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Industrial preparation and performance testing of property-modified prebaked carbon anodes for aluminum electrolysis^①

XIAO Jin(肖 劲), LI Jie(李 杰), ZOU Zhong(邹 忠), HU Guo-rong(胡国荣),
LAI Yan-qing(赖延清), LIU Ye-xiang(刘业翔)

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

Abstract: On the base of filtering composite additives in laboratory, the industrial property-modified prebaked carbon anodes containing composite additives were prepared in factory. The performance tests show that this kind of anodes not only have the same excellent physical performance as common (contrasting) ones used in aluminum electrolysis production at the present time, but also have better chemical and electrochemical performance than that of the common ones. Furthermore, the industrial preparation of the property-modified prebaked anode lays the foundation of electrolysis test. It can be forecasted that property-modified anodes will have good behavior in aluminum electrolysis production.

Key words: aluminum electrolysis; property-modified prebaked carbon anode; industrial preparation; performance

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1 INTRODUCTION

It is well known that aluminum electrolysis is a "large family" of electroenergy consumption. In the meantime, carbon anodes are used up continuously in the process of electrolysis, so the aluminum electrolysis is also called "large family" of carbon consumption. For a long time, it has been a focus, to which aluminum metallurgical researchers and relative specialists give much attention. As for energy consumption, many ways were adopted to save electric energy, such as enlarging volume capacity of single cell, popularizing and developing large-scale prebaked anode electrolysis cell^[1-3], optimizing technical condition of electrolysis process, enhancing autocontrol level of electrolysis production in order to reduce manmade influence^[4-6], improving cathode structure and performance of electrolysis cell in order to prolonging using life of cathode^[7, 8] and so on. Furthermore, Much laboratory research by adopting anode doping technology has been done to reduce anodic overvoltage in process of electrolysis^[9-14]. For recent ten years, the anode additive technology used in Söderberg cell had brought considerable economic and social benefit, and had been recognized by many aluminum factories. By using the experience obtained in Söderberg cell, people began to aim at prebaked anode cell, and obtained some study results in laboratory. As for carbon consumption, a lot of research results were obtained on how to reduce unit carbon consumption of anode. One of the economical and valid

methods, which benefits the factories where the technical conditions are difficult to be changed and the quality of raw materials used for production is not steady, is modifying anodic property. It is also one of the aluminum electrolysis research fields. The authors of this article acquired some results through several years' laboratory research, and pushed it to industrial test. The final goal is to extend it in large scope on the base of successful industrial test.

2 INDUSTRIAL PREPARATION

2.1 Pretreatment of additives

The additives must be pretreated before being added into anodes. It's a simple mechanical mixing of raw material (the compounds of Al, Mg, F and O), but it influences the property-modified effect of anodes. The three-dimensional mixing machine was adopted to mix additives (30-50 kg raw material) for 4.5 h in industrial test.

2.2 Industrial preparation

The preparation procedure of prebaked anodes includes crushing, calcining, grading, preheating, malaxating, shaping, baking and installing. The technological process is shown in Fig. 1. Thereinto, molten pitch was added into a malaxating machine from the entrance. Green crushing storage was chosen for feeding additives. The additives flowed into screw malaxating machine through electro-balance, and were mixed with raw materials of α

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Correspondence: XIAO Jin, Associate professor, Ph. D., + 86-731-8830984; bosun@public.cs.hn.cn

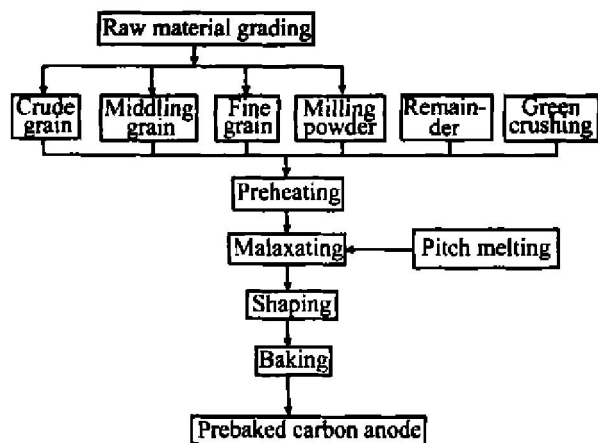


Fig. 1 Production flow of prebaked carbon anode

nodes (coke and pitch). After being shaped, the green anodes containing additives were prepared. These anodes would become property-modified ones when they were baked for enough time.

During industrial test, more than 700 blocks of property-modified anodes were prepared. Appearance examining showed that 98% of the property-modified anodes were up to grade, and the passing rate was higher than that of common ones prepared under the same technical conditions (as listed in Table 1).

Table 1 Comparison between property-modified anodes and common ones

Anode type	Passing rate/ %	Average mass/ kg
Property-modified	98.78	737.2
Common	98.54	744.8

3 PHYSICAL PERFORMANCE

3.1 Sampling of testing anode

Table 2 Physical performance of property-modified anodes and common anodes

Sample	w (ash) / %	Real density / (g·cm ⁻³)	Bulk density / (g·cm ⁻³)	Compression strength / MPa	Resistivity / (Ω·m)
P-M A1	1.28	2.07	1.49	31	58
P-M A2	0.81	2.07	1.48	29	59
P-M A3	1.16	2.06	1.46	30	59
Contrast anode 1	0.41	2.05	1.48	32	57
Contrast anode 2	0.38	2.05	1.46	33	59
Contrast anode 3	0.38	2.06	1.51	32	58
TY-1	≤0.5	≥2.0	≥1.5	≥29	≤55
TY-2	≤1.2	≥2.0	≥1.5	≥29	≤63

P-M A —Property-modified anode; TY —Standard anode

The mass of an industrial anode is ≥700 kg with a large surface area (the size of an anode is 1 450 mm × 660 mm × 540 mm). In order to enhance the reliability and comparability of testing results, the samples were got from the place of central line on the top of anode. The testing items include physical, chemical and electrochemical performance. The size of the sample is $d50$ mm × 150 mm.

3.2 Physical performance

The physical performance of property-modified anodes and common ones were tested in factory (as listed in Table 2). The physical performance examining standard of anodes used in carbon factory is also listed in Table 2.

From Table 2, we can see that, the ash content of property-modified anodes is higher than that of the common ones. The reason is that the additives are powder materials. Of course, these “ash” will not affect other physical performances such as resistivity, bulk density and so on. Furthermore, they will not “pollute” electrolysis products. In addition, the compression strength of property-modified anodes reduce slightly comparing with the common anodes, but they are still satisfy the standard. So do the resistivity and real density. In conclusion, the physical performances of property-modified anodes accord with the production demand.

4 CHEMICAL PERFORMANCE

The chemical performance includes the reaction rate of anodes with air and CO₂. The testing condition was as follows. The reaction time was 7 h; the reaction temperature was 970 °C (reacting with CO₂) and 500 °C (reacting with air), respectively; the size of samples was $d 50$ mm × 50 mm.

Table 3 lists the results of the reaction rate (*R*) of industrial property-modified anodes and the common ones with air and CO₂. Table 3 also lists the boiling rate of air and CO₂ in industrial property-modified anodes and the common ones.

Table 3 Chemical performance of industrial property-modified anodes and common ones

Anode	R_{Air} (mg·cm ⁻² ·h ⁻¹) (550 °C)	Boiling rate of air/ %	R_{CO_2} (mg·cm ⁻² ·h ⁻¹) (980 °C)	Boiling rate of CO ₂ / %
P-M A1	18.79	99.52	17.20	98.66
P-M A2	19.66	99.74	17.83	98.74
CA1	41.56	97.77	24.90	91.05
CA2	40.84	97.54	28.45	90.60

P-M A—Property-modified anode; CA—Common anode

Table 3 shows, under the same preparation condition, the industrial property-modified anodes have more excellent resisting capability being corrupted by air and CO₂ than that of the common ones. Furthermore, the air oxidation rate (R_{Air}) of industrial property-modified anodes is less than that of the common ones, and the CO₂ oxidation rate (R_{CO_2}) of the former is about 60%–70% of that of the later. From these, it can be forecasted that industrial property-modified anodes can reduce carbon consumption when they are used in aluminum electrolysis production.

5 ELECTROCHEMICAL PERFORMANCE

The electrochemical performance of carbon anodes is related greatly to electro energy consumption. After finishing industrial preparation, the electrochemical performance of industrial property-modified anodes was tested in laboratory. So did the common ones under the same condition. The testing system was Na₃AlF₆-Al₂O₃ molten electrolyte (with 10.9% AlF₃-5% CaF₂, mass fraction), the electrolysis temperature was 970 °C, and the analytical pure Na₃AlF₆ and α-Al₂O₃, the industrial pure AlF₃ and CaF₂ were adopted. In experiment electrolysis cell was set in the Ar ambience, and the anode area was controlled by sintering alumina thimble fixed on anode. The tested anode was fixed on the middle axes of graphite crucible through a piece of corundum with a hole in the middle part in order to keep the current density of anode distributing evenly. The lateral of anode uncovered by sintering alumina thimble was employed as experiment anode and the inner lateral of graphite crucible was employed as cathode. It was convenient for the carbon dioxide produced in anode reaction to separate out, and it could reduce the fluctuating of anode voltage.

The testing current was supplied through Model 273A Potentiostat/Galvanostat. The voltage between carbon anode and aluminum reference electrode was determined by cut current technology. Model 800 current interrupters

(made in Electrosynthesis Company, Virginia, USA) with fast switching times were used. The performance parameter is as follows. The permitted maximum current was 10 A. The switching time was 1 μs. The duration of current interruption was 10⁻⁴–40 μs.

Fig. 2 shows the relation between overvoltage and current density of property-modified anodes and the common ones, and linear regression was adopted to deal with the Tafel curve in Fig. 2. From the results, we can know, when the anode current density is 1 A/cm², the average overvoltage of property-modified anodes is lower by 52 mV than that of the common ones. It indicates that property-modified anodes have good result of reducing anode overvoltage.

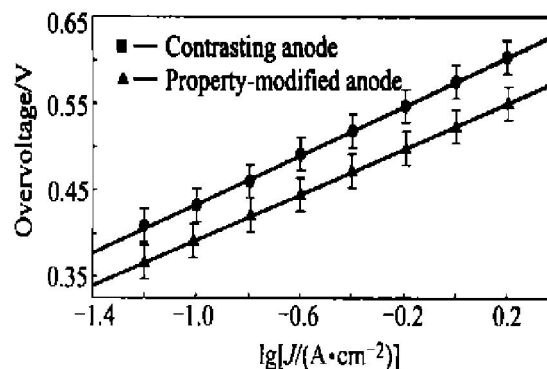


Fig. 2 Comparison of Tafel curve between property-modified anode and common one

As a result, the property-modified prebaked anodes which prepared in industrial production have good physical, chemical and electrochemical performance, and they can be applied for aluminum electrolysis production.

6 CONCLUSIONS

- 1) With ordinary production process, accessional equipment and logical entrance for additives, batch of industrial property-modified anodes are prepared successfully.
- 2) The physical performances of property-modified prebaked anodes satisfy the demand of production.
- 3) Under the same condition, the property-modified prebaked anodes have better performance of resisting air and CO₂ corruption than the common ones.
- 4) When the anode current density is 1 A/cm², the average overvoltage of property-modified anodes is lower by 52 mV than that of the common ones, which indicates that property-modified anodes have good result of reducing anode overvoltage.

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