DISSOLVED STATES OF DIVALENT METAL CHLORIDES
IN AlCl3-NaCl MELTS

T. Ishikawa, T. Sasaki, S. Konda and M. Noguchi
Faculty of Engineering, Hokkaido University,
Sapporo 060, Japan

ABSTRACT

Solubilities of the divalent metal chlorides, MnCl2, MgCl2, CdCl2, CoCl2, and PbCl2, in binary chloride melts (AlCl3 + NaCl) were measured in the concentration range from 55 to 59 mol% of AlCl3 at 200°C. The equilibrium constants for dissolution were derived as a function of solubilities and the mole fraction of AlCl3 on the assumption of the dissolution reaction being

\[ \text{AlCl}_3^- + \frac{1}{2}\text{MeCl}_2(s) = \frac{1}{2}\text{Me}^{2+} + 2\text{AlCl}_4^- \]

The equilibrium constants calculated from experimental results suggest that divalent metal chlorides dissolve in the melts as free Me\(^{2+}\) cations forming complex anions.

INTRODUCTION

Many experimental studies on electrowinning and electrorefining of aluminum from chloride melts containing over 50 mol% of AlCl3 have been carried out because the melting points of the melts are low as about 150°C and it may possible to work at a relatively low temperature. But there are difficulties, as the deposits easily grow in a dendritic and/or sponge-like fashion. Recently, it was reported that smooth deposition could be attained by addition of MnCl2 to the melts as noted from the viewpoint of surface treatments for steel.(1) But the factors affecting the morphology of the deposits have not been elucidated yet mainly because of a lack of information on the dissolved states of the chlorides in the melts.

The objectives of this work were, first, to determine solubilities of several divalent metal chlorides (MeCl2) in binary AlCl3 - NaCl melts and next, to elucidate the dissolved states of the chlorides by means of estimations of equilibrium constants of dissolutions of the chlorides under the assumption of equilibrium equations.

EXPERIMENTAL

All chlorides for the solvent were thoroughly purified before usage. The equipment for purification of AlCl3 is depicted in Fig.1. Crude AlCl3 (usually yellow) in a hopper was supplied to a boiler containing a small amount of NaCl by a rotary feeder with desired constant speeds and melted to form a low-temperature binary melt. Part of the AlCl3
beyond the equilibrium concentration in the melts at the prescribed temperature sublimated, leaving impurities with low vapor pressure. The vapor of Al$_2$Cl$_6$ carried by Ar gas was solidified as fine particles in a cooling zone and collected in a flask. These purified particles were kept under evacuated conditions.

The purification equipment for the binary mixture of AlCl$_3$ - NaCl is shown in Fig. 2. The mixtures with prescribed concentrations of AlCl$_3$ and NaCl (about 2 kg) were melted in a glass vessel and chips of high-purity Al were added for purification of the melts by reducing water and so on. As shown in the figure, the lower part of the vessel with a small diameter was heated in an electric furnace at 250 - 300°C while the upper part of the vessel with a large diameter was open to the atmosphere and was left to cool. The temperature differences between upper and lower parts of the melts induced a thermal convection and mixing of the melts by this convection led to elevation of the rate of purification. After two- or three-day purification, the melts were filtrated with a sintered glass to remove suspended aluminum particulates and kept in flasks under vacuum. Three kinds of melts were prepared in this manner. AlCl$_3$ concentrations of 55.2, 57.3 and 59.1 mol% in these melts were determined, by the usual chelate titration method. The sample chlorides, MnCl$_2$, MgCl$_2$, CdCl$_2$ and PbCl$_2$, were preliminarily prepared as rods 6 mm in diameter by melting and solidifying followed by drying under evacuated conditions. A CoCl$_2$ rod was similarly prepared except for drying and melting under an Ar atmosphere.

For solubility tests, 15 g of binary mixtures (AlCl$_3$ and NaCl) of containing 55-59 mol% AlCl$_3$ were introduced into a glass ampoule together with a large excess of the divalent metal chloride samples. The ampoule is presented in Fig. 3. The salts were melted under vacuum and the ampoules were also sealed under vacuum. The ampoule was set in an oven equipped with a vibration system as shown in Fig. 4. The vibration equipment could, at once, give six ampoules a tilt motion of inclination of 30 degrees and frequency of 60 times a minute. This vibration promoted dissolution of the salts and the experiments were carried out for various periods up to 20 hours at 200°C. After a vibration for the prescribed period the ampoules were allowed to stand perpendicularly for 30 minutes to settle undissolved divalent samples in the bottom, after which they were inclined carefully to transfer the supernatant liquid to the stems of sampling spaces. The sample holder made it possible to carry out the course of sampling procedures mentioned above in the oven. After precise scaling the samples were dissolved into distilled water for analysis and the solubilities of the divalent metal chlorides were determined. The sample containing PbCl$_2$ was dissolved in 2 N HCl and analyzed through the same procedure.

**RESULTS AND DISCUSSION**

In alkali metal chloride, XCl (X = Na or K) - AlCl$_3$ melts the equilibrium of the chemical reaction between AlCl$_3$ and XCl [1] shifts very much to right,

$$\text{AlCl}_3 + \text{XCl} = \text{X}^- + \text{AlCl}_4^-$$

The excess AlCl$_3$ on the left hand side of Eq.[1] reacts with AlCl$_4^-$ to produce Al$_2$Cl$_7$ as follows,
\[ \text{AlCl}_3 + \text{AlCl}_7^- = \text{Al}_2\text{Cl}_7^- \]  

[2]

The equilibrium of this reaction also shifts to the extreme right, and this indicates that the system is almost entirely composed of X+, \( \text{AlCl}_4^- \), and \( \text{Al}_2\text{Cl}_7^- \); the amount of Cl is very small.(2)

The divalent metal chlorides (MeCl₂) under investigation are assumed to react with \( \text{Al}_2\text{Cl}_7^- \) and dissolve as follows,

\[ \frac{1}{2} \text{MeCl}_2 + \text{Al}_2\text{Cl}_7^- = \frac{1}{2} \text{Me}^{2+} + 2\text{AlCl}_4^- \]  

[3]

The equilibrium constant (K) for this reaction is given as

\[ K = \frac{[\text{Me}^{2+}]^\frac{1}{2} \cdot [\text{AlCl}_4^-]^2}{[\text{Al}_2\text{Cl}_7^-]} \]  

[4]

where \([\ ]\) represents the mole fraction in the melts.

Consider the solubility of MeCl₂ is Q moles in one mole solvent (AlCl₃ + XCl), then the K value is given as follows,

\[ K = \frac{1}{Q^2(2 - 3\alpha + 4Q)^2 \cdot (2\alpha - 1 - 2Q)^3} \]  

[5]

where \( \alpha \) is a mole fraction of AlCl₃ in the solvent. In this equation the last term on the right is added to convert amounts of ionic components expressed by mole numbers to mole fractions. By measuring the solubility of MeCl₂ we can estimate K from the equation.

The results of solubility tests on the divalent samples of CdCl₂ and CoCl₂, are shown in Fig. 5. The numbers of moles dissolved per one mole of the solvent melt are presented with vibrating time in the oven at 200°C. For each case, numbers of dissolved moles increased with the mole fraction of AlCl₃ in the solvent melt. Nearly constant values, regarded as saturated solubility, were obtained in the range of 5 hours to 20 hours.
The relation between solubilities of various divalent chlorides and the mole fraction of AlCl$_3$ at 200°C is presented in Fig.6. The solubilities of all chlorides increase with the concentration of AlCl$_3$. The dotted line in the figure indicates the maximum amount of dissolution of the chlorides under the assumption that the chlorides react with all Al$_2$Cl$_7$ in the melts.

Next, the equilibrium constants of MeCl$_2$ were calculated from the solubility data in Fig.6 and plotted against the AlCl$_3$ concentrations in Fig.7. The calculated values remained constant within the experimental concentration ranges of AlCl$_3$, as shown in the figure. This suggests that the added divalent metal chlorides react with Al$_2$Cl$_7$ and dissolve in the melts as a Me$^{2+}$ cation and a complex anion.

**CONCLUSIONS**

Solubilities of five kinds of divalent metal chlorides in AlCl$_3$ + NaCl melts were examined by using a special oven with a vibration system. The divalent metal chlorides were saturated within 5 hours and the solubilities were determined in the concentration range from 55 to 59 mol% of AlCl$_3$ at 200°C. The equilibrium constants for dissolution derived on the assumption that the divalent metal chlorides dissolved in the reaction with Al$_2$Cl$_7$ complex showed constant values on the basis of the solubility data in the entire experimental concentration range of AlCl$_3$.

This leads the conclusion that the dissolution reaction is expressed as

$$\frac{1}{2}\text{MeCl}_2(s) + \text{Al}_2\text{Cl}_7 = \frac{1}{2}\text{Me}^{2+} + 2\text{AlCl}_4^-.$$

**REFERENCES**

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Fig. 1. Equipment for purification of AlCl₃.

Fig. 2. Equipment for purification of solvent (AlCl₃ + NaCl).
Fig. 3. Ampoule for solubility tests. Fig. 4. Schematic diagram of the oven and vibration equipment for solubility tests.

Fig. 5. Time variations in the amounts of dissolved CdCl$_2$ and CoCl$_2$ in one-mole solvent melts of different concentrations of AlCl$_3$ at 200 °C.
Fig. 6. Relation between the solubility of divalent metal chlorides and the AlCl$_3$ concentrations at 200 °C.

Fig. 7. Relation between the equilibrium constants for dissolution and the AlCl$_3$ concentrations at 200 °C.