

CHEMICAL AND PHYSICAL PROPERTIES OF EXPANDED GRAPHITE MODIFIED BY BORON OXIDE

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Introduction

Flexible graphite foil (GF) is widely used to produce different types of sealing materials, shields for electromagnetic and thermal emission, resistive elements in electrical heaters [1], bipolar plates in hydrogen-air fuel-cell elements [2] and other. GF is stable up to $T \sim 3000^\circ\text{C}$ in inert atmosphere or in vacuum but its appreciable oxidation starts at 450°C in air. Boron oxide is also widely used for protection of different carbon materials from oxidation [3, 4]. To distribute B_2O_3 uniformly by the surface and all porous of the sample, carbon material is usually exposed to melt B_2O_3 in inert atmosphere at high pressure over a long period of time. This method is unsuitable for inserting B_2O_3 into expanded graphite (EG) because it leads to EG's significant densification and change of its physical and chemical properties. We report a new method of boron oxide inserting which can be applied to EG: expandable graphite (ExpG) is exposed to boron acid solution and then is subjected thermal treatment. This way boron oxide particles are uniformly spread on EG surface, which leads to increase of GF oxidation stability.

Experimental

The natural graphite with an average flake size of $0.3\text{-}0.4\ \mu\text{m}$ and an ash content of about 0.3%, pure nitric (98%) acids, boric acid were used as initial substances. Second stage graphite intercalation compound (GIC) with nitric acid was synthesized by reaction between NG and nitric acid (98%) (liquid phase technique). ExpG1 obtained from nitrate GIC was treated by the different quantity of 5% boron acid water solution in order to obtain EG with different content of B_2O_3 (ExpG2-ExpG5). All samples were dried at room temperature to constant weight. EG samples (EG1-EG5) obtained by exfoliation of ExpG1-ExpG5 and GF (GF1-GF5 with the bulk density $1\ \text{g/cm}^3$) were obtained on the laboratory device by thermal shock treatment at 950°C with further cold rolling without binder.

XPS surface analysis was carried out on Kratos AXIS Ultra DLD spectrometer. Monochromatic emitter ($\text{Al K}\alpha$) with emission energy of $1486.9\ \text{eV}$ was used. Spectra was recorded in energy range $5\text{-}160\ \text{eV}$ with increment of $0.05\text{-}0.5\ \text{eV}$. Full elemental analysis was performed on a laser mass-analyzer EMAL-2. The process was hold in scanning mode at $5 \times 5\ \text{mm}$ areas; the fraction of ionic current of each element was calculated from full ionic current of all elements, registered on the film. The sum of all analytical signals was considered 100%. The microstructure of the GF modified by 4.2 % B_2O_3 was studied using a Jeol JEM-5510 scanning electron microscope equipped with an EDX spectrometer (INCA

Energy+, energy resolution below $1\ \text{eV}$) at a $20\ \text{kV}$ acceleration voltage. Thermogravimetry (TG) was carried out on STA 449 Jupiter[®] NETZSCH at a heating rate of $10^\circ\text{C}/\text{min}$ in air atmosphere. The samples were examined at an air flow rate of $40\ \text{ml}/\text{min}$ at temperatures ranging from room temperature to 950°C . The specific surface area of EG samples ($S_{\text{BET}}, \text{m}^2/\text{g}$) was determined by nitrogen adsorption measurements using the Brunauer–Emmett–Teller (BET) equation *via* an Qsurf Surface Area Analyzer 9600 (Thermo Electron Corporation). Tensile strength properties were measured on Hounsfield H100K-S universal testing machine.

Results and Discussion

Elemental analysis of the obtained GF samples (Table 1) has shown the presence of oxygen and boron. B:O mass ratio does not exactly correspond to stereochemical ($\text{B}:\text{O} = 1:2,22$) due to presents of oxygen (up to 0.3%) in unmodified GF.

Table 1. Elemental contents of pressed EG ($\rho=1.0\ \text{g/cm}^3$).

Element	GF1	GF2	GF3	GF4	GF5
C, wt. %	99.521	99.162	98.054	98.040	95.133
B, wt. %	0.0012	0.0902	0.4272	0.4417	1.2837
O, wt. %	0.3331	0.5945	1.2979	1.3093	3.2528
N, wt. %	0.0032	0.0475	0.0515	0.0323	0.0498

In X-ray photoemission spectrum only component with bond energy of $193\ \text{eV}$ can be distinguished, which according to the literature data corresponds to oxygen-boron bonding energy [5] and significantly differs from carbon-boron bonding energy ($188\text{-}189\ \text{eV}$) [6].

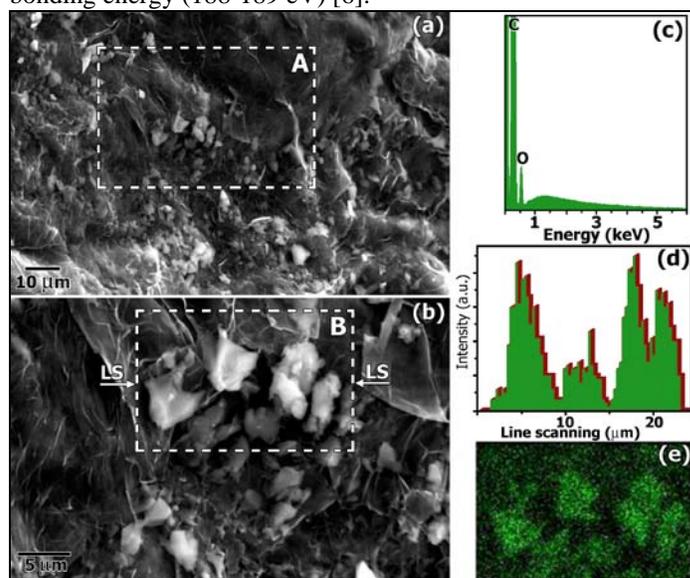


Fig. 1 SEM images of inside part of GF modified by 4.2 % B_2O_3 (a, b); (c) EDX spectrum from the area A; (d) Intensity of $\text{OK}_{\alpha 1}$ line along line scanning (LS); (e) $\text{OK}_{\alpha 1}$ map from the area B.

On SEM (Fig. 1a, 1b) images $2\text{-}5\ \mu\text{m}$ particles are present, which represent solid phase that contains oxygen (EDX, Fig. 1d, 1e). On EDX spectrum of the same area there are almost no signals corresponding to elements with atomic number above oxygen. Boron atom signal cannot be resolved

because of higher intensity of carbon atom signal. Therefore, it is reasonable to make a conclusion that particles observed on SEM images – are boron oxide particles.

XPS, elemental analysis and SEM with EDX data allows to draw a conclusion that during thermal treatment of ExpG exposed to boron acid two processes occur simultaneously: the thermal decomposition of ExpG particles and the decomposition on boron acid to boron oxide.

Thermal stability of the boron oxide-modified GF at the air atmosphere increases significantly in comparison to regular GF (Fig. 2a), and oxidation onset temperature shifts by ~200°C. As it is shown on the diagrams (Fig. 2a) increasing of antioxidant amount leads to increasing oxidation stability of GF. Correlation between temperature $T_{1\%/min}$ (temperature at which mass loss speed reaches 1%/min) and boron oxide amount is linear till $\omega(B_2O_3) \approx 5\%$, as it is shown on Fig. 2b. It testifies to uniform enough distribution of particles B_2O_3 on defects (the active sites) graphite crystallite in EG particle.

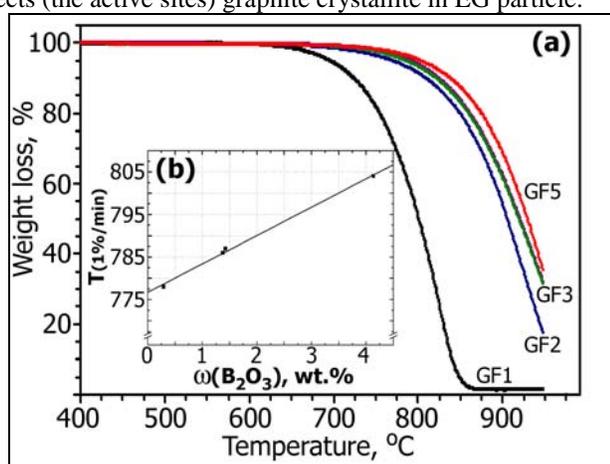


Fig. 2 (a) TG curves of GF ($\rho = 1 \text{ g/cm}^3$) with different contents of boron oxide; (b) the relationship between temperature at which oxidation speed of the GF sample reaches 1% per minute and B_2O_3 content.

During oxidation of any graphite-like material the most susceptible areas where oxidation starts are so-called active sites [7]: graphene edges, point defects in graphene plane, dislocations, functional groups on graphite crystal surface. It is obvious that EG contains a lot of active sites. Boron oxide particles, formed during decomposition of boron acid, are basically found on edges of graphite crystalline (fig. 1a). That is why the most susceptible places are being blocked which prevents access of oxygen to the places. As a result oxidation onset temperature shifts towards great values (Fig. 2).

Table 2. Bulk density (d) and surface area (S) of obtained EG and tensile strength (σ) of GF ($\rho = 1,0 \text{ g/cm}^3$) produced from these EG.

Sample	d (EG), g/l	S, m^2/g	σ , MPa
EG1	1.6	34	6.1
EG2	1.7	25	6.0
EG3	1.9	23	8.2
EG4	2.0	20	7.6
EG5	3.5	15	3.0

Adding of small amount (~1-2 wt.%) of boron oxide increase of GF tensile strength (Table 2). However adding yet 4-5% of B_2O_3 leads to tensile strength dramatical decrease down to tensile strength lower than initial GF has. Degradation of tensile strength is connected to forming of relatively big B_2O_3 agglomerates which act as foreign inclusions and are stress concentrators like impurities which lead to decrease GF tensile strength [8]. The most probable mechanism of blocking of the active sites of a graphite material by particles of B_2O_3 can be offered: formation of chemical bonds with “active” carbon C–O–B [9]. If to follow this supposition chemical bonding of two EG particles through the boron oxide seem possible and the tensile strength increase is caused by it.

Conclusions

In summary we offer a new method of modified EG and GF obtaining from ordinary ExpG by the exposing to boron acid and further thermal treatment. The usage of this method has shown that insignificant additive of boron oxide significantly increase thermal stability of GF and EG at air flow and shifts oxidation onset temperature on ~200 °C. It was investigated that 1-2 wt.% boron oxide concentration is optimal to obtain material with higher oxidation resistance and higher tensile strength.

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