AL18 - Application of Nano-Ceramic Anti-Oxidation Coating on Anodes of Aluminum Reduction Pots

Boyi Wang[1] and Bo Hong[2]
1. Hunan Bable Material Technology Co. LTD, Changde, Hunan, China
2. CHALIECO GAMI, Guiyang, Guizhou, China
Corresponding author: 2705967@qq.com

Abstract

Anodes are the heart of aluminium reduction pots. The reduction of anode oxidation and anode oxidation rate and the improvement of anode service life have always been a topic of great interest in aluminum reduction research. This article introduces the anti-oxidation mechanism of nano-ceramic-based anode anti-oxidation coating materials and presents: the results of in-depth research on the anode anti-oxidation effect of these materials in different bath systems and pot types; the testing of the impact of carbon block baking weight loss rate on anode anti-oxidation; and finally, a set of testing methods and application standards established for nano-ceramic-based anode anti-oxidation coatings. The recognition and application of this product in smelters have effectively reduced the instability of aluminum reduction pots, and also improved the quality of liquid aluminum. Practice has proven that this product can reduce the anode gross consumption by 15-25 kg/t Al and the power consumption by 20-50 kWh/t Al.

Keywords: Aluminium reduction pot anodes, Anode anti-oxidation nano-ceramic coating material.

1. Introduction

In a cryolite-alumina prebaked pot, the quality of carbon anodes has a direct influence on the production index of aluminum reduction. When the carbon anode fails to meet the quality requirement, it will generate abundant carbon residues in the bath and bring a series of hazards to pot [1-2]. To reduce carbon residues, high-quality carbon anodes must be used, and a careful operation and a meticulous process management must be adopted. As the availability of high-quality calcined coke decreases and the production costs need to be cut down, high-sulfur and high-vanadium cokes are widely used, resulting in poor anode quality and lower oxidation resistance, which have negative influence on aluminum production. In order to improve the oxidation resistance of anodes and reduce carbon residues, anode coating technologies have been extensively tested in China [3-6].

Currently, nano-ceramic-based anti-oxidation technology is the most widely applied anti-oxidation coating technology in China [7-8]. This technology involves the application of an anti-oxidation coating on the surface of a carbon anode, which has the advantages of being able to solidify at room temperature, quick drying, convenient construction, non-toxic, high-temperature resistance, excellent anti-corrosion performance, high hardness, good adhesion, non-stick, etc. Based on field data from different pot lines, this paper digs into the influence of the nano-ceramic-based coating on aluminum production index, so as to provide reference for application of this technology on a large scale [9-10].

2. Anti-oxidation Mechanism of Nano-Ceramic-Based Anode Coating

Nano-ceramic-based anti-oxidation anode coating mainly consists of a matrix, a solvent and an additive. The main components include:

- Alumina components: Al_2O_3, accounting for 45-50 % of the total mass of the coating.

- Alkali metal grain boundary fusion components: composed of plagioclase ore powder, albite, and sodium fluorosilicate, accounting for 2 to 3 % of the total mass of the coating.
- Silicone sol reinforcement components: silica sol, accounting for 25-30 % of the total mass of the coating.
- Continuous modification components of silane coupling agent: silane coupling agent, accounting for 0.3-0.8 % of the total mass of the coating.
- Crystal control components: composed of ytterbium(III) oxide and erbium(III) oxide, accounting for 0.001 % of the total mass of the coating.
- Flow control components: water, accounting for 16.2-27.7 % of the total mass of the coating.

Nano-ceramic-based anti-oxidation anode coating uses aluminum oxide as the basic structure skeleton, and silica sol as the reinforcing component to obtain the basic body with: dense structure, high strength, strong viscosity, self-healing. The alkali metal grain boundary fusion component, which constitutes of a certain proportion of plagioclase ore powder, albite, and sodium fluorosilicate, enables the basic body to be sintered at a low temperature of 400~420 ℃ to form a dense sintered body. At the same time, alumina is modified with silane coupling agents to improve the dispersion, stability, film-forming ability, heat resistance, and other properties of the coating components. By controlling the addition of components through crystal morphology, the high strength and toughness of the entire coating after sintering can be improved.

When nano-ceramic-based anti-oxidation anode coating is sprayed on the surface of an anode, as the anode temperature increases, the grain of coating material shrinks and the crystal gap decreases. Pre-sintering is completed at 400~500 ℃, and a high-strength and dense-network-structure sintered body is formed around the anode. The sintered body can withstand high temperatures above 900 ℃ for a long time, and can resist the carbon loss due to air, hydrogen fluoride gas, and high concentration CO_2, ultimately achieving the goal of preventing anode oxidation.

3. Anti-oxidation Tests for Different Pots and Bath Systems

The nano-ceramic-based anti-oxidation anode coating has been tested at multiple smelters ranging from 240~500 kA and in different bath systems including a pure bath system and a complex bath system. The testing result can be seen as Table 1 shows.

Table 1. Anode coating test results.

Test elements	Smelter 1	Smelter 2	Smelter 3	Smelter 4	Smelter 5
Current (kA)	240	300	400	500	500
Bath system	pure	complex	complex	pure	pure
Voltage (V)	3.96	3.99	3.97	4	3.99
Noise (mV)	17	19	18	18	20
Pot temperature (°C)	948	925	930	950	952
Anode carbon dioxide reactivity (%)	76	81	71	80	83
Anode cycle(day)	32	33	34	33	35
Quantity of test pot	10	4	4	48	37
Test period (months)	5	5	6	6	12
Reduction in carbon residues (%)	54	43	61	45	38
Extension in anode change schedule (day)	1.33	1	1.66	1	1

From Table 1, it can be seen that the nano-ceramic based anti-oxidation anode coating can extend the anode change schedule for more than one day regarding different pot lines and bath systems. The discrepancies in current intensity and bath components do not affect the anti-oxidation effect of the anode coating. For pots with worse anode qualities, the anode coating has a better effect on reducing carbon residue and extending anode change schedule. For pots with louder noise and poor stability, the effect of the anode coating is weakened.

4. Technical Standard of Nano-Ceramic-Based Anti-Oxidation Anode Coating

To improve the applicability of the anode coating, a technical standard has been established on the basis of tests on multiple pot lines as seen in Table 2.

Table 2. Technical standard of nano-ceramic anti-oxidation anode coating.

S.N.	Test elements	Standard	Test method
1	Anti-oxidation performance detection: baking losses	＜1.5 %	Weight loss of carbon rods coated with the coating material after 72 hours of calcination at 900 ℃ in a muffle furnace.
2	pH value	12.0～13.0	Glass rod, universal pH test paper, alkaline pH precision test paper (or acidity meter)
3	Viscosity	＞10000 mPas	Viscometer at 20 ℃
4	Density	1.90～2.00 g/cm^3	Mixer, stirring paddle, electronic scale, 500 mL measuring cylinder

The most important parameter in Table 2 is the anti-oxidation performance detection (baking losses), which is measured from the weight loss of the coated carbon rod after 72 hours of calcination at a temperature of 900 ℃. The greater the weight loss of the carbon rod is, the poorer the anti-oxidation effect of the coating is, and the smaller the effect of reducing the carbon residue is. The anode coatings with different anti-oxidation performances (baking losses) are tested, and the results are shown in Table 3.

Table 3. Comparison of the effect of coatings with different baking losses.

Test elements	Anti-oxidation performance detection (baking losses) (%)	Changes in carbon residue (%)	Increase in butt thickness (mm)	Extension in anode change schedule
Coating 1	8	no change	2	can be ignored
Coating 2	6	no change	3-4	4-6 hours
Coating 3	3	10-20	7-8	8-12 hours
Coating 4	2	20-30	7-9	12 hours
Nano-ceramic-based coating 1	1.5	30-70	14-16	more than 1 day
Nano-ceramic-based coating 2	1	30-80	15-18	more than 1 day

From Table 3, it can be seen that the lower the anti-oxidation performance detection (baking losses) is, the better the effect of reducing the carbon residue is, and the thicker the butt is. When the baking losses are lower than 1.5 %, the anode change schedule can be extended by one day, bringing greater economic benefits.

5. Influence of Nano-Ceramic-Based Anti-Oxidation Anode Coating on Pot Performance

Tests over a period of 12 months have been carried out in three of the six sections with 400 kA pot lines while the remaining three sections were kept the same for comparison (standard). This pot line applies three purification systems for sections 1-1 and 2-1, 1-2 and 2-2, and 1-3 and 2-3, respectively. In order to have a better comparison, each purification system was applied to one experimental section, and the sections are distributed in different smelters. The overall statistical results are shown in Table 4.

Table 4. Average production index (June 2021 ~ May 2022).

Section		Noise (mV)	Current consumption (kWh/t Al)	CE (%)	Gross anode loss (kg/t Al)	Primary aluminum mass	
						Si (%)	Fe (%)
Coated sections	1-1	15	12819	91.3	463	0.03	0.08
	1-2	15	12872	92.0	467	0.03	0.07
	1-3	16	12858	92.0	466	0.03	0.07
	Avg. value	15	12850	91.8	465	0.03	0.07
Standard sections	2-1	15	12847	92.0	485	0.03	0.08
	2-2	17	12911	90.8	480	0.03	0.09
	2-3	17	12899	91.4	476	0.03	0.09
	Avg. value	16	12886	91.4	481	0.03	0.08
Difference		1	-36	0.4	-15.4	0.00	-0.01

5.1 Influence on Noise Level

The noise data of coated sections and the comparison with those of standard sections are shown in Figure 1.

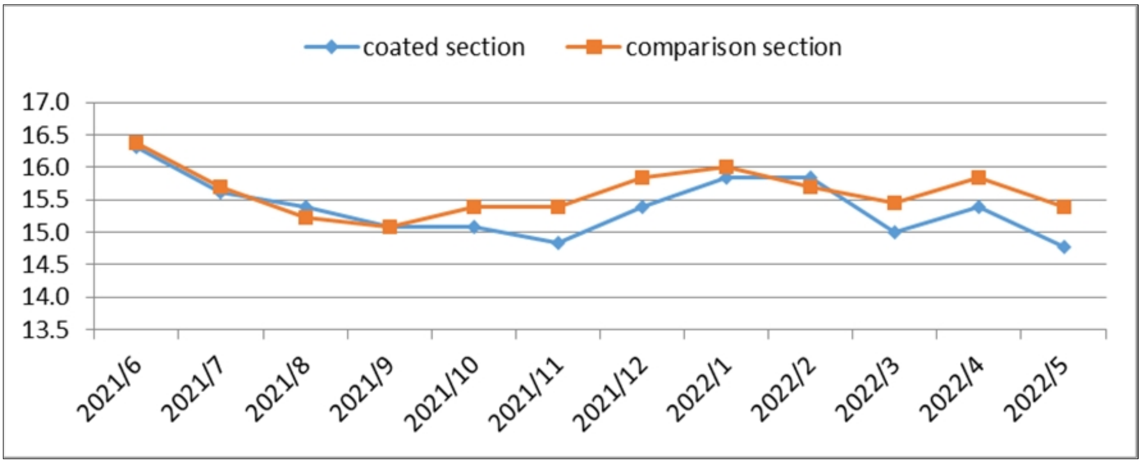

Figure 1. Noise (mV) of coated sections and standard sections.

From Figure1, it can be seen that the noise of the coated sections and the standard sections were basically similar before using the anode coating. After 4 months of applying the anti-oxidation anode coating, the noise of coated sections was significantly lowered. The coating can reduce the carbon content in the bath, lower the bath resistance, increase effective anode-cathode distance, and improve the pot stability. The noise is a comprehensive reflection of pot stability; when the pot stability increases, the pot cavity will be more regular and the noise level will drop.

5.2 Influence on Power Consumption

The power consumption data of coated and standard sections are shown in Figure 2.

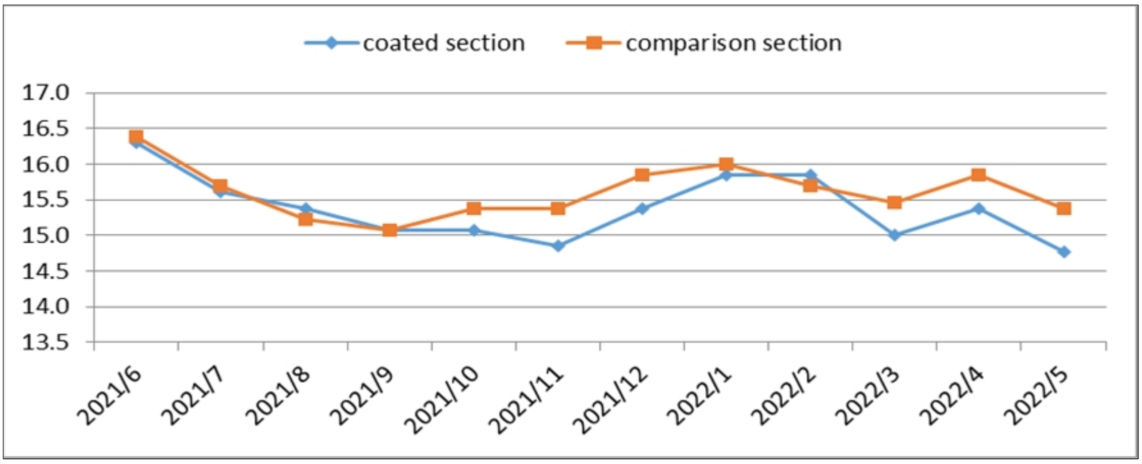

Figure 2. Power consumption of coated and standard sections.

From Figure 2, it can be seen that the power consumption data of coated sections and standard sections were basically similar before using the anti-oxidation anode coating. After 4 months of applying the coating, the power consumption of coated sections decreased compared to standard sections. After one year, the power consumption of coated sections was reduced by 36 kWh/t Al. The coating helps reduce the surface oxidation of anode carbon block and carbon residues and decrease the bath resistance, which are beneficial for the reduction of power consumption. Meanwhile, the coating can prolong the anode change schedule for one day so that one anode change operation can be saved, reducing interference for pot and additional voltage for anode change. This way, the power consumption can be decreased as well.

6. Influence on Current Efficiency

The current efficiency data of coated and standard sections are shown in Figure 3.

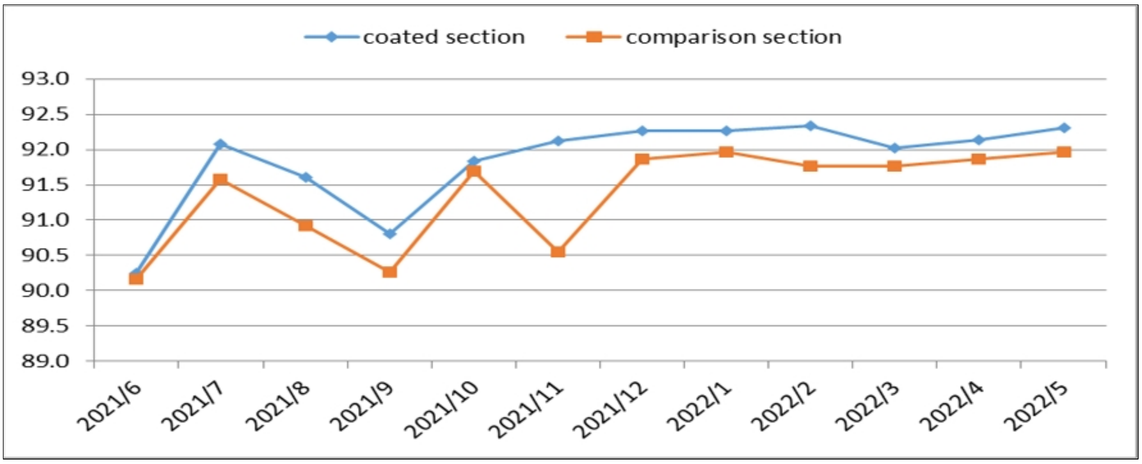

Figure 3. Current efficiency (%) of coated and standard sections.

From Figure 3, it can be seen that the current efficiencies of coated sections and standard sections were basically similar for the first month. From the second month on, the current efficiency of coated sections was higher than that of standard sections, and it increased by 0.4 % after one year.

After applying the anti-oxidation anode coating, the anode oxidation has been reduced, the anode shape was more regular, and the anode current density was lower. Under the same voltage, effective anode distance is higher and current efficiency is improved.

6.1 Influence on Gross Anode Consumption

Anode gross consumption data of coated section and comparison are shown in Figure 4.

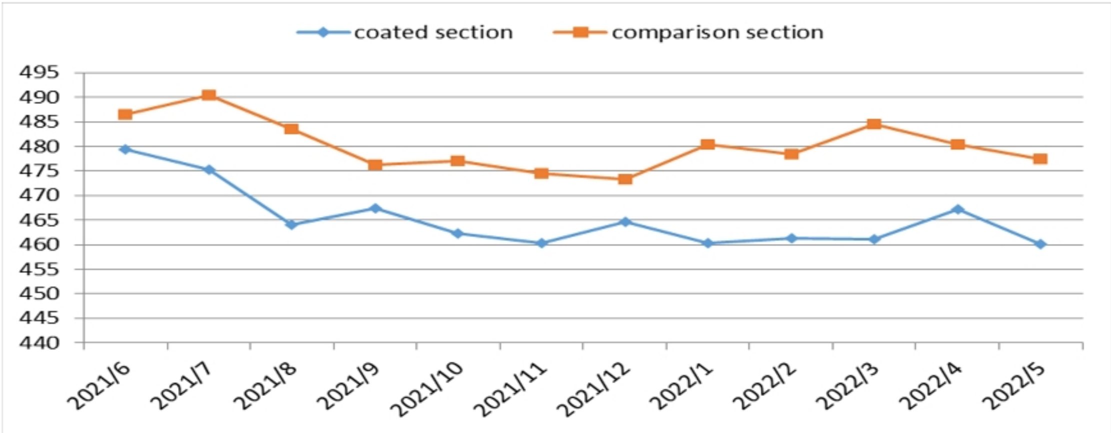

Figure 4. Gross anode consumption (kg C/t Al) of coated and standard sections.

Coating can notably reduce the gross anode consumption up to 15.4 kg C/t Al after one-year application. The anode surface is sprayed with the coating material to form a high-strength, dense-network-structure body, which can isolate the anode and prevent any contact with air and CO_2 so as to avoid the redox reaction between anode and oxidizing gas as well as the Boudouard reaction between anode and CO_2. This way, the gross anode consumption is also reduced.

6.2 Influence on Si and Fe Contents of the Aluminum Produced

From Table 4, it can be seen that there is a little difference between the coated and standard sections in the silicon content of the aluminum produced. Although the application of nano-ceramic based anti-oxidation anode coating (containing silicon elements) may introduce some silicon, the small amount has limited the impact on the silicon content in the aluminum produced. The comparison of iron content in aluminum produced in the coated and standard sections is shown in Figure 5.

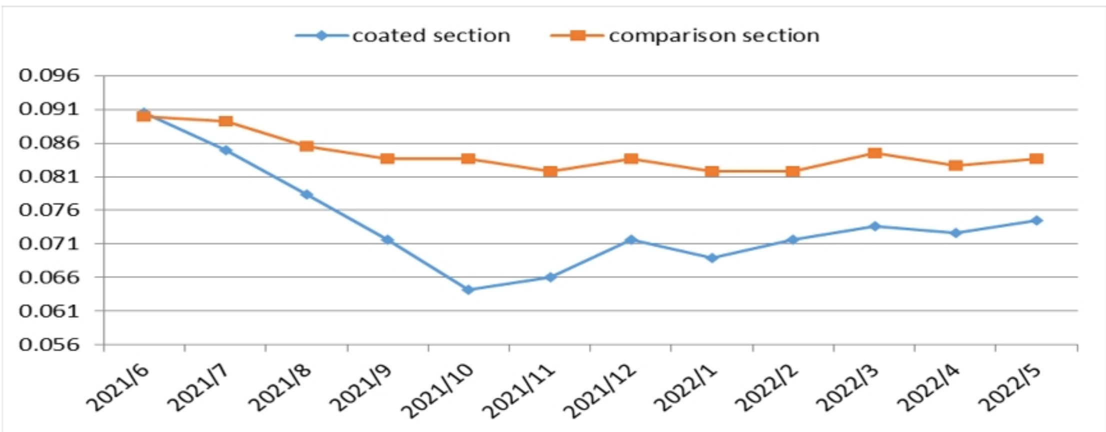

Figure 5. Iron content (%) in aluminum produced in the coated and standard sections.

From Figure 5, it can be seen that the coating can reduce the iron content of aluminum produced. After one year, the iron content of coated sections is 0.01 % lower than that of standard sections. After applying the coating, the thickness, length, and the width of the butt in the coated sections were less consumed than those in the standard sections on the condition that the anode change cycle is extended for one day. As the thickness of the butt is relatively greater, the ability to resist scratching, melting, and bottom penetration is enhanced, and the iron content in the aluminum produced is reduced. At the same time, the stability of the pot in the coated sections is improved, and the pot cavity is more stable, which is also beneficial for improving the quality of the aluminum.

7. Conclusions

A technical standard has been established through tests on nano-ceramic-based anti-oxidation anode coating applied to different pot lines and bath systems.

The conclusions are as follows:

1. The anti-oxidation performance detection (baking losses) shall be less than 1.5 % for the nano-ceramic-based anti-oxidation anode coating to extend anode the change schedule for one day.
2. The application of nano-ceramic-based anti-oxidation anode coating has a positive effect on reducing noise level, power consumption, and gross anode consumption, as well as improving current efficiency and quality of aluminum produced.
3. The nano-ceramic-based anti-oxidation anode coating can reduce the gross anode consumption by 15-25 kg/t Al, and reduce the energy consumption by 20-50 kWh/t Al, which would generate economic benefits.

8. References

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