

# Structural and thermal studies on metalized carbon fibres\*

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The objects studied are oxidized poly-acrylonitril fibres and carbon fibres prepared at the University "Prof. Dr. Assen Zlatarov"- Bourgas from a poly-acrylonitril fibre 6K product of Courtaulds Ltd, England and fibres chemically metalized with nickel and copper. Combined thermal analysis, scanning electron microscopy and elemental analysis were carried out with thermally treated and non-treated samples. The effect of the deposited thin metal layer on the thermal stability, structural and other physical characteristics of the fibres and non-woven carbon textile were studied. The effective kinetic parameters of the thermo-oxidative destruction of the samples and the most probable mechanisms of the thermo chemical reactions were determined under the experimental conditions.

(Received November 5, 2008; accepted December 15, 2008)

*Keywords:* Carbon fibres, PANOX fibres, Thin layer, Thermal analysis, Structure

## 1. Introduction

Oxidized poly-acrylonitril (PANOX) fibres and carbon fibres can be obtained at different stages of treatment of poly-acrylonitril (PAN) fibres [1, 2]. The materials obtained at each stage are of high technological value due to their good tensile and friction properties, heat, thermal and chemical resistance, low density and good electrical properties. This gives them potential for modern technology [3, 4], medicine, and renewable energy sources and offers their use as individual products or in composite materials [5, 6]. Under heating in air, however, their performance worsens. This drawback can be overcome to great extent by surface modification, like deposition of thin carbide layers [7], metal coatings [8] or introduction into metal [9] and polymer matrices [1, 10], which is itself a separate field of research.

The aim of the present paper is to study the effect of chemically deposited nickel and copper coatings on the change in thermal and morphological behaviours of carbon and PANOX fibres, as a result of their linear heating in an oxidizing medium.

## 2. Experimental

The objects studied were carbon fibres obtained from PANOX fibres modifying [11] before carbonization in an

experimental gradient installation in the University of Bourgas, in a nitrogen medium at flow rate of 300 l/h, carbonization rate of 30 m/h and an end temperature of carbonization of 1400<sup>0</sup> C. The carbon fibres obtained had a tensile strength of 3.2 GPa, a density 1.7 g/cm<sup>3</sup>, a diameter of 8 µm and an acoustic modulus of 10 GPa. Three samples were investigated: C1 – initial carbon fibres; C2 – metalized with Ni; C3 – metalized with Cu, as well as three samples of non-woven carbon textile based on cellulose with an area weight 120 g/m<sup>2</sup> and having been carbonized at 1000°C: T1– initial; T2 – metalized with Ni and T3– metalized with Cu.

For comparison, PANOX-fibres obtained from PAN fibres 6K (Courtaulds - England) and subjected to thermal treatment at 280°C for 2 h [12] were also studied. Three samples were prepared: P1–initial PANOX fibres; P2–metalized with Ni; P3–metalized with Cu.

The thermal curves (TG- thermo-gravimetric, DTG-differential thermo-gravimetric, DTA-differential thermo-analytic) were registered on a digitalized derivatograph (MOM, Hungary) in the temperature interval 20 to 950°C, at a heating rate of 10 deg/min, and a sample weight of 50 ± 1mg in air (Figs. 1 and 2). A number of thermal, kinetic and thermodynamic characteristics [13-16] of the thermal destruction were determined (Table 1).

The metallization with nickel and copper was carried out by a chemical method [17-19].

\* Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008

The microscope observations were performed by scanning electron microscopy - SEM (TESLA BS340-Czech Republic) (Fig. 3, 1-12).

The elemental analysis (EA) was carried out on an automatic analyzer (1004 Karlo Erba – Italy) where the composition of the initial carbon fibre was determined to be: C- 92.50%, N-3.64%, H- 0.55%, and for the initial PANOX fibre: C- 64.56%, N- 19.28%, H- 3.61%, which is close to the data published in the literature [1, 2].

### 3. Results and discussion

The shapes of the thermal curves of the carbon materials studied (Figs.1 A, B, C and Fig. 2) reveal the thermal processes occurring within a wide temperature interval. For the initial PANOX fibres and carbon textile, most of the adsorbed moisture (about 5-7 mass% of the initial weight) was released from 50 to 150°C, due to the existence of C-N bonds in the former and a highly developed surface of the non-woven textile. The unstable fragments of PANOX-fibres remaining outside the cyclic structures formed during the oxidation of PAN fibres were oxidized in the interval 180°C - 350°C. For the metalized fibres, the beginning of the destruction was shifted to higher temperatures by about 50°C. However, it did not proceed to the full extent, contrary to the case for non-metalized fibres ( Figs. 1 A, B, C ). According to the thermal

PANOX fibre and carbon textile samples were considered to be due to the influence of hydrolytic reactions. The limiting mechanism of destruction of the non-metalized fibres was assumed to be three-dimensional diffusion ( $D_5$ ) or cylindrical symmetry ( $D_4$ ) according to the equation of Ginstling-Brownstein [15]. The TG curves for samples P2 and P3 metalized with nickel and copper, as well as sample C3 metalized with copper, showed significant weight increase (3-11 mass %) due to oxidation of the metal layer. Accordingly, the limiting mechanism in this case was considered to be A1F1, according to the equation of Avrami- Erofeev – random generation and growth of nuclei at order  $n = 1$  [15].

Table1. Thermo-physical and kinetic characteristics

Spl	$E_a^*$ kJ/ mol	$\Delta H^\#$ kJ/ mol	$\Delta S^\#$ J/ mol. K	$\Delta G^\#$ kJ/ mol	Mecha- nizm
C1	147	139	-172	291	$D_5^{**}$
C2	112	111	-213	330	$D_4^{***}$
C3	123	116	-162	253	$A_1F_1^{****}$
P1	117	109	-202	292	$D_4^{***}$
P2	86	74	-214	251	$A_1F_1^{****}$
P3	125	119	-151	238	$A_1F_1^{****}$

Spl – sample; \* Correlation coefficients are above 0.997; \*\* three-dimensional diffusion; \*\*\* three-dimensional diffusion or cylindrical symmetry; \*\*\*\* random law,  $n=1$ .

analysis – TA, the oxidation of the metal coating of sample C3 (density  $\rho=0.23\text{g/cm}^3$ ) began before the destruction of the fibre itself, and for samples P2 ( $\rho=0.08\text{g/cm}^3$ ) and P3 ( $\rho = 0.13\text{g/cm}^3$ ), simultaneously with the destruction. It can be seen that the weight loss was affected by the relative content and density of the coating.

The main phase of all the samples studied was destroyed in the interval 400-700°C and, therefore, the effective kinetic parameters of the thermo-oxidative destruction and the limiting mechanisms of the summary reactions were determined in this interval, under the analysis conditions (Table 1).

The values of the activation energies  $E_a$  varied from 147 kJ/mol for the initial carbon fibre, 117 kJ/mol for the initial PANOX fibre and from 86 to about 120 kJ/mol for the metalized samples. The lower values of  $E_a$  for the

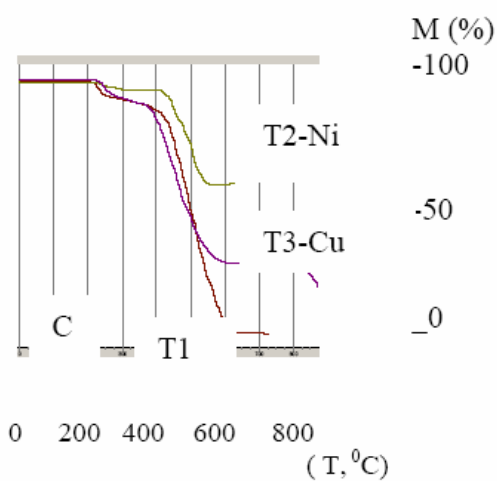
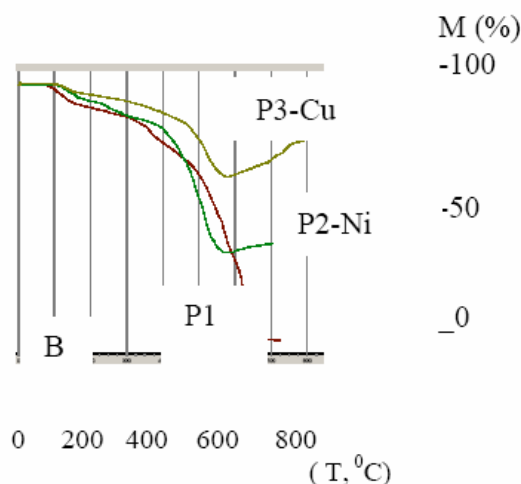
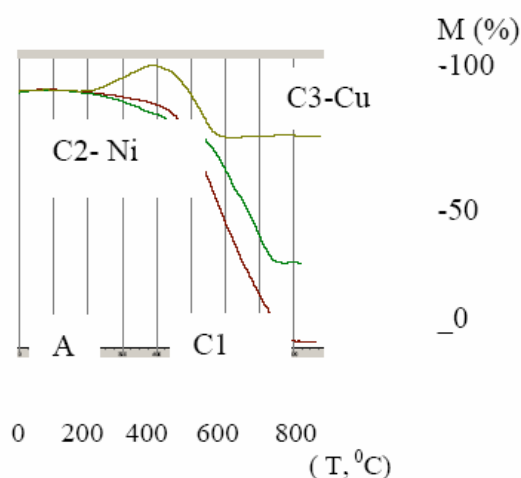


Fig.1. TG - curves of carbon fibres - PANOX fibres - B; carbon textile - C.

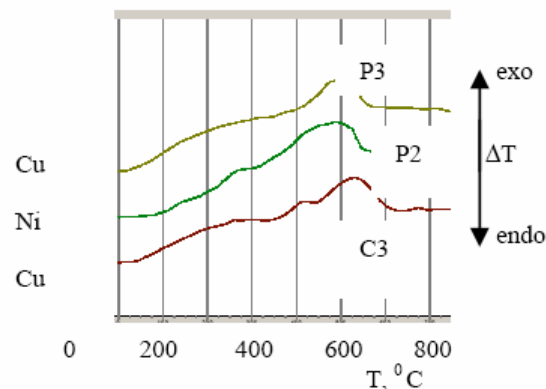


Fig. 2. DTA-curves of the samples P2, P3 and C3.

The entropies of thermal oxidation for all the samples studied decreased, which indicated that the “activated complex” in the transition state had a higher degree of arrangement compared to the initial state of the system.

The oxidative character of the reactions taking place was reflected in the DTA curves for these samples (Fig.2) through a number of exothermic maxima in the corresponding temperature intervals. This was also confirmed by the light-green colouring of the residue after the thermal treatment of nickel coated samples, characteristic for NiO<sub>2</sub>, and the yellow-green colour of CuO for sample P3, due to partial oxidation of Cu because of the disturbing influence of the gases released from the destruction of the PANOX fibre, and the black colouring due to the almost full oxidation of copper to CuO<sub>2</sub> for sample C3.

The SEM microphotographs of metalized carbon fibres (Fig. 3, 2-6) show better adhesion than that of metalized PANOX fibres (8-12). There are no gaps between the fibre and the coating. The photos 8-12 of Ni and Cu coated PANOX fibres samples, taken before and after thermal treatment up to 600°C, showed that parts of the fibres were preserved even after the heating, which confirmed the protective effect of the metal coating. PANOX fibres could be observed (Fig. 3, 10), which remained within the nickel oxide casing. A change of the copper coated PANOX fibres could be seen (11, 12). The fibres observed underwent structural processes, resulting in shrinkage to dense individual nuclei along the axis. The residue obtained from copper coated carbon fibres and PANOX fibres treated up to 600°C in air had carbon contents of 23.79% for sample C3 and 5.06% for sample P3. After thermal treatment at 950°C in air, the fibres were burnt, while the oxidized metal coating remained as an empty cylindrical casing (4, 6).

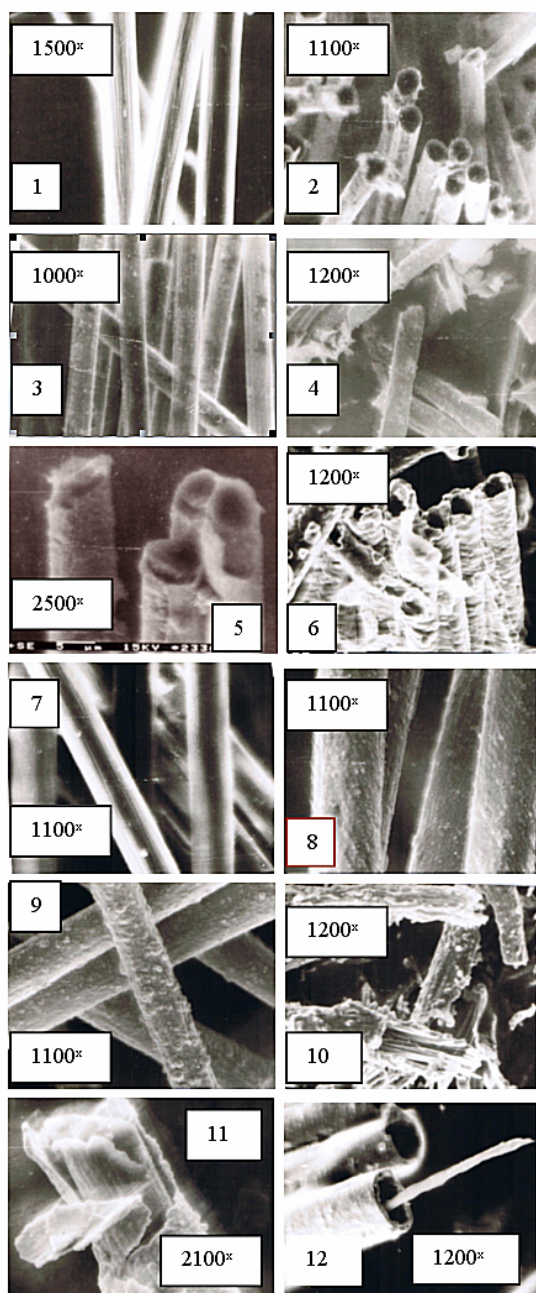


Fig. 3. SEM microphotographs of initial carbon fibres (1); carbon fibres - Ni before (2) and after heating to 950°C (4); carbon fibres -Cu before (3, 5) and after heating to 950°C (6); PANOX fibres -initial (7), PANOX fibres -Ni before (8) and after heating to 600°C (10), PANOX fibres -Cu before (9,11), and after heating to 600°C (12)

#### 4. Conclusions

The effect of chemical metallization of carbon fibres and PANOX fibres with nickel and copper was studied under a non-isothermal regime of heating in the temperature interval 20-950°C, in air. The coatings deposited were found to shift the commencement of the oxidative destruction to higher temperatures by about 50°C, and helped in the partial preservation of the fibres.

The effective kinetic parameters, i.e. the activation energy, change of entropy, enthalpy and Gibbs energy were calculated at the temperature of the highest rate of destruction, and the limiting mechanisms of the thermo-oxidative destruction were determined for the fibres studied.

Aiming at an optimum thermal protection effect and other useful properties of the fibres, further studies on multi-layer coatings are planned.

#### Acknowledgement

The present study was carried out with the financial support of the University "Prof. Dr. A. Zlatarov" – Bourgas under project NI 04/08.

We wish to express our gratitude to senior research fellow R. Pavlov for the SEM microphotographs.

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