Determination of Liquidus Temperature of Aluminium Electrolysis Electrolyte by Conductivity Method

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Abstract

This paper introduces a method to determine the liquidus temperature based on electrical conductivity variation curves, designed to overcome the challenges in measuring the liquidus temperature of low-temperature aluminium electrolysis electrolyte in the NaF-KF-AlF_3 system. The conductivity of molten electrolyte is measured at multiple temperature points within a defined range both above and below the presumed liquidus temperature using the Continuous Variation of Cell Constant method (CVCC). The liquidus temperature is then identified from the "inflection point" on the conductivity-temperature variation curve. This method was applied to industrial electrolytes, and the results were compared with those obtained via the stepwise cooling curve method, showing a deviation less than 0.17 %, thus validating the method accuracy. Additionally, this method was used to determine the liquidus temperature of the NaF-KF-AlF_3 system at various molecular ratios, revealing clear and consistent patterns. This method is applicable to various electrolyte systems and has the advantage of measuring both liquidus temperature and electrical conductivity.

Keywords: Low-temperature aluminium electrolysis electrolyte, Liquidus temperature, Bath Conductivity, CVCC method, NaF-KF-AlF_3 system.

1. Introduction

The liquidus temperature of aluminium electrolysis electrolyte is a critical parameter in aluminium electrolysis production [1, 2], as it governs the temperature control during the electrolysis process. Common experimental approaches for determining this temperature include visual observation [3, 4], stepwise cooling curve method [5–7], and differential thermal analysis [8, 9]. The visual observation method incurs substantial errors due to factors such as electrolyte volatilization and subjective interpretation by the experimenter. Therefore, the stepwise cooling curve method or differential thermal analysis is commonly used to measure the liquidus temperature of electrolytes. The principles of the stepwise cooling curve method and differential thermal analysis are basically the same; that is, the electrolyte is first melted in a high-temperature-resistant crucible, and then a temperature sensor immersed in the molten electrolyte tracks the temperature changes of the electrolyte. Due to heat release during the phase change solidification process of the electrolyte, an inflection point appears on the cooling curve of the electrolyte, which helps determine the liquidus temperature of the electrolyte.

Traditional industrial electrolytes are mainly composed of sodium cryolite, excess AlF_3, CaF_2 and alumina, with relatively straightforward electrolyte compositions. The inflection point on the cooling curve during their cooling process is more distinct and clearer, allowing the stepwise cooling curve method or differential thermal analysis to accurately measure the liquidus temperature of these electrolytes. However, for electrolytes in the NaF-KF- AlF_3 system, especially at low molecular ratios, there is no distinct inflection point on the cooling curve, or the inflection point is not at the liquidus temperature. The presumed reason is that during the cooling and solidification process of molten electrolyte in the NaF-KF- AlF_3 system, multiple phases such as $KAlF_4$, K_2NaAlF_6, $K_2NaAl_3F_{12}$, $Na_5Al_3F_{14}$, and Na_3AlF_6 exist, each with different solidification and phase transition heat release temperatures. The NaF-KF- AlF_3 electrolyte system is a commonly used low-temperature electrolyte system in the research of inert anode aluminium electrolysis technology [10–12], and accurate measurement of the liquidus temperature of low-temperature electrolytes is becoming increasingly important.

In this study, a novel method based on electrical conductivity variation curves is proposed to determine the liquidus temperature, addressing the limitations of conventional approaches for low-temperature electrolyte in the NaF-KF-AlF_3 system. This method exploits the fact that the molten electrolyte remains clear above the liquidus temperature and becomes turbid below it, combined with the characteristic changes in conductivity with temperature between these two states, to accurately identify the liquidus temperature. This method successfully validated its accuracy in measuring the liquidus temperature of industrial electrolytes and was used to measure the liquidus temperature of the NaF-KF-AlF_3 system at different molecular ratios.

2. Experimental Method

2.1 Determination of Temperature Range

Before the experiment, the electrolyte to be tested was crushed and mixed evenly, then dried at a constant temperature of 200 °C for more than 48 hours in a vacuum drying oven and stored in a desiccator for later use.

The electrolyte was placed in a lidded corundum crucible, heated and held in a well-type furnace until completely melted. Then the crucible lid was opened, and a thermocouple was inserted into the molten electrolyte to measure its temperature in real time. After turning off the furnace and allowing it to cool naturally, the transition process of the molten electrolyte from a clear to a turbid state was observed visually. The temperature at the inflection point, at which the liquid changed from clear to significantly turbid was recorded (rough value, assumed liquidus temperature), and the temperature range for measurement was determined based on the temperatures of the molten aluminium electrolyte in its clear and turbid states respectively.

2.2 Conductivity Measurement

The Continuous Variation of Cell Constant method (CVCC) is a commonly used technique for measuring the conductivity of molten electrolytes. Its principle is as follows: in a fixed molten salt circuit, an alternating current signal of constant frequency is applied, and the total resistance of the circuit has a linear relationship with the cell constant. The linear coefficient is a constant related to the molten salt conductivity, and the change in cell constant is caused by the change of the conductivity cell, namely (Equation (1)):

$$\kappa = 1 \Big/ A\left(\frac{dR}{dL}\right)_{average} \quad (1)$$

where:

κ	Conductivity, S/cm
A	Electrode area of the conductivity cell, cm^2

electrolyte increases with molecular ratio. Specifically, each 0.1 increase in molecular ratio leads to an average rise of 0.036 S/cm in conductivity.

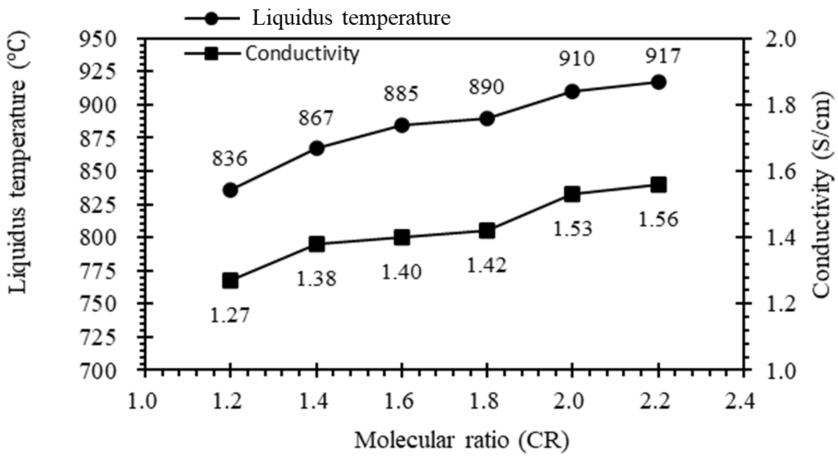

Figure 12. Liquidus temperature and conductivity variation curves of low-temperature electrolytes with different molecular ratios.

5. Conclusions

The method of determining the liquidus temperature from the electrical conductivity variation curve has an error less than 0.17 % compared to the stepwise cooling curve method, indicating its high accuracy. This method can be used not only to measure the liquidus temperature of industrial electrolytes but also for the NaF-KF-AlF3 low-temperature electrolyte system. It effectively addresses the limitations of the traditional stepwise cooling curve method, which struggles to accurately measure the liquidus temperature of low-temperature electrolytes in the NaF-KF-AlF3 system. Additionally, it provides conductivity data during the measurement of the liquidus temperature.

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