Application Research of Nano-Ceramic-Based Anti-Oxidation Technology for Anodes and Stubs in Aluminium Electrolysis Cells

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Abstract

This paper conducts an anode anti-oxidation test by spraying nano-ceramic-based high-temperature anti-oxidation coating material on the surface of pre-baked anodes and stubs. The test lasted for five anode changing cycles (about half a year). The test results show that the long-term application of the anode anti-oxidation coating material can effectively reduce the oxidation of carbon blocks and stubs. It plays a significant role in maintaining the regularity of the anode shape. The coated anode can extend the anode changing cycle by one day compared with the uncoated anode. After long-term application, the anode anti-oxidation coating material has no side effect on the quality grade of aluminium.

Coated anode stubs increase smoothness of the stub surface and decrease the occurrence of “narrow neck”. The lifespan of the coated stubs can be extended by 2.9 times. The metal purity can significantly increase by reducing the iron content in aluminium by 280 ppm.

Keywords: Aluminium electrolysis cells, Anode anti-oxidation nano-ceramic-based coating, Anode stubs anti-oxidation nano-ceramic-based coating, Long-term industrial tests.

1. Introduction

At present, the aluminium industry production uses the cryolite-alumina molten salt electrolysis method, in which molten cryolite serves as the solvent and alumina as the solute. Using a carbon body as the anode, after passing a strong direct current, an electrochemical reaction occurs at both poles in the electrolytic cell at a high temperature of approximately 950 °C, i.e., electrolysis. The anodic oxidation products are mainly CO_2 and CO gases, which contain a certain amount of harmful gases such as hydrogen fluoride and solid dust [1]. These gases easily react with the carbon anode and steel stub at high temperatures, leading to the oxidative consumption of the carbon anode and the oxidative corrosion of the steel stub.

In recent years, the main anti-oxidation research on anodes and steel stubs has included: (1) Anode anti-oxidation: anode production process management, anode production formula and process anti-oxidation technologies, and coating material anti-oxidation technologies [2–6]; (2) Steel stub anti-oxidation: anode covering material management, anode steel stub protection rings (divided into residual pole powder, carbon, aluminium ash, alumina, metal-based, covering material-based protection rings), coating technologies, wrapping technologies, etc.[7–15]. Among these methods and technologies, the coating anti-oxidation technology has shown better application effects.

As a surface treatment anti-oxidation method, the nano-ceramic-based coating anti-oxidation technology is a newly emerging technology in recent years. The coating has the advantages of room-temperature curing, rapid drying, convenient construction, non-toxicity, high temperature resistance, excellent corrosion resistance, high hardness, good adhesion, and non-stickiness. As the temperature gradually increases, the coating material grains shrink and the crystal gaps decrease, completing pre-sintering at 400–500 °C. Finally, a high-strength and dense networkstructured sintered body is formed on the surfaces of the anode and steel stub. This sintered body can withstand high temperatures above 900 °C for a long time and resist the erosion of air, hydrogen fluoride gas, and high-concentration CO_2, ultimately achieving the purpose of preventing the oxidation of the anode and steel stub.

The author's paper published in ICSOBA 2023 [16] focuses on exploring the anti-oxidation mechanism of nano-ceramic-based anode anti-oxidation coating materials, conducting in-depth research on their anti-oxidation effect in different bath systems and pot types, and testing the impact of carbon block baking weight loss rate on anode anti-oxidation. It sets testing methods and application standards for such coatings, proving they can reduce aluminium reduction pot instability and improve primary aluminium quality, cutting anode gross consumption by 15–25 kg C/t Al and power consumption by 20–50 kWh/t Al.

This paper conducts a large-scale industrial application study on anode and steel stub anti-oxidation using the BY series nano-ceramic-based anti-oxidation technology [17, 18], aiming to provide data reference and economic accounting for the popularization and application of anti-oxidation coating materials for anodes and steel stubs.

2. Anode Anti-Oxidation Coating

2.1 Anode Anti-Oxidation Application Process

2.1.1 Industrial Tests

This long-term industrial application test was carried out on 400 kA electrolytic cells in an aluminium plant in Shaanxi. The test included 4 test cells (No. 4321, No. 4322, No. 4323, No. 4324) and 4 comparison cells (No. 4315, No. 4316, No. 4317, No. 4318). The test lasted for 5 anode changing cycles from 25 September 2019 to 15 March 2020 and the results of the long-term industrial application were continuously tracked.

The first test cycle (25 September–28 October): The anode changing cycles of both the test cells and the comparison cells were 34 days. Before the new anodes were put into the cells, the heights of the coated new anodes in the test cells and the uncoated new anodes in the comparison cells were measured. The main test purpose of this cycle was to gradually replace the uncoated anodes in the test cells with coated new anodes.

The second test cycle (29 October–1 December): The anode changing cycles of both the test cells and the comparison cells were 34 days. The dimensions (length, width, and height) of the butt anodes in the test cells and the comparison cells that were put into the cells in the first cycle were measured every day. The main test purposes of this cycle were: 1) to stabilize the cell condition and reduce the impact of the mixture of coated and uncoated anodes on the test results in the early stage; 2) to provide data basis for whether to extend the service cycle of the coated anodes in the third cycle by measuring the dimensions of the butt anodes in the test cells and the comparison cells.

The third test cycle (2 December–5 January): The anode changing cycle of the test cells was 35 days, and that of the comparison cells was 34 days. The dimensions (length, width, and height) of the butt anodes in the test cells and the comparison cells that were put into the cells in the second cycle were measured every day. The main test purpose of this cycle was to provide experimental data results for extending the service cycle of the coated anodes by measuring the dimensions of the butt anodes in the test cells and the comparison cells.

The fourth test cycle (6 January–10 February): The anode changing cycle of the test cells was 35 days, and that of the comparison cells was 34 days. The dimensions (length, width, and height) of the butt anodes in the test cells and the comparison cells that were put into the cells in the third cycle were measured every day. The main test purpose of this cycle was to provide data basis for the long-term application of the coated anodes by measuring the dimensions of the butt anodes in the test cells and the comparison cells.

The fifth test cycle (11 February–15 March): The anode changing cycle of the test cells was 35 days, and that of the comparison cells was 34 days. The dimensions (length, width, and height) of the butt anodes in the test cells and the comparison cells that were put into the cells in the fourth cycle were measured every day. At the same time, the weights of some butt anodes in the test cells and the comparison cells were randomly checked. The main test purposes of this cycle were to provide experimental data results for the long-term application of the coated anodes by measuring the dimensions of the butt anodes in the test cells and the comparison cells; and to judge the impact of the coating material on the cell condition during the long-term application period.

The quality of primary aluminium was tracked during the five cycles.

2.1.2 Consumption of the Coating Material

The consumption of the coating material is determined by the roughness of the anode surface and the spraying method. During this application process, the average consumption of the coating material was 1.85 kg/m^2, the coating area of each anode was 2.03 m^2, and the average spraying consumption per anode was 3.76 kg. The average consumption per tonne of aluminium was about 1.76 kg. Since this test was carried out in winter, the room temperature during spraying was low, resulting in poor fluidity of the coating material. In addition, the number of anode blocks sprayed each time was small, and there were many bonding issues in the spraying equipment. After large-scale implementation, the consumption per tonne of aluminium should not exceed 1.6 kg.

2.1.3 Figures of Application

Figure 1 shows a coated new anode and Figure 2 anode butts.

Figure 1. Coated new anode, before enter the cell (left) and during entering the cell (right).

From Figure 2, it can be seen that the butt of the coated anode is thicker and its shape is more regular, while the butt of the uncoated anode is thinner and its corner oxidation is more severe than that of the coated anode.

Figure 2. Coated anode butt in test cell (left) and uncoated anode butt in comparison cell (right).

2.2 Application Results and Analysis

2.2.1 Butt Dimensions in the Second Cycle

Comparison of butt dimensions in the second cycle is shown in Table 1.

Table 1. Butt dimensions in the second cycle (all average values within the cycle).

Project	**Butt length/mm**	**Butt width/mm**	**Butt height/mm**	**New anode height/mm**	**Actual consumption height/mm**
A: Test Anode	1622.0	638.9	556.6	1001.3	444.3
B: Comparison Anode	1606.6	621.3	544.6	1005.4	460.8
A-B	15.4	17.6	12.0	-4.1	-16.5

Comparison of Other performance data of the butts			
Project	A: Test anode	B: Comparison anode	Difference A-B
Corner oxidation rate	1 %	14 %	-13 %
Proportion of consumption over 480 mm	0.5 %	10.4 %	-9.9 %
Number of shadows	0	0	0
Number of anodes with exposed stubs from bottom	0	0	0
Height standard deviation (mm)	16.5	18.2	-1.8
Minimum height of 10 % of thinnest anodes (mm)	147.1	127.4	19.7

Notes:

1. In the table, A represents the test cell, and B represents the comparison cell.
2. For convenient measurement, the measured heights of the new anodes and the butt anodes are the distances from the bottom of the carbon block to the upper surface of the yoke.
3. Corner oxidation rate: The probability of oxidation at the four corners of the butt anode, reflecting the integrity of the geometric shape of the butt anode.
4. Proportion of consumption over 480 mm: The proportion of the number of anodes with a consumption height greater than 480 mm in the butt anodes. 480 mm is the safe consumption height for the anode to penetrate the bottom, and the proportion should not exceed 10 % of the total number of butt anodes.
5. Number of shadows: The number of anodes whose oxidation is about to expose the stubs but has not yet exposed them when viewed from the bottom, with the unit of "piece".

From Table 1, we can conclude that:

1) The test anode has met the requirement of extending the anode cycle by one day and yet, the probability of exposed stubs from bottom is very low.

2) The geometric shape of the test anode is better maintained, which plays a certain role in maintaining the stability of the electrolytic cell condition (reducing the electrolyte resistance, reducing the anode current density, reducing the electrolyte temperature, and reducing anode.
3) The anode butt thickness of test anodes is more uniform.

Comparison of the consumption heights of anodes in the second cycle is shown in Figure 3. We can see that the average consumption height of the test anodes is significantly below that of the comparison anodes.

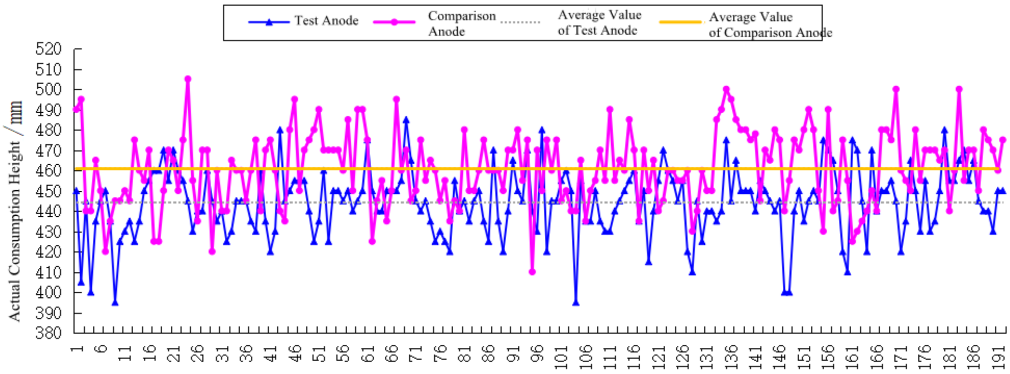

Figure 3. Consumption heights of test and comparison anodes in the second cycle. Horizontal axis is anode number.

2.2.2 Application Data of the Third Cycle

Comparison of butt dimensions in the third cycle is given Table 2.

Table 2. Butt dimensions in the third cycle (all average values within the cycle).

Project	Butt length/mm	Butt width/mm	Butt height/mm	New anode height/mm	Actual consumption height/mm
A: Test Anode	1631.7	633.8	542.8	997.9	455.1
B: Comparison Anode	1617.9	627.7	543.6	1002.0	458.4
A-B	13.8	6.1	-0.8	-4.1	-3.3

Comparison of Other performance data of the butts

Project	A: Test anode	B: Comparison anode	Difference A-B
Corner oxidation rate	1.6 %	8.3 %	-6.8 %
Proportion of consumption over 480 mm	4.2 %	9.9 %	-5.7 %
Number of shadows	8	7	1
Number of anodes with exposed stubs from bottom	0	0	0
Height standard deviation (mm)	18.5	18.1	0.3
Minimum height of 10 % of thinnest anodes (mm)	136	129	7

From Table 2, we can conclude that:
1) The dimensions of the butt of the test anode after extending the anode changing cycle by one day still have a slight advantage over those of the comparison anode.
2) The risk of bottom stub exposure of the test anode does not increase significantly due to the one-day extension of the anode changing cycle.

3) The test anode has a lower corner oxidation rate after extending the cycle by one day, and the test anode still has an advantage in maintaining the regularity of its geometric shape.
4) Among the thinnest 10% of butts in the total amount, the average thickness of the test group (coated anodes) exceeded that of the comparison group (uncoated anodes) by 7 mm using the same statistical method. This improvement is even more pronounced compared to the overall average thickness difference of -3.3 mm (Test Group - Comparison Group), indicating that the anode coating has significant effect on butt anode thickness. That means, the coating demonstrates a superior capability to increase thickness for thiner butt anodes.

Comparison of the anode consumption in the third cycle is shown in Figure 4. We can see that the consumption height curves of the test anode and the comparison anode intersect with each other. However, it can still be observed that after extending the cycle of the test coated anode by one day, its average consumption height is still slightly lower than that of the uncoated comparison anode.

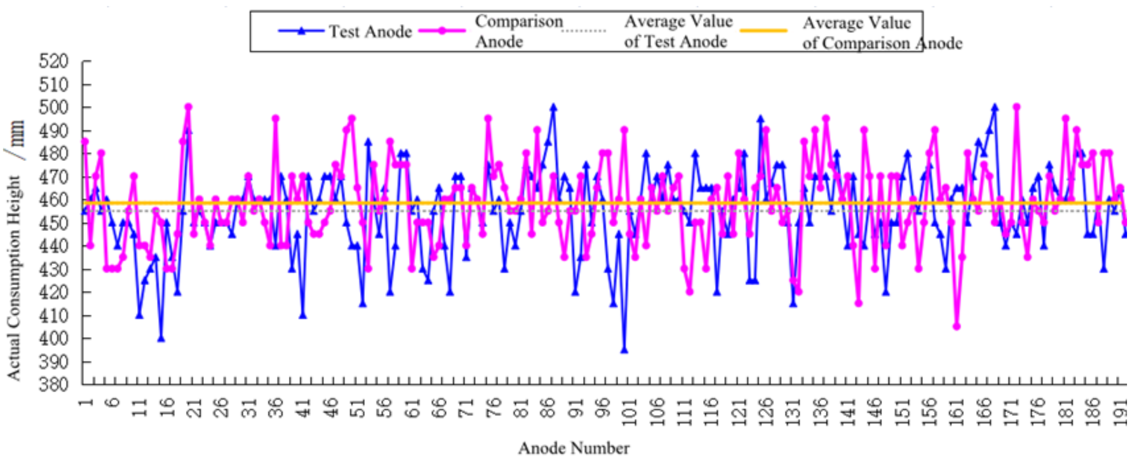

Figure 4. Consumption heights of test and comparison anodes in the third cycle.

2.2.3 Application Data of Fourth and Fifth Cycles

Comparison of butt dimensions in the fourth cycle is shown in Table 3.

Table 3. Butt dimensions in the fourth cycle (all average values within the cycle).

Project	Butt length/mm	Butt width/mm	Butt height/mm	New anode height/mm	Actual consumption height/mm
A: Test Anode	1618.9	630.9	548.3	998.6	450.3
B: Comparison Anode	1617.4	627.5	545.5	1003.4	457.9
A-B	1.5	3.4	2.8	-4.8	-7.6

Comparison of Other performance data of the butt

Project	A: Test anode	B: Comparison anode	Difference A-B
Corner oxidation rate	4 %	11 %	-7 %
Proportion of consumption over 480 mm	0.0 %	6.3 %	-6.3 %
Number of shadows	2	2	0
Number of anodes with exposed stubs from bottom	0	0	0
Height standard deviation (mm)	16.9	17.8	-0.9
Minimum height of 10 % of thinnest anodes (mm)	144.6	129.2	15.4

Comparison of the anode consumption in the fourth cycle is shown in Figure 5.

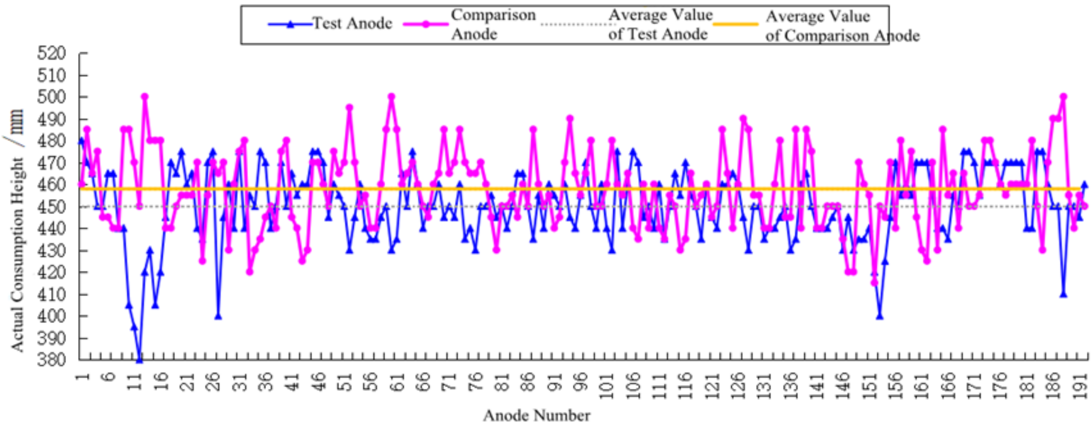

Figure 5. Consumption heights of test and comparison anodes in the fourth cycle.

Comparison of butt dimensions in the fifth cycle is shown in Table 4.

Table 4. Butt dimensions in the fifth cycle (all average values within the cycle).

Project	Butt length/mm	Butt width/mm	Butt height/mm	New anode height/mm	Actual consumption height/mm
A: Test Anode	1631.6	634.4	544.6	997.8	453.2
B: Comparison Anode	1627.4	630.7	544.4	1000.9	456.5
A-B	4.2	3.7	0.02	-3.1	-3.3

Comparison of Other performance data of the butt

Project	A: Test anode	B: Comparison anode	Difference A-B
Corner oxidation rate	3 %	7 %	-3 %
Proportion of consumption over 480 mm	4.2 %	14.1 %	-10.0 %
Number of shadows	1	1	0
Number of anodes with exposed stubs from bottom	0	0	0
Height standard deviation (mm)	15.2	20.5	-5.3
Minimum height of 10 % of thinnest anodes (mm)	143.0	132.0	11.0

From Tables 3 and 4, we can see that the test cell with an extended anode changing cycle of one day (35-day cycle) still has advantages over the comparison cell without extension (34-day cycle) in terms of actual consumption height, geometric shape regularity (length, width, corner oxidation rate), proportion of consumption over 480 mm, number of shadows and number of exposed stubs at the bottom.

It can be concluded that with the continuous test, the anti-oxidation effect of the coating material on the anode is still obvious. That is, the long-term application of the anode anti-oxidation coating material has a positive effect on reducing the carbon consumption of the anode.

Comparison of the anode consumption in the fifth cycle is shown in Figure 6.

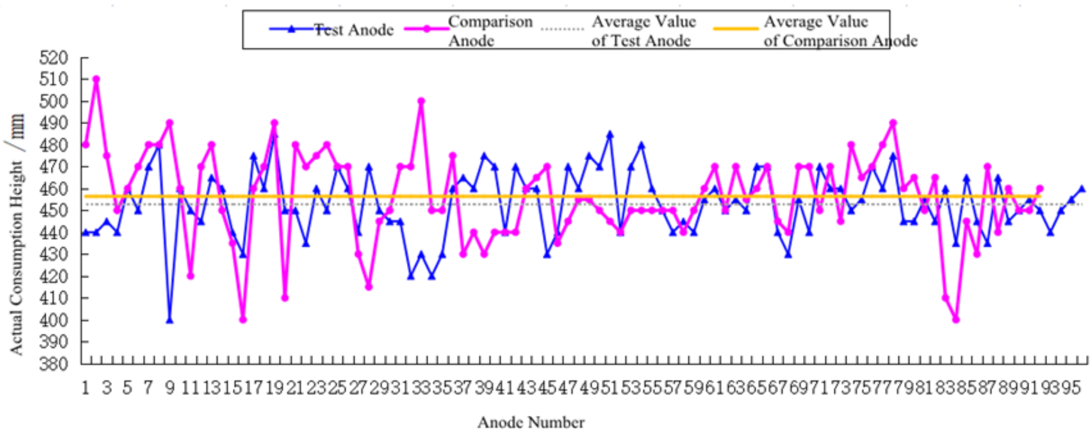

Figure 6. Consumption heights of test and comparison anodes in the fifth cycle.

2.3 Quality of Primary Aluminium

2.3.1 Results

Fe content in primary aluminium is shown in Figure 7 and Table 5.

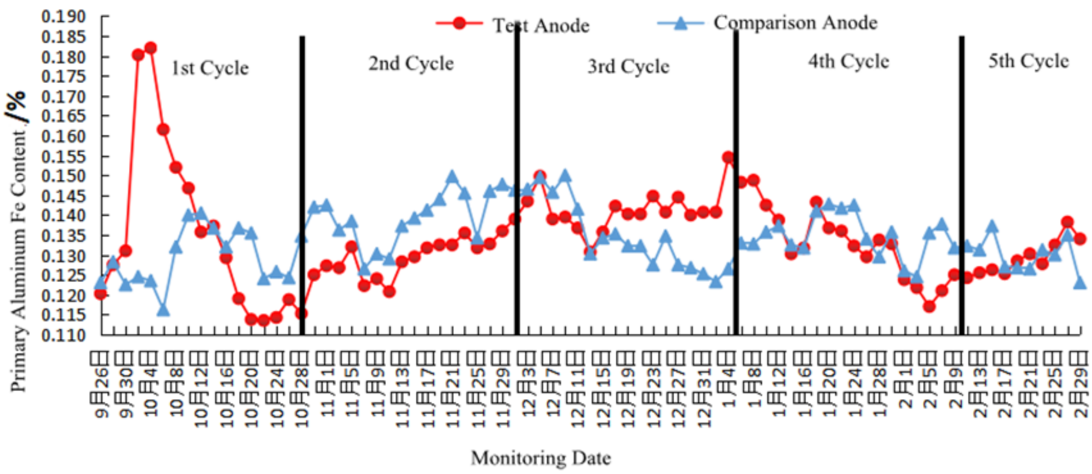

Figure 7. Average Fe content in primary aluminium.

Table 5. Average Fe content (%) in each cycle.

Time Period	Test Cell A	Comparison Cell B	A-B
The 1st Cycle	0.135	0.129	0.006
The 2nd Cycle	0.130	0.140	-0.010
The 3rd Cycle	0.141	0.135	0.007
The 4th Cycle	0.133	0.135	-0.002
The 5th Cycle	0.129	0.130	-0.001
Average situation after cycle extension (the 3rd to 5th Cycle)	0.135	0.134	0.001

Si content in primary aluminium is shown in Figure 8 and in Table 6.

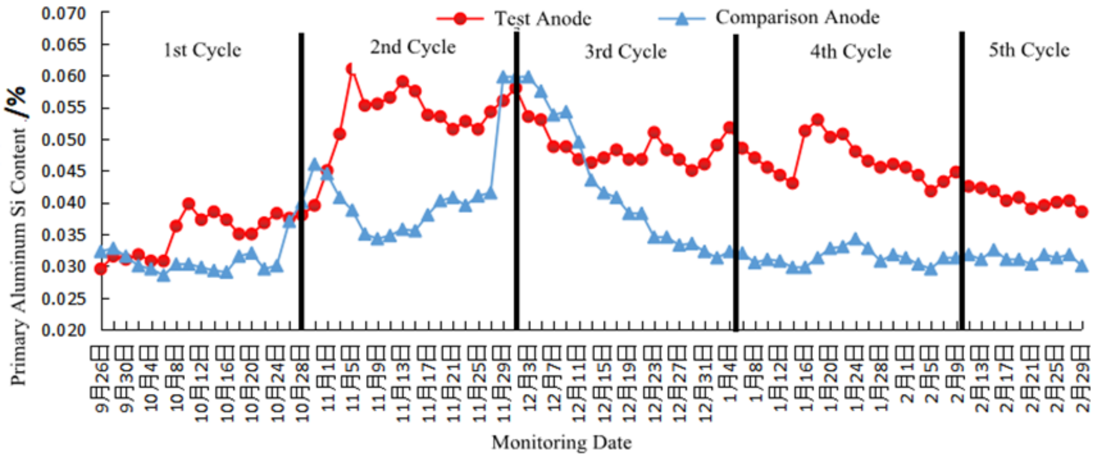

Figure 8. Average Si content in primary aluminium.

Table 6. Average Si content (%) changes in each stage.

Project	**① Pre-test period (6 September – 6 October)**	**② Post-Test Period (19 February – 29 February)**	**②-①**
A Test cell	0.0309	0.0397	0.0088
B Comparison cell	0.0308	0.0310	0.0003
A-B	0.0001	0.0087	0.0085

2.3.2 Data Analysis of Primary Aluminium Quality

1. As can be seen from Figure 7: 1) The Fe content in the test cell showed a significant downward trend in the first test cycle. 2) In the second cycle, the Fe content in the test cell was generally lower than that in the comparison cell. 3) In the third, fourth, and fifth cycles, the Fe contents in the test cell and the comparison cell fluctuated in an orderly manner, but the fluctuations were not significant.
2. As can be seen from Table 5: In the first cycle, the Fe content in the test cell was 0.006 % higher than that in the comparison cell. In the second cycle, it was 0.010 % lower. In the third cycle, it was 0.007 % higher. In the fourth cycle, it was 0.002 % lower, and in the fifth cycle, it was 0.001 % lower. This indicates that the Fe content in the test cell with coated anodes can be well controlled. Under the condition of an additional one-day anode changing cycle, the average Fe content in the test cell gradually decreased and became better than that in the comparison cell.
3. As can be seen from Figure 8: In the first two cycles, the Si contents in the test cell and the comparison cell fluctuated greatly. This was mainly because during this period, Cell no. 4337 in the work area was started up, the voltage was increased, causing the temperature of the furnace bottom plate to rise to 220 °C, and the silicon - iron increased rapidly. Starting from the third cycle, the Si contents in the test cell and the comparison cell gradually decreased and tended to be stable. However, the Si content in the test cell was slightly higher than that in the comparison cell, and the Si contents in both the test cell and the comparison cell were within the allowable range.
4. As can be seen from Table 6: The Si content in the test cell was higher in the later stage of the test than in the early stage, while that in the comparison cell was basically stable. The Si content in the test cell increased by 0.0085 % compared with that in the comparison cell. This was mainly related to the fact that the coating material (which contains silicon elements) brought in some silicon. However, overall, the Si content in the test cell tended to be stable and was within the normal range, indicating that the impact of the coating material on the

change of Si content was limited.

In conclusion, after using the coated anodes in the electrolytic cell, the Fe content in the primary aluminium decreased, the Si content increased slightly and tended to be stable, and the long-term application of the coating material had no impact on the quality grade of the primary aluminium.

2.4 Estimation of Economic Benefits

The economic benefit of anti-oxidation coating is given in Table 7.

Table 7. Economic benefit estimation (unit: 10 000 yuan/year).

Project			Two potlines (total production capacity 600 kt/a)
Revenue	Explicit revenue	Reduction in anode gross consumption, reduction of anode cost per tonne of aluminium	Approximately 4 100 (5.67 MUSD 2025 approx..)
		Value of alumina in the coating material as raw material	Approximately 180 (249 kUSD 2025 approx.)
	Implicit revenue	Reduction in anode gross consumption, reduction of carbon dioxide emissions by approximately 30 500 tonnes per year, with significant social benefits	
		Reduction in the amount of carbon residue and electrolyte loss. Since no data were statistically analysed, the revenue was not calculated	
		Reduction in the amount of carbon residue helps to reduce electrolyte resistance, improve the solubility of alumina, reduce furnace bottom deposits, increase current efficiency, and reduce power consumption. The revenue is temporarily difficult to quantify, so it was not calculated	
	Total revenue:		4 280 (5.92 MUSD 2025 approx.)
Cost	Coating material cost		Approximately 1 780 (non-fixed asset investment)
	Purchase and use cost of spraying equipment		10 (fixed asset investment)
	Spraying labour cost		130
	Total cost		1 920 (2.66 MUSD 2025 approx.)
Direct economic benefit			2 360 (3.27 MUSD 2025 approx.)

Note: Anode carbon blocks are calculated at 5000 yuan per tonne (including ex-factory price, transportation cost, and assembly cost, equivalent to 692 USD/t anode in 2025); implicit revenue is not included in the economic benefit.

2.5 Anode Application Conclusions

1. The long-term application of the anode anti-oxidation coating material can effectively reduce the oxidation of carbon blocks and plays a significant role in maintaining the regularity of the anode geometry.
2. After using the anode anti-oxidation coating material, the coated anode can extend the anode changing cycle by one day compared with the uncoated anode.
3. After the long-term application of the anode anti-oxidation coating material, the Fe content in the primary aluminium decreased, the Si content increased slightly and tended to be stable, and the long-term application of the coating material had no impact on the quality grade of the primary aluminium.
4. Based on an electrolytic aluminium production capacity of 600 kt/y, the long-term application of the anode anti-oxidation coating material can bring a direct economic benefit of approximately 23.6 million RMB/y (3.27 MUSD/y approx.).

3. Stub Anti-Oxidation

3.1 Stub Anti-Oxidation Industrial Application Process

3.1.1 Industrial Tests

This industrial application test was carried out on 500 kA electrolytic cells in an aluminium plant in Guangxi from 25 April 2019 to 8 July 2019. 12 groups of assembled anodes were selected as test stubs and numbered SY1-12 respectively, and 12 groups of assembled anodes were selected as comparison stubs and numbered DB1-12 respectively. The test lasted for two anode changing cycles, and the results of the industrial application were continuously tracked (Figures 9 to 11).

First, the residual iron oxide on the stubs was cleaned thoroughly, and the circumferences of the test and comparison stubs were measured respectively. Then, the anti-oxidation coating material was painted on the surface of the anode stubs to ensure that the coating was uniform without exposure or shadows.

Both the test and comparison stubs replaced in the first cycle were cleaned and their circumferences were measured. Then, the test stubs were coated again. After being replaced in the second cycle, they were cleaned, and their circumferences were measured again. The measurement position of the stub circumference was selected 8 cm below the lower edge of the steel beam.

The coated stubs were put into the cell for use after 8 h of drying maintenance.

3.1.2 Consumption of Coating Material

The consumption of the coating material per square meter is 1.5 kg, the painting thickness of the coating material is about 0.75–0.80 mm, and four stubs of an anode yoke are painted with about 730 g of coating material.

3.1.3 Figures of Industrial Application

Figure 9. Mixing of coating material in open containers (left) and coating material brushing operation (right).

It can be seen from Figure 10 (left) and Figure 11 (left) that the surface of the stub using the coating material is smoother and free of agglomeration compared with that of the stub without the coating material, and the "narrow neck" phenomenon hardly occurs.

Figure 10. Stubs with materials but not coated yet (left) and coated stubs right.

Figure 11. Surface of uncoated stubs (left) and uncoated stubs with "narrow neck" (right).

It can be seen from Figure 11 (right) that the stub without the coating material has a serious "narrow neck" problem after long-term air oxidation and corrosion. This phenomenon is more obvious in aluminium plants in humid southern regions. The reason for this may be the combined effect of the temperature and humidity in the electrolytic cell. The upper part of the stub has a low temperature (400–500 °C) and high humidity; the middle part of the stub has a moderate temperature (500–800 °C) and moderate humidity; the lower part of the stub has a high temperature (800–900 °C) and low humidity. Therefore, it is inferred that the stub is vulnerable to gas oxidation and corrosion in an environment at temperatures of 500–800 °C and moderate humidity.

3.2 Results and Analysis of Industrial Application

3.2.1 Test Data

In the first cycle, the data of the test stub SY9 could not be measured due to the failure of the broken suspension controller, and the comparison stub DB10 was corroded severely. Therefore, there were 11 groups of data for both the test and comparison stubs.

In the second cycle, due to factors such as severe corrosion and maintenance, there was no data for the test stubs SY4, 7, 8, and 9, leaving 8 groups of data. For the comparison stubs, there was no data for DB4, 6, 10, and 12, leaving 8 groups of data.

After two anode changing cycles, the comparison of the circumference of the stub is shown in Table 8.

Table 8. Measurement data of stubs perimeter after two cycles (unit: mm).

Test stub No.	**Before Experiment A**	**After 1st cycle B**	**Difference B-A**	**After 2nd cycle C**	**Difference C-A**	**Comparison stub No.**	**Before Experiment a**	**After 1st cycle b**	**Difference b-a**	**After 2nd cycle c**	**Difference c-a**
SY1	567.5	565.5	-2.0	563.3	-4.3	DB1	521.3	496.8	-24.5	477.0	-44.3
SY2	540.0	535.0	-5.0	530.8	-9.3	DB2	565.0	553.0	-12.0	540.0	-25.0
SY3	563.8	557.5	-6.3	555.0	-8.8	DB3	578.8	565.5	-13.3	546.3	-32.5
SY4	×	543.3	-6.8	×	×	DB4	×	552.8	-17.3	×	×
SY5	577.5	564.3	-13.3	561.8	-15.8	DB5	576.3	552.3	-24.0	531.8	-44.5
SY6	561.3	560.3	-1.0	558.8	-2.5	DB6	×	570.0	-10.0	×	×
SY7	×	551.8	-5.8	×	×	DB7	570.0	552.0	-18.0	538.8	-31.3
SY8	×	579.3	-4.5	×	×	DB8	565.0	556.0	-9.0	541.8	-23.3
SY9	×	×	×	×	×	DB9	558.8	535.0	-23.8	521.8	-37.0
SY10	542.5	532.5	-10.0	529.3	-13.3	DB10	×	×	×	×	×
SY11	580.0	577.0	-3.0	573.0	-7.0	DB11	585.0	569.0	-16.0	551.8	-33.3
SY12	560.0	557.0	-3.0	551.3	-8.8	DB12	×	565.0	-7.5	×	×
Average Value	561.6	556.7	-5.5	552.9	-8.7	Average Value	565.0	551.6	-15.9	531.2	-33.9

3.2.2 Data Analysis

After two anode changing cycles, the comparison of the average circumferences of stub is shown in Table 9.

Table 9. Comparison table of average data of stub perimeter after two cycles (unit: mm).

Project	**First cycle**		**Second cycle**		**Comparison before and after two cycles**	
Test stubs	Before experiment A	562.2	After 1st cycle B	556.1	Before experiment A	561.6
	After 1st cycle B	556.7	After 2nd cycle C	552.9	After 2nd cycle C	552.9
	Difference B-A	-5.5	Difference C-B	-3.3	Difference C-A	-8.7
Comparison stubs	Before experiment a	567.5	After 1st ycle b	547.5	Before Experiment a	565.0
	After 1st Cycle b	551.6	After 2nd cycle c	531.2	After 2nd cycle c	531.2
	Difference b-a	-15.9	Difference c-b	-16.3	Difference c-a	-33.8
Test - comparison (difference in change values)	—	10.4	—	13	—	25.1
Test ÷ comparison (ratio of change values)	—	34.6 %	—	20.2 %	—	25.7 %

The analysis of the application test data in Table 9 is as follows:
1) As shown in Table 9, after the 1st anode changing cycle, compared with before the experiment, the average circumference of the test stubs oxidized by 5.5 mm, and that of the comparison stubs

oxidized by 15.9 mm. The test stubs oxidized 10.4 mm less than the comparison stubs. The average oxidized circumference of the test stubs is 34.6 % of that of the comparison stubs, which means the test stubs reduced oxidation by 65.5 % compared with the comparison stubs.
2) As shown in Table 9, after the 2nd anode changing cycle, compared with when they were put into the cell in the 2nd cycle, the average circumference of the test stubs oxidized by 3.3 mm, and that of the comparison stubs oxidized by 16.3 mm. The test stubs oxidized 13 mm less than the comparison stubs. The average oxidized circumference of the test stubs is 20.2 % of that of the comparison stubs, which means the test stubs reduced oxidation by 79.8 % compared with the comparison stubs.
3) As shown in Table 9, after 2 anode changing cycles, compared with before the experiment, the average circumference of the test stubs oxidized by a total of 8.7 mm, and that of the comparison stubs oxidized by a total of 33.8 mm. The test stubs oxidized 25.1 mm less than the comparison stubs in total. The average oxidized circumference of the test stubs is 25.7 % of that of the comparison stubs, which means the test stubs reduced oxidation by 74.3 % compared with the comparison stubs, and the lifespan of the stubs was extended by 2.9 times.

3.3 Improvement of Primary Aluminium Quality

By statistically analysing the monthly average Fe content of a potline in an aluminium plant in Guangxi in the past 6 years (excluding abnormal cells), it can be seen that since the second half of 2020, the Fe content in the system has shown a significant downward trend, as shown in Figure 12.

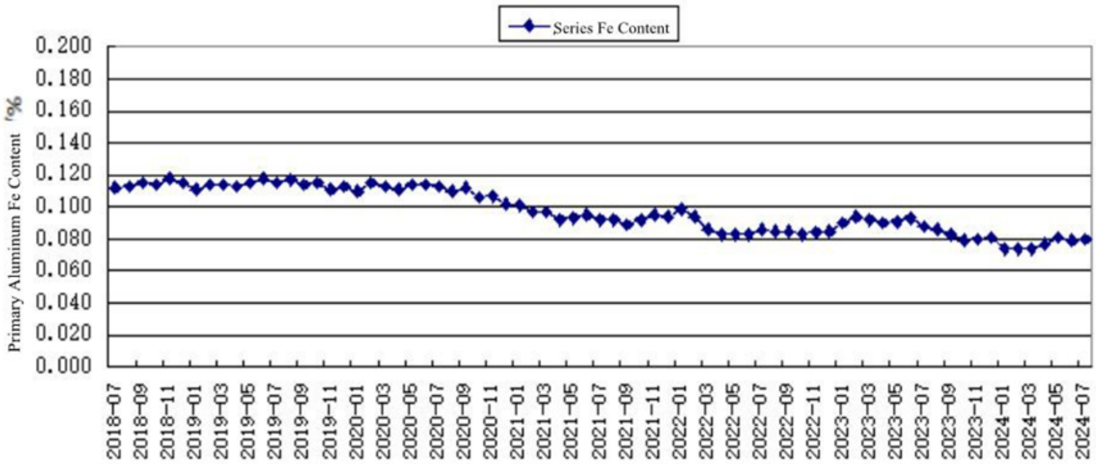

Figure 12. Trend of monthly average Fe content in the past 6 years.

Large-scale application of stub coatings started in May 2020. Table 10 shows the comparison of the Fe content in the series of primary aluminium (excluding abnormal cells) in the year before the promotion (May 2019 - April 2020) and in the most recent year (August 2023 - July 2024).

Table 10. Fe content in primary aluminium before and after stub coating large scale implementation.

Project	Time	Fe content, %	Project	Time	Fe content, %	Difference
One year before stub coating	2019-05	0.115	Application of stub coating for nearly a year	2023-08	0.086	—
	2019-06	0.118		2023-09	0.083	—
	2019-07	0.115		2023-10	0.079	—
	2019-08	0.117		2023-11	0.080	—
	2019-09	0.114		2023-12	0.081	—
	2019-10	0.115		2024-01	0.074	—
	2019-11	0.111		2024-02	0.074	—
	2019-12	0.113		2024-03	0.074	—
	2020-01	0.110		2024-04	0.077	—
	2020-02	0.115		2024-05	0.081	—
	2020-03	0.113		2024-06	0.079	—
	2020-04	0.111		2024-07	0.080	—
Average		0.114	Average		0.079	-0.035

The average Fe content in the potline of primary aluminium in the most recent year is 0.079 %, which is 350 ppm lower than the 0.114 % in the year before application the stub coating materials. Since the anti-oxidation coating materials for anodes were also implemented at the same time, the Fe content was reduced by 180 ppm (see reference [19], page 34, 2.5.2 Data Analysis of Primary Aluminium Quality for details). Therefore, the Fe content in primary aluminium reduced by using the stub coating materials is 170 ppm. During this period, the aluminium plant adopted a five-stage iron-removal technology, and the proportion of iron removal by magnetic separation of the covering material increased from the original 50–60 % to about 76 %. If the iron removal by magnetic separation had not been upgraded, the use of the stub coating materials could have reduced the Fe content in primary aluminium by up to 280 ppm.

3.4 Economic Benefit Estimation

(1) Replacement data of coated stubs:

The data of replacing damaged stubs in the past two years (2023–2024) are shown in Table 11.

Table 11. Replaced damaged stubs in the past two years.

Month / Year	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug	Sep.	Oct.	Nov.	Dec.	Total	Monthly average
2023	446	623	479	506	440	485	509	561	567	496	402	498	6012	501
2024	601	527	482	526	479	/	/	/	/	/	/	/	2615	523
Total average	—	—	—	—	—	—	—	—	—	—	—	—	8627	508

(2) Service life of coated stubs:

There are 19 600 yokes in the smelter and each yoke has 4 stubs (14400 yokes sealed on anodes and 5200 spare yokes as rotation stock). The average number of replaced stubs from 2023 and 2024 is 508 stubs/month, i.e., 127 yokes/month. Therefore, the service life of yokes with coated stubs is:

$$\text{Service life of yokes} = \frac{19600\ \text{(total number of yokes)}}{127\ \text{(average number of yokes/month)} \times 12\ \text{(months/year)}} = 12.86\ \text{(years)}$$

(3) Service life of uncoated yokes:

Based on the fact that the coating can reduce the oxidation rate of stubs by 74.4 % and the service life of coated yokes is 12.86 years, the service life of yokes with uncoated stubs is calculated as: 12.86 × (100 % - 74.4 %) = 12.6 x 25.6 % = 3.29 years.

(4) Annual cost reduction for replacing stubs after using the coating:

The annual number of replaced uncoated yokes is: 19600/3.29 years = 5957 units/y.

The annual reduction in the number of stub replacements after using the coating is: (5957 - 127 × 12) yokes × 4 stubs/yoke = 17 732 stubs.

Calculated at a replacement cost of 580 yuan per stub (80 USD/stub approx.; 300 yuan for the stub and 280 yuan for labour), the annual cost reduction for replacing stubs after using the coating is: 17 732 stubs × 580 yuan/stub = 10.285 million yuan (1.42 MUSD/y approx.).

(5) Annual comprehensive cost:

Annual coating cost = 48 (number of anodes per cell) / 37 (days of anode changing cycle) x 300 (number of cells) x 365 (days in a year) × 0.73 (kg of coating used per set of stubs) × 16.5 (yuan per kg of coating, 2.28 USD/kg approx.) = 1.711 million yuan; annual labor and tool cost is 301 000 yuan.

Therefore, the annual comprehensive cost is: 1.711 + 0.301 = 2.012 million yuan (278 kUSD/y approx.)

(6) Annual direct economic benefit: 10.285 – 1.711 – 0.301 = 8.273 million yuan (1.14 MUSD/y approx.)

3.5 Conclusions for Stub Anti-Oxidation Application

Through the analysis of the test data of the anti-oxidation coating for anode stubs and the relevant data of large-scale industrial applications, the following conclusions can be drawn:

1. The use of anti-oxidation coatings for anode stubs can increase the smoothness of the stub surface and reduce the occurrence of the "narrow neck" phenomenon of the stubs.
2. The use of anti-oxidation coatings for anode stubs can extend the lifespan of the stubs by 2.9 times.
3. The use of anti-oxidation coatings for anode stubs can significantly improve the quality of primary aluminium, reducing the Fe content in primary aluminium by 280 ppm.
4. Taking an electrolytic aluminium plant with an annual production capacity of 400 kt/y as an example, the use of anti-oxidation coatings for anode stubs can bring a direct economic benefit of 8.273 million yuan per year (1.14 MUSD/y approx.).

4. Conclusions on the Application of Anti-oxidation Technology

Nano ceramic-based anti-oxidation coating materials can effectively reduce the oxidation of anode carbon blocks and carbon dust generation, while significantly contributing to maintaining the regularity of anode geometry. When applied to anodes, this coating enables the coated anodes to extend the anode changing cycle by one day compared to uncoated ones. Additionally, its use on stubs can reduce their surface oxidation, enhance surface smoothness, and minimize the occurrence of the "narrow neck", thereby extending stub lifespan by 2.9 times. In large-scale smelters, the coating's ability to reduce oxidation and carbon dust deposition on anode carbon blocks has reduced carbon consumption and decreased anode cost per ton of aluminium.

Environmentally, the technology contributes to sustainability goals by curbing excessive carbon consumption. Additionally, the 280 ppm reduction in iron content in primary aluminium not only improves metal purity, but also reduces the need for post-production purification processes, further saving energy and reducing emissions.

Hunan Bable Material Technology Co. nano ceramic-based anti-oxidation coating materials, presented in this paper, are used in over a dozen smelters in China and sold to four smelters in Malaysia and India.

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