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

(II) THE SYSTEM NICKEL-SILICON

KOKICHI SANO, KAZUHISA OKAJIMA and NAOKI OKUDA

Department of Metallurgical Engineering

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I. Introduction

Despite of the fact that there has been an important increase in our understanding of the nature of molten alloys in recent years, the difficulty of accurate measurements at high temperatures, at which slags are molten, has prevented the precise determination of thermodynamic quantities. However, the e.m.f. methods of using slags have thrown a new light on the measurements of thermodynamic activities of molten alloys.

The only reported measurement of the thermodynamic quantity for molten Ni-Si alloys is that of the heat of mixing by Oelsen and Sampson-Himmelstjerna.[1] The present work was undertaken with a view of making further quantitative study of the thermodynamic property in molten Ni-Si alloys.

In a previous paper,[2] the authors reported the result of an electromotive force study in relation to the activities of molten Cu-Si alloys. By the similar method, the activities of molten Ni-Si alloys were measured.

The system Ni-Si has a very similar phase diagram[3] to that for the system Cu-Si and compounds are formed in a solid state. In general, compound-forming systems give marked negative deviations from Raoult's law. From measured results, it was made clear that the activity curve in the molten Ni-Si alloys shows large negative deviation from Raoult's law.

II. Experimental Procedure

Nickel used as electrode was made from a high purity nickel wire. The same cell construction and slag were used as in the previous study.

The large difference in free energies of formation[4] of oxides, NiO and SiO_2, makes it possible to study this system in a reversible galvanic cell.

The actual operational procedure was analogous to that used in the case of the Cu-Si alloys, with the exception for a special technique on the high nickel alloys and for another modification as mentioned in the following.

Since graphite is soluble in appreciable quantities in liquid nickel, the possible effect of dissolved graphite on the e.m.f. values must be considered. It was reported that the solubility of graphite in nickel at about 1,500° C is about 2.4%.[5] However, it is known that silicon additions cause a marked decrease in the solubility[6] of graphite in liquid iron. Since iron and nickel are like, we may expect the same effect on nickel as iron. Accordingly, the experimental procedure was

modified to minimize this error on the high nickel alloys. For this reason, moreover, no measurements within $N_{Si} = 0.17$ were carried out.

In the case of concentration range $N_{Si} = 0.17 \sim 0.3$, the graphite lead inserted into the less fine silica tube keeping a reducing atmosphere, allowed to attain thermal equilibrium just above the surface of alloy. The lead was then dipped into the alloy and the potential reading was taken as soon as possible.

The other modified operation is as follows; the cell container having only slag was introduced into a siliconit resistance furnace and then was held at the experimental temperature for about 30 min. before constructing the cell.

III. Experimental Results

The experimental value of electromotive force for each alloy having various compositions is given in Table 1 and is plotted in Fig. 1 against the mole fraction of silicon.

Reference to Fig. 1 shows that e.m.f.$-N_{Si}$ relation at 1,470° C is an anomalous curve over the concentration range of $N_{Si} = 0.3$ to 0.6, but it becomes smoother at

TABLE 1. Experimental Results

(i) 1,470° C

N_{Si}	E(mv)	a_{Si}	N_{Si}	E(mv)	a_{Si}
0.227	224.0	0.003	0.460	63.8	0.183
0.269	202.5	0.005	0.480	61.0	0.197
0.307	152.0	0.017	0.483	62.3	0.190
0.323	121.9	0.039	0.553	63.2	0.186
0.378	76.6	0.130	0.567	50.0	0.264
0.379	112.1	0.051	0.614	45.0	0.302
0.384	78.3	0.124	0.661	41.4	0.332
0.390	90.4	0.090	0.838	4.8	0.880
0.445	53.3	0.242			

(ii) 1,510° C

N_{Si}	E(mv)	a_{Si}	N_{Si}	E(mv)	a_{Si}
0.173	263.0	0.001	0.599	68.9	0.166
0.184	260.0	0.001	0.639	40.8	0.346
0.204	237.2	0.002	0.643	48.0	0.287
0.207	255.5	0.001	0.656	65.1	0.184
0.240	236.2	0.002	0.682	41.8	0.337
0.282	222.0	0.003	0.689	58.3	0.219
0.285	202.0	0.005	0.710	21.6	0.569
0.346	154.5	0.018	0.717	38.0	0.372
0.366	108.5	0.059	0.721	17.2	0.639
0.393	141.0	0.026	0.732	27.2	0.493
0.395	175.3	0.010	0.742	22.0	0.564
0.410	138.0	0.028	0.746	26.3	0.504
0.434	139.3	0.027	0.754	15.4	0.670
0.457	108.0	0.060	0.768	16.9	0.644
0.470	75.0	0.142	0.788	23.0	0.549
0.485	78.1	0.131	0.789	10.3	0.765
0.511	102.6	0.069	0.818	7.5	0.823
0.546	72.7	0.151	0.820	10.5	0.761
0.554	55.7	0.235	0.841	3.9	0.904
0.598	52.5	0.255	0.847	7.0	0.834

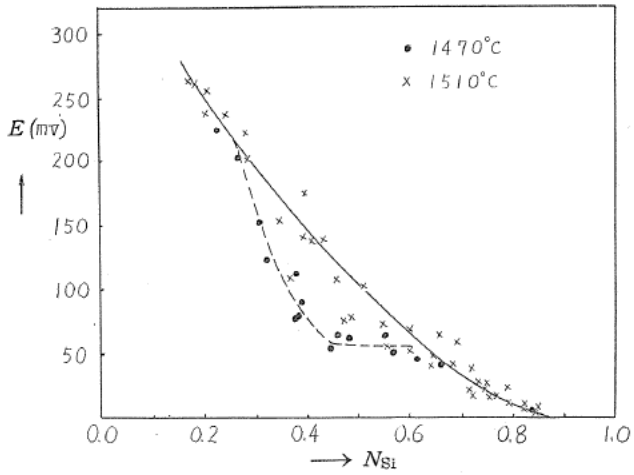
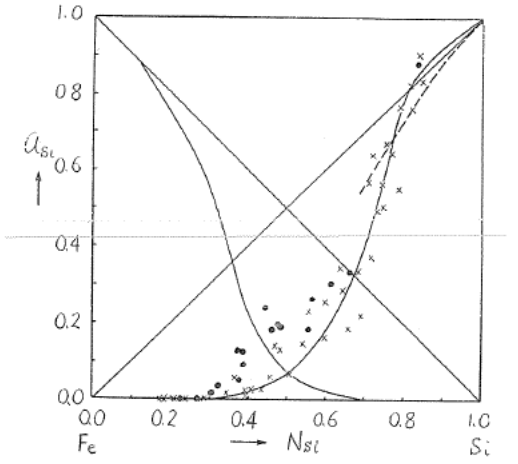


FIG. 1. e.m.f.$-N_{Si}$ relations for Ni-Si alloys.



• 1,470° C
× 1,510° C
– · From phase diagram (1,510° C)

FIG. 2. Activities of silcon and of nickel in Ni-Si alloys.

TABLE 2. Calculated Activity Values for Ni-Si Alloys at 1,510° C

N_{Si}	a_{Si}	N_{Ni}	a_{Ni}
0.1	0.0005	0.9	0.900
0.2	0.0015	0.8	0.747
0.3	0.004	0.7	0.543
0.4	0.020	0.6	0.225
0.5	0.072	0.5	0.080
0.6	0.185	0.4	0.025
0.7	0.385	0.3	0.006
0.8	0.780	0.2	0.0007
0.9	0.920	0.1	0.0003

1,510° C. It seems very likely that this phenomenon is understood to be related to the formation of unstable phase or of stable two phases. However, further various experimental works would be required to justify such a conclusion since we cannot decide from our data only whether it is correct or not. At any rate, we note that this anomalous behavior diminishes with the increase of temperature.

Based on this set of the experimental data at 1,510° C and the assumption of Si^{+4} ion, the activities of silicon were calculated from the smooth curve drawn through the experimental points. Using the Gibbs-Duhem equation, the activities of nickel were calculated from the observed activities of silicon assuming that Henry's law is applicable up to $N_{Si} = 0.1$. The results of these calculations are shown in Fig. 2 and in Table 2.

By the essentially same method as that for Cu-Si alloys, the activities of silicon in Ni-Si alloys assuming the regular solution from the location of the liquidus line in Ni-Si phase diagram[3] were calculated and is plotted in Fig. 2 in comparison with the experimental results. The agreement between the two curves is not necessarily good.

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