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LIQUIDUS TEMPERATURES OF THE SYSTEM Na_3AlF_6-K_3AlF_6-AlF_3

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Abstract

Liquidus temperatures for the primary crystallization of the molten salt system Na_3AlF_6-K_3AlF_6-AlF_3 for aluminium electrolysis were determined by thermal analysis. The data were fitted to an empirical equation:

$$T = 3478-1867\times[KR]^{0.12}-12.97\times[AlF_3]^{1.14}$$

$$+3.538\times[AlF_3]\times[KR]^{0.98}-0.505\times[AlF_3]^{1.24}\times[KR]^{1.23}$$

where T is the liquidus temperature in °C and the square brackets denote wt% of components in the system Na_3AlF_6-K_3AlF_6-AlF_3. with $[KR]=K_3AlF_6/(K_3AlF_6+Na_3AlF_6)$ The composition limitations are $20\%<AlF_3<30\%$, and $15\%<KR<30\%$.

The isothermal diagram of the molten salt system Na_3AlF_6-K_3AlF_6-AlF_3 was obtained in this composition limitation.

Introduction

Hall-Héroult process is the most important method of primary aluminum production. It has been used more than a century. But the disadvantage of this method is obvious. In theory the energy consumption of producing aluminum is about 6320 kWh per tonne. But in fact the energy consumption is more than 13000 kWh per tonne. Because of high energy consumption and serious environmental pollution, aluminum electrolysis industry is facing tough challenges. The use of low-temperature electrolysis would optimize production processes, reduce energy consumption, improve energy efficiency, eliminate emission of greenhouse gases, cut investment cost prolong cell life [1-3], and it became the research focus recently.

However, the temperature of producing aluminum depends on the liquidus temperature of the electrolyte for aluminum electrolysis which is highly dependent on its composition. So, it is necessary to find an appropriate low-temperature bath to implement the low-temperature electrolysis. As a general trend Na_3AlF_6 has a melting point of 1011 °C [4], additives such as AlF_3, CaF_2, LiF, can decrease the liquidus temperature. However, with these additives, alumina solubility of the melt decreases, which is leading easily to alumina deposition on the cathode surface, and this is detrimental for aluminum electrolysis. By comparison, alumina is highly soluble in the KF-AlF_3 melt. And the mixture of potassium and sodium cryolites melt is attractive since the system has a eutectic point at 560 °C [1]. To obtain low liquidus temperature and high alumina solubility electrolyte system; the mixture might be used [5-6]. Therefore, it is necessary to study on Na_3AlF_6-K_3AlF_6-AlF_3 system to develop environmentally friendly and energy-saving technologies for aluminum production.

The liquidus temperature of electrolyte is a basic parameter for aluminum electrolysis. Phase diagram of traditional electrolyte have been researched and some model equations describing liquidus temperatures have been derived based on the experimental data. Early studies on the NaF-KF-AlF_3 ternary system were presented by Belyaev et al. [7] and Barton [8]. David A.Chin et al. studied the portion of liquidus curves for Na_3AlF_6-K_3AlF_6-Al_2O_3 system by visual method [9]. Part of the NaF-KF-AlF_3 ternary system in the range of up to 50 mol pct AlF_3 was measured by Danielik and Cabcova [10]. Liquidus temperatures of cryolite melts with low cryolite ratio were researched by Alexei Apisarov et al. [11]. Compared some methods for testing temperature of primary crystallization in aluminum electrolyte melt, a classical thermo-analysis method was chosen by Wang et al. to measure the temperature of primary crystallization in the Na_3AlF_6-K_3AlF_6-AlF_3 [5]. But from published literatures, the research on liquidus temperatures of this system is rare.

Therefore, the aim of this paper is to obtain basic data for developing low temperature electrolyte for aluminum production process based on the system Na_3AlF_6-K_3AlF_6-AlF_3. The liquidus temperatures of Na_3AlF_6-K_3AlF_6-AlF_3 within the composition range of $K_3AlF_6/(K3AlF_6+Na_3AlF_6)$ (the value was defined as KR in this paper) 15%~30% and AlF3 20%~30%(without special explanation, % denotes weight percent all through in this paper) was investigated and a new equation describing liquidus temperatures was derived from these data.

Experimental

Chemical

The composition of electrolyte, Na_3AlF_6 and K_3AlF_6 were all of reagent grade. AlF_3 was purified by sublimation for three times and its purity was above 99.5%. All the raw materials were pre-processed for 48 hours under 120°C before being used.

Thermal Analysis

Comparing thermal analysis (TA), differential thermal analysis (DTA) , visual observations , quenching techniques and thermodynamic method, which have been used as the method to test phase equilibriums in cryolite-based melts, TA has been proven to give accurate freezing point depression data [5] In order to minimize the error due to undercooling of the melt, it is necessary to have vigorous stirring and a relatively low cooling rate (0.4 °C to 0.5 °C /min). So, the method of TA was adopted and the cooling rate was controlled at 0.5 °C /min in this work.Figure1 shows the experimental device.

The experimental crucible was made of high strength and purity graphite. Before the experiment the crucible must be dried for 24 hours in the oven under 100 °C. All experiments were carried out in an inert atmosphere. In the cooling process, temperature data was collected and processed.

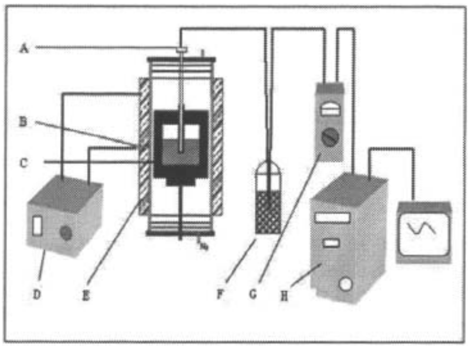

Figure 1. Experimental installation for determination of liquidus temperatures.

A- Thermocouple for temperature measurement; B- Thermocouple for temperature control, C- Experimental crucible; D- Temperature controller; E- Experimental furnace; F- Freezing point; G- Digital multimeter; H- Data collecting and processing system

Theoretically, liquidus temperatures of samples could be obtained in the cooling curves. To test the stability and reliability of this device, liquidus temperature of the melt NaCl (reagent grade) was measured three times. Their liquidus temperatures were 800.4 °C, 801.4 °C and 801.4 °C, which are close to the theoretic melting point 801 °C.One of the cooling curves of NaCl is shown in Figure 2. Repeating the experiment three times the results were close to the theoretical value, so the experimental equipment and methods are reliable and stable. More experimental details and experimental procedures can be found in the relevant papers [12-13]

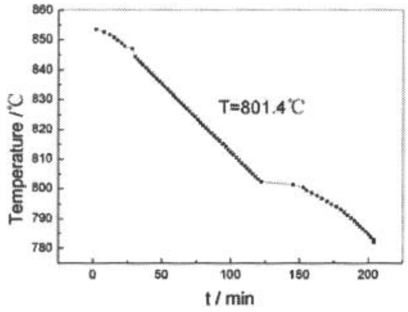

Figure 2. Cooling curve of the melt NaCl.

Results and Discussion

Characteristics of cooling curves

For pure substances, such as NaCl, the system composed of only one phase at the beginning of the experiment, the degree of freedom in system is 1. As the system temperature decreases, solid phase precipitates continuously, and then there is a system of solid and liquid phases. Known by the phase rule, freedom of the system is zero at this time. Temperature no longer change over time, until all the liquid has been turned into a solid phase, so temperature plateau appeared. When the liquid has been completely changed into solid phase, the system temperature continues to decline over time. This phenomenon is due to the crystallization process where latent heat compensates for reduced calories. But, the temperature plateau of complex system is not obvious, because the latent heat of crystallization process in this system is lower than in pure materials. For most experimental results, there is only a turning point, rather than plateau in the cooling curves. Some of the cooling curves for samples had been shown in Figure 3.

From Figure 3 the turning point in the cooling curve of the melt Na_3AlF_6-K_3AlF_6-AlF_3 (KR 30%, AlF_3 26%) is obvious, but it is difficult to find it when KR is 18%.Therefore, in order to obtain the results clearly it is necessary to repeat the testing and take derivation of the cooling curve [14].

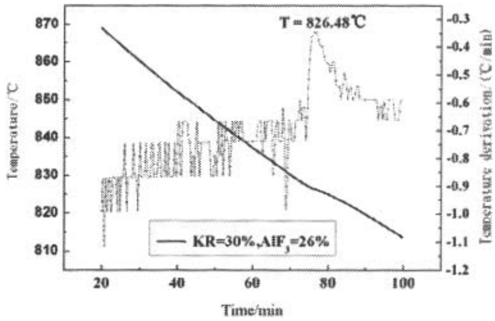

Figure 3. Cooling curves of the melt Na_3AlF_6-K_3AlF_6-AlF_3.

The ternary system Na_3AlF_6-K_3AlF_6-AlF_3

Figure 4.describes the effect of AlF_3 on liquidus temperatures of the system Na_3AlF_6-K_3AlF_6-AlF_3. It can be seen from the figure, adding aluminum fluoride can effectively reduce the liquidus temperature of the system Na_3AlF_6-K_3AlF_6-AlF_3. The impact of aluminum fluoride varies with KR. When KR was 15%, 18%, adding aluminum fluoride has a similar impact on the liquidus temperature of the system. However, the rate of temperature changes of the system with KR 21%, 24%, 27% increases when adding aluminum fluoride.

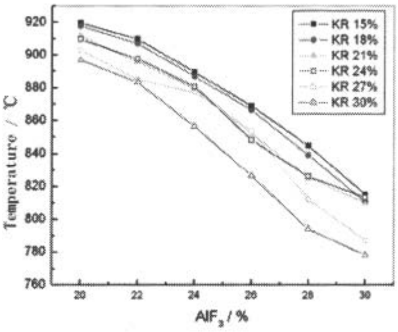

Figure 4. The effect of AlF_3on liquidus temperatures of the system Na_3AlF_6-K_3AlF_6-AlF_3.

In Figure 5 the curves represent the effect of KR on liquidus temperatures. The curves can be divided into three categories: (i) when the content of AlF_3 is 20% to 22%, KR has less impact on the system temperature, (ii) when the content of AlF_3 is 24% to 26%, the liquidus temperatures will reduce obviously when KR increases from 27% to 30%, (iii) when the content of AlF_3 in the system is 28% to 30%, the region in which temperature reduces rapidly will extend and in these systems when KR increases from 24% to 30%, the liquidus temperatures will reduce obviously.

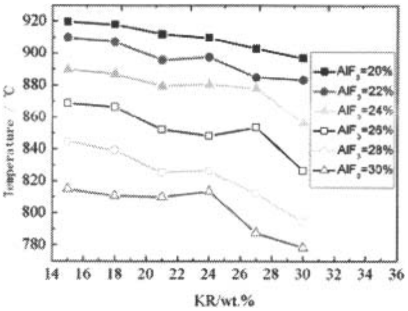

Figure 5. The effect of KR on liquidus temperatures of the system Na_3AlF_6-K_3AlF_6-AlF_3.

Empirical equation describing liquidus temperatures and isothermal diagram

Based on the present study, the data were fitted to an empirical equation:

$$T = 3478\text{-}1867 \times [KR]^{0.12}\text{-}12.97 \times [AlF_3]^{1.14} +3.538 \times [AlF_3] \times [KR]^{0.98}\text{-}0.505 \times [AlF_3]^{1.24} \times [KR]^{1.23} \quad (1)$$

Where T is the liquidus temperature in °C and the square brackets denote wt% of components in the system Na_3AlF_6-K_3AlF_6-AlF_3.The composition limitations are 20%< AlF_3 <30%, and 15%<KR<30%.Correlation coefficient of the equation is 0.992.

Some experimental data was selected and compared with the results which were calculated from different liquidus equations. The liquidus equation derived in the present work is in good agreement with the equation:

$$T=1003.508\text{-}0.081 \times A^{2.3159}\text{-}5.87 \times B^{0.657} \text{-}0.024 \times A^{2.2} \times B^{1.4}+0.035 \times A^{2.17} \times B^{1.084} \quad (2)$$

This equation is derived by Wang et.al. A denotes the weight percent of $AlF_3$and B denotes the weight percent of KR.

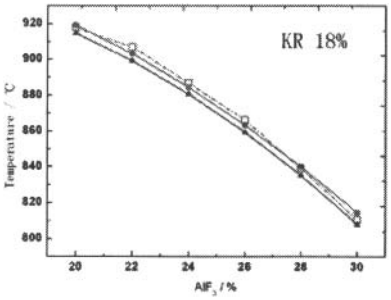

Figure 6. The liquidus temperatures of the system Na_3AlF_6-K_3AlF_6-AlF_3, Hollow square-Experimental data of this work, Solid square-Eqs. (1), Solid triangle -Eqs. (2).

In Figure 6 the curves that calculated by equation (1) and (2) have the same trend with the experimental results. And the curve which is calculated by equation (1) is well agreement with the experimental results than the curve that calculated by equation (2). This is because that dates which are used for fitting equation (1) are more intensive.

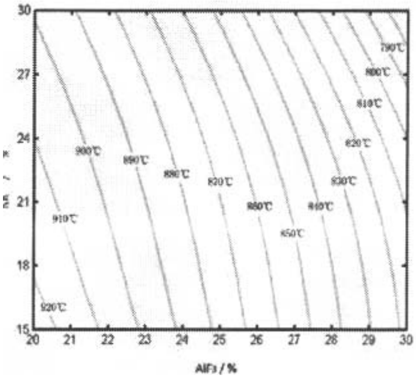

Figure 7. Isothermal diagram of the system Na_3AlF_6-K_3AlF_6-AlF_3 (KR=15%-30%, AlF_3=20%-30%).

According to equation (1), the ternary isothermal diagram is shown as Figure7. The figure shows that, the liquidus temperature will decrease with the addition of aluminum fluoride. Adding K_3AlF_6 had similar effect, but the impact is smaller than adding AlF_3.

Conclusions

Thermo-analysis method was chosen to test the temperature of the system Na_3AlF_6-K_3AlF_6-AlF_3. Due to the phase-change, latent heat is low; the inflection point of the cooling curve is not obvious. Calculating derivative is an important and effective method to obtain a more evident inflection point.

Liquidus temperature equation is derived based on experimental data in the present work of the system

Na_3AlF_6-K_3AlF_6-AlF_3.The range in which the equation is suitable is proposed to be KR: 15% to 30%, AlF_3:20% to 30%. Correlation coefficient of the equation is 0.992.The influence of KR on liquidus temperature depends on AlF_3. Isothermal diagram which is gained base on the equation (1) gives an intuitive method to choose low-temperature aluminum electrolysis.

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