

Exfoliated graphite with a low thermal conductivity

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Abstract – Exfoliated graphite of two types was obtained by thermal exfoliation of expandable graphite samples synthesized by hydrolysis of graphite nitrate of the II stage (“chemical route”) and anodic polarization of graphite in 60% HNO₃ (“electrochemical route”) correspondingly. The crucial influence of electrochemical oxidation and thermal treatment on graphite morphology and structure, i.e. high dispersion and amorphization, was revealed by means of X-Ray diffraction, scanning and high resolution transmission electron microscopy, Raman spectroscopy and electron energy loss spectroscopy. Thermal conductivity of “electrochemical” compacted exfoliated graphite is ~ 1 W/m·K which is 7 times lower than that of “chemical” one.

Exfoliated graphite (EG^T), obtained by a momentary thermal treatment of expandable graphite (EG), is a material of growing technological importance due to its numerous applications [1]. Obviously physicochemical properties of EG^T and related materials strongly depend on the synthesis conditions of expandable graphite. Herein we report the comparative study of the process of EG^T formation obtained by means of standard “chemical” and novel “electrochemical” techniques coupled with the investigation of thermal properties of compacted EG^T. The “chemical” technique lied in thermal exfoliation of EG synthesized by hydrolysis of graphite nitrate of the II stage, the “electrochemical” one – in exfoliation of expandable graphite synthesized by anodic polarization of graphite in 60% HNO₃.

Scanning electron microscopy and X-Ray diffraction experiments revealed the dramatic change of graphite particle shape and crystalline size (10 times reduction) as the result of graphite long-term electrochemical oxidation whereas chemical oxidation makes a slight impact on particle shape and crystalline size. Besides the peaks accounted for graphitic reflections the wide halo attributed to (001) reflection of graphite oxide was detected in the XRD pattern of “electrochemical” EG. Raman spectra of “chemical” EG and EG^T samples are almost similar to those of crystalline graphite whereas broad D- and G-lines of similar intensities are detected in the spectra of both “electrochemical” EG and EG^T samples suggesting the intensive formation of structural defects and partial amorphization of original graphite. According to electron energy loss spectroscopy data the content of amorphous carbon is ~ 60% in “electrochemical” EG^T. High resolution transmission electron microscopy experiments pointed out that the planarity of graphene layers is preserved in “chemical” EG^T. Electrochemical oxidation coupled with thermal exfoliation leads to constitutive graphite dispersion especially along c-direction: 5-10nm-thick turbostratic graphite lamina crystals are formed. These crystals are covered by ~1nm amorphous carbon layers being apparently the product of graphite oxide thermolysis. Delamination cracks, misorientation bands and loops in graphite are also observed in “electrochemical” EG^T.

EG^T compacts were prepared by uniaxial compression of worm-like EG^T particles of both types. Specific heat C_p and parallel thermal conductivity λ (relative to the direction of compression) of EG^T compacts were measured. C_p of “chemical” EG^T in the temperature range of 373K-648K was shown to coincide with C_p of HOPG. The accumulation of structural defects in “electrochemical” EG^T lead to 7-10% increase of C_p in comparison with that of HOPG in the mentioned temperature range. In contrast, thermal conductivity at 298 K of “electrochemical” EG^T samples is much lower than that of “chemical” samples in a wide range of densities. The room temperature λ of EG^T compacts of 0,2-1,2 g/cm³ density is about 1 W/m·K whereas for “chemical” samples it appears to be 7 W/m·K in agreement with Bonnissel [2]. The low thermal conductivity of compacted “electrochemical” EG^T is attributed to its high dispersity and defectiveness, i.e. enormous quantity of boundaries and different defects are proposed to be responsible for phonon predominant boundary and defect scattering. “Electrochemical” EG^T thermal conductivity temperature independence in the range of 298-1273 K is congruent with the proposed suggestion.

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[2] M. Bonnissel, L. Luo, D. Tondeur. Compacted exfoliated natural graphite as heat conduction medium. Carbon 39 (2001) 2151.