

Physico-chemical Behaviour of Southern Indian Graphite Used for Refractory Manufacture

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Graphite is a soft, black crystalline form of naturally occurring carbon. In India it is abundantly available and there are three major sources namely Palamau of Jharkhand, Bolangir of Orissa and Sivaganga of Tamil Nadu. Refractory industry is the major consumer of graphite and in India Palamau and Tamil Nadu sources are used as additive for refractory industry. In this paper an attempt has been made to investigate the physico-chemical properties of Tamilnadu graphite and also behaviour of the graphite in oxidising atmosphere was investigated. Oxidation behaviour was studied in DTA/TGA by oxidising two size fractions of the graphite in controlled atmosphere to understand the effect of size on oxidation and it was found that the behaviour is independent of the size fractions considered for investigation.

Introduction

Graphite is a soft, black crystalline form of naturally occurring carbon. Natural graphite occurs generally in large masses but found as nodules in eruptive rocks and in veins through cracks in sedimentary rocks. Natural graphite is often found in connection with carbonates and other carbon compounds and could be the result of their decomposition under conditions of high pressure and high temperature. Properties of graphite are given in Tab. 1. The oxidation reactivity of graphite and the structure of the carbon are interrelated. The influential factors are the optical texture, the crystallinity, the pore structure and catalytic impurities. The former two factors are related to the orientation and the graphitizability respectively, influencing the reactivity of carbon atoms in the

graphite layers. The third defines the access of oxidants to carbon. The reactivity of edge carbon atoms in the hexagonal sheet is larger than that of the atoms within the sheet, therefore, its reactivity with the gaseous oxidants generally decreases with better orientation (larger anisotropic development) and graphitization. The surface area including the walls of the small pores contributes to the reaction. The rate of reaction competes with that of diffusion at higher temperatures and at further higher temperatures, the diffusion becomes rate determining. Thus, the pores affect the rate of reaction, the smallest pores becoming unimportant to the reaction. In India refractory industry is the main user of graphite and consumes about 60 % of total graphite production for making carbon bearing refractories

for different industries. Indian refractory industries use graphite from three sources, i.e., Sivagangai district of Tamil Nadu, Palamau belt of Jharkhand and Sambalpur/Bolangir district of Orissa apart importation from China. As per the National Mineral Inventory [1] as on 1 April 1990, total recoverable reserves of graphite in India are placed at 4,8 Mt with an average grade of 10 to 40 % fixed carbon, occasionally rising to 60 %. Out of that about 400 000 t are available in Tamil Nadu state in Southern India. The Tamil Nadu graphite at latitude of 9,8° and longitude of 79,6° was originally having 20 % fixed carbon at the mine head and taken out from the mines in lump form. They are then crushed, and purified by floatation in Outokumpu Cell. Washing, centrifuging, drying, screening process and with repeated floatation for three times fixed carbon content proved to 96,2 % and sample was collected from this lot.

Literature review

The ideal crystal lattice is the hexagonal α -form. The basal planes consist of open hexagons (interatomic spacing = 0,1415 nm) stacked in an alternating sequence with a lattice spacing of 0,33539 nm [2]. Use of graphite as carbon additive in refractory imparts good corrosion resistance to the refractor but in oxidizing atmosphere it is susceptible to high oxidation. Oxidation of carbon by oxidising agents is popularly known as "gasification"

Tab. 1 Typical properties of graphite

Properties	Values
Density [g/cm ³]	~2,26
Thermal conductivity [W/m·K]	~5,2
Coefficient of thermal expansion [$\times 10^{-9}/K$]	1~0
Tensile strength [kPa]	14~21
Modulus of elasticity [kN/mm ²]	50~60
Electric resistivity [M Ω cm]	50~60
Hardness (Rockwell)	90~100

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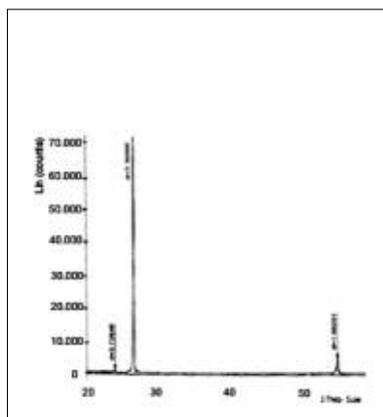


Fig. 1 X-ray diffraction pattern of Tamil Nadu graphite

and the rate at which carbon loses weight is generally termed as “reactivity”. Gasification reaction is characterized by high activation energy indicative of chemical control of the reaction. However, it has been established that mass transfer also tends to contribute significantly towards the rate of reaction specially at high temperature [3–5]. As chemical control dominates the gasification reaction, the mechanism of the same has been developed on the basis of adsorption of reactant gases on the surface, reaction on the surface and desorption of the product gas. It has been found [4–5] that migration of carbon atoms in the solid state is too slow at practically all the temperatures. Thus an oxidation reaction involves:

- initiation step
- succession steps.

In the initiation step, the oxidizing agent gets attached to the part of the carbon network, either on the edge site or on the sur-

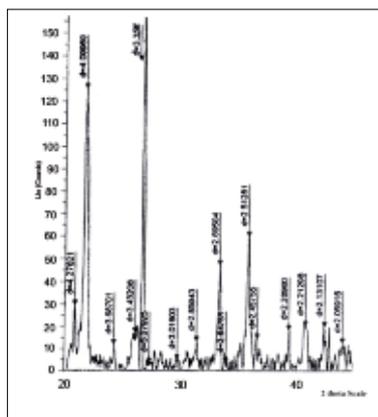


Fig. 2 X-ray diffraction pattern of ash of Tamil Nadu graphite

face and in that process satisfies the localized unbalanced valences. Following the attachment of oxidizing agent to the carbon network in the “initiation step” of some kind, the solid product will, if the temperature is sufficiently high, rearranges its bond to give a volatile product. This will leave back an active site in the carbon network. Further bond rearrangement may then follow and if oxidizing agent can be attached to the carbon in the same way as before, a succession sequence of oxidation step will be established. It is apparent from the above discussion that besides other parameters, such as porosity, which determines the access of the oxidizing gas inside the sample, surface area which determines the available area for reaction, structural imperfection or defects play a significant role for gasification of carbon. This is because the extent of defects in the structure of the sample will dictate the number of active sites available. If,

somehow, the structural imperfections are removed, then it is evident that there will be reduction in active sites. This, in turn, should improve the oxidation resistance of carbon.

Experimental

Chemical analysis of ash by XRF method and proximate analysis of graphite were measured and given in Tabs. 2–3. Grain density was measured by pycnometer method (using xylene as immersion liquid) and surface area of graphite was measured by BET’s method. Fusion temperature of ash was measured. X-ray diffraction analysis of graphite and its ash were done in BRUKER AXS model no. DN8 and shown in Figs. 1–2 and then using *Maire and Mering’s* formula degree of graphitization was determined. SEM/EDAX of the sample was done in JEOL JSM-840A microscope and shown in Figs. 3, 6. Optical microscopy was done under crossed and plane polar with 10× magnification and shown in Figs. 7–8. The extent of oxidation

Tab. 3 Chemical analysis of graphite ash

Constituent [mass-%]	Tamil Nadu
SiO ₂	67,54
Al ₂ O ₃	14,67
Fe ₂ O ₃	13,52
CaO	0,87
MgO	0,96
TiO ₂	0,37
Na ₂ O	0,29
K ₂ O	0,46
P ₂ O ₅	0,24
S	0,45

Tab. 2 Proximate analysis of graphite sample

Sample No.	Sample Size (BSS)	Moisture [%]	Volatile Matter [%]	Ash [%]	Fixed Carbon [%]
TG ₂	–60+150	0,23	1,77	3,2	94,8
TG ₁	–30+60	0,2	1,1	2,5	96,2

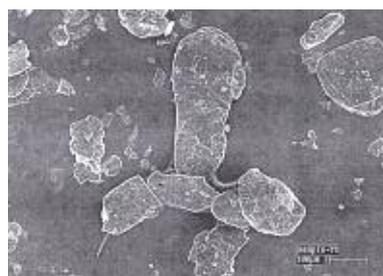


Fig. 3 Topographic view of Tamil Nadu graphite in SEM

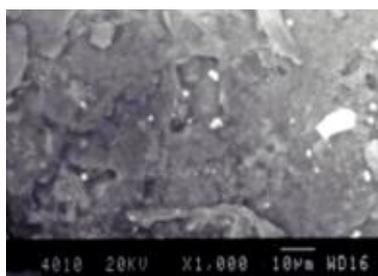


Fig. 4 SEM of Tamil Nadu graphite in SEM

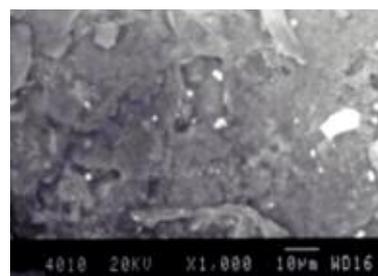


Fig. 5 SEM/EDAX showing distribution of impurities in Tamil Nadu graphite

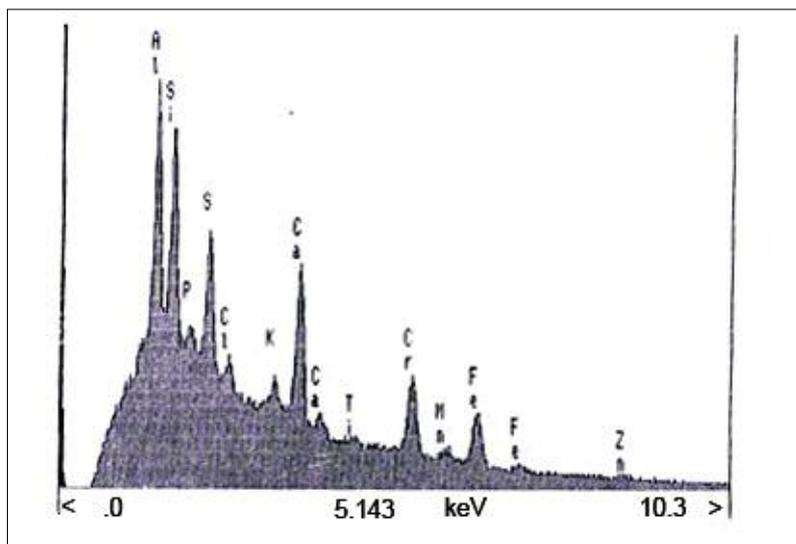


Fig. 6 EDAX of above sample

of graphite sample as a function of time was followed gravimetrically and isothermally at temperatures from 735 to 830 °C in both air and oxygen atmosphere under controlled condition in NETZSCH (STA-90) DTA/TGA apparatus and taking two fractions of graphite i.e., (-30+60) BSS i.e., TG1, and (-60+150) BSS* fractions i.e., TG2. (*BSS-sieves: 30 = 0,500 mm; 60 = 0,251 mm; 150 = 0,104 mm). These two fractions are normally used as additive for refractory making. The temperature was monitored by means of a platinum/rhodium thermocouple located directly below the specimen. Argon was used for flushing the reaction chamber before and after the experiments to ensure an inert atmosphere in the chamber. Oxygen and air used for oxidation of graphite. The air and oxygen used for oxidation was passed through flow meter where the flow rate of gas was registered. Gases emerging out

from flow meter finally entered into the reaction chamber. Figs. 9, 12 show the plots of fraction of graphite (α) oxidized against time at various temperatures with two fractions of graphite in oxygen and air atmosphere. Flow rate of air and oxygen (i.e. 0,25 bar) inside the furnace was kept constant by means of flow regulator.

Results

Grain density found to be of 2,25 g/cm³ and average surface area is 1,4 m²/g. Fusion temperature of ash was found to be 1105 °C. X-ray diffraction analysis of ash sample shows the presence of quartz, corundum, feldspar and alkali-aluminium-iron-silicate hydrate complex. The interlayer distance of the graphite sample was calculated from the average of $d_{(002)}$ and $d_{(004)}$ values obtained in X-ray diffraction. The d-values obtained are given in Tab. 4. It is seen that in-

Tab. 4 Degree of graphitization in the graphite samples

Sample No.	$D_{(002)}$ [Å]	$D_{(004)}$ [Å]	C [Å]	G
Tamil Nadu	3,356	3,365	6,721	0,87

Tab. 5 Reactivity of Tamil Nadu graphite

Sample No.	Temperature [°C]	$K \times 10^4$ [s ⁻¹]	
		Air	Oxygen
TG ₁	735	0,00004 (=0,4)	0,00008 (=0,8)
	785	0,00009 (=0,9)	0,0001 (=1)
	830	0,0004 (=4)	0,0004 (=4)
TG ₂	735	0,00005 (=0,5)	0,00007 (=0,7)
	785	0,0001 (=1)	0,0002 (=2)
	830	0,0003 (=3)	0,0006 (=6)



Fig. 7 Photomicrograph of Tamil Nadu graphite (plane polar)

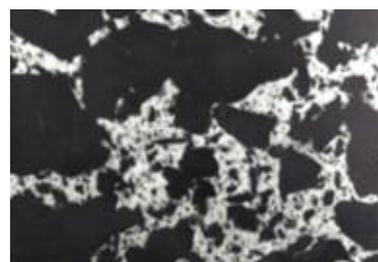


Fig. 8 Photomicrograph of Tamil Nadu graphite (cross polar)

terlayer distance are very close and corresponds to the value of pure graphite structure. It is also seen from the XRD-analysis that no other phases are present which indicates that the impurity percentage in the sample is very less. It is apparent from the result that sample is graphitized and degree of graphitization is 87,0 %. From the position of the (002) line, it was found in this study that the d-spacing in the sample was greater than the characteristic value of 3,354 Å for purely crystalline graphite which shows that some non-crystalline graphite are also present in the samples. SEM/EDAX were done and indicates large amount of pores in the grains as shown in Fig. 3. It was found by surface topography study that there were wide variation in size and shape of the particles. There are few cracks in bigger size grains and it was found that cracks are present at edges. Individual particle size has been calculated using the surface dimension of the respective particles. Average

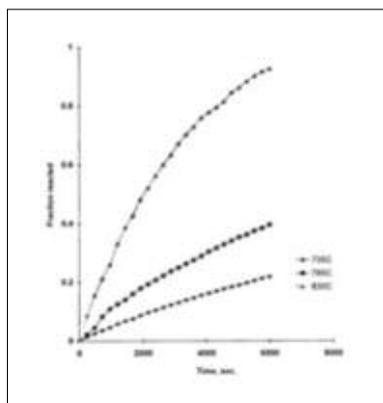


Fig. 9 Fraction graphite reacted as a function of time TG_1 (air)

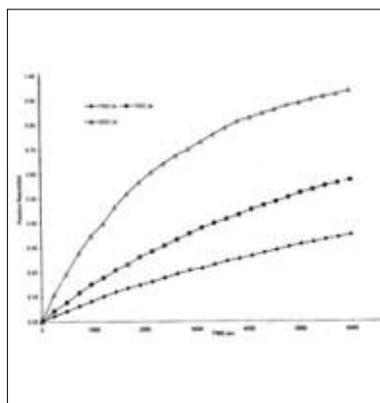


Fig. 10 Fraction graphite reacted as a function of time TG_1 (oxygen)

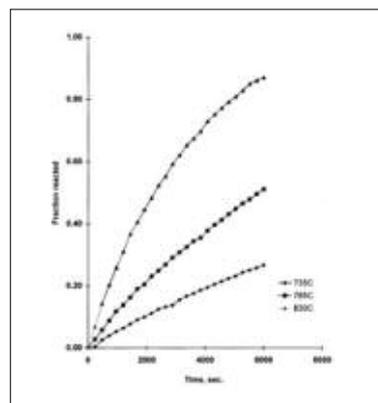


Fig. 11 Fraction graphite reacted as a function of time TG_2 (air)

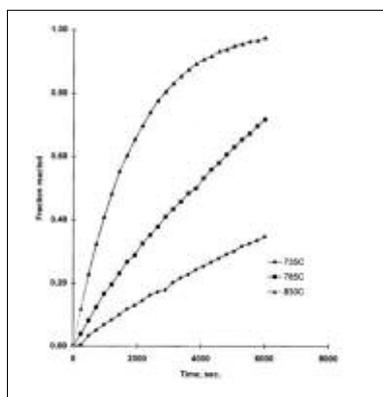


Fig. 12 Fraction graphite reacted as a function of time TG_2 (oxygen)

equivalent diameter of the particle has been obtained from a large number of randomly chosen particles. The average equivalent diameter of particle is 115 μm . Petrographic studies were carried out under transmitted light. Tamil Nadu graphite was black to steel grey and medium to fine grained. Most of the grains show columnar and radiated, others are rhombohedral. The mineral has well developed basal cleavage and metallic lusture. Fig. 9 and 12 show the plots of fraction of graphite (α) oxidized against time at various temperatures with two fractions of graphite in oxygen and air atmosphere. Flow rate of air and oxygen (i.e. 0,25 bar) inside the furnace was kept constant by means of flow regulator. The rate decreased with extent of reaction at any temperature and the effect of temperatures, atmosphere and grain size is evident. The reactivity of graphite at different temperatures in air and oxygen atmosphere is given in Tab. 5. At higher temperature, the α -time curve is very sharp and shapes of the α -time plots at dif-

ferent temperatures are different. The exact form of " α " against " t " plot is determined by the geometry of the reaction interface. In most homogenous reactions, the whole range of decomposition fits one kinetic law but in heterogeneous reactions, one expression may hold for the initial few percent of the reaction to be followed by a second in the accelerating stage of the reaction and a third or fourth expression may be found to be described the reaction in the decelerating stage of reaction.

Reaction of porous carbon solids in oxidizing gases frequently shows three temperature regimes [6]. At low temperature rate is controlled by the reaction at the interface, the rate of diffusion of reacting gaseous species to the internal surfaces of the solid being rapid, so that no concentration gradient exists within the pore structure, which is uniformly eroded.

As the temperature increases, the rate of reaction first becomes comparable with the rate of diffusion through the pore structure so that the concentration of reactant falls to zero within the pore structure and then the reaction at higher temperature is controlled by mass transport of reactant and product gases across the boundary layer at the external surface of the porous solid. These processes have been discussed by Walker Jr., P.L. et al. [7].

Conclusion

- Grain size does not have impact on fraction decomposed for both size fractions. From the (t) curves, it is apparent that curves for two fractions in both ranges are superimposed, which suggest that oxidation of graphite is independent of size fractions of

(-30+150 BSS).

- Tamil Nadu graphite used here contains ash to the tune of 2–3 % with higher amount of iron oxide and sulphur in it i.e., 13,5 % and 0,45 % respectively.
- Degree of graphitization is high, i.e. 87 %.
- Ash contains impurities like quartz, feldspar, corundum, alkali-iron-aluminium-silicate hydrates.
- Large number of pores are present in the sample as depicted by SEM.

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References

- [1] Indian Mineral Book. Indian Bureau of Mines, Nagpur
- [2] Bailer, J.C. et al. (Ed.): Comprehensive inorganic chemistry. Vol. 1. 1973, 1178
- [3] Adschiri, T.; Furusawa, T.: Relation between CO_2 -reactivity of coal char and BET surface area. Fuel **65** (1986) [7] 927
- [4] RDCIS-NML Jt. project report on "Increasing oxidation resistance of carbon/graphite products by high temperature heat treatment". Report No. 2384, March 1995
- [5] Bandopadhyay, D.: Kinetics of gasification of carbon and carbothermic reduction of iron oxide, PhD-Thesis, IIT Kanpur, 1989
- [6] Ozgen, O.S.; Rand, B.: Kinetics of oxidation of the graphite phase in alumina/graphite materials. Brit. Ceram. Trans. J. **84** (1985) 70–76
- [7] Walker Jr., P.L.; Rusinko Jr., F.; Austin, L.G.: Chemistry and physics of carbon. Advances in Catalysis **2** (1966) 275