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A KINETIC MODEL FOR GRAPHITE OXIDATION IN COLD LIQUID MEDIUM

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Abstract—Graphite oxidation in a cold liquid medium was studied by means of the oxidizing properties of graphite oxidation products. These solid products were obtained with Staudenmaier reagent at 0°C over various periods of time. They were dehydrated over phosphorous pentoxide and their oxidizing capacities against KI–H_2SO_4 solutions were measured. A combustion model involving an unreactive nucleus has been applied to explain these measurements which may be useful to point out textural differences among graphites.

Key Words—Cold graphite oxidation, Staudenmaier reagent, oxide graphite.

1. INTRODUCTION

The process of graphitization, or transformation of non-graphitic carbons into graphite by thermal treatment, is of great technological significance because it is used in the production of synthetic graphite. This process has been studied by means of several techniques. Monitoring cold oxidation in a liquid medium provides useful information[1] about textural and structural features of graphites and graphitizable carbons. López-González, Carpenter and Deitz[2] have shown that natural and synthetic graphite exhibit different behaviours. Later, more remarkable differences were observed in a number of intermediate products obtained by cold oxidation from graphites of different origin[3,4]. The treatment of graphite with strong oxidizing agents in a liquid medium leads to graphite oxide (GO), but partly oxidized graphites can be also obtained by oxidation during shorter periods of time. These intermediate preparations are able to react with reducing agents such as KI in an acidic medium[5], their oxidizing capacities indicating the extent to which they have been oxidized. Based on these oxidizing capacities against KI a kinetic model has been fitted to this particular type of oxidation.

2. EXPERIMENTAL

Two different kinds of graphite were used. Both graphite samples were ultrapure and polycrystalline materials, one a natural graphite (N) from Degussa (Germany) and the other a synthetic (A) made by Sigri Elektrographite GmbH (Germany). Basically the treatment was the Staudenmaier method[6] using an oxidizing mixture of $KClO_3$, nitric and sulfuric acids.† The particle size ranged from 44 to 60 μm. The beaker was kept at 0°C during the reaction. The oxidation attack was interrupted at different times for each sample by dilution with 10 l of distilled water at 0°C. The samples so obtained were washed with dilute HNO_3 and distilled water. The samples were dried in an oven at 40°C. A particle size of 40–60 μm was then chosen for the subsequent experiences. These preparations were dehydrated in desiccator with phosphorous pentoxide under vacuum until they attained constant weight.

The oxidizing capacities were measured by reaction between 80–150 mg of sample dehydrated over phosphorous pentoxide and KI solution (110 g/l) in sulfuric acid. The reaction progressed for six hours at 55°C under a slow flow of Ar. Iodine released from solution was condensed in a Dimroth refrigerant. Then the iodine in solution and that extracted from solid residue by HCl + ethanol solution was titrated. Finally, the carbonaceous residue was burnt in a sealed flask previously filled with oxygen. The iodine evolved was collected in alkali solution and then completely oxidized to produce iodate by means of bromine. The remaining bromine was removed using a formic acid solution, then an amount of iodine proportional to the initial quantity was regenerated in an acid medium with potassium iodide and titrated. The total amount of iodine produced was so determined.

Carbon and hydrogen percentages in the reduced samples were also determined by means of a Carlo Erba 1106 elemental analyzer. Diffraction (110) lines of both graphites and (220) line of α–Al_2O_3 as a reference were recorded by means of a Siemens set model D-500 using Mo K_α radiation, entrance slits of 0.3° and receiving slits of 0.3 and 0.05°, and a graphite monochromator. The 2θ scanning rate was 0.2°/min.

3. RESULTS AND DISCUSSION

The products obtained by the cold oxidation of graphite were characterized by chemical analysis, X-ray diffrac-

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†Caution: $KClO_3$ must be added in small amounts to avoid explosion.

tion and IR spectroscopy[5]. Their oxidizing capacities against KI in sulfuric acid solution are listed in Table 1. These values are expressed in millimole of iodine per gram of dehydrated sample. It is possible to consider that oxidizing capacities are nearly constant for N-72, A-64 and stronger oxidized samples in both series. But functional evolution of groups inserted in layers delays the complete conversion into graphite oxide[5] at least to N-84 in the Natural series and A-72 in the Artificial series. During oxidation very fine graphite powder was plunged into a fluid where $KClO_3$ was present as oxidizing agent. Oxidation by means of $KClO_3$ transformed graphite to graphite oxide and partly oxidation also produced soluble and volatile products. The chemical process can be represented by the equation:

$$D + bB(\text{solid}) \rightarrow B'(\text{solid}) + \text{other products.} \quad (1)$$

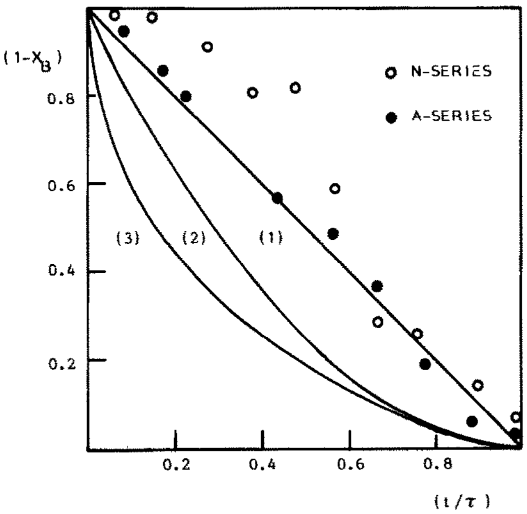

Fig. 1. Conversion grade to graphite oxide in cold oxidation of graphite. (1) Predicted behaviour when the rate-determining step is film diffusion. (2) Predicted behaviour when the rate-determining step is diffusion in layers already converted. (3) Predicted behaviour when the rate-determining step is chemical reaction.

Before chemical reaction would take place D must diffuse through a liquid film, which envelops the particle, and then inside the particle to get the lamellar edges. In a second stage it must diffuse between two layers already converted into graphite oxide. The third stage is the proper chemical reaction leading to GO. Nonsolid products must diffuse returning over the same path that the reagent did. Actually, it causes desintegration but in this approximation we will consider that the crystals maintain their form whilst they are progressively converting into GO with an increasing of L_c parameter. Thus, an ideal plate-like crystal, which conserves an unchanged core, has been taken as representative model of such intermediate preparations. Under the above conditions, the kinetic model conceived by Yagi and Kunii[7] has been used to describe graphite oxidation. In Fig. 1 the three different equations predicted according to the rate-determining step are represented. Three controllers are possible; film diffusion (curve 1), diffusion in layers already converted (curve 2) and chemical reaction (curve 3). Liquid film diffusion seems to be the one which controls the process (see Fig. 1). Consequently kinetics follows the simple equation:

$$t/\tau = X_B \quad (2)$$

where X_B is the degree of conversion or fraction of GO formed and t/τ is fraction of time required for complete conversion. τ could be expressed as follows

$$\tau = (\rho_B \cdot R)/(2 \cdot b \cdot k \cdot c_D) \quad (3)$$

where b has the same meaning as in eqn (1) above, ρ_B is molar density of solid, R the mean radius of plates, k a transport coefficient of mass and c_D the concentration of reagent D, which is nearly constant in this case.

The degree of conversion, X_B, has been estimated as the ratio between the oxidizing capacity of an interme-

Table 1. Oxidizing capacities of graphite oxidation products (time in hours)

Sample	Oxidizing Capacity (mmole I_2/gram)	Sample	Oxidizing Capacity (mmole I_2/gram)
N-6	0.00	A-6	0.69
N-12	0.17	A-12	2.07
N-24	1.07	A-24	4.41
N-32	2.49	A-32	6.51
N-40	2.31	A-40	7.48
N-48	5.69	A-48	9.27
N-56	9.93	A-56	11.97
N-64	10.40	A-64	13.79
N-72	12.63	A-72	14.25
N-84	12.90	A-84	15.00
N-96	14.79	A-96	14.70
N-108	13.74	A-108	14.63
N-120	14.46	A-120	14.76

diate preparation and the mean value calculated for the most strongly oxidized samples (14.0 mmole/gram in N-series and 14.7 mmole/gram in A-series).

Obviously this model overlooks many features that are actually involved in a more complicated situation. It has been tested following a method in which crystal size determinations have been performed. Assuming similar values of ρ_B, b, k and c_D in both cases, we find from eqn (3) the R_N/R_A ratio to be given by

$$(R_N/R_A) = (\tau_N/\tau_A) = (84\ \text{h}/72\ \text{h}) = 1.17.$$

The Scherrer formula may be used to determine crystal size of small crystals from three-dimensional reflections of the appropriate indices[8,9]. The line breadth of the (110) reflection has been chosen to calculate the diameter, L_a, of the crystal, considered as a right cylinder. Thus broadening was measured in the low angle region ($2\theta = 33.77°$), and a suitable curve for diffractometer line profile[8] was used to obtain the true diffraction broadening from the breadth at half the maximum intensity. This correction was based on instrumental breadth measured on the (220) line of α-Al_2O_3, which had been previously annealed for 24 h at 1300°C. Assuming a Scherrer constant close to unity[9] the values of L_a were calculated in order to compare to R values. We found that

$$(L_a{}^{110})_N/(L_a{}^{110})_A = (944\ \text{Å})/(787\ \text{Å}) = 1.20.$$

The absolute value of the mean layer dimension L_a must be taken with caution but the ratio will be more reliable. This second procedure, which gives approximately the same value for the ratio of crystal sizes, should give a certain confidence in the reaction mechanism.

4. CONCLUSIONS

The rate-determining step in the cold oxidation of graphite in a liquid medium must be the diffusion of the oxidizing agent $KClO_3$ through the liquid film surrounding the polycrystalline particle until it arrives at the crystal edges. The reagent must then diffuse rapidly between layers, which have been already transformed into GO, to react with graphite in the core. This mechanism involves two final steps for the reverse route of products. The time required for complete conversion into GO for A graphite is about 90% of that required for N graphite although a precise definition of τ is difficult.

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