Journal of the European Ceramic Society **18** (1998) 1953–1960
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PII: S0955-2219(98)00135-6
0955-2219/98/$—see front matter

Oxidation Inhibition of Carbon Fibre Preforms and C/C Composites by H_3PO_4

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Abstract

Carbon preforms and C/C composites were treated with a H_3PO_4 aqueous solution in order to lower their oxidation rate. H_3PO_4 groups are adsorbed on carbon at room temperature. Rising the temperature results in the decomposition of the adsorbates and the formation at 600°C of C–O–P bonds. Hence, carbon active sites are blocked and oxidation of carbon is limited. Further, phosphate groups neutralize catalytic impurities present at the surface of the carbonaceous material. Nevertheless, the desorption and the elimination of phosphate groups which occur at 950°C, limit the efficiency of this treatment to lower temperatures. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Applications of carbon–carbon (C/C) composite materials at high temperature in oxidizing atmospheres are limited by oxidation of the carbonaceous constituents. Phosphorus oxyhalides and particularly oxychloride which appears to be the most active, are commonly used as oxidation inhibitors.[1–3]

By using Fourier Transform Infrared Spectroscopy (FTIR), McKee and co-workers[4] showed that phosphate and phosphite groups were strongly adsorbed on graphite by C–O–P bonds attached to the 'zigzag' $\{10\bar{1}0\}$ faces of graphite where oxidation normally occurs.

Oh and Rodriguez[5] studied, by controlled atmosphere transmission electron microscopy (TEM), the oxidation as a function of temperature, of a single-crystal of graphite pretreated with a 0·2% aqueous solution of methyl-phosphonic acid. Direct observation showed that the additive completely inhibited the reaction below 830°C. At higher temperatures, phosphorus species were bound preferentially to the graphite 'armchair' $\{11\bar{2}0\}$ faces leaving the 'zigzag' $\{10\bar{1}0\}$ faces vulnerable to attack by oxygen. In situ electron diffraction analysis indicated the formation of a chemical bond between phosphorus and the graphite edge atoms, which involved the formation of a complex thought to be responsible for the observed thermal stability of P–O species on graphite at temperatures up to 1050°C.

The present research aimed at understanding the oxidation mechanisms for two carbon fibre preforms and related C/C composites.

2 Experimental procedure

2.1 Materials

Two kinds of ex-PAN carbon fibre 3D-preforms were used.† The first was fabricated from Tenax HTA carbon fibre from AKZO and further heat treated at 1600°C under vacuum (HTA preform). The second was produced from oxidized PAN fibres (RK-SGL) and was further heat treated at 1600°C under vacuum (RK preform).

RK preforms were densified by pyrocarbon by chemical vapour infiltration (CVI). C/C specimens ($10\times10\times1\,mm^3$) were cut from these materials. Their surface were carefully polished with diamond pastes of decreasing size (successively 30/15/6/3 μm). Then, the as-prepared specimens were washed with distilled water in an ultrasonic bath and finally heat treated at 950°C under high vacuum in order to remove the impurities introduced during polishing.

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† Supplied by SEP, Le Haillan, France.

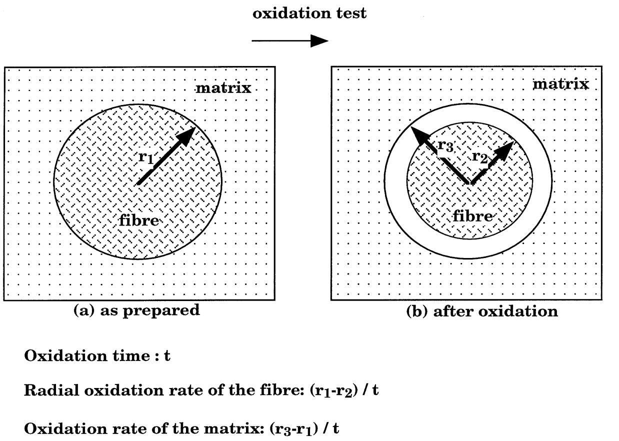
The anisotropy of the CVI-pyrocarbon matrix was investigated by means of optical microscopy (MEF_2 from Reichert-Jung) on polished cross-sections under polarized light as described by Diefendorf and Tokarsky.[6] The so-called extinction angle, A_e, is an indirect measurement of the reflecting power of the carbon. For graphite, a maximum of 22° is found whereas isotropic carbon yields a value of 0°. (In this study a value of 11° was measured, suggesting that the pyrocarbon deposit was Smooth Laminar).Fibre preforms and C/C specimens were impregnated with a 10 vol% distilled water solution of orthophosphoric acid. Then, the samples were dried in air at 150°C for 2 h and treated at 600°C under an argon atmosphere during 1 h (H_3PO_4-pretreatment).

2.2 Techniques

Conventional elementary trace analyses were carried out on RK and HTA fibre preforms.* FTIR and Raman spectroscopies were used to analyse the sample surface before and after the H_3PO_4-pretreatment. The FTIR spectra were recorded between 4000 and 600 cm^{-1} with a Nicolet FT 20 SXC spectrometer and the Raman spectra with a Dilor OMARS 89 spectrometer coupled to a Spectra Physics ionized argon laser (150 mW; $\lambda = 514.5$ nm; slit width: 3 cm^{-1}).

X-Ray elementary analysis (wave dispersive spectrometry mode) was conducted with a Camebax electron probe microanalyser (EPMA) from CAMECA. A Pentaerytritol (PET) crystal was used for the analysis of calcium and phosphorus, a Thallium Acid Phthalate (TAP) crystal for that of phosphorus, magnesium, sodium and finally a pseudo crystal multilayer (PC1) for the quantification of carbon and oxygen.

Fibre surfaces of oxidized preforms were examined using a high resolution scanning electron microscopy (SEM) (S 4500 from Hitachi). SEM was also used to record micrographs of fibres perpendicular to the surface of the C/C specimens before and after different oxidation treatments under same observation conditions. The radial oxidation rates of the fibre and the oxidation rate of the pyrocarbon matrix were calculated from the r_1, r_2 and r_3 radii measurements, as shown in Scheme 1.



Scheme 1. Radial oxidation of fibre and matrix at the interface F/M in a C/C composite.

The oxidation of carbon fibre preforms and C/C specimens were performed with a Setaram TAG 24 thermogravimetric analyser (TGA) under dry air flow (50°C/min heating rate up to the test temperature). Moreover for C/C specimens, isothermal treatments at 600°C were carried out until 4 wt% burn off. The oxidation rate is defined as $R = -(1/m_o)\,(\delta_m/\delta_t)$ (expressed in % s^{-1}), where δ_m is the weight variation observed during a time δ_t for a sample of initial weight m_o at time t (when R becomes constant).

Thermal treatments were carried out in the TGA apparatus under argon. The temperature of the furnace was raised to 1100°C at a constant heating rate (10°C min) and the weight loss of the sample was recorded as a function of time.

3 Results

3.1 Oxidation of ex-PAN fibre preforms

From chemical analysis data shown in Table 1, it appears that HTA fibre preforms contain more impurities than their RK counterparts.

In order to select an oxidation temperature, the thermal variations of the oxidation rate, R, for the HTA preforms were determined, and are shown as an Arrhenius plot, in Fig. 1. From the values of the related apparent activation energies, it will be assumed that oxidation is controlled by reaction kinetics for $T < 700$°C. Thus, the thermogravimetric experiments were carried out on the fibre preforms mostly at 650°C in order to study the kinetic phenomena.

The weight loss $\Delta m/mo$ and the oxidation rate R of the fibre preforms are reported in Fig. 2. It

Table 1. Chemical analyses conducted on RK 2 and HTA preforms

Impurities	*RK(in ppm)*	*HTA(in ppm)*
Ca	150	900
Na	9	38·7
Fe	10	57
Al	5·4	27
Si	5	0·5
Mg	3·3	4
Cl	40	
Cu	4·7	
K	2	
Zn	0·55	

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*Analyses performed at CNRS-Vernaison, France.

appears from the data that (i) the oxidation rate first increases and then becomes constant for the RK fibre preforms whereas (ii) it first decreases rapidly and becomes constant for the HTA preforms. Furthermore, the oxidation rates of the two carbon fibres are about the same after stabilisation ($R = 1{\cdot}6 \times 10^{-3}$ % s^{-1} for $t = 10^4$ s).

The same TGA experiments were carried out on fibre preforms pretreated with orthophosphoric acid (H_3PO_4). Figure 3(a) and (b) shows that this treatment improves the oxidation resistance of the carbon fibre preforms. The oxidation rate of the H_3PO_4-pretreated preforms is six times lower than that of their untreated counterparts. Moreover, the rate of oxidation of the H_3PO_4-pretreated HTA preforms no longer increases rapidly at the beginning of the oxidation test as observed for that of the untreated ones.

The thermal variations of the oxidation rate are shown as an Arrhenius plot in Fig. 4, for both the

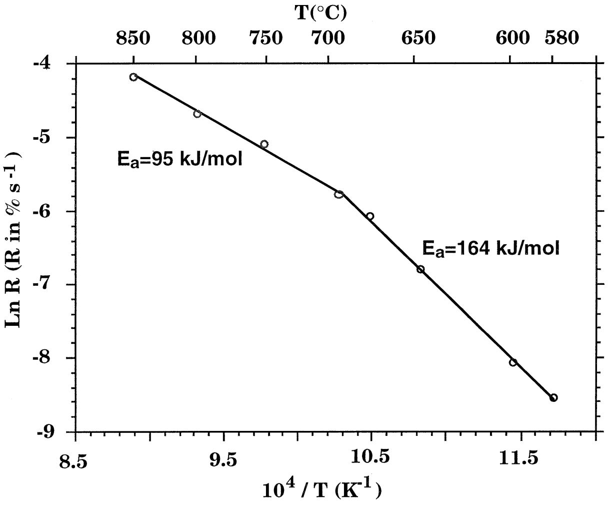


Fig. 1. Arrhenius plot for the oxidation under dry air flow of untreated HTA preforms.

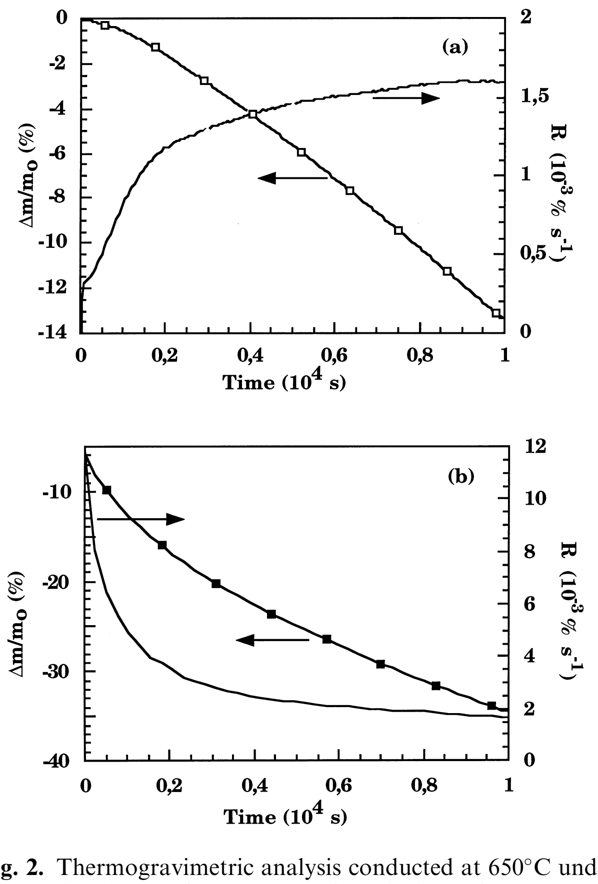


Fig. 2. Thermogravimetric analysis conducted at 650°C under dry air flow for RK (a) and HTA (b) preforms.

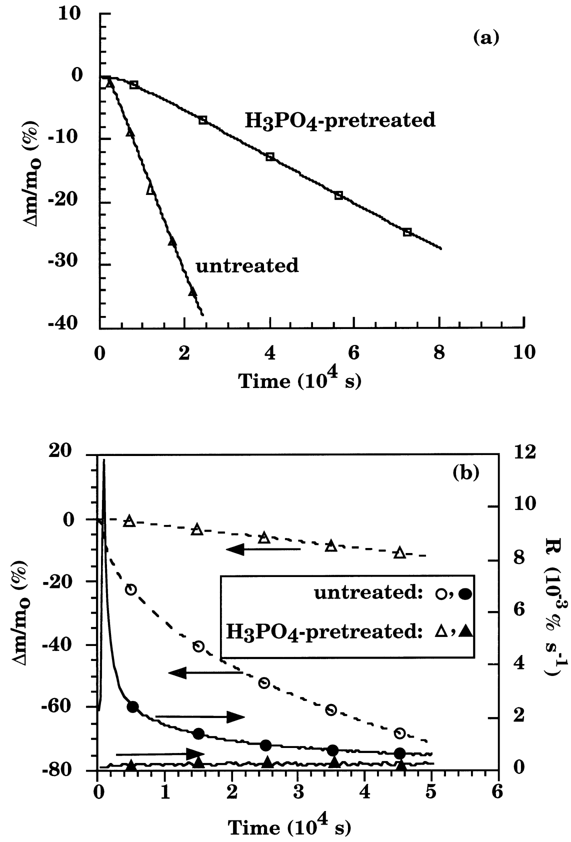


Fig. 3. Thermogravimetric analysis conducted at 650°C under dry air flow for untreated and H_3PO_4-pretreated RK (a) and HTA (b) preforms (○,●: untreated; △,▲: H_3PO_4-pretreated).

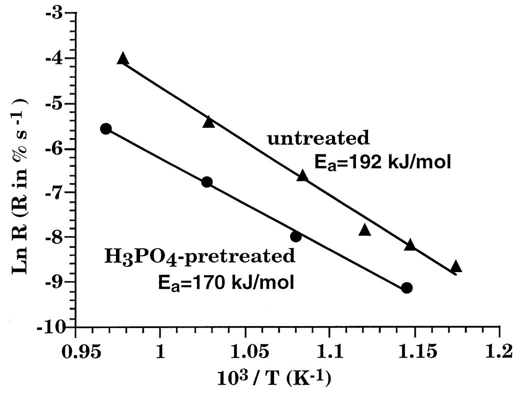


Fig. 4. Arrhenius plots of the oxidation rate under dry air flow of untreated and H_3PO_4-pretreated RK preforms.

as-received and H_3PO_4-pretreated RK fibre preforms. The slopes of the two lines are similar, the related apparent activation energies being 192 kJ mol^{-1} for RK untreated preforms (164 kJ mol^{-1} for untreated HTA preforms) and 170 kJ mol^{-1} for pretreated ones. The curve corresponding to the treated material lies below that for the untreated preform, confirming that the orthophosphoric treatment improves the oxidation resistance of ex-PAN carbon fibres. Moreover, H_3PO_4 impregnated preforms, washed with distilled water until quasi removal of excess phosphoric acid, show better oxidation resistance than the untreated ones.

Scanning electron microscopy was performed on RK fibre preforms oxidized at 20 wt% burn off [Fig. (5a)]. Pitting features, characteristic of a catalytic oxidation, are observed. Figure 5(b) shows the same fibre pretreated with orthophosphoric acid and then oxidized at the same burn off. Catalytic attack is no longer observed on these preforms. The same behaviour was observed for HTA fibre preforms.

A thermal treatment was carried out on the H_3PO_4-pretreated preforms in the TGA apparatus using a 30°C min heating rate between each plateau of about 12 min from 25 to 1100°C under argon (Fig. 6). A first weight loss is observed between 100 and 400°C. More important weight losses occur at 500°C and then at 950°C. SEM images recorded from fibres after this thermal treatment show some aggregates at the fibres surface (Fig. 7).

Thermal treatments of H_3PO_4-pretreated preforms were carried out at respectively 600, 800 and 1000°C during 1 h under an argon atmosphere. The materials were then oxidized at 650°C under a dry air flow. TGA data reported in Fig. 8 show that oxidation rates are very low for samples treated previously at 600 or 800°C. On the other hand, the oxidation rate of the fibre preform which was heat-treated at 1000°C before the oxidation test is equal to that of the untreated material.

3.2 Oxidation of C/C composites

TGA was conducted on pretreated polished C/C samples. As shown in Fig. 9,orthophosphoric acid pretreatment reduces dramatically the oxidation rate of the C/C composites

Fibres perpendicular to the sample surface were observed in as-prepared C/C composites and after

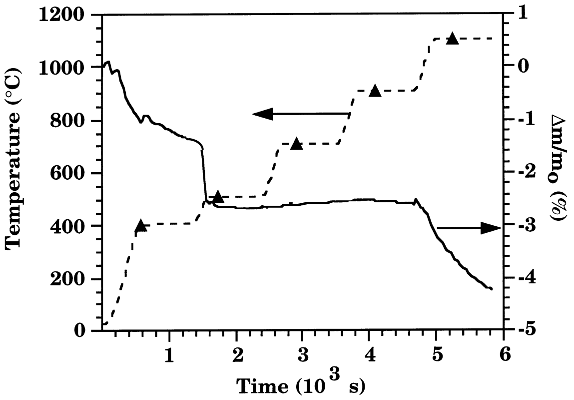


Fig. 6. Thermogravimetric analysis conducted under pure argon flow (1 atm., 1 l h^{-1}) for H_3PO_4-pretreated RK preforms.

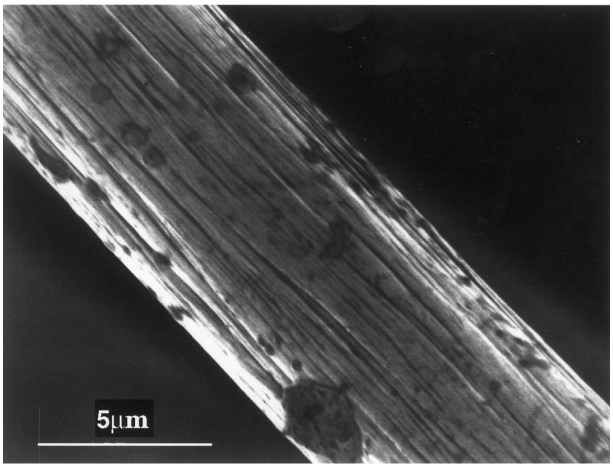


Fig. 7. Surface of H_3PO_4-pretreated HTA fibre after a 1 h thermal treatment under pure argon flow.

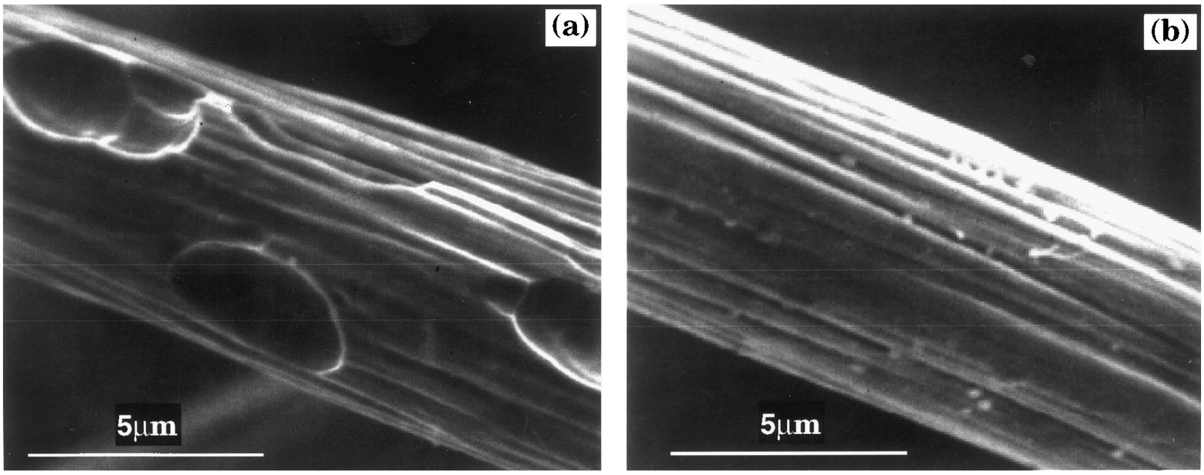


Fig. 5. Fibre surfaces after oxidation of untreated(a) and H_3PO_4-pretreated (b) preforms.

4 wt% burn off at 600°C (Fig. 10). Oxidation takes place preferentially at the fiber-matrix (FM) interfacial zones as already mentioned by Yasuda *et al.*[7] and to a lesser degree at limits of pyrocarbon growth zones (limits of Voronoï zones). In order to quantify oxidation damages at the C/C sample surface, diameters of 30 fibres were measured before oxidation test and after 4 wt% burn off. Fibre radius decreases at a rate of 0·05 μm h^{-1} and the matrix is oxidized at a rate of 0·07 μm h^{-1}.

Figure 11(a) and (b) shows the same fibre cross-sections before and after H_3PO_4-pretreatment. The difference consists principally in the presence of solidified droplets at the fibre-matrix interface. After an oxidation of 20 min, the interfacial zones of the H_3PO_4 pre-treated composites do not look oxidized compared to the untreated samples. Figure 11(c) and (d) shows the same fibre cross-sections after 6 and 15 h of oxidation, the fibre radius was reduced at a rate of 0·01 μm h^{-1}. The matrix was oxidized at a rate of 0·02 μm h^{-1} and the interfacial zones were as well oxidized at the limits of Voronoï zones.

EPMA and FTIR data have shown that oxygen and phosphorous elements, on the one hand, as well as P–O–P and O–H bonds, on the other hand, were present at the surface of C/C samples impregnated with H_3PO_4 and dried at 160°C.

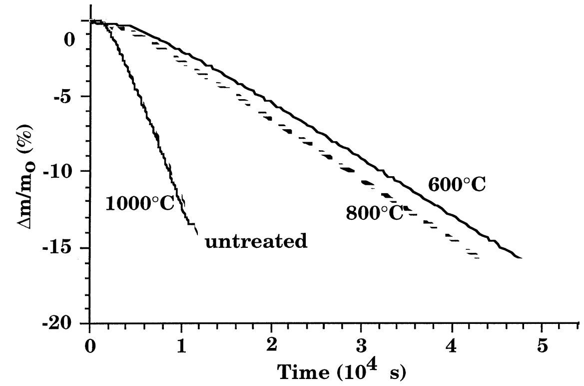


Fig. 8. Thermogravimetric analysis conducted at 650°C under dry air flow for untreated RK preforms and H_3PO_4-pretreated preforms thermally treated under argon at different temperatures before the oxidation tests.

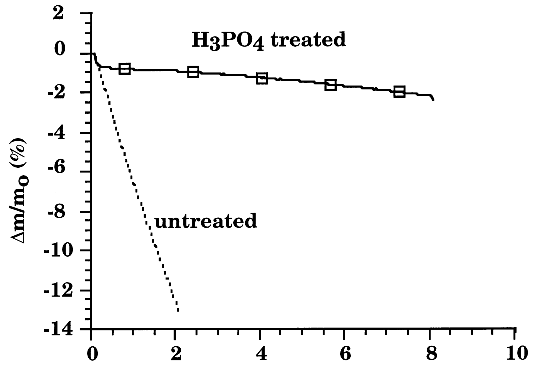


Fig. 9. Thermogravimetric analysis conducted at 600°C under dry air flow for untreated and H_3PO_4-pretreated C/C composite (ex Rk fibre preforms).

After the thermal treatment at 600°C, analyses were carried out on droplets located at the interfacial zone [Fig. 11(b)] and on the carbonaceous surface (Table 2). Catalytic impurities (such as Ca, Na and Mg), as well as phosphorus and oxygen are present in the interfacial zones. Raman spectrum shows a peak at 924 cm^{-1} characteristic of $(PO_4)^{3-}$ tetrahedra. Moreover, an increase of the 1450 cm^{-1} carbon peak intensity of the Raman spectrum may be due to the formation of a bond between the phosphorus species and the surface of the carbonaceous material. In a similar manner, the occurrence of an absorption band at 784 cm^{-1} in the FTIR spectrum may be characteristic of C–O–P bonds. Finally, EPMA data from regions without droplets show only phosphorus and oxygen heteroatoms but no catalytic impurities. Raman spectrum peak at 640 cm^{-1} and FTIR absorption band at 727 cm^{-1} were tentatively attributed to C–P bonds.

4 Discussion

4.1 Carbon fibre preforms

The difference in the oxidation behaviour of the HTA and RK fibre preforms may be attributed to differences in catalytic impurity concentrations.

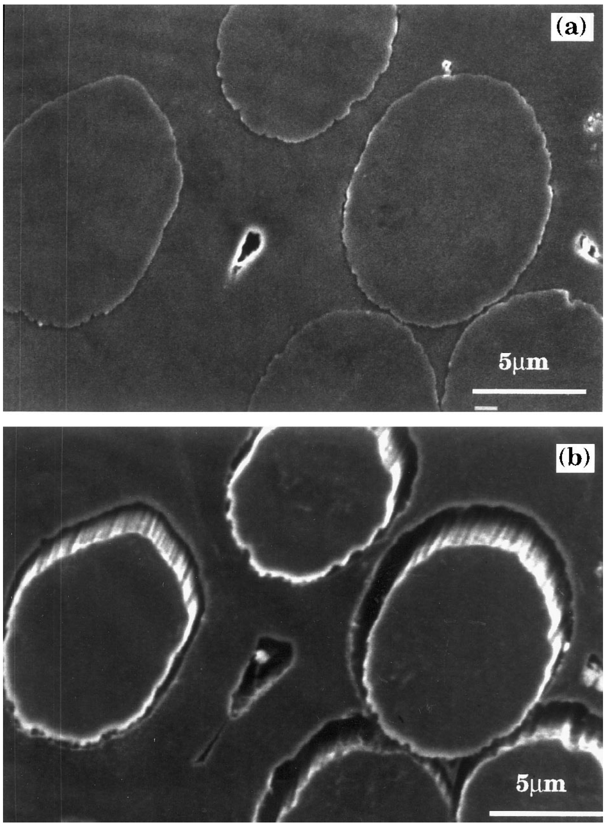


Fig. 10. Surface of a C/C composite surface before (a) and after (b) an oxidation test conducted under dry air flow air 600°C during 6 h (ex RK fibre preforms).

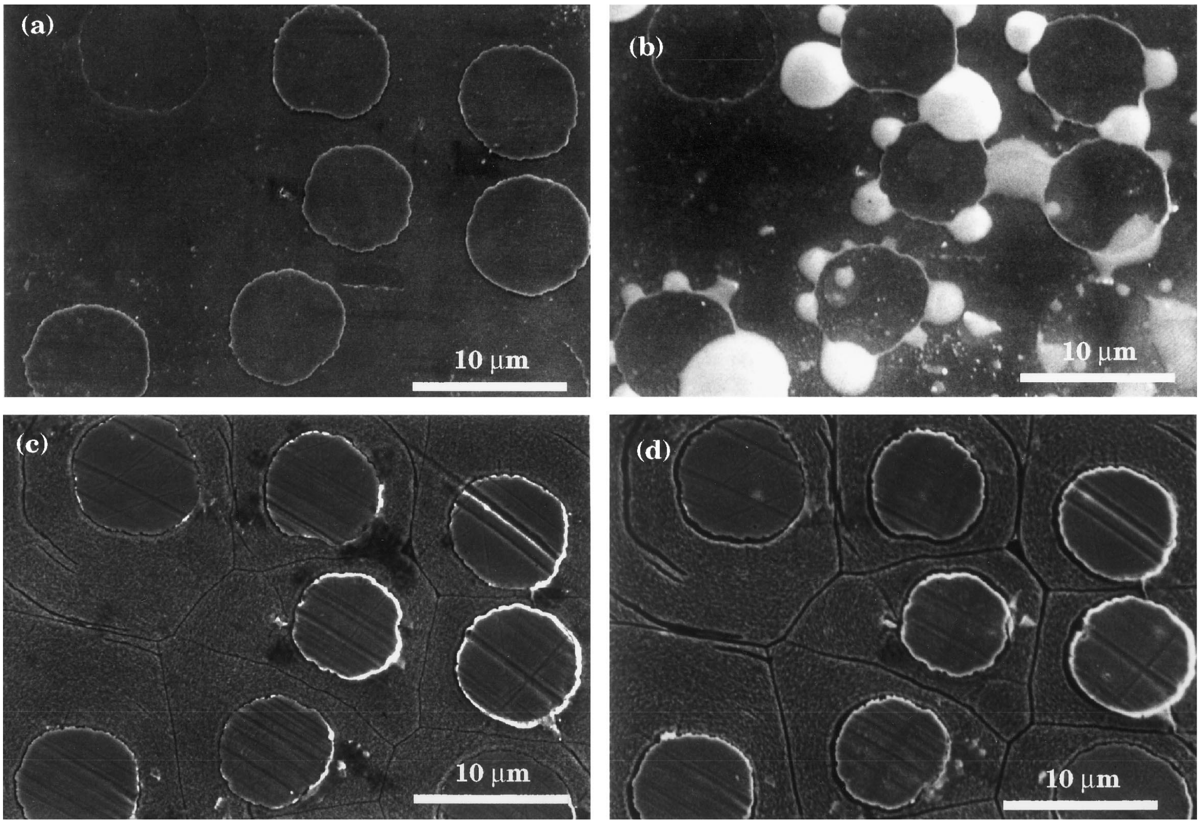


Fig. 11. Surface of C/C composite surface : (a) reference, (b) after H_3PO_4 treatment (c) and (d) after subsequent oxidation during 6 and 15 h at 600°C under dry air flow.

Table 2. Analytical data obtained by different experimental techniques on treated C/C platelets

	EPMA	*Raman*		*Ftir*	
	Elements detected	*Band* (cm^{-1})	*Bond*	*Band* (cm^{-1})	*Bond*
Interface (droplets)	O, Ca,Na, Al, Mg, Si and P	640	C–P	784	C–O–P
		924	$(PO4)^{3-}$	948	P–O–P
Carbonaceous surface	P, O	640	C–P	727	C–P
		850	P–O	969	P–O–P

The concentrations in Ca and Na (which are very active catalytic species in carbon oxidation[8]), are higher for HTA preforms than for their RK counterparts. Therefore at the beginning of an oxidation test, the oxidation rate of the HTA fibre preform presents a peak characteristic of a catalyzed oxidation [Fig. 2(b)] as already reported by Duvivier.[9]

Many authors[5,10–12] have shown that H_3PO_4 treatments neutralize catalytic impurities. Indeed after such a pretreatment and a subsequent oxidation test, the HTA fibres present no pitting contrary to untreated fibres (Fig. 5). Moreover, phosphorus species neutralize the catalytic impurities and form droplets at interfacial zones in C/C composites [Fig. 11(b)].

For untreated samples, FM interfacial oxidation is faster than oxidation at the limits of Voronoï zones (Fig. 10) because the catalytic impurities segregate preferentially at the FM interfaces. On the other hand, FM interfacial zones oxidize as fast as limits of Voronoï zones for H_3PO_4 pretreated samples [Fig. 11(d)]. Under such conditions, the catalytic species present at FM interfacial zones are neutralized and oxidation occurs at about the same rate at the different decohesion zones (FM interfaces and limits of Voronoï zones) where the density of carbon plane edges accessible to oxygen is high.

At ambient temperature, the phosphorus species fix the catalytic impurities. A H_3PO_4-impregnated sample subsequently washed with distilled water presents a better oxidation resistance than an untreated one. Catalytic impurities present at the ppm level and linked to phosphorus species are eliminated during the washing treatment as already shown by Secondary Ion Mass Spectroscopy (SIMS) by Hippo *et al.*[13]

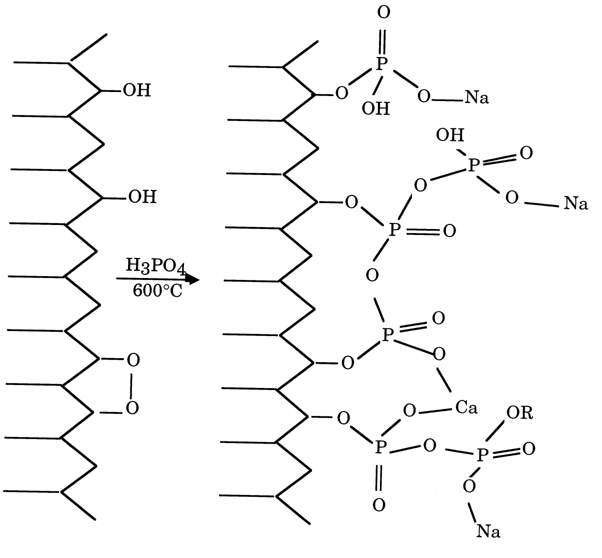
At ambient temperature, no strong bond exists between the carbonaceous material surface and phosphorus species, only $(PO_4)^{3-}$ tetrahedra were observed suggesting the presence of alkali and alkaline earth orthophosphates (Table 2).

The weight loss observed during the thermal treatment at about 300–400°C may be attributed to an evolution of water associated with hydrophilic alkali and alkaline earth orthophosphates (Fig. 6).

At these temperatures, no link with carbon was observed from Raman or FTIR spectra (Fig. 2). That is in agreement with the results of Chesneau[13]on carbon samples treated with $POCl_3$ at 300°C.

At 500–600°C carbon reduces phosphorus-bearing species. An important weight loss is observed at this temperature during the thermal treatment under argon atmosphere (Fig. 6). Moreover Raman and FTIR spectra show clearly the formation of bonds between carbonaceous and phosphorus-bearing species (Table 2). C–O–P bonds are obvious (Scheme 2 shows a representation of this feature) and C–P bonds might be present at carbon active sites until about 900–950°C. At this temperature, oxygen evolution from the carbonaceous surface occurs[13]. Hence, phosphorus species bound by oxygen leave the carbonaceous surface (Fig. 6). Thermogravimetric analysis conducted at 700, 800 and 1000°C shows that phosphorus species protect carbonaceous materials only at temperatures lower than 1000°C (Fig. 8). It is noteworthy that some aggregates are present at the fibres surface after a thermal treatment at 1000°C (Fig. 7). They may be residual catalytic impurities left at the carbon surface after departure of the phosphorus species. Indeed, the oxidation resistance of a 1000°C pretreated sample is similar to that of an untreated one (Fig. 8).

Finally, the Arrhenius plots of the oxidation rate (Fig. 4) show similar slopes for H_3PO_4 pretreated or untreated preforms, only oxidation rate being changed. Such a result could be due to the neutralization of catalytic impurities by phosphorus-bearing species and to the graft of phosphorus radicals on the active sites without changing oxidation mechanisms.



Scheme 2. Schematic representation of phosphorus groups formed after thermal treatment at 600°C of H_3PO_4 treated preforms.

5 Conclusion

H_3PO_4 molecules are adsorbed on the carbon fibre surface at room temperature. Subsequent heat treatment at a temperature of about 600°C, decomposes adsorbates and C–O–P bonds are created at the surface on the zigzag faces of the carbonaceous material. Strongly attached phosphate groups have already been mentioned by McKee and co-workers.[4] Active sites are blocked and oxidation of the carbon fibres in air at high temperature is limited. Moreover, phosphate groups at the surface of the carbonaceous material neutralize catalytic impurities which are one of the principal causes of oxidation.

At 650°C the time necessary to reach a 10 wt% burn off can be multiplied by ≈ 5 and more than 50 for RK and HTA preforms respectively, after an orthophosphoric acid treatment. This difference is essentially due to the high impurities concentration in untreated HTA preforms. The effect of this treatment is still more accentuated for the related C/C composites.

The efficiency of this inhibition treatment is limited to temperatures lower than 950°C due to the desorption and the elimination, at 950°C, of the phosphorus radicals bonded to the carbon surface. As a result, fibres could not be treated with phosphorus-bearing inhibiting species before the infiltration of a pyrocarbon matrix by chemical vapor infiltration, CVI being performed at or beyond 950°C during several hours. A solution could be to entrap phosphorus groups by a CVD deposit carried out at low temperature (700°C) or to treat the C/C composite with phosphorus-bearing species infiltrated subsequently in the core of the material, as shown by Roy and Dietz[14] with metal phosphate treatment.

Finally, in C/C composites, phosphorus-bearing species tend to be fixed preferentially at interfacial zones where both the catalytic impurities content and the density of edges of carbon planes are large.

Acknowledgements

This work has been supported by CNRS and SEP through a grant to S.L. The authors are indebted to J.M. Jouin and J. Thébault from SEP and M. Lahaye from CECAMA for assistance and valuable discussion.

References

1. McKee, D. W., *Chemistry and Physics of Carbon*, ed. P. L. Walker and P. A. Thrower. Dekker, New York, 1981, p. 1.
2. Hawtin, P. and Gibson, J. A., Conf. on Industrial Carbon and Graphite, Society Chemical Industry, London, 1970.

3. McKee, D. W., Savage, R. H. and Gunnoe, G., Chemical factors in carbon brush wear. *Wear*, 1972, **22**, 193.
4. McKee, D. W., Spiro, C. L. and Lamby, E. J., The effects of boron additives on the oxidation behavior of carbons. *Carbon*, 1984, **22**, 193.
5. Oh, S. G. and Rodriguez, N. M., In situ electron microscopy studies of the inhibition of graphite oxidation by phosphorus. *J. Mater. Res*, 1993, **11**(8), 2879.
6. Diefendorf, R. J. and, Tokarsky, E. W., Relationships of structure to properties in graphites fibers, Air Force Report AF 33 (615)-70-C-1530 (1971).
7. Yasuda, S., Kimura, S. and Shibusi, Y., *Trans. Jpn. Soc. Comp. Mat.* 1980, **6**, 14.
8. McKee, D. W., The catalysed gasification reaction of carbon,chemistry and physics of carbon, ed. P. C. Walker Jr. and P. A. Thrower. Marcel Dekker, New-York, 1981, p. 1.
9. Duvivier E., Cinétique d'oxydation d'un composite C/C, PhD Thesis, n° 1692, University of Bordeaux, April 2, 1997.
10. Magne, P., Amariglio, H., and Duval, X., Etude cinétique de l'oxydation du graphite inhibée par les phosphates. *Bull. Soc. Chim.,* 1971, **Fr, 6,** 2005.
11. McKee, D. W., Effect of absorbed phosphorus oxychloride on the oxydation behavior of graphite. *Carbon*, 1972, **10**, 491.
12. Baker, R. T. K., *Carbon and Coal Gasification*, ed. J. I. Figueiredo and J. A. Moulijn. NATOASI series, 1986.
13. Hippo, E. J., Murdie, N. and Kowbel, W., The effect of acid treatments on subsequent reactivity of carbon-carbon composites. *Carbon*, 1989, **27**(3), 331.
14. Chesneau M., Comportement des matériaux carbonés dans les mécanismes de l'oxydation et de son inhibition, PhD Thesis, University of Orléans, 1992.
15. Roy, S. E. and Dietz, R. P., Inhibition of catalysed oxidation of carbon/carbon composites, European patent application 94-100138.0, 7 Jan 1994.