

STUDIES ON THE RESISTANCE TO ALKALI METAL PENETRATION OF BINDERS FOR TiB₂-C COMPOSITE CATHODE MATERIALS

FANG Zhao¹, ZHANG Kai², LAI Yan-qing², LI Lin-bo¹, ZHU Jun¹

¹School of Metallurgical Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China

²School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China

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Abstract

Thermal gravimetric analysis (TGA) and X-ray diffraction (XRD) were used to analyze the pyrolysis of pitch, furan, phenolic aldehyde and epoxy binders. Their micro-structures after carbonization were also studied. The relationship between alkali metal penetration resistance of binders, their pyrolysis activation energy (E_a) and micro-structure after carbonization was investigated. The results show that for binders containing turbostratic graphite or a transitional structure between turbostratic graphite and graphite, the higher the degree of graphitization the better the penetration resistance of the binder. When the binder micro-structure is in a transitional stage from amorphous or other non-graphitic structures to turbostratic graphite, the penetration resistance of the binders deteriorates. For these microstructures, the higher the E_a , the better the penetration resistance. The E_a of pitch, furan, phenolic aldehyde and epoxy are 47.20 kJ/mol, 93.11 kJ/mol, 178.11 kJ/mol and 780.32 kJ/mol respectively.

Abstract

Owing to many advantages such as good wettability by molten aluminum, less use of TiB₂, excellent conductive properties and easy large-scale preparation, TiB₂-C composite cathodes have become key materials for promoting industrial applications of inert electrolysis systems [1-5]. Although TiB₂-C composite cathode materials offer a number of attractive properties, it has been widely reported that short service life is a problem which has not yet been fundamentally resolved [6]. Considering the composition of the material, we know that the main components of TiB₂-C composite cathodes after high temperature heat-treatment are TiB₂, carbon aggregates and coking carbon from the binder (binder coke). Whilst the resulting TiB₂ phase and carbon aggregates in the high temperature heat treated composite cathode material have excellent corrosion resistance and good stability in liquid aluminium, the binder coke phase is weaker and easily suffers from erosion.

At present, the main binder used in conventional cathode blocks for aluminium electrolysis is coal tar pitch [7]. Coal tar pitch coats the surface and penetrates into the pores of the coke and anthracite particles well, making the various ingredients conglomerate with each other and form a paste with good plasticity. This paste can be made into the expected shapes easily and the obtained green body will become rigid after cooling, allowing the shape to be maintained. During the baking process of the green body, the coal tar pitch will be pyrolyzed gradually and finally carbonized, making the aggregate particles bond together firmly. The carbonization rate of pitch is relatively high and the pitch coke generated in the carbonization process is graphitized easily. Therefore, coal tar pitch plays an important role in the production of cathode materials used for aluminium electrolysis. However, as is typical for viscoelastic materials, the mechanical

properties of pitch are affected by temperature greatly and exhibit stress relaxation and creep phenomena [8]. After carbonization, the structure of the pitch phase is turbostratic graphite [9]. This structure is vulnerable to the penetration and erosion of alkali metals such as K and Na, and therefore carbon materials using pure pitch as a binder cannot be used for a long periods of time. The reason is that, after carbonization, the microstructure of the pitch is layered, but it is a more chaotic layering rather than a well orientated layer. Under this circumstance, the penetration of K and Na will induce an increase of the d spacing of the carbon layers and lead to severe expansion of the cathode, which can ultimately result in cracking and thus short service life.

Reported research has proven that corrosion of conventional cathode materials used for aluminium electrolysis is often started in the binder phase. When the binder has been eroded, aggregate particles in the composite cathode can detach from the bulk [7, 10]. That is to say, during aluminium electrolysis, the failure of binder is an important reason that causes the particle detachment and wear, inducing the breakage and fracture of the cathode. Nowadays, aluminium reduction cells are developing toward super large-scale, high current pots. Under this background, the higher performance requirements for binders used in the cathode have been put forward. Therefore, changing the existing binder system and improving the corrosion resistance of binder phase is very necessary.

Under the condition of CR=1.6 (CR: cryolite ratio) and KR=0.3 (KR: Potassium Cryolite Ratio), Fang et al investigated the corrosion resistance of TiB₂-C composite cathode materials [11]. It was found that when the addition of binders are optimal, electrolysis expansion of the TiB₂-C composite cathode using furan, phenolic aldehyde and epoxy as binders are reduced by 15.44%, 20.81% and 38.26% respectively, when compared with a TiB₂-C composite cathode using pitch as the binder. Ibrahim et al's study confirmed that furan based TiB₂-C cathode coatings have a stronger alkali metal penetration resistance than pitch based TiB₂-C cathode coatings [12]. However, research aimed at industrial application have failed to involve the mechanism problem in regards to the resistance to alkali metal (K, Na) penetration of binders for TiB₂-C composite cathodes. This has bottlenecked the further optimization of binder performance. Therefore, pitch, furan, phenolic aldehyde and epoxy are employed as the research materials in this paper and the mechanism around their resistance to alkali metal (K, Na) penetration was investigated. This is helpful for optimizing the binder system used for wettable TiB₂-C composite cathode materials.

Experimental

Because TiB₂, petroleum coke and other carbonaceous aggregates are heat-treated in advance at high temperature, the structures of these components will no longer change. Only the binder in the green body will undergo a series of physical and

chemical changes during baking [13-15]. According to the different microstructures after heat treatment, the binders can be divided into two categories: one is the soft carbon material (pitch), while the other is the hard carbon material (furan, phenolic aldehyde, and epoxy) [9]. The most important factor which affects the electrolysis expansion and corrosion resistance of the cathode is the binder and this may be the combined effect of structure and chemistry. The structure of composite cathode is affected by the baking process of the green body, so TGA can be adopted to analyze the dynamics of the binders' heat-treatment process, in order to study the influence of binder type on the electrolysis expansion and corrosion resistance of the cathode material at the micro-scale.

X-ray diffraction is a common method used to characterize the structure of carbon materials used in aluminium electrolysis and related research. XRD is also adopted to characterize the level of calcining of raw materials for quality control [16]. In this investigation, in order to further study the difference in resistance to alkali metal penetration among various TiB₂-C composite cathodes with different types of binders, X-ray diffraction techniques are used to study the structure of coking carbon generated by the heat treatment process of various binders.

Pitch, furan, phenolic aldehyde and epoxy were respectively placed in a corundum crucible. Under the conditions of isolation from the air (the specimens were buried in graphite powder), the binders were heat treated and the heating curve was consistent with those reported in literature [17]. After crushing, grinding and screening, the obtained coking carbon powder (-250 mesh) was used for the X-ray diffraction test analysis.

TGA was carried out on a Dupont 9900 thermal analysis apparatus. The specimens were pitch, furan, phenolic aldehyde and epoxy. In every test, the weight of the specimen was approximately 30 mg, which was placed in a corundum crucible. All tests were carried out in an argon atmosphere (100 ml/min) and between the temperature ranges, room temperature to 1000 °C. The heating rate used was 5 °C /min.

A Rigaku D/Max-RA X-ray diffractometer was adopted to analyze the microstructure of the specimens under Co target. Under 50 kV accelerating voltage conditions, the basic parameters of the XRD patterns were obtained through the (002) diffraction peak combined with equations (1) and (2).

$$D = \frac{K\lambda}{B \cos \theta} \quad (1)$$

$$d_{002} = \frac{\lambda}{2 \sin \theta} \quad (2)$$

Where D denotes grain size, d₀₀₂ denotes d spacing concerning (002) diffraction peak, K is a constant (0.89) λ denotes wavelength of X ray (0.154056 nm), B denotes half-height width of the diffraction peaks (rad) and θ denotes diffraction angle (rad).

Results and Discussion

Dynamic Analysis of Pyrolysis Process for Different Binder Types

Figure 1 shows the TG curves of pitch, furan, phenolic aldehyde and epoxy obtained under the same test conditions. Due to the volatilization of water and some other small molecules within the range of 200 °C to 500 °C, each specimen has a large weight loss range. Following this stage, every specimen's weight

loss rate reduces greatly and the mesophase quickly combines, generating coking carbon. On this basis, impurity atoms and groups will discharge from the periphery of the macromolecules and the remaining molecules are rearranged.

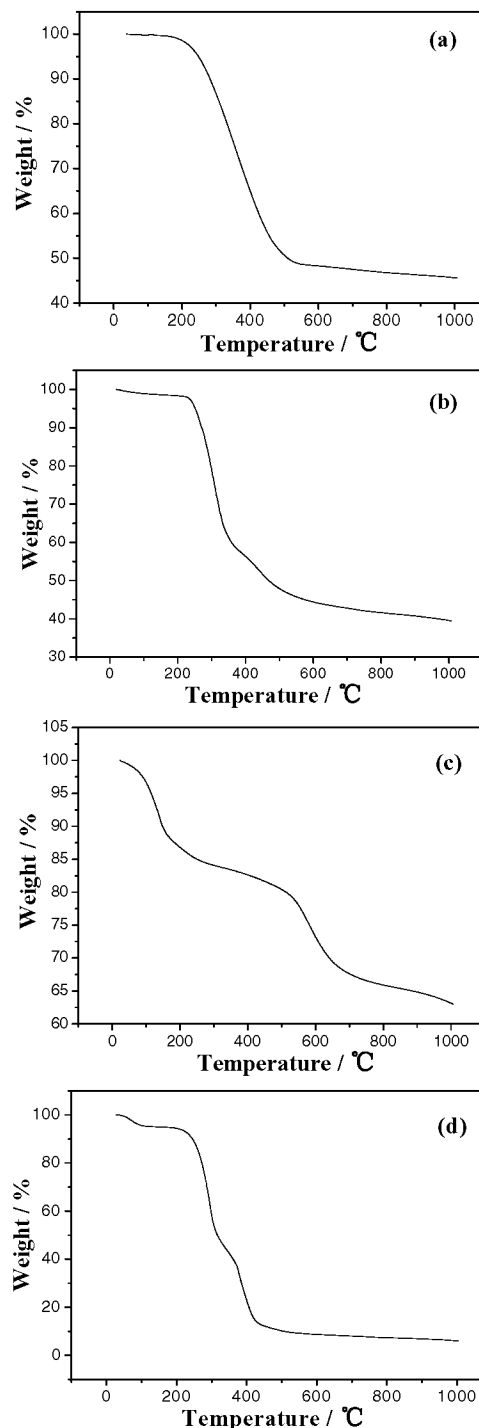


Figure 1. TG curves of binders in the argon atmosphere: (a) pitch; (b) furan; (c) phenolic aldehyde; (d) epoxy.

The heat-treatment process of the binder is complex and therefore is difficult to describe by a simple dynamic model. In this paper, the thermal weight loss process of the specimens is only used to carry out dynamic analysis and discuss the pyrolysis

process of various binders so that a correlative dynamic equation and research method referring to the pyrolysis process can be used for reference, shown in equation (3).

$$\ln\{[1-(1-\alpha)^{1-n}]/[(1-n)T^2]\}=a+b/T \quad (3)$$

Where, $a=\ln\{(AR/\Phi E)[1-(2RT/E)]\}$, $b=-E_a/R$, α denotes change rate of weight, n denotes the reaction order, T denotes temperature (K); R denotes gas constant and A is a constant. According to literature [18-21], if n equals 8, the result shown in Figure 1, Figure 2 can be obtained.

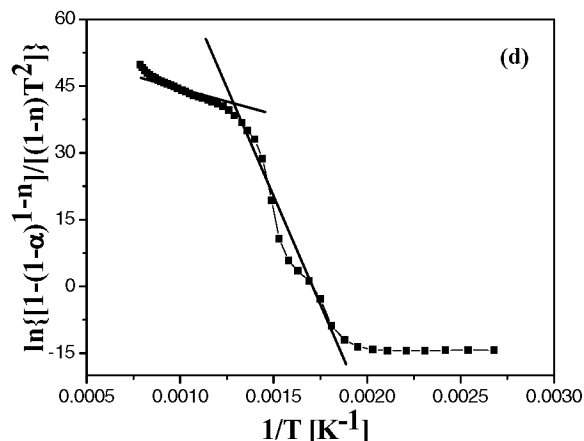
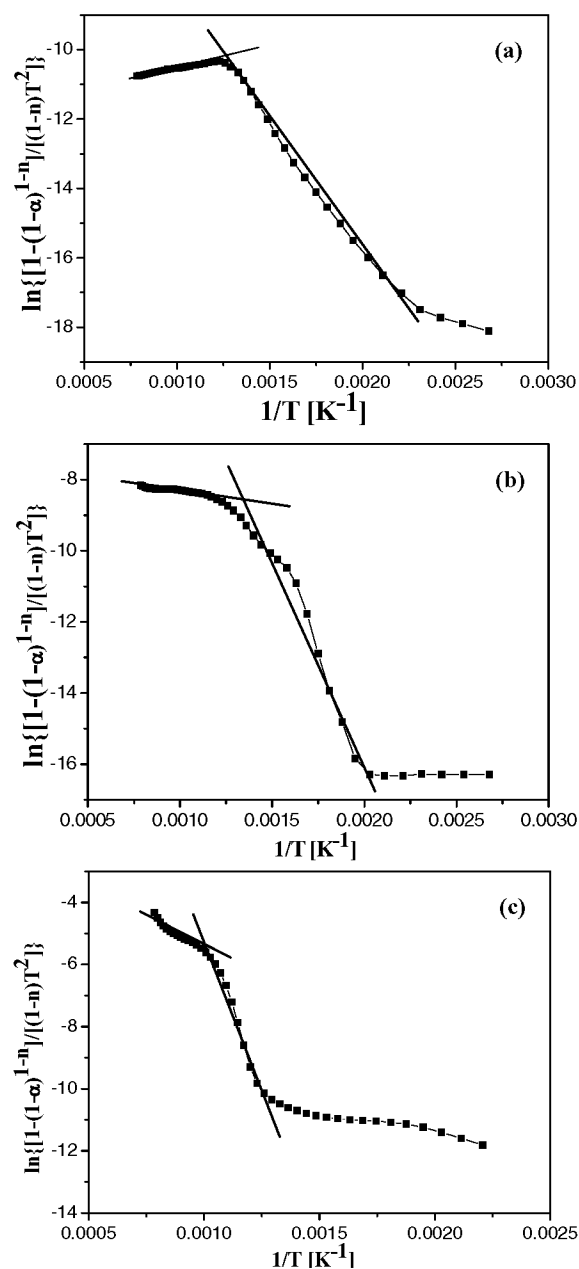


Figure 2. Curves of $\ln\{[1-(1-\alpha)^{1-n}]/[(1-n)T^2]\}$ vs. $1/T$ refer to different binders: (a) pitch; (b) furan; (c) phenolic aldehyde; (d) epoxy.

The data shown in Figure 2 was fitted and then a straight line can be obtained. From the slope of the straight line, the E_a of the various binders can be calculated. The E_a of pitch, furan, phenolic aldehyde and epoxy referring to this pyrolysis process are shown in Table I.

Table I: Apparent activation energy of pitch, furan, phenolic aldehyde and epoxy refer to pyrolysis process

Category	Pitch	Furan	Phenolic aldehyde	Epoxy
$E_a \backslash$ kJ/mol	47.20	93.11	178.11	780.32

The binder pyrolysis process is essentially a process to get the densest remnants. Aromatic structure is the densest and most solid structure, so therefore the pyrolysis process is the aromatization process of the non-volatile residue. During the pyrolysis process, binders undergo large number of complex reactions such as decomposition, polymerization, cyclization and aromatization, transforming binder to coking carbon, where decomposition and polymerization reactions occur simultaneously. Owing to the thermal decomposition of the molecules, unpaired electrons will exist at the point of fracture. It is effortless for them to combine together when they contact each other, and then at the higher temperature, heterogeneous atoms or relative groups will be released and combine with other molecules possessing the unpaired electrons. Because decomposition and aggregation occur constantly as previously described, the firmest molecules accumulate in the non-volatilized residue, forming large planar molecules. Different binders have different microstructures after carbonization, and this has much to do with the E_a of the binders' pyrolysis process. The higher the pyrolysis activation energy, the stronger the heat resistance of binder, making the pyrolysis process more difficult, which makes it difficult to discharge the heterogeneous atoms, promoting the formation of transverse bond between aggregate and binder in the cathode. In this circumstance, directional alignment of planar molecules is inhibited, resulting in solidification of the binder in advance or directly transforming it into coking carbon rather than through the liquid phase. Figure 3(a) shows the micro-structure of the obtained coking carbon. The lower the pyrolysis activation energy, the poorer the heat resistance of the binder and therefore the process is easier and the heterogeneous atoms of binder

discharge fully. Following the formation of the polycyclic condensation structure through constant combination of aromatic rings, plane atomic layers will be formed and carbon atoms closely distribute in each corner of the hexagon. On account of obvious unequal axes, these layers are oriented parallel to each other easily, forming an accumulative atomic layered structure, as shown in Figure 3(b) [13-15].

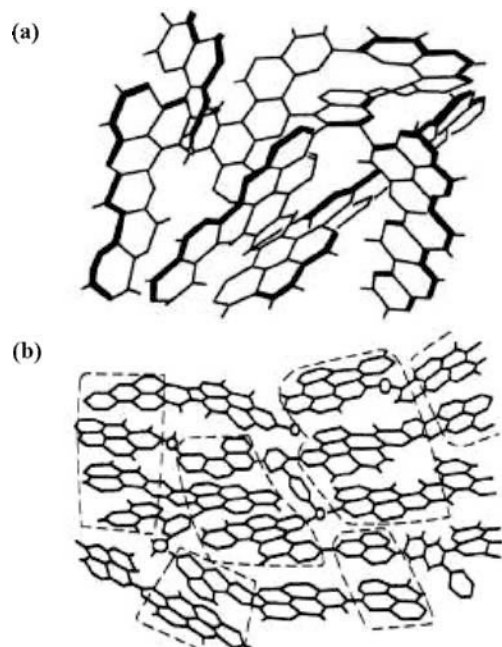


Figure 3. Maternal structure schematic of carbon material: (a) three-dimensional disordered carbon; (b) good orientation carbon.

Structure shown in Figure 3(b) is the layered structure carbon which is in the transition stage from turbostratic graphite to graphite structure and during electrolysis process, alkali metal and the electrolyte can easily penetrate into them, resulting in corrosion of the cathode. Whereas structure shown in Figure 3(a) is an aromatic bridge structure carbon which also comprises tetrahedral three dimensional structured carbons in which for alkali metal and the electrolyte is more difficult to penetrate, and therefore the erosion to the cathode is relatively small. Combined with the data in Table I, in decreasing order the E_a of binders are epoxy, phenolic aldehyde, furan, pitch. This indicates that, when the addition of binders are optimal, the composite cathode using resin as the binder will have the stronger corrosion resistance, while the corrosion resistance of the composite cathode using the pitch as binder is relatively poor.

The Micro-structure After Carbonization of Different Types of Binders

The graphitization process of amorphous carbon is not a mutation process. In the range of 1000 °C~3000 °C, physical and chemical properties of carbonaceous material change gradually [22]. In the view of crystallography, this is mainly because the change of carbon microstructure. Carbon after high-temperature heat treatment, C_0 (lattice constant) is shortened. While the d spacing of the a -axis and b -axis become larger, close to the structure of natural graphite. Figure 4 shows the XRD patterns of various binders after carbonization. Where half-height width of

the diffraction peaks refer to pitch, furan, phenolic aldehyde and epoxy are 0.267, 0.232, 0.278 and 5.436, and 2θ of the diffraction peaks about them are 26.409°, 26.447°, 26.435° and 25.686° respectively.

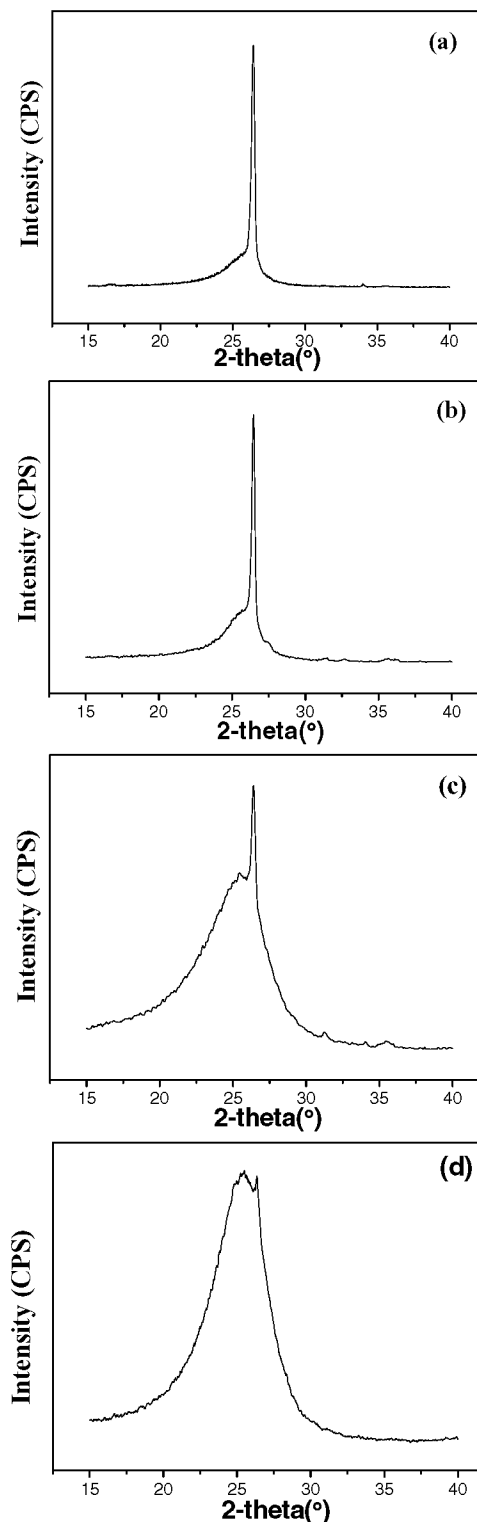


Figure 4. XRD spectrum of different binders after carbonization: (a) pitch; (b) furan; (c) phenolic aldehyde; (d) epoxy.

The basic parameters of the XRD patterns can be obtained through analysis of the (002) diffraction peak combined with the equations (1) and (2), shown in Table II

Table II: Basic parameters of XRD spectrum of different binders

Category	2- θ (°)	d_{002} (Å)	D(Å)	Crystallinity /%
Pitch	26.409	3.3721	366	28.69
Furan	26.447	3.3673	421	25.01
Phenolic aldehyde	26.435	3.3689	352	11.86
Epoxy	25.686	3.4654	18	×

Note: Crystallinity denotes the degree of graphitization degree for each specimen.

It can be seen from Table II that after high-temperature heat treatment, the degree of graphitization of the pitch, furan and phenolic aldehyde are 28.69%, 25.01% and 11.86% respectively. After the carbonization of the epoxy, the obtained coking carbon has no components with graphite structure and thus no crystallinity results reported. Pitch was found to be the easiest material to graphitize, while furan, phenolic aldehyde and epoxy were more difficult. It should be noted that difficult graphitization does not mean that the material can not be graphitized, thus the results shown in Table II are not difficult to understand, however, there is still a problem to be explained. It can be seen from the experimental results that the degree of graphitization of the pitch is higher than that of the resins mentioned above, but the resistance to alkali metal penetration of the pitch is worse than that of the resins. In order to solve this problem, the microstructure of heat-treated pitch under different temperatures is required to be analyzed.

With increasing heat treatment temperature the variation of microstructure of pitch is shown in Figure 5 [22, 23] and this variation can be divided into four regions: *a*, *b*, *c*, *d*.

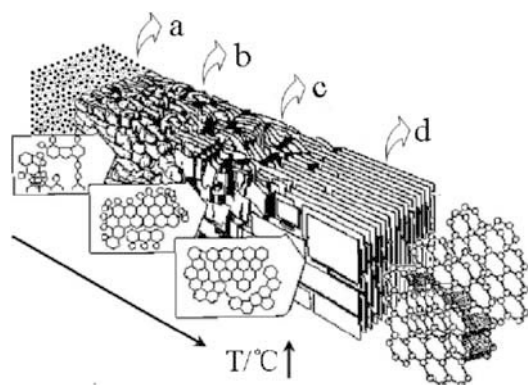


Figure 5. Structural diagram of carbon materials heat-treated under different temperatures [24].

Pitch in region *a* has non-graphitizing structure, while pitch in region *b* and *c* has a turbostratic graphite structure and the content of turbostratic graphite in region *b* is higher than that in region *c* and pitch in region *d* has a complete graphite structure. These four kinds of structures have their own characteristics. For expansion during electrolysis, the structures shown in region *b* and *c* are the worst. Whilst for corrosion resistance, the structures shown in region *a*, *b* and *c* are all poor. In this paper, heat

treatment temperature of pitch was 1000 °C, and under this circumstance the micro-structure of pitch is in a transition state from region *a* to region *b*. When the micro-structure of the material is in this region, the corrosion resistance of material is very poor, and during electrolysis, carbon with this kind of structure can react with electrolyte under the action of alkali metal, forming Al_4C_3 . For expansion, carbon materials with structures in region *b* are worse than that with structures in region *a*. This is mainly because in region *a*, no graphite lamellar structure exists and carbon materials do not have the prerequisite to swell even if alkali metals penetrate into them. However, when the micro-structure of carbon materials transforms from region *a* to region *b*, electrolysis expansion of carbon materials becomes worse. This illustrates that although the degree of graphitization of coking carbon obtained through heat-treatment of pitch at 1000 °C is 28.69%, it's electrolysis expansion is still poor.

On the contrary, although the degree of graphitization of the resin binder (furan, phenolic aldehyde and epoxy) is low, their resistance to alkali metal is still stronger. Because the structure of resin will change after carbonization to the obtained structure shown in Figure 3(a), which is different from the microstructure of pure graphite. This kind of structure can not be characterized using the degree of graphitization test using XRD. On the other hand, after carbonization, the degree of graphitization of coking resin is not equal to zero (shown in Table II). The existence of the layered structure makes electrolysis expansion caused by alkali metal penetration possible. That is to say, if the structure of the coking resin is a complete three-dimensional cross-linked structure it is more different to swell for coking resin. In the view of electrolysis expansion, the complete three-dimensional cross-linked structure is helpful. The test results show that coking resin (resin after carbonization) also has some component which is the layered structure, this makes electrolysis expansion possible. Compared with pitch coke, the degree of graphitization of resin coke is low. This improves the corrosion resistance of resin coke and also reduces the electrolysis expansion of resin coke remarkably. In the view of traditional opinion, with the increase of the degree of graphite, performance in regards to resistance to alkali metal will be improved. In order to obtain this conclusion, a prerequisite must be realized. Namely, when turbostratic graphite exists in the carbonaceous material, or when micro-structure of the carbonaceous material is in the transition state from turbostratic graphite to pure graphite, the higher the graphite degree, the stronger the resistance to alkali metal penetration of materials. While, when the micro-structure of the carbonaceous material is in the transition state from amorphous or other completely non-graphitic structures to turbostratic graphite, the electrolysis expansion of carbonaceous material will deteriorate instead.

Conclusions

With a traditional viewpoint, the increase of the degree of graphite will result in the electrolysis expansion of the binder decreasing. That is to say, corrosion resistance of the binders improves with the increase of the degree of graphite. However, binders which are hard to graphitize such as the furan, phenolic aldehyde and epoxy discussed in paper do not absolutely accord with this conclusion. For binders used in the cathode blocks for aluminium electrolysis, when the turbostratic graphite exists or their structure is in the transition stage from turbostratic graphite to graphite structure, the higher the degree of graphitization the smaller the electrolysis expansion of binders. However, when the

binders micro-structure was in the transition stage from amorphous or other completely non-graphitic structures to turbostratic graphite, the electrolysis expansion of binders will deteriorate. Under this circumstance, the higher the E_a , the stronger the performance of binder's resistance to alkali metal penetration. E_a of pitch, furan, phenolic aldehyde and epoxy are 47.20kJ/mol, 93.11kJ/mol, 178.11kJ/mol and 780.32kJ/mol respectively.

Compared with pitch, resistance to alkali metal penetration of resin binders is better, but use of pure resin as a binder in cathode blocks for aluminium electrolysis still have some problems that need to be solved. Firstly, the price of resin is relatively high, about 4-8 times the price of the pitch. This cost is too high for industrial application. Secondly, after carbonization, the micro-structure of resin will change, forming an aromatic bridge structure carbon which also comprises tetrahedral three dimensional structure carbons. Composite cathodes using pure resin as binder have greater brittleness and higher electrical resistivity which will need to be solved. Considering the characteristics of pitch and resin, further studies on a modified pitch obtained through combination of pitch and resin will be made. The aim of this study will be to achieve complementary advantages of pitch and resin and improving the resistance to alkali metal penetration of TiB₂-C composite cathode.

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