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Short communication

A modification of Ozen's first order diffusion kinetics reaction during carbon oxidation at higher temperatures

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Abstract

The present work is a modification of Ozen's first order diffusion kinetics equation incorporating imperfections (pores, cracks and voids, etc.) in the established relationship between weight loss, particle size and time. The differences in oxidation behaviour of different varieties of graphite at higher temperatures could be well explained from the modified equation.

Keywords: Diffusion kinetics; Carbon oxidation; High temperatures

1. Introduction

It was observed [1] earlier that the discontinuities present in the graphite particles namely pores, cracks, voids and various other imperfections result in characteristic differences of graphite, obtained from different sources leading to differences in their oxidation behaviour. In the present article, the first order diffusion reaction as reported by Ozen et al. [1] valid for carbon oxidation at higher temperatures has been corroborated further with weight loss equation. This attempt resulted in a modification of Ozen's equation such that a term relating to porosity of the particles could be correlated with wt.loss and time measurements. The experimental data points were analyzed through the modified equation to verify validity of the equation.

2. Theory

The weight loss (α) during burning, time (t), particle size (r), and density (ρ), are related as

$$\alpha^2 = \mathrm{k}t/r^2 \quad (1)$$

due to Ozen et al. Weight, α, particle size, r, density, ρ, and porosity p are related as

$$\alpha = 4/3\pi r^3 \rho(1-p) \text{ (assuming spherical particle)} \quad (2)$$

$$\mathrm{d}\alpha = Kr^2(1-p)\mathrm{d}r - Kr^3\mathrm{d}p \quad (3)$$
$$(K = \text{constant, includes } 4/3\pi \text{ and } \rho)$$

$$= Kr^2\{3(1-p)\mathrm{d}r - r\mathrm{d}p\} \quad (4)$$

substitution of (4) into (1) gives

$$\mathrm{d}\alpha/3(1-p)\mathrm{d}r - r\mathrm{d}p = t/\alpha^2 \quad (5)$$

or

$$3(1-p)\mathrm{d}r/\mathrm{d}\alpha - r\mathrm{d}p/\mathrm{d}\alpha = \alpha^2/t \quad (6)$$

The physical significance of $\mathrm{d}p/\mathrm{d}\alpha$ which relates to relative change of porosity/voids with respect to change of weight has no physical significance and can be eliminated leaving modification of Eq. (6) into

$$3(1-p)\mathrm{d}r/\mathrm{d}\alpha = \alpha^2/t \quad (7)$$

or

$$\mathrm{d}r/\mathrm{d}\alpha = 1/3(1-p)\alpha^2/t \quad (8)$$

The term $\mathrm{d}r/\mathrm{d}\alpha$ relates to relative change of particle size with respect to relative change in weight loss. At $p=0.0$ (dense particle), $\mathrm{d}r/\mathrm{d}\alpha=$(constant) α^2/t, and gives "parabolic rate law" equation. A plot of α^2 vs. t should give a straight line and the variations in slope $1/3(1-p)$, will denote the changes in $\mathrm{d}r/\mathrm{d}\alpha$, as effected with change of porosity in the particles during experimental heat treatment process.

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3. Experimental

The $\alpha^2 - t$ plot of two different natural graphite from Indian origin were obtained from DTA–TGA analysis (NETZSCH DTA-TGA Thermoanalyser, Model STA 7630) at isothermal temperatures of 750 and 850 °C separately in air and in oxygen atmosphere. Plot of α^2 vs t were made for the two different varieties with respect to (1) change of particle origin (PG1, Palamou Graphite, particle size 0.2–0.5 mm and SG1, Sambalpur Graphite, particle size 0.2–0.5 mm), temperature (750 and 800 °C), but same atmosphere (oxygen) (2) change of atmos-

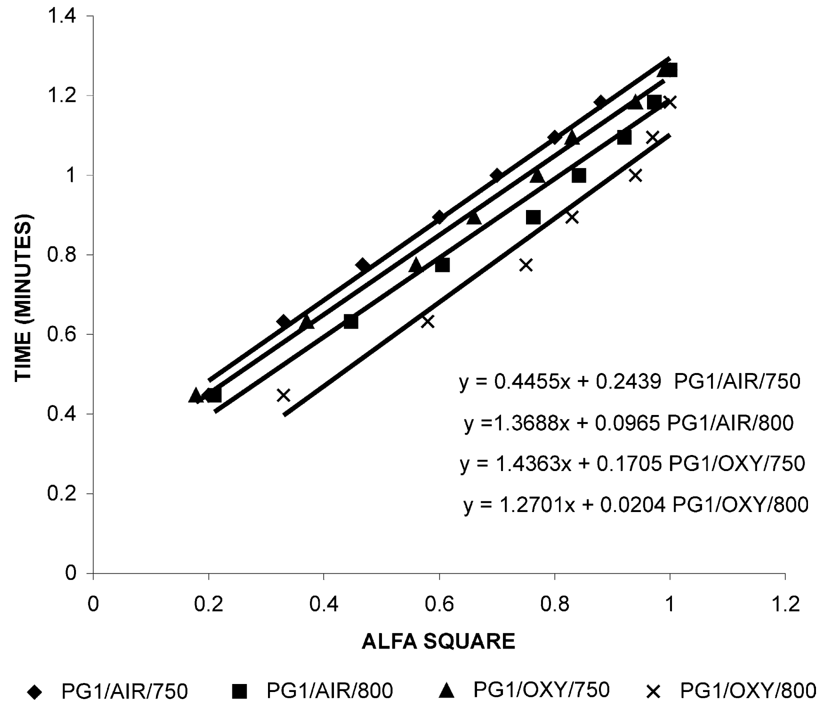

Fig. 1. Weight loss with time plot for Palamou graphite in air and oxygen atmosphere at two temperatures.

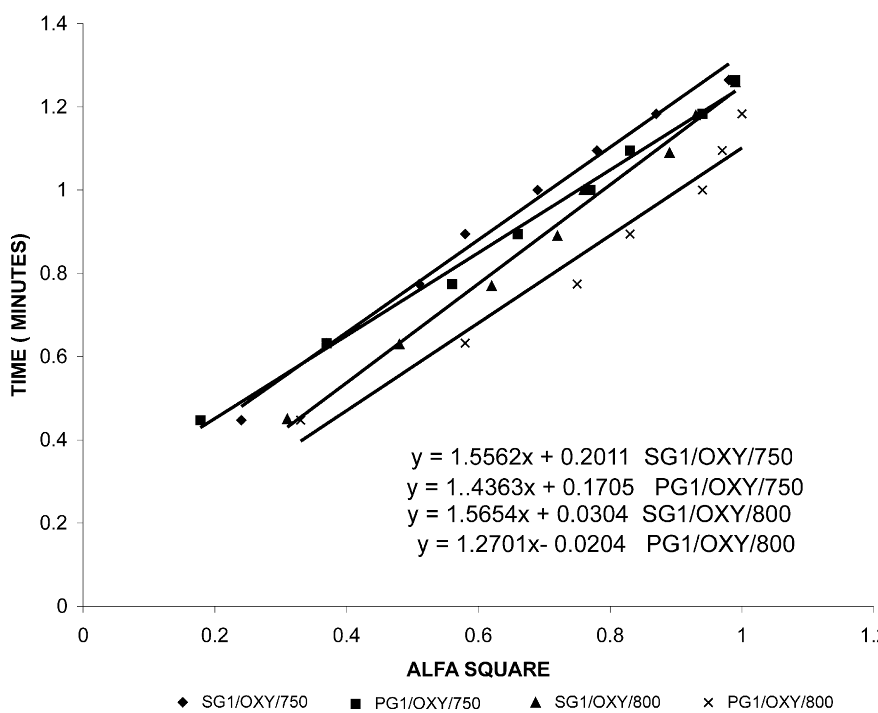

Fig. 2. Weight loss with time plot for Palamou and Sambalpur graphite in oxygen atmosphere at two temperatures.

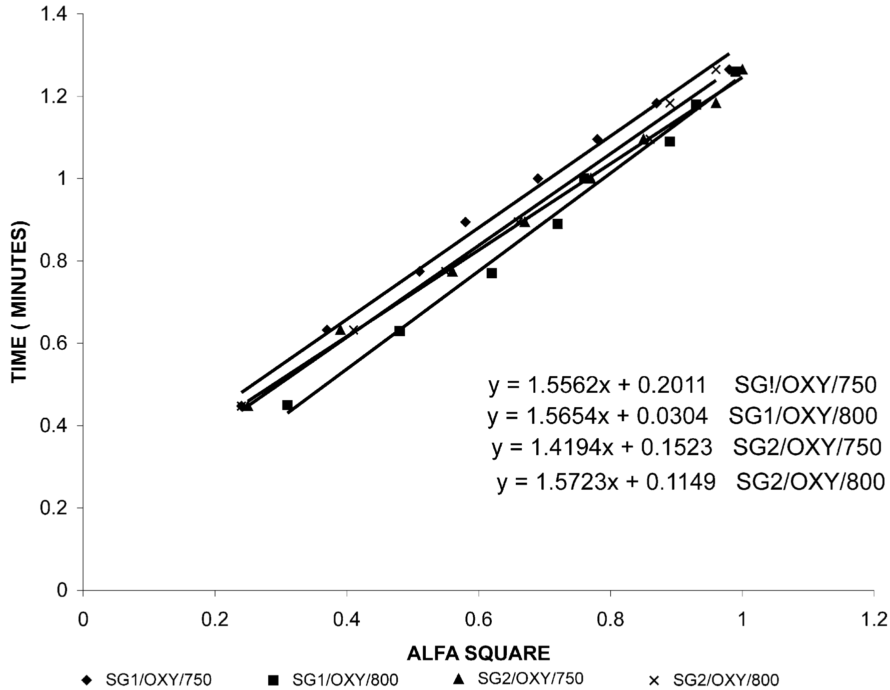

Fig. 3. Weight loss with time plot for Sambalpur graphite in oxygen atmosphere at two temperatures.

phere (air/oxygen), temperatures (750 and 800 °C) but same particle size and origin (PG1) and (3) change of particle size (SG1 and SG2, Sambalpur Graphite, particle size 0.1–0.25 mm), temperature (750 and 800 °C) but the same atmosphere (oxygen). These are shown in Figs. 1–3.

4. Results and discussion

A straight line plot of the data points indicate validity of the ‘‘parabolic rate law equation’’, while the change in slope, $1/(1-p)$, is associated with imperfections in the solids. Fig. 1 indicates that the SG1 variety is insensitive towards temperature variations as compared to PG1 variety in oxygen atmosphere, while Fig. 2 indicates that the PG1 variety is more sensitive towards temperature variations. Fig. 3 indicates that with variation of particle size in SG variety variation in temperature from 750 to 800 °C affects the slope significantly in oxygen atmosphere. Finer SG2 variety is more sensitive as compared to coarse SG1 variety.

It is interesting to note that depending on origin significant variation in oxidation behaviour is observed with different graphite samples. While one variety is insensitive even in small particle size the other variety exhibits sensitivity with temperature variations.

These observations demonstrate significant contribution of particle imperfection present in graphite as dependent on origin and these characteristic differences exhibit their effect at progressively higher temperatures.

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