Observation of Alumina Dissolution and Bubble Behavior in Molten Salts with High Temperature Transparent Electrolytic Cell

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Abstract

The method of high temperature transparent electrolytic cell, which was developed by Prof. Zhuxian Qiu, was further developed and it played an important role in investigating the physical-chemical phenomena in molten salts. Two topics including dissolution of alumina in molten salts and anodic bubble behavior during aluminum electrolysis are described in this paper. The high temperature transparent cell was used for observing the dissolution behavior of alumina, including comparison of dissolution behavior between the secondary alumina and the primary alumina, physical-chemical properties of alumina on dissolution rate and crust dissolution dynamics. Another type of laboratory scale transparent aluminum electrolytic cell was used to observe the bubble dynamics beneath the anode in an electrolytic environment like that of an industrial cell. Some factors, such as anode design, anode current density, and bath composition on anodic bubble behavior are discussed.

Keywords: Aluminum electrolysis, transparent electrolytic cell, alumina dissolution, bubble behavior, molten salts.

3. Introduction

At present, the electrolysis of cryolite-alumina molten salts, also known as Hall-Héroult process, is the only industrial process for the primary aluminum production. The temperature of electrolysis is usually in the range of 940 to 970 °C. The cathodic product is liquid aluminum and the anodic product is a mixture of CO/CO_2 gas. The energy consumption is about 13.5 kWh/kg Al.

In 2018, the global primary aluminum production is estimated to be around 64.34 million tonnes. China produced 36.49 million tonnes accounting for 56.7 % of global production [1]. Currently, the largest prebake cell operating at 600 kA was started in China in 2014 [2]. Such great achievements were based on the development of fundamentals on aluminum electrolysis, including bath chemistry, cell magnetohydrodynamic (MHD) stability of the aluminum metal, energy balance and mass balance, electrochemical process of super large anode, materials selection and engineering.

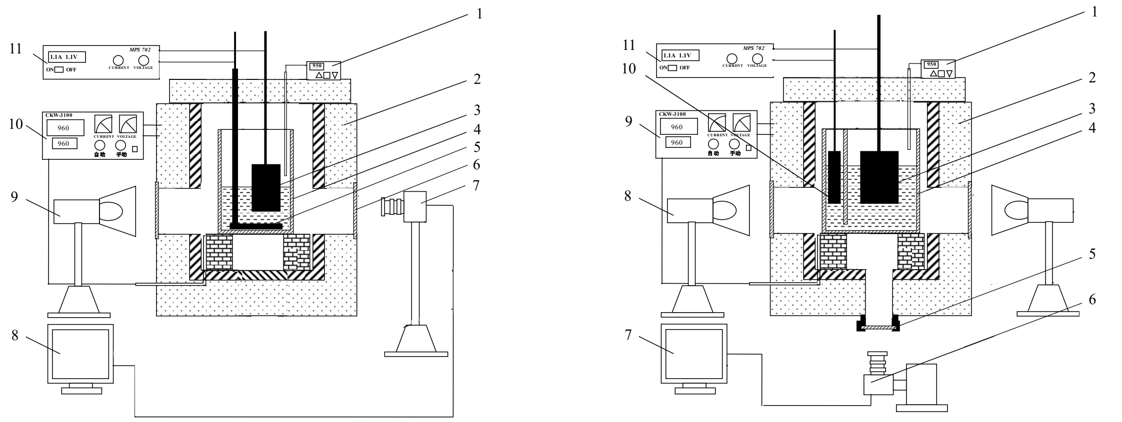
In this paper, some fundamental developments in understanding physical and chemical phenomena in the cryolitic melt are presented, such as dissolution of aluminum oxide in molten salts and anodic bubble behavior during aluminum electrolysis. A special instrument, called high temperature transparent cell was used to investigate these phenomena.

4. Introduction of the High Temperature Transparent Cell

Restricted by the high temperature and heavily corrosive environment of the molten salt, studies of industrial aluminum electrolytic cells are very difficult and expensive, particularly for detailed bubble dynamics and alumina dissolution process.

Haupin invented the first generation of transparent cell used for observation of molten salt electrolysis [3]. He employed sapphire windows held in a graphite crucible to 'see' the electrolysis process. This kind of transparent cell was limited due to high cost and small viewing window. For better viewing, Zhuxian Qiu [4 - 5] applied square-shaped quartz crucibles to study the metal fog, anode effect and other electrolysis phenomena, e.g., alumina dissolution. The cell enables us to observe experimental phenomena through side window, therefore it is called side-view transparent cell, as shown in Figure 1(a). This design of cell was limited in time and current density as metal fog rapidly arose and led to an opaque electrolyte. Qiu [5] improved the transparent cell design using double-chamber crucibles by positioning a square-shaped quartz tube inside the quartz crucible. Gao [6] further improved the cell design by implementing two chambers in one quartz crucible with a slot at the bottom of the middle wall connecting the two chambers. The cell can be operated more conveniently.

A new transparent cell with a bottom viewing window was developed at Northeastern University, as is shown in Figure 1(b) [7]. To observe the bubble behavior in the anode-cathode distance (ACD), a new viewing window at the bottom of furnace was opened. The experimental situations are recorded by an Industrial Camera (MV-VS078FC) with 15 frames per second (FPS) from bottom viewing window.



a) Side-view transparent cell **b) Bottom-view transparent cell**

Figure 1. The schematic diagram of side-view transparent cell and bottom-view transparent cell [7].

5. Dissolution of Alumina in Molten Salts

Industrial aluminum smelters use alumina as the raw material for electrolysis. The dissolution of alumina in molten cryolite bath has been a long and challenging topic. The high temperature transparent cell was used for observing the dissolution behavior of alumina, including comparison of dissolution behavior between the secondary alumina and the primary alumina, physical-chemical properties of alumina on dissolution rate as well as crust dissolution dynamics [8 - 11].

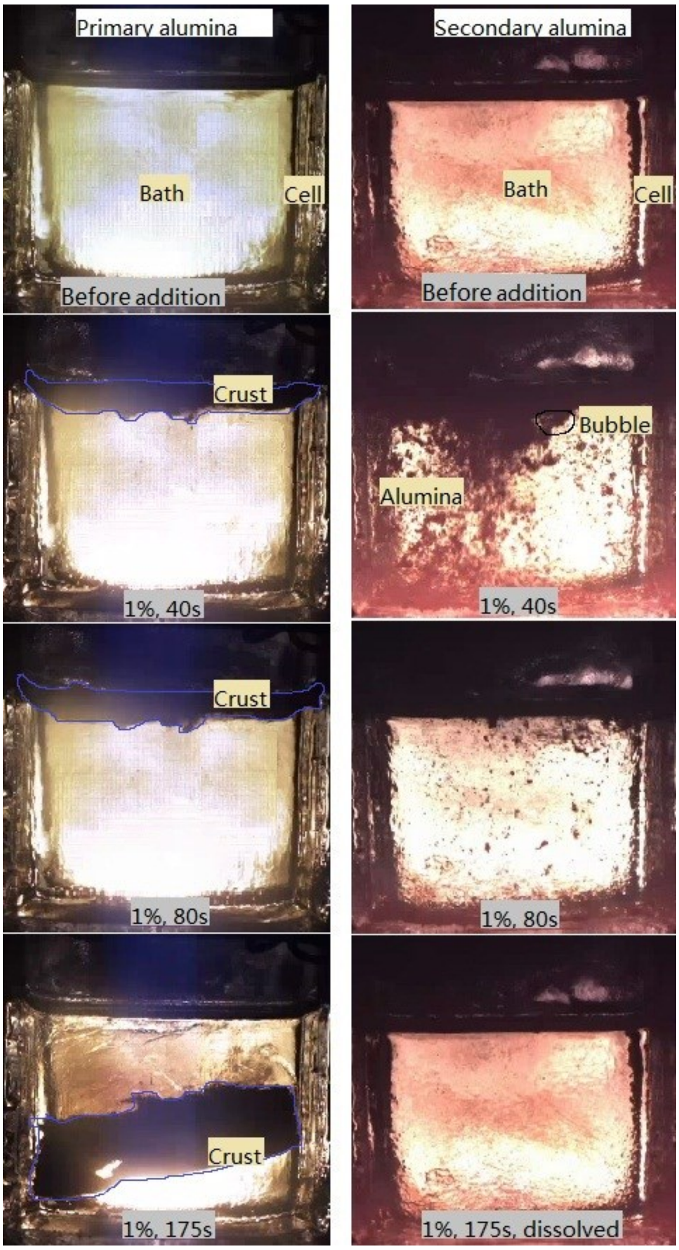


Figure 2. Comparison of the dispersion of primary alumina and secondary alumina in cryolite-electrolyte at 955 °C.

Figure 2 shows snapshots of the dissolution of primary alumina and secondary alumina. The secondary alumina floated on the surface of the melt first, and then dispersed into the melt gradually in the forms of particles and fine fragments. After 175 seconds, the dissolution of secondary alumina was completed. It was noticed that there was no crust formed during the dissolution process of secondary alumina. Moreover, gas bubbles were released at the interface of the liquid melt and floating particles.

During the first 20 seconds after addition of primary alumina, some of the alumina dispersed through the electrolyte and dissolved quickly in 20 seconds. The undissolved alumina particles, however, formed a layer of boat-like white crust with a dimension of 55 mm x55 mm x 0.5 mm and floated on the surface of the electrolyte for over 2 minutes. Then the crust sank to the bottom of the crucible and dissolved completely after 600 seconds, 425 seconds slower than the secondary alumina

The real reason for disappearance of agglomerate is the damage of connection formed on the surface of molten cryolite between alumina particles. Carbon dust trapped in the secondary alumina burned as soon as it reached the surface of molten electrolyte, the heat of combustion preheated the alumina and then reduced the temperature gradient between the cold alumina and molten salts; the instantly generated carbon dioxide played a role of agitation, both of which give active help to alumina dissolution [11]. The gas bubbles generated between alumina particles break up the connections between alumina particles. Small pieces of alumina result in faster wetting by the molten electrolyte and longer floating time in electrolyte. After sinking through the melt, much bigger contact area with the melt makes it easier to dissolve.

Our findings encouraged the Chinese aluminum smelters to use the secondary alumina instead of primary alumina for getting better dissolution in the reduction cells. Because the secondary alumina is obtained by absorbing fluorides in the duct gas using primary alumina in the Gas Treatment Center, the smelters have greater motivation to recover the fluorides in the duct gas even if the gas scrubbing procedure consumes a lot of energy accounting for 3 % of energy consumption for aluminum smelting.

6. Anodic Bubble Behavior during Aluminum Electrolysis

Carbon anode is considered as the heart of the aluminum reduction cell. Carbon dioxide bubbles are generated under the anode from an anodic electro-chemical reaction, they are then released at the anode edges and rise to the bath surface in the side channel. In our lab, the bubble dynamics beneath the anode was observed directly from a bottom view, using a laboratory scale transparent aluminum electrolytic cell in an electrolytic environment like that of an industrial cell. The relationships between bubble coverage and cell voltage and current density and its induced resistance have been discussed. Combined with industrial measurement, we gained valuable insight of anodic bubble behavior on carbon anode [7, 12 - 14].

Figure 3 shows some characteristic bubble morphologies in a bubble life cycle at the fixed current density of 0.9 A/cm^2. It appears that the slot divides the entire anode surface into separated parts: The longitudinal slot divides the original anode (length to width aspect ratio 2.27) into two slim parts (aspect ratio 5.56 for each part), and the two transverse slots divide the original anode (aspect ratio 2.27) into three parts (aspect ratio 1.57 for each part). On the unslotted anode, the bubbles coalesce into larger bubbles as they meet with each other as shown in Figure 4(a). However, it is interesting to notice the bubbles on slotted anodes cannot move through the slots for further coalescence. The unslotted anode leads to the maximum bubble size among three types of anodes, the transverse slots significantly decrease it, and the longitudinal slot makes a further reduction. These observations indicate that the slot in width of 4 mm can prevent bubbles from coalescing into larger bubbles and allows the release of smaller bubbles from slotted anodes. While the common slot width in industrial cells is now approximately 10 to 15 mm wide, the current investigation provides valuable evidence for possible use of narrower slot width in a real cell, though more work is needed to optimize the slot width in industrial anodes.

At all current densities, anode slots decrease the oscillations of the cell voltage. At current density of 0.9 A/cm^2, the average oscillation of cell voltage is about 24.5 mV for the unslotted anode; it decreases to 15.5 mV for the longitudinally slotted anode and to 16 mV for the transversely slotted anode.

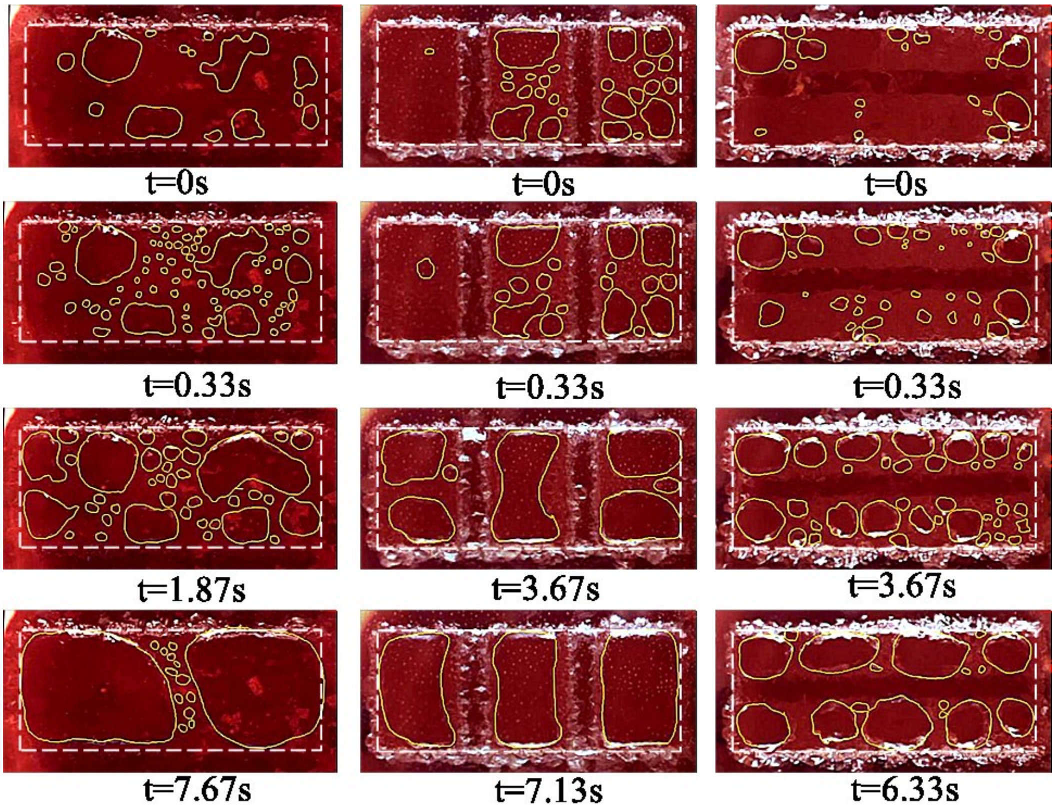


Figure 3. Bottom view of the characteristic bubble morphologies for three types of anodes at current density of 0.9 A/cm^2: (a) unslotted case (left) (b) transversely slotted case (centre) (c) longitudinally slotted case (right).

The anode slot affects the bubble behavior and the resultant voltage drop significantly. With the presence of a 4 mm wide longitudinal slot, the mean bubble coverage was reduced by about 38 % and the maximum coverage by 33 % at a current density of 0.9 A/cm^2. The bubble induced voltage drop and its fluctuation were reduced consequently, while the mean fluctuation was reduced by 37 %. The bubble coverage on the slotted anode was much lower than that on the un-slotted anode when the current density was less than 1.1 A/cm^2. At the highest current density of 1.3 A/cm^2 performed in this experiment, the difference was reduced. These findings provide potentials for designing new anode for industrial process.

7. Conclusions

Using the high temperature transparent electrolytic cell, we have showed the nature of some important phenomena in the high temperature molten salts. The cell provided us a lot of information for understanding the physical chemistry and electrochemistry of molten salts. There is still large room to improve this method continuously. Combined with other important techniques, such as high-speed photography technology, Raman spectroscopy or spectral analysis technology, the high temperature transparent cell may find its unique and eminent role in the field of molten salt chemistry and technology.

8. Acknowledgements

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