THERMODYNAMIC STUDIES ON THE FORMATION OF MOLTEN SILICON ALLOYS USING THE GALVANIC CELLS

(1) THE SYSTEM COPPER-SILICON

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I. Introduction

To make progress in understanding liquid alloys, we have to examine the thermodynamic properties of a great number of alloys. From this consideration the study was undertaken to determine the activities in molten Cu-Si alloys.

Recently, Sanbongi and Ohtani[1] have reported the results of an electromotive force study with regard to molten Fe-Si alloys using the slag containing SiO_2 as the electrolyte. The principle employed in this study was essentially the same as that described by them, but certain modifications regarding to the method of measurement have been made.

From the results of experiment, it was made clear that the activity curves in molten Cu-Si alloys show negative deviation from Raoult's law.

II. Materials

Metals: Copper used in the present experiment was made from a high purity copper wire and silicon was commercial pure metallic silicon.

Slag: Silica, alumina and calcium carbonate were the materials used which were of commercially pure quality. Lime was prepared from a commercial carbonate by heating in the nichrom resistance furnace at about 1,000° C.

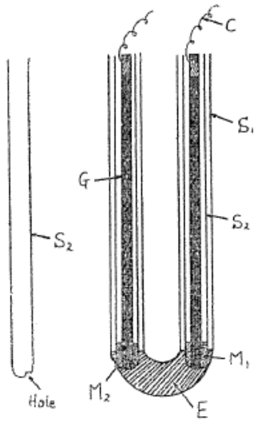
The slag, of which the composition was SiO_2 61.5%, CaO 23.5% and Al_2O_3 15.0%, was melted in graphite crucible at about 1,600° C using Tammann furnace and was used after ground to fine powder.

III. Experimental Apparatus

The construction of the cell is shown in Fig. 1. In the cell, we made the molten slag electrolyte contact with the metal or the alloy electrode through the holes made in the end of two silica tubes. Owing to high viscosity of the slag, the metal and the alloy in the electrodes can not escape through the holes.

The cell used consists of U-shaped silica tube and two less fine silica tubes. Graphite rods are used as connecting leads from the molten electrodes to the outside potentiometer circuit.

The leads must be virtually insoluble in the electrode metal and alloy, and the electrolyte must exhibit ionic conductance.



M_1 : Pure Si electrode
M_2 : Cu-Si alloy electrode
E : Slag electrolyte
S_1 : U-shaped silica tube (Dia. 13 mm)
S_2 : Silica tube (Dia. 8 mm) having hole (Dia. 0.8 mm)
G : Graphite rod
C : Copper wire lead

FIG. 1. The cell for e. m. f. measurement.

IV. Experimental Procedure

At an early stage in the work, the slag was put in the U-shaped cell container and was dehydrated by heating with a burner to avoid trouble arising from moisture.

The furnace used to obtain the experimental temperature was the "siliconit" resistance furnace (made in Japan) of the vertical type and its uniformity of temperature was constant over a considerable distance within the furnace. The Temperature of the slag in the container was held at about 1,570° C for about 1 hr. to eliminate gas bubbles in it before constructing the cell and then was lowered to the experimental temperature. Two silica tubes which contained graphite rods to avoid oxidation of the metal and the alloy by converting the oxygen in the tubes to carbon monoxide were inserted into two sides of the U-tube and after a time the graphite rods were removed. Then, the weighed amount of silicon and mixture of silicon and copper in certain percentage were dropped into one tube for formation of the pure metal electrode and the other tube for the alloy electrode respectively. The average weight of the total silicon metal was about 1 g and the volume of the alloy electrode was approximately of the same size as that of the pure silicon electrode. After construction of cell had been completed, the potential between the alloy and the pure silicon electrode was measured by means of the potentiometer.

The duration taken for a complete run was ordinarily 20 min. to 80 min.. All the final values of electromotive force were obtained by taking the averages of twice or more readings. A few alloys having different composition could be studied simultaneously in the same cell by adding pure copper or silicon into the alloy electrode one after another. Temperatures were measured with a Pt, Pt-Rh thermocouple of which the junction was located in the furnace at the same level as the cell.

The temperature control was of the order of ±10° C.

V. Experimental Results and Comparison with Other Data

The data were summarized in Table 1. The weighed compositions of these series were used in the computations.

The accuracy of the measured values may be generally within ± 5 mV in the concentration range in which Nsi is between 0.7 and 0.1. On the other hand, above $N_{Si} = 0.7$, the accuracy is within ± 2 mV, but it is hard trying to obtain the normal value by reason of the singular trouble. From these data, the activities of silicon in the molten Cu-Si alloy were calculated under the consideration of Si^{+4} ion and were plotted against the mole fraction in Fig. 2.

TABLE 1. Experimental results

(*a*) 1,470° C

N_{Si}	E (mV)	a_{Si}
0.0783	163.2	0.013
0.0917	155.3	0.016
0.1061	146.9	0.020
0.1118	135.3	0.027
0.1455	120.0	0.041
0.4418	57.2	0.218
0.4520	61.8	0.193
0.5274	36.3	0.380
0.5779	23.2	0.540

(*b*) 1,510° C

N_{Si}	E (mV)	a_{Si}
0.1073	160.9	0.015
0.2193	100.0	0.074
0.2226	87.2	0.103
0.2358	101.6	0.071
0.3048	85.5	0.108
0.3680	72.4	0.152
0.4439	54.2	0.244
0.4765	52.5	0.255
0.5263	36.1	0.391
0.5643	27.9	0.484
0.5779	28.0	0.482
0.7062	14.1	0.693
0.8190	4.2	0.897
0.8739	4.8	0.883

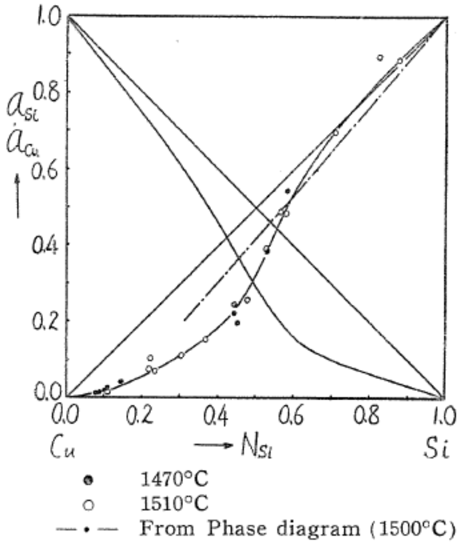


FIG. 2. The activities in molten Cu-Si alloys.

Activity curve of copper calculated by the Gibbs-Duhem equation was shown together with the activity of silicon in Fig. 2. The same calculated results were also shown in Table 2.

TABLE 2. The calculated activity values of molten Cu-Si alloys (1,470°–1,510° C)

N_{Si}	a_{Si}	N_{Cu}	a_{Cu}
0.9	0.910	0.1	0.027
0.8	0.799	0.2	0.063
0.7	0.687	0.3	0.097
0.6	0.537	0.4	0.155
0.5	0.322	0.5	0.285
0.4	0.181	0.6	0.459
0.3	0.108	0.7	0.607
0.2	0.060	0.8	0.731
0.1	0.023	0.9	0.863

It is found that the activity curves in the Cu-Si alloy studied show negative deviations from ideality.

It is possible to determine approximately the activity of silicon in copper assuming the regular solution from the location of the liquidus line of Cu-Si phase diagram,[2] since, on the silicon side, the solubility in the solid is negligible small.

We take the heat of fusion reported of 11,100 cal[3] per g-atom and make the reasonable assumption that $\Delta C_p = 0$ because of the lack of data for the specific heat of undercooled liquid silicon.

To aid comparison, the calculated curve was also plotted in Fig. 2. The values calculated from the phase diagram do not agree with the experimental values. While this disagreement may be ascribed to inaccuracies in the data used in the calculation and in the assumption of Si^{+4} ion, it is considered readily that it may be caused by the deviation of entropy from ideality in the Cu-Si alloy.

References

1) K. Sanbongi and M. Ohtani: Sci. Rep. Tohoku Univ., **A5** (1953), 350.
2) Metals Handbook, A. S. M., Cleveland, (1948).
3) O. Kubaschewski and E. L. Evans: Metallurgical Thermochemistry, Pergamon Press, London, (1956).