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Surface oxidation by microwave-induced plasma of candidate composite materials for space shuttle protection

R. I. BEN-AIM, J. L. BONARDET*, A. M. DIAMY, J. FRAISSARD*,
J. C. LEGRAND
*C.N.R.S. URA 870, Laboratoire de Chimie Générale, and *Laboratoire de Chimie des Surfaces, Université Pierre et Marie Curie, 4 Place Jussieu, Tour 55, 75252 Paris Cedex 05, France*

Oxidation resistance of composite materials (SiC/SiC, C/SiC and C/C) which can be used to protect shuttles is studied in oxygen microwave-induced plasmas (MIP). These plasmas contain the same energetic species (electrons, ions, radicals, excited atoms or molecules) as those produced by the shock wave resulting from re-entry into the atmosphere. The plasma is sustained in a silica tube located in a resonant cavity and microwave energy is supplied by a generator operating at 2450 MHz with variable power from 15 to 1000 W. Experiments are conducted at pressures from 100 to 1000 Pa with temperature ranging from 1100 to 1300° C. The atomic oxygen flow rate is about 6.10^{19} at sec^{-1} cm^{-2}. The wafers are exposed to the plasma for 10 to 25 h for periods of 15 or 30 min. Kinetic behaviour of the material is studied by gravimetry and surface characteristic modifications are analysed by BET Krypton isotherms at 77 K and electron spectroscopy for chemical analysis (ESCA). Gravimetric results, measurements of specific surface area by krypton adsorption and ESCA analysis show that the samples of SiC/SiC and C/SiC are quite resistant to the oxygen plasma even after 25 h exposure. The mass loss is small and the specific surface area (BET) increases but is always lower than $1\ \text{m}^2\ \text{g}^{-1}$. ESCA analysis shows that the surface evolves by change of the superficial silicon carbide into silica. The C/C samples behave quite differently: without any protection they disappear in less than 5 min. With an antioxidant protective layer, this material can be oxidation resistant. The BET and ESCA measurements show that the attack leads to a sintering of the silica which gathers on the fibres, reducing the protection of the matrix.

1. Introduction

When space vehicles return to earth, the friction of the dense layers of the atmosphere causes heating of the structure of the device which is raised to temperatures between 500 and 2000° C. The shock wave accompanying re-entry produces energetic species such as electrons, ions, atoms, excited or reactive molecules (mainly atomic oxygen and nitrogen oxides) which can attack the surface materials.

For certain exposed parts of the device, three options can be considered: thermal protection added to the structure, integrated in the structure or mixed. In the latter two cases, the protective materials are involved in the mechanical behaviour of the whole. The problem of choosing the materials is one of the crucial points in preliminary studies on the design of space vehicles. During recent years, important progress has been achieved in the development of such materials [1]. When considering the various possibilities, the following criteria must be taken into account: temperature and thermal flow; re-entry duration; attack of the materials by partially ionized air; mechanical stress.

It is possible to create plasmas in the laboratory which can be used to simulate partially the chemical environment and the conditions of pressure and temperature encountered by a space vehicle re-entering the atmosphere. We have used air or oxygen plasmas induced by microwaves (MIP) to study the resistance to oxidation of small test pieces of composite materials which could be employed for thermal protection. In this paper, results only concern experiments with oxygen MIP.

We have tested three sorts of composite materials (SiC/SiC, C/SiC and C/C). The fibres can be woven in two or three dimensions (2D or 3D). The samples may or may not be covered with a protective antioxidant layer (PAOL).

2. Apparatus (Fig. 1)

2.1. Plasma production

The microwave energy producing the discharge is supplied by a Thompson-CSF generator, the power of which can be adjusted continuously from 15 to 1000 W at 2450 MHz. A two-directional coupler fitted with two 60 dB captor-attenuators placed in line is used to measure the incident and reflected power. Wave-matter coupling is achieved in silica tube located in a

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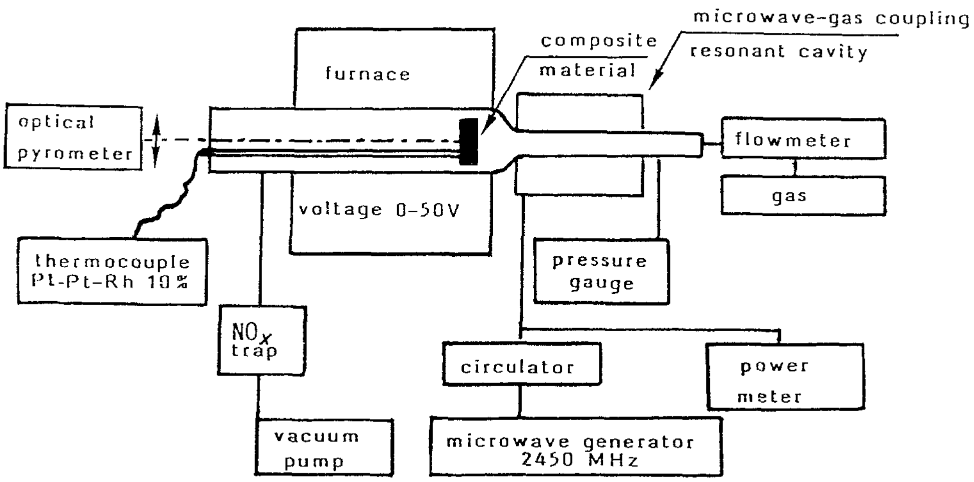

Figure 1 Experimental apparatus.

resonant cavity [2] or in a wave-guide. In a fairly narrow tube reactor, the discharge fills the tube almost completely, but when the diameter is increased, the plasma forms near the walls (surface plasma).

2.2. Reactor

So that the solid samples are entirely in the plasma we used a reactor consisting of two concentric silica tubes fused end to end. The smaller tube (i.d. = 10 mm) passes through the microwave cavity while the diameter of the larger tube, containing the composite material, depends on the size of the test pieces.

Transfer of heat towards the exterior is limited by placing the larger tube in a furnace and by lagging. The sample is held by a silica or alumina support at the exit of the resonant cavity. After each experiment, it is necessary to check by microscopic inspection of the surface that there has been no interaction between the sample and the support.

3. Conditions for studying solid samples

3.1. Plasma characteristics

Under the experimental conditions used in the present study, the main characteristics of the plasma are summarized as followed: electron density, $N_e = 10^{11}$ to 10^{12} part/cm^3; electron temperature, T_e = 40 000 to 50 000K; gas temperature, T_g = 500 to 1300 K; dissociation $(O)/(O_2)_0$ = 15% to 20%; neutral species O_2, O, O_3; atomic oxygen flow rate $\simeq 6 \times 10^{19}$ at sec^{-1} cm^{-2}; ions O_2^-, O^-, O_3^-, O_2^+, O^+, O_3^+; metastables $O_2(^1\Delta_g)$, $O_2(^1\Sigma_g^+)$, $O_2(v)$, $O(^1D)$, $O(^1S)$, $O(^5S)$.

In the case of an air plasma, we also find these species: N, NO_x, N_2^+, NO^+, NO_x^-, $N_2(A^3\Sigma_u^+)$, $N_2(v)$.

3.2. Temperature

Cold plasmas such as MIP are typically non-equilibrium systems where translational, T_g, rotational, T_r, vibrational, T_v, and electron, T_e, temperatures are different; so local thermodynamic equilibrium is not established. Generally, $T_e > T_v > T_r > T_g$. This comes from the fact that energy is first transferred to chemical species via electron impact and is then converted into vibrational, rotational and translational energies.

Transfers from different types of energy determine surface temperature. The main mechanisms are:

(i) transfer of translation, rotation and vibration energies, either by direct impact or by chemisorption, from neutral or charged species;

(ii) transfer of electronic energy from metastable species;

(iii) chemical reactions on the surface such as atoms and radical recombination;

(iv) heat losses from the surface;

(v) heating of a solid by absorption of microwave power depending on its dielectric constant.

The contribution of ions and electrons is negligible because of their weak concentration (10^{11} to 10^{12} part/cm^3) compared with that of neutral species (10^{16} to 10^{17} part/cm^3). The metastable species concentration depends on pressure and their contribution may become more important in the low-pressure range [3].

It is possible to control the temperature at the surface of the materials by modifying the microwave power and the reactor lagging. The surface temperature is followed by means of a disappearing filament pyrometer. This latter was chosen after trying several types of pyrometer (total radiation, colour temperature) and by comparison with thermocouple measurements. The results show that the radiation observed corresponds to thermal emission of the material and that the discharge does not perturb the pyrometer measurement. The study was carried out at 1250° C.

3.3. Pressure

With air, nitrogen or noble gases, the apparatus can operate at pressures from a few pascals to atmospheric pressure. With oxygen it is not possible to exceed 20 kPa (200 mbar) because beyond this, the temperature of the gas is high enough to melt the silica discharge tube. For this study on the oxidation of composite materials the pressures used are in the range 0.1 to 5 kPa (a few mbar to 50 mbar); these values are representative of re-entry conditions.

3.4. Absorbed microwave power

It is assumed that line loss is small. The power absorbed corresponds to about 75% incident power; it is deduced

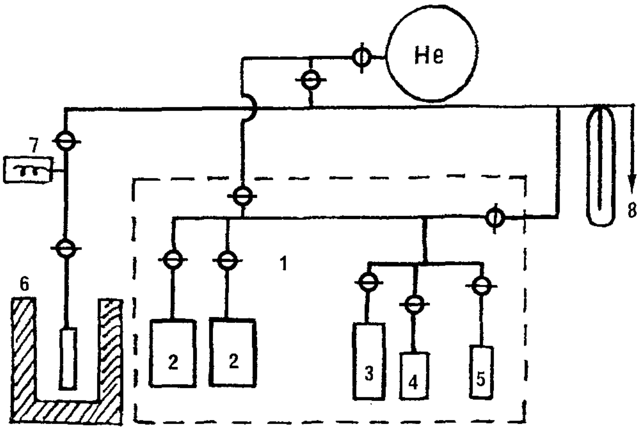

Figure 2 Isothermal adsorption apparatus. 1, Isothermal space; 2, capacitive gauges; 3, krypton gas; 4, standard volume; 5, sample; 6, treatment furnace; 7, Pirani's gauge; 8, vacuum.

from the difference between the measured incident and reflected power.

3.5. Plasma exposure time

Once the plasma is established, it can operate for several hours consecutively. To simulate re-entry into the atmosphere the materials are exposed for periods of 15 to 30 min for a total of several hours (up to 25 h).

3.6. Flow rate

The experimental arrangement does not give flow rates comparable to the real values during re-entry. Experiments have been carried out at 4.2 l h^{-1} (STP) which corresponds to a flow speed of 76 m sec^{-1}. This is much slower than that of a vehicle re-entry. Consequently, ablation phenomena do not arise with our apparatus.

4. Analytical methods

The behaviour of a material with respect to oxidation is characterized by: variation of the mass with time (weighing); modification of the porosity (BET); study of the composition of the superficial layer by photoelectron spectroscopy (ESCA).

4.1. Gravimetry

After each period of exposure to the plasma the sample is returned to ambient temperature and pressure and then weighed. In this way curves can be drawn of the weight loss (or gain) and the rate of weight loss per unit surface and time, as a function of exposure time.

4.2. Specific-area measurement

Measurement of the specific area provides information about the roughness, the porosity, the division and the dispersion of a solid. It is based on the theory of Brunauer *et al.* [4], namely that the adsorption of an inert gas is multilayer right from the beginning of the process.

The most common method used experimentally consists of measuring volumetrically the amounts of nitrogen adsorbed on the solid at 77 K for different equilibrium pressures. The volume of nitrogen required to cover the entire surface of the solid with a monolayer can be determined from the $V = f(P)$ isotherm (BET isotherm). However, given the nature of the materials studied, the specific areas are small even after exposure to oxygen plasma and, in this case, it is necessary to use an adsorbate whose vapour pressure is small at the temperature of liquid nitrogen. Several authors [5–7] have used xenon or krypton. We adopted the latter gas (P_0 = 232 Pa (1.8 torr)) which allows us to work at low equilibrium pressures, between 13 and 80 Pa, i.e. within the range in which the BET isotherm is valid.

The measurements are carried out in an adsorption microapparatus where the dead spaces are minimized (Fig. 2). This device is connected to two capacitive pressure captors operating between 10 and 10^5 Pa or 10^{-1} and 10^3 Pa. The vacuum in the vessel is maintained by means of a two-stage rotary pump in series with an oil diffusion pump, providing a pressure of 10^{-3} Pa. The apparatus is fitted with a greaseless bellows tap. The static leak ratio is less than 2×10^{-4} Pa sec^{-1}. The chief impurities of the krypton N 35 (Air Liquide) are xenon (< 200 p.p.m.) and water (< 5 p.p.m.).

The solid–krypton equilibrium time being about 10 to 20 min, the error on the pressure estimate is less than 0.2 Pa.

The method is as follows: the previously degassed (10^{-3} Pa) disc is placed in a bulb of known volume, V_A, which is immersed in a constant level liquid nitrogen bath. A known volume, V_M, of krypton at an initial pressure, P_i, is released into the volume, $V_M + V_A$, the equilibrium pressure settling at P_i^e.

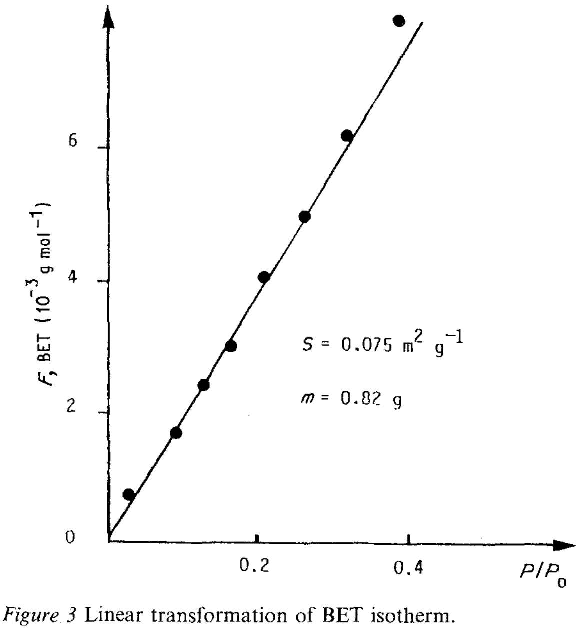

Figure 3 Linear transformation of BET isotherm.

TABLE I

Material	Treatment time (h)	Surface area ($m^2 g^{-1}$)	Analysis of the superficial layer			
SiC/SiC 1	0	8.4×10^{-3}	C $Si_{0.045}$	$O_{0.145}$	$Na_{0.015}$	
SiC/SiC 1	10	51.7×10^{-3}	-	-	-	
SiC/SiC 1	25	53×10^{-3}	C $Si_{2.5}$	O_4		
SiC/SiC 2	0	4×10^{-3}	C $C^*_{0.23}$	$Si_{0.07}$	$Si^*_{0.26}$	$O_{0.4}$
SiC/SiC 2	25	18×10^{-3}	C $Si_{0.4}$	$O_{1.2}$	$B_{0.65}$	$Na_{0.14}$
C/SiC	0	7.5×10^{-2}	C $C^*_{0.4}$	$Si_{0.16}$	$Si^*_{0.52}$	O_4
C/SiC	25	1.9×10^{-1}	C $Si_{2.4}$	$O_{4.2}$		
C/C 2D NP	0	0.2	C			
C/C 2D	0	21.7	C $Si_{3.5}$	O_7		
C/C 2D	7	1.13	C $Si_{1.6}$	O_4	$Na_{0.08}$	$Ca_{0.13}$
C/C 3D	0	31				
C/C 3D	10	1.3				

NP non protected; C* carbon carbide; Si* silicon carbide.

Taking into account the correction for the volume of gas immersed in liquid nitrogen, one determines the amount of krypton adsorbed by means of the equation for a perfect gas. With a value of $V_M = 90\,cm^3$ it is possible to measure surface areas of about $10^{-2}\,m^2$. As an example, Fig. 3 shows the linear transform of the BET isotherm for a sample with a specific area of $7.5 \times 10^{-2}\,m^2\,g^{-1}$.

4.3. ESCA analysis

ESCA analysis is performed on a VG ESCALAB MK 1. The X-ray source is the $K\alpha$ emission of aluminium or magnesium.

Each sample was analysed before and after heating at 100° C and 10^{-6} Pa. The superficial layer analysed is about 5 nm thick.

5. Results and discussion

The resistance of a material to oxidation obviously depends on its nature, on the effectiveness of the protective antioxidant layer (PAOL) which may cover the surface, as well as experimental conditions.

The experimental apparatus described earlier allows one to test the resistance to oxidation and to interpret the behaviour of the material.

The experimental results of specific area and ESCA surface analysis are given in Table I. Changes in a sample mass are studied by exposing the material to a plasma for a time corresponding to the re-entry period of the space shuttle. One can deduce the rate of attack defined as the loss of mass per square metre per minute.

5.1. SiC/SiC materials

With the first series of materials we observe a quite significant mass loss at the beginning of exposure to the oxygen plasma and then this tended to stabilize (Fig. 4a). On the other hand, another series of SiC/SiC samples shows a slight increase in mass during the same treatment (Fig. 4b).

Gulbransen *et al.* [8, 9] showed that the oxidation of SiC could correspond either to a "passive" oxidation (mass gain) or an "active" oxidation (mass loss) depending on the temperature and pressure conditions.

Active oxidation is due to the attack by oxygen on the material along with vaporization of the products formed, whereas passive oxidation corresponds to the formation of an oxide layer of SiO_2 on the surface of the sample.

The first material before exposure to the plasma has a very low specific area, at the detection limit of the apparatus. However, measurements after oxidation reveal a fairly large increase in area which depends on the exposure time. This increase may be due to the formation of a thin, slightly porous silica, as confirmed by ESCA analysis. The original disc shows a disymmetric 2p electron peak (100.7 and 102.6 eV) corresponding to two types of silicon: silicon oxide and silicon carbide. After treatment this peak becomes symmetrical, the bounding energy corresponding to that of the 2p electrons in silica. The formula of the superficial layer is then close to $C(SiO_2)_2$. At the same time, surface impurities are eliminated.

The second SiC/SiC material behaves in the same way, but with specific surface areas even smaller (4×10^{-3} and $18 \times 10^{-3}\,m^2\,g^{-1}$). ESCA analysis, however, reveals that foreign atoms have migrated towards the surface after exposure to plasma (Table I).

5.2. C/SiC materials

This material resists oxidation fairly well, as the mass loss is small after 25 h exposure. Moreover, the oxidation rate stabilizes after 6 h (Fig. 5).

The specific surface areas are always small; plasma treatment results in an increase by a factor of less than 3. ESCA analysis shows that oxidation leads to the formation of a silica layer which, according, to BET analysis, is of very low porosity (see Table I).

5.3. C/C materials

In the case of non-protected C/C, the material disappears almost completely in less than 5 min.

We then studied a first series of C/C material with an experimental PAOL. The mass loss remains high but the geometry and the appearance of the sample are unchanged. This phenomenon can be attributed to the diffusion of oxygen within the material; the oxygen can then attack either carbon fibres or the matrix [7]. During the first hours of treatment the weight decreases markedly, then it stabilizes but the sample has become very fragile (Fig. 6).

Further series of C/C materials with other PAOLs

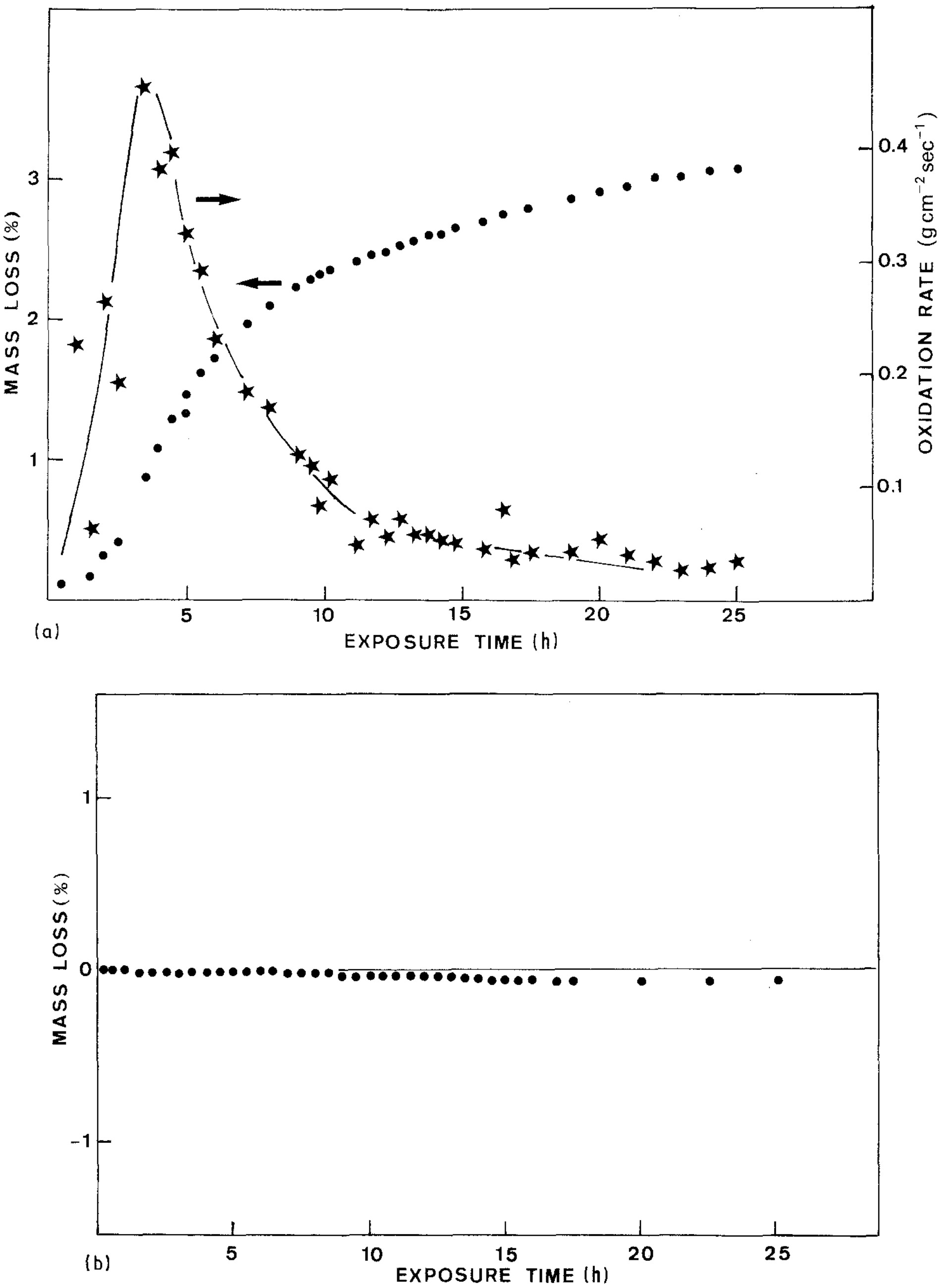

Figure 4 SiC/SiC mass loss and oxidation rate as a function of time. (a) material type I, 1250° C, O_2 10 mbar and 700 cm^3 min^{-1}; (b) material type II, 1250° C, O_2 10 mbar and 700 cm^3 min^{-1}.

are being studied; they behave very differently and resist oxidation very well.

The behaviour of the C/C specimens with PAOL of the first series can be interpreted as follows. The antioxidant layer has a BET area of 20 to 30 m^2 g^{-1} depending on the weave of the fibres. This layer is therefore very porous. After plasma treatment, the specific area decreases sharply ($\simeq 1$ m^2 g^{-1}). ESCA and BET analysis show that the protective layer consists of porous silica which, because of the temperature (1250° C) to which it is raised by the plasma, undergoes fritting. The formation of a fritted silica layer could explain the evolution of the mass loss which stabilizes after a few hours exposure.

Medford [10] proposed a model to describe the oxidation of a C/C sample with PAOL. This model takes into account the diffusion of oxygen and by-products inside the fissures of the PAOL. Depending on the experimental conditions, the kinetics will be controlled by the chemical reaction at low temperatures or by diffusion at high temperatures. In addition, it is necessary to take into account the oxidation of the PAOL to silica.

Curry *et al.* [11] reworked and improved the Medford model by considering three kinetic regimes: the chemical reaction, diffusion, and a transition zone between the two. Curry's results are shown schematically in Fig. 7.

6. Conclusion

The evolution of the mass during oxidation of the material is the result of several phenomena: the method of preparing the material; the presence of a PAOL or formation of a protective oxide layer; the presence of fissures in the protective layer.

Recently, materials were tested in an air MIP under similar conditions. The oxidation rate and the ESCA analysis are similar to the results obtained with an oxygen plasma. In the surface analysis, we find nitrogen atoms only at the highest temperature.

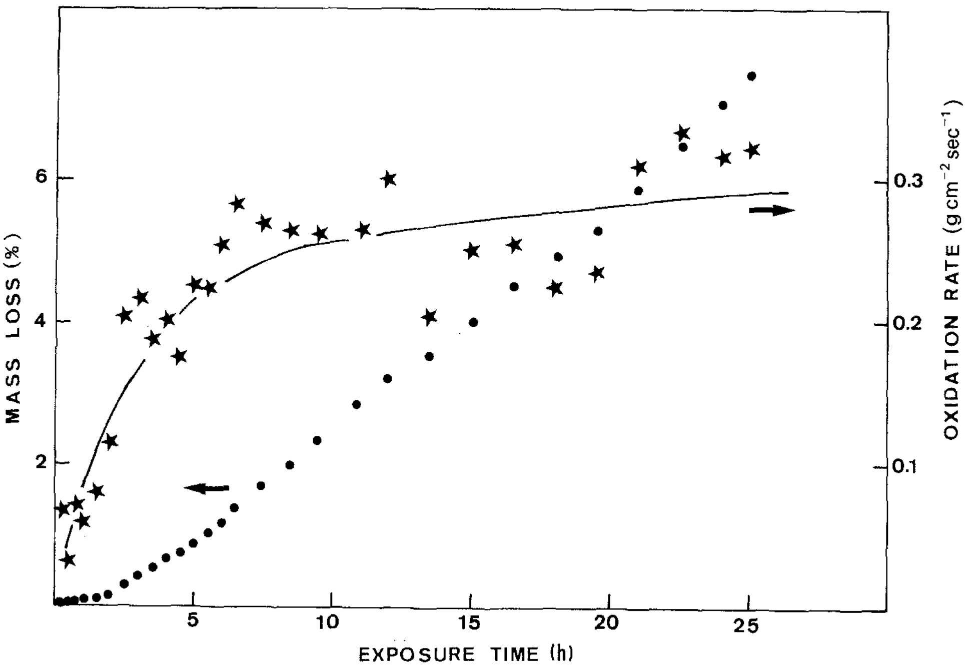

Figure 5 C/SiC mass loss and oxidation rate as a function of time; 1250° C, O_2 10 mbar and 700 cm^3 min^{-1}.

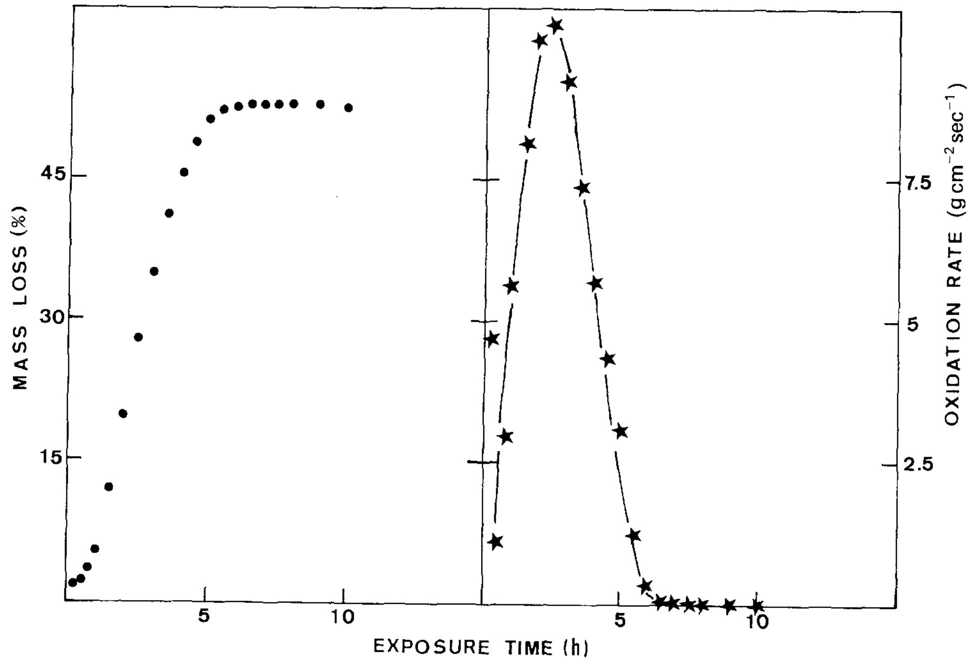

Figure 6 C/C mass loss and oxidation rate as a function of time; 1250° C, O_2 10 mbar and 700 cm^3 min^{-1}.

The specific surface areas determined by the BET method depend on the type of material and the nature of the PAOL. Attack at high temperature can lead to a sintering of the PAOL which can be seen by the diminution of the specific surface area. This sintering can favour the protection of the material against oxidation. Certain materials without PAOL can be covered by a protective oxide layer [8, 9] and, in this case, the specific surface area, which was small at first, rises slightly.

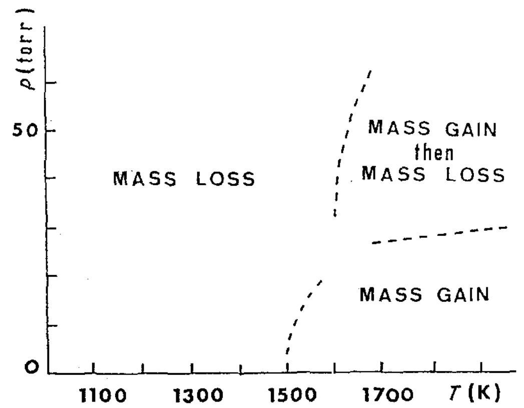

Figure 7 Reinforced carbon/carbon oxidation behaviour.

ESCA analysis allows one to follow the changes suffered by the surface layer during oxidation. For example, by studying the 2p electron peaks of silicon, one can distinguish silicon bonded to oxygen (102.7 eV) from silicon bonded to carbon (100.7 eV). This technique also indicates that migration of atoms from the bulk to the surface occurs.

The preceding techniques have been applied to samples of possible materials for the construction of the *Hermes* space shuttle. Some of the results obtained are considered industrial secrets and cannot be disclosed in this paper. For the same reason, we cannot give more details about the structure and composition of the materials studied.

The use of oxygen plasmas induced by microwaves allows the partial simulation of conditions experienced by a space vehicle during re-entry. These experiments have the advantage of being easy to do, and relatively inexpensive; they make it possible to test various materials, to analyse their evolution, and interpret the process of attack or protection of the surface.

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