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STUDIES ON THERMAL DECOMPOSITION OF ELECTROCHEMICALLY OXIDIZED GLASS-LIKE CARBON

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Glass-like carbon (GC) tiles were electrochemically oxidized in 1 mol · dm^{-3} H_2SO_4 solution at a potential of 2.3 V/SCE. The surfaces of the oxidized samples were examined by scanning electron microscopy (SEM). The solid oxidation products were studied by derivatographic (TG, DTG and DTA) and elemental analyses. The solid products of electrochemical oxidation of GC, with the general formula $C_8O_{4.2}H_{2.3}$ were thermolabile and revealed properties similar to those of graphite oxide. They are hydrophylic and their thermal decomposition proceeds in three steps: (i) evaporation of chemisorbed water (320–400 K), (ii) exothermic decomposition of graphite oxide (370–430 K), and (iii) gradual decomposition of the oxidation products (>430 K).

Glass-like carbon (GC) is a carbon material (99% C) whose mechanical properties are typical of those for glassy materials, but whose chemical reactivity is characteristic of that for carbon. Thanks to its unique physicochemical properties, this material has been finding ever wider applications in ultra-high-purity materials technology, electrochemistry, laboratory techniques, and medical technology [1–3]. Further studies on the technology and properties of GC are connected with the dynamic development of carbon–carbon composites in which GC may play the role of matrix [4]. Different applications of GC have been extensively investigated, usually with considerable success as far as the stability of the carbon is concerned. Under the influence of oxidizing agents (gases at >750 K or liquids), GC undergoes chemical or electrochemical corrosion. The oxidation of GC in air or oxygen results in a significant decrease in mass of the material and in its strongly lowered mechanical strength [5], the oxidation kinetics having an anisotropic character [6]. The chemical or electrochemical oxidation of GC in the liquid phase produces corrosion of the material, consisting in a characteristic cracking and peeling of the surface [2, 7–11]. The solid products of anodic oxidation of GC peel off from the surface in solution or during drying of the oxidized samples. The physicochemical properties of these products have not as yet been subjected to systematic examination.

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The present paper gives the results of derivatographic investigations of GC and its anodic oxidation products, and is a contribution to a study on the properties of electrochemically oxidized carbon materials.

Experimental

The GC used in this study was of WS–1 type, manufactured by the Carbon Electrode Plant in Racibórz (Poland). Tiles with dimensions of 30 × 30 × 2 mm were produced by the carbonization of phenolic resin (the final temperature was ca. 1300 K).

The samples were polished with SiC abrasive paper (800) and next with diamond paste until a mirror-like surface was obtained. After polishing, the tiles were sonicated for 5 minutes in bidistilled water and subjected to electrochemical oxidation in a 1 $\text{mol} \cdot \text{dm}^{-3}$ H_2SO_4 solution at a potential of 2.3 V *vs.* a saturated calomel electrode (SCE). The surface of the oxidized GC was examined by scanning electron microscopy (SEM).

During electrochemical oxidation, the surface of the GC cracked and peeled off. After the removal of two layers with a total thickness of about 10 μm, the next layers of GC oxidation products were collected, thoroughly washed and dried in vacuum at 320 K.

Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves were obtained for as-received GC and for the solid products of its anodic oxidation. The OD–102 MOM derivatograph was used. The material to be tested was granulated in an agate mortar and the fraction with grain size of $0.4 < \phi \leq 0.6$ mm was used. Prior to testing, it was kept in a desiccator at 293 K for 30 days in air of 0%, 50% or 80% humidity, ensured by using sulfuric acid solutions of appropriate density. All the measurements were made on 100 mg samples, heated over the temperature range 293–1200 K in a dynamic air or high-purity (less than 5 vpm $O_2 + H_2O$) argon atmosphere. The heating rate was varied from 1.25 to 9 $\text{deg} \cdot \text{min}^{-1}$; the sensitivities used were TG — 100 mg, DTG — 1 : 15 and DTA — 1 : 10. α-Al_2O_3 was used as reference material.

Further information on the thermal decomposition of the GC oxidation products was obtained from TG studies carried out on 2 mg samples in argon and oxygen atmospheres. In these investigations, a Perkin–Elmer TGS–1 thermobalance was used.

The gases (H_2O, CO_2 and CO) evolved during heating of the 100 mg samples were measured in parallel experiments by a chromatographic method.

Elemental analysis of the oxidized and dehydrated samples was carried out by means of a Carlo Erba analyzer. The oxygen content was determined directly, according to a method described elsewhere [12].

Results and discussion

Surface morphology

The anodic polarization of GC tiles in dilute sulfuric acid solution at a potential of $E \geqslant 2.0$ V *vs.* SCE for about 12 minutes resulted in distinct corrosion of the material, consisting in cracking of the surface and the detachment of flat grains of the oxidation products [9, 11]. The thickness of the peeling layers was 0.5 μm to 30 μm and depended on the density of the electric charge passed through the tile. The physical properties of the GC oxidation product differed significantly from those of the initial material.

Figure 1 shows a SEM micropattern of a GC tile oxidized electrochemically at a potential of 2.3 V for 120 min. The visible solid products of anodic oxidation of GC constitute the third successive layer. They are black and shiny and cracked at random. Dübgen observed a similar form of corrosion of GC after chemical oxidation of the material in boiling nitric acid [2]. Figure 2 depicts the surface of GC after detachment of the layer of electrochemical oxidation products. We see etched circular craters with varying diameter and depth. Peng [5] observed very similar morphologic changes of the GC surface after its exposure to vigorous oxidation in air at > 800 K, while Laušević and Jenkins registered such changes when GC was electrochemically oxidized in brine [9].

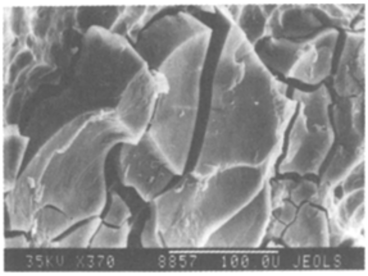

Fig. 1 SEM micropattern of electrochemically oxidized (E = 2.3 V, 120 min) GC

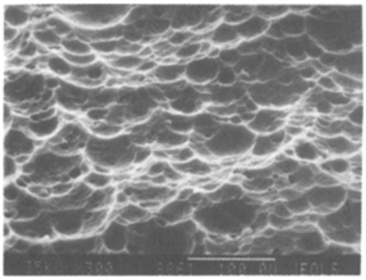

Fig. 2 SEM micropattern of oxidized GC after detachment of layer of oxidation products

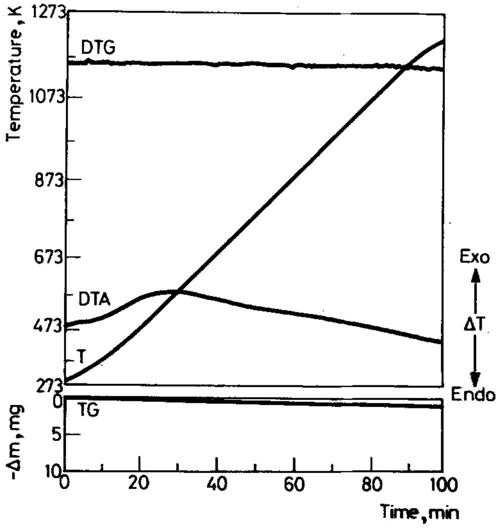

Fig. 3 Thermoanalytical curves of GC, obtained in argon atmosphere

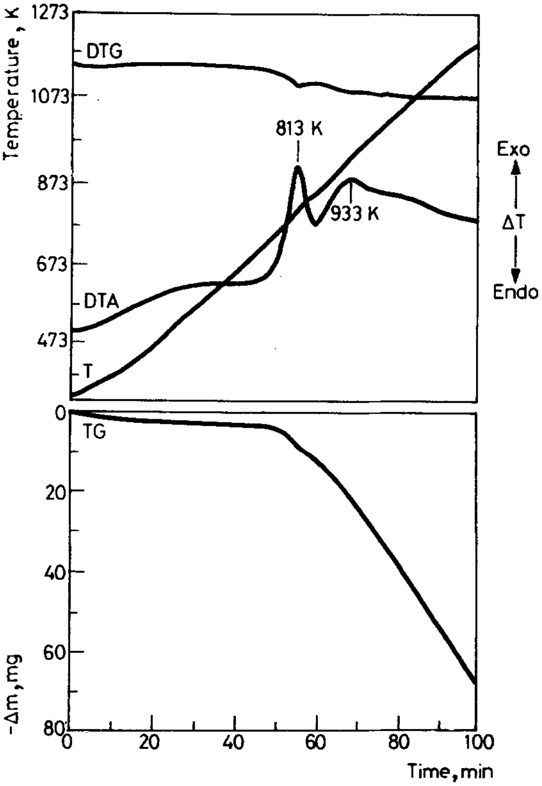

Fig. 4 Thermoanalytical curve of GC, obtained in air

Thermal analysis of GC

Figures 3 and 4 present thermoanalytical curves of as-received GC, obtained in argon and air. In the argon atmosphere, we observe a small (1%) decrease in sample weight, due to thermal decomposition of the granulated GC. The wide maximum in the DTA curve is due to the difference in specific heats between GC and the α-Al_2O_3 used as reference material.

When heated in air up to 720 K, GC oxidized very slowly (Fig. 4). Above 720 K, the oxidation rate increased several-fold. At 812 K and 933 K, two inflections appear in the TG curve, which correspond to two distinct exothermal effects in the DTA curve. These effects may be related to the occurrence in the GC structure of trigonally hybridized (sp^2) and tetragonally hybridized (sp^3) carbon atoms, as has been suggested by various authors on the basis of structural investigations [1, 13, 14]. This would also explain the occurrence in GC of regions with distinctly increased resistance to oxidation, and the characteristic morphology of the surface of oxidized GC (Fig. 2).

Thermal analysis of electrochemically oxidized GC

Figure 5 presents thermoanalytical curves obtained in the course of heating of GC electrochemical oxidation products (which were kept for 30 days over concentrated H_2SO_4, $d_{20} = 1.84$ g$\cdot$cm^{-3}) in argon atmosphere. The DTA curve reveals that up to 373 K an endothermic process takes place, caused by the evaporation of surface bonded water. This effect is better visible in Fig. 6, which shows a selection of TG and DTA curves of GC oxidation products which were kept in atmospheres of 0%, 50% or 80% humidity. The higher the air humidity, the more distinct is the endothermal effect observed. A rapid decrease in the mass of the samples is simultaneously observed in the TG curves.

Above 373 K, an exothermal process starts, caused by the thermal decomposition of oxidized GC. The maxima appear in the DTA curves at 413 K and are accompanied by a sharp drop in sample weight in the TG curve (Figs 5 and 6). From the DTA and TG curves in Figs 5 and 6, we see that the decrease in the exothermal effect with elevation of the humidity of their air in which the samples were kept is due to the superposition of an additional endothermal effect, most probably the evaporation of intercalated water. Above 413 K, the rate of decrease in weight of the samples heated in a neutral atmosphere becomes lower. The total decrease in weight of samples heated to 450 K reached 30%. The exothermal decomposition of oxidized GC in the temperature range 370–430 K involves combustion of the carbon material under the action of molecular (or atomic) oxygen introduced into the internal structure of GC in the course of anodic polarization.

Analysis of the gases evolved in the course of thermal decomposition of the

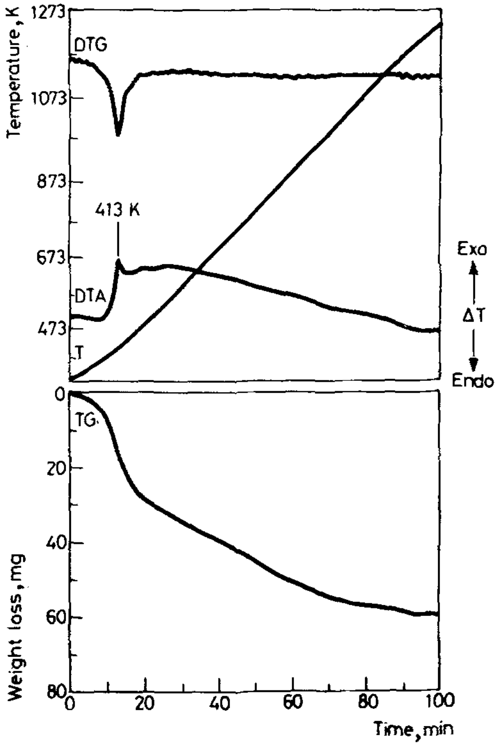

Fig. 5 Thermoanalytical curves of electrochemically oxidized GC, obtained in argon atmosphere

samples (Fig. 7) shows that in the temperature range up to 500 K water and CO_2 are the main products. The water evolution maxima are at 360 K and 400 K. Above 500 K, only the evolution of CO_2 and CO is observed.

The exothermal effect of decomposition of the GC oxidation products is related to the rate of heating of the samples. As the heating rate is lowered, the maximum in the DTA curve gradually disappears. At a heating rate of 1.25 deg·min^{-1}, the maximum in the DTA curve is no longer visible. This confirms the argument that the process of thermal decomposition of GC oxidation products, in the temperature range 370–430 K, is chemical in character [15, 16].

The process studied in the present work takes place in a similar manner to the thermal decomposition of graphite oxides obtained by chemical oxidation of various kinds of graphite [15–19]. The authors of the quoted works found that the positions of the maxima in the DTA curves of the graphite oxides depend on the kind of graphite used and on the way it is oxidized. As a result of anodic oxidation, GC oxidation products with properties similar to those of graphite oxide are formed. Though unexpected, this indicates that significant numbers of regions exist

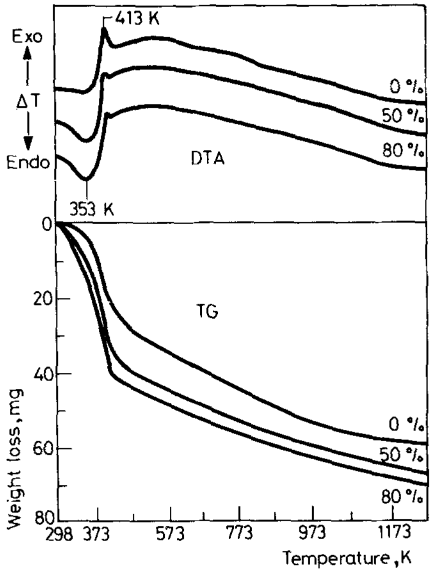

Fig. 6 DTA and TG curves of GC anodic oxidation products kept in air atmospheres of 0%, 50% or 80% humidity

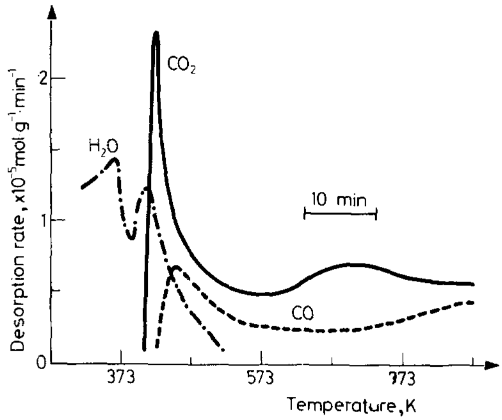

Fig. 7 Temperature-programmed desorption of H_2O, CO_2 and CO from electrochemically oxidized GC dried over concentrated H_2SO_4

in GC with turbostratic, graphite-like ordering of the carbon atoms. Such an ordering, in the form of a tangled ribbon-like lattice of graphite-like crystallites, is postulated on the basis of structural investigations of GC [1, 13, 14]. Recently, Honjo and Shindo [20] reported that graphite oxides are formed on carbon fibers in the course of electrochemical oxidation.

Elemental analysis of GC oxidation products dried in vacuum at 323 K has shown that the composition of this material is non-stoichiometric and can be represented by the molecular formula $C_8O_{4.2}H_{2.3}$. The stoichiometric formula $C_8O_2(OH)_2$ is suggested for graphite oxide [21]. It should be taken into account, however, that the studied material might contain a certain quantity of strongly chemisorbed or intercalated water that is difficult to remove in view of the thermal instability of GC.

Above 450 K, the weight of samples heated in a neutral atmosphere gradually decreased, at 1220 K reaching 40–30% of their initial weight (Figs 5 and 6). In this temperature range no thermal effects were observed in the DTA curves, and the weight deficit was related to the thermal decomposition of graphite oxide and the carboxylic and carbonyl groups formed on the edges of the graphite-like crystallites of the internal GC structure [22]. Further derivatographic studies of the same sample of oxidized GC, conducted in argon atmosphere, have shown that the process of thermal decomposition of the material is irreversible.

Figure 8 shows thermogravimetric curves obtained when samples were heated in air. Up to 500 K, the course of the curves was similar to that of the curves obtained in argon. The strong exothermal effect (DTA curve) and the accompanying rapid deacrease in weight of the sample (TG curve) point unequivocally to the combustion of the carbonaceous residue.

Thermogravimetric investigation of 2 mg samples

The results of TG investigations of 2.0 mg samples of GC and the products of its electrochemical oxidation are given in Fig. 9. Despite the fact that the samples used in the tests were 50 times smaller than those in the thermoanalytical studies, the relevant TG curves are very similar. This proves that the initial and oxidized samples were homogeneous and that diffusion had only a minor effect on the results of thermal decomposition of the samples. In oxygen, the combustion of GC oxidation products proceeds vigorously at 660 K, while GC is oxidized rapidly at >800 K. The much lower ignition point of the GC oxidation products than that of the initial GC suggests an increased microporosity and disintegration of the internal structure of the oxidized material.

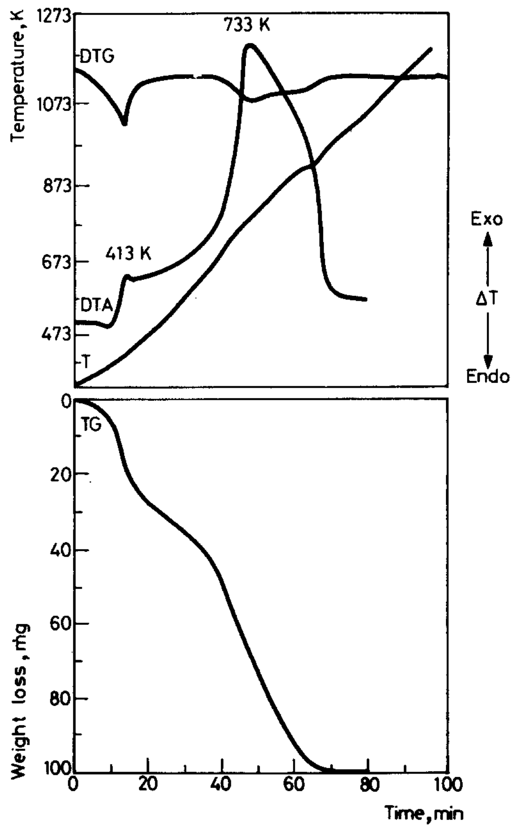

Fig. 8 Thermoanalytical curves of electrochemically oxidized GC, obtained in air

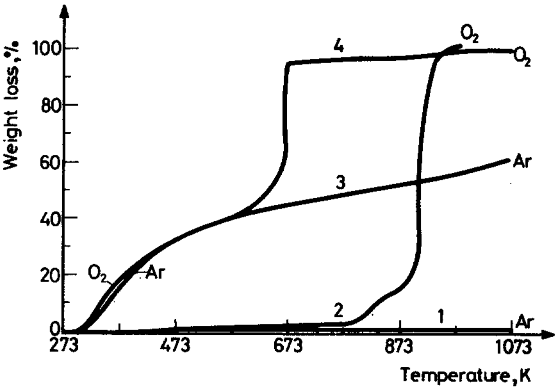

Fig. 9 Thermogravimetric curves of GC (1 and 2) and its anodic oxidation products (3 and 4). Curves 1 and 3 were obtained in argon atmosphere. Curves 2 and 4 were obtained in oxygen atmosphere

Conclusions

As a result of the electrochemical oxidation of GC, solid thermolabile products with molecular formula $C_8O_{4.2}H_{2.3}$ are formed, which display properties similar to those of graphite oxide. The thermal decomposition of these products proceeds in three steps. In the first endothermal step (320–400 K), the chemisorbed water is evolved. In the second step (370–430 K), exothermal decomposition of graphite oxide takes place, with the evolution of CO_2, H_2O and CO. The water evolved in this step is probably that intercalated between the graphite oxide layers. The exothermal effect is due to the combustion of carbon with oxygen trapped in the bulk of the oxidized GC. The third step (above 430 K) consists in the gradual decomposition in a neutral atmosphere of graphite oxide and of the functional groups chemisorbed on the edges of the graphite-like crystallites present in the material. In an oxygen-containing atmosphere, the rapid combustion of carbon takes place. Electrochemically oxidized GC is more liable than the initial GC to oxidation.

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Zusammenfassung — Glasähnliche Kohlenstoff (GC) Ziegel werden in einer 1 mol·dm^{-3} H_2SO_4 Lösung bei einem Potential von 2,3 V/SCE elektrochemisch oxydiert. Die Oberfläche der oxydierten Proben wurde mittels Scanning-Elektronen-Mikroskopie (SEM) untersucht. Die festen Oxydationsprodukte wurden mittels Derivatografie (TG, DTG, DTA) und Elementaranalyse untersucht. Es konnte gezeigt werden, daß die Feststoffprodukte der elektrochemischen Oxydation von GC thermolabil sind und ähnliche Eigenschaften zeigen wie Graphitoxid der allgemeinen Formel $C_8O_{4,2}H_{2,3}$. Diese sind hydrofilen Charakters und zersetzen sich thermisch in drei Schritten: (I) Verdampfen des chemosorbierten Wassers (320–400 K), (II) exotherme Zersetzung von Graphitoxid (370–430 K) und (III) allmähliche Zersetzung der Oxydationsprodukte (>430 K).

Резюме — Плитки из стеклообразного углерода электрохимически окислялись в 1 М растворе серной кислоты при потенциале напражения 2,3 В/эдс. Поверхность окисленных образцов была исследована методом сканирующей электронной микроскопии, а твердые продукты окисления были изучены методом ТГ, ДТГ, ДТА и элементным анализом. Показано, что продукты электрохимического окисления стеклообразного углерода термически неустойчивы и проявляют свойства, подобные окиси графита с общей формулой $C_8O_{4,2}H_{2,3}$. Эти продукты являются гидрофильными и их термическое разложение протекает в три стадии: а) выделение в интервале 320–400 К химически сорбированной воды, б) экзотермическое разложение окиси графита в температурном интервале 370–430 К и в) постепенное разложение продуктов окисления выше 430 К.