JOURNAL OF MATERIALS SCIENCE 27 (1992) 3206–3210

High-temperature oxidation of silicon carbide in simulated atmospheric re-entry conditions

B. BERTON
Dassault Aviation, 78 Quai Marcel Dassault, 92214 Saint-Cloud, France

M. P. BACOS, D. DEMANGE
Office National d'Etudes et de Recherches Aérospatiales (ONERA), 29 Avenue de la Division Leclerc, 92320 Chatillon, France

J. LAHAYE
Centre de Recherches sur la Physico-Chimie des Surfaces Solides, 24 Avenue du Président Kennedy, 68200 Mulhouse, France

Oxidation tests on silicon carbide samples were carried out in a facility specifically developed at ONERA partly to simulate atmospheric re-entry conditions. Thermogravimetric data and surface analyses have shown the effect of low pressure and dissociated species on the oxidation of SiC. The transition between active and passive oxidation is well related to thermodynamic equilibrium between SiC and SiO_2 and does not seem influenced by low dissociated oxygen. On the contrary, atomic oxygen has a drastic effect on the kinetics of formation as well as the structure of the oxide layer and the phenomenon of silica vaporization.

1. Introduction

Silicon carbide is a major component of space shuttles such as *Orbiter* or *Hermès*. This material keeps its mechanical properties up to around 1400 °C and several workers verified its good resistance to oxidation in air at atmospheric pressure. However, the behaviour of SiC in simulated re-entry conditions has been little studied.

Thermal oxidation of silicon carbide occurs in two ways depending on the thermochemical conditions. At high pressure and medium temperature, SiC reacts with oxygen to form a solid layer of silica SiO_2. This layer is protective and leads to a mass gain of the material. This reaction is called passive oxidation and has been largely studied [1, 2]. At low pressure and high temperature, oxidation of silicon carbide produces the gaseous primary product SiO; this reaction is called active oxidation. In this case, the material exhibits weight loss which means erosion of the surface.

The transition between an active region and a passive region is then of special importance for the use of silicon carbide, especially in thermal protection systems. Unfortunately, the study of this transition in different gases is extremely complex and published literature is scarce.

Gulbransen *et al.* [3] studied the thermodynamical transition phenomena in comparison with Wagner's theory of silicon oxidation [4]. Three possible reactions between silicon carbide and silica were considered

$$SiC + 2SiO_2 \rightarrow 3SiO + CO \qquad (1)$$

$$SiC + SiO_2 \rightarrow C + 2SiO \qquad (2)$$

$$2SiC + SiO_2 \rightarrow 3Si + 2CO \qquad (3)$$

For each reaction, the gaseous equilibrium pressures against temperature were calculated. This is shown by the straight lines in Fig. 1. By comparison with experimental results on silicon carbide oxidation, it was concluded that the boundary line of Reaction 3 determines the transition.

The approach of Rosner and Allendorf [5] was very different. Silicon carbide filaments were oxidized under low pressures of molecular or atomic oxygen with very high flow rates ($\approx 100\ \mathrm{m\ s^{-1}}$). Their results are mostly interpreted by the phenomena of silica vaporization. With criteria different from those of Gulbransen *et al.*, the Pi–T diagram of the transition for molecular and atomic oxygen was determined (Fig. 1). According to this work, oxidation with dissociated species greatly extends the passive domain, i.e atomic oxygen would be more favourable than molecular oxygen.

The present work aimed to elucidate the behaviour of SiC in simulating re-entry conditions in order to describe thermal systems materials (C/SiC, SiC/SiC). We attempted to determine the influence of low pressure and dissociated species on the active/passive transition, on the oxidation kinetics and on the nature of the oxides produced.

2. Experimental procedure

2.1. The oxidation facility

The oxidation facility specifically developed for these tests is named the BLOX (laser oxidation bench) and is shown in Fig. 2. Its principal characteristics are:

(i) a CILAS ALCATEL CO_2 laser (1500 W) used to provide high temperature levels (up to 2000 °C) and quick heating and cooling of materials;

(ii) a test chamber (Fig. 3) where the sample is heated and submitted to the gaseous environment. The laser beam is collimated on the front face of the sample so that the area of the laser spot covers the whole sample surface;

(iii) a regulation system of pressure and gas flow which allows tests under 0.1–90 kPa with different mixtures of gas;

(iv) a microwave apparatus (2.4 GHz, 1.2 kW) for dissociating gaseous molecules into atoms (plasma);

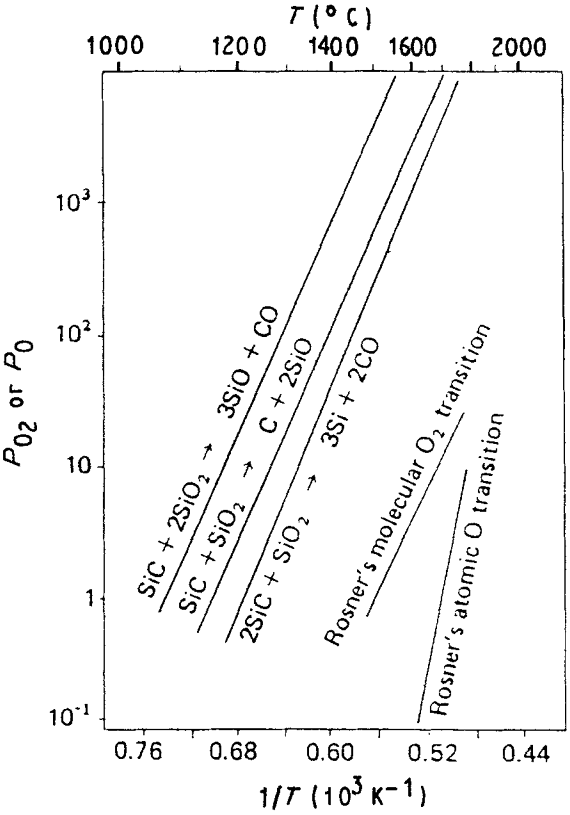

Figure 1 Thermodynamic plot of SiC/SiO_2 reactions and Rosner's transitions.

(v) three optical pyrometers (Fig. 2) for measuring temperatures of the front and rear face of the sample;

(vi) a microbalance for controlling the mass of the sample with an accuracy of 0.1 mg.

2.2. Materials tested

In order to limit the effect of porosity and chemical impurities on the oxidation kinetics of SiC [6], samples of commercial sintered α-SiC coated with a layer of chemical vapour deposited (CVD) SiC were prepared.

These samples were cylinders of 25 mm diameter and 2 mm thickness (~ 3 g). Some morphological analyses, such as optical micrographs and specific area measurements, showed that the CVD coating was regular and continuously formed with a thickness of around 20 μm [7].

2.3. Experimental conditions

The oxidation tests were performed between 1200 and 1650 °C at a constant pressure of 1 kPa. These conditions correspond to the hottest parts of the *Hermes* shuttle during re-entry. Two types of gas were used: molecular oxygen and dissociated oxygen produced by a microwave power of 400 W. Diagnosis of the BLOX plasma showed that, for this power, the atomic concentration in the area of the sample (after-glow) is quite low, around 3% or 4%. In addition to atomic and molecular oxygen, singlet oxygen and ozone may exist in relatively large amounts. For these tests, the gas velocity normal to the sample was about 10 m s^{-1}.

The different samples were submitted to a series of cycles including heating in argon from room temperature to the temperature of the experiment (~ 5 min), oxidation at constant temperature for 30 or 60 min, cooling to room temperature under argon (~ 5 min).

2.4. Measurements and analyses

During experiments, two parameters were continuously controlled: the mass of the sample and its temperature. Pyrometric temperatures are recorded

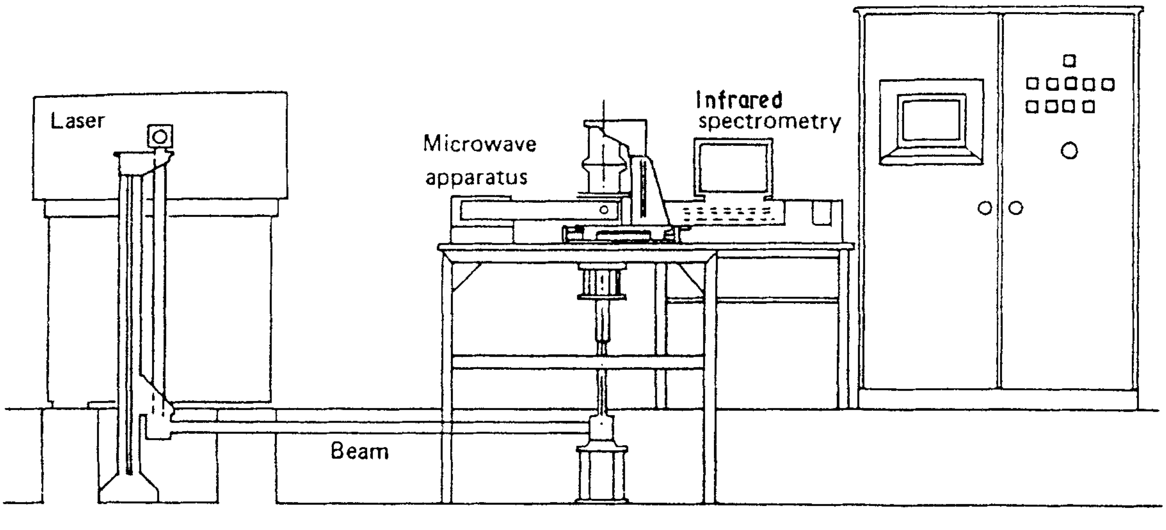

Figure 2 The laser oxidation facility (BLOX).

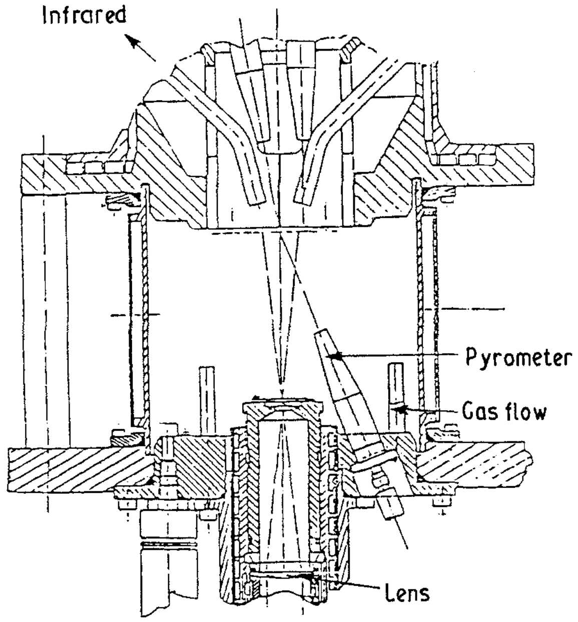

Figure 3 The test chamber.

with an emissivity of 0.8 for SiC materials. Owing to the heating by laser, some thermal gradients exist in the thickness of the sample. Indeed, the temperature difference between its two faces varies from 10 °C at 1200 °C, to 50 °C at 1500 °C.

After oxidation, surface analysis by X-ray diffraction was used to characterize the oxide layer.

3. Results and discussion

For the utilization of SiC in space, it is important to determine the regime of oxidation. The regimes of passive and active oxidation correspond to a mass gain and mass loss, respectively. The conditions of passive–active transition must be accurately determined. Fig. 4 represents the rate of oxidation after 1 h reaction under a total pressure of 1 kPa for temperatures between 1200 and 1650 °C. The vertical lines correspond to the temperatures for which the reactions between SiC and SiO_2 occur according to Gulbransen's computation (Fig. 1).

Up to 1400 °C the oxidation rate is positive (weight gain) and increases with temperature. Between 1400 and 1500 °C, the oxidation rate falls but remains positive, which means passive oxidation. This decrease is related to the crossing of the thermodynamic line of the first chemical reaction between silicon carbide and silica (Reaction 1). Between 1500 and 1570 °C, the oxidation rate still decreases to nearly zero corresponding to the crossing of the second thermodynamic line. Above 1570 °C, as the third thermodynamic line is crossed, the oxidation rate becomes negative and increases sharply in absolute value. As shown in Fig. 4, the variation of oxidation rate with temperature for dissociated oxygen is similar to that for molecular oxygen.

It appears that the transition between active and passive regime for molecular oxygen as for low dissociated oxygen is well related with the thermodynamic equilibrium of Reaction 3 between silicon carbide and

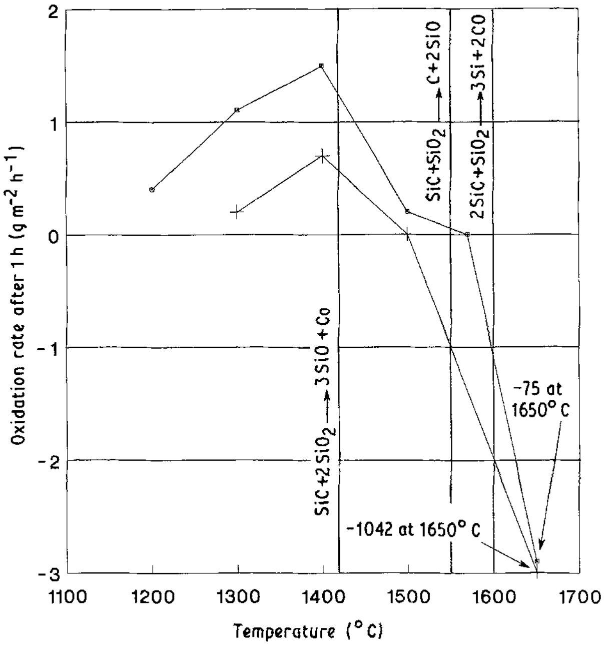

Figure 4 Temperature dependence of the oxidation rate in (■) molecular and (+) dissociated oxygen. (1 kPa).

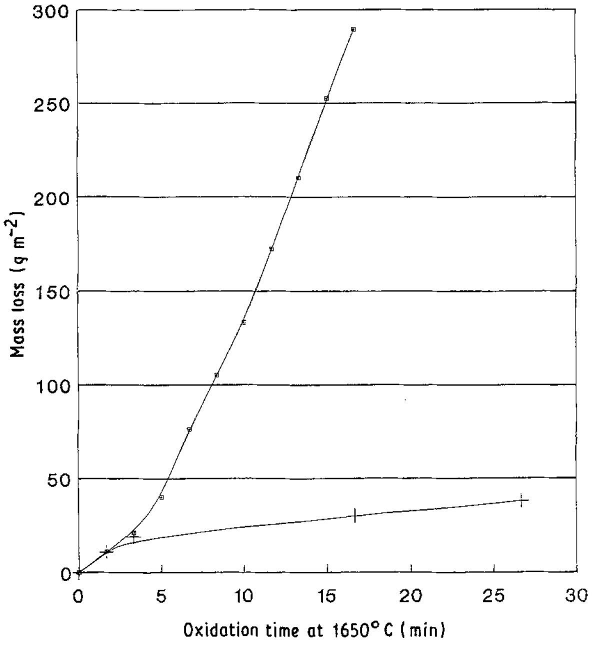

Figure 5 Mass loss curves in the active regime. (■) Atomic oxygen, (+) molecular oxygen.

silica theoretically computed. This result agrees with Gulbransen's work. In addition, before the passive–active transition, the oxidation rate starts to decrease slowly when the other two chemical reactions between SiC and SiO_2 become thermodynamically possible (intermediate zone).

3.1. Kinetics of SiC oxidation

Experimental results for a pure active regime at 1650 °C are shown in Fig. 5. Mass losses are nearly linear with time and are greatly enhanced with atomic oxygen. The rates are 0.039 g m^{-2} s^{-1} for molecular oxygen and 0.34 g m^{-2} s^{-1} for dissociated gas. Linear law has generally been observed in the active regime

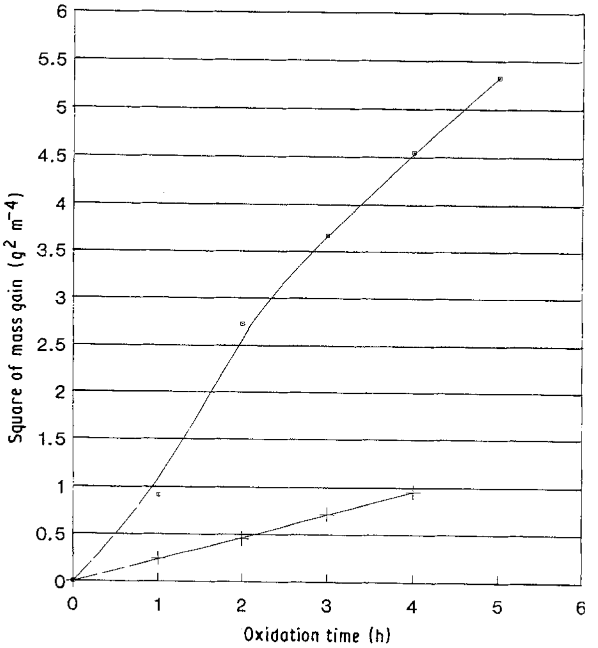

Figure 6 Oxidation isotherms in the passive area at 1300 °C (parabolic plot). (■) Molecular oxygen, (+) atomic oxygen.

[8]. As carbon and silicon atoms are considered to react from the SiC surface, the increase in mass loss rate with atomic oxygen can be compared with the oxidation of pure carbon: reactivity can be enhanced by factors between 5 and 80 for temperatures in the range 1000–1800 °C [9].

Examples of mass measurements for passive oxidation are shown in Fig. 6. The square of the mass gain is plotted against time.

This type of mass variation is related to an oxidation controlled by the solid diffusion through the oxide layer. Mathematically, the growth of the oxide layer responsible for the mass gain is expressed by the following relation: $s^2 = 2kt$, where s is the film thickness, t the time and k is the parabolic constant. This constant can be theoretically calculated from the diffusivity through silica [10].

This mathematical relation has been applied to the experimental results of the pure passive domain except in the intermediate area (Section 3.1). While the correlation is excellent up to 1300 °C, the mass gains are not purely parabolic above this temperature. The parabolic law has then to be corrected with a linear contribution. This deviation can be assumed to be the effect of silica vaporization. Indeed, some tests on pure silica samples have shown that this phenomenon is not negligible at 1350 °C under a pressure of 1 kPa [7]. Moreover, this vaporization seems to be faster under dissociated oxygen than under molecular oxygen.

The parabolic constants obtained by numerical exploitation of the experimental results are plotted on the Arrhenius diagram of Fig. 7 in comparison with the results of Fitzer and Ebi [1]. The most interesting point is the influence of the dissociated species on oxidation rate. The parabolic constant is then reduced by nearly one order of magnitude in comparison with the molecular constant. This effect can be attributed to the interactions and recombinations of atomic and excited species with the silica lattice, which slow down the diffusion. Such phenomena are observed during plasma anodization of silicon and gallium arsenide for microelectronics [11].

As already shown in Fig. 4, parabolic constants increase with temperature. For molecular oxygen, two temperature ranges are found: below 1300 °C, an activation energy of 67 kcal mol^{-1} is calculated while it is reduced to 37 kcal mol^{-1} for higher temperatures. This behaviour, also observed by Fitzer and Ebi [1], can be explained by the structure of the oxide layer (Section 3.2). For dissociated gas, an activation energy of 90 kcal mol^{-1} is calculated between 1300 and 1400 °C.

3.2. Structure of the oxide layer

X-ray diffraction analyses have been performed with a copper anticathode apparatus. For non-oxidized samples, the SiC structure of the substrate is verified and the CVD layer is found to be β-SiC.

For oxidized samples, (i) at 1200 °C, a wide diffused line is seen corresponding to amorphous silica; (ii) at 1300 °C, the peaks of cristobalite appear. They are more intense on the sample face which has been exposed to the laser beam; (iii) at 1400 °C, cristobalite peaks are stronger than at 1300 °C and the amorphous phase is reduced again. The diffraction patterns of samples from molecular oxidation and dissociated gas oxidation are nearly the same.

In view of these analyses, the change of oxidation kinetics for molecular oxygen at 1300 °C is related to the formation of cristobalite. For relatively low times of oxidation, in agreement with Fitzer and Ebi [1], the oxidation rate is reduced because the diffusion through cristobalite is more difficult than in pure amorphous silica (the lattice of cristobalite is more

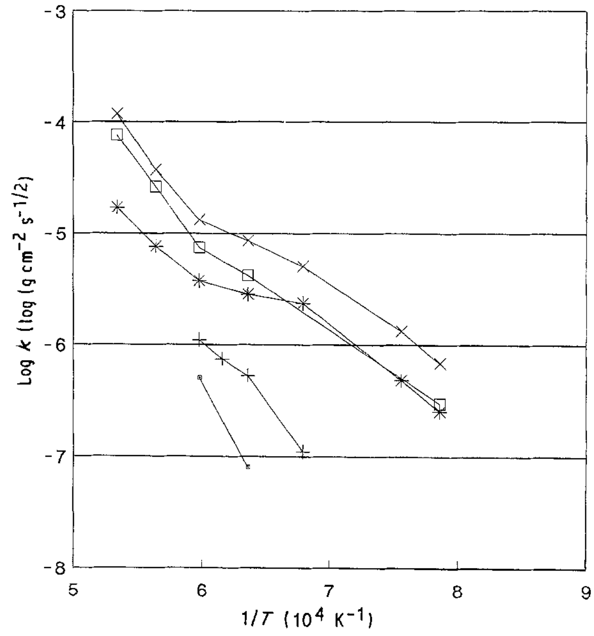

Figure 7 Arrhenius plot of parabolic constants in molecular and dissociated oxygen. (■) SiC, 1 kPa, O [7]; (+) SiC, 1 kPa, O_2 [7]; (*) Si_3N_4, 100 kPa, O_2 [1]; (□) SiC, 100 kPa, air [1]; (×) SiC, 100 kPa, O_2 [1].

compact). When the oxide layer grows, the formation of thermal stresses between cristobalite and glass cause its fracture. The transport of oxygen through these fissures is then easier and the oxidation rate is enhanced. In this case, the effect of cristobalite is harmful.

For dissociated gas oxidation, the apparently similar structure of the oxide layer confirms that the difference in kinetics is due to particular transport mechanisms of these species.

4. Conclusion

In the conditions of this study, which partly simulate atmospheric re-entry, silicon carbide is likely to undergo active oxidation. The transition occurs at around 1600 °C for 1 kPa molecular oxygen, which is coherent with the thermodynamic equilibrium between SiC and SiO_2. The transition zone does not seem to be influenced by low dissociated oxygen. Before this abrupt transition, an intermediate zone is observed where the oxidation rate is reduced due to the occurrence of Reaction 1 between SiC and SiO_2.

From a kinetic point of view, the mass loss rates in the active regime are greatly increased by dissociated oxygen. On the contrary, the parabolic mass gain rates in a passive regime are reduced when oxidized with dissociated gas. This would be due to the transport mechanisms of these species through silica. In addition, two other phenomena have a real influence on kinetics in the passive regime: (i) the transformation of the oxide layer from amorphous silica to cristobalite which initially reduces the oxidation rates, and (ii) the vaporization of this silica which becomes noticeable above 1350 °C at a pressure of 1 kPa.

References

1. E. FITZER and R. EBI, in "Silicon Carbide", Proceedings of the Third International Conference, Miami Beach, FL, 17-20 Sept 1973, edited by R. C. Marshall, J. W. Faust and C. E. Ryan (University of South Carolina Press, 1974) p. 320.
2. G. ERVIN, *J. Amer. Ceram. Soc.* **41** (1958) 347.
3. E. A. GULBRANSEN and S. A. JANSSON. *Oxid Metal* **4** (1972) 181.
4. C. WAGNER, *J. Appl. Phys.* **29** (1958) 1295.
5. D. E. ROSNER and H. D. ALLENDORF, *J. Phys. Chem.* **74** (1970) 9.
6. J. SCHLICHTING, NASA TM 76608 (1981).
7. B. BERTON, PhD thesis, University of Haute Alsace (1990).
8. E. A. GULBRANSEN, F. A. KENNETH and F. A. BRASSAROL. *J. Electrochem. Soc.* **113** (1966) 1311.
9. D. E. ROSNER and H. D. ALLENDORF, *AIAA J.* **6** (1968) 650.
10. K. MOTZFELDT, *Acta Chem. Scand.* **18** (1964) 1596.
11. S. K. GANDHI, "VLSI fabrications principales" (Wiley, 1983).

Received 12 February
and accepted 20 June 1991