EFFECTS OF COKE TYPES AND CALCINING LEVELS ON THE PROPERTIES OF BENCH-SCALE ANODES

Ning Fang[1], Jilai Xue[1], Xiang Li[1], Guanghui Lang[2], Chongai Bao[2], Shoulei Gao[2], Baiyuan Xia[2], Jinlong Jiang[2]

[1] School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing
Xueyuan Road 30, 100083, Beijing, China
[2]Sunstone Development Co., Ltd; 100029, Beijing, China

Keywords: Carbon Anodes, Coke, Under-calcined, Reactivity, Conductivity，Compressive Strength，Shear Strength

Abstract

The anode with under-calcined cokes have better component homogeneity and smaller carbon consumption in aluminum electrolysis. In this study, three types of petroleum cokes were calcined at 800, 900, 1000 and 1100 °C, respectively. The content of S and volatiles of cokes were measured against the calcining temperature. The air/CO_2 reactivity, electrical conductivity, density, porosity, compressive/shear strength of the bench-scale anode sample made by these cokes were optimized as a function of calcining temperatures. In addition, the L_C value and real density of cokes were tested to show calcining level of the cokes. Based on the results above, the optimum calcining level of cokes for the prebaked anodes was obtained.

Introduction

Carbon anode manufacturers traditionally adopt the method that the calcining temperature was higher than baking temperature. In this baking process, pitch transformation usually occurs with a minimal coke transformation [1].

During aluminum electrolysis, the consumption rate of binder phase is much higher than that of the skeleton in the anode [1]. The binder phase is consumed by O_2 and CO_2 in comparison with small consumption of the coke, which results in failure in the connection function or disappearance of part of binder phase. Then the rest of skeleton in anode will shed because of the absence of binder phases [2], which will again increase the anode consumption.

Therefore, some researchers and anode makers used under-calcined coke to reduce the difference in reactivity between skeleton and binder phase [1-6]. In their studies, it was found that the skeleton and binder phase had the same transformation in the baking process when the calcining temperature was lower than the baking temperature. The reduced difference between the reactivity of two phases made their anodes more uniform [1, 3].

Compared with the anode using ordinary calcined cokes, the anode using under–calcined coke had lower reaction rate [1-4], better thermal shock resistance [2], and lower consumption in the pots[1-2, 4]. In certain cases, the use of under-calcined coke could even reduce the number of problem anodes in the pots (ahead of schedule, dust, spikes, and cracks) [1]. However, some important properties, such as electrical conductivity, compressive strength, shear strength, etc, of the under-calcined cokes have not received much attention in open literature. Also it is known that the anode properties may become worse when coke calcining level is lower than a certain value. The calcining level has not been reported on the under-calcined cokes. Lack of the information mentioned above may limit the possible utilization of this type of coke for their technical and economic benefits in anode making.

In this paper, three types of petroleum cokes with different sources and compositions have been investigated at several calcining temperatures of 800, 900, 1000, 1100 °C, respectively. The anode properties, such as reactivity, electrical conductivity, density, porosity and compressive/shear strength were measured, and the crystallite size (L_C) and the real density (RD) of the coke and the anodes were determined for their potential applications.

Experimental

Materials

The properties and elements content of three types of petroleum coke (Petroleum Coke-L, Petroleum Coke-H, and Petroleum Coke-M) were shown in Table I and Table II. Petroleum Coke-L and Petroleum Coke-H each had its own supplier. Petroleum Coke-L was low sulfur petroleum coke and its S content is 1.91%. Petroleum Coke-H was a high sulfur petroleum coke and its S content was 4.81%. In industrial production, the petroleum cokes used in anode manufacturing came from different materials suppliers and production areas.

Table I. Properties of Petroleum Cokes for Anode Production

Types	Ash (wt%)	Volatile (wt%)	S content (wt%)
Petroleum Coke-L	0.14	12.32	1.91
Petroleum Coke-H	0.22	12.14	4.81
Petroleum Coke-M	0.16	11.35	2.84

Table II. Metals Contents in Petroleum Cokes

Elements（ppm）	Petroleum Coke-C	Petroleum Coke-J	Petroleum Coke-H
V	162	184	184
Ni	187	202	172
Si	69	98	173
Fe	139	148	125
Al	90	95	196
Na	35	44	27
Ca	90	91	120
Zn	7	6	9
Pb	3	3	3

Table III. Properties of Coal Pith

SP[a] (°C)	Volatile (wt%)	TI[b] (wt%)	QI[c] (wt%)	β (wt%)
100.8	55.9	27.44	7.28	20.16

[a] Softening point
[b] Toluene insoluble
[c] Quinoline insoluble

To simulate the actual conditions of industrial application, different types of petroleum coke from various suppliers were mixed to obtain Petroleum Coke-M. The open porosity of coke used was about 18-30%, which was determined by image analysis method [7]. Only one type of coal pitch was used in this study. Coal pitch properties used here are shown in Table III.

Calcinations and Baking

Four calcining temperatures of petroleum coke were 800, 900, 1000, 1100 °C, respectively. The calcining furnace containing the materials was heated according to the following temperature/time profile: (i) heating at 400 °C/h up to 200 °C; (ii) from 200 °C to the desired temperatures at 100 °C/h; (iii) and keeping it for 20 h to soak.

The baking temperature of anodes was 1100 °C, and the heating rate in baking process was purposely the same as that in calcining process.

Anode Preparation

The formula of the skeleton for using these cokes is listed in Table IV, where15 % of coal pith is added in mixing the skeleton to form the anode paste. 12 types of anodes were prepared using 3 types of petroleum cokes with various calcinations temperatures.

Table IV: Grain Size of Carbon Skelton

Granularity	8-5mm	5-2mm	2-0mm	Fines
%	12	20	33	35

The anode paste kneaded at 175 °C was formed as cylinder (Φ50 mm×110 mm) by extrusion molding under constant pressure, and then the green samples were baked in the baking furnace. In order to test each property for 2-3 parallel measurements, 10 samples were made for one type anode each.

For convenience of descriptions, Coke-L, Coke-H and Coke-M were expressed for the cokes which calcined from Petroleum Coke-L, Petroleum Coke-H and Petroleum Coke-M, respectively. Anode-L, Anode-H and Anode-M were expressed for the anodes which were made of Coke-L, Coke-H and Coke-M, respectively.

Characterization Methods

The anode properties in this study were characterized using various standard methods for density (ISO12985-1:2000), porosity (ISO12985-2:2000), electrical conductivity (ISO11713:2000), shear strength (ISO 12986-1:2000), compressive (ISO18515:2007), real density (ISO 21687:2007), L_C (ISO 20203-2006), CO_2 reactivity (ISO12988-1: 2000) and air reactivity (ISO12989-1:2000).

Results and Discussion

Coke Properties at Varying Calcinations Temperature

The range of calcinations levels of cokes which commonly used in the aluminum industry can be divided into 3 categories by the real density (RD) and the crystallite size (L_C) [1]:

• Under-calcined coke: RD <2.05 g/cm^3 (L_C<25.3 Å)
• Standard-calcined coke: 2.05 g/cm^3<RD<2.09 g/cm^3
                          (25.3 Å <L_C<32.7 Å)
• Highly-calcined coke: RD>2.09 g/cm^3 (L_C>32.7 Å)

The value of RD and L_C of calcined cokes increases with increasing calcining temperature. Among the values of L_C and RD of calcined cokes, as shown in Table V, it can be found that cokes which were calcined in 800, 900, 1000 °C are under-calcined coke and coke which was calcined in 1100 °C is standard-calcined coke. It shows that the value of RD and L_C of Coke-H are slightly greater than the other two kinds of cokes in the same calcining temperature. The value of RD and L_C of Coke-L and Coke-M are almost same. The reason for these results is the variation in the specific compositions of three types of petroleum cokes. However, there is difference in property of anodes made by three types of petroleum cokes. These differences have no effect on the conclusion in this work, so it is no further discussion in this paper.

Table V: Values of RD and L_C of Calcined Cokes with Varying Temperature.

Calcining Temperature (°C)	Cokes-L		Cokes-H		Cokes-M	
	L_C (Å)	RD (g/cm^3)	L_C (Å)	RD (g/cm^3)	L_C (Å)	RD (g/cm^3)
800	17	1.879	18	1.892	17	1.892
900	19	1.967	20	1.975	20	1.985
1000	22	2.029	25	2.057	23	2.036
1100	27	2.076	30	2.088	27	2.080

Table VI shows the content of volatile and S of cokes with small difference at various calcining temperatures. This suggests that the three types of petroleum coke have been basically completed for removal of volatile and the free sulfur before 800 °C. The rest of S in sulfur compound may need a temperature higher than the standard calcining temperature (1200 °C) in order to remove it completely [8].

Table VI: Contents of Volatiles and S of Cokes

Calcining Temperature (°C)	Coke-L		Coke-H		Coke-M	
	Volatile (wt%)	S (wt%)	Volatile (wt%)	S (wt%)	volatile (wt%)	S (wt%)
800	1.03	1.71	0.97	4.29	1.04	2.59
900	1.06	1.69	1.04	4.35	1.12	2.49
1000	1.06	1.71	0.99	4.41	1.04	2.64
1100	1.09	1.60	0.98	4.25	0.96	2.56

Anode Properties with Varying Coke Calcining Temperatures

Table VII show the values of RD and L_C of 12 kinds of anodes show only small variation. Because four kinds of calcining temperatures were lower than or equal to the baking temperature in this experiment, so cokes which have different calcining levels

ultimately achieved similar values in RD and L_C at the same baking temperature.

Table VII: Value of RD and L_C of Anodes

Calcining Temperature (°C)	Anodes-L		Anodes-H		Anodes-M	
	L_C (Å)	RD (g/cm³)	L_C (Å)	RD (g/cm³)	L_C (Å)	RD (g/cm³)
800	29	2.080	31	2.076	28	2.068
900	28	2.068	29	2.076	29	2.063
1000	29	2.077	32	2.080	29	2.072
1100	29	2.080	32	2.083	29	2.076

Figure 1 show anodes have minimum density when calcining temperature is 800 °C. The density of anodes becomes the maximum when calcining temperature is 900 °C. After 900 °C, the value of anode density decrease with increasing calcining temperature. The density of carbon anode is an important factor determining the lifetime of anode in the pots. The greater the anode density is, the longer the lifetime will be [2]. Therefore, the under–calcined coke can extend the service life of anode, especially when calcination temperature is at 900 °C.
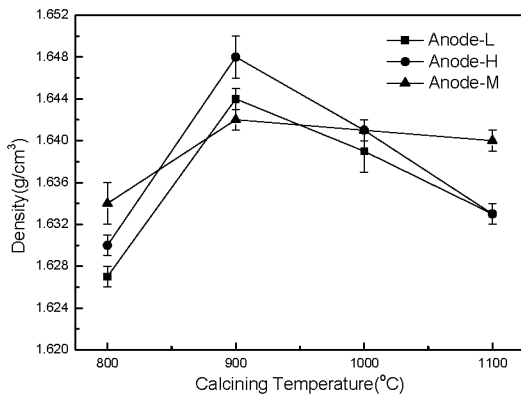
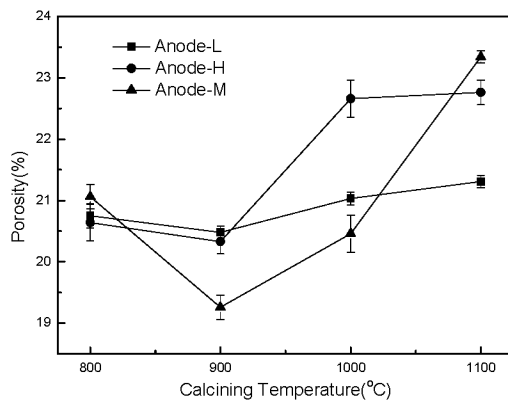Figure 1. Densities of anodes as a function of coke calcining temperature

Figure 2. Influence of coke calcining temperature on porosity of anodes

In Figure 2, the porosity of anodes calcined decreases with increasing calcining temperature from 800 °C to 900 °C, while it increase again as the calcining temperature further increasing up to 1100 °C. The changes, as mentioned above, in both the density

and the porosity can be attributed to the difference in shrinkage behaviors between the skeleton and the binder phase in the same anodes. The lower the calcining level of the coke with limits, the longer the transformation undergone jointly by the skeleton and the binder phase during baking [1]. Thus，there is a smaller porosity in anode. However, the porosity of anodes calcined at 800 °C is greater than anodes calcined at 900 °C. This might be because the shrinkage of coke calcined at 800 °C is too high and lead to the opposite effect.

Figure 3 and Figure 4 show that the anode has minimum loss from the tests of anode-air and anode-CO_2 reactions with calcining temperature of 900 °C, while the mass loss becomes larger with the calcining temperature of 800 °C. The mass loss increases with further increasing the calcining temperature up to 1100 °C.

Figure 2-4 show that trends from test results of the anode porosity and reactivity are similar, and the reason is: the reactivity of anode is related to three basic structural elements as carbon microstructure, porosity and impurities [9]. The reactivity difference generated from carbon microstructure and impurities in anodes made by same petroleum coke with same baking temperature and varying coke calcining temperatures is very small. Thus, the porosity has the biggest effect on the anodes reactivity.
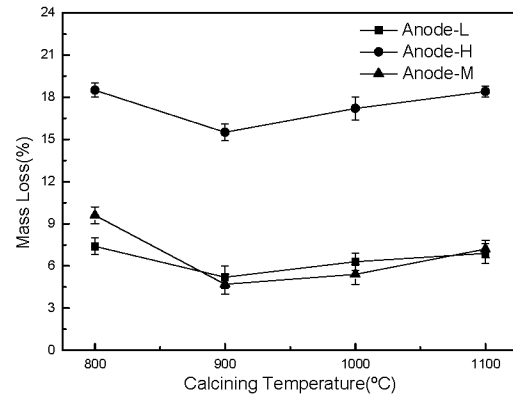

Figure 3. Mass loss (air) of anodes samples produced with cokes calcined at various temperatures (oxidation at T = 525 °C)
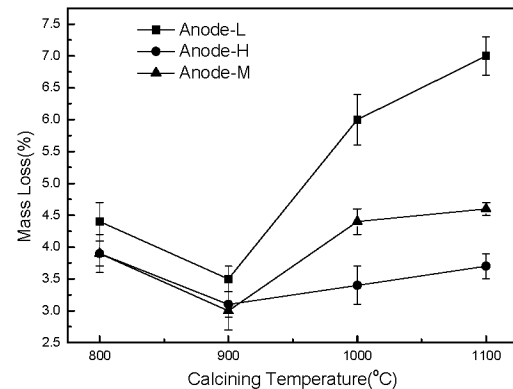

Figure 4. Mass loss (CO_2) of anodes samples produced with cokes calcined at different temperature (oxidation at T = 960 °C)

Figure 5 to Figure 7 show the optimal value of anode electrical conductivity and compressive/shear strength with the calcining temperature of 900 °C. These tests results may be attributed to the

1155

changes of anode porosity like the results of anode reactivity test. The air inside pores of the anode will increase the anode electrical conductivity. The pores also reduce the bonding performance of the binder phase and anode compressive/shear strength.
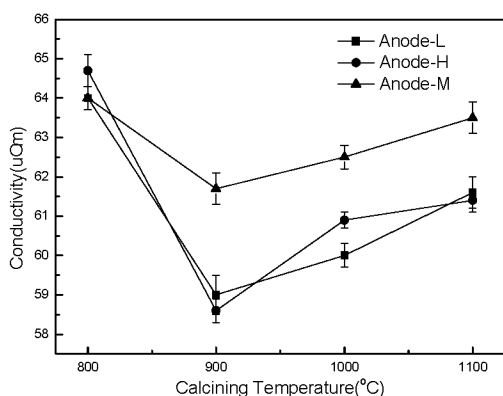

Figure 5. Influence of coke calcining temperature on electrical conductivity of anodes
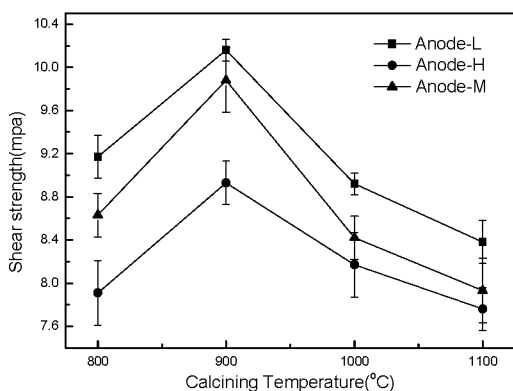

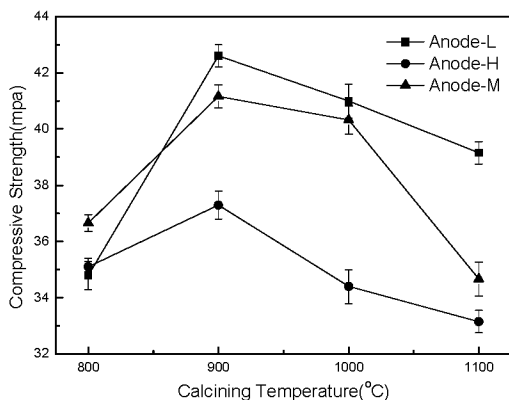Figure 6. Influence of coke calcining temperature on shear strength of anodes

Figure 7. Compressive strength of anodes as a function of coke calcining temperature

Combining results of all the anode properties tests (electrical resistivity, compressive strength, shear strength, porosity and reactivity), it can be found that properties are the best with coke calcining temperature of 900 °C. Regardless of using low sulfur petroleum cokes, high sulfur petroleum cokes, or mixed petroleum

cokes, the test results are the same. This is show that the optimum calcining temperature is 900 °C for the anode preparation. According to Table V, the optimum value of L_C and RD of cokes are 19~20 Å, 1.967~1.985 g/cm^3, respectively.

Because these experiments were conducted in laboratory scale, some problems might exist if the under-calcinated cokes is applied in the industrial production,.The most important one is that the relationship among shrinkage, size, and cracks of industrial anode, which is still absent so far. The problems from the shrinkage of bench-scale anode may not be very clear. The shrinkage of the industrial anode is big, it can make the anode generate huge cracks. The relationship among the shrinkage, size and cracks of anode still need further study.

Conclusion

1. Three types petroleum cokes which come from different sources and have various compositions are calcined at 800, 900, 1000 and 1100 °C, respectively, in which the removal of volatile and the free sulfur can be been completed at a temperature as low as 800 °C.

2. Base on the measurements on the anode properties (electrical resistivity, compressive strength, shear strength, porosity, and reactivity), the calcinations temperature of 900 °C can make optimal results among the cokes tested; the optimum value of L_C and RD of cokes are 19-20 Å, 1.967-1.985 g/cm^3, respectively.

Acknowledgements

References

[1] J Lhuissier, L Bezamanifary, "Use of under-calcined coke for the production of low reactivity anodes," *Light Metals*, (2009), 979-983.
[2] B Samanos, C Dreyer, "Impact of coke calcination level and anode baking temperature on anode properties," *Light Metals*, (2001), 681-688.
[3] M J Chollier, A Gagnon, and C Boulanger, "Anode reactivity: effect of coke calcinations level," *Light Metals*, (2009), 905-908.
[4] D Sulaiman, R Garg, "Use of under calcined coke to produce baked anode for aluminium reduction lines," *Light Metals*, (2012), 1147-1151.
[5] Tran K N et al., "Crystalline structure transformation of carbon anodes during gasification," *Energy and Fuels*, 22(200 8), 1902-1910.
[6] T Muftuoglu, R Fernandez, "The effects of feedstock and coke calcination degree on the properties of bench scale anodes," *Light Metals*, (1990), 511-519.
[7] X Li, J Xue, and T Chen, "Characterization of porous structure and its correlation to sodium expansion of graphite cathode materials using image analysis," *Light Metals*, (2013), 1263-1267.
[8] L Edwards, K Neyrey, L Lossius, "A review of coke and anode desulfurization," *Light Metals*, (2007), 895-900.
[9] B A Sadler, S H Algie, "A porosimetric study of sub-surface carboxy oxidation in anodes," *Light Metals*, (1990), 637-698.