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Ceramics International 29 (2003) 967–969

CERAMICS INTERNATIONAL

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Short communication

Oxidation reaction in graphite—role of particle characterstics

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Received 28 May 2002; received in revised form 20 September 2002; accepted 12 December 2002

Abstract

Diffusion controlled reactions involve square of the particle size as a significant controlling factor and great attention should be given to characterize the particles. Common observations are that imperfections present within pores, cracks, voids, etc., play a critical role in further reactions, leading to anisotropic reaction behaviour.

Two different graphites of different physico-chemical properties and having different particle sizes were studied and it was found that the particles, irrespective of their initial particle characteristics, exhibit the same time period for completion of reaction, and the rate of reaction towards completion is variable with particle characteristics and atmosphere employed.

Keywords: C. Diffusion; Graphite; Oxidation; Kinetics; Particle

In their work on kinetics of oxidation on graphite, Ozen and Rand [1] have shown that in diffusion controlled reaction of graphite (temperature > 950 °C) diffusion of oxygen and gaseous products controls further reaction. The α–t plot (α = amount of weight loss and t = time) they observed was dependent on specimen geometry, and, kinetics of diffusion controlled reaction in porous system by Szekely [2] et al. involving diffusion reaction equations was applied by them for data analysis. These equations are

$$\alpha^2 = (8k/x_o^2)t = k_1 t - (\text{1st order diffusion reaction})$$

$$\alpha + (1-\alpha) = (4k/r_o^2)$$

$$= k_2 t \ (\text{2nd order diffusion reaction})$$

where k = constant, x_o = height of the cylindrical sample, r_o = radius of the cylindrical sample and t = time; k_i = 1,2 can be determined from the concentration gradient across the de-carbonized layer, effective diffusivity of the de-carbonized layer and the volume fraction of the unreacted core. The rate constant ratio $(k_1/k_2) = 2r_o^2/x_o^2$ was approximately 1.0, but the diffusion reactions showed anisotropy in directions parallel and perpendicular to the cylindrical axis. Ozen and Rand [1] concluded that preferred orientation of the graphite flakes is responsible for this anisotropic diffusion.

Diffusion controlled reactions (1st order, 2nd order, Jander and Ginstling and Brounstein equations) involve square of the particle size as a significant controlling factor (in the denominator) and great attention should be given to characterize the particles. Common observations indicate that the imperfections present within pores, cracks, void size, etc. play critical role in further reactions, leading to anisotropic reaction behaviour

Fig. 1. SEM image of Palamou graphite.

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0272-8842/03/$30.00
doi:10.1016/S0272-8842(03)00037-3

besides presence of trace amounts of impurities. Moreover, common observations indicate that burning of flaky materials involve exfoliation of the flakes during burning and the equations of diffusion controlled reactions in these particles loses its significance, being valid for granular materials.

We have analysed through SEM two natural Indian graphites (Palamou graphite, PG, and Sambalpur graphite, SG) regarding their particle sizes (70 μ and 165 μ, Figs. 1 and 2 respectively). Their physical and chemical characteristics are shown in Tables 1 and 2. The samples exhibited cracks and porosities to different degrees, under SEM studies, in addition to their varying particle size. They were subjected to DTA-TGA analysis (Netzsch simultaneous DTA-TGA thermo-analyser Model STA 409) in two different particle size ranges namely 0.2–0.5 mm (Palamou graphite, PG 1, and Sambalpur graphite, SG 1) and 0.1–0.25 mm (Palamou graphite, PG 2, and Sambalpur graphite, SG 2) separately in air and in oxygen atmosphere.

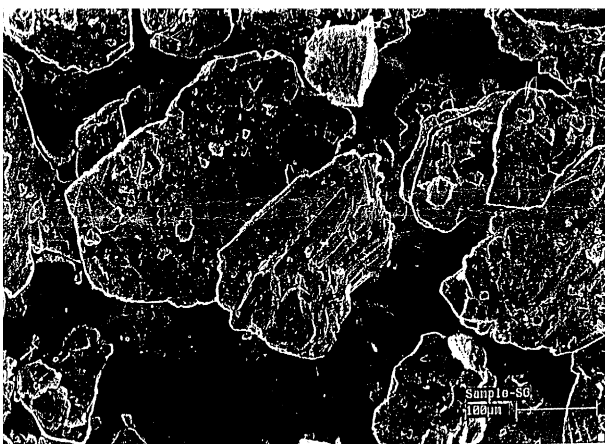

Fig. 2. SEM image of Sambalpur graphite.

Table 1
Chemical properties of graphite samples and analysis of ash samples (percentage)[a]

Constituents	Palamou	Sambalpur
SiO_2	64.52	50.54
Al_2O_3	23.85	33.42
Fe_2O_3	4.87	11.33
CaO	0.45	0.84
MgO	1.08	1.44
Na_2O	0.17	0.21
K_2O	3.93	0.41
TiO_2	0.35	0.90
P_2O_5	0.08	0.21
S	0.005	0.34
V_2O_5	0.16	0.04
MnO	0.021	0.05
Cuo	0.04	0.04
ZnO	0.02	0.01
ZrO_2	0.03	0.01
Cr_2O_3	0.31	0.08
Co_3O_4	0.003	0.01
Rb_2O	0.02	0.004
SrO	0.005	0.004

[a] Ash percentages: Palamou 18%, Sambalpur 12.5%.

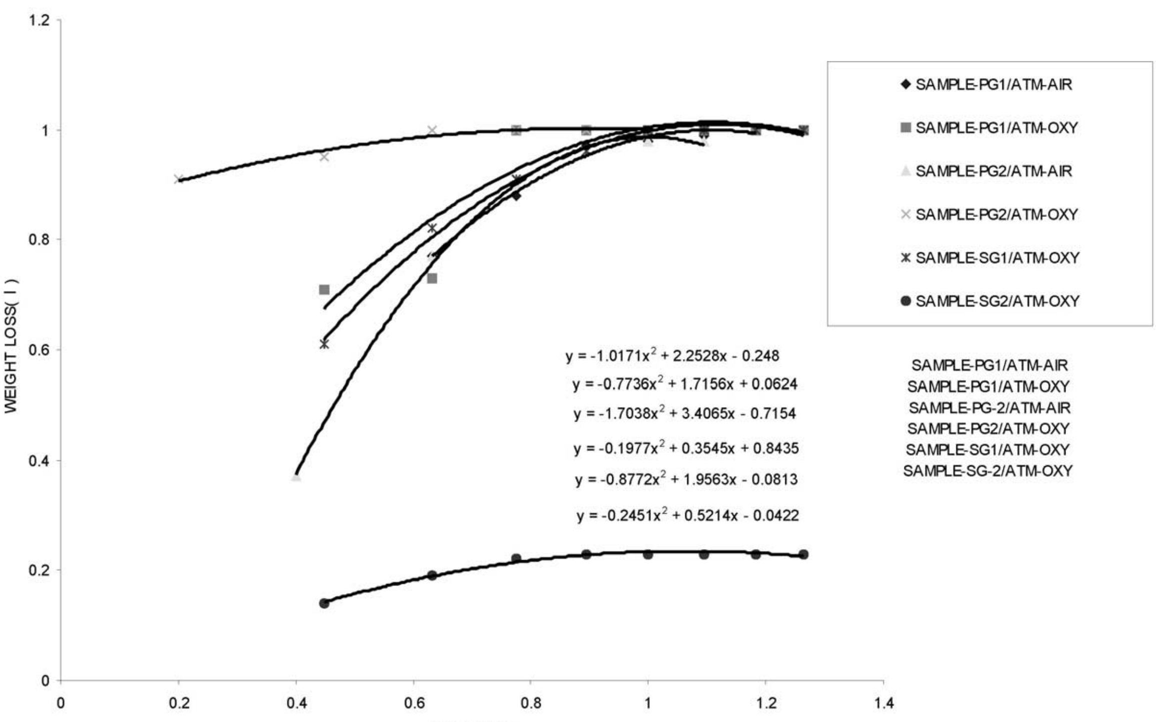

Fig. 3. Plot of α vs. square root of time.

At an isothermal temperature of 850 °C, the chart gave loss in wt. (α) against time (t) plot and the data points were plotted as (α) vs. t^{05} plot with the help of a personal computer (EXCEL program). Fig. 3, give line tracings and the relevent equations of the curves . Analysis of the equations yielded the following table, as shown below.

Following, Ozen and Rand [1], 1st order diffusion reaction: $\alpha^2 = (8k/x_o^2)t = k_1 t$) was applied for data point analysis, and the results are shown here:

Sample/ atmosphere	Value of "x" at point of inflexion ($dy/dx = O$)	Value of slope, c, on a plot of $dy/dx = cx + d$
PG1/oxygen	1.11	1.54
PG2/oxygen	1.08	0.38
PG1/air	1.11	2.02
PG2/air	1.0	3.4
SG1/oxygen	1.12	1.74
SG2/oxygen	1.08	0.48

The conclusion from these are: (i) the particles irrespective of their initial varying characteristics exhibit the same time period for completion of reaction and (ii) the rate of reaction towards completion is variable with particle characteristics and atmosphere employed. Therefore, we conclude that the role of particle characteristics is significant in oxidation reaction of graphite at higher temperatures. For example, small value of dy/dx (0.38 and 0.48 observed with PG2/oxygen and SG2/oxygen respectively) and a comparatively high value of dy/dx (1.54 and 1.74 observed with PG1/oxygen and SG1/oxygen respectively) indicate role of particle size while similar effects with variations of atmosphere (in both PG and SG varieties) indicate the role of atmosphere in oxidation reactions.

Table 2
Physical properties of graphite sample

Surface Area		
(BET apparatus)		
Sample	M^2/gm	
Palamou	1.1	
Sambalpur	0.4	
Size range (μ)	Palamou (%)	Sambalpur (%)
Grain size analysis		
2–5	1.0	11.0
6–10	11.5	16
11–20	14.0	21
21–30	22.5	13
31–50	10.0	25
51–100	31.0	14
>100	10.0	–
Analysis under SEM		
Palamou sample—No porosity but cradks present within the sample.		
Particle size 70 μ		
Sambalpur sample—Small no. of porosities but no cracks.		
Particle size 165 μ		

Acknowledgements

The authors are grateful to the RDCIS management for their help at different stages of the work and allowing permission to publish the article.

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