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THE STATUS AND DEVELOPMENT TRENDS OF CARBON CATHODE MATERIALS IN CHINA

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Abstract

China is the largest producer and consumer of carbon cathode blocks and ramming pastes. Various grades and qualities of carbon cathode materials are now produced and used in China, among them some have reached the world advanced levels with regards to the qualities. The present paper describes the raw material selection, production equipment, standards and specifications of the carbon cathode materials in China. Although the carbon cathode materials are overall over-supplied, the demand for high quality graphitized blocks and environment friendly ramming pastes is increasing. The application of graphitized cathode blocks in 300kA and 400kA potlines in Wanji Aluminum and the development of high density graphitized blocks in Shanjin Carbon are simply introduced respectively. As the pressure on energy saving, productivity and environment is increasing, graphitized cathode blocks and cold ramming pastes are becoming more and more popular, which will in return promote the Chinese aluminum smelting industry to new level.

1. Introduction

China has become the largest aluminum producer and consumer in the world since 2002. The output of primary aluminum in 2013 in China exceeded 22 million tons. As the fast development of the aluminum industry, the related carbon cathode industry has fast expanded too. China is now the largest carbon cathode producer and exporter in the world. There are altogether more than forty carbon cathode producers in China. As the aluminum pot capacity increases, the technology advances, the market competition becomes more intensive and saving energy and environment protection become more important, the requirement to the carbon cathode materials becomes higher. Cathode blocks of higher conductive and more resistant to attack and environment friendly ramming pastes are expected. After the development of over 60 years, especially in the recent ten years, the production technology, equipment and product quality of carbon cathodes in China have all reached the world advanced levels. China has established a complete set of standards and analysis methods of raw materials, semi-products and finished products for production of carbon cathode materials. Due to over capacity and too many small-scale producers, the profit of the industry is low and the quality of quite many producers is not very stable.

The present paper describes in general the production, standards, qualities, problems and development of the carbon cathode materials in China.

2. The present status

The carbon cathode materials for the aluminum industry include cathode blocks, sidewall blocks and ramming pastes. They are the main materials of the pot lining in direct contact with metal and bath. Their qualities have a great effect on the pot performance and lifetime.

2.1 The industry outline

There are presently 47 carbon cathode producers in China, including carbon bottom blocks, sidewall blocks and ramming pastes, excluding silicon carbide sidewall blocks [1]. They are distributed in 16 provinces and autonomous regions in China (refer to Table 1). Among these 47 producers, nine belong to aluminum smelters, the remaining 38 are independent producers.

The total capacity of the carbon cathode materials exceeded 750,000 tons in 2013. There are five producers with capacity over 50,000 tons and 26 producers with capacity less than 10,000 tons. The total output in 2013 is about 530,000 tons. The domestic consumption was about 480,000 tons and another 45,000 tons were exported in 2013. There were only two producers with output over 50,000 tons and 32

producers with output less than 10,000 tons in 2013. Among these 530,000 tons, bottom blocks amounted to about 320,000 tons, sidewall blocks about 60,000 tons and ramming pastes 150,000 tons. Please note that quite a lot of carbon cathode producers also produce carbon electrode pastes and blocks for ferroalloy and other high temperature furnaces. The statistics here may not be very accurate.

Among the cathode bottom blocks, more than 80% were semi-graphitic blocks with 30% or 50% graphite content. The remaining less than 20% were graphitic or graphitized blocks.

Various qualities of carbon sidewall blocks were produced in 2013, and the majority were combined with silicon carbide blocks constituting SiC-C composite sidewall blocks.

Various qualities of ramming pastes (i.e.: cold, tepid and hot) were produced in 2013, the majority were tepid and hot ramming pastes, cold ramming pastes amounted to about 15%. As the government tightens the environment policy and more people realize the importance of the environment, the cold ramming pastes are becoming more and more popular. Now aluminum projects (new or expansion) mainly use cold ramming pastes.

Table 1. Distribution of carbon cathode producers in China

Seq. no.	Location	No. of producers	Seq. no.	Location	No. of producers
1	Shanxi	21	9	Shanghai	1
2	Henan	4	10	Sichuan	1
3	Ningxia	3	11	Inner Mongolia	2
4	Jilin	1	12	Guizhou	2
5	Liaoning	1	13	Yunnan	1
6	Hebei	2	14	Shan'xi	1
7	Shandong	2	15	Gansu	1
8	Hunan	3	16	Qinghai	1

2.2 Technology

2.2.1 Raw materials

The main raw materials for manufacturing carbon cathodes are ECA, coke (mainly from petroleum oil, some from coal tar) and coal tar pitch. A complete set of standards for the raw materials have been established, including "Graphitized coke by an electrical calciner" (YS/T763-2011), "Coal tar pitch" (YB/T5299-2009), "coal tar" (YB/T 5075-2010), "Technical requirement of petroleum coke for making graphitized cathode blocks" (YS/T842-2012), and "Electrically calcined anthracite for making cathode blocks" (GB/T2290-2012). These standards stipulate the value limits of the regular analyses like ash content, volatile content and real density, and analyses of reference properties like particle size distribution, calcination or graphitization degree, sulphur content, microstructure, isotropic and anisotropic properties and powder electrical resistivity.

2.2.2 Equipment

Most cathode block producers in China are equipped with computer-controlled and closed crushing, screening and batching systems, vibrators with hydraulic and vacuum systems, mixers with preheating systems and computer-controlled ring baking furnaces. Some are equipped with lengthwise graphitization furnaces and automatic machining lines.

2.2.3 Qualities and dimensions

Most cathode producers can produce semi-graphitic (typically with 30% or 50% graphite) and graphitic blocks, some can produce graphitized blocks. Various sizes of cathode blocks can be produced. The maximum dimensions have reached length more than 4 meters, width up to 0.8 meter and height up to 0.6 meter.

2.3 System of test methods and standards

It is common practice in China that the buyers select products according to the property limits stipulated in the standards, while the sellers or producers use the standards as the specifications of their products. The appropriate national or industrial test methods and standards are usually the most important technical part of the contracts between the buyers and sellers. These test methods and standards are also used in arbitration when resolving disputes. It is therefore that the national and the industrial test methods and standards play a very important role on the market.

2.3.1 Quality standards of finished products

There are two quality standards for cathode bottom blocks and sidewall blocks: YS/T623-2012 (Semi-graphitic and graphitic blocks for aluminum electrolysis) and YS/T699-2009 (Graphitized blocks for aluminum electrolysis). The quality standard for the ramming pastes is YS/T65-2012 (Cathode pastes for aluminum electrolysis). The standard YS/T623-2012 is shown in Table 2. Most carbon cathode producers have stricter quality standards than the industrial standards. The industrial standards should be regarded as minimum requirements and are used as specifications by the producers.

2.3.2 Standards

Organized by SAC/TC243 (The standardization Committee of Non-Ferrous Metals), and based on the standards issued by

ISO/TC226, the main research institutes and the main producers of

Table 2. Specifications of semi-graphitic and graphitic cathode blocks (YS/T 623-2012)

Grade	Regular analysis					Reference analysis			
	Real density, g/cm^3	Apparent density, g/cm^3	Electrical resistivity, μΩ·m	Compressive strength, MPa	Ash, %	Bending strength, MPa	Yang's modulus, GPa	CTE, 1×10^{-6}/K (20-300^{0}C)	Sodium expansion, %
	≥	≥	≤	≥	≤	≤	≤	≤	≤
GS-1	1.91	1.56	39	32	8	10.0	10.0	4.2	1.0
GS-3	1.95	1.57	35	24	5	7.0	7.0	4.0	0.8
GS-5	1.99	1.57	30	24	4	7.0	7.0	4.0	0.7
GS-10	2.08	1.59	21	26	2	7.5	6.5	4.0	0.5
GS-C	1.91	1.56	/	32	8	/	/	4.2	1.0

Table 3. Sampling and test methods of carbon materials for the aluminum industry

Chinese number	Name	Corresponding ISO number
Sampling methods		
GB/T 26297.1-2010	Sampling method: Part 1 bottom blocks	ISO 8007-1：11999
GB/T 26297.2-2010	Sampling method: Part 2 sidewall blocks	ISO 8007-3：11999
GB/T 26297.4-2010	Sampling method: Part 4 ramming pastes	ISO 14422：1999
Test methods		
YS/T 63.1-2006	Determination of baking loss and apparent density of green samples	ISO 20202：2004
YS/T 63.2-2006	Determination of electrical resistivity at room temperature	ISO 11713：2000
YS/T 63.3-2006	Determination of thermal conductivity: comparison method	ISO 12987：2004
YS/T 63.4-2006	Determination of coefficient of thermal expansion	ISO 14420：2005
YS/T 63.5-2006	Determination of sodium expansion with pressure	ISO 15379-1：2004
YS/T 63.6-2006	Determination of open porosity: hydrostatic method	ISO 12985-2：2000
YS/T 63.7-2006	Determination of apparent density: dimension method	ISO 12985-1：2000
YS/T 63.8-2006	Determination of density in xylene: picknometer	ISO 9088：1997
YS/T 63.9-2006	Determination of real density: helium gravimeter	ISO 21687：2007
YS/T 63.13-2006	Determination of Yang's modulus	/
YS/T 63.14-2006	Determination of bending strength: three points	ISO 12986-1：2000
YS/T 63.15-2006	Determination of compressive strength	ISO 18515：2007
YS/T 63.17-2006	Determination of volatile content	ISO 9406：1995 / ISOTS 14425：1999
YS/T 63.18-2006	Determination of water content	ISO 11412：1998
YS/T 63.20-2006	Determination of ash content	ISO 8005：2005 / ISO 14428：2005
YS/T 63.21-2007	Expansion/shrinkage during baking of a ramming paste	ISO 14427：2004
YS/T 63.25-2012	Determination of sodium expansion without pressure	ISO 15379-2：2004
YS/T 700-2009	Grinding test	/
YS/T 733-2010	Determination of graphitization degree	/
YS/T 735-2010	Determination of ash content in carbon glue	/
YS/T 736-2010	Determination volatile content in carbon glue	/
GB/T 26293-2010	Determination of rammability of ramming pastes	ISO 17544：2004
GB/T 26294-2010	Determination of binder and aggregate in ramming pastes	ISO/TS 14423：1999
GB/T 26295-2010	Bending strength: four points	ISO 12986-2：2005
*YS/T XXX-201X	Inspection method of the interior defects of carbon cathode blocks	/

*: Not published yet

the carbon materials for the aluminum industry cooperatively started drafting the standards and test methods. Now there are 75 standards or test methods for the carbon materials [2], among them, 27 are China national standards (GB), 48 are the non-ferrous industry standards (YS). The standards related to the carbon materials for the aluminum industry and corresponding ISO standards are listed in Table 3.

It can be seen from Table 3 that there are altogether 28 standards, 6 national and 22 the industrial. There are 24 standards having corresponding ISO standards.

Regarding the analysis equipment, China has imported a lot of advanced equipment from Switzerland, USA and Germany in the last two decades. In the recent years, China has developed a lot of advanced equipment. These imported and domestically developed equipment helped a lot in writing and execution of the standards and test methods.

It must be pointed out that all these quality standards and test methods are still under modification. For the quality standards, China is trying to make them similar to the specifications of Western aluminum companies. For the test methods, China is trying to make them similar to the ISO standards.

3. Application of graphitized cathode blocks and development trend

3.1. Application of graphitized cathode blocks

From the mid of 1990s to 2006, a few Chinese aluminum smelters tried graphitized cathode blocks in small scales, i.e.: 3 to 10 pots per trial. In 2006, Wanji Aluminum started to use graphitized cathode blocks (supplied by Wanji Graphite) in potline scale and cold ramming pastes (supplied by Elkem Carbon) in potline scale as well. Since then Wanji has been using graphitized cathode blocks and cold ramming pastes all the time for relining and expansion projects. Wanji has achieved the following result [3]: a) No early failures (pot life < 3 years). b) The average pot life of the 300kA potline (204 pots, the anodic current density is 0.73A/cm^2) has reached 3089 days with only 38 relinings, meaning that the pot life of most pots has exceeded 3000 days. The average pot life of the 400kA potline (198 pots, the anodic current density is 0.81A/cm^2) has reached 1994 days with only 10 relinings. c) The cathode voltage drop (CVD) of most pots is initially about 200mV and stabilized between 220mV and 300mV after one year's operation.

In the recent years, more and more Chinese aluminum smelters use graphitized cathode blocks in potline scale for their expansion or new projects. The anodic current density has been increased to slightly over 0.80A/cm^2. In the meantime, the environment friendly cold ramming pastes have been getting more and more popular and now widely used in the expansion and new projects.

3.2. Development trend

There is no doubt that the development trend of the carbon cathode materials in China is to high quality of graphitized blocks for the cathode blocks and high quality of cold ramming pastes for the ramming pastes. This is the requirement of both export and domestic markets. Shanjin Carbon conducted an industrial production trial of graphitized cathode blocks of high density with domestic materials. Here is the introduction to the trial.

3.2.1 Targets

The following targets were set for the trial: apparent density ≥ 1.68 g/cm^3, compressive strength ≥ 22 MPa, electrical resistivity ≤ 11 μΩ·m, bending strength ≥ 8 MPa and open porosity ≤ 25%.

3.2.2 Raw materials

The binder is coal tar pitch with a softening point of 105℃ (R&B). The isotropic coke is coal tar pitch based from a local supplier and the sponge coke is a regular low sulphur coke from the market. The properties of the two cokes are listed in Table 4 and Table 5. The dry aggregate of the trial blocks was the mixture of 50% isotropic coke and 50% sponge coke, while the dry aggregate of the regular blocks was 100% sponge coke. Thirty blocks were produced for each recipe. The blocks were all formed with a horizontal vibrator with vacuum system, baked in an open ring baking furnace and graphitized in a lengthwise graphitization furnace.

Table 4. Comparison of vibration density between the isotropic coke and the sponge coke

Particle size, mm	Isotropic coke, g/cm^3	Sponge coke, g/cm^3
6-8	0.844	0.782
4-6	0.855	0.803
2-4	0.926	0.892
0-2	1.010	0.900
-0.5	1.102	1.010

It can be seen from Tables 4-5 that the isotropic coke is denser than the sponge coke, and other properties of both cokes are quite similar.

Table 5. Comparison of other properties between the isotropic coke and the sponge coke

Property	Isotropic coke	Sponge coke
Ash, %	0.42	0.47
Real density, g/cm^3	2.08	2.09
Powder resistivity, μΩ·m	498	415
Sulphur, %	0.47	0.45

3.2.3 Result and discussion

The apparent green density, graphitized density and bending strength of the trial blocks are shown in Figures 1, 2 and 3 respectively. The comparison between the trial blocks and the regular blocks is shown in Table 6.

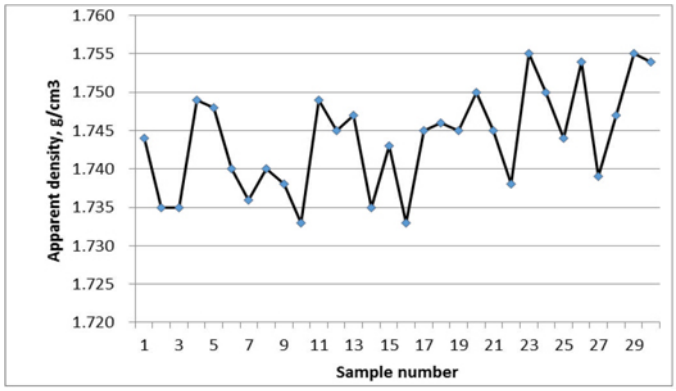

Figure 1. Apparent green density after forming, g/cm^3

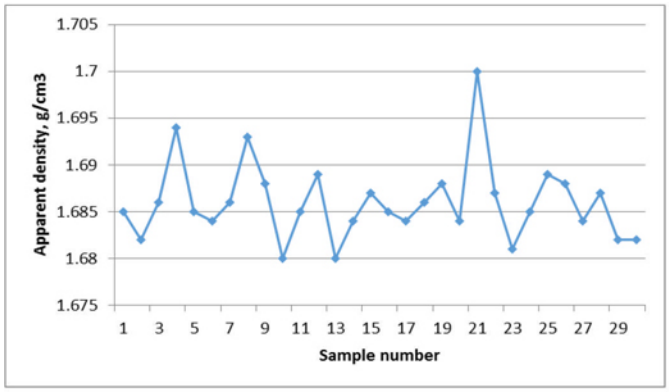

Figure 2. Apparent density after graphitization, g/cm^3

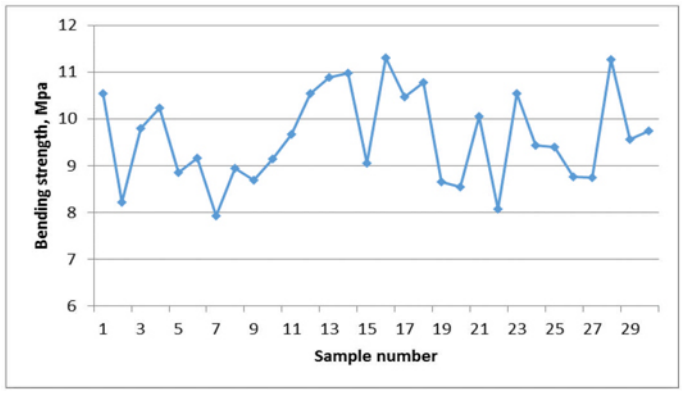

Figure 3. Bending strength after graphitization, MPa

It can be seen from Table 6 that the density and the strength of the trial blocks are higher than that of the regular blocks, and the open porosity of the trial blocks is lower than that of the regular blocks. The electrical resistivities at room temperature of both groups of blocks are quite similar.

Table 6. Property comparison between the trial blocks and the regular blocks produced in the same period

Property	Unit	No. of samples	Average of the trial blocks	Average of the regular blocks
Apparent density	g/cm^3	30	1.686	1.610
Open porosity	%	30	17	20
Electrical resistivity	μΩ·m	30	10.5	10.7
Compressive strength	MPa	30	24	19
Bending strength	MPa	30	9.6	7.6
Real density	g/cm^3	30	2.20	2.19
Ash	%	30	0.30	0.35

4. Concluding remark

Various qualities of carbon cathode materials are produced and used in China. The production equipment and the technology have been improved a lot over last two decades. A complete set of test methods and standards have been established. The market competition is intensive due to oversupply and the profit is low. The quality

variation is sometimes quite big, especially for small producers. As the Chinese aluminum industry intends to creep the current density and attach more and more importance to the quality and the environment, carbon cathode materials of high qualities are getting more and more popular, which promotes the development of the carbon cathode industry towards graphitized blocks and cold ramming pastes. We expect that the market of the graphitized cathode blocks and cold ramming pastes in China will exceed 50% of the total market of carbon cathode materials within ten years to come.

Reference

1. Henglong Li. "Technology Handbook of Aluminum Production", Metallurgical Industry Press, Beijing: 2011

2. Cunzhen Ma, "Collect and Edit of Standards of Carbon Materials for Aluminum Production". China Standard Press, Beijing: 2013

3. Baoguo Chen, "The Application of Graphite Cathodes in Aluminium Reduction Cells", Qinjinshu, 2012, 9:45