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ELECTROLYSIS EXPANSION PERFORMANCE OF MODIFIED PITCH BASED TiB_2–C COMPOSITE CATHODE IN $[K_3AlF_6/Na_3AlF_6]–AlF_3–Al_2O_3$ MELTS

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Abstract

Electrolysis expansion of pitch, modified by furan, phenolic-aldehyde and epoxy, based TiB_2-C composite cathodes in $[K_3AlF_6/Na_3AlF_6]–AlF_3–Al_2O_3$ melts were investigated, and TGA was used to study dynamics of pyrolytic process about various modified pitch. The results show that, compared with electrolysis expansion of unmodified pitch based composite cathode, pitch modified by furan, phenolic-aldehyde and epoxy based composite cathodes all exhibit lower electrolysis expansion which are 1.61 %, 1.62 % and 1.68 % respectively. The maximum depressed amplitude can reach 13.77 %. Apparent activation energy (AAE) concerning pyrolysis process of pitch is related to electrolysis expansion of composite cathodes. The higher the AAE, the lower the electrolysis expansion, and the AAE of unmodified pitch is 47.21 kJ/mol, while the AAE of pitch modified by furan, phenolic-aldehyde, and epoxy are 66.25 kJ/mol, 57.07 kJ/mol and 63.24 kJ/mol severally. The values of them can account for test result of electrolysis expansion mentioned above.

Introduction

Since the turn of the century, aluminum electrolysis industry of China experienced a period of rapid growth. Large-scale prebaked aluminum electrolysis enterprises have been built and put into production. Presently, China's production and consumption of primary aluminum have been more than 30 wt.% of global total and per capita consumption of aluminum has reached 9.7 kg, which makes China become one of the most important force to promote the development of the world aluminum industry [1]. According to statistics [2], in China, power consumption of aluminum electrolysis has accounted for 80 % of non-ferrous metal industry's total consumption which bring us tremendous pressure on energy saving and pollution alleviation. However, challenges and opportunities coexist. High energy consumption makes the aluminum electrolysis industry become the greatest potential sub-sector.

Hall-Heroult process, the exclusive way to produce primary aluminum, has many problems to be solved such as high energy consumption, which severely restrict the future development of aluminum industry [3-4]. The new technique for aluminum production based on the inert electrode is expected to change conventional production and achieve energy saving by a large margin and the zero emissions of greenhouse gases during electrolysis process. As an important component of an inert electrode system, wettable cathodes have the greatly important effect to promote the industrial application of inert electrode system. However, as far as the current TiB_2-C composite cathode is concerned, the problem referring to the short service life and easy to crack etc. have not been solved thoroughly, which can not meet the requirements of the inert electrode system, and become an obstacle to baffle its industrial application [5-6].

During the baking process of green-bodies of TiB_2-C composite cathode, As TiB_2, petroleum coke and other carbonaceous aggregate have been pre-heat treatment, and its temperature is higher than cathode green bodies, so that, in addition to the binder in the green bodies, other components' structure and composition do not change, only the binder occur a series of physical and chemical changes [7-8]. Moreover, studies have shown that [9-10], because of the polarization, alkali metals will generate on the surface of the cathode and penetrate into the cathode from the exterior to the interior during the electrolysis process, causing cathode corrosion. In this process, binder in the cathode bears the brunt of alkali metals' destruction. In summary, it can be seen that, the binder is the weak link in the cathode, corrosion resistance performance's pros and cons of which determines that of the cathode.

As pitch can wet and penetrate into the surface and pores of various aggregate commendably, and cause all kinds of granular components bond each other, forming the paste with good plastic performance, so that, it is still widely used in the cathode production process. But, pitch is the soft carbon material [11-12], which embodies a high content of aromatic compounds before baking process. During the baking process, as the temperature increases, a number of layered structures generate gradually in the internal, finally, forming moderate or large pores mostly after carbonization. This structure has poor performance on resistance to alkali metal penetration. In view of pitch's microstructure after carbonization, there is still some room for improving pitch's resistance to alkali metal penetration.

In order to further enhance the corrosion resistance of TiB_2-C composite cathode and extend its service life, taking into account the microstructure of binder after carbonization, pitch modified by furan, phenolic-aldehyde and epoxy were used as binder to prepare TiB_2-C composite cathode for aluminum electrolysis. Electrolysis expansion performances of them were tested in $[K_3AlF_6/Na_3AlF_6]-AlF_3-Al_2O_3$ melts. At the meantime, Thermo-gravimetric analysis (TGA) was adopted to study the dynamics of coking process about various modified pitch, providing sustentation to promote industrial application of TiB_2-C composite.

Experimental

Preparation of Modified Pitch

Firstly, a certain amount of acetone was used to dilute a certain ratio of resin, and then, pitch was added into them with the required ratio by forming slurry. Subsequently, acetone was evaporated under 45 ℃ The resins used in this paper are furan, phenolic-aldehyde and epoxy, application amount of resin in the modified pitch were all 12 wt.%. FAP_{12} represented pitch modified by furan. PFP_{12} represented pitch modified by phenolic-aldehyde. EPP_{12} represented pitch modified by epoxy.

Preparation of Modified Pitch Based TiB_2-C Composite Cathode

Cathode Formulations. TiB_2 powder (average particle size 12 μm): 75 wt.%; modified pitch (self-made): 14 wt.%; petroleum coke (average particle size 10 μm): 11 wt.%.

Preparation Technology. First, place a certain proportion of TiB_2 powder, petroleum coke into the three-dimensional motion mixer, kneading and then mixing them with pitch binder in the pot. After weighing, the materials will be put into the all-powerful hydraulic pressure machine (WE-300C) for molding; the molding pressure is 150 MPa, and the obtained cathode with specifications of Φ20 × 50 mm. Finally, put the samples into the alumina crucible, being embedded by coke and placed in program control box resistance furnace to conduct heat-treatment. The heating program is shown in Figure 1.

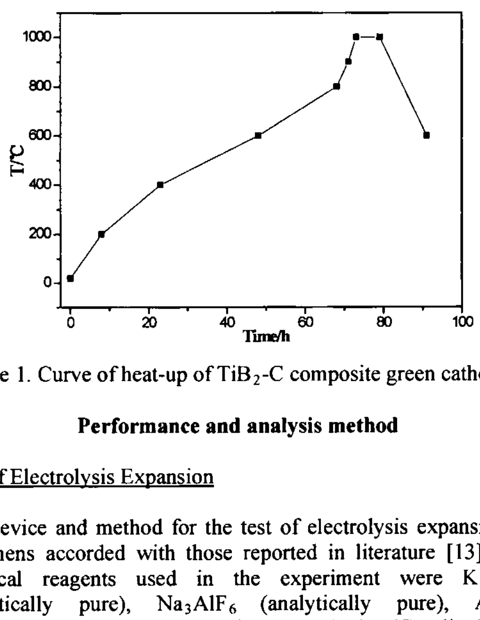

Figure 1. Curve of heat-up of TiB_2-C composite green cathodes.

Performance and analysis method

Test of Electrolysis Expansion

Test device and method for the test of electrolysis expansion of specimens accorded with those reported in literature [13]. The chemical reagents used in the experiment were K_3AlF_6 (analytically pure), Na_3AlF_6 (analytically pure), Al_2O_3 (analytically pure), AlF_3 (analytically pure). CR (Cryolite Ratio) of electrolyte was 1.6 and KR [nA/(nA+nB), where nA and nB are the mass of K_3AlF_6 and Na_3AlF_6 severally] was 0.3. The concentration of alumina in the electrolyte was saturated in every experiment. The current density (ρCD), the liquidus temperature (tL) and the superheat (tS) were 0.8 A/cm^2, 873 ℃ and 50 ℃ respectively. The specimens were subjected to electrolyte for 1.5 h. Testing temperature was determined by tL and tS. The whole experimental process was taken in the high-purity argon atmosphere.

Thermo-gravimetric Analysis

As mentioned above, during the electrolysis process, binder will have a greater impact on electrolysis expansion of cathode. This impact may be combined action refer to both structure and chemistry. Moreover, structure of composite cathode is affected by the baking process of cathode green bodies. In an effort to reveal the relationship between binder and electrolysis expansion of composite cathode from the microstructure, in this paper, TGA was adopted to study the dynamics of heat-treatment process of modified pitch.

TGA was carried out at Dupont 9900 thermal analysis apparatus. The specimens were pitch modified by furan, phenolic-aldehyde and epoxy respectively. These specimens were the same as the binders mentioned above which were used to prepare TiB_2-C composite cathode. In every test, the weight of the specimen was about 30 mg, and then it was put into the corundum crucible. All test were carried out in the argon atmosphere(100 ml/min) and between the same temperature region (room temperature to 1000 ℃). The heating rate is 5 ℃/min.

Results and Discussion

Electrolysis Expansion of Modified Pitch Based TiB_2-C Composite Cathodes

Figure 2 shows the curves of low temperature electrolysis expansion of modified pitch based TiB_2-C composite cathodes as a function of electrolysis time in $[K_3AlF_6/Na_3AlF_6]$-AlF_3-Al_2O_3 melts, where abscissa is the electrolysis time(h) and ordinate is the linear electrolysis expansion(ρ, %) of specimens. As shown in the figure, using FAP_{12}, PFP_{12} and EPP_{12} as binder, electrolysis expansion of the obtained TiB_2-C composite cathode are 1.61 %, 1.62 % and 1.68 %, respectively, and differences in values are not significant.

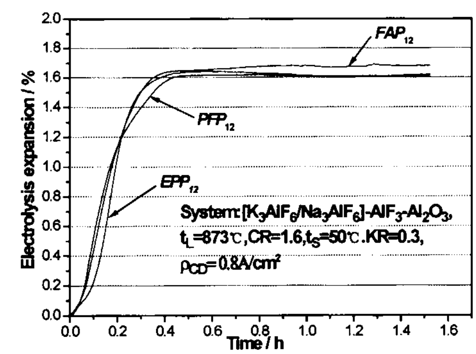

Figure 2. Electrolysis expansion of modified pitch based TiB_2–C composite cathode.

Previous studies have shown that [13], when the pure resin was used as binder to prepare TiB_2-C composite cathodes, the differences of electrolysis expansion among them are very large. However, being enslaved to application amount of resin in the modified pitch and the similar micro-structure of furan, phenolic-aldehyde, and epoxy after carbonization, the electrolysis expansion of TiB_2-C composite cathode, using the three modified pitch mentioned above as binder, is also similar. But, compared with the composite cathode using unmodified pitch as binder, the electrolysis expansion of which is 1.87 %, TiB_2-C composite cathodes using EAP_{12}, PFP_{12}, and EPP_{12} as binder exhibit the smaller electrolysis expansion, in contrast, decreasing by 12.97 %, 12.43 % and 9.19 %, respectively. This is mainly affected by the micro-structure of resin after carbonization, which is three-dimensional network structure. As for resin, with temperature increasing, one kind of cross-linking phenomenon emerges in the interior, and forming a kind of rigid three-dimensional network structure. This cross-linking phenomenon spur the random layer stacking, and then causing the formation of some "nano-pores". These nano-pores are beneficial for the cathode, whether in view of its great resistance to alkali penetration, or with an eye to its good effect on structural strength of the cathode.

Dynamic Analysis of Pyrolysis Process about Modified Pitch

Figure 3 shows the TG curves of the three modified pitch obtained under the same test condition. It can be seen that TG curves of these three modified pitch are similar to the TG curves of unmodified pitch or pure resin [14]. Within the range of 200 ℃to 500 ℃, each specimen has a large range refer to weight loss, and then, every specimen's weight loss rate reduce greatly, and generating coking carbon gradually.

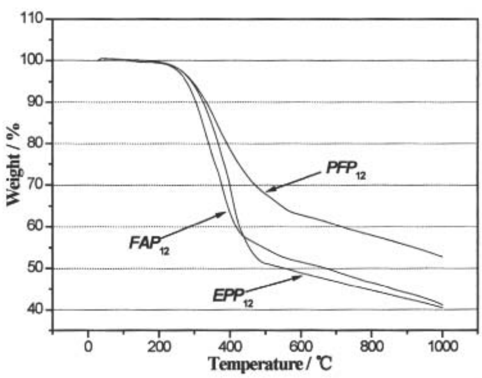

Figure 3. TG curves of binder in the argon atmosphere.

Dynamic Analysis of Pyrolysis Process about Modified Pitch

Heat-treatment process of binder is more complicated, and it is difficult to be described by using a simple dynamic model. But, in this paper, thermal weight loss process of specimens is only used to carry out dynamic analysis and discuss the pyrolysis process of various binders. So that, correlative dynamic equation and research method refer to pyrolysis process can be used for reference. According to the literature [15-16], if the pyrolysis process was regarded as 8 grade, dealing with the result shown in Figure 3, the curves refer to $\ln\{-[1-(1-\alpha)^{-7}]T^{-2}/7\}$ — 1/T can be obtained, as shown in Figure 4. The data of pyrolysis process shown in Figure 4 was fitted, and then, a straight line can be obtained. According to the slope of the straight line, the AAE of various binder refer to their pyrolysis process can be calculated, and denoted by E.

The AAE of FAP_{12}, PFP_{12} and EPP_{12} referring to the pyrolysis process are shown in Table I.

Table I. Apparent Activation Energy of Pitch Modified by Furan, Phenolic-aldehyde and Epoxy Refer to Pyrolysis Process

Category	FAP_{12}	PFP_{12}	EPP_{12}
E \ kJ/mol	66.25	57.07	63.24

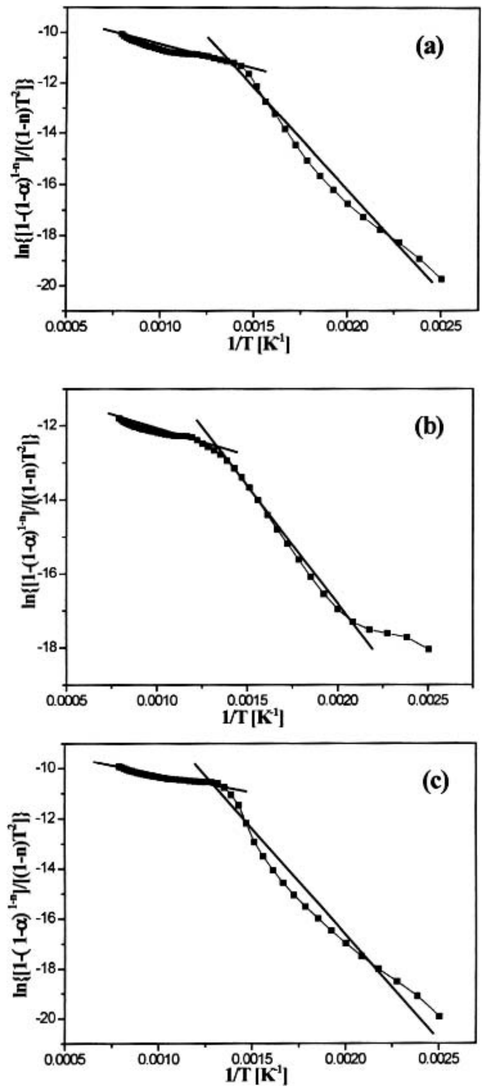

Figure 4. Curves of $\ln\{-[1-(1-\alpha)^{-7}]T^{-2}/7\}$ *vs.* 1/T refer to different binders: (a) pitch modified by furan; (b) pitch modified by phenolic-aldehyde; (c) pitch modified by epoxy.

Binder pyrolysis process is essentially a process to get the densest remnants. Aromatic structure is the most dense and solid structure, so that all the pyrolysis process are the aromatization process of non-volatile residue. During pyrolysis process, binders carry out large number of complex reactions such as decomposition, polymerization, cyclization and aromatization, making binder form coking carbon, where decomposition and polymerization reactions occur simultaneously. Owing to the thermal decomposition of 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 atom 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, moreover, forming huge planar molecule.

Different binder have different microstructure after pyrogenation, this has much to do with the AAE of binders pyrolysis process. The higher the pyrolysis activation energy, the stronger the heat resistance of binder, pyrolysis process is more difficult, which would be difficult to discharge the heterogeneous atoms, promoting the formation of transverse bond between aggregate and binder in the cathode. At this circumstance, directional alignment of planar molecule is inhibited, resulting in solidification of binder in advance or directly transforming into coking carbon rather than through the liquid phase. Figure 5(a) shows the micro-structure of the obtained coking carbon. The lower the pyrolysis activation energy, the poor the heat resistance of binder, pyrolysis process is easier and the heterogeneous atoms of binder discharge fully. Following the formation of polycyclic condensation structure through constant combination of aromatic ring, plane atomic layer will be formed and carbon atoms closely distribute in each corner of hexagon. On account of obvious unequal axes, these layers are oriented parallel to each other easily, forming accumulative atomic layered structure, as shown in Figure 5(b) [7-8].

(a)

(b)

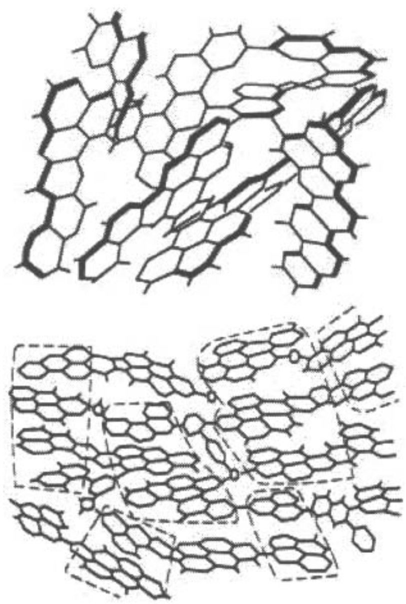

Figure 5. Maternal structure graph of carbon material: (a) three-dimensional disordered carbon; (b) good orientation carbon.

Structure shown in Figure 5(b) is the layered structure carbon in the process of augmentation 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 5(a) is aromatic bridge structure carbon which also comprises tetrahedral third structure carbon, alkali metal and the electrolyte is more difficult to penetrate into this structure, therefore, the erosion to cathode is relatively small.

Combined with the data in Table I, it can be seen that pyrolysis activation energy of the three modified pitch mentioned above are 66.25 kJ/mol, 57.07 kJ/mol and 63.24 kJ/mol respectively, Exhibiting little difference, however, compared with unmodified pitch, they all have the higher pyrolysis activation energy (pyrolysis activation energy of unmodified pitch is 47.21 kJ/mol).

Based on the previous analysis, it can be known that the micro-structure of binder after carbonization, which is directly relative to corrosion resistance of cathode in the electrolysis process, is determined by the values of pyrolysis activation energy. The values of pyrolysis activation energy of the three modified pitches are more or less the same, exactly explaining the experimental result as shown in Figure 2.

Conclusions

Application of pitch modified by furan, phenolic-aldehyde and epoxy is very useful to reduce the electrolysis expansion of TiB_2-C composite cathode in $[K_3AlF_6/Na_3AlF_6]$-AlF_3-Al_2O_3 melts. The electrolysis expansion of TiB_2-C composite cathode using these three modified pitch as binder are 1.61 %, 1.62 % and 1.68 %. Compared with the cathode using unmodified pitch as binder, electrolysis expansion is improved obviously, which is decreased by 12.97 %, 12.43 % and 9.19 %. This is mainly affected by the AAE of pyrolysis process. When the AAE is higher, after carbonization, binder tends to generate coking carbon with the three-dimensional network structure, which has the good corrosion resistance. But when the AAE is lower, binder tends to generate coking carbon with layered structure, the corrosion resistance of which is poor. The AAE of the three modified pitch are 66.25 kJ/mol, 57.07 kJ/mol and 63.24 kJ/mol, more or less the same, just accounting for the test result of electrolysis expansion mentioned above.

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