SOLUBILITY OF ALUMINA IN MOLTEN CHLORIDE-FLUORIDE MELTS

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ABSTRACT

In secondary aluminum production, salt flux is often used to protect the metal from oxidation during melting, to strip oxide layer from the scrap, to promote the metal coalescence and further to dissolve or intake impurities. Al_2O_3 is the most encountered oxide impurity, and the commonly used salt flux is the NaCl-KCl-Na_3AlF_6 system. With the increasing rate of recycling and the varying scrap quality, the solubility of alumina in molten chloride-fluoride melts is increasingly gaining importance for proper salt flux selection and for better understanding of the melting behavior.

In the present study, equilibrium experiments were conducted to determine the solubility of alumina in the chloride based system. The effects of temperature and various additives on the solubility of oxides in NaCl-KCl based salt flux were investigated. The results prove that the solubility of alumina in the molten chloride system is quite low, and generally the temperature and cryolite addition increase the solubility of oxides in the chloride melt. Other additives of AlF_3, KF and NaF have also positive effects on the solubility of alumina. In addition, the solubility data in various salt mixtures in literature are analyzed. The solubility of alumina in the molten salt has been calculated using the FACT commercial thermochemical databases, and compared to the experimental results. The general trend of the present measurements can be fairly reproduced by thermodynamic simulations. The additives with decreasing effect on the solubility of alumina in the chloride based melt are in following sequence: $AlF_3 \rightarrow CaF_2 \rightarrow MgF_2 \rightarrow Na_3AlF_6 \rightarrow NaF$.

INTRODUCTION

In recent years, the share of the secondary aluminum production has been constantly growing world wide, and recently increased to over 40% in western Europe. Secondary aluminum has been widely used in the field of transportation, building, and packaging industries etc. Aluminum scrap is normally processed in a rotary furnace or a hearth furnace. The whole recycling process includes scrap collection, scrap pre-treatment, melting in the furnace, refining and alloying of liquid aluminum in holding furnaces, casting or transportation to the industrial end-users. The operation temperature is normally around 800°C. Salt flux is used to protect metal from burning and to absorb and remove contaminants and oxides.

In the secondary aluminum industry, due to the complexity of compositions and contaminants in the various types of aluminum scraps, an understanding of the behavior of oxide impurities from the scraps during melting is important in the recycling process. The salt flux absorbs the oxides and contaminants from the scrap and protects the aluminum melt from oxidation loss (burn-off). The salt flux consists mainly of NaCl and KCl, and some additional cryolite or CaF_2. After melting, aluminum metal and salt slag are tapped from the furnace. A large amount of salt slag is generated which contains mainly oxides, carbides, nitrides, chlorides and some residual aluminum metal or alloys. Usually high salt flux factor is used to reach a higher metal recovery for melting lower grade scrap, which leads to an increased quantity of the salt slags. Due to the high consumption of the salt flux and thus high generation of salt slags, it has to be cleaned and recycled. The salt slag is actually not slag but rather a slurry, which contains the salt flux and the products from the chemical reactions that occur between the scrap and the salt flux during melting. The entrained phases affect viscosity and the viscosity of the salt flux is increased with the amount of entrapped non-metallic components, which influence the settling of heavier materials [11]. A high slag viscosity will lead to more fine aluminum metal entrapped in the salt slag, and thus increase the load of salt slag recycling. In aluminum recycling, metal loss is a crucial factor which depends also on the salt properties. Since the properties of the salt flux affect the separation efficiency of the metal from salt slags and the metal loss, research was carried out to understand the dissolution reactions between aluminum oxide and molten salt.

Reviewing the information in literature, solubility data of aluminum oxide in NaCl-KCl based salt system was limited [3]. The information of the solubility of Al_2O_3 in the molten salt system is important to understand the impurity intake of the molten salt during the aluminum scrap smelting. In the present work, to provide the fundamental knowledge for aluminum recycling, the solubility of Al_2O_3 in NaCl-KCl based molten salt system was experimentally determined. The effects of temperature and various additives in the salt system are investigated. The thermodynamic calculation with the FACT commercial thermo-chemical databases was conducted and compared to the experimental results.

EXPERIMENTAL

Raw Materials

Alumina powder (μ-Al_2O_3) with 99.98 % purity and >100 μm in size was used in the solubility experiments. The halides (NaCl, KCl, Na_3AlF_6, NaF, AlF_4, KF, and $AlCl_3$) were of laboratory reagent grade with purity of 99.7%. The chemicals were stored and handled in a glove box in an argon atmosphere.

Solubility Measurements

The solubility was determined by the isothermal equilibrium method. In the experiment, about 50 gram of the salt mixture with additional 6 wt% alumina was homogeneously mixed and charged in the crucible, and placed into a high temperature gas-tight chamber furnace. The furnace was closed and flushed with 2 l/min Ar, and heated to the designed temperature. After equilibrium for 5 hours, the melt was quenched with nitrogen. The samples were taken and ground into powder and leached in 100ml of 1N HCl for 24 hours. The leachate was analyzed by Atomic Absorption Spectrophotometry (AAS) for the dissolved amount of aluminum ions in the molten salt. The solubility of Al_2O_3 in the system was calculated based on the AAS results and the input compositions. Two types of crucibles were used: graphite for containing cryolite and fluoride bearing salt systems, and alumina for containing the salt mixtures without cryolite and fluoride. A lid was placed on the crucible to minimize vapour loss. To obtain a representative result for each salt system, some equilibrations were repeated. In addition, during each equilibration test, three samples were analysed from different locations in the crucible. The average of the analyzing results was determined as the solubility of the reaction system.

RESULTS AND DISCUSSION

In order to obtain a better understanding of the molten chemistry of alumina in various salt fluxes, the solubility of Al_2O_3 over a wide range of additives was measured in NaCl-KCl based salt system at 750°C, 850°C and 950°C, respectively. The alumina saturated molten salt was sampled, dissolved and analyzed to determine the solubility of Al_2O_3. The measured solubility results are given in Table 1.

Table 1: Solubility of Al_2O_3 in various molten salt fluxes

T (°C)	Salt compositions (wt%)	Al_2O_3 solubility (wt%)
850	NaCl (50) + KCl (50)	0.00
850	NaCl (45)+KCl (45)+ Na_3AlF_6 (10)	1.20
850	NaCl (42.5)+KCl (42.5)+ Na_3AlF_6 (15)	1.60
850	NaCl (40)+KCl (40)+ Na_3AlF_6 (20)	2.14
750	NaCl (45)+KCl (45)+ Na_3AlF_6 (10)	1.10
750	NaCl (42.5)+KCl (42.5)+ Na_3AlF_6 (15)	1.81
750	NaCl (40)+KCl (40)+ Na_3AlF_6 (20)	2.27
950	NaCl (45)+KCl (45)+ Na_3AlF_6 (10)	1.26
950	NaCl (42.5)+KCl (42.5)+ Na_3AlF_6 (15)	1.86
950	NaCl (40)+KCl (40)+ Na_3AlF_6 (20)	2.32
850	NaCl (45)+KCl (45)+ AlF_3 (10)	2.02
850	NaCl (45)+KCl (45)+ KF (10)	1.29
850	NaCl (45)+KCl (45)+ NaF (10)	0.08

The System of NaCl-KCl-Al_2O_3

The phase diagram of the binary system NaCl-KCl is extensively studied [5]. The salt flux on equimolar composition (44 wt% NaCl - 56 wt% KCl) has the lowest melting point, which corresponds to the eutectic temperature of about 656°C. In the present study, the equal-weight salt mixtures, with additional 6wt% Al_2O_3, were used. The mixtures were homogeneously mixed and melted at 850°C, after equilibrium the samples were quenched with air. The solidified melt of NaCl + KCl + Al_2O_3 had two separated layers, the bottom layer with precipitated white alumina and the bulk melted salt flux with a pale pink color. It was found that there is almost no solubility of Al_2O_3 in the NaCl-KCl binary system.

The System of NaCl-KCl-Na_3AlF_6-Al_2O_3

As practiced in the secondary aluminum industry, cryolite was added into the equal-weight NaCl-KCl salt mixtures to dissolve the alumina. The determination of aluminum ions was calibrated against the NaCl-KCl-Na_3AlF_6 melt without alumina addition. The results are shown in Figure 1.

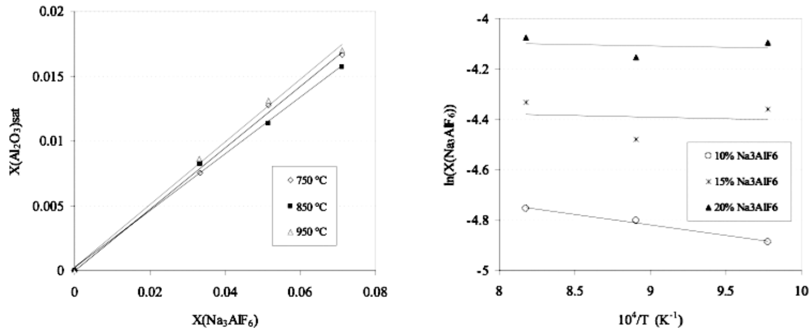

Figure 1: Measured Al_2O_3 solubility and its temperature dependence in NaCl-KCl-Na_3AlF_6 system

With 10 wt% of cryolite addition, the solubility of Al_2O_3 was increased from 0 to 1.20 wt% at 850°C. Increasing temperature from 750°C to 850°C has resulted in a slightly increased solubility of Al_2O_3 , from 1.1 to 1.2 wt%, possibly due to the high fusion enthalpy of alumina. Temperature has little influence on the Al_2O_3 solubility for 15 wt% and 20 wt% of cryolite additions. On the other hand, it is clear that addition of cryolite from 10 to 20 wt% has more significant effect on the alumina solubility than the temperature. Comparing the solubilities of aluminum oxide in the molten cryolite, ~12 wt% at 1000°C [10], the results are reasonable.

Thus to recover aluminum metal from scrap in aluminum recycling, cryolite in the salt flux plays important role not only in lowering the interfacial energy between oxide layers and the aluminum melt, but also in increasing the solubility of oxide in the molten slag. Higher solubility of oxide in the salt melt normally leads to higher metal recovery.

The Effect of Additives

The effect of various additives on the solubility of Al_2O_3 was investigated, as shown in Figure 2. Comparing various additives at 10wt% level, AlF_3 gives highest solubility (2.0 wt%) for Al_2O_3, followed by KF (1.3 wt%), Na_3AlF_6 (1.2 wt%) and NaF (0.08wt%) at 850°C. However, with 50 g salt mixture, 10wt% additives are equivalent to 0.024 mole Na_3AlF_6, 0.060 mole AlF_3, 0.086 mole KF and 0.120 mole NaF respectively. It is obvious that the alumina dissolution is positively affected by the concentration of F^- in the melt. Meanwhile the cations play also certain roles on the reactivity of alumina in the molten salt. The mechanism of alumina dissolution in chloride-fluoride based salt system is not clear, and further research is still required to understand the ionic interactions in the melt.

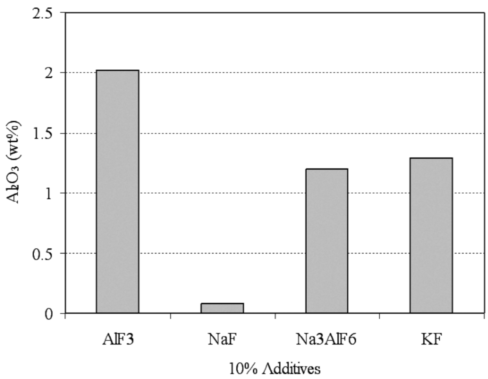

Figure 2: Effect of additives on the solubility of Al_2O_3 in the equal-weight NaCl-KCl based fluxes at 850°C

In general, no stirring was applied in the present experimental research. A uniform concentration was confirmed through the samples taken at different locations in the melted salt flux and the repeated AAS analysis. The effect of salt vaporization on the solubility was considered small, thus ignored. For the $AlCl_3$ containing system, the solubility data are not included, due to the uncertainty of the results and the significant mass loss during melting.

Experimental Data in the Literature

Solubilities of Al_2O_3 in the NaCl-KCl-NaF system in the temperature range of 700-850ºC using isothermal saturation method have been reported in the literature [3]. The alumina solubilities are somewhat lower than the present measurements, as seen in Table 2. The extrapolation of their results to the NaF-free chloride system also confirms the zero solubility of Al_2O_3 in the equalmolar NaCl-KCl mixture.

Table 2: Solubility of Al_2O_3 in molten salt fluxes [3]

T (°C)	Salt compositions (wt%)	Al_2O_3 solubility (wt%)
750	NaCl (39.5)+KCl (50.4)+ NaF (10)	0.007
800	NaCl (39.5)+KCl (50.4)+ NaF (10)	0.009
850	NaCl (39.5)+KCl (50.4)+ NaF (10)	0.012
700	NaCl (36.6)+KCl (46.7)+ NaF (16.6)	0.010
750	NaCl (36.6)+KCl (46.7)+ NaF (16.6)	0.017
800	NaCl (36.6)+KCl (46.7)+ NaF (16.6)	0.020
850	NaCl (36.6)+KCl (46.7)+ NaF (16.6)	0.023
700	NaCl (34.6)+KCl (44.1)+ NaF (21.3)	0.014
750	NaCl (34.6)+KCl (44.1)+ NaF (21.3)	0.023
800	NaCl (34.6)+KCl (44.1)+ NaF (21.3)	0.027
850	NaCl (34.6)+KCl (44.1)+ NaF (21.3)	0.029

The solubility of Al_2O_3 in molten cryolite is well established [4, 6, 9, 10]. Solubility of Al_2O_3 in NaF-AlF_3-CaF_2-LiF-MgF_2 molten fluorides was thermodynamically assessed by Chartrand and Pelton [2] using the modified quaschemical model. The measured and calculated solubility of Al_2O_3 in molten cryolite is shown in Figure 3. The phase diagrams and thermodynamic behavior of the Li, K, Na, Ca, Mg//Cl, F and K, Na, Al/Cl systems were also assessed by the same group [1, 7]

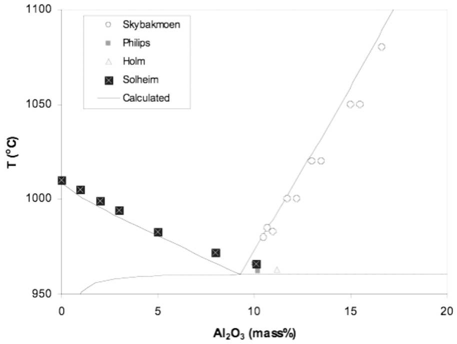

Figure 3: Solubility of Al_2O_3 in molten cryolite from the literature [4, 6, 9, 10] compared with calculated solubility using a quasichemical model by Chartrand [2]

The liquidus projection of the Al_2O_3-NaCl-Na_3AlF_6 system was studied in the 1950's [6]. As can be seen from Figure 4, solubility of Al_2O_3 decreases monotonously with the increase of NaCl content. By extrapolating the solubility curves to the NaCl-end one may conclude that the alumina is not soluble in pure NaCl, and this is in good agreement with the present investigation.

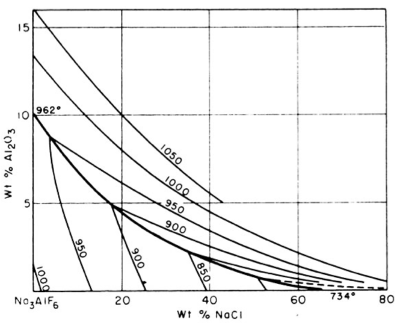

Figure 4: Liquidus projection of the Al_2O_3-NaCl-Na_3AlF_6 system [6]

The Al_2O_3-MgF_2 pseudo-binary system was also reported by Sharma [8] and shown in Figure 5. Pure magnesium fluoride is able to dissolve Al_2O_3 at temperatures higher than 1250ºC.

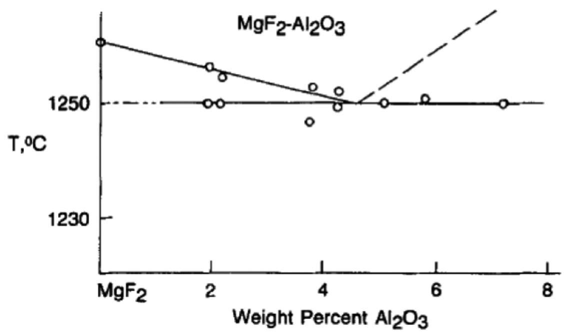

Figure 5: The Al_2O_3-MgF_2 pseudo-binary system [8]

THERMODYNAMIC SIMULATIONS

Solubility of Al_2O_3 in the equal-weight NaCl-KCl based salt mixture has been simulated using the FactSage™ software package. The FACT salt and Hall-Héroult databases were used to calculate the Al_2O_3 solubility in molten salts. Since the commercial databases [1, 2, 7] are not able to fully cover the Al, Na, K, Ca, Mg // Cl, F, O system, the calculations are only a priori from the model. The results are shown in Figure 6. The calculated Al_2O_3 solubilities in different molten fluxes fairly agree with the present experimental results. The effect of various additives on the Al_2O_3 solubility can be sorted in the following sequence: $AlF_3 \rightarrow CaF_2 \rightarrow MgF_2 \rightarrow Na_3AlF_6 \rightarrow NaF \rightarrow KF$, which is in good agreement with the present measurements, except for the KF additive. Figure 7 shows the calculated effect of temperature on the Al_2O_3 solubility in the equal-weight NaCl-KCl-Na_3AlF_6 melt. The model gives more significant impact of temperature on the alumina solubility than the experimental results. A comparison between the model calculations and experimental results [3] on Al_2O_3 solubility in the equalmolar NaCl-KCl-NaF fluxes also shows the similar tendency, as illustrated in Figure 8. To better understand the behavior of alumina in the molten salt, further investigation is in need in the future.

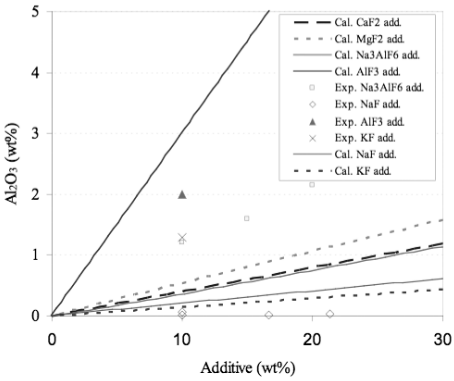

Figure 6: Comparison of calculated and measured effects of various additives on the solubility of Al_2O_3 in the equal-weight NaCl-KCl based molten fluxes

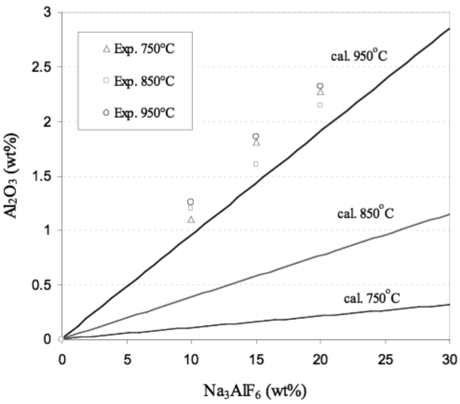

Figure 7: Comparison of calculated and measured effects of temperature on the solubility of Al_2O_3 in the equal-weight NaCl-KCl based molten fluxes with Na_3AlF_6 additive

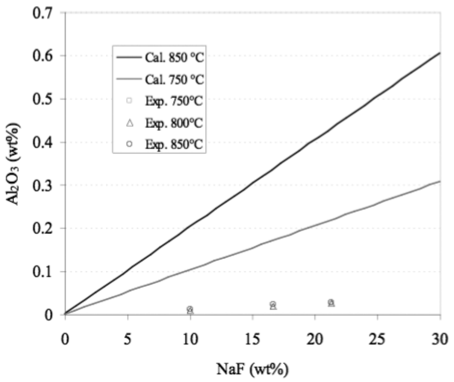

Figure 8: Comparison of calculated and measured effects of temperature on the solubility of Al_2O_3 in the equalmolar NaCl-KCl molten fluxes with NaF additive

CONCLUSIONS

Solubility of Al_2O_3 in various equal-weight NaCl-KCl based fluorochloride mixtures has been determined in the laboratory. The experimental results are compared to that calculated by using the commercial thermochemical databases. The following conclusions have been obtained from the present investigation:

- Within the experimental uncertainty, the equal-weight NaCl-KCl chloride mixture is not able to dissolve a measurable concentration of aluminum oxide in the temperature range 750-950°C. This is in good agreement with the literature.
- Cryolite addition and temperature rise increase the solubility of Al_2O_3 in the chloride melt. The influence of temperature is less significant than the cryolite addition. The solubility of Al_2O_3 in NaCl-KCl-Na_3AlF_6 system increases from 1.2 to 2.3 wt%, when the Na_3AlF_6 increases from 10 wt% to 20 wt% in the chloride melt. In the NaCl-KCl-Na_3AlF_6 system containing 10wt% of cryolite, when temperature increases from 750 to 950°C, the solubility of Al_2O_3 increases from 1.1 to 1.26 wt%.
- Comparing various additives at 10 wt% level, AlF_3 gives the highest solubility of Al_2O_3 (2.0 wt%), followed by KF (1.3 wt%), Na_3AlF_6 (1.2 wt%) and NaF (0.07 wt%) at 850°C. Effect of different additives can be sorted in the sequence: $AlF_3 \rightarrow KF \rightarrow Na_3AlF_6 \rightarrow NaF$.
- The experimental results have been compared with predictions using the FACT commercial thermochemical databases. The present measurements can be fairly reproduced by thermodynamic simulations. Effect of various additives can be sorted in following sequence: $AlF_3 \rightarrow CaF_2 \rightarrow MgF_2 \rightarrow Na_3AlF_6 \rightarrow NaF \rightarrow KF$, which is in good agreement with the present measurements, except for the KF additive. Temperature has significantly higher impact on the alumina solubility from the model calculation.

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