Electrical Resistivity Measurements of Carbon Electrodes

by

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Abstract. Due to the reactivity of coke filler with binder during baking, low electrical resistivity was obtained from carbon electrode specimen made of uncalcined petroleum coke and a binder. The carbon specimen had 44 micro ohm meter electrical resistivity vs 60 micro ohm meter for a regular calcined coke carbon when both were baked at 1100°C. The low value suggests chemical bonding occurred among carbon aggregates in contrast with physical bonding in calcined coke-binder system which has substantial micro cracks in the binder layer coke around filler coke grain boundaries.

Introduction

Carbon electrodes used in the aluminum industry are made with coke aggregates, precalcined at temperatures not exceeding 1300°C and a binder, usually coal tar pitch. The mixture was shaped into large blocks and baked to 1150°C. Good bonding among coke aggregates by the binder carbon is an indication of carbon block quality which can be determined by measurements of electrical resistivity of a carbon specimen. Industrial carbon specimens with calcined coke as filler have electrical resistivity values as low as 60 μΩm (micro ohm meter). It is of interest to determine experimentally the lower limit of electrical resistivity value of a carbon specimen which had thermal treatment(s) history not exceeding 1150°C (1).

According to Mrozowski (2) the energy gap decreases from 0.3 eV for a molecular solid to 0.15-0.03 eV for a carbon baked to 900°-1700°C. The corresponding electrical resistivity measured at room temperature should be approximately 50 μΩm. Many published papers reported the dependence of physical properties of carbons with formulation of the green mix (3). Some established relationships of mechanical strength, electrical conductivity particularly depended on the density of the carbon specimen. Seldin (4) focused on density-resistivity relationship for baked carbons, some of which have been reimpregnated for several times. The lowest value of electrical resistivity was approximately 50 μΩm for a carbon specimen with 4 successive reimpregnations and bakings to 1150°C. The corresponding baked apparent density was 1.6 g/cm^3.

Uncalcined petroleum coke or green coke, still containing approximately 4.2% hydrogen, is very reactive during baking. In presence of a binder, green coke would react with the latter and form chemical bonds. The electrical conductivity of such material would be more uniform because less micro cracks occurred in the carbon specimen.

Experimental

Properties of Starting Materials

Table I gives analytical results of raw materials. Two types of green cokes with different volatile matter content were used in the experiments. Petroleum residue with low coking yield (10%) was used as binder with green coke "A" and "C".

Table I: Properties of Starting Materials

	Filler Green Coke "A"	Filler Green Coke "C"	Binder Pet. Resid.
Volatile Matter (%)	14.9	9.20	85.6
Elemental Analysis (%)			
C	91.9	92.1	90.3
H	4.27	4.10	7.37
N	1.44	1.53	0.41
S	--	1.68	0.79
Coking Yield (%)	90.2	92.1	10.0
Softening Point (°C)	--	--	20
Specific Gravity (g/cm^3)	1.36	1.38	1.02

Processing

Samples of starting materials were processed in laboratory scale. Cokes were crushed and sized into fractions suitable for anode manufacture. Carbon aggregates pastes were mixed in a sigma blade mixer. Mixing and pressing temperatures were set at 140°C for calcined coke-binder pitch system. Mixing and pressing were performed at room temperature for green coke-petroleum resid binder system. Green anode samples (about 400g) were baked under N_2 purge to 1125°C with a standard 25°C/hr heating rate and held at 1125°C for 10 hours before allowing the furnace to cool.

Electrical measurements were determined by calculating the voltage drop measured at room temperature by the four-point method using a set of probes separated by 25.4 mm and passing 6A of direct current through the anode.

Table II: Properties of Anodes Using Green Coke "A" (14.9% VM) and Green Coke "C" (9.2% VM) and petroleum resid binder

% Binder	Density (g/cm^3) GAD "A"	GAD "C"	BAD "A"	BAD "C"	Electrical Resistivity (μΩm) "A"	"C"
0	1.13	--	1.33	--	135	--
3	1.13	--	1.34	--	108	--
8	1.14	1.10	1.41	1.29	68	433
12	1.23	1.17	1.49	1.38	51	150
16	1.25	1.27	1.54	1.55	45	62

GAD: green apparent density
BAD: baked apparent density

Discussion

Petroleum resid was used as binder when green cokes were filler. The binder can ultimately dissolve partially the surface of the filler aggregates. During carbonization, cracking of weak bonds and formation of new stable bonds simultaneously occurred. Above 500°C, the carbonaceous material starts to shrink. Since the whole body of the small sample shrinks uniformly, no micro cracks occurred, thus better electrical conductivity was allowed in the carbon.

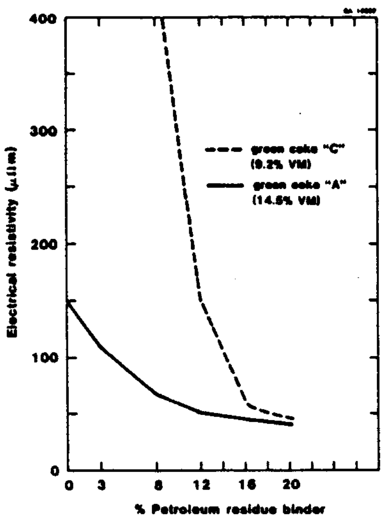

Figure 1. Evolution of anode electrical resistivity with different binder levels.

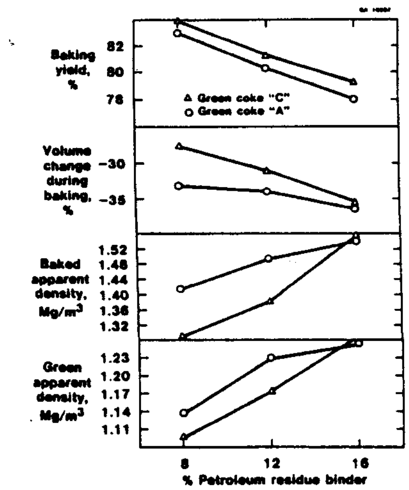

Figure 2. Green coke anode properties made of two types of green cokes and petroleum resid binder.

The amount of liquid binder is important because the volume of the binder occupied in the aggregates would determine the extent of dissolution of green coke. It appeared that approximately 12% to 16% binder is required for best chemical reactivity among filler and binder during baking (See Figure 1 and Table II).

Volatile matter content of each green coke also determines the extent of dissolution of green coke by the binder. Low volatile matter content green coke displayed higher electrical resistivity in anodes than high volatile matter content coke. This again indicates good bonding among aggregates dictates the quality of a carbon anode which was also proved by different chemical reactivity tests (e.g. air burning, CO_2 gasification, Al_2O_3 electrolysis...) (1).

Conclusion

Chemical bonding among carbon aggregates resulted in low electrical resistivity values measured on a carbon anode made with petroleum green coke and a binder. The lowest value was 44 μΩm for this specimen. The amount of binder should be adjusted to a volume that would occupy the empty space of the aggregates. The uniform shrinkage of the filler and the binder during baking made a crack-free carbon specimen which allowed the electrical current to pass without interruption.

References

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