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Trans. Nonferrous Met. Soc. China 23(2013) 1847−1853

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn

Alkali metals (K and Na) penetration and its effects on expansion of TiB_2−C composite cathode during aluminum electrolysis

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Received 2 December 2012; accepted 30 January 2013

Abstract: The behavior of alkali metals (K and Na) penetration in TiB_2−C composite cathode and the induced electrolysis expansion under various conditions in KF melt, NaF melt and their composite melts were investigated. The most important influence factor on the electrolysis expansion properties of the cathode was revealed, and the elements micro-analysis of cathode profiles was performed. The results indicate that, under the condition of non-polarization and Al free, no electrolysis expansion occurs. The alkali metal produced by direct discharge reduction is the most important factor causing the electrolysis expansion, and the maximal expansion is 20.40%. Electrolysis expansion in electrolyte with K is higher than that in electrolyte without K, and the maximal excess magnitude is 35.13%. Compared with pure potassium salt, composite electrolyte has less destructive effects on the cathode. In addition, no matter under the condition of polarization or non-polarization, electrolysis expansion in electrolyte with Al is always greater than that in electrolyte without Al, and the increase amplitude of electrolysis expansion in non-polarization conditions with Al is significantly greater than that in polarization conditions with Al.

Key words: aluminum electrolysis; alkali metals; K; Na; TiB_2−C composite cathode; electrolysis expansion

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1 Introduction

Aluminum electrolysis industry is one of the pillar industries for national economic development. It accounts for about 80% of entire power consumption of the non-ferrous metals industry in China, and is the most "energy saving" potential sub-sectors in the industry [1,2]. During these years a great deal of research works have been done on energy saving of aluminum electrolysis. Low-temperature electrolytic process which can reduce heat loss, heat erosion, lower power consumption and secondary reaction has become one of the most active research topics in aluminum industry [3,4]. However, there are many problems for low temperature electrolysis, such as for low alumina solubility/dissolution rate in melts, incrustation at the bottom of cell during electrolysis, which are detrimental to the normal operation of the electrolysis. Since $[K_3AlF_6/Na_3AlF_6]-AlF_3-Al_2O_3$ melt can maintain high Al_2O_3 solubility and good operational stability to ensure stable operation of low-temperature electrolytic process, it has become the focus of the low temperature aluminum electrolysis research [5−7]. Compared with Na in ordinary electrolyte system, K in the system has a lower ionic potential, which is easier to penetrate into the cathode's interior and form C_xK intercalation compounds. This behavior deteriorates the cathode during electrolytic process and accordingly injures the service life of aluminum reduction cells and normal industrial production significantly [8−10]. Based on semi-graphitic cathode, NAAS et al [11] investigated the influence of KF on electrolysis expansion properties of the cathode under the condition of CR(Cryolite ratio)=2.2 and Current density ρ=0.7A/cm^2 at 970 °C. It was reported that electrolysis expansion of semi-graphitic cathode was only 0.3%, when KF addition was lower than 5% (mole fraction), which had little effect on the electrolysis expansion properties of cathode; but when KF addition was 20%, the electrolysis expansion was twice that of 5% KF addition under the same test conditions. LI et al [12] also confirmed that the addition of potassium cryolite should not be more than 10% (mass fraction), otherwise it would cause large electrolysis

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Foundation item: Project (2009BAE85B02) supported by the National Key Technology Program of China; Project (QN1221) supported by the Science and Technology Funds of Xi'an University of Architecture and Technology, China

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DOI: 10.1016/S1003-6326(13)62669-2

expansion of semi-graphitic cathode. TiB_2-based cathodes with good wettability, which can resist strong corrosion from low temperature potassium electrolyte melts [13−15], were emerged as a promising cathode material used in aluminum electrolyte-inertia electrode system. FANG et al [16] studied the electrolysis expansion properties of TiB_2−C composite cathodes in the low temperature potassium electrolyte melts. Compared with the electrolysis expansion of semi-graphite cathode measured in the same electrolyte system and electrolytic process conditions, the electrolysis expansion of pitch, furan, phenolic aldehyde and epoxy based TiB_2−C composite cathode were smaller (9.0%−56.4%). ZHANG et al [17] also reported that the average annual erosion rates of pitch, furan, phenolic aldehyde and epoxy based TiB_2−C composite cathode were 7.29, 5.84, 2.31 and 2.63 mm/a, respectively, which was reduced significantly compared with that of semi-graphitic cathode(15 mm/a).

However, because of the complicated compositions and structure of $[K_3AlF_6/Na_3AlF_6]-AlF_3-Al_2O_3$ melt, it is difficult to distinguish the different influences of alkali metals K and Na on the electrolysis expansion properties of TiB_2−C composite cathode. There are only some primary reports that the penetration ability of potassium salts on carbon-based materials was about 10 times larger than that of sodium [10,11]. It would impede further optimization of the electrolyte composition as well as the design of the TiB_2−C composite cathode with high resistance to penetration. ADHOUM et al [18] investigated the electrochemical intercalation of alkali metal Na from NaF melt into graphite cathode at the temperature of 1025 °C, and found that part of alkali metal Na formed on the surface of the cathode during the electrolysis went into the graphite layer in the form of intercalation and become intercalation compounds, and the other part deposited in the pores of the cathode materials but then reached the position of intercalation by diffusion, also became intercalation compounds ultimately. At the temperature of 1163 K, LIU et al [19] studied the electrochemical intercalation of graphite cathode by alkali metal K in KF melt. They revealed that K just went into the graphite layer in the form of intercalation, and confirmed that C−K graphite intercalated compound would not only lead to the electrolysis expansion but also the erosion on the cathode which would produce peeling flakes on the surface of cathode. Further understanding the difference of the behavior of alkali metals (K and Na) penetration and clarifying the principal influencing factors of electrolysis expansion will help to the early industrialization of low temperature electrolyte melt containing K, and development of wettable TiB_2−C composite cathode with high resistance to penetration.

In this work, the effects of alkali metals K and Na penetration on the electrolysis expansion properties of pitch-based TiB_2−C composite cathode were investigated in 100% NaF, 100% KF and 50% NaF+50% KF melts under varius conditions. The most important effect on the expansion properties in cathode electrolysis was revealed, and the element micro-analysis of cathode cross section was performed.

2 Experimental

The formulae of TiB_2−C composite cathodes are shown in Table 1. The average particle size of TiB_2 powder was 12 μm, and that of the petroleum coke was 106−300 μm.

Table 1 Pitch-based formula of TiB_2−C composite cathode (mass fraction, %)

TiB_2 powder	Petroleum coke	Pitch
75	11	14

First, a certain proportion of TiB_2 powder and petroleum coke were mixed and kneaded in a three-dimensional motion kneader in order to mix with pitch binder in the pot. After being weighed, the materials were molded under the molding pressure of 150 MPa by a universal hydraulic press machine. The size of the obtained cathode was *d*20 mm×50 mm. Finally, the cathode samples were put into the alumina crucible via coke landfill, and sequentially heated according to the heating procedure shown in Fig. 1 in a box resistance furnace to obtain the TiB_2−C composite cathodes.

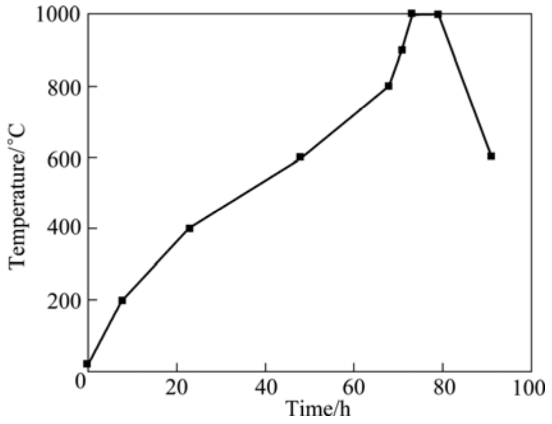

Fig. 1 Curve of heat-up of TiB_2−C composite green cathodes

The chemical reagents and materials used in the electrolysis tests were NaF, KF and aluminum block (99.99%). The specific electrolyte composition, electrolytic temperature and other test parameters are shown in Table 2.

Table 2 Composition of melts, electrolysis temperature and correlative test condition

Item No.	Electrolysis temperature/°C	Composition/%			Current density/(A·cm^{-2})
		NaF	KF	Al	
N_P	1013	100	0	0	0.8
N_N		100	0	0	0
N_{AP}	1013	100	0	20	0.8
N_{AN}		100	0	20	0
K_P	878	0	100	0	0.8
K_N		0	100	0	0
K_{AP}	878	0	100	20	0.8
K_{AN}		0	100	20	0
KN_P	800	50	50	0	0.8
KN_N		50	50	0	0
KN_{AP}	800	50	50	20	0.8
KN_{AN}		50	50	20	0

Rapoport apparatus used to test the linear expansion displacement of specimen and the cathode electrolysis expansion was figured out by

$$\rho=\Delta L/L \tag{1}$$

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

The cross sections of specimens after electrolysis were analyzed by a JEOL JSM−5600LV SEM in backscatter electron image (BEI) mode. NORAN VANTAGE4105 X-ray energy dispersive spectrometry (EDS) was used to analyze the element distribution in the cross sections of specimens.

3 Results and discussion

3.1 Influence of alkali metal K and Na on cathode properties

Figure 2 shows the expansion curves of cathode during electrolysis in pure fluoride system. Three obvious characteristics are as follows.

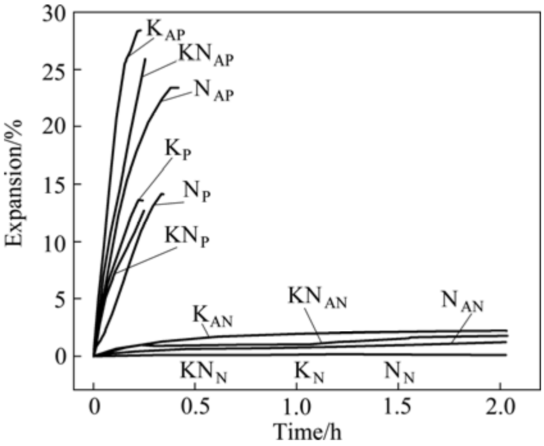

Fig. 2 Curves of cathodic electrolysis expansion obtained in fluoride system

Firstly, expansions of all the electrolyte melts under polarization are much larger than that under non-polarization. As a result of pure fluoride, the electrolysis expansion will be beyond the expansion measurement range after a very short test time. In order to facilitate the comparison, the electrolysis expansion data obtained after 10 min of electrolysis were used. Under polarization, after 10 min of electrolysis, the decreasing order of cathode electrolysis expansion is K_{AP}>KN_{AP}>N_{AP}>K_P>K_{NP}>N_P (28.40%, 23.27%, 18.43%, 13.56%, 11.65% and 10.41%, respectively). Under non-polarization, the electrolysis expansion is very small. 2 h later, cathode electrolysis expansion in the K_{AN}, KN_{AN} and N_{AN} melts are only 0.91%, 0.43% and 0.22%, respectively, and the electrolysis expansion in the KN_N, K_N, N_N melts can even be ignored. The main reason of this phenomenon is that alkali metal is produced on the cathode surface according to Eq. (2) under polarization when aluminum precipitates. The aluminum would not precipitate under non-polarization. Therefore, the electrolysis expansion of polarization is much larger than that of non-polarization, indicating that alkali metal generated by direct discharge reduction is the most important factor of the electrolysis expansion.

$$\mathrm{Na^+/K^+ + e^- = Na/K(dissolved)} \tag{2}$$

Secondly, in addition to KN_N, K_N and N_N electrolyte melts, whether under polarization or non-polarization, electrolysis expansion in electrolyte melt with potassium is greater than the expansion in melt without potassium, such as K_{AP}>N_{AP}, K_P>N_P, KN_{AP}>N_{AP} and KN_P>N_P, the former is higher than the latters by 35.13%, 23.21%, 20.82% and 10.61%, respectively. This is because of the following aspects: 1) Electrochemical equivalent of K and Na is different (1.46 g/(A·h) for K and 0.86 g/(A·h) for Na), and therefore the precipitation amount of K is greater than that of Na under the same current density. This leads to the fact that the impact of K on the cathode is more significant than that of Na. 2) Larger atomic radius of K (227.2 pm) than that of Na (190 pm) makes expansion which is caused by infiltration of K precipitation on the cathode surface greater than that of Na. It is the necessary condition that the impact of K is greater than that of Na on cathode. 3) C−Na intercalation compounds generated by the reaction between Na penetrated into cathode and carbon mostly are high-end (such as $C_{64}Na$, 8 bands), while C−K intercalation compounds generated by the reaction between K and carbon mostly are low-end (such as C_8K, 1 band). This results in the concentration of C−K intercalation compounds in carbonaceous component of the cathode higher than that of C−Na intercalation compounds, causing a greater expansion of the cathode and becoming the decisive factor for greater impact of K than Na on cathode. In addition, it can be seen that, $KN_{AP}<K_{AP}$, $KN_P<K_P$, $KN_{AN}<K_{AN}$, respectively fell 18.07%, 14.10% and 5.52%, indicating that the use of composite electrolyte can help reducing the destruction on the cathode from pure potassium melt.

Finally, under polarization and non-polarization conditions, cathode electrolysis expansion obtained in melts including Al is larger than that of free Al electrolyte melt, for example, $K_{AP}>K_P$, $N_{AP}>N_P$ and $KN_{AP}>KN_P$. Besides, K_{AN}, KN_{AN} and N_{AN} were also greater than KN_N, K_N, and N_N. This is mainly due to the occurrence of replacement reaction between Al and electrolyte melt according to Eq. (3).

$$\text{Al(l)+3NaF/KF(in electrolyte)=}\\ \text{3Na/K(g)+AlF}_3\text{(in electrolyte)} \qquad (3)$$

Equation (3) will occur when Al is added into the melts. Under this circumstance, besides alkali metal obtained through direct discharge reduction, additional alkali metals obtained through Eq. (3) are also generated no matter under polarization or non-polarization. Some of these additional alkali metals dissolve or evaporate, but the others penetrate into the cathode and impact the expansion of cathode. Thus, adding Al to the melt leads to larger expansion.

In addition, it can be seen that, for pure fluoride melt, electrolysis expansion caused by the addition of Al under non-polarization conditions is much larger than that under polarization conditions, for example, N_{AN} is 94.58% higher than N_N, while N_{AP} is only 43.49% higher than N_P. Likewise, K_{AN} is 90.99% higher than K_N, but K_{AP} is only 52.26% higher than the K_P. These results show that alkali metals produced by replacement reaction under non-polarization conditions have greater impact than that under polarization conditions. This is mainly because that there is no discharge reaction of alkali metal ion in non-polarization conditions. At this circumstance, the replacement reaction occurs sufficiently, finally exhibits greater impact on the cathode. While in polarization conditions, the discharge reaction of alkali metal ion plays dominant role and inhibits the replacement reaction. Based on the above analysis, it is confirmed that the alkali metal generated by direct discharge reduction is the most important factor of electrolysis expansion.

3.2 Element micro-analysis of cross-section of cathode

Figure 3 shows the element surface scan images of the cross-section of TiB_2−C composite cathode after electrolysis expansion test in polarization and non-polarization conditions. Fig. 3(a) indicates that Na does not penetrate into the carbon aggregates, which just congregates in the mixed area of binder and TiB_2 under non-polarization conditions without Al. No element can penetrate into TiB_2, and accordingly Na is essentially present in the binder phase. It can also be seen that element F is present in the binder phase, which indicates that Na in the binder phase is in ion form and penetrates together with the electrolyte. In non-polarization conditions, there is no evidence of the formation of Na, which is the prerequisite for electrolysis expansion. Figure 3(b) shows that Na infiltrates into both the binder and the carbon aggregates at polarization conditions without Al. Figure 3(c) shows that, under non-polarization conditions with Al, similar to Fig. 3(b), Na also infiltrates into both the binder and the carbon aggregates, but the content of Na in the aggregate carbon is less than Fig. 3(b), which confirms that alkali metal generated by direct discharge reduction is the most important factor of electrolysis expansion. At the same time, it is failed to detect the F in the aggregate carbon. This indicates that Na penetrates into the cathode in the form of alkali metal which confirms the replacement reaction between Al and electrolyte. Unlike Figs. 3(b) and (c), Fig. 3(d) displays that the permeability of Na is very intense, and the content of Na in any region of the cross section is almost the same. Neither the region of aggregate carbon nor the region of binder can be distinguished.

Alkali metals are generated by direct discharge reduction and replacement reaction under polarization conditions with Al. Compared with N_P and N_{AN} melts, large amount of alkali metals are generated. Therefore, it leads to the fact that the impact on the cathode is also large, which is in consistent with the results in Fig. 2.

Figure 4 shows the EDS analysis of different points in radial section of specimen KN_{AP} after electrolysis. Firstly, it can be seen from Fig. 4(b) that, as for petroleum coke, both K and Na penetrate into it in various degrees, but the penetration of F is not found. This indicates that K and Na penetrating into the petroleum coke are not ionic, but the elementary substance. Secondly, Fig. 4(c) shows that, as for coking carbon of binder, F, Al, K and Na all penetrate into cathode in various degrees, indicating that K and Na penetrate into the coking carbon in the form of electrolyte or elementary substance. From Fig. 4(d), it can be found that no element penetrate into TiB_2, revealing the good corrosion resistance of TiB_2. Table 3 shows the elements content of different zones in the

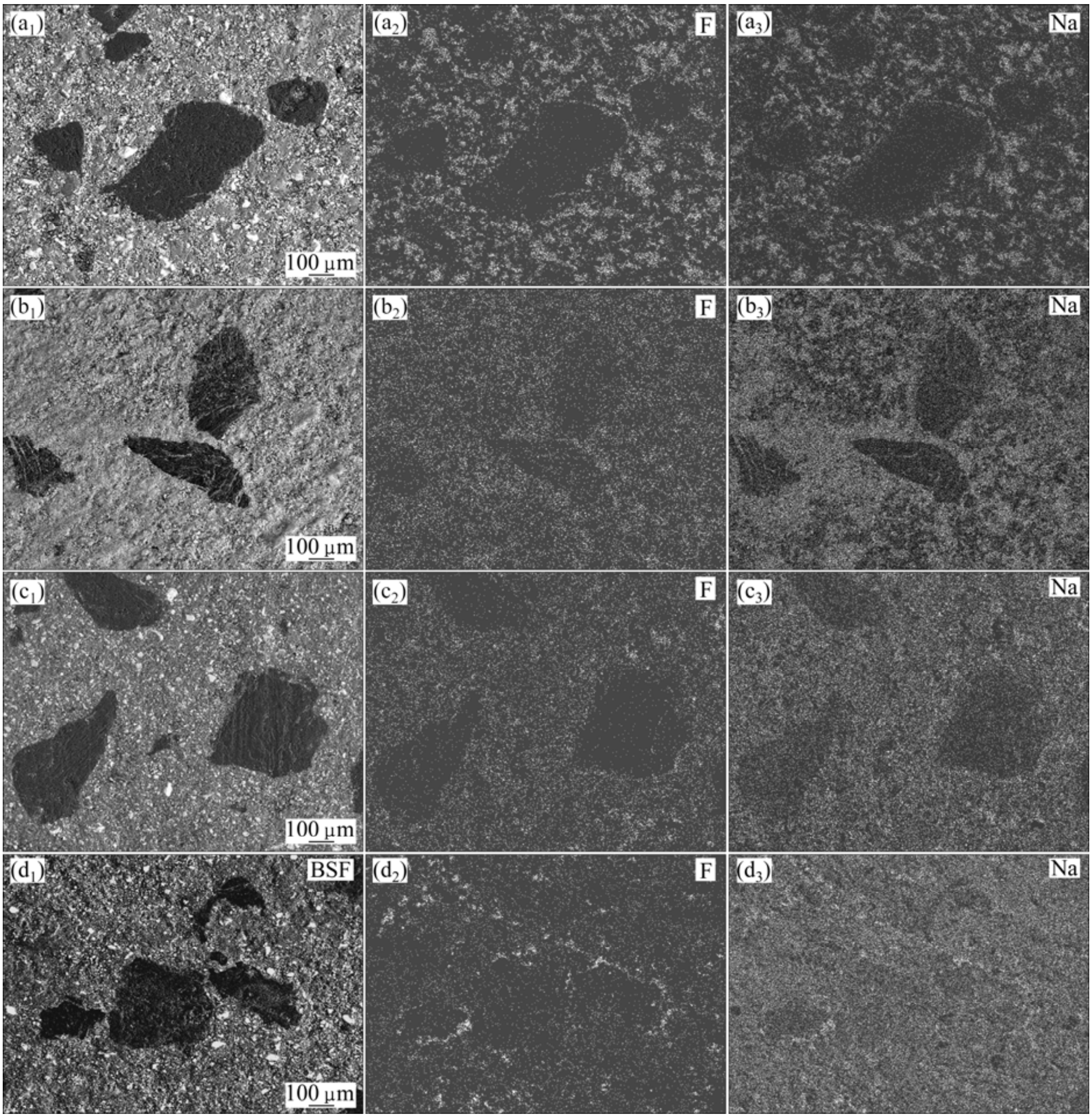

Fig. 3 Element micro-analysis of cross-section of cathode after electrolysis expansion test in different fluoride melts: (a_1, a_2, a_3) N_N; (b_1, b_2, b_3) N_P; (c_1, c_2, c_3) N_{AN}; (d_1, d_2, d_3) N_{AP}

cross section of specimen KN_{AP} after electrolysis. The content of K and Na in the petroleum is larger than that in the coking carbon of binders. This suggests that during the electrolysis process in low temperature electrolyte containing potassium, coking carbon of binders in the composite cathode is the easiest to be corroded, and the corrosion resistance of which determines the holistic performance of the cathode. Furthermore, the content of K is larger than that of Na in the same region, indicating that K has stronger penetrate ability than Na.

In the process of electrolysis, because of the cathode polarization effect, potassium and sodium are precipitated on the surface of cathode. Subsequently, they will penetrate into carbon cathode under the bonding action between the electron in orbit S of alkali metal and electron π in carbon, forming alkali-graphite intercalation compounds. These compounds show a typical structural character that is the order phenomenon: the intercalation complexes are arranged in the host body between the graphite layers with certain period.

As for sodium precipitated on the surface of cathode in the process of electrolysis, when it penetrates into the cathode, the obtained C−Na intercalation compounds generated by the reaction between Na and carbon are mostly high-end (such as $C_{64}Na$, 8 bands). But C−K intercalation compounds generated by the reaction between K and carbon are mostly low-end (such as C_8K, 1 band), which makes the concentration of C−K

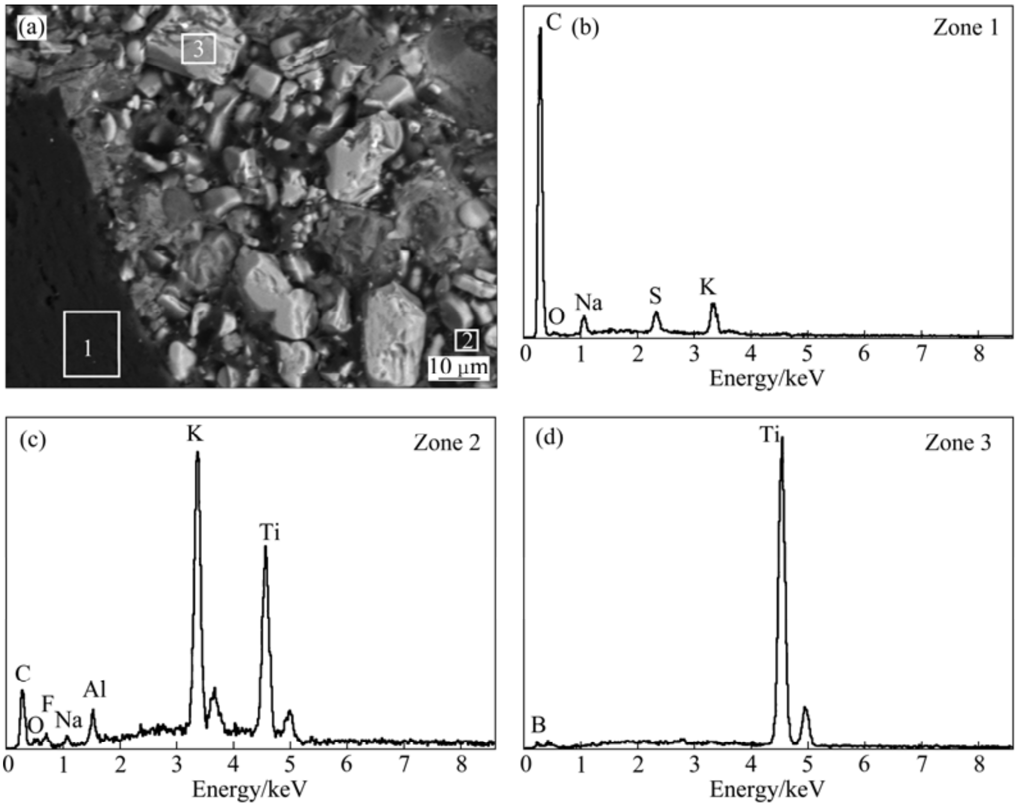

Fig. 4 XDS of radial section of specimen KN_{AP} after electrolysis: (a) SEM images; (b) Petroleum coke; (c) Coking carbon of binder; (d) TiB_2

Table 3 Elements content of different points in cross section of specimen KN_{AP} after electrolysis (mole fraction, %)

Element	Petroleum coke	Coking carbon	TiB_2
C	96.54	75.41	−
O	2.08	10.94	−
Na	0.11	1.69	−
S	0.14	−	−
K	1.13	3.30	−
F	−	6.72	−
Al	−	1.94	−
B	−	−	93.53
Ti	−	−	6.47

intercalation compounds in the cathode larger than that of C−Na intercalation compounds, leading to a greater destructive effects on the cathode, and becoming the decisive factor for more significant impact of K than Na on cathode [21,22]. Because cathode materials contain a certain amount of open porosity, electrocapillarity will exist in the process of electrolysis. At this circumstance, a mass of electrolyte would penetrate into the cathode, and fill the pores, making the interface between electrolyte and cathode increase. Consequently, the penetration of K, Na to the cathode is aggravated.

4 Conclusions

1) Electrolysis expansion obtained under the condition of polarization is much larger than that obtained under the condition of non-polarization and the maximal expansion is 20.40%. Direct discharge reduction is the most important factor causing the electrolysis expansion.

2) No matter under polarization or non-polarization, electrolysis expansion obtained in electrolyte melt containing potassium is greater than that in melt without potassium and the maximal excess magnitude is 35.13%. Composite electrolyte consisting of sodium cryolite and potassium cryolite can reduce the destruction to the cathode resulting from melts.

3) Under the conditions of co-existence of Al and electrolyte, Al will have effect on the electrolysis expansion of cathode, but its influence is far less than that of polarization and potassium cryolite. In addition, electrolysis expansion caused by addition of Al under non-polarization conditions is much larger than that under polarization conditions. Polarization inhibits the replacement reaction between Al and electrolyte.

4) After electrolysis, K and Na penetrate into the coking carbon of binders in the form of elementary

substance and ionic, while, in the carbon aggregates, K and Na only exist in the form of coking carbon of binders. In contrast, the penetration ability of K and Na to binder phase is stronger than that to carbon aggregates. Binder phase is the weak links in TiB_2−C composite cathode and strengthening the corrosion resistance of binder helps to promoting the overall performance of cathode.

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TiB_2−C 复合阴极中碱金属(K、Na)的渗透及其对阴极电解膨胀的影响

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摘 要：在不同电解条件下，研究纯 KF 熔体、纯 NaF 熔体及其复合电解质熔体中，碱金属(K、Na)在 TiB_2−C 复合阴极中的渗透迁移行为及其引起的阴极电解膨胀。揭示影响阴极电解膨胀性能的主要因素，同时对阴极剖面进行元素微区分析。结果表明：在非极化以及不含铝的电解质熔体中，阴极不会发生膨胀；直接放电所生成的碱金属是造成阴极膨胀的主要因素，引起的阴极最大电解膨胀率可达 20.40%；含钾电解质熔体中阴极的电解膨胀率远高于不含钾电解质熔体中阴极的电解膨胀率，最高超出 35.13%；与纯钾盐相比，复合电解质对阴极的破坏作用降低；此外，无论是在极化条件还是在非极化条件下，含铝电解质熔体中阴极的电解膨胀率均大于不含铝电解质熔体中阴极的电解膨胀率；同时，在非极化条件下电解质熔体中加入铝后比极化条件下电解质熔体中加入铝后所引起的阴极电解膨胀的增加更为明显。

关键词：铝电解；碱金属；钾；钠；TiB_2−C 复合阴极；电解膨胀

(Edited by Chao WANG)