Light Metals 2015
Edited by: Margaret Hyland
TMS (The Minerals, Metals & Materials Society), 2015

The Resistibility of Semi-Graphitic Cathode to Alkali Metal (K and Na) Penetration

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Keywords: Aluminum Electrolysis, Electrolysis Expansion, Low Temperature Electrolyte, Potassium Cryolite, Empirical Formula, Ternary Isotherm Diagram.

Abstract

The electrolysis expansion of semi-graphitic cathode blocks was studied in (Na, K) cryolite-alumina melts. A self-made modified Rapoport apparatus was used to study the effects of *CR* (cryolite ratio) and *KR* (potassium cryolite content divided by the total amount of potassium cryolite and sodium cryolite) on the expansion. The empirical formula linking *CR*, *KR* and expansion was obtained from the experiment results. When *CR* is in the range between 1.4 and 3.0, *KR* 0.1 and 0.5, the formula can be used to reveal the relationship between electrolysis expansion of semi-graphitic cathode and melts composition. On this basis, the ternary isotherm diagram refer to electrolysis expansion is also drawn. From this diagram, the electrolysis expansion of semi-graphitic cathode in low temperature electrolyte containing potassium can be directly obtained, which corresponds to the different electrolyte compositions; conversely, the electrolysis expansion of semi-graphitic cathode can be designed as expected through selecting the appropriate *CR* and *KR* according to the ternary isotherm diagram. This has some help on choosing the components of low temperature electrolyte containing potassium.

Introduction

Because of the application of traditional Hall-Héroult electrolysis process, the current aluminum electrolysis industry still has several deficiencies such as high energy consumption and large emissions of greenhouse gases etc. In this case, energy-saving and emission-reduction become the very important considerations which must be studied unremittingly. Low temperature electrolysis can effectively reduce energy consumption of aluminum electrolysis process, improve current efficiency, increase purity of primary aluminum, and prolong lifespan of the cell. So it has become one of the most active research topics in current international aluminum sphere [1-4]. Researches show that [5-6], in a certain temperature range, if the electrolysis temperature decrease by 10℃, the current efficiency will be increased by 1~2% with the remarkable energy savings. However, the low electrolysis temperature is not propitious to the dissolution of alumina in the electrolyte and can lead to the formation of lots of precipitation in the bottom of the cell. At this circumstance, electrolysis process does not work normally. As for low temperature aluminum electrolysis, selecting suitable low temperature electrolyte is key to realize energy saving. Potassium cryolite-alumina, as a typical low temperature electrolyte system [7-10], has excellent ability to dissolve alumina at relatively low temperature and has good operation stability in the electrolysis process. However, it can be seen that potassium has strong penetration ability on carbon materials, which is about decuple of sodium [11, 12]. So, it can make cathodes severe dilapidated and shorten the lifespan of the cell markedly. As the key equipment, the service life of electrolytic cells not only affects the output and production costs of primary aluminum, but also concern the environmental pollution and other issues caused by waste cathode lining [13, 14]. This implies that pure potassium cryolite can not be used as electrolyte to substitute for sodium cryorite wholly. Considering the two factors of cathode life and alumina solubility of electrolyte, composite electrolyte being composed of potassium and sodium cryolite will become the more potential new low temperature electrolyte system. Therefore, it is extraordinarily necessary to study electrolysis expansion performance of cathode in the composite electrolyte being composed of potassium and sodium cryolite.

In order to research the K/Na penetration characteristics of this composite electrolyte composed of potassium cryolite and sodium cryolite, semi-graphitic cathode was employed as the research object, which is widely used in the aluminum electrolysis plant of china. The self-made modified Rapoport apparatus was introduced to systematically study the effects of *CR* and *KR* on the performance of cathode electrolysis expansion in low temperature molten electrolyte containing potassium. Furthermore, through mathematical calculations, the empirical formula was acquired from the experimental results which describe the influence of *CR* and *KR* on electrolysis expansion of semi-graphitic cathode. Next, the ternary isotherm diagram refer to electrolysis expansion is also drawn, which can help to choose the component of low temperature electrolyte more directly.

Experimental

<u>Cathode specimens</u>

Semi-graphitic cathode widely used in electrolytic aluminum industry in china was selected as cathode specimen, the quality of which accords with criterion YS/T287-2005. the cathode was machined into the cylinder of 20×60mm (diameter×length), and a circle hole with diameter 5mm in one end surface was drilled in order to connect steel rod with specimen.

<u>Test of electrolysis expansion</u>

A self-made modified Rapoport apparatus (as shown in Fig.1) was used to test the linear expansion displacement of specimen. 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 25mm. The specimen (10) and the graphite crucible (11) was separated by a corundum plate (13). The graphite crucible was used as anode and the specimen was used as cathode. The current flows into the cathode through the side wall of the specimen and the current density can be figured out through the side wall area of specimen which was immersed in the molten electrolyte. The electrolysis expansion of cathode was figured out through Eq.1 [15, 16].

$$\rho = \Delta L / L \qquad (1)$$

where ρ is the electrolysis expansion of cathode, ΔL is the linear displacement of cathode expansion, L is the initial length of specimen.

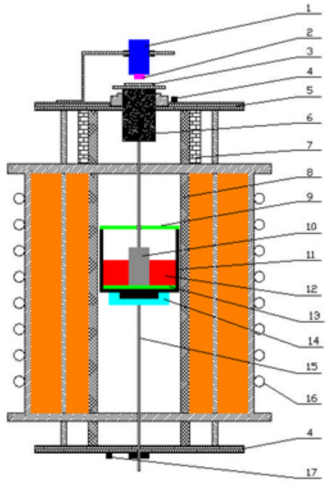


Fig.1 Testing apparatus for electrolysis expansion

1—Spiral rod; 2—Transducers; 3—Stainless steel strip; 4—Gas outlet; 5—Ring flange; 6—Graphite piston; 7—Insulation casing; 8—Corundum furnace tube; 9—Corundum lid; 10— Test specimen (cathode); 11—Graphite crucible; 12—Cryolite melt; 13—Corundum plate; 14—Graphite base; 15—Steel rod; 16—Cooling pipe; 17—Gas inlet

Experiment conditions

According to the difference of *CR*, the experiments could be grouped into eight teams. In each team, *CR* was constant but *KR* was 0.1, 0.2, 0.3, 0.4, 0.5 respectively, as shown in Table 1. The chemical reagents used in the experiments were: K_3AlF_6 (analytically pure), Na_3AlF_6 (analytically pure), Al_2O_3 (analytically pure) and AlF_3 (analytically pure). The concentration of alumina in the electrolyte was saturated in every experiment. The current density (ρ_{CD}) was 0.8A/cm^2 and the superheat (t_S) was 50℃. The specimens were subjected to electrolysis for 1.5 hours. Testing temperature was determined by the liquidus temperature (t_L) and t_S of each electrolyte. The whole experimental process was taken in the high-purity argon atmosphere.

Table 1 *CR*, *KR* and t_L of electrolyte in each experiment

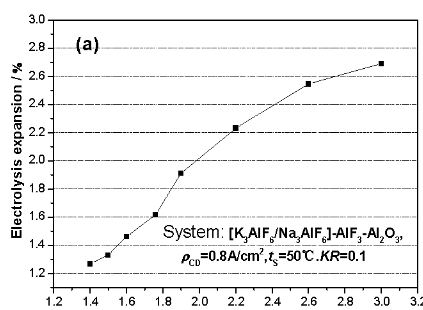
Serial number	A_1	A_2	A_3	A_4	A_5	B_1	B_2	B_3	B_4	B_5	C_1	C_2	C_3	C_4	C_5
CR			1.4					1.5					1.6		
KR	0.1	0.2	0.3	0.4	0.5	0.1	0.2	0.3	0.4	0.5	0.1	0.2	0.3	0.4	0.5
t_L/℃	805	808	803	727	673	821	827	818	751	723	895	869	873	805	815
Serial number	D_1	D_2	D_3	D_4	D_5	E_1	E_2	E_3	E_4	E_5	F_1	F_2	F_3	F_4	F_5
CR			1.76					1.9					2.2		
KR	0.1	0.2	0.3	0.4	0.5	0.1	0.2	0.3	0.4	0.5	0.1	0.2	0.3	0.4	0.5
t_L/℃	900	893	890	840	852	938	931	933	903	892	960	950	946	924	915
Serial number	G_1	G_2	G_3	G_4	G_5	H_1	H_2	H_3	H_4	H_5	/	/	/	/	/
CR			2.6					3.0					/		
KR	0.1	0.2	0.3	0.4	0.5	0.1	0.2	0.3	0.4	0.5	/	/	/	/	/
t_L/℃	975	955	942	927	928	980	960	941	940	939	/	/	/	/	/

Results and discussion

The influence of *CR* on the electrolysis expansion of semi-graphitic cathode

Fig.2 shows the curves of electrolysis expansion of specimens as a function of *CR* in low temperature electrolyte containing potassium under different *KR*, where abscissa is *CR* and ordinate is the linear electrolysis expansion(ρ/%) of specimens. When *CR*=1.4 and *KR*=0.1, the electrolysis expansion of cathode is minimum, which is 1.27%; when *CR*=3 and *KR*=0.5, the electrolysis expansion of cathode is maximum, which is 9.68%. Meanwhile, with the increase of *CR*, the electrolysis expansion of cathodes exhibits a tendency to increase. Under different *KR*(*KR* equals 0.1, 0.2, 0.3, 0.4, 0.5 respectively), when *CR* increase from 1.4 to 3.0, the electrolysis expansion of cathode thereupon increase from 1.27%, 1.52%, 1.78%, 1.34% and 1.47% to 2.69%, 3.44%, 4.77%, 6.11% and 9.68% respectively.

Besides, under different *KR*, the increase amplitude of electrolysis expansion is different. When *KR*=0.5, the influence of *CR* on the increase amplitude of electrolysis expansion is greatest, when the growth of *CR* is 0.1 averagely, the electrolysis expansion of semi-graphitic cathode will increase by 0.51%. But, when *KR*=0.1, the influence of *CR* on the increase amplitude of electrolysis expansion is least, and when the growth of *CR* is 0.1 averagely, the electrolysis expansion of semi-graphitic cathode will only increase by 0.09%.



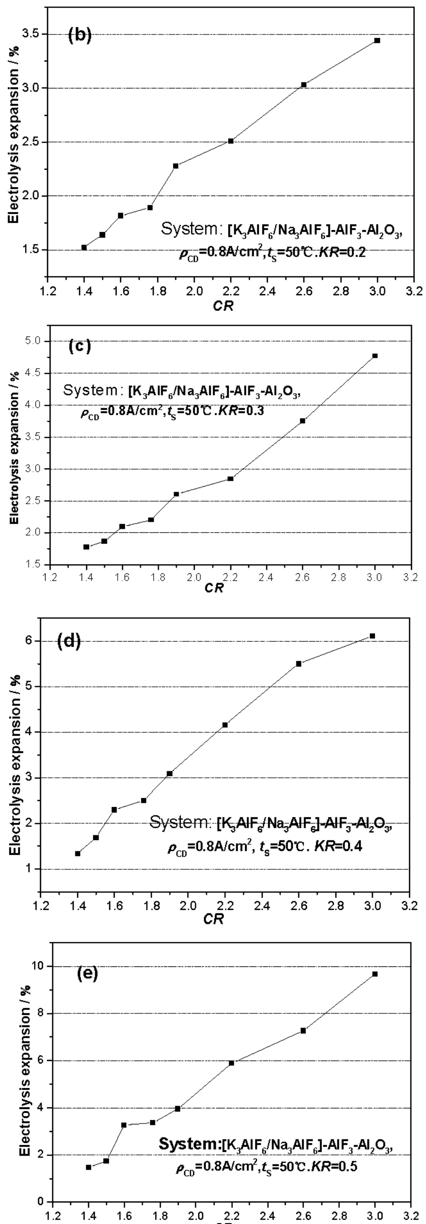


Fig.2 Effect of *CR* on the electrolysis expansion of semi-graphitic cathode under different *KR*: (a) *KR*=0.1; (b) *KR*=0.2; (c) *KR*=0.3; (d) *KR*=0.4; (e) *KR*=0.5

The process of aluminum electrolysis needs high temperature which may lead to the replacement reaction between liquid aluminum and NaF or KF in the molten bath, and also lead to the precipitation of K and Na. Meanwhile, in some condition, Na^+ and K^+ in molten bath can directly discharge on the surface of cathode, precipitating K and Na. Evolution reactions of sodium and potassium in molten bath are shown as Eq.2 and Eq.3 [16]：

$$Na^+/K^+ + e^- = Na/K(dissolved) \quad (2)$$

Or

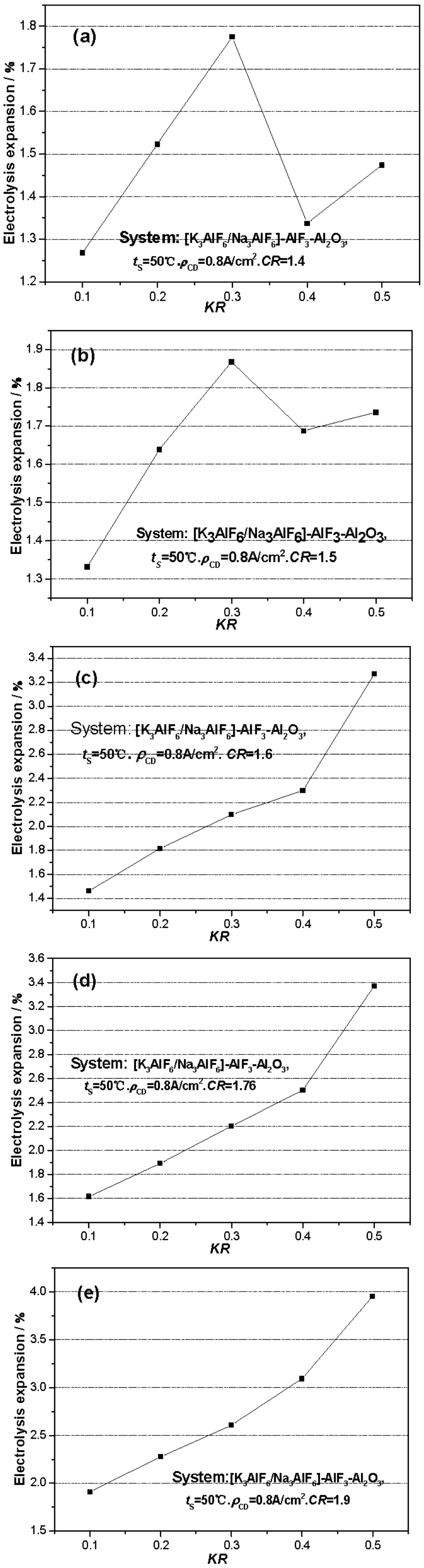
$$Al(l) + 3NaF/KF(l) = 3Na/K(dissolved) + AlF_3(l) \quad (3)$$

The precipitated sodium and potassium will penetrate into the inner part of cathode through pores and carbon lattice, and react with the carbon, forming the Graphite Intercalation Compounds (GICs) and resulting in the increase of interlayer spacing of graphite. In macroscopic view, the expansion and failure of cathode can be observed. Therefore, the amount of the precipitated sodium and potassium will directly influence the concentration of potassium and sodium on the cathode surface, and then influence the diffusion kinetic parameters of potassium and sodium, finally making a great impact on the performance of cathode electrolysis expansion. With the increasing *CR*, the evolution potential difference among potassium, sodium and aluminum decreases[17], and directly this results in the increase of potassium and sodium's precipitation amount, thereby aggravating the penetration of potassium and sodium to cathode and impelling the generation of GICs, finally causing the increase of cathode electrolysis expansion. Meanwhile, *CR* also influences the balance of chemical reactions (3). As *CR* goes up, the content of K^+ and Na^+ in the electrolyte increases, and chemical reactions (3) will move to the right side, which will also cause the increasing amount of precipitated potassium and sodium, consequently causing the increase of cathode electrolysis expansion.

<u>The influence of *KR* on the electrolysis expansion of semi-graphitic cathode</u>

Fig.3 shows the curves of electrolysis expansion of specimens as a function of *KR* in low temperature electrolyte containing K under different *CR*, where abscissa is *KR* and ordinate is the linear electrolysis expansion(ρ/%) of specimens. It can be seen that the influence of *KR* on the electrolysis expansion is different with various *CR*. When *CR*=1.6, 1.76, 1.9, 2.2, 2.6 and 3.0, with the increase of *KR*, the electrolysis expansion of semi-graphitic cathode increase gradually and when each average growth of *KR* is 0.1, the electrolysis expansion of cathode will increase by 0.45%, 0.44%, 0.51%, 0.92%, 1.18% and 1.75% respectively. The more the *CR*, the greater effect the *KR* has.

When *CR* maintains a certain value, the increase of *KR* can be considered that the equivalent potassium cryolite is substitute for sodium cryolite. Atomic radius of potassium is 227.2pm, while that of sodium is 190pm. The former preponderates over the latter. Therefore, when the same amount of potassium penetrates into carbon cathode and generates GICs, the electrolysis expansion it causes is comparatively larger than that caused by sodium. That is to say, so long as the *CR* keeps constant, the increase of *KR* will cause larger expansion of cathode. Therefore, the cathode electrolysis expansion gradually increases with the increasing *KR*. But it also can be seen from Fig.3 that, potassium does not exhibit decuples penetration ability to sodium, which is different from that mentioned in literatures [11, 12]. The reason is that when electrolysis is conducted under correspondingly lower temperature, The evolution potential difference among potassium, sodium and aluminum increase, and the precipitation amount of potassium and sodium reduces, so does the penetration ability[17]. Further more, the current density used in the experiment is $0.8A/m^2$. At this circumstance, the wettability of liquid aluminum to carbon cathode can be improved. During the process of electrolysis, the surface of cathode may be covered by a flat of aluminum film, thereby preventing the penetration of potassium and sodium in a certain extend[18, 19].



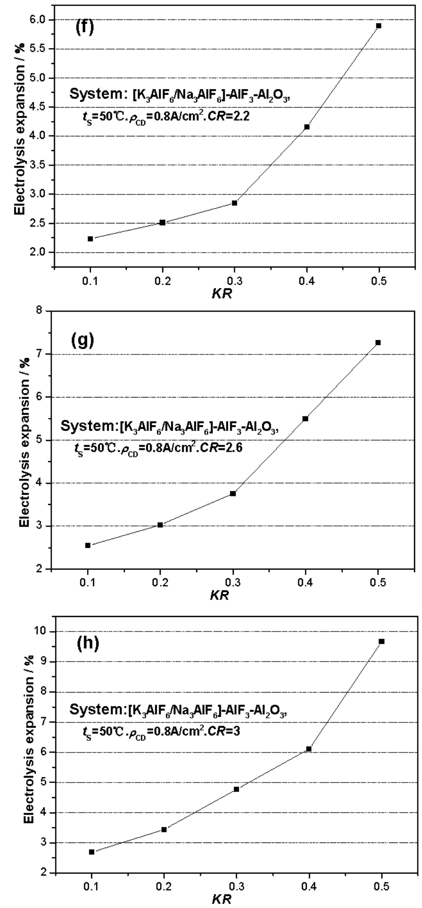


Fig.3 Effect of *KR* on the electrolysis expansion of semi-graphitic cathode under different *CR*: (a) *CR*=1.4; (b) *CR*=1.5; (c) *CR*=1.6; (d) *CR*=1.76; (e) *CR*=1.9; (f) *CR*=2.2; (g) *CR*=2.6; (h) *CR*=3

When *CR*=1.4 and 1.5, the electrolysis expansion of the cathode doesn't increase with increasing *KR*， but present a phenomenon, firstly increment, then decrement and next increment again. That is to say, when *KR* increase from 0.1 to 0.3, the electrolysis expansion of cathode exhibit a tendency to increase; while, when *KR* continue to increase to 0.4, the electrolysis expansion of cathode decrease drastically; subsequently, when *KR* increase to 0.5, the electrolysis expansion of cathode increase again. The reason for this phenomenon is as follows: the boiling point of K is 757℃ and the boiling point of Na is 881℃. When *KR* increase to 0.4, the actual electrolysis temperature is between the boiling point of sodium and potassium, while, when *KR* increases to 0.5, the actual electrolysis temperature is below the boiling point of sodium and potassium. Electrolysis is carried out at such a low temperature, so, the vapor pressure of K and Na is also low relatively, resulting in the reduction of the penetration ability of K and Na deservedly. Besides, the lower temperature will affect evolution potential difference among potassium, sodium and aluminum. With the decrease of electrolysis temperature, the evolution potential difference among potassium, sodium and aluminum will increase, making K and Na harder to precipitate, resulting in the poor destructive power of K and Na to cathode. Therefore, affected by the electrolysis temperature, when *KR* increase to 0.4 and 0.5, the electrolysis expansion of cathode doesn't increase, but decrease, which indicates that, under this condition, the influence of temperature on the electrolysis expansion is greater than that of *KR*.

The empirical formula and the ternary isotherm diagram refer to electrolysis expansion of semi-graphitic cathode

(1) The empirical formula

The multivariate nonlinear regression is used to analyze the results shown in Fig.2 and Fig.3, and the empirical formula is acquired, as shown in Eq.4:

$$\rho = -52.18 + 53.89CR^{2\times10^{-2}} - 11.02KR^{1.1} - 6.38CR^{1.38}KR + 15.27CR^{1.28}KR^{1.27} \quad (4)$$

Where ρ denotes electrolysis expansion of semi-graphitic cathode(%). The implication of *CR* and *KR* is interpreted in the abstract. The correlation coefficient of this formula is 0.987. The experimental parameters (*CR* and *KR*) are substituted into the empirical formula, and the calculation results and the experimental data are shown in Table 2.

It can be seen from Table 2 that, the calculation results are in good agreement with the experimental values. When *CR*=3.0, *KR*=0.5, the absolute error(| C_d-E_d |) between the calculation result and the experimental datum is maximum, which is 0.19, and the relative error (| C_d-E_d | /E_d×100%) is 1.96%. When *CR*=2.2, *KR*=0.4, the absolute error between the calculation result and the experimental datum is minimum, which is 0.01, and the relative error is only 0.24%. The average of all deviations between the calculation results and the experimental values is 0.008%. It can be seen that, the fitting of experimental data through multivariate nonlinear regression is successful, and within certain experimental condition, Eq.4 can be used to describe and forecast the experimental results.

(2) The ternary isotherm diagram

Eq.4 is used to get a series of calculated results, and through them, the ternary isotherm diagram of semi-graphitic cathode in $[K_3AlF_6/Na_3AlF_6]$-AlF_3-Al_2O_3 melts refer to certain composition of electrolyte and electrolytic parameters is drawn(as shown in Fig.4). Within a certain range, If electrolyte composition and electrolytic parameters are known, through the ternary isotherm diagram, the corresponding electrolysis expansion can be read out directly. Conversely, according to the known electrolysis expansion, also the corresponding electrolyte composition and electrolytic parameters can be acquired from the diagram. This has some significance for the promotion of low temperature electrolyte containing potassium to apply in the industry.

The influence of *CR* and *KR* on the electrolysis expansion of semi-graphitic cathode can be seen obviously from Fig.4. When *KR* remains unchanged, with the increase of *CR*, the electrolysis expansion of cathode exhibit a tendency to increase, and under different *KR*, *CR* indicates little difference on the growth slope of electrolysis expansion. But the influence of *KR* on the growth slope of electrolysis expansion is different with various *CR*. When *CR* is less than 1.6, with the increase of *KR*, the electrolysis expansion of cathode present a tendency, firstly increment, then decrement and next increment again. While, when *CR* is between 1.6 and 3.0, with the increase of *KR*, the electrolysis expansion of cathode exhibits a tendency to increase.

Table 2 Experimental data and calculation results refer to electrolysis expansion of semi-graphitic cathode in $[K_3AlF_6/Na_3AlF_6]$-AlF_3-Al_2O_3 molten electrolyte

KR		*CR*							
		1.4	1.5	1.6	1.76	1.9	2.2	2.6	3.0
0.1	E_d/%	1.27	1.33	1.46	1.62	1.91	2.23	2.55	2.69
	C_d/%	1.29	1.35	1.50	1.66	1.88	2.20	2.49	2.61
	E_r	0.02	0.02	0.04	0.04	0.03	0.03	0.06	0.08
0.2	E_d/%	1.52	1.64	1.82	1.89	2.28	2.51	3.03	3.44
	C_d/%	1.50	1.61	1.78	1.86	2.24	2.46	3.05	3.50
	E_r	0.02	0.03	0.04	0.03	0.04	0.05	0.02	0.06
0.3	E_d/%	1.78	1.87	2.10	2.20	2.61	2.85	3.75	4.77
	C_d/%	1.74	1.84	2.05	2.14	2.58	2.90	3.83	4.87
	E_r	0.04	0.03	0.05	0.06	0.03	0.05	0.08	0.10
0.4	E_d/%	1.34	1.69	2.30	2.50	3.09	4.16	5.50	6.11
	C_d/%	1.36	1.73	2.26	2.56	3.14	4.15	5.58	6.28
	E_r	0.02	0.04	0.04	0.06	0.05	0.01	0.08	0.17
0.5	E_d/%	1.47	1.74	3.27	3.37	3.95	5.90	7.26	9.68
	C_d/%	1.50	1.77	3.21	3.31	3.92	5.79	7.14	9.49
	E_r	0.03	0.03	0.06	0.06	0.03	0.11	0.12	0.19

Notes: E_d denotes experimental data; C_d denotes calculation results; E_r denotes absolute error(| C_d- E_d |).

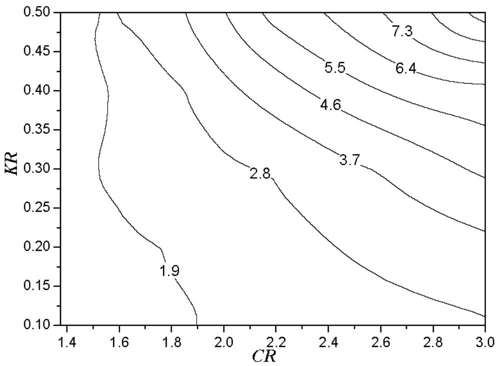


Fig.4 The ternary isotherm diagram of semi-graphitic cathode in $[K_3AlF_6/Na_3AlF_6]$-AlF_3-Al_2O_3 molten electrolyte

Conclusion

Semi-graphitic cathode used in aluminum electrolysis was employed as the research object and the effect of *CR* and *KR* on its electrolysis expansion was studied in low temperature molten electrolytes containing potassium. Based on the experimental result, through mathematical calculations, the empirical formula was acquired, which describes the relationship among *CR*, *KR* and electrolysis expansion of semi-graphitic cathode in low temperature molten electrolyte (as shown in Eq.4). The correlation coefficient of this formula is 0.987, and the results are in good agreement with the experimental data. When *CR*=1.4～3.0 and *KR*=0.1～0.5, Eq.4 can be used to describe and forecast the experimental results. On this basis, according to Eq.4, the ternary isotherm diagram refer to electrolysis expansion is drawn. From this diagram, the electrolysis expansion of semi-graphitic cathode in low temperature electrolyte containing potassium with different composition can be directly acquired; conversely, the electrolysis expansion of semi-graphitic cathode can be designed as expected through selecting the appropriate *CR* and *KR* according to the ternary isotherm diagram. This has some help on choosing the component of low temperature electrolyte containing potassium.

Acknowledgement

Project supported by the National Natural Science Foundation of China(51304152), Natural Science Basic Research Plan in Shaanxi Province of China(2013JQ7016) and Shaanxi Provincial Education Department of China(2013JK0904).

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