ENHANCEMENT OF THE OXIDATION RESISTANCE OF CARBON FIBRES IN C/C COMPOSITES VIA SURFACE TREATMENTS.

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Introduction

This work deals with the protection of carbon fibres from oxidation between 600 and 1000°C. Two kinds of methods were investigated to protect carbon fibres: (i) surface treatment with aqueous solutions (e.g. of H3PO4) and (ii) Chemical Vapour Deposition (CVD) of SiC coatings. Oxidation resistance of the as treated preforms was studied under dry air atmosphere.

Experimental

Preforms made of PAN based carbon fibres were used in this work. (a) Preforms were impregnated with 10 vol. % distilled water solution of orthophosphoric acid. The samples were then dried in air at 150°C for 2 hours and treated at 600°C under an argon atmosphere. In order to understand the chemical phenomena occurring between H_3PO_4 and carbon, C/C composite materials (tablets) were carefully polished and treated with a H_3PO_4 solution. (b) Preforms were coated with SiC using a methyltrichlorosilane (MTS)/H_2 mixture (950°C-3 kPa-H_2/MTS=0,7).

Thermogravimetric analyses (TGA) were performed on the treated preforms under argon or dry air atmospheres in the 650-1000°C temperature range. Scanning electron microscopy (SEM), electron probe microanalysis (EPMA), Raman and Fourier transform infrared (FTIR) spectroscopies were carried on C/C composites polished surfaces.

Results

H_3PO_4 treatment of PAN preforms

TGA curve (figure 1) recorded under an argon atmosphere on H_3PO_4-impregnated carbon fibres of the preform shows three weight losses: (i) at low temperatures (Θ<400°C), adsorbed water is eliminated, (ii) at 400-500°C carbon reduces phosphorus species, and finally, (iii) above 900°C, phosphorus species (C-O-P) and C-O groups are desorbed.

Oxidation tests were performed on H_3PO_4-impregnated and thermally treated preforms. Thermal tests were carried out at respectively 600°C, 800°C and 1000°C during one hour under an argon atmosphere. The carbon materials were then oxidized at 650°C under dry air. Thermogravimetric results are reported in figure 2. Oxidation rates are low for samples treated at 600 and 800°C. On the contrary, the oxidation rate for a carbon material treated at 1000°C under argon is as high as oxidation rate for the untreated carbon material.

EPMA, Raman and FTIR spectroscopies were carried out on H_3PO_4 impregnated C/C tablets. Only P-O-P and O-H bonds are observed by FTIR spectroscopy. EPMA analyses show the presence of oxygen and phosphorus at the surface of the sample .

Analyses of the surface of C/C tablets thermally treated at 600°C are reported in table 1 and SEM micrograph shows droplet at interfacial zones (figure 3). EPMA analyses show the presence of catalytic impurities (such as Ca, Na and Mg), phosphorus and oxygen at interfacial zones. Raman spectrum shows a peak at 924 cm^{-1} characteristic of $(PO_4)^{2-}$ tetraedra. Moreover, an increase of the 1450 cm^{-1} C-C peak of the Raman spectrum let us suppose a bond of the phosphorus species at the surface of the carboneous material. On FTIR spectrum, a peak at 784 cm^{-1} may be characteristic of C-O-P bonds. It is interesting to note that for untreated samples a catalytic oxidation occurs at interfacial zones due to the presence of catalytic impurities (figure 4). On the contrary for H_3PO_4 treated samples, all the catalytic species present at interfacial zones are neutralised and no pitting was observed after the oxidation test.

At ambient temperature, phosphorus-bearing species fix the catalytic impurities. Indeed, an orthophosphoric acid impregnated sample washed with distilled water presents a better oxidation resistance than an untreated sample [1]. No kind of bonds exists between carboneous species and phosphorus species at ambient temperature. Only $(PO_4)^{2-}$ tetraedra were observed suggesting the presence of alkali and alkaline earth orthophosphates [2].

Raman and FTIR spectra show clearly the formation of C-O-P bonds at 600°C between carbone- and phosphorus-bearing species. Phosphorus-bearing species are linked at carbon active sites up to 900°C. At this temperature, oxygen leaves from the carboneous surface [2] and so C-O-P species leave the carboneous surface. Moreover, phosphorus-bearing species neutralise catalytic impurities at interfacial zones: droplets rich in catalytic impurities are observed in these zones.

In summary: (i) at low temperatures, phosphorus bearing species react with catalytic impurities to form alkali and alkaline earth orthophosphates with a weight loss corresponding to water evolution. **Phosphorus species neutralise catalytic impurities,** whereas at (ii) higher temperature (600°C) phosphorus-bearing species hold on carbon active sites and **inhibit carbon oxidation**. For temperature higher than 900°C

phosphorus-bearing species leave the carboneous surface and no carbon fibres protection is any longer observed.

CVD coating

Thermogravimetric tests were carried out under dry air at **650°C and at 1000°C on SiC coated carbon preforms** (figure 5). SiC deposit oxidises slowly at 650°C and protect efficiently carbon fibres. At 1000°C, the SiC deposit is still very efficient. At the beginning of the oxidation test, oxidation occurs through the cracks of the deposit; then the deposit is oxidized and a glassy silica seals cracks and limits oxygen access to the carbon surface. It thus appears that in the 600°C-1000°C temperature range, SiC CVD deposits protect efficiently carbon fibre from oxidation. Oxygen access to the carboneous surface is stopped, the deposit oxidation rate being very slow.

Conclusion

Surface treatment with aqueous solution (e.g. H3PO4 or H3BO3) that are very easy to use protect carbon fibres in the 600-800°C temperature range. At higher temperature, only coatings obtained by CVD method have improved carbon fibres oxidation resistance by limiting oxygen access to the carboneous surface.

Aknowledgements

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References

[1] Hippo E.J., Murdie N., Kowbel W., Carbon, 27(3)331 (1989).
[2] Chesneau E., Thesis, Orleans university, 1989.

Table 1: Results obtained by different experimental techniques.

	EPMA	Raman Band	Raman bond (cm-1)	Infrared Band	Infrared bond (cm-1)
Interface (droplets)	O, Ca, Na, Al Mg, Si et P	640	C-P	784	C-O-P
		924	$(PO_4)^{2-}$	948	P-O-P
Carbonaceous surface	P	640	C-P	727	C-P
		850	P-O	969	P-O-P

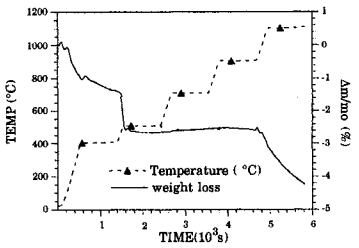

Figure 1: thermogravimetric analysis conducted under argon atmosphere on a H_3PO_4 treated sample.

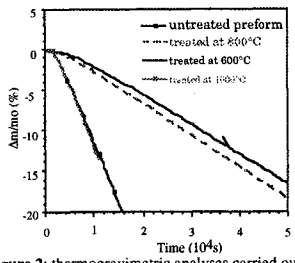

Figure 2: thermogravimetric analyses carried out at 650°C under dry air. H_3PO_4 treated samples were previously thermally treated under an argon atmosphere at different temperatures.

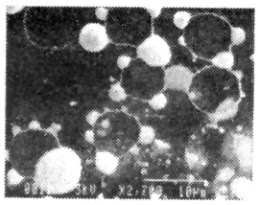

Figure 3: Aspect of the C/C composite surface after the H_3PO_4 treatment.

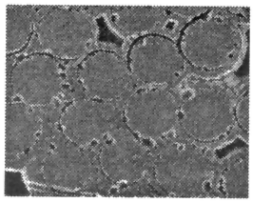

Figure 4: Untreated C/C composite surface after oxidation under dry air at 600°C.

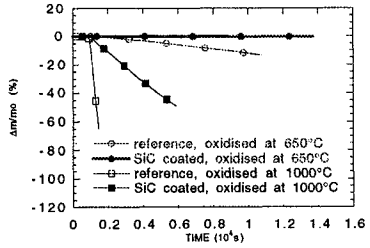

Figure 5: oxidation resistance of SiC coated carbon fibre preforms. Thermogravimetric tests were carried out under dry air at 650 or 1000°C.