Journal of Thermal Analysis, Vol. 35 (1989) 2225–2233

THERMAL ANALYSIS STUDIES ON ELECTROCHEMICALLY OXIDIZED CARBON FIBERS

Part 1. Thermal decomposition in air atmosphere

S. Neffe

DEPARTMENT OF CHEMISTRY AND TECHNICAL ENGINEERING,
MILITARY TECHNICAL ACADEMY, 00–908 WARSAW 49, POLAND

(Received May 25, 1988)

The results are presented of studies on the effect of electrochemical oxidation of carbon fibers (CFs) in 1 $mol \cdot dm^{-3}$ H_2SO_4 on their thermal decomposition in air.

The resistance to oxidation of the as-received fibers increases with increasing ordering of their internal structure, characterized by the interlayer spacing $\bar{d}_{002}$ of the graphite crystallites.

After anodic oxidation, the resistance to oxidation of CFs in air is markedly decreased. It is shown that in the course of anodic polarization of CFs with a current density of more than 5 $A \cdot m^{-2}$, the regions of the material with highest ordering convert to graphite oxide, which is hydrophilic and thermally unstable.

The chemical and physical nature of carbon fiber surfaces plays an important role in their reactivity during their high-temperature use in corrosive environments. Various physical and chemical methods have been used to examine the structure and surface of the fibers [1].

The surface oxidation of carbon fibers has been proposed as a means of modifying or studying their surface properties and internal structure [2–9]. Anodic oxidation allows the most accurate maintenance of the required oxidation conditions and easy control of the process rate. Most examinations of the electrochemical oxidation of carbon fibers had the aim of producing a physical and chemical modification of their surface that would ensure the removal of some of the surface defects and at the same time generate surface functional groups [3, 5, 6, 8, 10]. For this reason, the anodic oxidation of carbon fibers was conducted under mild conditions which did not lead to essential morphological changes of their surface. The intense chemical or electrochemical oxidation of carbon fibers brings about a mass loss and produces surface etching or splitting [1, 7, 9]. These processes, in acidic media, are often accompanied by conversion of the surface graphite

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

crystallites of the carbon material into graphite oxide [2, 5, 7, 9]. Graphite oxide is known to be a lamellar thermolabile and somewhat nonstoichiometric substance [11].

A knowledge of the resistance of carbon fibers to oxidation, in a broad range of temperatures, is essential for an assessment of the possibility of their application in different composite materials.

The aim of the present work is to study the effects of the structure and electrochemical oxidation of carbon fibers on their thermal decomposition in air.

Experimental

Samples

Six types of carbon fiber were investigated; these are tabulated in Table 1, together with the values of their physical properties. The carbon fibers K–1, B–1–1820, B–1–2200 and B–1–2800 were produced in Poland, on a semicommercial scale, from polyacrylonitrile. K–1 was manufactured in a periodic process with a weak tension of the fibers during carbonization. B–1–1820 was obtained in a continuous process with a strong tension of the fibers during carbonization. B–1–2200 and B–1–2800 were obtained by heat treatment of B–1–1820 at 2200 K and 2800 K, respectively. Grafil XAS (HP) and Celion carbon fibers are manufactured by Hysol Grafil Ltd. and Celanese Co., respectively.

The sizing was removed from the commercially surface-treated carbon fibers by extraction with boiling acetone and next toluene, followed by distilled water extraction.

Table 1 The mechanical and physical properties of carbon fibers

Kind of carbon fiber	Diameter $\bar{d}$*, μm	Tensile strength, GPa	Young's modulus, GPa	Elongation, %	Interlayer spacing, $\bar{d}_{002}$, nm	Temp. of half decomposition, $T_{1/2}$, K
K–1	8.3	1.13	195	0.68	0.360	830
B–1–1820	7.8	3.10	215	1.63	0.351	905
**B–1–2200	7.6	2.60	250	1.50	0.349	960
**B–1–2800	7.6	1.15	350	0.70	0.344	990
Grafil XAS (HP)	6.8	3.58	221	1.65	0.348	970
Celion	6.7	3.10	224	1.77	0.348	940

* Standard deviation 0.40–0.50 μm

** Heat-treated in the laboratory.

The average interlayer spacing $\bar{d}_{002}$ in the studied carbon fibers was determined from the 002 X-ray diffraction line by using CuK_{α} radiation and an Al filter. The fiber axis was perpendicular to the X-ray beam. TheT602 values of the studied carbon fibers are listed in Table 1.

Electrochemical oxidation

Electrochemical oxidation of carbon fibers was carried out in a standard three-electrode measuring vessel. A bundle of ca. 3000 filaments, 10 cm long, was used as the working electrode. The filaments were tied together with platinum foil, which served as a current connection. A platinum plate of 4.20 cm^2 constituted the counter electrode. A saturated calomel electrode was used as the reference electrode. Oxidation was carried out in a sulfuric acid solution of 1 mole$\cdot$dm^{-3} concentration. The constant polarization current was ensured by the PG 30/1 potentiostat. After electrochemical treatment, the fibers were carefully rinsed in double distilled water and dried at 320 K in vacuum. Next, they were kept in a desiccator at 293 K over concentrated (d_{20} = 1.84 g$\cdot$cm^{-3}) sulfuric acid.

Thermal analysis

Thermal analysis curves (TG, DTG and DTA) were obtained for as-received carbon fibers and for the electrochemically oxidized ones. The Q–1500 D MOM derivatograph, was used. The measurements were made on 50–60 mg samples, heated over the temperature range 293–1200 K in a dynamic air atmosphere. The heating rate was 5 deg$\cdot$min^{-1}. α-Al_2O_3 was used as the reference material.

Results and discussion

The mechanical properties and average interlayer spacings ($\bar{d}_{002}$) of the tested carbon fibers are given in Table 1. From these data it follows that the K–1 fibers have a strongly defective internal structure with poorly developed graphite crystallites. The B–1–1820 fibers have a better ordered internal structure, which is reflected by the much higher tensile strength. These results are in agreement with the results of earlier studies on the surface morphology of these fibers [9]. After thermal treatment of the B–1–1820 fibers at 2200 K and 2800 K, the ordering of their crystalline structure improved further and the increase of Young's modulus took place at the expense of a decrease in the tensile strength. The B–1–1820, B–1–2200, Graphil XAS (HP) and Celion fibers have high tensile strength, while B–1–2800 has a high modulus.

Thermal analysis of as-received carbon fibers

Thermogravimetric (TG) and differential thermal analysis (DTA) curves obtained in the course of heating of as-received fibers are shown in Fig. 1. From the shape of the TG curves, we see that distinct oxidation of the tested fibers begins only above about 800 K. K–1 constitutes an exception here, since its slow oxidation starts at 400 K and its rapid combustion begins at 690 K. From the shape of the TG curves, it can be concluded that the susceptibility to oxidation of the carbon fibers decreases with the degree of ordering in the material, characterized by the parameter d_{002}. This becomes obvious if we consider the fact that highly ordered graphites are more resistant than amphoteric carbons to various oxidizing agents [2]. Among the tested carbon fibers, the high-modulus B–1–2800 was most resistant to oxidation, which is due to the high ordering of its internal structure generated in the course of thermal treatment. The half decomposition temperatures of the studied carbon fibers are given in Table 1.

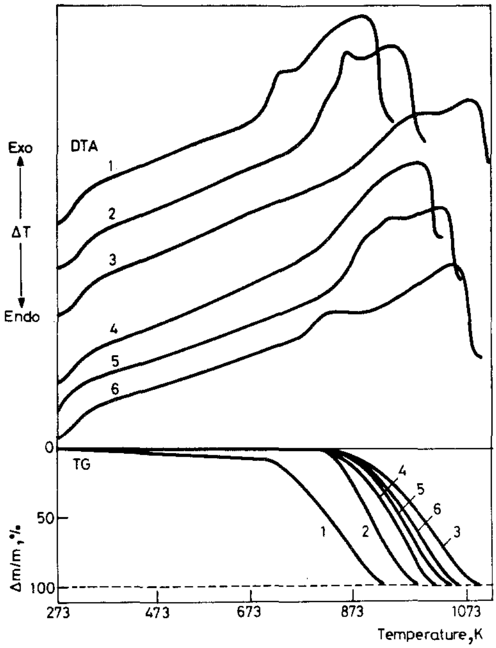

Fig. 1 Thermal analysis curves of different types of carbon fibers: 1 – K–1, 2 – B–1–1820, 3 – B–1–2800, 4 – Celion, 5 – B–1–2200 and 6 – Grafil XAS (HP)

The DTA curves (Fig. 1) of all the tested carbon fibers (with the exception of Celion reveal two exothermic maxima in the temperature range up to 700 K. This is probably due to the heterogeneous skin/core type of the tested carbon fibers [9]. The skin of the fibers consists of well-developed graphite crystallites arranged parallel to the fiber axis, while the core is characterized by a much poorer random ordering of the crystallites [1, 12].

Thermal analysis of electrochemically oxidized carbon fibers

Depending on the density of the applied polarization current, the electrochemical oxidation of carbon fibers produces changes in the chemical condition of the surface and the generation of surface layers of graphite oxide. The latter process proceeds in acid solutions at high current densities, the thickness of the graphite oxide layer depending on the electric charge passed through the fiber [1, 2, 9]. Figure 2 presents

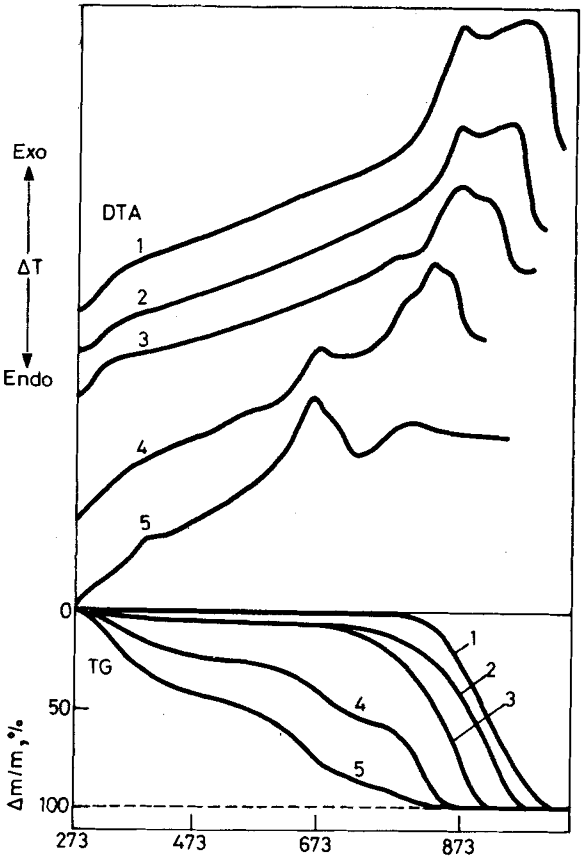

Fig. 2 Thermal analysis curves of B–1–1820 carbon fibers electrochemically oxidized with different electric charges: 1 – as-received, 2 – 100 $C\cdot g^{-1}$, 3 – 230 $C\cdot g^{-1}$, 4 – 1000 $C\cdot g^{-1}$ and 5 – 5000 $C\cdot g^{-1}$

the TG and DTA curves obtained for B–1–1820 carbon fibers oxidized galvanostatically at a polarization current density of 5 A · m^{-2}. The charge passing through the fibers was controlled by the duration of polarization. The TG curves in Fig. 2 show that the resistance of the fibers to oxidation in air decreases strongly with increasing charge of polarization. A qualitative change occurs in the character of the TG and DTA curves when the carbon fibers are oxidized with a charge of more than 500 C · g^{-1} (curves 4 and 5 in Fig. 2).

Figures 3 and 4 depict thermal analysis plots of K–1 and B–1–2800 carbon fibers, respectively, oxidized anodically with an electric charge of about 1000 C · g^{-1} and 5000 C · g^{-1}, respectively. The TG curves of the carbon fibers oxidized in this way exhibit three distinct inflection points, which correspond to three steps of thermal decomposition of the tested materials in air. The mass loss percentages in the successive steps for carbon fibers oxidized with an electric charge of about 1000 C · g^{-1} or 5000 C · g^{-1} are given in Table 2.

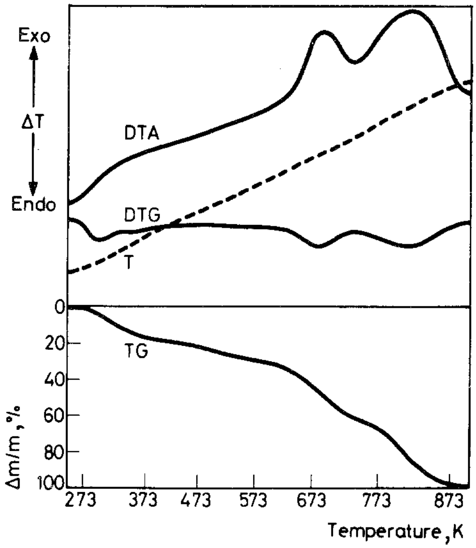

Fig. 3 TG, DTG, DTA and T curves of K–1 carbon fibers electrochemically oxidized with an electric charge of about 1000 C · g^{-1}

In the first step (293–473 K), the loss in mass is due chiefly to the evaporation of water strongly chemisorbed on the surface and intercalated inside the material, and also to the decomposition of the unstable graphite oxide. The thermal effect of graphite oxide decomposition is visible in the DTA curves (curve 5 in Fig. 2 and the DTA curve in Fig. 4) for B–1–1820 and B–1–2800 carbon fibers, in the form of a weak maximum in the range 373–450 K. Similar effects of exothermic decom-

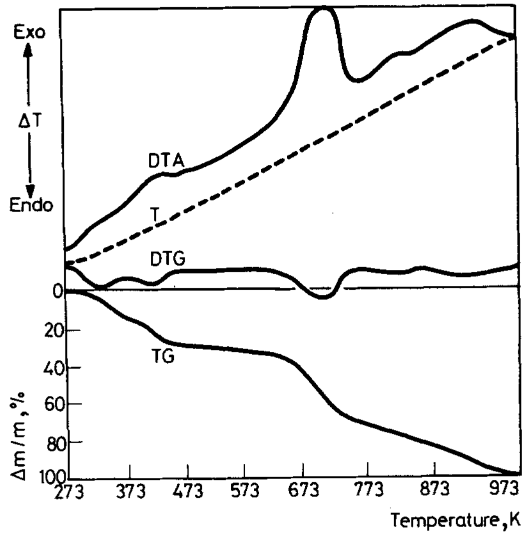

Fig. 4 TG, DTG, DTA and T curves of B-1-2800 carbon fibers electrochemically oxidized with an electric charge of about 5000 C·g^{-1}

Table 2 Thermal analysis data on electrochemically oxidized carbon fibers

Kind of carbon fiber	Anodic charge, C·g^{-1}	Weight loss, %		
		Step 1 293–473 K	Step 2 473–750 K	Step 3 750 K
K-1	1000	21	39	40
B-1-1820	5000	40	50	10
B-1-2200	5000	32	45	23
B-1-2800	5000	30	41	29
Grafil XAS (HP)	5000	28	50	22
Celion	5000	26	47	27

position of graphite oxide have been observed for various kinds of graphites oxidized chemically [13–16] and for glass-like carbon oxidized electrochemically [17].

The second step of thermal decomposition of oxidized carbon fibers proceeds in the temperature range 473–750 K; in this step, the graphite oxide produced in the course of anodic polarization of the carbon fibers reacts with oxygen. The higher the electric charge passed through the oxidized fibers and the greater the degree of ordering of the inner structure of the material, the greater is the mass that converts to graphite oxide. In the temperature range considered, we see a well-developed exothermic maximum in the DTA curves.

The third step of thermal decomposition of electrochemically oxidized carbon fibers proceeds above 750 K and consists in the oxidation of carbon not converted to graphite oxide in the electrochemical process. This relates primarily to the fiber cores not converted to graphite oxide due to the poorly developed internal crystalline structure. The phenomenon of the selective conversion of carbon material with varying degrees of graphitization [18] and of various types of carbon fibers [7, 9] to graphite oxide has been noted in earlier works, on the basis of oxidation kinetics studies [18] and observation of the morphologic changes of the surface [7, 9].

Conclusions

Thermal analysis of as-received and electrochemically oxidized carbon fibers provides considerable indirect information about the internal and surface structures, as well as about the degree of oxidation of the material. Electrochemical oxidation in a 1 $\text{mol}\cdot\text{dm}^{-3}$ sulfuric acid solution with an electric current density of 5 $\text{A}\cdot\text{m}^{-2}$ and a charge of more than 500 $\text{C}\cdot\text{g}^{-1}$ produces conversion of the best-ordered regions of carbon fibers to graphite oxide. The degree of this conversion depends on the internal structure of the material and on the electric charge passed through the carbon fibers.

The thermal decomposition of anodically oxidized carbon fibers in air may be divided into three steps: (i) 293–473 K: evaporation of strongly chemisorbed and intercalated water, and exothermic decomposition of graphite oxide; (ii) 473–750 K: combustion and thermal decomposition of graphite oxide; (iii) >750 K; combustion of carbon not-converted to graphite oxide in the electrochemical process.

The thermal decomposition of electrochemically oxidized carbon fibers proceeds in a similar manner to that of electrochemically oxidized glass-like carbon [17].

* * *

The author is indebted to Miss Lucyna Hrynczyszyn for experimental assistance during the derivatographic measurements. This study was carried out with support from Government Research Programme 01. 15.

References

1 J. B. Donnet and R. Ch. Bansal, Carbon Fibers, Marcel Dekker, Inc., New York, 1984.

2 J. B. Donnet, Carbon, 20 (1982) 266.

3 P. Ehrburger and J. B. Donnet, in Hnadbook of Composites, Eds W. Watt and B. V. Perov, Vol. 1, p. 577, Elsevier Science Publishers 1985.

4 J. B. Donnet, M. Breudle, T. L. Dhami and O. P. Bahl, Carbon, 24 (1986) 757.

5 E. Fitzer and R. Weiss, Carbon, 25 (1987) 455.

6 C. Kozlowski and P. M. A. Sherwood, Carbon, 25 (1987) 751, and references therein.

7 K. Honjo and A. Shindo, Carbon, 24 (1986) 230.

8 N. L. Weinberg and T. B. Reddy, J. Appl. Electrochem., 3 (1973) 73.

9 S. Neffe, Carbon, 25 (1987) 761.

10 W. Scholtz and H. P. Boehm, Z. Anorg. Allg. Chemie, 369 (1969) 327.

11 L. B. Ebert, in Annual Review of Materials Science, Ed. R. A. Huggins, Vol. 6, p. 181, 1976, Palo Alto, California.

12 S. C. Bennett and D. J. Johnson, Carbon, 17 (1979) 25.

13 J. H. de Boer and A. B. C. van Doorn, Konik. Ned. Akad. Wet. Ser., B 61 (1958) 160.

14 A. V. Nikolayev, A. S. Nazarov and V. V. Lisitsa, Zh. Neorg. Chim., 19 (1974) 3396.

15 A. Martin Rodriguez and P. Valerga Jimenez, Thermochim. Acta, 78 (1984) 113.

16 A. Martin Rodriguez and P. S. Valerga Jimenez, Carbon, 24 (1986) 163.

17 S. Neffe, J. Thermal Anal., 35 (1989) 1387.

18 P. Ehrburger and J. B. Donnet, Carbon, 11 (1973) 309.

Zusammenfassung — Es werden die Ergebnisse einer Untersuchung über den Einfluß der elektrochemischen Oxydation von Kohlefiber (CF) in 1 molarer H_2SO_4 auf dessen thermische Zersetzung in Luft dargelegt. Ihre Oxydationsbeständigkeit wächst mit steigender innerer Strukturordnung, charakterisiert durch den Zwischenschichtabstand $\bar{d}_{002}$ zwischen den Graphitkristalliten. Nach anodischer Oxydation ist die Oxydationsbeständigkeit von CF in Luft deutlich niedriger. Es wurde gezeigt, daß sich die Materialregionen mit der geordnetsten Struktur im Verlauf der anodischen Polarisation von CF mit einer Stromdichte von mehr als $5\ \mathrm{A \cdot m^{-2}}$ in hydrophiles und thermisch instabiles Graphitoxid umwandeln.

Резюме — Представлены результаты исследования влияния электрохимического окисления графитных волокон в растворе 1 М серной кислоты на их термическое разложение в атмосфере воздуха. Устойчивость к окислению исходных волокон увеличивается с увеличением упорядочения их внутренней структуры, характеризуемой межслоевым расстоянием $\bar{d}_{002}$ в графитовых кристаллитах. После анодного окисления устойчивость к окислению графитовых волокон в атмосфере воздуха заметно уменьшается. Показано, что в процессе анодной поляризации волокон с плотностью тока более чем $5\ \mathrm{A \cdot м^{-2}}$, участки волокон с наиболее высокой упорядоченностью превращаются до окиси графита, являющейся гидрофильной и термически неустойчивой.