

PHYSICAL AND CHEMICAL PROPERTIES OF CARBON-CARBON COMPOSITE BASED ON EXPANDED GRAPHITE

A.I. Gabelchenko, D.V. Savchenko, A.I. Sizov, S.G. Ionov

Department of Chemistry, Moscow State University, 119991, Moscow, Russia

Introduction

Flexible graphite foils (GF), fabricated by binder free cold rolling of the thermolysis products of hydrolyzed graphite intercalation compounds (GICs) with nitric or sulfuric acid, are widely used as gasketing materials, electromagnetic interference shields, thermal insulation, resistive elements of electrical heaters [1], bipolar plates of hydrogen–air fuel cells [2], etc. The physical and mechanical properties of GFs can be tuned by varying the chemical composition of the GIC, the particle size composition of the starting graphite, the heating rate of the GIC, etc. [3]. There is considerable interest in techniques for modifying GFs, which allow one to substantially vary the physicochemical properties of the material. The purpose of this work was to study the mechanical and electrical properties of GFs slightly densified via methane pyrolysis or decomposition of polymeric carbon precursors in an exfoliated graphite (EG) matrix.

Experimental

As initial materials we used purified natural graphite (ash content <0.2%; particle size 0.2–0.4 mm) and fuming nitric acid ($\rho = 1.5 \text{ g/cm}^3$). Second stage GICs with nitric acid were prepared by a standard solution method [4]. GFs were produced on a laboratory size rolling mill by binder free cold rolling of EG produced by thermal destruction of hydrolyzed obtained GICs with nitric acid at 900°C. The GFs were densified with pyrolytic carbon (PC) through pulsed methane pyrolysis at a temperature of 1060°C and a methane pressure of 20 kPa using a purpose designed apparatus. The amount of deposited pyrolytic carbon was controlled by varying the reaction time. The polymeric precursors poly(hydridocarbyne) (PHC) and poly(naphthylhydridocarbyne) (PNHC) were synthesized in an argon atmosphere using standard procedures for handling reactive substances. PHC was prepared as described elsewhere [5], via an ultrasonically activated reaction of bromoform with the KNa alloy in a mixture of THF and DME. PNHC was prepared from bromoform and sodium naphthalenide, the latter synthesized by reacting sodium and naphthalene in THF [6]. The synthesized polymers were characterized by elemental analysis, ^1H NMR, EPR, and IR spectroscopy, and their structure and composition were shown to be identical to those reported previously [5,6]. The samples impregnated with the polymer solutions were dried in air, roll pressed to a density of 1.0 g/cm³, and placed in a quartz reactor, which was then pumped down, filled with argon, and heated to a temperature of 600°C at a rate of 2°C/min.

Mechanical tests (tensile strength, Young's modulus) were carried out on a Hounsfield H100KS universal testing machine. The resistivity of the samples was measured by a standard four probe dc method. The current and voltage leads were attached to the sample faces with silver paste. To rule out thermoelectric effects, all of the measurements were made for the two opposite directions of the current through the sample. The specific surface area and total open pore volume were determined from 77 K nitrogen adsorption isotherms on a Qsurf 9600 surface analyzer. The specific surface area was evaluated using BET polymolecular adsorption analysis. Thermogravimetric (TG) analyses were carried out at temperatures from 30 to 800°C in flowing air (50 ml/min) at a heating rate of 5°C/min using a Netzsch STA 449 Jupiter simultaneous thermal analyzer

Results and Discussion

The deposition of pyrolytic carbon increases the tensile strength σ_p of the foil and reduces its resistivity ρ_a (Fig. 2). The curves in Fig. 2 can be divided into two distinct portions: 1) weight gains within 2–3%, the mechanical and electrical properties of the foils are strong functions of pyrolytic carbon content; 2) weight gains above 3%, both σ_p and ρ_a vary little.

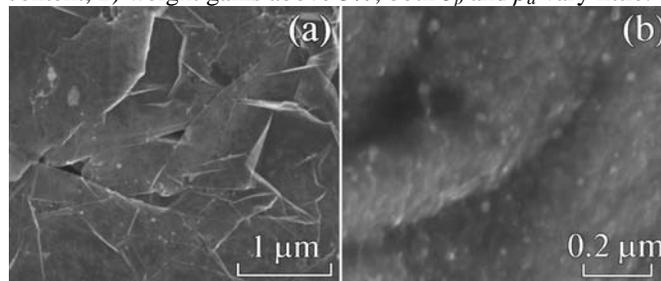


Fig. 1. SEM images of (a) the initial GF surface and (b) the surface of foil containing 4.0 wt % pyrolytic carbon.

In the early stages of the process ($\tau < 120 \text{ min}$) the densification of the GF with pyrolytic carbon was a three dimensional process: the pyrolytic carbon deposits both in pores and at the boundaries between EG particles, which is accompanied by chemical bonding between the EG particles and the development of a closed pore structure. As a result, the initial stages of the process see a marked increase in the tensile strength (from 4 to 11 MPa) and Young's modulus (from 1.9 to 5.5 GPa) of the GF. Reducing the contact resistance between the EG particles leads to raising the conductivity of the material. That the conductivity of the composites rises only slightly is due to the fact that the large contribution to the resistivity of the samples is made by the carrier scattering by point defects, which are generated during chemical and thermal processing of graphite in the GF fabrication step [7].

But after $\tau > 120 \text{ min}$ (3–4% PC), the deposited pyrolytic carbon closes most of the accessible pores (Fig. 1b), preventing methane from penetrating into the porous material. And pyrolytic carbon subsequently deposits only on the surface of the material. The thickness of the pyrolytic carbon film is about 30–50 nm, which is four orders of magnitude less

than the sample thickness (300 μm). Such film has an insignificant effect on the strength and conductivity of the GF.

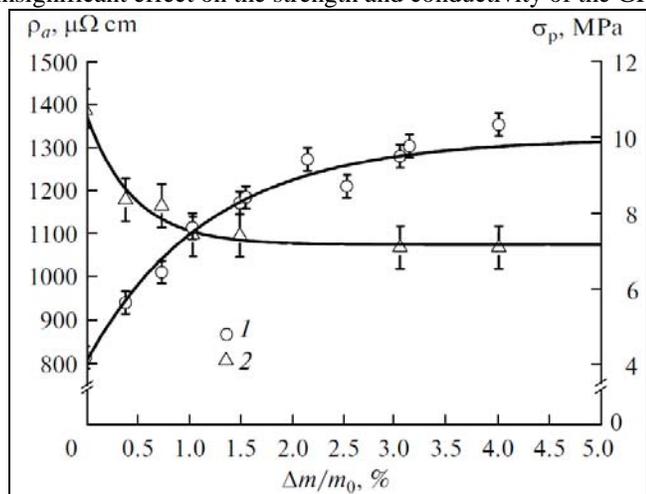


Fig. 2. Tensile strength σ_t and resistivity ρ_a of GFs as functions of weight gain due to pyrolytic carbon deposition.

A thin pyrolytic carbon layer markedly enhances the chemical and thermal stability of the GF. TG results demonstrate that the oxidation rate of the GFs also decreases markedly with increasing pyrolytic carbon content. The rise in the oxidation resistance of the material is due to the decrease in the concentration of active centers (microcrystallite boundaries and point defects) for oxidation, which become covered with pyrolytic carbon film, so that the surface area accessible to the oxidant decreases. Pyrolytic carbon deposition reduces the specific surface area by a factor of 4 and the pore volume by a factor of 7. This also indicates that the pyrolytic carbon closes some of the pores and that the concentration of closed pores increases.

Because of PHC and PNHC special structural features, these polymers possess an excess energy and readily decompose on heating to form various carbon structures [5]. The strength of GFs increases when either PHC or PNHC is decomposed in the EG matrix, but the former polymer ensures a substantially greater increase in tensile strength: 3.1 MPa for the as-prepared GF, 6.0 MPa for the PHC-modified material, and 3.9 MPa for the PNHC-modified material. This may be related to the difference in weight gain upon synthesis (3.7% for PHC and 2.5% for PNHC), but also this may be a result of differences of polymers decomposition mechanisms. Electron microscopic examination indicates that, after PHC thermolysis, the GF surface is covered with a film which ensures bonding between the EG particles (Fig. 3a). Clearly, this process also takes place within the pores of the sample, substantially raising the strength of the material. At the same time, judging from the electron micrograph of the material modified with PNHC (Fig. 3b), this polymer differs in destruction mechanism from PHC. Most likely, the first step of the process is decomposition of the PNHC macromolecules into fragments of lower molecular weight, followed by thermolysis of the forming fragments. This complex decomposition process gives small clusters, instead of a

continuous film characteristic of PHC, which reduces the efficiency of EG particle bonding.

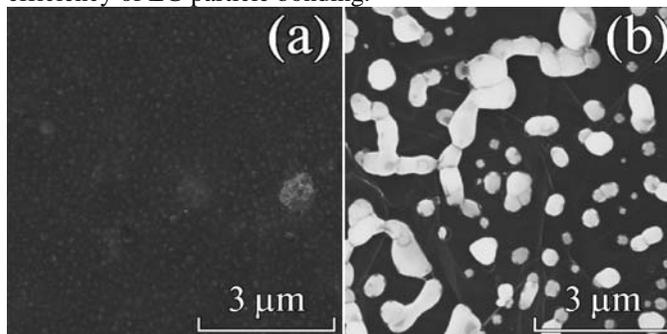


Fig. 3. SEM images of the (a) PHC-modified, and (b) PNHC-modified GFs.

Conclusions

Thus, in this work it was shown that impregnation of small amount (1-4 weight.%) of PC results in increasing tensile strength and modulus of elasticity in 2,5 times, decreasing electrical resistivity on 25%, essentially increasing chemical and thermal resistance of GF. Decomposition of preceramic polymers also leads to increasing tensile strength of GF in 2 times. So, these techniques of GF modification allow physical and chemical properties of the material to be improved without significant change in composition.

References

- [1] Chung DDL. Flexible graphite for gasketing, adsorption, electromagnetic interference shielding, vibration damping, electrochemical applications, and stress sensing. *J. of Materials Engineering and Performance* 2000;9(2):161-163.
- [2] Middelma E, Kout W, Vogelaar B, Lenssen J, de Waal E. Bipolar plates for PEM fuel cells. *J. of Power Sources* 2003;118(1-2):44-46.
- [3] Dowell MB, Howard RA. Tensile and compressive properties of flexible graphite foils. *Carbon* 1986;24(3):311-323.
- [4] Dresselhaus MS, Dresselhaus G. Intercalation compounds of graphite. *Adv. Phys.* 2002;51(1):1-186.
- [5] Bianconi PA, Joray SJ, Aldrich BL, Sumranjit J, Duffy DJ, Long DP, Lazorcik JL, Raboin L, Keams JK, Smulligan SL, Babyak JM. Diamond and diamond-like carbon from a preceramic polymer. *J. Am. Chem. Soc.* 2004;126:3191-3202.
- [6] Rieke RD. US Patent 5 463 018 1995
- [7] Ionov SG, Kulbachinskii VA, Kytin VG, van Schaijk RTF, de Visser A. Magnetotransport in carbon foil fabricated from exfoliated graphite. *Phys.Rev. B* 1998;57(15):8900-8906.