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STUDIES ON THE GRAPHITIZATION OF CALCINED PETROLEUM COKE IN NITROGEN ARC PLASMA

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Abstarct*:The present work deals with the laboratory scale production of 4-H graphite by the heat-treatment of the homogeneous mixture of calcined petroleum coke powder (CPC) and boron catalyst in nitrogen and hybrid nitrogen cum argon arc plasma in the extended argon arc plasma reactor (EAAPR).The graphite product obtained from the heat treatment of homogeneous raw material mixture consisting of 99.5% CPC and 0.5 wt %, boron powder in the EAAPR by the application of hybrid nitrogen cum argon arc plasma for 45 minutes showed real density of 2.15 g/cc, electrical resistivity of 0.022 Ωcm. The XRD studies on the plasma heat-treated product showed 100 % relative intensity peak of 4-H graphite at d_{002} =3.37Å.Where as the graphite product obtained after heat treatment of homogeneous mixture of 99.5%CPC and 0.5 % boron in pure nitrogen arc plasma for 45 minutes showed density of 2.24 g/cc, electrical resistivity of 0.023 Ω cm. The XRD studies on the plasma heat-treated product also showed 100 % relative intensity peak of 4-H graphite at, d_{002} =3.37Å. The product yield in both the cases was as high as 92.0%.*

[Key words: Calcined petroleum coke, Graphitization, Nitrogen plasma, Argon plasma]

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Introduction:

In recent years synergetic efforts are being made to synthesize high temperature advanced materials employing novel thermal arc plasma devices. Its specific advantages have been highlighted in the literature [1-3]. The thermal plasmas render the task of graphitization of amorphous carbon (a-carbon) much easier, because the charge can be rapidly heated to graphitization temperatures of 2600 to 3500 ºC in inert nitrogen or argon atmospheres. In our earlier investigations we have reported graphitization behavior of CPC powder in argon arc plasma and mention was made on the effect of addition of transition element catalysts on the degree of graphitization of CPC during its plasma heat treatment [4]. Several worker,[5- 8] have tried to improve the kinetics of graphitization by the addition of the transition element catalyst and they have also established the beneficial

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effect of addition of boron in lowering the temperature of graphitization of a-carbon during high temperature catalytic graphitization. The mechanism of catalytic graphitization has been discussed by several authors in the literature[8].

The nitrogen as a catalyst also plays the role of boron when it is introduced in to the CPC charge in the ionic state from nitrogen plasma i.e it forms solid complexes such as CN,C_3N_4 at high temperature which might help the process of diffusive graphitization. The use of nitrogen plasma in place of argon arc plasma is expected to reduce the cost of production of graphite powders. Oya et al,[9] have discovered the effect of addition of transition element catalysts on the rate of graphitization of a-carbon derived from resins. The present work describes the graphitization behavior of homogeneous mixture of CPC powder and boron catalyst during its heat treatment in nitrogen and hybrid nitrogen cum argon arc plasma in the EAAPR and characterization of heat-treated graphite powder products.

Experimental :

Materials & Methods: The calcined petroleum coke powder (CPC) supplied by M/s Nalco Ltd, Bhubaneswar, India., was used as one of the raw materials. The fixed carbon content of CPC was found to be 98%. The amorphous boron powder of 99.0% purity supplied by M/s Merck India Ltd., was used as catalyst in these experiments. The plasma forming argon gas of 99.9 % purity and nitrogen gas of 99.0% purity supplied by M/s. Industrial Gas Company, Bhubaneswar, Orissa were used for the generation of argon arc plasma and nitrogen arc plasma respectively.

In order to render the charge more effective for the graphitization, the CPC powder of –60 +100 BSS mesh size was dry mixed with requisite quantity of boron catalyst in a rotary ball mill for 15 to 30 minutes in dry conditions. The schematic cross sectional diagram of extended argon arc plasma reactor (EAAPR) used in this investigations is shown in fig -1. Two types of plasma heat treatment experiments were carried out on the CPC charge mixture.

In the first batch of plasma heat treatment experiments,200.0g of the homogeneous charge mixture consisting of CPC powder and 0.5 % boron powder was poured into cylindrical graphite crucible kept on graphite anode and to begin with the graphite cathode tip was made to contact the inner bottom of the graphite crucible then DC voltage was of 50 V was supplied across the electrodes and hybrid plasma arc was generated by passing nitrogen gas a rate of 0.5l/min and argon gas at rate of 1.5l/min into hollow cathode and withdrawing the cathode to optimum height with the help of rack and pinion gear to a optimum height thus plasma arc was stabilized. The charge was subsequently heat treated in EAAPR in argon plus nitrogen hybrid arc plasma for the isothermal time duration of 45 minutes. After heat treatment, the

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electrical power to plasma reactor was put off and hot charge was cooled in argon gas stream to 773 K and the semi cooled charge was further furnace cooled to room temperature.

In the second batch of plasma heat treatment experiments, the homogeneous charge consisting of 99.5%CPC and 0.5 wt % B, stored in a cylindrical graphite crucible was heat treated in static bed EAAPR in nitrogen arc plasma for the isothermal time duration of 45 minutes. The nitrogen plasma arc was generated over the CPC charge mixture in the graphite crucible by passing dry N_2 at flow rate of (1.5 lpm) through hollow cathode and simultaneously applying ripple free D.C potential of 50 V, across the electrodes and the stabilization of plasma arc was effected by raising the tip of the hollow cathode to optimum height of 7-8 cm over the charge with the help of rack and pinion gear. After heat treatment, the electrical power to plasma reactor was put off and hot charge was cooled in argon gas stream to 773 K and further furnace cooled to room temperature.

The bench scale experiments on high temperature graphitization using 2.0 Kg CPC raw material charge consisting of 0.5 wt % boron catalyst were also carried out in nitrogen plasma in 2.5 liter capacity hearth crucible in a similar manner employing input electrical voltage of 35 volts, and input electrical current of 250 amperes for 1h to determine the electrical power consumption per kilogram of the graphite product produced.

The plasma heat-treated graphite product was leached in 5% v/v HCl for 30.0 minutes, rinsed with distilled water and dried in an electrical oven at 100 ^{0}C for 1h.

Measurement of density

The apparent density of graphite powder samples was determined using density bottle and distilled water as dispersing media.

XRD measurements

The lattice parameters of heat treated powder products were determined employing Philips PW –3710 based' X 'pert X- ray system. The CuKα radiations were utilized to record the XRD spectrum of samples over spectral span of 10 to 70^o. X -rays were generated by imposing 35.0 kV biasing voltage across the cathode, while maintaining a generator current of 20.0 mA. The wave length of X rays emitted from cathode was maintained at α_1= 1.54056 Å.

Proximate analysis

The moisture, volatile matter, ash and fixed carbon present in the CPC and plasma heat treated samples were determined using LECO 601, TG apparatus.

Measurement of electrical resistivity

The electrical resistivities of CPC and different graphite powder samples were measured using electrical micro- ohm meter (Model: DOT-405 Indian make) in a capillary glass cell with aluminium electrodes as per ASTM (126) procedure.

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SEM studies

The microstructures different graphite samples obtained after plasma heat treatment were observed using JEOL-8100, EPMA scanning electron microscope

The degree of graphitization of plasma heat treated sample is calculated using Maire et Mering [10] formula i.e P=3.44 - d_{002}/ 3.44-3.354*100,

Where, P = Degree of graphitization in percentage and d_{002}= Interlayer distance between the successive basal planes of graphite powder sample in (Å). The constant 3.354 Å corresponds to interlayer distance between the successive basal planes of perfect graphite crystal.

Results and discussion:

The ash analyses of CPC and graphite samples obtained by different plasma heat treatments are shown in Table I. The volatile matter in plasma heat treated graphite product is decreased after plasma heat treatment of CPC sample in nitrogen plus argon plasma environment. In the plasma heat treatment of CPC charge mixture for graphitization, there is small increase in ash content which may be attributed to the oxidation of B_4C (formed during plasma heat treatment) to B_2O_3 phase during heating of the same to high temperature of 900 ^{0}C in air during ash determination. This phase does not volatilize even at high temperature hence ash content is slightly increased. The variation of ash content and volatile matter shows same trend for the graphite powder prepared in nitrogen plasma. Table II, evinces density, electrical resistivity, degree of graphitization of graphite product and electrical parameters of plasma heat treatment in EAAPR. The results, of thermal plasma graphitization of CPC in nitrogen arc plasma experiments shown in Table-II, indicate same level of graphitization of CPC as that of hybrid nitrogen cum argon plasma arc heating of similar charge under the identical electrical power loading conditions and catalyst concentration. Nitrogen being cheaper, graphite powder can be produced at lower cost in nitrogen plasma. The mode of graphitization of CPC in nitrogen plasma can be depicted from the following XRD data.

Fig 2a.evinces XRD spectrum of CPC sample mixed with 0.5 % boron and heat treated in hybrid nitrogen cum argon arc plasma for 45 minutes at an electrical power input of 200 amperes and 35 volts (Table-2). The XRD spectrum shows peaks of 4-H graphite. The product sample shows a density of 2.15 g/cc, electrical resistivity of 0.022 Ω cm and degree of graphitization of 81.39 %.

Fig 2b.evinces XRD spectrum of CPC sample mixed with 0.5% boron and plasma heat treated in nitrogen plasma at an input electrical power loading conditions of 35 volts and 350 amperes (Table-II), for 45minutes. The

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XRD pattern shows peaks of 4-H graphite. The product sample shows a density of 2.24 g/cc, electrical resistivity of 0.023 Ω cm and degree of graphitization of 81.39%.

The micro-structural features of graphite powder obtained after thermal plasma heat treatment of homogeneous mixture of CPC and 0.5 % boron on argon arc plasma for 45 minutes are described else where in the literature. [4]

Fig 3a. Evinces low magnification SEM photomicrograph of graphite particles obtained after plasma heat treatment of homogeneous mixture of CPC and 0.5% boron catalyst in nitrogen arc plasma at 350 amperes for 45 minutes. The irregular platy particles with layered structure having wide size distribution of particles are observed in the micro structure. Considerable number of flaky particles are stacked in layered structure.

Fig 3b, evinces high magnification SEM photomicrographs of same graphite sample. The majority of particles show flaky morphology with the layered arrangements of graphitic plates. Very small number of second phase inclusion particles are also observed on the surface of graphite flakes.

Conclusions :

1) The use of nitrogen arc plasma heating in place of argon arc plasma heating method lowers the cost of production of graphite from CPC. Bench scale experiments carried out in this investigations show that nitrogen plasma heating method gives a graphite product with a degree of graphitization of 81.39 % and associated electrical power consumption for the graphitization of CPC is around 4.35 KWh/Kg. The addition of 0.5% boron catalyst enhances the kinetics of the graphitization of CPC charge.

2) Use of, hybrid nitrogen cum argon arc plasma heating method for the production of graphite from homogeneous mixture of CPC and 0.5% boron catalyst, shows same degree of graphitization (81.4%) but the cost of production increases due to higher cost of argon gas.

3) The physical and electrical properties of graphite powder obtained by heat treatment in nitrogen and hybrid nitrogen cum argon arc plasma are comparable to the commercially available graphite samples. But the use of nitrogen plasma reduces the cost of production.

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help rendered in taking SEM photographs of different samples.

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TABLE-I

Analyses of ash, volatile matter and fixed carbon present in CPC and graphite samples produced from plasma heat treatment of CPC.

Sample description	Constituents. wt%		
	Volatile matter	Ash content	Fixed carbon
CPC	1.7	0.2	98.1
CPC powder mixed with 0.5% boron and heat treated in hybrid nitrogen cum argon plasma for 45.0 minutes at 200 amperes in the EAAPR	0.4	0.4	99.2
CPC powder mixed with 0.5% boron and heat treated in nitrogen plasma for 45.0 minutes at 350 amperes in EAAPR for 45 minutes	0.4	0.4	99.2

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TABLE-II

Physico –electrical properties of graphite powders, produced from heat treatment of CPC in nitrogen and hybrid nitrogen cum argon arc plasma for 45 minutes at different electrical loading conditions

Sl No	Sample Details	Density g/cc	Electrical Resisitivity Ω cm	Volts	Amperes	100% XRD Peak d_{002} (Å)	Degree of Graphitisation %	Product Yield, %
1)	CPC+0.5% boron, in Ar+ N_2 plasma	2.15	0.022	35	200	3.37	81.37	90
2)	-do-	2.15	0.022	35	350	3.37	81.39	92
3)	CPC+0.5% boron, in N_2 plasma	2.24	0.023	35	350	3.37	81.39	92

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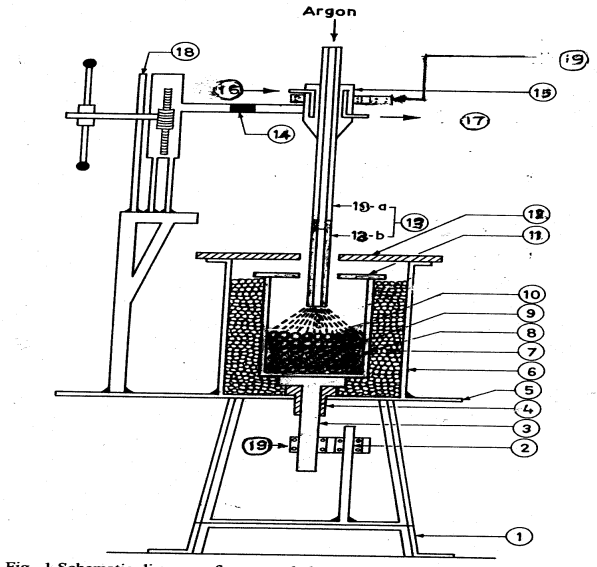

Fig –1 Schematic diagram of an extended argon arc plasma reactor 1)M.S stand 2) Electrical connection to lower graphite anode 3) Lower graphite electrode 4)Alumina bush 5) MS supporting plate 6) MS cover 7) Bubble alumina insulations 8) Graphite crucible 9) cpc charge 10) Plasma arc 11) Graphite lid 12) Alumina board 13)a) Copper holder for cathode ,b) Hollow graphite cathode 14)Horizontal arm 15) Water cooled copper holder , 16) Cooling water inlet 17) Hot water out let 18) Rack and pinion gear with handle. 19) Electrical connections to cathode and anode

8

Fig.1) Cross-sectional diagram of extended argon arc plasma reactor (EAAPR)

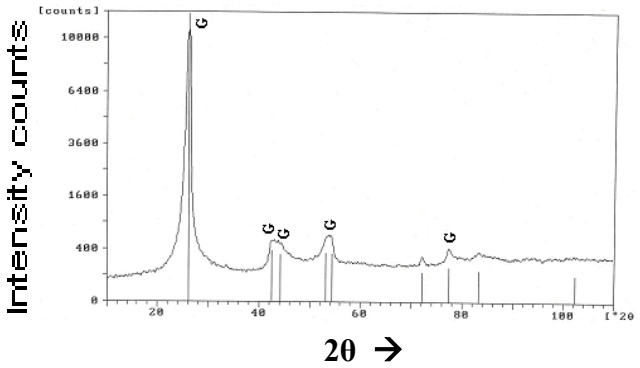

Fig- 2 a), XRD spectrum of (a) CPC mixed with 0.5 wt% boron and heat treated in hybrid nitrogen cum argon arc plasma for 45 minutes at 200 amperes.

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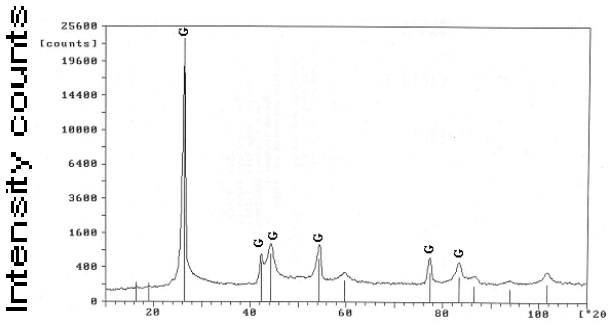
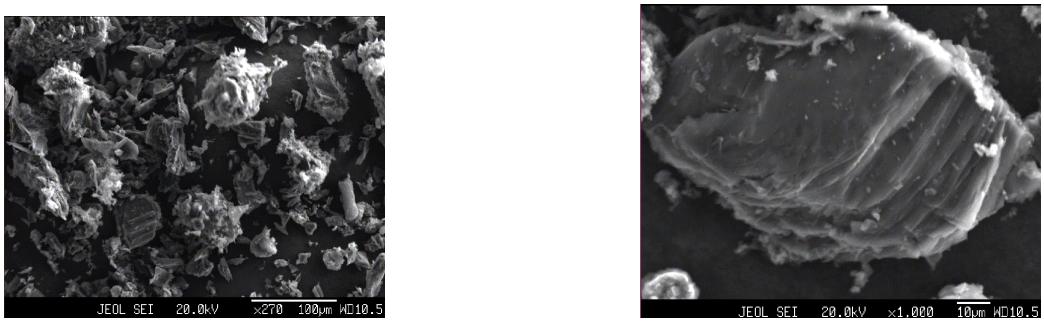


2θ →

Fig -2b), XRD spectrum of CPC mixed with 0.5% boron and heat-treated in nitrogen plasma for 45 minutes at 350 amperes.



(a) **(b)**

Fig -3, SEM photomicrograph of (a) CPC mixed with 0.5% boron, heat treated in nitrogen arc plasma for 45 minutes at 350 amperes (270X) and b) CPC mixed with 0.5 wt%, boron and heat treated in nitrogen plasma for 45 minutes at 350 amperes(at 1000X) ,

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