EFFECT OF KF ADDITIONS IN NA_3ALF_6-AL_2O_3 ELECTROLYTES ON EXPANSION OF CATHODE BLOCKS

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Abstract

Effects of K and Na on expansion of cathode carbon block were studied through an improved instrument for measurement of expansion rate. For a 30% graphitic cathode block, based on the results, in KCl-NaCl electrolysis system K and Na are reacting with graphite and forming graphite intercalation compounds (GICs) during penetration from surface to inside of the cathode block, and K plays more important role in expansion and penetration than Na. The results show that for a NaF-AlF_3-Al_2O_3 system, containing 7% Al_2O_3 and with CR = 6.5, during electrolysis at 1000℃ the expansion rate of the 30% graphitic cathode block is increased from 0.47% to 0.82% with 0 to 7% KF addition to the electrolytes. It is also shown that the expansion due to K and Na penetration in cathode becomes lower with increasing content of graphite in cathode material, and that expansion of fully-graphitized cathode is very low.

Introduction

Bauxite is the raw material of produce alumina, which is used for electrolytic aluminum production. But impurity content of K in China bauxite is high, which results in high concentration of KF in electrolyte [1-3]. Na_3AlF_6-Al_2O_3-AlF_3 system is usual electrolyte to produce aluminum, and for improving physicochemical property of electrolyte and increasing the current efficiency and electrical conductivity of electrolyte, MgF_2 and LiF are usually added into the electrolyte [4,5]. It is generally acknowledged that KF should not be added into the electrolyte process, because K damages the cathode [6,7].

There is a lot of research focusing on the system of low temperature electrolyte, while few study the effect of KF in the electrolyte and the damage to cathodes. High KF and LiF is found in the electrolyte of some aluminum smelters, because of using high K-Na alumina [8,9].Thus, the study of rich K and Li in electrolysis system become necessary.

The composition of electrolyte, materials and characteristics of cathode are important factors which influence expansion rate of cathode. The trend is to use cathode blocks produced with high content of graphite material (high percentage graphitic cathode blocks) and graphitized cathode blocks instead of anthracite based carbon cathode blocks and low percentage graphitic cathode blocks as in the past. The effect of KF in molten electrolyte on the expansion of cathode blocks produced with different materials is studied in this paper.

Experiments

Experimental materials

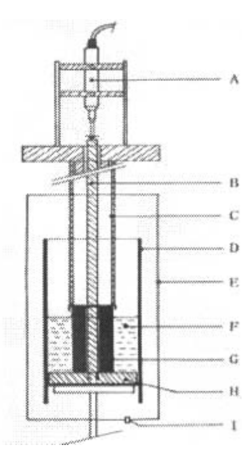
Cathode of electrolytic cell was supplied by San Menxia China. Graphite crucibles being the anode of the experimental electrolytic cell were supplied by Shenyang China. And boron nitride, diameter 4 mm and height 55 mm, was supplied by Shan Dong Pengchen Special Ceramics Co. Ltd.

Composition of the electrolyte

The composition of the electrolyte was KCl-NaCl; with 87% cryolite Na_3AlF_6, 3% Al_2O_3 and KF (0 - 7%). Mole ratio of NaF: AlF_3 was 6.5.

Experimental procedures

Figure 1 schematically shows the experimental apparatus for aluminum electrolysis. The cathode is a vertical cylinder, diameter 25 mm, and height 50 mm. The electrolytic cell is heated by a tube type resistance furnace and its temperature is controlled at the heating rate of 15℃/min. The power is DC power supply used for controlling cathode current density with argon inlet into the heating system to protect the cathode from oxidization. The phases of cathode are analyzed by X-ray diffractometer and surface topography of the cathode is analyzed by scanning electron microscope.



A - sensor, B - boron nitride stick, C-Ni-Cr alloy cathode tube, D - graphite crucible, E-furnace, F-cryolite melts, G - cathode, H - boron nitride, I - shielding gas entrance
Figure1. Schematic of experimental apparatus.

Analysis of experimental results

Analysis of graphite cathode after electrolysis

Figure 2 shows two the expansion curves of cathode in 100% KCl system and in 100% NaCl system, respectively. After 30 min electrolyzing in KCl system, the expansion rate reach 6.2% and the cathode was destroyed. While the maximum expansion rate of cathode was only 0.53% in 100% NaCl system with experiment lasting 4 h without being crashed.

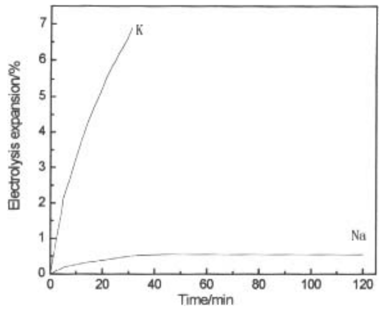


Figure 2. Effect of K and Na on expansion of cathode.

Figure 3 shows the photographs of cathodes after electrolysis at 850℃ with different content of KCl-NaCl (0 - 7%). The results show that the cathode becomes perforated and fragile when the content of KF increases.

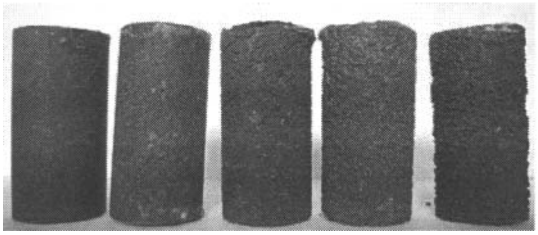


Figure 3. Effect of KCl on macro morphology of cathode.

Figure 4 shows phases of original cathode and cathodes after electrolysis in electrolyte with different K content. The results show that 2θ is 26.44, indicating a characteristic peak of graphite laminated structure. Na and K penetrating into graphite could extend the distance of graphitic layers and cause 2θ to change when the content of K^+ is increasing. At the same time penetration of Na and K also caused expansion of graphitic layers along the C axis which results in enlarging d_{001}. The peak of d_{001} moved forward to lower angle, which meant that the graphitic cathode was destroyed and graphite intercalation compounds (GICs) were generated by Na and K penetration into the graphite layers [10-12].

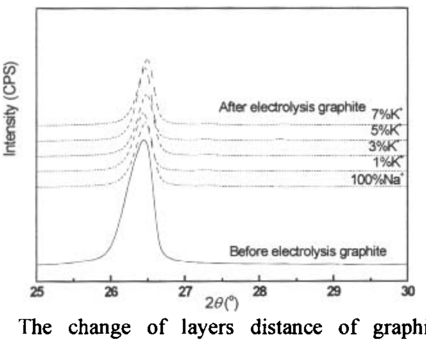


Figure 4. The change of layers distance of graphite after electrolysis.

Figure 5 shows the structure of GICs which is formed by Na and K. Na penetration into graphite could form a kind of chemical compound as $C_{32}Na$ (4 ranks GICs), where one Na atom is implanted per four carbon atoms: the distance between two Na-graphitic layers increased by 0.46 nm, the others were 0.34094 nm and average distance was 0.37, as shown in Figure 5. K penetration into graphite could form a kind of chemical compound as $C_{24}K$ (3 ranks GICs), with one K atom implanted per three carbon atoms. Atomic diameters of K, 0.4544 nm, is larger than the distance between graphitic layers, 0.34094 nm, so it is difficult for K to enter into the graphitic layers.

The activation energy of reaction with K atom and C is bigger with rising temperature. Firstly, K atom reacted at edge of carbon layers, which enlarged the distance of reaction points. When $C_{24}K$ is formed, the distance between graphitic layers is increased by 0.62 nm, so K atom can implant into graphitic layers and react with C successively. Finally, crystal lattice of graphite is damaged seriously and the cathode carbon becomes fragile.

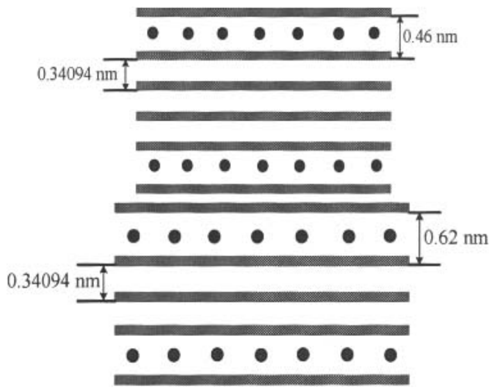


Figure 5. Structure model of intercalation compounds in graphitized carbon.

Effect of K on expansion of cathode

Figure 6 shows the effect of different content of KF on the expansion rate of the cathode. The curve has a parabolic shape which means that the expansion rate increases fast at the beginning of the electrolysis and the expansion become slow even invariable as the process of electrolysis develops. The expansion rate of the cathode is 0.47% in the electrolyte without KF and it reaches 0.82% in the electrolyte containing 7% KF.

Figure 7 is the relationship between content of KF and expansion rate of cathode after 90 min electrolysis. It is shown that the expansion increases with content of KF increasing.

Na^+ is the major conductive ion in the aluminum electrolysis process. And K, Na and Al can deposit together on the cathode when the concentration of K+ is high enough. The K and Na diffuse through holes or crystal lattice of C and react with cathode to form GICs finally. For the cathode, expansion or cracks occur because of the above mechanism. Electrolyte containing high concentration of KF reacts with K at the cathode and the expansion rate of the cathode is serious due the high concentration of K+ in the nearby cathode

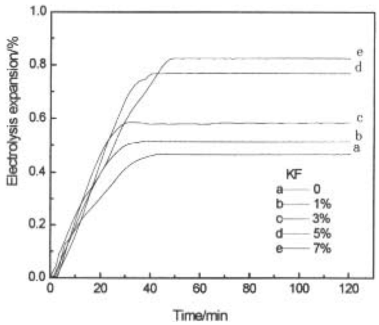


Figure 6. Expansion curves of cathode in different electrolytes during electrolysis.

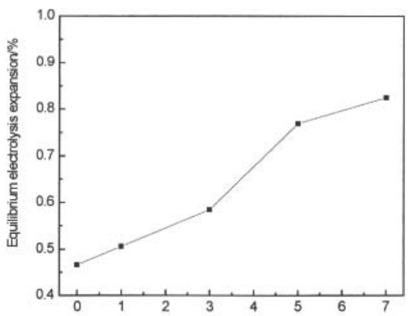


Figure 7. Expansion of cathode in electrolyte with different contents of KF after electrolyzing.

Expansion of different cathode materials

For carbon blocks, submitted to high temperature the first expansion step is thermal expansion, which is related to the carbon block material. The thermal expansion increases until the temperature stabilizes. A rapoport Na-expansion tester was used for testing expansion rate of cathodes with different materials being heated at a rate of 15℃/min to 850℃.

The curves of expansion rate of the cathode vs. heating-up time are shown in Figure 8. The expansion of the cathode increases with heating-up time, but becomes invariable at last. Table 2 shows the maximum expansion rate of different type of cathode.

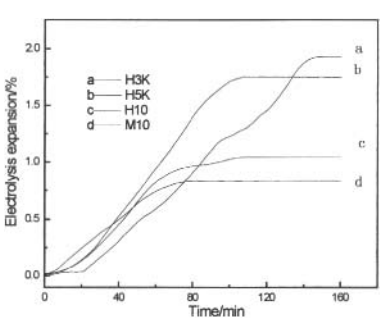


Figure 8. Expansion curves of cathode during heating-up process.

Figure.9 shows the expansion rate of cathode vs. electrolysis time. The curve has a parabolic shape with the maximum expansion rate shown in Table 1. The expansion rate of cathode decreases when the content of graphite in cathode increases. The minimum expansion rate of full-graphitization was shown to be 0.32%.

Table 1 Expansion rate of cathode

No.	Expansion rate (%)	
	Heating-up	electrolysis
30% graphitic (H3K)	4.7	1.56
50% graphitic (H5K)	3.0	1.23
full-graphitic (H10)	2.4	0.74
full- graphitization (M10)	2.1	0.32

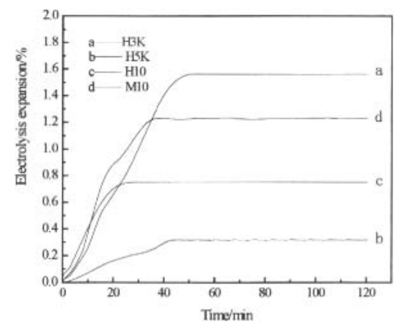


Figure 9. Curves of expansion of cathode during electrolysis.

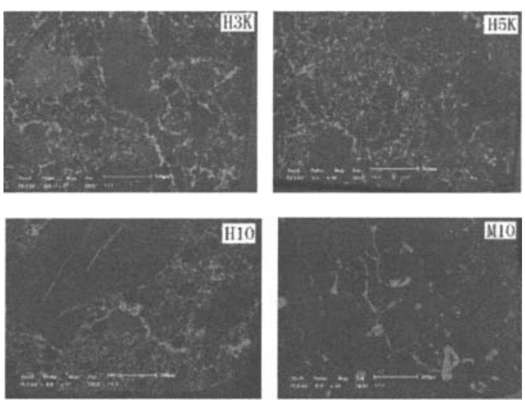


Figure 10. Appearance of cathode after electrolysis.

Figure 10 shows stereoscan photographs of different cathode materials after electrolysis. The results show that white areas (meaning shape of penetration of the electrolyte) decreased with content of graphite increasing due to less penetration of the electrolyte into the cathode. Fully-graphitic and fully-graphitized cathodes have excellent anti-penetration performance, but they are soft and expensive. In spite of higher thermal and electrolysis expansion rate than the graphitized blocks, 30% graphitic (H3K) blocks should be widely used by the enterprise.

Conclusions

K and Na can penetrate into the cathode and form graphite intercalation compounds during aluminum electrolysis process. The expansion ability of cathode material with K is 10 times greater than with Na and can even destroy the cathode block.

The expansion rate of the cathode increases with the content of KF increasing in a $KF-Na_3AlF_6-Al_2O_3$ electrolyte system. The expansion rate of cathode was 0.47% with 0% KF content and 0.82% with 7% KF content.

The expansion rate of the cathode decreases, due to the lower penetration capacity of Na and electrolyte when the graphite content of the cathode increases. The expansion rate was 1.56% with 30% graphite content in the cathode and with 120 min of electrolysis. The expansion rate was only 0.32% with a fully-graphitized cathode.

Acknowledgement

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References

1. Yang J H, et al., "Aluminum Electrolysis Tests with Inert Anodes in $KF-AlF_3$-based Electrolytes",Light Metals, 2006, 421–424.
2. Yuril Z et al., "Interaction of Heat Resistance Concrete with Low Melting Electrolyte $KF–AlF_3$ (CR=1.3)", Light Metals, 2007: 369–372.
3. Wang Y. "An analysis and study of potassium fluoride and lithium fluoride in aluminum electrolyte", Light Metal, 1993 (3):30-33.
4. Kan H M et al., "Effect of NaCl and LiF on liquidus temperature of molten cryolite based aluminum electrolyte", Metallurgical Analysis, 2007, 27(3): 13–17.
5. Zhang C S. "The effects of MgF_2, CaF_2 and LiF on Electrolyte chemical and physical properties and microstructure", Light Metal, 1997, (10): 34–37.
6. Galasiu I, Galasiu R, Thonstad J. "Inert Anodes Foraluminium Electrolysis", Düsseldorf: Aluminium-Verlag, 2007. 23–24.
7. Li J, Fang Z, Lai Y Q, et al.,. "Electrolysis Expansion Performance of Semigraphitic Cathode in $[K_3AlF_6/Na_3AlF_6]$–AlF_3–Al_2O_3 Bath system",Journal of Central South University of Echnology, 2009, 16(3): 422–428.
8.Chen F Q. "The effects of KF and LiF contents on Pre-baked production slot", Journal of Materials and Metallurgy, 2010, 6(9): 148–149.
9. Feng N X. "Aluminium electrolysis", Beijing: Chemical Industry Press, 2006: 98-140.
10. Qiu Z X, et al., "Aluminum electrolysis interface and interface reaction in the phenomenon", Shengyang: House of northeast institute, 1986, 170-177.
11. Ge J Y, et al., "Recent progress of graphite-intercalation-compounds superconductors", Chinese journal of low temperature physics, 2008, 30(1): 1–7.
12. Zhou M S, et al., "Properties and preparation of an $HClO_4$ - CrO_3 -Graphite intercalation compound", New carbon materials, 2010, 25(5): 389–393.