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

(III) THE SYSTEM IRON-SILICON

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I. Introduction

The following investigation represents a series of continued investigations which started in order to secure more data on the thermodynamic properties of molten silicon alloys. This system is especially significant in ferrous metallurgical field and, there have been reported the values of heat of formation[1] and some data of activities of this system by several workers.

Chipman[2] employed the phase diagram to determine the activities of silicon in molten Fe-Si alloys, and also studied with his collabrators[3] the distribution of silicon between liquid iron and silver to obtain its thermodynamic properties. In dilute silicon alloys, the activities of silicon can be obtained from the equilibrium relation[4] of silicon in liquid iron with gaseous mixtures. Recently, Sanbongi and Ohtani[5] applied the galvanic cell to the measurement of activities of silicon. Nevertheless, a survey of the literature shows that some disagreement exists in the activity values reported by the different investigators.

II. Experimental Procedure

Metallic iron used as sample was electrolyzed pure one.

The solubility of graphite in Fe-Si alloy was determined by Chipman *et al.*[6] and it was found that it decreases as silicon content increases. Therefore, there was needed some special experimental technics in the dilute silicon range and no attempt was made to obtained data at the compositions higher than $N_{Fe} = 0.9$ because of the complication associated with the dissolution of graphite in the alloy.

The experimental run was carried out in a manner similar to the procedure adopted in the case of Ni-Si alloys[7] and it will not be described further since no significant modifications were made.

III. Experimental Results and Consideration

The results obtained in each run are shown in Table 1.

Details of the comparison of the results obtained by different investigators is presented in the following:

Activities of silicon were calculated under the consideration of Si^{+4} or Si^{+8} ion and are given in Fig. 1, 3 and in Table 2. In Fig. 1, activity curve for silicon shows positive deviations from $N_{Si} = 0.54$ to 1.0 and negative deviations over the

TABLE 1. Experimental Results

1,470° C		1,510° C	
N_{Si}	E(mv)	N_{Si}	E(mv)
0.189	263.0	0.236	187.3
0.298	126.5	0.270	160.0
0.305	137.8	0.297	172.5
0.355	105.8	0.305	191.0
0.357	116.2	0.308	135.8
0.399	92.4	0.326	136.0
0.430	69.5	0.362	127.5
0.460	84.6	0.407	102.6
0.488	51.8	0.419	69.0
0.497	51.4	0.459	74.7
0.505	29.9	0.479	68.9
0.519	39.7	0.493	41.0
0.554	37.4	0.494	30.1
0.557	31.7	0.524	43.7
0.590	13.6	0.534	32.7
0.630	12.5	0.536	42.8
0.655	10.3	0.558	16.5
0.688	5.4	0.585	11.7
0.763	4.4	0.591	13.4
		0.609	11.2
		0.642	10.7

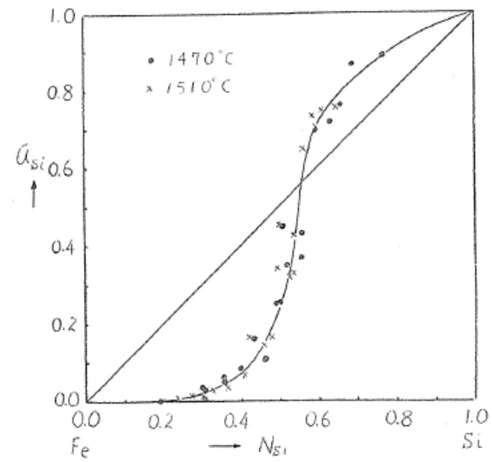
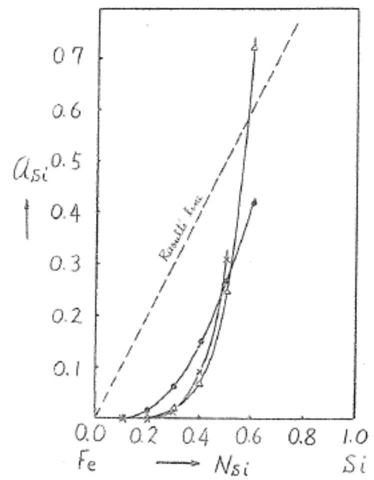


FIG. 1. Activities of silicon in Fe-Si alloys (Si^{+4} ion, $n=4$).



△ Authors (Si^{+4} ion, $n=4$)
× Chipman *et al.* (Calculated from the activity coefficient data in their report)
● Sanbongi, Ohtani

FIG. 2. Comparison between author's and other data for Fe-Si alloys.

rest of the concentration range. In Fig. 2, the authors' data are plotted together with the experimental values obtained by Chipman *et al.*[3] and by Sanbongi and Ohtani. For the lower silicon contents which are plotted in the figure, our value is below Sanbongi and Ohtani's and almost coincides with Chipman's data. In contrast to the close agreement between the authors' and Chipman's experimental activities, there is a large discrepancy between the activities measured experimentally and those calculated from the phase diagram. However, the activity values calculated under the assumption of Si^{+8} ion (namely, $n=8$), which are shown in Fig. 3, are in comparatively good agreement with those from the phase diagram though the structural interpretation for such assumption remains open to question.

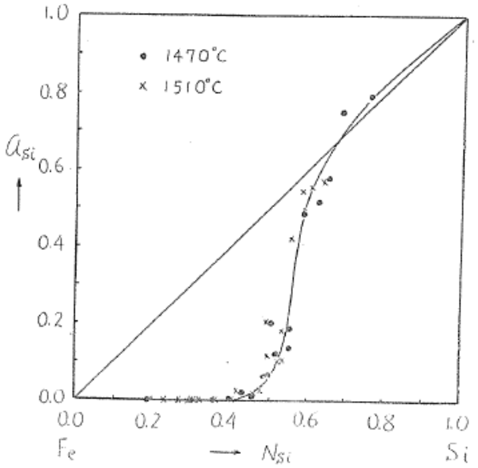


FIG. 3. Activities of silicon in Fe-Si alloys (Si^{+8} ion, $n=8$).

TABLE 2. Activity Values for Fe-Si Alloys (1,470°-1,510° C)

N_{Si}	$a_{Si}(n=4)$	$a_{Si}(n=8)$
0.1	0.0003	9×10^{-8}
0.2	0.002	4×10^{-6}
0.3	0.020	0.0004
0.4	0.072	0.005
0.5	0.250	0.063
0.6	0.725	0.526
0.7	0.840	0.706
0.8	0.910	0.828
0.9	0.960	0.922

At present, it is impossible to say something about the exact structure of liquid silicate and, the details of it await clearification. Herasymenko[8] and King[9] appear to postulate the existence of a few Si^{+4} ions in the liquid silicate, but the results of the transport number obtained experimentally by Bockris *et al.*[9] do not agree with this view. It is to our regret, therefore, that no further conclusions can be drawn from these data although either of them would represent a suitable activity values.

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