

## Fire Protection Performance of Oxidized Graphite Modified with Boric Acid

M. I. Saidaminov, N. V. Maksimova, N. G. Kuznetsov, N. E. Sorokina, and V. V. Avdeev

*Moscow State University, Moscow, 119899 Russia*

*e-mail: mahsudmsu@gmail.com*

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**Abstract**—We have studied intercalation in the graphite– $\text{H}_2\text{SO}_4$ – $\text{H}_3\text{BO}_3$ – $\text{K}_2\text{Cr}_2\text{O}_7$  system with the acids in the weight ratio 1 : 0, 12 : 1, 6 : 1, or 3 : 1. The results demonstrate that, with decreasing sulfuric acid (active intercalant) concentration in solution, the stage number of the resultant graphite intercalation compounds increases. Boric acid modification raises the oxidation onset temperature of oxidized graphite by 200–300°C and improves its fire protection performance, with little or no effect on the bulk density of exfoliated graphite.

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### INTRODUCTION

Graphite, a layered material in which the interatomic interaction within the layers is considerably stronger than that between the layers, is capable of forming intercalation compounds containing various species in their interlayer spaces.

Graphite intercalation compounds (GICs) with strong Brönsted acids (nitric and sulfuric acids) are of greatest practical importance because the hydrolysis of such compounds yields oxidized graphite (OG). OG has a unique property: when rapidly heated, it markedly increases in volume (exfoliates), transforming into exfoliated graphite (EG).

EG has a number of valuable properties, such as low bulk density, large specific surface area, the ability to be compacted without binder, stability in aggressive media, and tunable thermal and electrical conductivity. Structural sealants based on EG (graphite foils, sealing braid) combine the properties inherent in graphite with elasticity and plasticity. Owing to its large specific surface area, EG can be used as an effective sorbent of heavy oil and petroleum derivatives [1].

There are several ways to modify OG and EG with the aim of imparting additional application-oriented properties to these materials. Of particular interest is a recently proposed procedure for modifying EG with iron compounds. This approach enables one to produce EG with magnetic properties, which would make it an indispensable sorbent for use in oil-polluted areas [2].

As mentioned above, OG considerably expands on heating. In connection with this, it has found application in fire protection coatings [3]. Structural components are coated with an OG-containing fire protection material. On heating (e.g., during a fire event),

OG exfoliates to form an EG layer, which protects the components from failure owing to its low thermal conductivity. At the same time, the use of such materials in air is limited to the onset of carbon oxidation, i.e., 450–550°C. In this context, an important practical issue is to eliminate this limitation by introducing an antioxidant additive.

There are several ways to modify carbon materials with antioxidants, such as SiC [4],  $\text{ZrO}_2$  [5], BN [6], and  $\text{P}_2\text{O}_5$  [7], with the aim of raising their oxidation onset temperature. Nevertheless, many researchers approach this problem using modifiers based on boron compounds.

In Ref. [8], a porous composite of carbon fibers and pyrolytic carbon was treated with an ethanolic solution of boric acid. The material was slowly dried and then annealed for 1 h at 500°C in a nitrogen atmosphere. Examination on a scanning electron microscope (SEM) indicated the formation of boron oxide clusters on the surface of the carbon fibers. The modified material exhibited high oxidation stability at 700°C.

Sogabe et al. [9] proposed boron oxide impregnation of carbon composites at 1200°C for 1 h in a nitrogen atmosphere. The material thus modified was stable to oxidation with atmospheric oxygen at 900°C for 1 h. The addition of elemental boron reduces the thermal stability of carbon materials because of the formation of boron carbide, which catalyzes carbon oxidation.

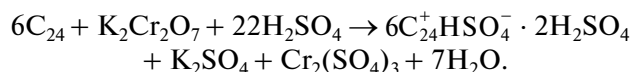
The reported approaches to the protection of carbon materials have a number of drawbacks: antioxidants cannot be applied as a uniform surface layer, and the process requires relatively harsh conditions, takes considerable time, and is rather expensive.

This paper presents a continuation of our studies of the effect of boric acid on the key features of GIC synthesis and the properties of OG and EG. In earlier studies, we showed using electrochemical GIC synthesis in the graphite–H<sub>2</sub>SO<sub>4</sub>–H<sub>3</sub>BO<sub>3</sub> system that boric acid was uniformly distributed over the surface of OG, without cointercalating with H<sub>2</sub>SO<sub>4</sub> into the graphite host. This markedly improved the fire protection performance of the OG. At the present stage, a highly promising approach is to add boric acid to graphite together with sulfuric acid in the chemical oxidation step. Chemical synthesis of GICs is attractive in that large amounts of GICs can be obtained, which cannot be achieved by electrochemical synthesis because of the highly nonuniform current distribution.

The purpose of this work was to study the distinctive features of GIC synthesis in the graphite–H<sub>2</sub>SO<sub>4</sub>–H<sub>3</sub>BO<sub>3</sub>–K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> system and the properties of OG and EG based on such GICs. It seems likely that boric acid modification of OG will ensure a uniform H<sub>3</sub>BO<sub>3</sub> distribution over the surface of the OG, thereby considerably improving the fire protection performance of the material.

## EXPERIMENTAL

To prepare GICs, 10 g of natural flake graphite ( $d_{001} = 3.354\text{--}3.359$  Å, 99.99% carbon) was mixed with a preprepared oxidizing solution (reagent-grade potassium dichromate solution in H<sub>2</sub>SO<sub>4</sub> (96%) + H<sub>3</sub>BO<sub>3</sub> (reagent grade), with the acids in the weight ratio 1 : 0, 12 : 1, 6 : 1, or 3 : 1). The oxidant and sulfuric acid were in threefold excess relative to the following reaction for the preparation of stage I graphite bisulfate:



The mixture was first constantly stirred for 10 min and then for 5 min every hour. The solid product was separated from the solution by decantation.

The resultant GICs were hydrolyzed by distilled water (100 ml) and then stirred for 15 min. After decantation, the precipitate was washed twice with water (30 ml) for 5 min. Next, the water was removed, and the material was dried at 60°C for 6 h.

The phase composition of the materials thus prepared was determined by X-ray diffraction (XRD) on an ARL X'TRA diffractometer (CuK<sub>α</sub> radiation,  $\lambda = 1.5418$  Å) in the angular range 20°–60° at a scan rate of 2°/min.

Thermal analysis (thermogravimetry (TG) + differential scanning calorimetry (DSC)) was performed with a Netzsch STA Jupiter 449 C simultaneous thermal analyzer in flowing air (40 ml/min) at tempera-

## Phase composition and identity period of GICs

Oxidizing solution	Stage number ( $I_c$ , Å)	Weight ratio
H <sub>2</sub> SO <sub>4</sub> (96%)	I (7.97)	1 : 0
	II (11.20)	1 : 0*
H <sub>2</sub> SO <sub>4</sub> : H <sub>3</sub> BO <sub>3</sub>	II (11.18)	12 : 1
	II (11.18)	6 : 1
	III (14.55)	3 : 1

\* Different oxidants.

tures from 40 to 1200°C and a heating rate of 10°C/min. The measurement accuracy was 3%.

The fire protection performance of OG was determined at the UNIKhIMTEK Research and Production Association using a system for the fire testing of small components of building structures. The general principle of the method is to evaluate the fire protection performance of a layered structure under a thermal influence and to determine the time it takes for a specimen to reach a limiting state. In our case, the limiting state was when the temperature on the back-side of the specimen reached 500°C. The fuel delivery/combustion system, parameter measurement/recording system, and thermal conditions met the requirements formulated in the RF State Standard GOST 30247.0.

EG was prepared from OG at three temperatures: 600, 800, and 900°C.

The bulk density of EG was determined as

$$d_{\text{EG}} = m_{\text{EG}}/V_{\text{EG}},$$

where  $m_{\text{EG}}$  (g) is the weight of the EG, and  $V_{\text{EG}}$  (l) is its volume.

## RESULTS AND DISCUSSION

**GIC synthesis in the graphite–H<sub>2</sub>SO<sub>4</sub>–H<sub>3</sub>BO<sub>3</sub>–K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> system.** GICs were synthesized in the graphite–H<sub>2</sub>SO<sub>4</sub>–H<sub>3</sub>BO<sub>3</sub>–K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> system. As shown in extensive studies [10–12], reducing the amount of an active intercalant (nitric or sulfuric acid) in the oxidizing solution increases the stage number of the resulting GIC (the stage number is the number of graphene layers between two successive intercalate layers). Similar behavior was found in the graphite–H<sub>2</sub>SO<sub>4</sub>–H<sub>3</sub>BO<sub>3</sub>–K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> system.

According to XRD results (table), mixed solutions of the H<sub>2</sub>SO<sub>4</sub>–H<sub>3</sub>BO<sub>3</sub> system (12 : 1 and 6 : 1) yield stage II GICs. Increasing the oxidant concentration and synthesis time did not lead to the formation of stage I (saturated) compounds. Reducing the sulfuric acid content in the H<sub>2</sub>SO<sub>4</sub>–H<sub>3</sub>BO<sub>3</sub> solution (3 : 1) resulted in the formation of stage III GICs. For com-

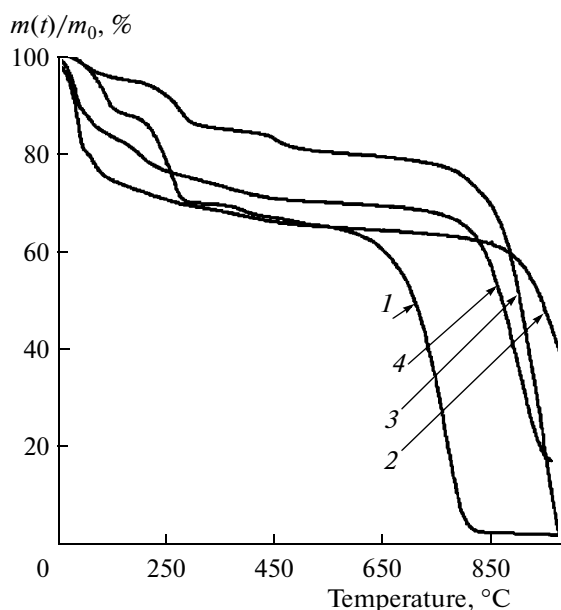


Fig. 1. TG curves of the OG samples (1) 1 : 0, (2) 3 : 1, (3) 6 : 1, and (4) 12 : 1.

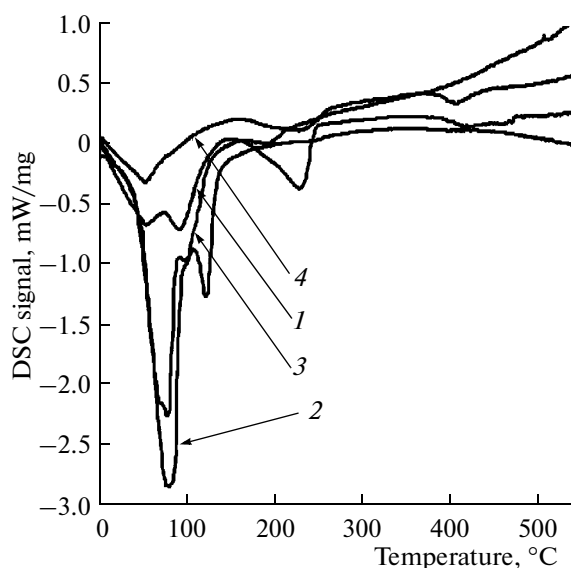


Fig. 2. DSC curves of the OG samples (1) 1 : 0, (2) 3 : 1, (3) 6 : 1, and (4) 12 : 1.

parison, we prepared classic samples of stage I and II graphite bisulfate in the graphite–H<sub>2</sub>SO<sub>4</sub>–K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> system. Stage II graphite bisulfate was obtained by varying the amount of potassium dichromate.

The filled layer thickness in the synthesized GICs in the graphite–H<sub>2</sub>SO<sub>4</sub>–H<sub>3</sub>BO<sub>3</sub>–K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> system is 4.50–4.60 Å. Since sulfuric and boric acids differ little in ion sizes (B–OH and S–OH bond distances are 0.145 and 0.154 nm, respectively), it is not possible to ascertain from the present XRD data whether or not H<sub>3</sub>BO<sub>3</sub> is intercalated into the graphite host.

**OG and PG.** OG was prepared by hydrolyzing GICs. It is worth pointing out that the OG modified with boric acid was not black (in contrast to classic OG based on graphite bisulfate) but gray, which was probably due to boric acid adsorption on its surface.

The weight gain of OG was evaluated as

$$\Delta m = (m_{\text{OG}} - m_{\text{G}})/m_{\text{G}} \times 100\%,$$

where  $m_{\text{OG}}$  and  $m_{\text{G}}$  are the weights of the OG and graphite, respectively. The weight gain of classic OG (1 : 0), prepared from graphite bisulfate, was 35%, and that of the modified OG materials (12 : 1, 6 : 1, and 3 : 1) was 40, 45, and 52%, respectively. Thus, the weight gain increases with increasing H<sub>3</sub>BO<sub>3</sub> content in the oxidizing solution, attesting to an increase in the percentage of boric acid in the OGs.

It was of most interest to study the behavior of OG during heating. The TG and DSC curves of the OG samples are presented in Figs. 1 and 2. Each curve can be divided into three distinct portions, with well-defined weight losses (in the TG curves) and thermal

events (in the DSC curves): 50–150, 150–300°C, and the oxidation onset (the third event does not show up in the DSC curves because of the large heat effect of graphite oxidation, which obscures the other thermal events). In the range 50–150°C, the likely process is water release from defects. The second temperature range seems to correspond to the decomposition of the residual sulfuric acid in intercrystalline spaces and the release of H<sub>2</sub>O, SO<sub>2</sub>, and CO<sub>2</sub>. As shown earlier, boric acid dehydration also takes place in this temperature range. The first two ranges almost coincide for the classic and modified OGs. The third event is the oxidation of the material, as pointed out above, and its temperature range depends on the OG synthesis procedure and conditions.

Clearly, the plateau between the second and third steps characterizes the thermal stability of the material. The TG curves demonstrate that the OG (1 : 0) oxidizes starting at 500–550°C, whereas the OGs (12 : 1) and (6 : 1) begin to oxidize at 750°C. The OG (3 : 1), prepared at the highest boric acid concentration in solution, offers the highest oxidation onset temperature: 850°C.

We believe that boric acid adsorbs not at random but on areas with increased energy, where otherwise oxidation would begin at 550°C. This is supported by the fact that the TG curves of the modified OGs show single-step oxidation. If our assumption were wrong, there would be two-step oxidation: at 550°C in areas free of boric acid and at higher temperatures where boric acid was adsorbed.

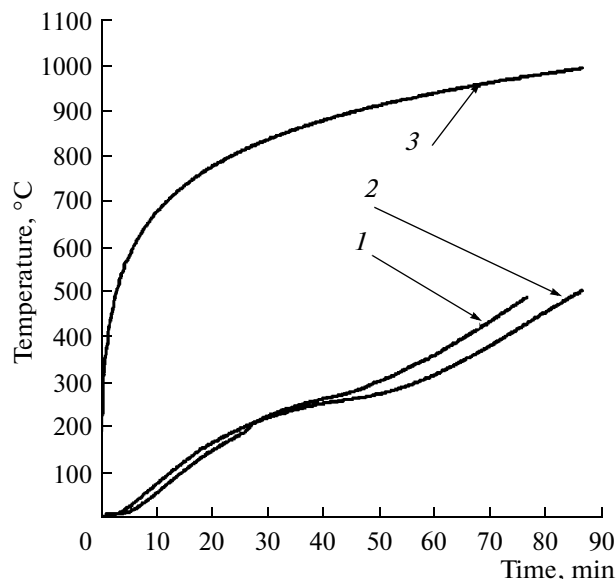


Fig. 3. Fire curves of the OG samples (1) 1 : 0 and (2) 6 : 1; (3) steady-state curve.

OG is not only a raw material for EG production but also a component of fire protection materials owing to its ability to rapidly expand and form an EG layer with low thermal conductivity. The fire protection performance of OG can be assessed using purpose-designed testing systems which determine the time it takes for a specimen to reach a limiting state under a thermal influence (by recording a so-called fire curve (Fig. 3)). In our case, the limiting state was when the temperature on the backside of a plate coated with an OG-containing material reached 500°C. Classic OG (1 : 0) based on stage I graphite bisulfate reaches the limiting temperature in 75 min, whereas the modified OG (6 : 1), in 85 min. The curves for the OG samples diverge starting at a temperature of 850°C in the steady-state curve. The divergence increases with temperature, demonstrating that the fire protection performance improves with increasing temperature.

Thus, not only does chemical modification with boric acid raise the oxidation onset temperature of OG but it also improves its fire protection effectiveness by 10 min. Moreover, this parameter increases with temperature.

The final OG expansion product is EG, which is used primarily to produce graphite foil by conventional binderless compaction. The ability to be pressed into graphite foil with no binder is one of the main advantages of EG.

EG offers many unique characteristics, the most important of which is its low bulk density, which in many respects determines the properties of EG and related materials. The effect of bulk density on mate-

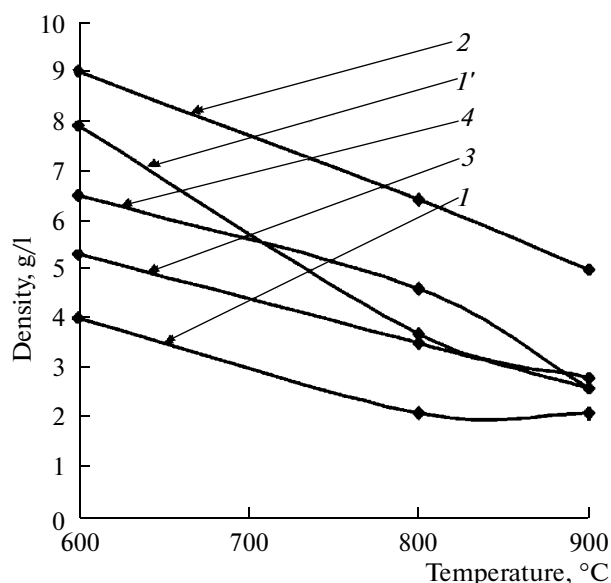


Fig. 4. Bulk density as a function of temperature for the EG samples (1, 1') 1 : 0, (2) 3 : 1, (3) 6 : 1, and (4) 12 : 1.

rials properties (e.g., on the sorption efficiency of EG and strength of graphite foil) has been the subject of extensive studies. Their main purpose was to produce a thermally stable material with other good characteristics, including bulk density. Figure 4 demonstrates that the EGs (1 : 0), (6 : 1), and (12 : 1) prepared from stage II GICs are almost identical in bulk density (curves 1', 3, and 4). The lower bulk density of the EG (1 : 0) represented by curve 1 and the higher bulk density of the EG (3 : 1) (curve 2) are attributable to the fact that these materials were prepared from stage I and III GICs, respectively.

## CONCLUSIONS

We have prepared GICs in the graphite-H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>BO<sub>3</sub>-K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> system.

The present results demonstrate that, with decreasing sulfuric acid concentration in solution, the stage number of the resultant GICs increases. Boric acid modification raises the oxidation onset temperature of OG (12 : 1) and OG (6 : 1) by 200°C and that of OG (3 : 1) by 300°C. Classic OG (1 : 0) prepared from stage I graphite bisulfate reaches the limiting temperature in 75 min, whereas the modified OG (6 : 1), in 85 min. The time difference increases with temperature.

Note that the modification did not reduce the bulk density of EG, one of its most important characteristics.

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