Electrolysis expansion performance of semigraphitic cathode in [K₃AlF₆/Na₃AlF₆]-AlF₃-Al₂O₃ bath system

LI Jie(李 健), FANG Zhao(方 钤), LAI Yan-qing(赖延清), LÜ Xiao-jun(吕晓军), TIAN Zhong-liang(田忠良)

(School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China)

Abstract: The electrolysis expansion of semigraphitic cathode in [K₃AlF₆/Na₃AlF₆]-AlF₃-Al₂O₃ bath system was tested by self-made modified Rapoport apparatus. A mathematical model was introduced to discuss the effects of αCR (cryolite ratio) and βKR (elpasolite ratio) on performance of cathode electrolysis expansion. The results show that K and Na (potassium and sodium) penetrate into the cathode together and have an obvious influence on the performance of cathode electrolysis expansion. The electrolysis expansion and K/Na penetration rate increase with the increase of αCR. When αCR=1.9 and βKR=0.5, the electrolysis expansion is the highest, which is 3.95%; and when αCR=1.4 and βKR=0.1, the electrolysis expansion is the lowest, which is 1.28%. But the effect of βKR is correlative with αCR. When αCR=1.6 and 1.9, with the increase of βKR, the electrolysis expansion and K/Na penetration rate increase. However, when αCR=1.4, the electrolysis expansion and K/Na penetration rate firstly increase and then decrease with the increase of βKR.

Key words: aluminum electrolysis; semigraphitic cathode; low temperature electrolysis; electrolysis expansion; K penetration; Na penetration

1 Introduction

Compared with the deficiency of high temperature, high energy consumption of current aluminum electrolysis, low temperature electrolysis can effectively improve the current efficiency, increase the purity of primary aluminum, lower energy consumption, and prolong the lifespan of aluminum reduction cell. So it has become one of the most active research topics in current international aluminum sphere [1–2]. At present, the research effort of low temperature electrolyte system has mainly focused on Na₃AlF₆-AlF₃-Al₂O₃ and K₃AlF₆-AlF₃-Al₂O₃ bath systems [3–8]. From the laboratory experiments, it can be known that based on Na₃AlF₆-AlF₃-Al₂O₃ and K₃AlF₆-AlF₃-Al₂O₃ bath systems, the solubility and solution rate of alumina decrease with decreasing electrolysis temperature. Comparatively, the solution properties of alumina are superior in K₃AlF₆-AlF₃-Al₂O₃ bath system. With decreasing electrolysis temperature, the solution properties of alumina are of great importance and related to the normal and reposeful operation of aluminum reduction cell. Therefore, the K₃AlF₆-AlF₃-Al₂O₃ bath system has considerable predominance in low temperature electrolysis. However, considering the actual carbon cathode, it will be greatly destroyed by pure elpasolite used to carry out low temperature electrolysis and the lifespan of cell will also be shortened markedly. At this circumstance, the application of composite electrolyte composed of elpasolite and sodium cryolite can not only lower the electrolysis temperature and ameliorate the solution properties of alumina, but also avoid the destructive effect of pure elpasolite on carbon cathode. From the literatures reported at home and abroad [9–12], it can be seen that researches about the penetration and destructive action of alkali metal to cathode mostly include the penetration of Na and the expansion and failure of cathode in macroscopic view during the conventional electrolysis process only, but those about performance of electrolysis expansion of cathode in the new type of low temperature electrolyte containing K were barely reported. There are only a few qualitative researches which believe that leopoldite has strong penetration ability on carbon material, which is about decuple of sodium salt [4–6]. Therefore, whether or not this new type of low temperature electrolyte can be applied in electrolytic aluminum industry, it is extraordinarily necessary to study the penetration characteristics of the electrolyte on the carbon cathode profoundly and quantificationally.

In order to research the K/Na penetration characteristics of this composite electrolyte composed of...
elpasolite and sodium cryolite, semigraphitic cathode was employed as the research object, which is widely used in the current electrolytic aluminum industry. A self-made modified Rapoport apparatus was adopted to review its performance of electrolysis expansion in \([\text{K}_3\text{AlF}_6/\text{Na}_3\text{AlF}_6]-\text{AlF}_3-\text{Al}_2\text{O}_3\) bath system, and the influences of \(\alpha_{CR}\) and \(\beta_{KR}\) on the performance of electrolysis expansion of semigraphitic cathode were studied. Moreover, the morphology and element distribution about the cross section of specimens after electrolysis were analyzed.

2 Experimental

2.1 Cathode specimens
Semigraphitic cathode widely used in electrolytic aluminum industry was selected as cathode specimen, and the quality of which accorded with criterion YS/T287—2005. The cathode was machined into the cylinder of 20 mm \(\times\) 60 mm (diameter \(\times\) length), and a circle hole with a diameter of 5 mm in one side surface was drilled in order to connect steel rod with specimen.

2.2 Experimental method and condition
The specimen was put into a cell made of high purity graphite in the vertical tube furnace, and the cylindrical cathode specimen was immersed into the molten electrolyte by 25 mm. The chemical reagents used in the experiment were: \(\text{K}_3\text{AlF}_6\) (analytical grade), \(\text{Na}_3\text{AlF}_6\) (analytical grade), \(\text{Al}_2\text{O}_3\) (analytical grade) and \(\text{AlF}_3\) (commercial grade). According to the difference of \(\alpha_{CR}\), the experiments could be grouped into three teams. In one team, \(\alpha_{CR}\) was constant and \(\beta_{KR}\) was respectively 0.1, 0.2, 0.3, 0.4 and 0.5, as shown in Table 1. The concentration of alumina in the electrolyte was saturated in every experiment. The current density \(\left(\rho_{CD}\right)\) was 0.8 A/cm\(^2\) and the superheat temperature \((t_{S})\) was 50 °C.

The specimens were subjected to electrolyte for 1.5 h. Testing temperature was determined by the liquidus temperature \((t_{L})\) of each electrolyte and superheat. The whole experimental process was taken in the high-purity argon atmosphere.

2.3 Test of electrolysis expansion
A self-made modified Rapoport apparatus was used to test the linear expansion displacement of specimen and the cathode electrolysis expansion was figured out by the following equation \([9−10]\):

\[
\rho = \Delta L / L
\]

where \(\rho\) is the cathode electrolysis expansion, \(\Delta L\) is the linear displacement of cathode expansion, and \(L\) is the initial length of specimen.

2.4 Characterization of cathode specimens after electrolysis
The cross sections of specimens after electrolysis were analyzed by a JEOL JSM–5600LV backscatter electron image (BEI). NORAN VANTAGE4105 X-ray energy dispersive spectrometry was used to test the element distribution in the cross sections of specimens.

3 Results and discussion

3.1 Morphology and element distribution of semigraphitic cathode after electrolysis
The obtained cathode specimen A4 was carved after electrolysis along the radial direction. The cross section is about 10 mm from the bottom. Japanese JEOL JSM–5600LV SEM was used to analyze the morphology of the margin and the central part of the cross section. Fig.1 shows the morphology and element surface analysis figures about the margin part of cross section. The white zone in morphology figure is mainly the electrolyte penetrating in cathode’s pores, and the grey zone is the semigraphitic cathode. It can be clearly seen that because of the electrocapillarity, a mass of electrolyte penetrates into the cathode and fills in the pores of it. It is this electrolyte existing in the pores of the cathode that makes the interface between electrolyte and cathode increment. Consequently, the penetration of K/Na to the cathode is aggravated. Meanwhile, in the process of electrolysis, once K and Na precipitate on the surface of cathode, they will penetrate into carbon cathode under the bonding action between the electron in orbit s of alkali metal and electron in orbit \(\pi\) in carbon. From elements surface analysis figures, it can be seen that both K and Na penetrate into the cathode, but K, Na,

<table>
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<tr>
<th>Serial number</th>
<th>(\alpha_{CR})</th>
<th>(\beta_{KR})</th>
<th>(t_{L}/\degree\text{C})</th>
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</tr>
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<td>808</td>
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<td>0.3</td>
<td>803</td>
</tr>
<tr>
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<td>1.4</td>
<td>0.4</td>
<td>727</td>
</tr>
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</tr>
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<td>903</td>
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