

FURAN RESIN AND PITCH BLENDS AS BINDERS FOR TiB₂-C CATHODES

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Abstract

Blends of furan resin and pitch were applied as the binder of TiB₂-C cathodes. Characteristic properties of both the binder and furan/pitch based TiB₂-C cathodes were studied. The actual coking value of furan/pitch binder was higher than the theoretical value calculated from the coking values of the two components. There was a synergistic effect between pitch and furan resin. This leads to TiB₂-C cathode materials with lower open porosity and electrical resistivity and higher bulk density and compressive strength than those of pure pitch based TiB₂-C cathode materials. In addition, the low-temperature electrolysis expansion of TiB₂-C samples was tested. Furan/pitch based TiB₂-C samples showed lower electrolysis expansion than pitch based TiB₂-C samples (1.68% and 1.87%, respectively). Molecular structure (FTIR) and semicoke morphology (SEM) analysis results indicated that after adding an appropriate amount of furan resin, the pitch binder had improved cohesion and flexibility.

Introduction

The poor wettability of carbon cathodes used in aluminum electrolysis requires the retention of a 19~30cm layer of molten aluminum and a high anode-cathode distance (ACD) in the electrolytic cell. The resulting smooth and steady surface of molten aluminum avoids short circuits but leads to a high energy consumption. However, it has been proved that applying wettable cathode materials of titanium diboride or composites based on TiB₂ can narrow the ACD effectively. The wettable cathode allows a lower ACD with a decreased thickness (3-5mm) of molten aluminum. The secondary reaction of Al and the interference of magnetic field are reduced, lowering the energy consumption substantially [1-4]. TiB₂-C composite material is considered one of the most promising inert wettable cathode materials [5] because it can reduce the usage of TiB₂ while retaining the good wetting with the molten aluminum. In addition, it can be prepared by baking at a temperature much lower than the sintering temperature of TiB₂.

Pitch was the binder of first choice for TiB₂-C cathode because of its high carbon yield, good fluidity, easy graphitization, and good compatibility with TiB₂ aggregate [6].

The commonly used pitch, however, expands during carbonization to produce porous and cracked carbons with random lamellar structure [7]. These pores and cracks not only degrade the mechanical and electrical properties of the TiB₂-C cathode materials, but also become the pathway for infiltration and erosion of electrolyte and molten aluminum during the electrolysis process. This makes the cathode materials more susceptible to deformation and expansion, with a shorter life. To overcome these shortcomings, a wide range of research has been completed. A variety of methods such as thermal oxidation, flash distillation, thermal polymerization or use of additives have been tried to modify pitch in order to enhance its performance as binder [8-12]. Only the process of using additives to modify the pitch was simple and easy to implement. Condensation resin, as an additive to pitch, was expected to substantially improve the effect of the modification of pitch binder for aluminum electrode. It contains reactive groups which can form chemical bonds linking with the pitch to produce a three-dimensional network structure on carbonization [13]. Therefore, further research on modifying pitch by resin for TiB₂-C cathode is necessary.

In this study, blends of furan resin and pitch were used for the binder of TiB₂-C cathodes. Characteristic properties of the binder and TiB₂-C cathodes were studied to assess the advantages of the furan/pitch binder.

Experimental

Pretreatment of pitch

The furan resin and pitch blends were mixed in the required ratio by forming a slurry in acetone. The solvent was then evaporated before moulding.

Preparation of cathode samples

The raw materials including TiB₂ power with an average particle size of 10 μm, petroleum coke (106-150μm) and binder paste were mixed by kneader for 30 minutes, and then formed into cylindrical samples (Φ20mm) under a pressure of 160 MPa by a hydraulic press. After moulding, the samples

were baked in a temperature controlled furnace according to the heating curve shown in Figure 1.

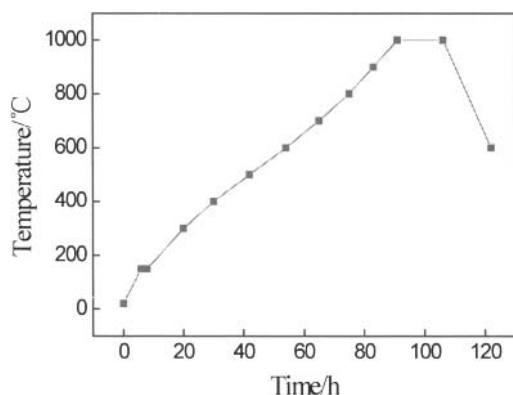


Figure 1. Heating curve for TiB₂-C cathode baking.

Research methods

The coking values of binders were measured according to GB 8727-88. The molecular structure of binders after curing at 150°C for 2h was studied using FTIR. SEM was also used to evaluate the topography of baked TiB₂-C composite cathodes and semi-cokes obtained from binders carbonized at 500°C for 60 min.

The bulk density, open porosity and compressive strength of baked TiB₂-C composite cathodes were determined according to ISO 12985-2: 2000. The electrical resistivity of baked samples was measured using the SZT-90 four point probe measuring system.

A modified laboratory Rapoport device [14] was used to test the electrolysis expansion of samples, the electrolysis was performed in [K₃AlF₆/Na₃AlF₆]-AlF₃-Al₂O₃ electrolyte melts at 923°C, the current density was 0.8A/cm² and the whole electrolysis process was taken in high-purity argon atmosphere.

Results and discussions

Properties of binders

Coking value:

The coking values of furan resin and pitch are shown in Table I. The theoretical coking values have been calculated using the individual component coking values and the furan/pitch ratio in the blend. The actual coking value and theoretical coking value of the furan/pitch binders tested are shown in Figure 2. The actual coking values of the furan/pitch binders were higher than theoretical values. This is related to a certain synergistic effect between pitch and furan resin during carbonization.

Table I. Coke values of pitch and furan resin

Binder	Pitch	Furan resin
Coking values/%	59.50	47.66

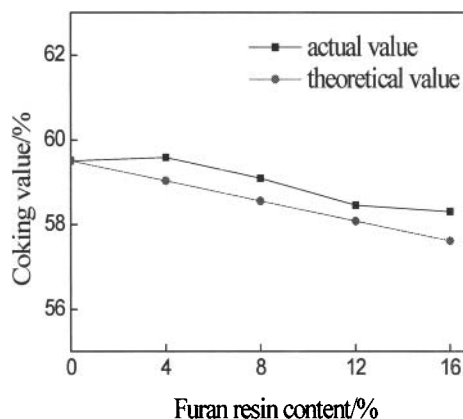


Figure 2. Dependence of actual coking value and theoretic coking value on furan resin content of furan/pitch binder.

On mixing the furan resin with pitch, a series of complex condensation and cross-linking reactions occurs as the temperature is increased. As the carbonization temperature of resin is lower than pitch, the furan resin is carbonized first to produce a microporous carbon with a certain extent of three-dimensional network structure produced. With a further increase in temperature, the pitch become more fluid and can infiltrate into the micropores of resin carbon. This combination suppresses the expansion and volatilization of the lighter components of the pitch. Therefore, the actual coking value of the modified pitch increased.

FTIR analysis:

To ensure the reactions between furan resin and pitch, and the cross-linking reaction of furan resin is completed, the furan/pitch mixed binder has been held at 150°C for 2 hours. The same process of holding at 150°C for 2 hours was used during the TiB₂-C cathode baking. The samples were the subjected to FTIR (Fourier Transform Infrared Spectroscopy) analysis. Figure 3 shows the FTIR spectra of pitch, furan/pitch (12wt% resin content) and furan resin binders after curing at 150°C for 2hours. The spectra show that several reactions take place between the furan resin and pitch that causes the C=O adsorption band of furan resin (a) at 1715cm⁻¹ to almost disappear. A new strong secondary alcohol C-O adsorption band (b) at 1010cm⁻¹ appeared in the spectra of the furan/pitch binder, and the aromatic ring skeleton C=C adsorption band (c) at 1593cm⁻¹ of modified pitch increased in intensity. The conversion of C=O to C-O and the increase in intensity of the aromatic ring skeleton C=C adsorption band of modified pitch show that this compositing treatment of furan resin and pitch promotes the condensation of the

aromatic rings. The cross-linking between the rings enhances the degree of aromatization of the binder. This may also explain why the actual coking value of furan/pitch binder was higher than theoretical value.

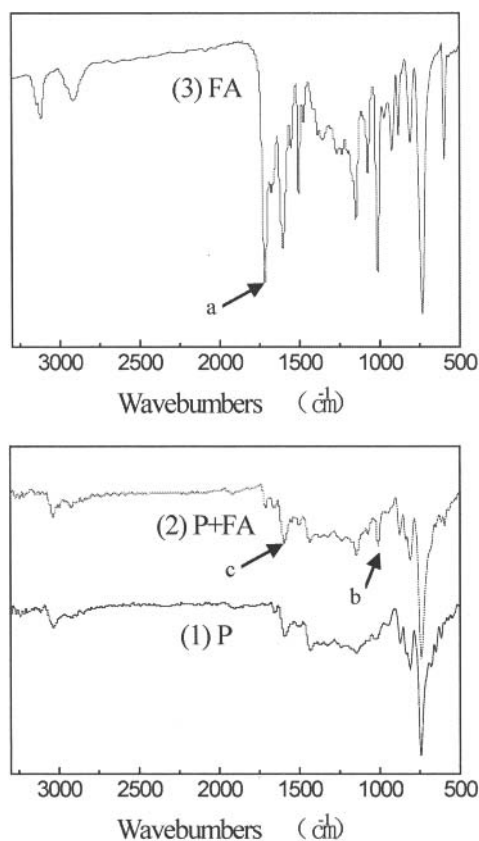


Figure 3. FTIR spectra of binders after curing at 150 °C for 2h: (1) Pitch; (2) furan/pitch (12wt% resin content); (3) furan resin.

SEM analysis of semi-cokes:

Figure 4 shows the SEM image of semi-cokes obtained from binders carbonized at 500°C of furan resin for 60 min. From Figures a₁ and a₂ many large pores can be seen in the semi-coke of pitch. Some of the pores are connected in series, and furthermore, many cracks and random lamellar structures are seen in Figure a₂. In contrast, the surface of the furan/pitch (12wt% resin content) semi-coke shown in b₁ and b₂ are smoother, with the pores mostly small or closed and surrounded by concaves. This shows that after modified by furan resin, the cohesion and flexibility of pitch binder were significant enhanced.

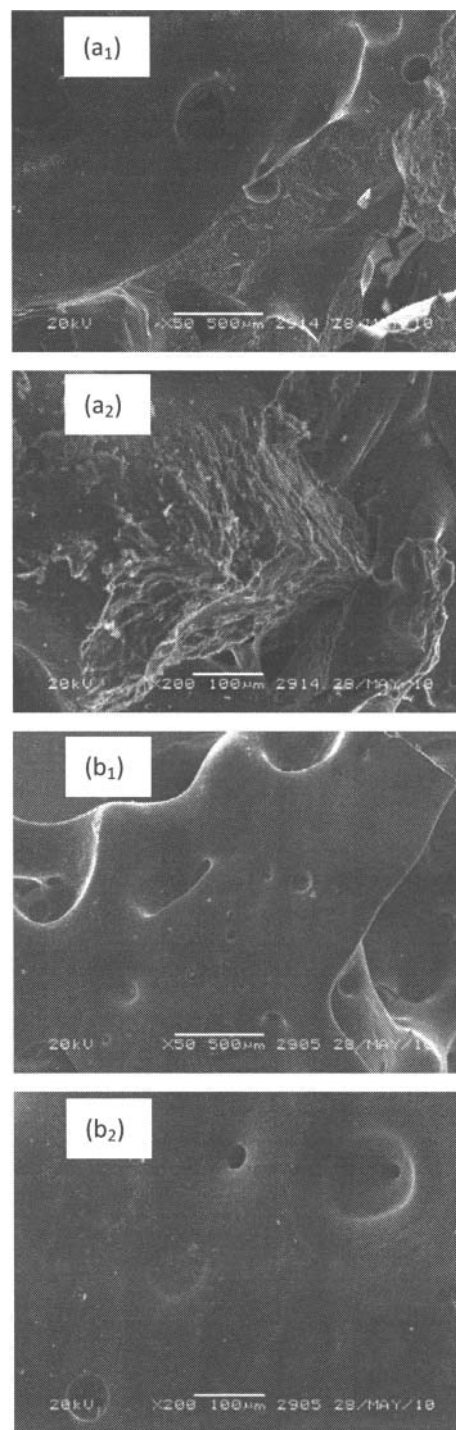


Figure 4. SEM image of resultant semi-cokes obtained from binders carbonized at 500°C for 60 min: (a) Pitch; (b) furan/pitch (12wt% resin content) (a₁, b₁ - 50 times magnification; b₁, b₂ - 200 times magnification).

Physical properties of TiB₂-C cathodes

From the results above we know that there is a synergistic effect between pitch and furan resin during carbonization.

These improvements in the coking value of the binder will have a large effect on the physical properties of TiB₂-C cathodes. As shown in Table II, the furan/pitch binder provided TiB₂-C cathodes of improved physical properties with lower open porosity and electrical resistivity and higher bulk density and compressive strength than those of pure pitch based TiB₂-C cathodes. However, the highest resin content produced brittle carbon which increased the electrical resistivity and reduced the compressive strength of the

cathodes. The optimal physical properties of the TiB₂-C cathodes are produced at a furan resin content of 12wt%. Figure 5 shows an SEM image (1000 times magnification) of the pitch and furan/pitch (12wt% resin content) based TiB₂-C cathodes. Many large pores are observed in the cathode using pitch alone as binder. In contrast, furan/pitch blending suppressed the expansion of pitch, resulting in lower porosity in the cathode.

Table II. Properties of baked TiB₂-C cathodes in the presence of 14 wt% binder of pitch and furan/pitch.

Binder	BD (g/cm ³)	OP (%)	ER (μΩ·m)	CS (MPa)
P0	2.25	36.99	51.41	22.78
P0*	2.50	29.61	48.68	29.07
4%FA+96%P	2.54	29.41	44.31	30.84
8%FA+92%P	2.53	29.30	43.58	36.52
12%FA+88%P	2.54	28.82	38.75	41.28
16%FA+84%P	2.55	28.44	39.76	37.59

P0: Mixed without acetone.

P0*: Mixed in acetone.

BD: bulk density, OP: open porosity, ER: electrical resistivity, CS: compressive strength.

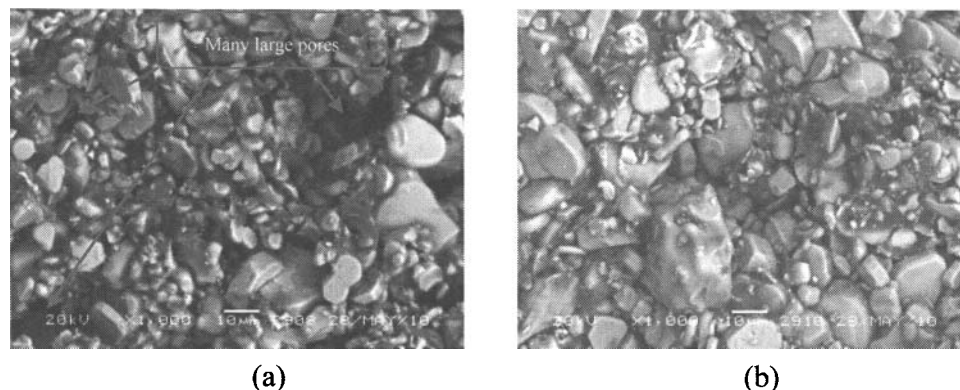


Figure 5. SEM image of TiB₂-C composite cathodes: (a) pitch (P0*) based; (b) furan/pitch (12wt% resin content) based.

Electrolysis expansion of TiB₂-C cathodes

Figure 6 shows the electrolysis expansion curves of pitch based and furan/pitch (12wt% resin content) based TiB₂-C cathodes tested in [K₃AlF₆/Na₃AlF₆]-AlF₃-Al₂O₃ melts. It can be seen that both the electrolysis expansion curves are a parabolic shape. At the beginning of electrolysis, the expansion of the cathode occurred rapidly. As the electrolysis continues, the rate of cathode expansion reduces and tends to a constant after a period of time. There was a significantly different behavior between the pitch and furan-based TiB₂-C cathodes in the electrolysis expansion experiments. After electrolyzing for 1.5h, the expansion rates of pitch and furan/pitch based composite cathodes were 1.87% and 1.68%, respectively.

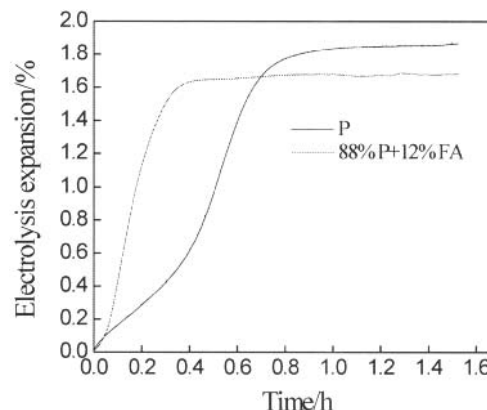


Figure 6. Electrolysis expansion of pitch, furan/pitch (12wt% resin content) based TiB₂-C composite cathodes.

Pitch is a kind of soft carbon material. During cathode baking, it expands and produces porous and cracked carbons with a random lamellar structure. This makes the TiB₂-C composite cathode more easily penetrated by electrolyte. The contact area of electrolyte and cathode increases, resulting in more sodium and potassium metal being produced on the surface of cathode. The K and Na are more likely to penetrate into the cathode through the lattice and grain boundaries of the carbon materials and form alkali metal-graphite intercalation compounds [C_xM (K, Na)] [15]. As a result, the layered structure of the carbon may deform or rupture, leading to a large expansion of the cathode. In contrast, furan resin is a hard carbon material. It undergoes less expansion during carbonization than pitch. The micropores and three-dimensional network structure produced during cathode baking reduced the formation of the intercalation compounds [C_xM (K, Na)]. Therefore, the furan/pitch based TiB₂-C composite cathode showed a smaller expansion rate after electrolysis.

Conclusions

- (1) There was a synergistic effect between pitch and furan resin during carbonization, with the actual coking value of furan/pitch binder being higher than the theoretical value.
- (2) After modification by furan resin, the cohesion and flexibility of pitch binder were significantly enhanced.
- (3) The synergistic effect between pitch and furan resin improved both the physical properties and electrolysis expansion resistance of TiB₂-C cathodes, with the optimal content of furan resin in binder being 12wt%.

Acknowledgement

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