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Effect of heat treatment on desulphurization of petroleum coke

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Calcined petroleum coke (CPC) is one of major constituent used for making graphite electrodes. Increasing demand of graphite electrodes requires more and more quantity of high quality-low sulphur calcined petroleum coke. The sulphur content of the petroleum coke strongly depends on the nature of the coking feed stock (crude oil) and its sulphur content. High sulphur coke (>1%) is not desirable for making graphite electrodes because evolution of sulphur causes puffing in the temperature range of 1,400-2,200 °C during graphitization. In this study, attempt has been made to reduce the sulphur of calcined petroleum coke by heat treatment to the acceptable level for making graphite electrodes. A high sulphur coke (approx. 2%) was heat treated up to 1,800 °C in inert atmosphere in order to reduce the sulphur content. It was observed that most of the sulphur goes off up to 1,800 °C. A sample of size 12x80 mm was prepared (by extrusion method) from desulphurized petroleum coke using coal tar binder pitch as binder at 125 °C. The extruded samples were carbonized at 900 °C, followed by graphitization at 2,900 °C. The graphitized rods were characterized for various properties such as apparent density (AD), electrical resistivity (ER), flexural strength (FS) and compared with the properties of samples made from electrode grade CPC.

Keywords: Calcined petroleum coke (CPC), Coal tar pitch, Extrusion, Carbonization, Graphitization, Flexural strength

1 Introduction

Petroleum coke, a solid residue of oil refining, is composed primarily of elemental carbon organised as a porous polycrystalline carbon matrix. The specific chemical composition of a petroleum coke is determined by the composition of the feed stocks used in the coking process, which in turn are dependent upon the composition of crude oil and refinery processing from which the feed stock is derived[1-2]. Coke produced from feed stocks, high in asphaltenes, will contain higher concentrations of sulphur and metals than cokes produced from high aromatic feed stocks. The sulfur content in petcoke varies widely from 1 to 6%, depending on the sulfur content of feedstock[3]. Sponge coke containing 4% is used for fuel, whereas less than 4% sulfur content is used in anode manufacturing. Needle cokes for electrode manufacturing are required to have less than 1% sulfur content[4]. High sulphur coke cannot be used for making graphite electrodes due to puffing, which may be reduced to an acceptance level by using puffing inhibitors like Fe_2O_3[5-6]. Thermal desulphurization is an effective method to reduce the sulphur of petroleum coke to an acceptance level to make it useful for making graphite electrodes.

Desulphurization is dramatically increased when coke is heated above 1,400 °C. The energy available above this temperature is sufficiently high for the decomposition of sulphur-hydrocarbon compounds of stabilities up to those of thiophene structure[7]. However, complete elimination of sulphur does not take place even at this high temperature[8-9].

2 Experimental Section

2.1 Raw material

High sulphur CPC (sulphur- 2.07%, real density (RD)-2.11g/cc, volatile matter-0.11%, ash-0.26%) were taken for this study

2.2 Heat treatment

High suphur CPC was heat treated at 1400, 1500, 1600, and 1800 °C for 2 h soaking time in the atmosphere of nitrogen gas. Heat treated coke samples were characterized for sulphur, wt. loss, real density (RD), mercury density (HgD) and vibrated bulk density (VBD). The properties of heat treated (desulphurized) cokes along with the electrode grade CPC were shown in Table 1.

2.3 Sample preparation

Samples of size 12x80 mm from heat treated high sulphur CPC (Exp. No.- HS-2, Table 1) were prepared using coal tar pitch as a binder by extrusion method.

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Table 1 — Properties of as such and desulphurized CPC.

Exp No.	Temperature (°C)	Sulphur (%)	Wt. loss (%)	RD (g/cc)	HgD (g/cc)	VBD (g/cc)
HS-0	As such	2.07	-	2.079	1.734	0.708
HS-1	1400	1.35	1.2	2.079	1.693	0.686
HS-2	1500	0.90	2.1	2.071	1.619	0.679
HS-3	1600	0.54	2.8	2.062	1.604	0.670
HS-4	1800	0.28	3.2	2.053	1.552	0.650
Electrode grade CPC		0.80	-	2.125	1.762	0.721

Table 2 — Properties of graphitized samples.

Properties	High sulphur CPC	Desulphurized CPC	Electrode grade CPC
Apparent Density (g/cc)	1.458	1.544	1.438
Volume change (%)	-1.10	-2.57	4.53
Electrical resistivity (μΩcm)	855	800	759
Flexural strength (DaN/cm^2)	144	150	128
CTE (mm/mm/°C)	2.39	2.20	1.81

All the samples were baked at 900°C for 2 hr soaking time in presence of nitrogen atmosphere and finally graphitized at 2800 °C for 3 h soaking time in presence of nitrogen atmosphere. Graphitized samples were characterized for apparent density (AD), electrical resistivity (ER, flexural strength (FS) and coefficient of thermal expansion (CTE). Similar samples were prepared from as such high sulphur coke and electrode grade coke and properties were compared with that of heat treated coke. Graphitized properties of all samples are summarized in Table 2.

Puffing samples of size 25x25 mm from as such high sulphur coke and heat treated coke (with and without iron oxide) using coal tar pitch as a binder by molding method. Samples were baked at 900 °C and puffing was carried out up to 2700 °C in nitrogen atmosphere.

2.4 Characterization

- **Apparent density -** Dimensional AD was measured using vernier caliper of least count 0.01mm and weighing balance of least count 0.01g. (AD=mass/volume, g/cc)
- **Electrical resistivity -** Electrical resistivity was measured by four probe method. (ER=RA/L, μΩcm, R-resistance, A-cross-sectional area, L-probe distance)
- **Flexural strength -** Flexural strength was measured by four point method. (FS=16FL/3d3, DaN/cm2, F-max force, L- load span, d-specimen diameter)
- **Coefficient of thermal expansion (CTE) -** CTE was measured from 25 to 520 °C using Dilatometer. (CTE=l/Lt mm/mm/°C, l-change in length, L-specimen length, t-change in temperature).

Puffing-puffing was carried out on baked samples by heating them from room temperature to 2,700 °C with controlled heating rate in nitrogen atmosphere. During heating, change in length was recorded and maximum percent expansion was calculated.

3 Results and Discussion

Sulphur is an undesirable element in calcined petroleum coke which causes puffing during graphitization. To a certain extent, puffing can be controlled by modifying electrode recipe, heating rate or by using puffing inhibitors[5-6]. As shown in Table 1, high sulphur coke (anode grade CPC) is inferior to electrode grade CPC in terms of sulphur, RD, HgD and VBD. Desulphurization started after calcination temperature (1200-1300 °C) and continued till 1800 °C. More than 50 % of sulphur was removed at 1500 °C, 85 % of sulphur was removed at 1800 °C and 15 % of sulphur still remained in heat treated coke. The desulphurized CPC of 0.90 % sulphur content was used for making graphite electrode samples and processed till graphitization.

Desulphurized CPC showed the maximum graphitized AD due to higher volume shrinkage (Table 2). It showed that there was no puffing took place in desulphurized coke samples whereas electrode grade samples showed an expansion of 4.57 %. The electrical resistivity of desulphurized coke decreased from 855 μΩcm to 800 μΩcm, while flexural strength was increased slightly from 144 DaN/cm^2 to 150 DaN/cm^2 due the higher density. The electrical resistivity of high sulphur coke after desulphurization was found to be comparable with electrode grade CPC, whereas CTE was not comparable because of the type of coke taken for the study was anode grade grade CPC.

The percentage expansion of high sulphur coke before and after desulphurization with respect to heat treatment temperature up to 2700 °C (Fig. 1). The initial expansion up to 1250 °C was due to CTE (coefficient of thermal expansion), from 1250 °C to 1500 °C the rate of expansion was slowed down because formation of crystalline structure started in this temperature range. The sudden expansion (called puffing) from 1500 °C to 1800 °C was due the release of sulphur. Highest puffing of 1.15 % was observed in high sulphur coke without adding iron oxide which

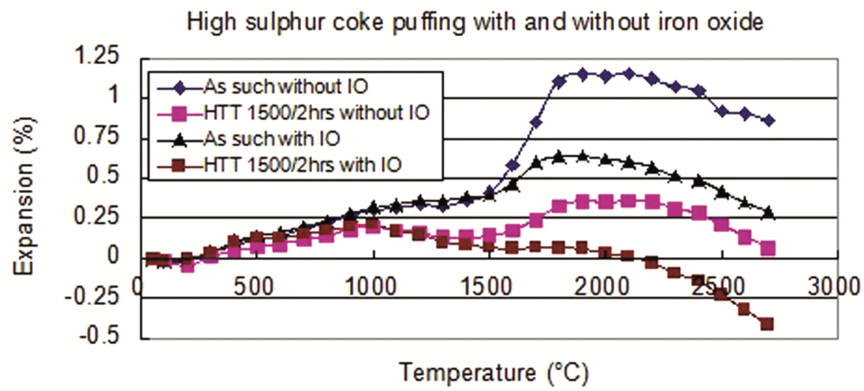

Fig. 1 — Puffing curve of high sulphur and desulphurized coke with and without iron oxide (IO).

was reduced to 0.6 % after adding iron oxide. The desulphurized coke showed puffing of 0.35 % without iron oxide and showed shrinkage (no puffing) after adding iron oxide.

2 Conclusions

Thermal desulphurization is an effective way to upgrade a poor quality coke (high sulphur coke) and to make it suitable for making graphite electrode. The sulphur content of CPC decreases on increasing the desulphurization temperature. At 1500 °C, the sulphur content was reduced to less than 1 % i.e. 0.90 %, which was found to be suitable for making graphite electrodes. The graphitized AD and FS of desulphurized coke were found to be higher than than the electrode grade CPC and electrical resistivity was comparable. Desulphurized coke showed much lower puffing and with iron oxide it showed shrinkage (no puffing) therefore it can be concluded that removing sulphur by heat treatment is an effective method to make the high sulphur coke suitable for making graphite electrodes.

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