabe: The Memo. Fac. Eng. Hokkaido Univ., 9(1952) No. 2, 125.

weight percentage of sulphur in copper, $[S]$ was as follows;

$$\log \frac{P_{H_2S}}{P_{H_2}} \frac{1}{[S]} = C(T) \quad (5)$$

The value of ZW_{Cu-Cu_2S} which is obtained from Eq. 3 and Eq. 5 is 0.34×10^{-12} erg. On the other hand, the values which are given from the mutual solubilities at 1150°C in the Cu-Cu₂S diagrams proposed by several investigators⁽⁹⁾⁽¹⁰⁾⁽¹¹⁾ are shown in Table 2. These values of ZW_{Cu-Cu_2S} as mentioned above are distinct from each other. Then the mean value of all of these data, 0.75×10^{-12} erg, is assumed to be the reliable

Table 2 Values of ZW_{Cu-Cu_2S} calculated from the solubilities at 1150°C on the Cu-Cu₂S diagrams by several investigation.

Investigator	Cu side		Cu ₂ S side	
	S, (wt %)	ZW_{Cu-Cu_2S} , (erg/mol)	S, (wt %)	ZW_{Cu-Cu_2S} , (erg/mol)
Yagihashi ⁽⁵⁾	1.5	0.715×10^{-12}	—	—
K. Sudo ⁽⁷⁾	1.0	0.796×10^{-12}	19.5	0.631×10^{-12}
Tanaka, et al ⁽⁸⁾	0.76	0.833×10^{-12}	—	—
Friedrich, et al ⁽⁹⁾	1.06	0.780×10^{-12}	19.5	0.631×10^{-12}
Bornemann, et al ⁽¹⁰⁾	1.94	0.672×10^{-12}	17.9	0.410×10^{-12}
Schumann, et al ⁽¹¹⁾	—	—	19.8	0.675×10^{-12}

value of ZW_{Cu-Cu_2S} . Then the activity of Cu₂S in copper, a_{Cu_2S} is calculated from Eq. 2 by substituting 0.75×10^{-12} erg. in ZW_{Cu-Cu_2S} . Fig. 7 shows the a_{Cu_2S} at the observed temperatures.

Fig. 7 a_{Cu_2S} at observed temperatures as a function of x .

Baes and his co-worker⁽²⁾ pointed out that if a plot of $\ln [S]$ against $\ln(\gamma^0 - \gamma)$ was drawn, it became a straight line, where γ^0 denotes the surface tension of pure copper and then $(\gamma^0 - \gamma)$ represents the surface tension-lowering by adding Cu₂S. While, in the present work, linear relationships were found between $\ln(100 \ln 1000 a_{Cu_2S})$ and $\ln(\gamma^0 - \gamma)$ as shown in Fig. 8. Thus Γ_{Cu_2S} as a function of a_{Cu_2S} is obtained as shown in Fig. 9. It seems that in Fig. 9 that with lowering temperature, Γ_{Cu_2S} approaches more rapidly a saturation value, while the saturation value of Γ_{Cu_2S} increases with rising temperature.

The excess surface concentration of Cu₂O on the surface

of liquid copper, Γ_{Cu_2S} , can be obtained in a similar way as described above. Vogel and his co-worker⁽¹²⁾ determined the mutual solubilities 0.058 and 0.825 (in mol-fraction of Cu₂O) respectively in a Cu-Cu₂O

Fig. 8 Relation between $\ln(\gamma^0 - \gamma)$ and $\ln(100 \ln 1000 a_{Cu_2S})$.

Fig. 9 Γ_{Cu_2S} at observed temperatures as a function of a_{Cu_2S} .

Fig. 10 a_{Cu_2S} as a function of x_{Cu_2S} .

system at 1200°C . Then ZW_{Cu-Cu_2O} is given by 5.6×10^{-12} erg. and the activity of Cu₂O in liquid copper (a_{Cu_2O}) at each observed temperature is obtained as a function of mol-fraction of Cu₂O in copper (x_{Cu_2O}) as shown in Fig. 10.** If a plot of γ from the data of

(12) R. Vogel & W. Pocher: Z. Metallk., 21 (1928), 333.

** K. Sano and his co-worker reported on the activity of oxygen in liquid copper. [J. Japan Inst. Met., 19 (1955) 435.] The value of ZW_{Cu-Cu_2O} calculated from the data mentioned above is 15.7×10^{-13} erg/mol, and from a similar equation to Eq. (4), the solubility of Cu₂O in liquid copper at 1200°C is calculated to be 0.0005 mol-%. But this value is about 1 % of the solubility determined experimentally.

(9) K. Friedrich & H. Wahlert: Met. u. Erz., 10 (1913), 976.

(10) K. Borneman & K. Wagnemann: Ferrum, 11 (1913/14), 276, 293, 303, 306, 310, 331.

(11) R. Schumann & O. W. Moles: J. Met., 3 (1951), 235.

Fig. 3, against $\ln a_{\text{Cu}_2\text{O}}$ is drawn, it becomes a straight line at each observed temperature as shown in Fig. 11, and from whose inclination and Eq. (1), $\Gamma_{\text{Cu}_2\text{O}}$ can be determined as a fixed value independently upon $x_{\text{Cu}_2\text{O}}$.

Fig. 11 Relation between γ and $\ln a_{\text{Cu}_2\text{O}}$.

We thus have $\Gamma_{\text{Cu}_2\text{O}}$ which is equal to 0.93×10^{-9} mol/cm² at 1150°C, 0.98×10^{-9} mol/cm² at 1230°C and 1.02×10^{-9} mol/cm² at 1300°C respectively. Of course, if the concentration of Cu_2O is very small, as shown in Fig. 11, the relationship between $\ln a_{\text{Cu}_2\text{O}}$ and γ deviates from the above-mentioned straight lines, and with decreasing $x_{\text{Cu}_2\text{O}}$, $\Gamma_{\text{Cu}_2\text{O}}$ decreases. The concentration corresponding to the beginning of the decreasing of

Fig. 12 Relation between $\log(\gamma_0 - \gamma)$ and $\log C_{\text{Se}}$.

Fig. 13 Relation between $\log(\gamma_0 - \gamma)$ and $\log C_{\text{Te}}$.

$\Gamma_{\text{Cu}_2\text{O}}$ may be estimated as an order of 0.01 wt % O_2 .

Activities of selenium and tellurium in liquid copper have not been determined experimentally. Therefore Γ_{Se} and Γ_{Te} shall be calculated approximately by the following equation.

$$\Gamma_{\text{Se or Te}} = \frac{-1}{RT} \frac{d\gamma}{d \ln c} = \frac{(\gamma_0 - \gamma)}{RT} \frac{d \log(\gamma_0 - \gamma)}{d \log c} \quad (6)$$

where c is the mol-percentage of selenium or tellurium in copper. If plots of $\log(\gamma_0 - \gamma)$ against $\log c$ are drawn from the data of Fig. 4 and Fig. 5, they become straight lines as shown in Fig. 12 and Fig. 13,*** from

Fig. 14 Γ_{Se} and Γ_{Te} as a function of x_{Se} and x_{Te} .

whose inclinations $d \log(\gamma_0 - \gamma) / d \log c \equiv \alpha$ are determined. The values of α are independent upon x , and α_{Se} is given by 0.245 both at 1150°C and at 1200°C, while α_{Te} is given by 0.285 at 1150°C and 0.295 at 1200°C. In Fig. 14, the curves of Γ_{Se} and Γ_{Te} vs. concentrations of selenium and tellurium are drawn by substituting α -values as above-mentioned and observed temperatures in Eq. (6).

As mentioned above, with increasing the concentration, Γ -values increase and seem to approach to an each saturation-value while the concentration of a solute in liquid copper arrives at the saturation-value. The rate of increasing of Γ till the saturation-value seems to be in the order of $\text{O} \leftarrow \text{S} \leftarrow (\text{Se, Te})$ and this order corresponds to that of electro-negativities of the solute elements. The estimated saturation-values of Γ at 1200°C are as shown in Table 3. These values compare favorably with the values expected for hexagonal close packed monolayers of sulphur-, selenium- and tellurium-ions as shown in Table 3. It is considered from these facts that the adsorption-layer at the surface of liquid copper consists of a monolayer of negative ions. However, the value expected for a hexagonal closed packed monolayer of O^{2-} (2.74×10^{-9} mol/cm²) is considerably distinct from the value of saturated $\Gamma_{\text{Cu}_2\text{O}}$ observed. That reason is considered as follows. The negative ions adsorped at the liquid surface may attract Cu^+ electro-statically. If the size of the

negative ion is considerably larger than that of Cu^+ (for example, $\text{Te}^{2-}/\text{Cu}^+ = 2.30$), the spacing of negative ions does not change so far by attraction of Cu^+ . While, if size of a negative ion is nearly equal to that of Cu^+ (for example, $\text{O}^{2-}/\text{Cu}^+ = 1.37$), the spacing of negative ions should be extended by attraction of Cu^+ .

*** Broken lines as shown in Fig. 13 may represent more reasonable relationships between $\log C_{\text{Te}}$ and $\log(\gamma_0 - \gamma)$.

On the other hand, the crystal structure of solid Cu_2O may be regarded approximately as CaF_2 -type, and the number of O^{--} at a (110) plane in Cu_2O crystal (the densest plane of O^{--}) is 1.3×10^{-9} mol/cm². This

Table 3 Excess surface concentration on the surface of liquid copper saturated with the group VI elements, Γ_{obs} , and calculation values expected for a hexagonal close-packed monolayer of these ions, Γ_{cal} .

Adsorbed element	Γ_{obs} , mol/cm ²	Γ_{cal} , mol/cm ²
oxygen	1.0×10^{-9}	2.74×10^{-9}
sulphur	1.6×10^{-9}	1.61×10^{-9}
selenium	1.4×10^{-9}	1.22×10^{-9}
tellurium	1.1×10^{-9}	1.14×10^{-9}

value compares favorably with the above mentioned $\Gamma_{\text{Cu}_2\text{O}}$ observed.

As for results, it is considered that the surface layer

of liquid copper containing a negative element consists of a monolayer of negative ions, just below which copper ions are attracted.

V. Summary

The effects of dissolved oxygen, sulphur, selenium and tellurium on the surface tension of liquid copper have been measured by the sessile drop method at various temperatures.

The elements of group VIb of the periodic table are highly "surface active" in liquid copper. The effects of negative elements on the surface-tension-lowering becomes more severe with lowering temperature.

The degree of adsorption of these negative elements on the surface of liquid copper has been calculated, and each adsorption-layer is considered to consist of a monolayer of negative ions attracting copper ions.