Protection against oxidation of C/SiC composites: oxidation behaviour of CVD TiB₂ coated substrates

Christian Courtois, J. Desmaison, H. Tawil

► To cite this version:

Christian Courtois, J. Desmaison, H. Tawil. Protection against oxidation of C/SiC composites: oxidation behaviour of CVD TiB₂ coated substrates. Journal de Physique IV Proceedings, 1993, 03 (C9), pp.C9-843-C9-853. 10.1051/jp4:1993987 . jpa-00252429

HAL Id: jpa-00252429

<https://hal.science/jpa-00252429>

Submitted on 1 Jan 1993

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Protection against oxidation of C/SiC composites: oxidation behaviour of CVD TiB₂ coated substrates

C. Courtois⁽¹⁾, J. Desmaison⁽¹⁾ and H. Tawil⁽²⁾

⁽¹⁾ Université de Limoges, Faculté des Sciences, Laboratoire de Céramiques Nouvelles, URA CNRS 320, 123, Avenue Albert Thomas, 87060 Limoges Cedex, France

⁽²⁾ SEP, 33165 Saint-Médard-En-Jalles Cedex, France

Abstract. — Titanium diboride coatings (20 or 30 μm thick), deposited by hydrogen reduction of TiCl₄ and BCl₃, are protecting C/SiC substrates against oxidation up to 1100 °C. The oxidation of TiB₂ leads to the formation of a protective low viscosity B₂O₃ glass filling the cracks of the primary CVD-SiC oxygen barrier. Above this temperature, the rapid consumption of the B₂O₃ glass by vaporization limits the duration of the protection system. A comprehensive description of the oxidation mechanism, based on a complementary experimental study of B₂O₃ evaporation, is presented.

1. Introduction.

The use of C/SiC composites, as structural materials for aerospace applications at high temperature involves the development of a reliable oxidation protection [1-3]. The current oxidation protection system is based on the use of a CVD-SiC coating, as primary oxygen barrier, coupled with an internal inhibitor. Since coatings are normally obtained at elevated temperatures, microcracked barriers result from thermal mismatch stresses.

Therefore, in order to create a full range oxidation protection system, it is necessary to seal the cracks in the range from the oxidation threshold for the C-SiC composite (< 500 °C) to the microcracking temperature of the silicon carbide coating ($700 < T < 1000$ °C).

Boron has proved to be the most important constituent for providing self-healing capabilities in coating systems since it oxidizes to give B₂O₃ (m.p. 450 °C) which can fill cracks and reduce permeation of oxidants.

The main aim of this work was to test a new oxidation protection system based on the use of an outer layer of titanium diboride able to produce a B₂O₃ glass.

A previous publication [4] dealt with the chemical vapor deposition of TiB₂ and presented preliminary results concerning the oxidation behaviour of C/SiC samples.

The purpose of this paper is to analyse in more detail the oxidation mechanism of such coated specimens.

2. Experimental.

2.1 COATINGS. — Titanium diboride was deposited by hydrogen reduction of TiCl₄ and BCl₃.

Fig. 1. — Non isothermal oxidation curves for Al_2O_3 and C/SiC samples coated with a $20\ \mu\text{m}$ thick deposit.

The deposition conditions are those defined in [4] :

- temperature: $800\ ^\circ\text{C}$;
- total pressure: $3.28 \times 10^3\ \text{Pa}$;
- H/Cl ratio: 10;
- Ti/B ratio: 0.5;
- thickness: ≈ 20 or $\approx 30\ \mu\text{m}$.

2.2 SUBSTRATES. — $5 \times 5 \times 5\ \text{mm}^3$ cubes of alumina (inert substrate) or C/SiC composite (coated with a $30\ \mu\text{m}$ thick layer of silicon carbide).

The oxidation kinetics of TiB_2 coated and uncoated specimens in pure flowing (5 l/h) oxygen (Prodair, 99,998%) were determined as a function of temperature using a symmetrical continuous recording thermobalance (MTB 50, Setaram, France). Samples were placed in an alumina crucible.

After oxidation, the quenched oxide layers were examined by optical scanning electron microscopy (SEM) and characterized by X-ray diffraction (XRD).

3. Results and discussion.

3.1 OXIDATION KINETICS OF COATED Al_2O_3 AND C/SiC SUBSTRATES. — Experiments were conducted with alumina and C/SiC substrates both coated with a $20\ \mu\text{m}$ thick layer of TiB_2 . The kinetic curves were obtained by plotting the weight change per unit area of reactive surface $\Delta m/S\ (\text{g}/\text{cm}^2)$, the relative weight change $\Delta m/m_o$ (m_o refers to the initial mass) or the fractional weight change ($\Delta m/\Delta m_\infty = \alpha$) vs. time. The weight gain Δm_∞ corresponds to the complete oxidation of TiB_2 according to the reaction (1) without any volatilization of B_2O_3 .

The non-isothermal oxidation curves (Fig. 1) show that reaction (1) becomes noticeable above 500 °C.

The isothermal kinetics indicate a passive behaviour below 1100 °C (Fig. 2). Above this temperature, the curves exhibit a maximum due to the vaporization of B₂O₃(2).

Fig. 2. — Oxidation kinetics of TiB₂ coated substrates: a) Al₂O₃; b) C/SiC.

Only a slight behaviour difference is observed between alumina and C/SiC substrates.

Figure 3, which compares the oxidation of the coated and uncoated substrates, confirms the protectiveness of the coating below 1100 °C. Indeed, the coating suppresses the weight losses due to the internal oxidation of the carbon fibers.

Fig. 3. — Comparison of the oxidation behaviour of coated and uncoated C/SiC substrates ($600 < T < 1000^{\circ}\text{C}$).

Fig. 4. — Influence of the TiB_2 coating thickness on oxidation protectiveness.

At higher temperatures, the influence of the thickness of the TiB_2 coating has been tested. For example at 1300°C (Fig. 4), the increase in thickness ($18\text{ }\mu\text{m} \rightarrow 31\text{ }\mu\text{m}$) of the coating results in a slight efficiency increase of the passive oxidation behaviour.

Therefore, in order to obtain a comprehensive understanding of the oxidation behaviour in the explored temperature range, it is necessary to determine the exact contribution of the B_2O_3 volatilization weight loss.

3.2 VOLATILIZATION KINETICS OF B₂O₃. — Due to the simultaneous oxide formation and vaporization of B₂O₃, the oxidation rate can be described as the sum of a parabolic diffusion-controlled scale thickening (x) and a time-dependent vaporization loss:

$$dx/dt = k_p/x - k_v \quad (3)$$

where k_p and k_v are respectively the parabolic rate constant and the rate constant for the vaporization loss. The first period of oxidation should be determined by a parabolic rate law because $k_p/x \gg k_v$. After extended oxidation, however, a steady state is established. It is characterized by the equality of the two terms on the right hand side of the equation. This means that:

$$dx/dt = 0 \quad (4)$$

and

$$x_{\max} = k_p/k_v \quad (5)$$

In thermogravimetric measurements of oxidation rates, this leads under the steady state conditions, to a continuous weight loss of the specimens. This behaviour explains the shape of the kinetic curves of figure 2. It has already been observed in other reactions characterized by the formation of compounds of appreciable volatility [5-7].

The maximum rate of evaporation of component i from a free surface into a vacuum is given by the Hertz-Langmuir equation:

$$k_v = A a_i p_i (M_i/T)^{1/2} \quad (6)$$

where: A is a constant, a_i is the evaporation coefficient ($a_i < 1$), p_i is the vapor pressure of i above the sample, and M_i is the molecular weight of i .

It should be emphasized that equation (6) is derived on the assumption that none of the evaporating molecules returns to the surface. As a rough guide, back reflection of escaping molecules will not be significant at pressures below 0.1-1 torr. Under these conditions the evaporation rate is controlled by the interface reaction rate.

A higher pressures, back-reflection reduces the vaporization loss relative to that predicted from the surface processes. The evaporation molecules may also form a boundary layer of thickness δ next to the surface. If the rate of evaporation is controlled by transport in the boundary layer, the flux J away from the surface of the melt may be defined by [8]:

$$J = -D dc/dx = D [(C_i - C_\infty) / \delta] \quad (7)$$

where D is the diffusion coefficient, C_i is the equilibrium concentration of component at the interface and C_∞ is the concentration at the external interface of the boundary layer ($C_\infty \neq 0$).

Because of this boundary layer of gaseous oxide molecules, the reaction conditions in general become a critical parameter in oxidation at atmospheric pressure where oxide volatilization occurs. Indeed, the evaporation rate becomes a complex function of the gas pressure, gas flow over the melt, geometry of the reactor... This explains why very different data may be found in the literature [8].

For all these reasons volatilization experiments were made in the thermobalance in the same experimental conditions as the oxidation runs, in order to determine the rate of evaporation.

Fig. 5. — Isothermal volatilization kinetics of B_2O_3 powder.

A pure and anhydrous B_2O_3 powder (99.998%, Aldrich chemical company, Inc) was placed in the same Al_2O_3 crucible as C/SiC substrates. Weight losses were plotted vs. time for several temperatures (Fig. 5).

The volatilization of B_2O_3 becomes noticeable above 900 °C. Up to 1100 °C, the rate of evaporation is approximatively constant for a given temperature. Above 1100 °C, the kinetic curves are decelerated suggesting either that the simple diffusion approach (Eq. (7)) is no longer valid or that the thickness of the boundary layer is increasing with time.

The corresponding Arrhenius plot (Fig. 6) leads to an apparent activation energy of evaporation ($E \approx 180$ kJ/mol) in accordance with Tsapuk's previous work [9]. Nevertheless, the evaporation rates determined in the present study are approximatively two orders smaller.

Fig. 6. — Arrhenius plot for B_2O_3 evaporation.

3.3 CALCULATED OXIDE GROWTH KINETICS.

Influence of the temperature. — We are now able to take into account the effect of vaporization on the global oxidation rate. Indeed, the contribution to the weight gain of reaction (1) can be calculated by summing point by point the weight losses derived from figure 5 and the experimental weight gain determined from figure 2:

$$\Delta m/S = \Delta m/S_{(\text{experimental})} - \Delta m/S_{(\text{volatilization})} \quad (8)$$

For the two types of substrates, the calculated curves (Fig. 7) present a parabolic type shape (Fig. 8), except around $T = 800^\circ\text{C}$ where they exhibit a cubic form (Fig. 9). Such a behaviour was previously observed by Münster [10] who attributed this evolution to a morphological transformation of the oxide layer. In the case of coated C/SiC substrates the transitory kinetic domain extends up to 900°C (Figs. 8 and 9).

Fig. 7. — Isothermal weight gains calculated after equation (8): a) Al₂O₃; b) C/SiC.

Fig. 8. — Parabolic plot of the calculated weight gain per unit area vs. time for TiB_2 oxidation.

Fig. 9. — Cubic plot of the calculated weight gain per unit time vs. time for TiB_2 oxidation at $T = 800^\circ\text{C}$.

No significant difference between the two substrates is observed. By extension, this means that the internal oxidation of the carbon fibers is negligible in the upper temperature region ($T > 900^\circ\text{C}$). The apparent activation energy determined from the Arrhenius plot of figure 10 ($E \approx 102 \text{ kJ/mol}$) is similar to that ($E \approx 93.6 \text{ kJ/mol}$) obtained by Münster [10]. In contrast, the value estimated in the lower temperature range, from a too limited number of data, is smaller (present work: $E \approx 75 \text{ kJ/mol}$, Münster [10]: $E \approx 106 \text{ kJ/mol}$).

Fig. 10. — Temperature dependence of the calculated parabolic constant for TiB₂ oxidation.

4. Nature and morphology of the reaction products.

Polished cross-sections of the reaction products are observed after 24 h oxidation.

4.1 ALUMINA SUBSTRATES. — Before the total oxidation of the TiB₂ coating, we observe an internal compact polyphase oxide (B₂O₃ + TiO₂) sublayer and an external non-protective porous rutile scale. This external layer results from the vaporization of B₂O₃, and is only observed above 600 °C. Its thickness, porosity and crystallinity (rutile form above 900 °C) increase with the oxidation temperature. Above 1000 °C, after the total consumption of TiB₂ and volatilization of B₂O₃, only the porous and non-protective TiO₂ scale is observed. A slight diffusion of boron in alumina was revealed by electron microanalysis and the formation of borooaluminate (2 Al₂O₃·B₂O₃ and 9 Al₂O₃·B₂O₃) phases was detected by XRD.

4.2 C/SiC SUBSTRATES. — The results, for different oxidation temperatures, are summarized on figure 11 for C/SiC substrates.

The nature and structure of the oxide layers are the same as for alumina substrates as long as a thin TiB₂ layer remains near the substrate. After the total consumption of TiB₂ ($T > 1000$ °C and 24 h oxidation time), important modifications are observed. Rutile (TiO₂) and titanium suboxide (Ti₂O₃) are detected. At 1300 °C, the polycrystalline oxide phase is surrounded by a borosilicate glass resulting from a slight oxidation of the CVD SiC sublayer (Fig. 11).

Therefore, it is clear that at high temperature, due to the rapid oxidation of the TiB₂ CVD coating (Figs. 2 and 4), the kinetic behaviour is directly linked to the transport properties and the thickness of the B₂O₃ glass scale (Fig. 4). After total vaporization of B₂O₃, the porous TiO₂ layer, present at the surface of the C/SiC substrates, no longer prevents the internal oxidation of carbon fibers (Fig. 4).

Fig. 11. — Nature and morphology of oxidation products in the case of C/SiC substrates.

5. Conclusion.

This work provides a better understanding of the oxidation mechanism of TiB_2 coated C/SiC composites.

Indeed, the protectiveness of C/SiC composites coated with TiB_2 occurs as long as B_2O_3 is still present in the oxide outer layer. Below 1100 °C, it acts as a low viscosity diffusion barrier having efficient healing capabilities of the primary CVD-SiC oxygen barrier. Above this temperature, the rapid consumption of the B_2O_3 glass by vaporization, limits the efficiency of the protection.

Acknowledgements.

The authors would like to thank B. Soulestin and D. Tetard for assistance in designing the CVD equipment, and D. Pezet and H. Lemerrier for their contribution to this work.

References

- [1] DESMAISON J., *Werskst. Korros.* **41** (1990) 749.
- [2] KNIGHTS C.F., New materials and their Applications 1990, Int. Phys. Conf. Ser. N° 111, D. Holland Ed. (Institute of Physics, Bristol, England, 1990) p. 163.
- [3] STRIFE J.R., SHEEHAN J.E., *Am. Ceram. Soc. Bull.* **67** (1988) 369.
- [4] COURTOIS C., DESMAISON J., TAWIL H., *J. Phys. IV* **1** (1991) C2-657.
- [5] KOFSTAD P., High temperature oxidation of metals (John Wiley, New York, 1966).
- [6] KOFSTAD P., High temperature materials corrosion in coal gasification atmospheres, J.F. Norton Ed. (Elsevier, London, 1984) p. 1.
- [7] HAUFFE K., HINRICHS, Oxidation of metals and alloys ASM Ed. (American Society of metals and alloys, American Society for Metal, Metals Park, Ohio, 1977) p. 87.
- [8] CABLE M., FERNANDES M.H.V., *Glass Technol.* **28** (1987) 135.
- [9] TSAPUK A.K., PODOBEDA L.G., KOVALEVSKII N.N., *Poroshk. Metall.* **183** (1978) 51.
- [10] MÜNSTER A., *Z. Phys. Chem. N.F.* **25** (1960) 116.