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Oxidation protection of carbon materials by acid phosphate impregnation

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Abstract

Acid phosphate impregnation, with ozone pre-treatment, improves the oxidation resistance of carbon materials (polycrystalline graphite and pitch-based carbon fiber), as shown by weight measurement in air up to 1500 °C. The impregnation involves using phosphoric acid and dissolved aluminum hydroxide in the molar ratio 12:1 and results in a rough, white and hard aluminum metaphosphate coating of weight about 20% of that of the carbon before the treatment. Without ozone pre-treatment, the impregnation is not effective. Without aluminum hydroxide, the impregnation even degrades the oxidation resistance of the carbon.

Keywords: A. Carbon fibers, Synthetic graphite; B. Oxidation, Impregnation; C. Thermal analysis

1. Introduction

The tendency for carbons to oxidize and become a vapor is a problem that limits the use of carbons at high temperatures. Structural carbons include carbon fibers, carbon–carbon composites and graphite. They are used in aerospace and various industrial applications. Much attention has been given to the development of methods of oxidation protection of carbon materials [1].

The dominant method of oxidation protection of carbons involves the use of a coating, such as SiC [2], silicon oxycarbide [3], TiC [4], TiN [5], TiO_2 [6], Si_3N_4 [7], B_4C [8], SiO_2 [9], $ZrSiO_4$ [10], ZrO_2 [11], Si–Hf–Cr [12], Al_2O_3 [13], Al_2O_3–SiO_2 [14], SiC/C [15], BN [16], Si–B [17], mullite [18], LaB_6 [19], $MoSi_2$ [20], Y_2SiO_5 [21] and glass [22]. These ceramic coatings are mostly applied by either chemical vapor deposition (CVD) or pyrolysis of a preceramic polymer [23].

Another method of oxidation protection of carbons involves surface treatment with an aqueous solution [24], such as oxyfluoride phosphate compounds [25], $POCl_3$ [26] and boric acid [27,28]. Immersion in the solution is followed by drying and sometimes heating as well. This method should be distinguished from the formation of a ceramic coating by dipping in a sol–gel [29]. The solution technique is simple compared to CVD, though it usually provides oxidation protection in a lower temperature range than the ceramic coating method [24].

Phosphate binder is widely used in the field of refractories. Phosphate bonding can be achieved by using either phosphoric acid or an acid phosphate. The latter is prepared by adding an acid (such as phosphoric acid) to a phosphate solution. The phosphoric acid acts as the bonding material, such that the addition of aluminum greatly increases its bonding power. Thus, aluminum phosphates are widely used as binders for ceramics. All aluminum phosphate binders contain phosphoric acid in excess of that needed to form aluminum phosphates, so they are called acid phosphates.

Phosphoric acid has been used to treat polyacrylonitrile (PAN) fibers (not carbon fibers) [30,31], carbon fibers [24] and glassy carbon [28]. Other phosphorus compounds, such as oxyfluoride phosphate, have been used to impregnate carbons for oxidation protection [25,26]. An acid phosphate in the form of a mixture of phosphoric acid and a metal phosphate, preferably $Al(H_2PO_4)_3$, such that the P/Al molar ratio is 5 or less in the acid phosphate, has been used for treating carbon–carbon composites for oxidation

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Table 1
Basic properties of graphite

Carbon content	98%
Flexural strength	16.5 MPa
Compressive strength	32.6 MPa
Yield strength (0.2% offset)	25.8 MPa
Electrical resistivity	2×10^{-3} Ω cm
Density	1.46 g/cm^3

protection [32,33]. This work uses a different acid phosphate, which is obtained by forming a solution of aluminum hydroxide and phosphoric acid, such that the P/Al molar ratio is 12 or more [34,35] and the reaction product formed after heating is $Al(PO_3)_3$. In contrast, Refs. [32,33] use $Al(H_2PO_4)_3$, which is present before heating, and the acid phosphate in Refs. [32,33] is a mixture rather than a solution. A solution is more attractive than a mixture for ease of impregnation.

Two types of carbon material were used in this work, namely polycrystalline graphite and mesophase-pitch-based carbon fiber. The graphite is relevant to electrode, electric brush, heating element and other industrial applications. The carbon fibers are relevant to composites for lightweight structures. They are less crystalline and more strongly textured than graphite. In addition, the fibers are much smaller in size than graphite, which is in bulk form.

2. Experimental methods

The polycrystalline graphite was Grade EG 389P from Carbone (Boonton, NJ, USA). Its properties are shown in Table 1. The carbon fibers were Thornel P-25 from Amoco Performance Products (Alpharetta, GA, USA). Their properties are shown in Table 2.

The surface treatment (impregnation) of the carbons involves immersion in a solution of phosphoric acid (H_3PO_4, from Morton Thiokol, Danvers, MA, USA) and aluminum hydroxide ($Al(OH)_3$, from Fisher Scientific, Fair Lawn, NJ, USA) at 150 °C for 10 h, with stirring. The solution is prepared by mixing phosphoric acid and aluminum hydroxide in a molar ratio of either 12:1 or 23:1 and heating at 150 °C to ensure complete dissolution of the aluminum hydroxide. After immersion, the carbon was dried in air at 110 °C for 2 h in order to remove water. This was followed by heating in nitrogen gas at a rate of 10 °C/min to 800 °C and holding at 800 °C for 20 min for the purpose of formation of type-A $Al(PO_3)_3$ [36]. Heat treatment at 500 °C instead of 800 °C gives type-B $Al(PO_3)_3$ [36] and results in less effective oxidation protection. Type A and type B are two crystal forms of $Al(PO_3)_3$.

Table 2
Basic properties of carbon fibers

Carbon content	97%
Tensile strength	1.38 GPa
Tensile modulus	159 GPa
Electrical resistivity	1.3×10^{-3} Ω cm
Density	1.9 g/cm^3

Table 3
Atomic content (in %) of surface functional groups on graphite

	C–H	C–O	C=O
As-received	90.1	9.9	0
After O_3 exposure	72.6	4.1	23.3

Prior to the impregnation described above, the carbons are subjected to an ozone surface treatment, which involves heating in air containing 0.3 vol.% ozone (O_3) at 175 °C for 6 min. The ozone treatment results in the formation of oxygen-containing surface functional groups, as shown by ESCA surface analysis (1000 μm spot size, monochromatized Al Kα X-rays). The surface concentration of C=O is increased, while that of C–O and C–H is decreased by the ozone treatment, such that the total surface oxygen concentration is increased, for both graphite (Table 3) and carbon fibers (Table 4). Consistent with the increase in surface oxygen concentration is the weight increase of 2.8% for graphite and 2.2% for carbon fibers.

In order to investigate the usefulness of the ozone pre-treatment, samples with and without the pre-treatment were evaluated. For each of graphite and carbon fibers, five samples were evaluated, namely Sample 1 (as received), Sample 1′ (ozone treated), Sample 2 (from Sample 1, followed by impregnation with $H_3PO_4+Al(OH)_3$ (23:1 molar ratio) and heating to 800 °C in N_2 for 20 min), Sample 3 (from Sample 1, followed by ozone treatment, impregnation with $H_3PO_4+Al(OH)_3$ (23:1 molar ratio) and heating to 800 °C in N_2 for 20 min), and Sample 4 (from Sample 1, followed by ozone treatment, impregnation with $H_3PO_4+Al(OH)_3$ (12:1 molar ratio) and heating to 800 °C in N_2 for 20 min). The graphite samples are accordingly labeled G-1, G-1′, G-2, G-3 and G-4, while the fiber samples are labeled C-1, C-1′, C-2, C-3 and C-4.

In order to investigate the usefulness of $Al(OH)_3$ in the acid phosphate, a carbon fiber sample was treated by impregnation in H_3PO_4 (2 vol.% in methanol, no $Al(OH)_3$) for 6 h, followed by drying at 110 °C for 2 h.

Table 4
Atomic content (in %) of surface functional groups on carbon fibers

	C–H	C–O	C=O
As-received	86.5	13.5	0
After O_3 exposure	76.0	5.1	18.9

The oxidation resistances of the carbons were evaluated by thermogravimetric analysis (TGA) conducted in air (30 cc/min flow) using a Perkin-Elmer (Norwalk, CT, USA) 7 Series Thermal Analysis System. The temperature was raised from 50 to 1500 °C at a rate of 10 °C/min.

The surface microstructure was examined by scanning electron microscopy (SEM), conducted using an Hitachi S-400 field emission SEM operated at 30 keV. Specimens were not coated prior to SEM examination.

X-ray diffraction was performed on the white coating (after removal from the black graphite substrate by scraping) using a Siemens X-ray diffractometer with Cu Kα radiation. The 2θ scan rate was 0.02° s^{-1}.

The mechanical hardness (Superficial Rockwell Hardness No.) was measured by using a 1/4 inch diamond ball indentor and a 15 kg major load. The testing was performed on Samples G-1, G-4 (after partial removal of the coating by mechanical polishing) and G-4 (after complete removal of the coating by mechanical polishing). Three measurements were made for each sample.

3. Results and discussion

The weight increase of the carbons due to impregnation and 800 °C heat treatment was 3.2, 24.1 and 22.7% for Samples G-2, G-3 and G-4, respectively, and 11.2, 19.4 and 19.3% for Samples C-2, C-3 and C-4, respectively. This means that the ozone pre-treatment greatly enhances the weight uptake during the subsequent impregnation. The use of $H_3PO_4 + Al(OH)_3$ at the two molar ratios gives similar values of weight uptake. With ozone pre-treatment, the weight uptake due to impregnation is higher for graphite than for carbon fibers; without ozone pre-treatment, the weight uptake due to impregnation is lower for graphite than for carbon fibers.

SEM photographs of Samples G-1, G-1′, G-2, G-3 and G-4 show that ozone treatment has little effect on surface morphology. Without ozone pre-treatment (G-2), impregnation causes surface roughening. With ozone pre-treatment (G-3 and G-4), impregnation causes surface coating, which is more complete when the acid content is higher (23:1 ratio). Similar effects are observed for the carbon fibers (Samples C-1, C-1′, C-2, C-3 and C-4). The fiber diameter is essentially unaffected by any of the treatments, although the fiber surface morphology (particularly the roughness) is.

Fig. 1 shows TGA results for Samples G-1, G-2, G-3 and G-4. The weight loss is similar for Samples G-1 and G-2, but is much less for Samples G-3 and G-4. Hence, ozone pre-treatment (not used in Refs. [32,33] is important for the subsequent impregnation to be effective for oxidation protection. The oxygen-containing functional groups imparted by the ozone pre-treatment are believed to

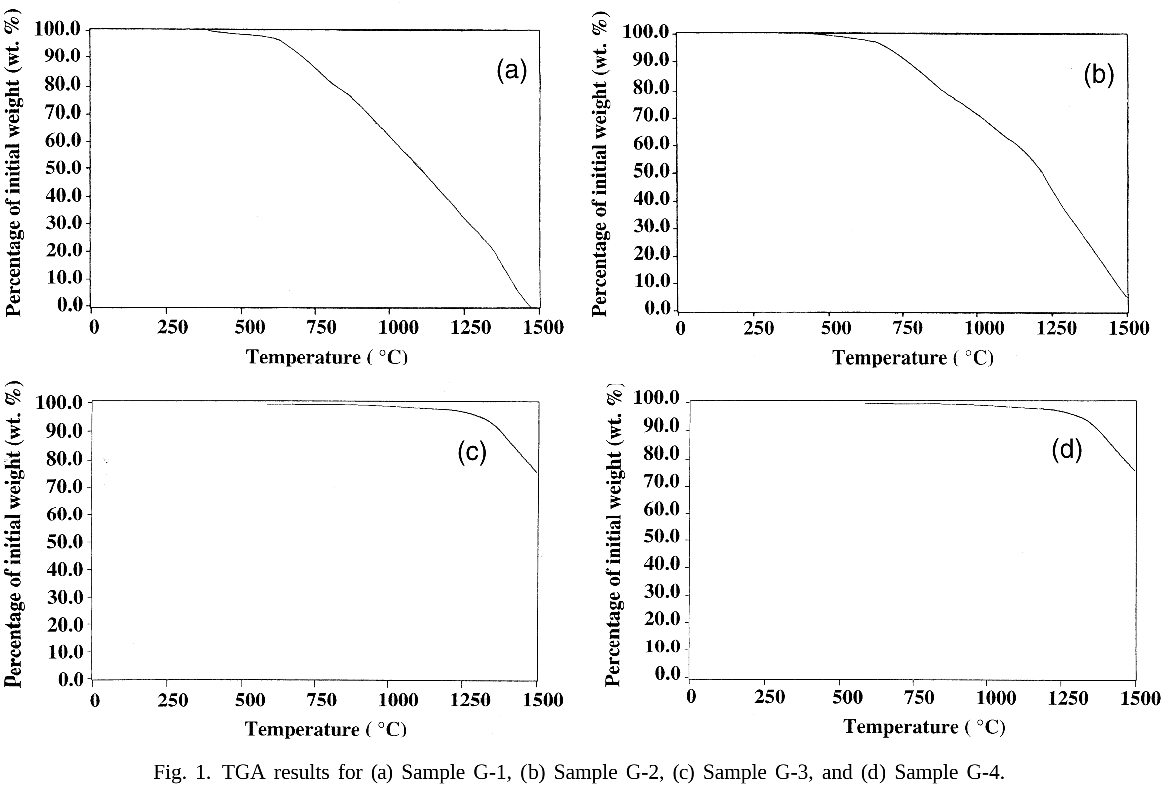

Fig. 1. TGA results for (a) Sample G-1, (b) Sample G-2, (c) Sample G-3, and (d) Sample G-4.

enhance the affinity between graphite and the acid phosphate [37]. The two ratios of H_3PO_4 to $Al(OH)_3$ give similar degrees of oxidation protection.

Fig. 2 shows TGA results for Samples C-1, C-2, C-3 and C-4. The weight loss is similar for Samples C-1 and C-2, but is less for Samples C-3 and C-4.

The fiber sample impregnated by H_3PO_4 in the absence of $Al(OH)_3$ gives a weight increase of 6.2% after impregnation, which actually degrades the oxidation resistance. As shown in Fig. 3, the weight loss during heating in TGA is slightly more than that of the as-received fiber (Sample C-1). This result is in disagreement with Ref. [24], which reported that phosphoric acid treatment improved the oxidation resistance of carbon fibers. That the acid treatment degrades the oxidation resistance of carbon fibers is expected from the expected formation of oxygen-containing functional groups. On the other hand, that phosphoric acid treatment improves the oxidation resistance of PAN fibers [30,31] is reasonable, since the oxidation causes a change in the chemical structure of the polymer.

Table 5 compares the oxidation resistance of the various graphite and carbon fiber samples in terms of the temperature (during heating at 10 °C/min) at which the weight loss is 10%. For the same treatment, the fibers are less oxidation-resistant than the graphite, but the treatments have similar effects on fibers and graphite. Impregnation by H_3PO_4 in the absence of $Al(OH)_3$ is damaging to the oxidation resistance.

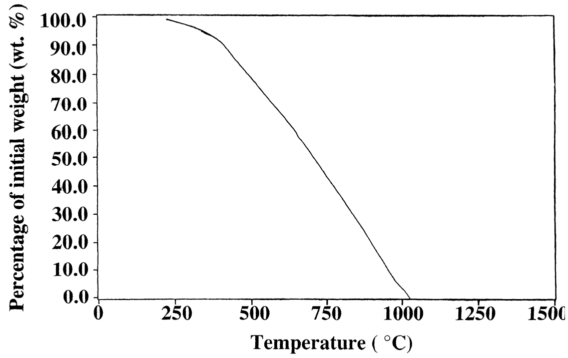

Fig. 3. TGA result for fiber sample impregnated with H_3PO_4 in the absence of $Al(OH)_3$.

Fig. 4 shows the X-ray diffraction pattern of Sample G-3. The pattern exactly matches that of type-A aluminum metaphosphate, $Al(PO_3)_3$.

The coating resulting from acid phosphate impregnation is white in color.

The Superficial Rockwell Hardness Number is 17±1, 42±1 and 18±1, respectively, for Samples G-1, G-4 (after partial removal of the coating) and G-4 (after complete removal of the coating). This means that the coating causes

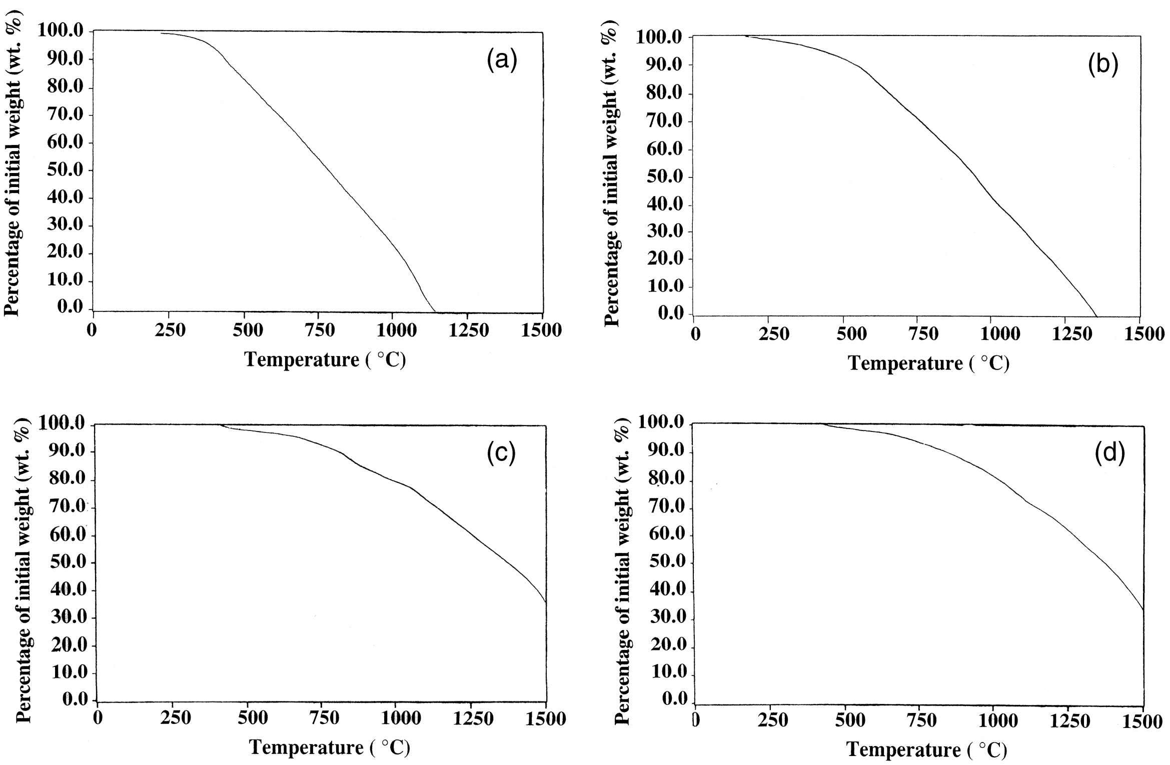

Fig. 2. TGA results for (a) Sample C-1, (b) Sample C-2, (c) Sample C-3, and (d) Sample C-4.

Table 5
Oxidation resistance of various graphite and carbon fiber samples, as indicated by the temperature (during heating at 10 °C/min) at which the weight loss is 10%

Sample	Temp. (°C)
G-1	750
G-2	760
G-3	1375
G-4	1375
C-1	450
C-2	550
C-3	825
C-4	865
–[a]	440

[a] Carbon fiber impregnated by H_3PO_4 in the absence of $Al(OH)_3$.

an increase of the hardness at the surface (due to the hardness of the coating material), but essentially does not affect the hardness of the underlying graphite.

4. Conclusion

Acid phosphate solution impregnation, with ozone pre-treatment, improves the oxidation resistance of polycrystalline graphite and pitch-based carbon fibers, as shown by thermogravimetric measurement in air up to 1500 °C. The impregnation involves using phosphoric acid and dissolved aluminum hydroxide in the molar ratio 12:1. The treatment results in a rough, white and hard aluminum metaphosphate (type-A $Al(PO_3)_3$) coating, such that the weight uptake is 23% for graphite and 19% for carbon fiber. The use of a molar ratio of 23:1 gives similar effects. In contrast, treatment with phosphoric acid alone (without $Al(OH)_3$) degrades the oxidation resistance. Without ozone pre-treatment, which increases the surface oxygen concentration, the impregnation is not effective for coating or for oxidation protection.

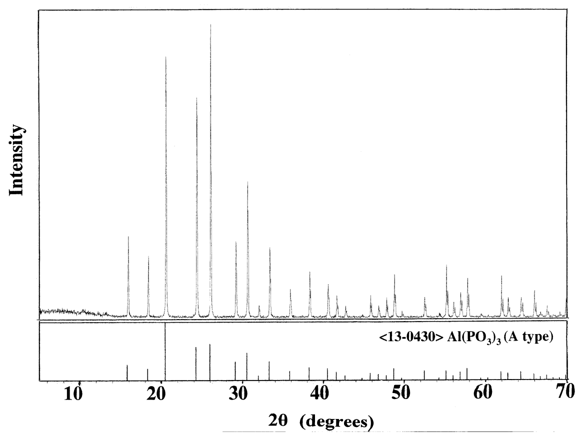

Fig. 4. X-ray diffraction pattern of Sample G-3. The bottom inset shows the known pattern for type-A $Al(PO_3)_3$.

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