Phase Diagram of NaCl-AlCl₃-SeCl₄ System and Electrical Conductivities of the Melts

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NaCl-AlCl₃-SeCl₄ melts are attractive for a Na/SeCl₄ battery, and the liquidus temperature of this system has been determined as a function of composition by differential thermal analysis. The ternary eutectic composition is (NaCl)₂₀(AlCl₃)₅₉(SeCl₄)₂₁ and its temperature is 42 °C. Phase relation of NaCl-AlCl₃-SeCl₄ system at 200 °C was also determined. Electrical conductivities of quasibinary (NaCl)₄₅(AlCl₃)₅₅-SeCl₄ melts tend to decrease with increasing content of SeCl₄.

1 INTRODUCTION

NaCl-AlCl₃-X ternary systems (x=third component such as LiCl, KCl, FeCl₂ and SeCl₄) make the low-melting molten salts with high ionic conductivity and are attractive for the practical application such as electrolytes for electrowinning of aluminum and for the battery¹⁻⁴⁾. In systems with X=KCl, LiCl, etc., phase diagram, density, electrical conductivity, transport number, Raman spectra have been reported by many investigators⁵⁻¹⁰⁾. Matsunaga et al¹⁾ and Hashiguchi et al⁴⁾ have recently reported a Na/SeCl₄ battery by using NaCl-AlCl₃-SeCl₄ melts. However, even the liquidus temperature is not clear in the ternary system.

Electrical conductivity of NaCl-AlCl₃ melt has been reported by Carpio et al⁶⁾. However, effect of SeCl₄ addition on the electrical conductivity of NaCl-AlCl₃ melt is also unknown.

In this work, the liquidus temperature of NaCl-AlCl₃-SeCl₄ system, the phase relation of the system at 200°C and the effect of SeCl₄ addition on the electrical conductivity of NaCl-AlCl₃ melt are studied.

2 EXPERIMENTAL

2.1 Sample preparation and phase diagram

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The chemicals used are AlCl₃ (high purity reagent, 99.999% purity), SeCl₄ (99.9%) and NaCl (99.99%, dried at 200°C for 15h under vacuum). The chemicals were weighed and mixed to a given composition in the glove box filled with dry N₂ gas (dew point <-70 °C) and sealed into an evacuated Pyrex glass cell for differential thermal analysis (DTA) described below, and then, were melted in a rocking furnace at 200°C from 1 to 5h to prepare the molten salts.

Differential thermal analyzer was assembled by referring that reported by Berg et al¹⁰⁾; the cryoscopic cell, containing 5g of molten salts, consists of a glass container (12mm in diameter and 70 mm in length) with a small glass pocket (2.6mm in diameter and 25mm in length) for inserting chromel-alumel thermocouple¹¹⁾. After preparing molten salt in the glass cell, the liquidus and solidus temperatures were determined by DTA at the heating and cooling rates of 0.2°C/min. Alumina powders were used as reference material for DTA. In several samples, DTA measurements were carried out by changing the heating and cooling rates from 0.1 to 1 °C/min, and it was found that the heating and cooling rates of 0.2 °C/min was enough for reproducing liquidus and solidus temperatures. The thermocouple was calibrated by measuring the melting point of indium metal (156.2°C). The accuracy of temperature measurement was ±0.5°C. Compositions of molten salts are represented by those of mixed raw chemicals.

Phase relation of NaCl-AlCl₃-SeCl₄ system at 200 °C was determined by the following method. The phase boundary of liquid phase at 200°C was determined by

Fig.1 Schematic diagram of conductivity cell;
a:capillary, b:tungsten spiral, c:melt,
d:Pyrex glass tube.

Fig.2 Liquidus temperatures of $(\text{NaCl})_m(\text{AlCl}_3)_{100-m}$ - SeCl_4 quasibinary systems as a function of SeCl_4 content. Small number in the figure shows a value of m .

direct observation whether the precipitates coexist or not in the melt during heating the molten salts at 200 °C for 1 to 5h in a transparent furnace. Crystal structure of the precipitates coexisted with liquid phase was determined by X-ray diffraction (XRD), after separating the precipitates from melts at 200°C. The glass tube, which was used for filtration of precipitates, consists of a pair of small reservoirs separated by glass filter at the center. After sample was melted in this tube, the melt was flowed down from one side of the tube to the other side through glass filter by turning the glass tube upside down at 200°C. These precipitates filtered were cooled and taken out in a glove box, and then, mounted in a specimen holder for XRD. This specimen was taken out from a glove box,

after covering by polymer film to avoid the effect of moisture, and the crystal structure was determined by using an X-ray diffractometer (Rigaku RAD system).

2.2 Electrical conductivity

Electrical conductivity was measured by the ac impedance method in the temperature range from 140 to 220 °C, using a conductivity cell shown in Fig.1. The conductivity cell was made of the H-type Pyrex glass tube, which consists of a capillary (3.0mm in inside diameter and 30mm in length) and two glass tubes (8mm in diameter and 70mm in length). The resistance for the migration of ions through capillary was analyzed by the complex impedance plot, separating from the electrode interface impedance. The ac impedance measurement was carried out by connecting a cell to a Tohogiken potentiostat 2000 which was connected to a NF Electronic Instrument 5720B frequency resonance analyzer, supplying 5mV ac perturbation with frequency sweeping from 0.1 to 10⁵ Hz. The cells were calibrated by measuring the electrical conductivity of 1mol/dm³ KCl solution. The cell constants were all on the order of 4100cm⁻¹. The error of electrical conductivity measurement was $\pm 0.05\text{S cm}^{-1}$.

3 RESULTS AND DISCUSSION

3.1 Phase diagram

Figure 2 represents the liquidus temperatures of several $(\text{NaCl})_m(\text{AlCl}_3)_{100-m}$ - SeCl_4 quasibinary systems as a function of SeCl_4 content. Small number in this figure indicates a value of m . By using these results, the liquidus surface of NaCl - AlCl_3 - SeCl_4 ternary system is given as depicted in Fig. 3. By plotting the lowest liquidus temperature of each quasibinary system of Fig.2 as a function of m -value, the ternary eutectic composition is estimated to be $(\text{NaCl})_{20}(\text{AlCl}_3)_{59}(\text{SeCl}_4)_{21}$, and its temperature is 42°C. In a region of large SeCl_4 content, composition dependence of liquidus temperature is very large as shown in Fig.2. Then, the liquidus temperature higher than 160°C was not drawn in a region of large SeCl_4 content, i.e. in a region of AlCl_3 content lower than about 50mol% in Fig. 3. Sodiumtetrachloroaluminate NaAlCl_4 melts at 153 °C. Sample with SeAlCl_7 composition is confirmed to melt at 160°C by DTA.

In order to clarify the phase relation of molten salt at the temperature of operating Na/SeCl_4 battery¹⁾, the phase relation of NaCl - AlCl_3 - SeCl_4 system at 200 °C was determined in a range of SeCl_4 content lower than 50mol% and in a range of AlCl_3

Fig.3 Liquidus diagram of NaCl-AlCl₃-SeCl₄ system. Small number in the figure represents the liquidus temperature. Heavy lines with arrows show the eutectic valleys. Open circles show the eutectic compositions.

Fig.4 X-ray diffraction patterns of precipitates and NaAlCl₄; □:NaCl, ●: NaAlCl₄, ▼:SeCl₄

- (a) Precipitates filtered from (NaCl)₄₄(AlCl₃)₄₄(SeCl₄)₁₂ melt at 200°C.
 (b) Precipitates filtered from (NaCl)₄₀(AlCl₃)₄₀(SeCl₄)₂₀ melt at 200°C.
 (c) NaAlCl₄ crystal solidified from (NaCl)₅₀(AlCl₃)₅₀ melt.

content from 20 to 80mol%. XRD patterns of the precipitates filtered at 200°C are shown in Fig.4, compared with that of NaAlCl₄. At (NaCl)₄₄(AlCl₃)₄₄(SeCl₄)₁₂ composition, the precipitates coexisted with liquid phase are found to be NaCl, as shown in Fig.4(a). In this sample, because small amounts of

Fig.5 Phase relation of NaCl-AlCl₃-SeCl₄ system at 200°C. L:Liquid, N:NaCl, S:SeCl₄.

melts are adherent to the precipitates, weak diffraction peaks of NaAlCl₄, which was formed by the solidification of melt, were also observed. At (NaCl)₄₀(AlCl₃)₄₀(SeCl₄)₂₀ composition, precipitates are considered to be NaCl and SeCl₄, judging from the XRD pattern in Fig.4(b).

Figure 5 shows the phase relation of NaCl-AlCl₃-SeCl₄ system at 200°C. Here, □, ▲, ● and ■ represents, respectively, the composition where only the liquid phase, coexistence of liquid+NaCl, coexistence of liquid+SeCl₄ and coexistence of liquid+NaCl+SeCl₄ have been observed at 200°C. In a range of AlCl₃ content higher than about 80mol%, the region of liquid phase separated into two phases is expected to exist⁵⁾, which has, however, not been studied in this work.

3.2 Electrical conductivity

In a Na/SeCl₄ battery, the molten salts with AlCl₃/NaCl molar ratio from 50/50 to 65/35 have been used¹⁾. Then, the effect of SeCl₄ addition on the electrical conductivity of NaCl-AlCl₃ melt with AlCl₃/NaCl molar ratio 55/45, which is in a range of AlCl₃/NaCl ratio used in the battery, has been studied

Figure 6 shows the electrical conductivities of the quasibinary (NaCl)₄₅(AlCl₃)₅₅-SeCl₄ melts as a function of temperature.

Specific conductivities of the quasibinary melts tend to decrease with increasing content of SeCl₄. As an origin of this phenomenon, it is considered that the electrical conductivity of molten salt is affected strongly by the concentration of Na⁺ ions, because the transport number of Na⁺ ions is considered to be much larger than those of other ions as suggested by Sato et al⁸⁾; they have shown that the transport number of Na⁺ ions in NaCl-AlCl₃ melt is 0.93 at 200°C in a

Fig.6 Specific conductivities of quasibinary $(\text{NaCl})_{45}(\text{AlCl}_3)_{55}\text{-SeCl}_4$ melts as a function of temperature.

- (a) $(\text{NaCl})_{45}(\text{AlCl}_3)_{55}$ melt.
- (b) $(\text{NaCl})_{42.75}(\text{AlCl}_3)_{52.25}(\text{SeCl}_4)_5$ melt.
- (c) $(\text{NaCl})_{40.5}(\text{AlCl}_3)_{49.5}(\text{SeCl}_4)_{10}$ melt.

range of AlCl_3 content from 52 to 65mol%, which is quite larger than that (0.07) of AlCl_4^- ions⁸⁾.

4 SUMMARY

The liquidus temperature of $\text{NaCl-AlCl}_3\text{-SeCl}_4$ system, phase relation of the system at 200°C and the electrical conductivity of $\text{NaCl-AlCl}_3\text{-SeCl}_4$ melts have

been studied. The following results were obtained.

- (1) In $\text{NaCl-AlCl}_3\text{-SeCl}_4$ system, the liquidus temperature is lower than 160°C in a range of AlCl_3 content from about 50 to 70mol%. The ternary eutectic composition is $(\text{NaCl})_{20}(\text{AlCl}_3)_{59}(\text{SeCl}_4)_2$, and its temperature is 42°C.
- (2) The electrical conductivities of the quasibinary $(\text{NaCl})_{45}(\text{AlCl}_3)_{55}\text{-SeCl}_4$ melts tend to decrease with increasing content of SeCl_4 .

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