

Thermal analysis of the oxidation of natural graphite — effect of particle size

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Abstract

The oxidation of natural graphite particles with a prismatic (flake-like) structure was investigated by thermal gravimetric analysis (TGA) and differential thermal analysis (DTA). The objective of this study is to examine the relationship between the relative fraction of edge sites and the oxidation behaviour of graphite. The approximate prismatic structure of the natural graphite provided a model geometry from which the relative fraction of edge and basal plane sites was determined. The three thermal parameters, ignition temperature (T_i), temperature maximum (T_m) in the DTA curves, and the temperature at which 15% carbon weight loss is attained (T_{15}), were determined for a series of natural graphite samples (average particle size, 2–40 μm) using simultaneous TGA/DTA. The results reported in this study support the observation that the fraction of edge sites has a strong influence on the thermal parameters (T_i , T_m and T_{15}) for the oxidation of graphite. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Graphite; Oxidation; Thermal; Active sites; Particle size

1. Introduction

Graphite has a crystallographic structure consisting of hexagonal graphene layer planes that are usually stacked in a sequence ABABA... Alternatively, a rhombohedral stack sequence of ABCABC... is observed, but to a lesser extent. The layer planes are often referred to as basal planes. The carbon atoms form s bonds with adjacent carbon atoms in the same plane. The so-called edge atoms containing unpaired s electrons are available to form chemical bonds at the

terminations of the layer planes. Hence, the carbon edge atoms are more reactive sites than the carbon atoms in the basal plane. Two types of edge sites exist at the terminations of the basal plane [1], which are called zig-zag ($\text{—}\backslash\text{—}$) and arm chair ($\text{—}\wedge\text{—}$). Detailed optical studies of the oxidation of graphite crystals at 846°C by Thomas [1] showed that the reaction rate of the zig-zag face is about 1.20 times more rapid than that of the arm-chair face. A comparison of the oxidation rates at 800°C of the surfaces parallel ('a') and perpendicular to the basal plane ('c') revealed that the rate is 26 times greater in the a-direction. The studies by Thomas [1,2] clearly demonstrate the anisotropy of the graphite surface to oxidation kinetics, which is indicative of the relative fraction of edge sites.

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One approach used to determine the relative fraction of edge or defect sites on carbon is to measure the amount of oxygen chemisorption. Here it is assumed that oxygen chemisorbs only on the active sites that are represented by carbon atoms at edge or defect sites, and the basal plane sites remain unaffected. The concept of active sites for oxidation reactions involving oxygen chemisorption or gasification was suggested by Radovic et al. [3], Laine et al. [4], Coltharp and Hackerman [5] and Brown et al. [6]. However, Lang and Magnier [7] reported that the oxidation rate of on the edge and basal planes is comparable, although they acknowledged this was contrary to other studies. These studies show that active sites, which are surface sites that are capable of dissociatively chemisorbing oxygen, are present on carbons and they are primarily associated with edge sites or defects on the carbon surface. This observation suggests that the chemical properties of carbonaceous materials should be influenced by the relative fraction of the active sites. It should be possible, then, to derive a better understanding of the physical properties of carbonaceous materials by investigating their thermal oxidation behaviour.

Oxidation studies involving thermal analysis techniques such as thermal gravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been used to characterise the properties of carbonaceous materials. For example, the oxidation rate and ignition temperature (T_i) of carbonaceous materials in air are strongly dependent on parameters such as the surface area and crystallographic structure [8–11]. Thermal analysis of the oxidation behaviour of carbon blacks showed a linear relationship between the temperature at which 15% carbon weight loss is attained (T_{15}) and the surface area [8]. High-surface-area carbon blacks exhibit low T_{15} and vice versa. However, the active surface area and not the total surface area (TSA) is the important parameter controlling the oxidation rate of carbons [4]. Therefore, graphitised carbons with a preponderance of basal plane sites are less reactive than disordered carbons that contain a larger fraction of edge or active sites. Radovic et al. [3] suggested that the emergence of the (1 1 0) peak at $2\theta=43^\circ$ in the XRD spectra of carbon is a strong indication of a decrease in the concentration of active sites. In the case of high-surface-area carbon blacks, a large frac-

tion of active sites is present on the surface. Welham and Williams [11] used TGA to investigate air oxidation of ball-milled graphite and active carbons. The ignition temperature decreased after prolonged ball milling, indicating the disordered carbon that was formed oxidised more quickly, i.e., reduction in crystallinity is associated with an increased reactivity to oxygen. Honda et al. [10] observed by DTA that the maximum temperature (T_m) in the exotherm during air oxidation was strongly influenced by the $d(0\ 0\ 2)$ spacing and L_c of the carbon; T_m increased with an increase in L_c and a decrease in the $d(0\ 0\ 2)$ spacing. For example, T_m of a carbon black (high $d(0\ 0\ 2)$ spacing, low L_c) was 511°C and that for spectroscopic graphite (low $d(0\ 0\ 2)$ spacing, high L_c) was 698°C . These trends are consistent with the hypothesis that a decrease in the concentration of edge sites or active sites on carbon results in slower oxidation kinetics and a shift in T_m to higher temperatures.

The parameters mentioned above are not the only ones that have been used to characterise the thermal properties of carbonaceous materials. For example, Kopp et al. [12] identified four TGA parameters for characterising the oxidation of coal: (i) temperature at which 1% weight loss was reached, (ii) temperature at the maximum rate of weight loss, (iii) temperature at which the slope of the weight loss reached 45° , and (iv) the percent weight loss at 1000°C .

The relative fraction of edge sites present on carbonaceous materials varies widely with the structure and particle size. Barton and Harrison [13] calculated the edge and total surface area of graphite crystallite from the crystallite parameters, L_c and L_a , obtained from XRD analysis. They assumed crystallites of cylindrical shape with height L_c of $90\ \text{\AA}$ and diameter L_a of $300\ \text{\AA}$. From this analysis, the total surface area is $160\ \text{m}^2/\text{g}$ and the edge plane area is $60\ \text{m}^2/\text{g}$. In this example, the percentage of edge sites is 37.5%. Coltharp and Hackerman [5] reported that the percent of edge sites on a high-surface-area carbon black is 68% of the BET surface area ($\sim 110\ \text{m}^2/\text{g}$). Such high percentages of edge sites are not likely to exist with large graphite particles that have dimensions greater than $1\ \mu\text{m}$. For example, Chung et al. [14] considered a circular disk as a representation of a graphite flake and calculated an edge fraction of $\approx 1\%$ for particle diameter of $10\ \mu\text{m}$ and thickness of $0.1\ \mu\text{m}$.

The purpose of this paper is to present the results of a study to show the relationship between the relative fraction of edge sites and the oxidation response of natural graphite. The approximate prismatic (flake-like) structure of the natural graphite samples provides a model geometry to calculate the relative fraction of edge and basal plane sites. Thermal analysis studies involving TGA and DTA were conducted to observe the oxidation of natural graphite of different average particle size, and these results are correlated with the fraction of edge sites. The three thermal parameters, ignition temperature (T_i), temperature maximum (T_m) in the DTA curves, and the temperature at which 15% carbon weight loss is attained (T_{15}), were determined for a series of natural graphite samples using simultaneous TGA/DTA. This effort is part of a larger program to investigate the role of carbon surface catalysis on the decomposition of non-aqueous electrolytes for lithium-ion batteries [15–17].

2. Experimental details

Five samples of natural graphite powders with average particle sizes of 2, 12, 20, 30 and 40 μm were obtained from a commercial source. These samples represent a wide range of particle size, but with similar particle morphology. The Brunauer–Emmet–Teller (BET) surface area was measured with a Quantachrome Autosorb automated gas sorption system using N_2 gas. X-ray diffraction (XRD) analysis (Siemens D500 Diffractometer) was used to determine the $d(0\ 0\ 2)$ spacing and the crystallite size, L_c . Scanning electron microscopy (SEM, Hitachi) was employed to determine the morphology and dimensions of the edge and basal plane. In this paper, the basal-plane dimension of the particle is used as the average particle size.

Raman spectroscopy measurements were carried out at room temperature in ambient atmosphere using an argon-ion laser (Coherent, Model Innova 70) tuned to 514.5 nm. The resolution of this instrument is approximately $1.7\ \text{cm}^{-1}$. The crystallite dimension, L_a , is obtained by using the method of Tuinstra and Koenig [18], i.e., $L_a = 44 / (I_{1372} / I_{1576})$, where I_{1372} and I_{1576} are the integrated intensities of the Raman peaks at 1372 and 1576 cm^{-1} , respectively.

The thermal analysis experiments were conducted using simultaneous TGA/DTA (SDT 2960, TA Instru-

ments, New Castle, DE) to monitor both the weight change (balance sensitivity, 1 μg) and temperature change (DT sensitivity, 0.001°C) of the samples. The experimental procedure consisted of heating the sample in flowing nitrogen (99.999% purity, 100 ml/min) at $10^\circ\text{C}/\text{min}$ to 1200°C to eliminate any surface oxygen groups. As the graphite samples were produced at temperatures above 1200°C , this heat-treatment step is not expected to change their crystallographic structure. The clean carbon was oxidised by heating at $10^\circ\text{C}/\text{min}$ to 1200°C in flowing air (100 ml/min) after the sample was cooled to room temperature. Preliminary experiments were conducted to identify the appropriate mass of graphite required to maintain the oxidation reaction under kinetic control. These measurements indicated that the oxidation rate was not diffusion controlled with a sample weight of 5–10 mg.

The parameters, T_i , T_m and T_{15} , were determined from the thermal measurements by the commercial software package that controlled the instrument. The computer program calculated T_i from the derivative dW/dT , where W and T are the weight and temperature of the sample, respectively. The temperature at which dW/dT first deviated from zero is designated as T_i . The other parameters, T_m and T_{15} , were determined by the computer software from the DTA and TGA curves, respectively. A commercial software program (KaleidaGraph, Synergy Software, Reading, PA) was used to analyse and plot the experimental data. Due to the limited number of graphite samples, no attempt is made to present statistical information. The software program was used to show the trend of the data, and this is noted in several of the figure captions.

3. Discussion of results

The physical properties of the natural graphite particles are reported elsewhere [17]. In brief, the BET surface area decreased from 12.1 to 2.3 m^2/g with an increase in the average particle size of 2–40 μm . X-ray diffraction analysis showed that the $d(0\ 0\ 2)$ spacing is 3.36 \AA , and L_c ranges from 54 to 80 \AA . The results obtained from Raman spectroscopy indicate L_a is in the range from 110 to 183 \AA .

The weight change observed during the oxidation of the natural graphite samples is illustrated in the TGA

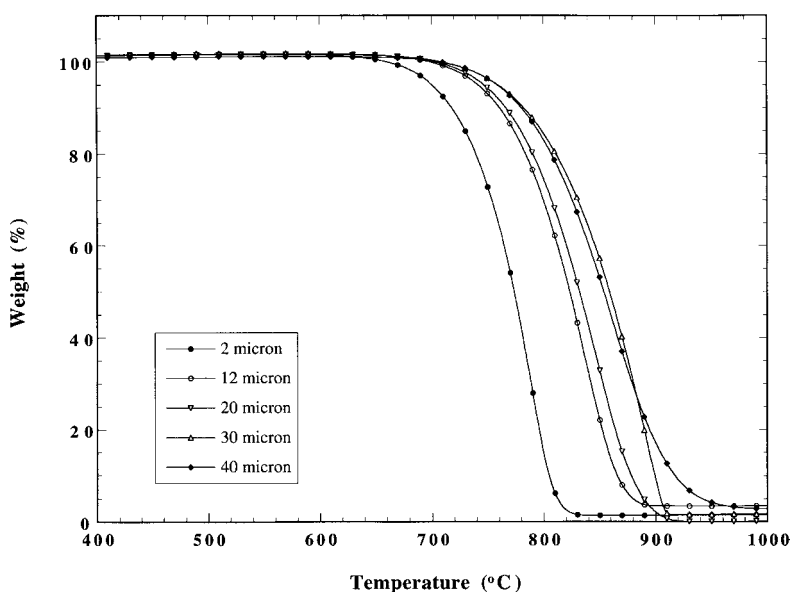


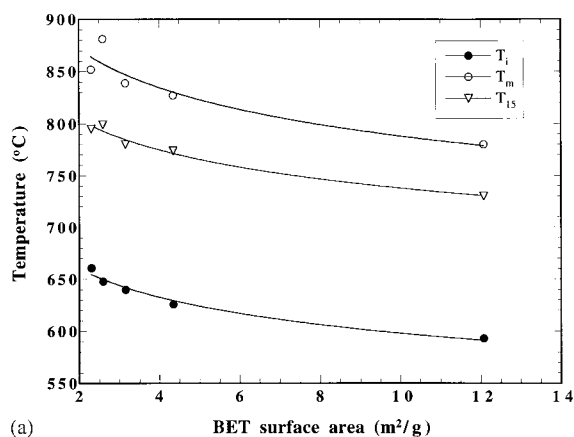
Fig. 1. TGA measurement of the oxidation of natural graphite in air. Heating rate 10°C/min.

curves shown in Fig. 1. The TGA curves show an initial gradual change in sample weight followed by a precipitous drop as the temperature increases. There is no evidence in the thermal analysis measurements to differentiate oxidation of surface basal or edge sites. The derivative dW/dT shows only a single peak as a function of T . When the sample contains a mixture of carbons that oxidise at different temperatures, the heterogeneity of the samples yields derivative dW/dT with discrete peaks as a function of temperature [19]. The more reactive component in the carbon mixture will oxidise at a lower ignition temperature. The major difference between the TGA curves in Fig. 1 is the increase in the ignition temperature (T_i) as the average particle size increases. The graphite particles with an average particle size of 2 μm has T_i of about 593°C, and it increases to 661°C for graphite with average particle size of 40 μm . The DTA curves showed a general trend with T_m increasing to higher temperatures as the average particle size increases. This trend was observed earlier by Honda et al. [10] in their DTA studies of graphite oxidation.

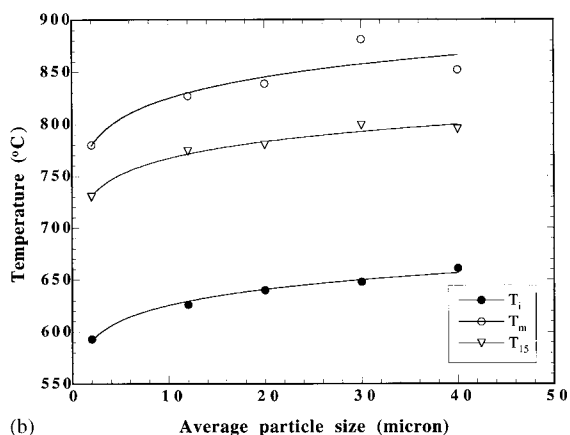
The parameters, T_i , T_m and T_{15} , which were derived from the TGA and DTA measurements, are plotted in Fig. 2 as a function of the BET surface area and average particle size. Trend lines obtained by using the KaleidaGraph plotting software are shown in Fig. 2.

The parameters all show a mild change as a function of surface area and average particle size. The thermal parameters decrease as the surface area increases and as the average particle size decreases. The thermal parameters in Fig. 3 increase with an increase in the crystallite dimension, L_a . Similar results (not plotted) were also observed with L_c , and in agreement with the observations by Honda et al. [10] with reactor-grade graphite. The trends indicated in Figs. 2 and 3 can be explained by considering the reactivity of edge sites compared to that of basal plane sites. The relative fraction of edge sites on carbon, as mentioned above, play an important role in its reactivity to oxygen. The trends displayed in Fig. 2 are consistent with the concept that the concentration of edge sites increases with an increase in surface area and a decrease in average particle size. The studies by Radovic et al. [3] suggested that the magnitude of the crystallite dimension, L_a , is a good measure of the fraction of active sites associated with carbons. Thus, the concentration of edge sites increases with a decrease in the magnitude of L_a , and the thermal parameters decrease.

The fraction of edge and basal plane sites was determined for ideal prismatic structures of different particle size and used as a model for the natural graphite particles. The details of this analysis are described elsewhere [17], and only a brief summary



(a)



(b)

Fig. 2. Variation in thermal parameters, T_i , T_m and T_{15} , as a function of BET surface area (a) and particle size (b). Line indicates trend of data using KaleidaGraph.

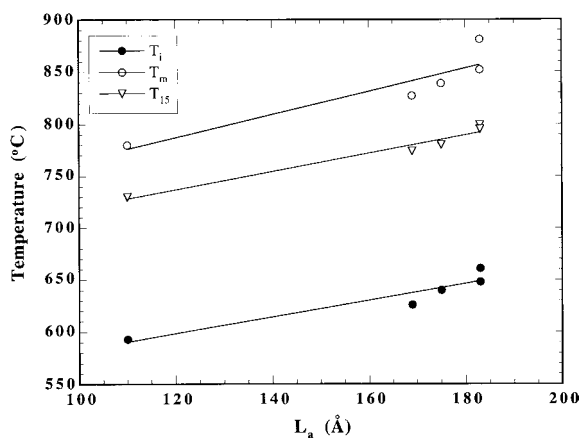


Fig. 3. Relationship between T_i , T_m and T_{15} and L_a . Line indicates trend of data from a linear plot using KaleidaGraph.

is presented here. The study by Fujimoto and co-workers [20,21] served as the starting point for the analysis. They derived a correlation between the size of the graphite crystallites and the crystallographic parameters, L_a , L_c , $d(0\ 0\ 2)$ and $d(1\ 0\ 0)$, starting from a model that consisted of hexagonal arrays of carbon (i.e., benzene rings) to represent the graphite layer planes. The size of the layer planes (L_a) increases by adding more benzene rings to the array. The size of the array is proportional to a parameter, n , which is a measure of the number of connected rings:

$$L_a = d(1\ 0\ 0) (2n + 1) \quad (1)$$

where $d(1\ 0\ 0)$ is the in-plane lattice constant (0.24612 nm). The crystallite parameter, L_c , is obtained by stacking m layers of the layer planes of the same dimensions on top of each other:

$$L_c = d(0\ 0\ 2) (m - 1) \quad (2)$$

where $d(0\ 0\ 2)$ is the distance between the layer planes (i.e., 0.3354 nm for graphite). These relationships were used to determine the edge-site concentration for graphite particles of different dimensions. A graphite particle is considered to be a collection of prismatic crystallites, which is arranged in a regular geometry. The dimension of the particle is a function of the crystallite size and the number of crystallites. For a prismatic structure with the length of basal planes, B (also referred to as the particle size), and with a thickness of edge planes, E , the fraction of edge carbon atoms (f_e) is expressed as

$$f_e = \frac{2B/L_a + E/d(0\ 0\ 2)}{2B/d(1\ 0\ 0) + E/d(0\ 0\ 2)} \quad (3)$$

Eq. (3) indicates that the fraction of edge carbon atoms is a function of several parameters that vary independently of each other. With graphitisable carbons, both L_a and L_c increase with an increase in the degree of graphitisation, i.e., decrease in $d(0\ 0\ 2)$ spacing [22]. Consequently, it is difficult to derive a simple relationship between f_e and an independent variable for the graphite particle.

The relationships between the average particle size and the thickness of the edge planes, E , and the crystallographic parameter, L_a , are illustrated in Fig. 4. The dimension of the edge planes increases linearly proportional to the average particle size. On the other hand, L_a increases dramatically for the lower

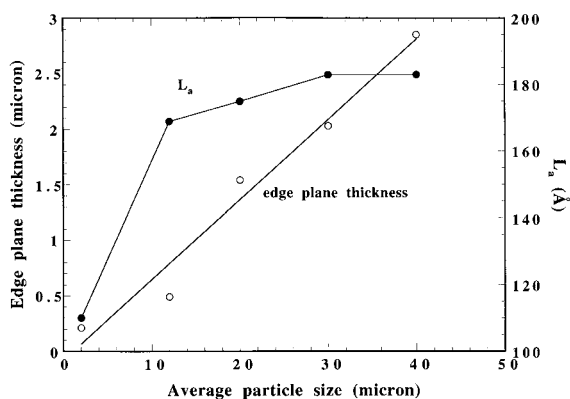
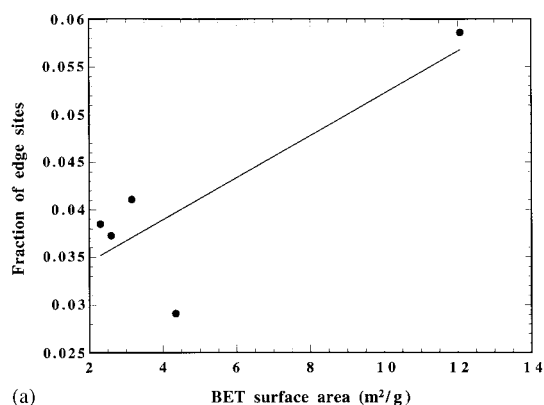


Fig. 4. Relationship between the average particle size and the dimensions of E and L_a .

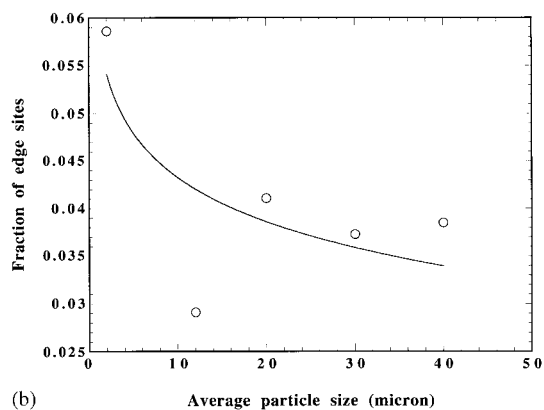
particle sizes and approaches a constant value of 183 \AA as the particle size approaches $40 \mu\text{m}$. These results illustrate that the dimensions of the crystallite (L_a) and particle thickness (E) can change independently of each other. Thus, the natural graphite used in this study exhibited a constant $d(002)$, and L_a increases with an increase in B and E .

The relationships between the fraction of edge sites and the BET surface area, average particle size and crystallite size L_a are presented in Fig. 5. The fraction of edge sites increases with an increase in the BET surface area and a decrease in the average particle size, as noted by the trends lines obtained from the software plotting program. These trends are consistent with the observations discussed above. The fraction of edge sites calculated from Eq. (3) decreases as the crystallite size represented by L_a increases. For a particle size of $10 \mu\text{m}$, an estimate from Fig. 5b for f_c is about 0.05. The simple analysis by Chung et al. [14] for a circular disk of $10 \mu\text{m}$ diameter yielded $f_c=0.01$. Considering the difference in geometry of the particles and the equations used in the calculation, the agreement is quite good. The trend observed in Fig. 5c indicates that the fraction of edge sites increases with a decrease in the crystallite size L_a . This result is in agreement with the observations by Radovic et al. [3] that L_a is a good measure of the fraction of active sites associated with carbon.

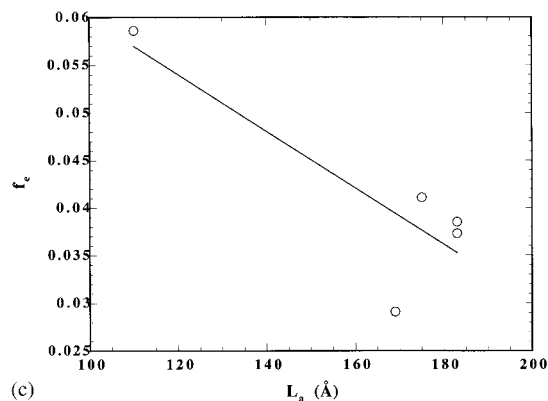
Fig. 6 shows the change in the thermal parameters (T_i , T_m , T_{15}) as a function of the fraction of edge sites. The solid lines illustrate the trend of the parameters as a function of f_c . It is evident that T_i , T_m and T_{15} decrease gradually with an increase in the fraction of edge sites.



(a)



(b)



(c)

Fig. 5. Dependence of the edge fraction on (a) surface area, (b) particle size and (c) L_a . Line indicates trend of data using KaleidaGraph.

The relationship between the thermal parameters and the fraction of basal plane sites (not plotted) shows the opposite trend as that observed with f_c . That is, T_i , T_m and T_{15} increase with an increase in the fraction of

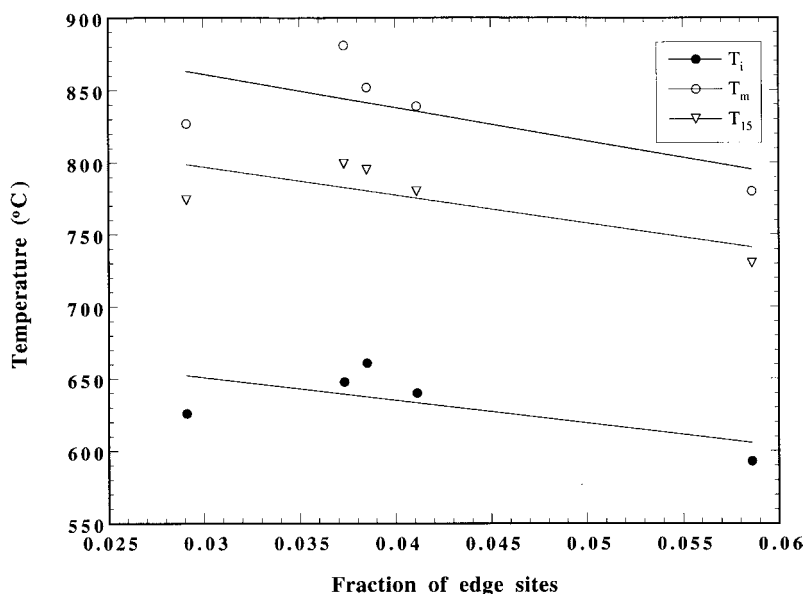
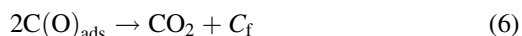


Fig. 6. Variation in thermal parameters, T_i , T_m and T_{15} , as a function of fraction of edge sites. Line indicates trend of data from a linear plot using KaleidaGraph.

basal plane sites, which is expected because f_e and f_b are complementary. These trends are consistent with the hypothesis that the reactivity of carbon increases with an increase in the amount of edge sites.

As we have discussed, the direct relationship between the fraction of edge sites and the thermal parameters for the oxidation of graphite is elusive because of the interdependency of the crystallographic properties. So far, only indirect evidence is presented to show the existence of such a relationship. However, other arguments can be presented to support the discussion. Thomas [1] summarised the observations of the microscopic studies of graphite oxidation, and he concluded that the reaction rate was anisotropic. Both CO_2 and CO were identified as primary reaction products of graphite oxidation [6,21]. The reaction mechanism leading to the formation of these gaseous species involves chemisorption of oxygen and subsequent desorption of the products [23–25]:



where C_f is a free carbon site and $\text{C}(\text{O})_{\text{ads}}$ is a site with a chemisorbed oxygen atom. Reaction (4) involves the

dissociative chemisorption of O_2 on the active sites, and Reactions (5) and (6) indicate desorption of the adsorbed oxygen species to form gaseous products. It is not the intent here to discuss the fine details of the reaction mechanism, but rather to illustrate that active sites play a role in the oxidation of graphite. As the active sites are associated with facile chemical reactions, C_f is most likely to be edge and defect sites on graphite. Scanning tunnelling microscopy and temperature-programmed desorption studies of graphites by Henschke et al. [26] clearly showed the significant role played by edge and defect sites on carbon oxidation. Laine et al. [4] suggested that the reaction rate (R) for the oxidation of graphitised carbon can be expressed by the equation

$$R = k_e[P_o](\text{ASA})(1 - \theta) + k_b[P_o](\text{TSA}) \quad (7)$$

where k_e and k_b represent the reaction rate constants at the edge and basal plane sites, respectively, P_o is the oxygen partial pressure, ASA is the active surface area, TSA is the total surface area and $1 - \theta$ is the fraction the ASA that is unoccupied by a surface complex. If $k_e \gg k_b$, then the reaction rate is dominated by the concentration of edge site. Radovic et al. [27] described the concept of the reactive surface area (RSA), which represents the surface concentration

of the $C(O)_{ads}$ species that show facile reactions (see Reactions (5) and (6)). The ASA represents the surface concentration of stable C–O complexes. Thus, the total concentration of C–O complex is equal to ASA+RSA. For the purposes of our discussion, what these studies illustrate is the significance of different surface sites (i.e., edge and basal plane sites) on the oxidation of graphitised carbons.

The TGA/DTA results obtained in the present study show that graphite with the highest fraction of edge sites has the lowest ignition temperature. Once ignition occurs, the graphite samples with a higher fraction of edge sites oxidise more rapidly as the temperature increases because of the enhanced heat that is generated by the exothermic oxidation reaction. More rapid oxidation kinetics will lead to a sharp increase in the weight loss and an earlier onset of T_m where the maximum heat generation is produced. Consequently, the measured thermal parameters are shifted to lower temperature with an increase in f_e . The decrease in the ignition temperature with an increase in the fraction of edge sites is in agreement with the TGA studies of air oxidation of ball-milled graphite by Welham and Williams [11]. They reported that T_i decreased with an increase in the amount of non-crystalline carbon and the relative amount of disordered carbon.

In summary, evidence obtained from TGA/DTA studies of graphite oxidation suggests that the ignition temperature is a function of the edge site concentration. The rapid kinetics associated with oxidation at the edge sites of graphite has a strong influence on the thermal parameters, T_i , T_m and T_{15} . The TGA/DTA measurements are conducted under dynamic conditions, that is under conditions where graphite is heated at 10°C/min. Therefore, it may not be valid to explain our results by using studies of graphite oxidation under isothermal conditions. However, the concepts developed on the mechanism of carbon oxidation in isothermal studies are useful in explaining our results on the role of surface sites on the thermal parameters for the oxidation of graphite.

4. Concluding remarks

For a prismatic graphite structure, the fraction of edge sites increases, and the fraction of basal plane sites decreases, as the particle size decreases. Using a

simple geometric model and analysis of the sites on the basal and edge surfaces, we derived the fraction of edge sites. Over the range of particle sizes (2–40 μm) considered in this study, the fraction of basal plane sites dominated, i.e., >0.94, and the edge sites represented only a minor fraction of the total surface sites. However, it is argued that the edge sites can play a major role in the oxidation of graphite.

The fraction of edge sites, f_e , derived from Eq. (3) is a function of several physical parameters (i.e., B , E , L_a , L_c , $d(002)$) which describe the properties of the graphite particle. The relationship between these parameters is complex, and it not possible to easily change one of these parameters without affecting the others. Consequently, an unequivocal relationship between the thermal parameters and the fraction of edge sites is not attainable. Instead, the collective observations from the research community, which are summarised in the Introduction, and the correlation reported in the present study, confirms that the fraction of edge sites has a strong influence on the thermal parameters (T_i , T_m and T_{15}) for the oxidation of graphite.

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