Activity Measurements of the Ternary Liquid Al-Si-Fe System by the EMF Method*

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In this report, the activities of Al in the ternary liquid Al-Si-Fe system were determined by emf measurements of the reversible concentration cell

in the range 750 ~ 1100°C.

Using the obtained activities of Al, the activities of Si and Fe at 1000°C were calculated by Schuhmann's tangent intercept procedure.

Judging from the obtained activities of Al, Si and Fe, the liquid Al-Si-Fe alloy with Fe/Si = 1.5 ~ 2.0 is most suitable to the subhalide process as the raw material.

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I. Introduction

The application of the subhalide reaction to Al refining has recently been a subject of increasing concern as a process to obtain pure Al from crude Al alloys. In this process, the ternary Al-Si-Fe alloy containing various amounts of Si and Fe which is produced^{(1)~(3)} by the direct reduction of bauxite or alumina-bearing ores is used as the raw material. Therefore, on obtaining pure Al from Al-Si-Fe ternary alloys by the subhalide process, it is very important to know the thermodynamic properties of ternary Al-Si-Fe alloys. On the subhalide reaction, the reactivity between AlCl_3 and Al in the alloys depends strongly on the activity of Al, so that it is indispensable to know the activities in the ternary Al-Si-Fe system. However, very little work has been reported about this system.

In this report, the activities of Al in the ternary liquid Al-Si-Fe system were determined by the emf method in the range 750 ~ 1100°C. Using the obtained activities of Al, activities of Si and Fe were calculated by Schuhmann's tangent intercept procedure⁽⁴⁾. With great emphasis on the reactivity between AlCl_3 and Al in the alloys, the compositions of Al-Si-Fe alloys suitable for the raw material to this process were selected using the obtained activities of Al, Si and Fe.

II. Experimental Procedure

1. Specimens

The chemical compositions of the ternary Al-Si-Fe alloys used for the emf measurement are shown in Fig. 1. The mother alloys for the ternary Al-Si-Fe alloys shown by A ~ G points in Fig. 1 were prepared by vacuum melting of high purity Al (99.99%), electrolytic iron and pure Si (99.9%). Seven alloy systems

Fig. 1 Compositions of alloy electrodes and their mother alloys.

- A ~ G Mother alloys of electrodes
- Chemical composition of electrodes

(A ~ G alloy systems) in which the ratios of Fe/Si in weight are 0.133, 0.338, 0.561, 1.000, 1.667, 3.040 and 6.940 were prepared by the addition of pure Al to the seven mother alloys. Such alloys lie on the straight lines which pass through the corner corresponding to pure Al.

2. Apparatus

The activities of Al in liquid ternary Al-Si-Fe alloys were measured by potentiometric measurements of the reversible emf of the cell as functions of temperature and composition of the alloy. The cell under study was as follows:

The activities of Al in the alloys (pure Al is made the standard state in all cases) are obtained directly from the equation

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(1) J. Glasser and W. Few: J. Metals, 14 (1962), 126.

(2) M. M. Striplin and W. M. Kelley: Chem. Eng. Prog., 43 (1947), 569.

(3) Y. Hayakawa: Denki Kagaku, 15 (1947), 19.

(4) R. Schuhmann, Jr.: Acta Met., 3 (1955), 219.

$$\mu_{\text{Al}} = RT \ln a_{\text{Al}} = -nEF. \quad (1)$$

Here

- μ_{Al} : chemical potential of Al
 R : gas constant
 T : absolute temperature
 a_{Al} : activity of Al
 n : number of electrons participating in the reaction
 E : electromotive force of the cell
 F : Faraday's constant.

A diagram of the experimental apparatus is shown in Fig. 2. Each cell contained three electrodes (5), one of which was composed of pure Al and the other two were of Al-Si-Fe alloys. A quartz tube (2) having an outside diameter of 70 mm contained the whole cell assembly and was fitted with a water cooled brass top (3). Suitable fittings in the top permitted insertions of leads (10), a thermocouple sheath (9) and the gas and vacuum connection, so that the cell could be evacuated or pressurized as desired. The most important problem in operating the cells at high temperature is the selection of contact lead material. Tantalum was used for the contacting lead because it was the only metal that was hardly attacked by liquid Al. The large cell case-containing crucible (7) and the sheathing for the tantalum lead wires were made of alumina of 97% purity. The eutectic mixture of sodium and potassium chlorides containing about 5% AlCl_3 was used as electrolyte.

3. Experimental procedure

Prior to the experimental runs, pure Al and the alloys were melted in high-purity alumina electrode crucibles (6) in a purified argon atmosphere, and then tantalum lead wires protected by a high alumina sheath were inserted into the melt and chilled quickly. After the solid electrolyte was transferred to the cell under a purified argon atmosphere, the cell was sealed in the quartz tube. The system was evacuated for 5 min to degas the electrode and the electrolyte, and then purified argon gas was introduced to the system until the pressure reached an atmospheric pressure + 5 mmHg. The temperature of the cell was then raised to 750°C under argon atmosphere. At the desired temperature the cell was held for at least 2 hr for the equilibration of temperature and composition and potential readings were started. The emf values were measured by means of a potentiometer until the values became constant with time. For each alloy investigated, potential measurements were made at seven different temperatures: 750, 800, 850, 900, 950, 1000, 1050 and 1100°C in a staggered sequence. Although potential measurements were made in a staggered sequence, the potential varied linearly with temperature above the liquidus. And the potential readings at a given temperature was highly reproducible even after the rise or fall in the cell temperature. In addition, consistent readings were obtained for different cells having the same compositions. Also, there were no perceptible drift of the potentials with time. All these observations indicated that the cell used was revers-

①Furnace	⑤Al electrode	⑨Thermocouple
②Quartz tube	⑥Alumina crucible	⑩Ta lead
③Brass cap	⑦Alumina crucible	⑪Radiation shield
④Alumina tube	⑧Electrolyte	⑫Alumina tube

Fig. 2 Schematic diagram of the experimental apparatus.

ible. At high temperature, tantalum slowly dissolved in liquid Al. Above 1000°C, therefore, the leads touched the electrodes only for a short time when a measurement was carried out.

III. Experimental Results

The emf measurements were carried out on the alloys of the binary Al-Si and Al-Fe systems, and of the above-mentioned seven ternary systems in the temperature range 750 ~ 1100°C. From the emf data, the activities of Al in the alloys are obtained directly by eq. (1). Based on the activities of Al, the activities of Si and Fe were calculated by Schuhmann's method.

1. Activities of Al in Al-Si and Al-Fe binary alloys

Kozuka et al.⁽⁵⁾ have determined the activities of Al in Al-Si binary alloys by emf measurement. Accordingly, similar measurements were carried out again as preliminary experiments for $N_{\text{Al}} = 0.823, 0.704, 0.628$ and 0.518. There was a good agreement between the two studies for a_{Al} in Al-Si binary alloys. Therefore, the data obtained by Kozuka et al. were used for subsequent calculations of the activities of Si in Al-Si binary system.

On the other hand, the experimental determination of the thermodynamic properties of Al-Fe binary system are difficult because of the high liquidus temperature and the complexity of the solid-state reactions. In

(5) Z. Kozuka, S. Yasugi, W. Nakajima and J. Moriyama: *Denki Kagaku*, **34** (1966), 35.

Fig. 3 Temperature dependence of emf for Al-Fe binary alloys and phase diagram.

our previous work, the activities of Al in liquid Al-Fe binary alloys were determined by the bubbling method. In order to confirm the propriety of the experimental results obtained by the bubbling method, the activities of Al in Al-Fe binary alloys were measured by the emf method. The experimental E vs T data for Al-Fe binary alloys ($N_{Al} = 0.956, 0.924, 0.908, 0.882$ and 0.857) are shown in Fig. 3. The dashed curve in this figure indicates the potentials of alloys along a portion of the liquidus of the Al-Fe system, which are calculated by using a phase diagram⁽⁶⁾ of the Al-Fe binary system and the eq. (2) derived by Hauffe and Wagner⁽⁷⁾.

$$\Delta\mu_{Al} = (\Delta H_f/\theta) \left[N_{Fe}\Delta T/(N_{Al} - X_{Al}) + X_{Fe} \int_{X_{Al}}^{N_{Al}} \Delta T dN_{Al}/(N_{Al} - X_{Al})^2 \right]. \quad (2)$$

The measured emf values of Al-Fe binary alloys increase along the calculated line (the dashed line) as the temperature increases in the solid-liquid equilibrium region and break at their melting points, and then increase linearly. Although the measured values in the solid-liquid equilibrium region are a little larger than the calculated values, there is a good agreement in shape between the two. Moreover, the activities of Al measured by the bubbling method agree with those obtained by the extrapolation of the values obtained in

this experiment to 1200°C. Therefore, it is confirmed that the activity values obtained by the bubbling method in our previous work are reliable.

2. Activities of Al in the ternary Al-Si-Fe alloys

The emf was measured for the above-mentioned seven alloy systems. Typical examples of the emf for the A-alloy system as a function of temperature are shown in Fig. 4. As can be seen from Fig. 4, the emf exhibits a larger value for the alloy which has a lower Al concentration. The emf values increase linearly and break at their melting points, and then increase linearly again. The activities of Al in the A-alloy system obtained in the present investigation are shown in Fig. 5. The activities of Al exhibit a slightly negative deviation from Raoult's law in the single liquid phase but show a tendency to a positive deviation in the solid-liquid equilibrium region. The activities of Al

Fig. 4 Temperature dependence of emf for A-pseudobinary alloys.

Fig. 5 Activities of Al in the A-pseudobinary alloy system, referred to liquid Al.

(6) M. Hansen and K. Anderko: *Constitution of Binary Alloys*, McGraw-Hill, New York, (1958).

(7) K. Hauffe und C. Wagner: *Z. Elektrochem. u. Angewante Phys. Chem.*, **46** (1940), 160.

Fig. 6 Isoactivity lines of Al at 1000°C.

were also determined in B-G alloy systems. Activity surface for Al in the ternary liquid Al-Si-Fe system at 1000°C are depicted by the isoactivity lines in Fig. 6. The isoactivity curves protrude at the E-F alloy systems. Therefore, the activities of Al in the E-F alloy systems exhibit the largest value at a constant composition of Al.

3. Activities of Si and Fe

Darken⁽⁸⁾, Wagner⁽⁹⁾ and Schuhmann⁽⁴⁾ recently showed how the Gibbs-Duhem equation can be applied to ternary systems to calculate the activities of two components from experimental data on the activities of the third component. However, very little has been reported about the activities on the Al-Fe or Fe-Si binary system. Therefore, based on the activity curves of Al obtained in this study, the activities of Si and Fe were calculated by Schumann's method. The activities of Si and Fe can be calculated according to the following equation:

$$\left[\mu_{\text{Si}}^{\text{II}} = \mu_{\text{Si}}^{\text{I}} - \int_{\mu_{\text{Al}}^{\text{I}}}^{\mu_{\text{Al}}^{\text{II}}} \left(\frac{\partial n_{\text{Al}}}{\partial n_{\text{Si}}} \right)_{\mu_{\text{Al}}, n_{\text{Fe}}} d\mu_{\text{Al}} \right] n_{\text{Fe}}/n_{\text{Si}} \quad (3)$$

In eq. (3), $\mu_{\text{Si}}^{\text{I}}$ and $\mu_{\text{Al}}^{\text{II}}$ represent the chemical potentials of Si and Al at a given point II, and $\mu_{\text{Si}}^{\text{I}}$ and $\mu_{\text{Al}}^{\text{I}}$ represent the chemical potentials at the starting point I. The values of $(\partial n_{\text{Al}}/\partial n_{\text{Si}})_{\mu_{\text{Al}}, n_{\text{Fe}}}$ are obtained as follows; a tangent drawn to the isoactivity curves of Al was extended to intersect the Al-Si side of the triangle, and then the composition read at the intersection from the composition scale along Al-Si was converted to a mole ratio of component Al to component Si. Equation (3) can be integrated along lines of constant ratio $n_{\text{Fe}}/n_{\text{Si}}$. On a composition triangle, such a path follows a straight line which passes through the corner corresponding to pure Al. When the chemical potential at a starting point I, $\mu_{\text{Si}}^{\text{I}}$, is known, the chemical potential of Si at a point I, $\mu_{\text{Si}}^{\text{I}}$, can be obtained by making an

Fig. 7 Isoactivity lines of Si at 1000°C.

Fig. 8 Isoactivity lines of Fe at 1000°C.

integration along a path such as I-II. Chemical potential of Fe can be also obtained by integration of the values of $(\partial n_{\text{Al}}/\partial n_{\text{Fe}})_{\mu_{\text{Al}}, n_{\text{Si}}}$. As the starting point I, the ternary alloys of 95 wt% Al were employed. On the assumption that the activities of Si and Fe obey Raoult's law at 95 wt% Al and decrease linearly to zero with the decrement of the composition of Si and Fe, $\mu_{\text{Si}}^{\text{I}}$ and $\mu_{\text{Fe}}^{\text{I}}$ were determined. Figures 7 and 8 show the isoactivity lines of Si and Fe at 1000°C respectively.

Since the Gibbs-Duhem equation shows that the manner in which one of chemical potentials can vary with composition is closely related to the manner in which the other two chemical potentials vary with composition, it is reasonable to expect that the directions or slopes of the three isoactivity curves at a given point must be related in a simple fashion. The three intersections ($T_{1,23}$, $T_{2,13}$, $T_{3,12}$) between the tangents of the three isoactivity curves at a given point and the ternary triangle must fall on a single straight line. Here, $T_{1,23}$ indicates the intersecting point between the tangent of the isoactivity curve of component 1 and the binary system of components 2 and 3. It was difficult to confirm the above relation because of the complexity of the isoactivity curves

(8) L. S. Darken: J. Amer. Chem. Soc., **72** (1950), 2909.

(9) C. Wagner: *Thermodynamics of Alloys*, Addison-Wesley Press, (1952), p. 19.

obtained in this work. However, the intersections fall on a single straight lines generally.

IV. Discussion

Alloys produced by the direct reduction of bauxite or alumina-bearing ores are reported to be ternary Al-Si-Fe alloys containing 40 ~ 70 wt% Al and various amounts of Si and Fe. As can be seen from our previous work, the reactivity between Al and AlCl_3 depends strongly on the activity of Al in the alloys. The results of this work show that the activity of Al in Al-Si-Fe alloys at constant aluminum composition depends strongly on the compositions of Si and Fe. Therefore, the concentration of the liquid Al-Si-Fe ternary alloys suitable for the subhalide process as the raw material was selected from the measured activities of Al.

Fig. 9 Concentration dependence of activity at constant aluminum composition.

In the subhalide reaction, as only Al in Al alloys reacts with AlCl_3 and decreases its concentration, the composition of Al in Al-Si-Fe alloys supplied to the reaction as the raw material decreases along the lines of the constant Fe/Si ratio in the Al-Si-Fe ternary system. When AlCl_3 reacts with Al-Si-Fe ternary alloys containing a constant amount of Al and various amounts of Si and Fe for a certain time, the retained Al in the alloys is shown to be minimum in the alloy in which the activity of Al in the starting material is large and the decrement in the activity of Al with decrease in Al content is minimum. Therefore, in order to make clear the relation between the activity and composition of Al at constant Fe/Si, the concentration dependence of the activity at a constant Al composition was obtained from Fig. 6 and is shown in Fig. 9. As can be seen from Fig. 9, it is concluded that the liquid Al-Si-Fe alloys with $\text{Fe/Si} = 1.5 \sim 2.0$ are most suitable for the subhalide process as the raw material.

V. Summary

(1) The activities of Al in the ternary liquid Al-Si-Fe system were determined by the emf method in the range 750 ~ 1100°C. The isoactivity curves protrude at E~F alloy systems, and then the activities of Al in these alloys with $\text{Fe/Si} = 1.5 \sim 2.0$ exhibit the largest value at a constant composition of Al.

(2) Based on the isoactivity curves of Al measured in this study, the activities of Si and Fe were calculated by Schuhmann's method. Although isoactivity curves of Si and Fe are complex in shape, the three intersections ($T_{1,23}$, $T_{2,13}$, $T_{3,12}$) fall on single straight lines generally.

(3) Judging from the activities of Al obtained in this study, it is concluded that the ternary liquid Al-Si-Fe alloys with $\text{Fe/Si} = 1.5 \sim 2.0$ are most suitable for this process as the raw material.

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