

Modification of the oxidation behaviour of $\text{Si}_3\text{N}_4\text{-TiB}_2$ composites by PECVD alumina coatings

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Abstract

A nearly fully dense (>98%) electroconductive silicon nitride—35 vol.% titanium diboride composite was obtained by hot isostatic pressing (HIP) in presence of a low content of sintering aids (0.5 wt.% Y_2O_3 + 0.25 wt.% Al_2O_3). To improve the oxidation behaviour of this composite material, a 3- μm thick protective coating of aluminium oxide was deposited on cubic samples (4 mm \times 4 mm \times 4 mm) by microwave plasma-enhanced chemical vapor deposition (PECVD) using an oxygen plasma and an organometallic precursor (trimethylaluminium). SEM images demonstrated that the coating was homogeneously distributed on the external surface of the specimens.

Non-isothermal and isothermal oxidation tests were carried out with a Setaram Microbalance under pure flowing oxygen (10 L/h) on both uncoated and coated $\text{Si}_3\text{N}_4\text{-TiB}_2$ samples. In the case of non-isothermal oxidation of a substrate without coating, the reaction started at 600 °C. Between 1100 and 1350 °C, a plateau was observed and above 1350 °C the weight gain increased significantly. In presence of an Al_2O_3 coating, the composite started to oxidize at higher temperature (1200 °C). Isothermal kinetics recorded for 24 h, at 1350 and 1400 °C, revealed that the presence of the Al_2O_3 coating improved drastically the oxidation resistance and changed the shape of the curves from globally parabolic to almost logarithmic. An explanation of this protective behaviour, based on the characterization by XRD, SEM and EDS of the reaction products, is proposed.

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1. Introduction

Advanced non-oxide ceramics (Si_3N_4 , SiC, AlN, Sialons) have outstanding properties such as high strength, toughness and thermal stability as well as thermal shock and oxidation resistance at elevated temperatures under aggressive environments. They may be used for several applications like engines and aerospace components. One of the limiting factors for the development of these materials is their shaping into complex parts. A possible solution is the use of electron discharge machining (EDM), which necessitates the incorporation of a suitable content of electroconductive secondary phases, such as borides, carbides or nitrides of transition metals, allowing to reach the percolation threshold.^{1–4}

However, in general, the addition of these more reactive phases is degrading the oxidation behaviour. In the case of the oxidation of $\text{Si}_3\text{N}_4\text{-TiB}_2$ composites, the evaporation of the liquid oxide B_2O_3 and the formation of a low viscosity glassy borosilicate layer are facilitating the inward transport of the reactive oxygen gas.^{1,3,5–7} In previous works, devoted to similar materials, an improvement of the oxidation resistance has been achieved by introducing an alumina former component in the composite, such as AlN in the case of SiC–TiB₂. The ternary composite AlN–SiC–TiB₂ forms a high viscosity glassy aluminoborosilicate layer, which can contain mullite and/or aluminoborate phases, which reduce the evaporation of boria.^{1,8}

The aim of the present work was to test an alternative route consisting in coating the binary $\text{Si}_3\text{N}_4\text{-TiB}_2$ composite with a sacrificial alumina layer rather than producing a ternary material.

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2. Experimental procedure

2.1. Composite elaboration

A nearly dense electroconductive silicon nitride—35-vol.% titanium diboride composite was produced by Hot Isostatic Pressing (HIP) in presence of a low content of sintering additives at a temperature (1710 °C), which limited the decomposition of silicon nitride and the reaction between powders. The two main powders (65% Si₃N₄ and 35 vol.% TiB₂) and aids (0.5 wt.% Y₂O₃, 0.25 wt.% Al₂O₃) were mixed in alcohol with ultrasonic assistance. The mixture was then dried, sieved at 32 μm and cold isostatically pressed at 200 MPa. The green moulded material was placed inside a silica container and degassed in vacuum at 500 °C for 10 h. The container was sealed and hiped at 1710 °C, 185 MPa, in an ABC ALSTHOM Atlantique press, for one-hour dwell time. A value of 98% relative density was reached.⁵

2.2. Deposition system

The alumina films were deposited on composite substrate cubes (4 mm × 4 mm × 4 mm) by a plasma enhanced chemical vapor deposition (PECVD) technique suitable for high rate deposition on complexes surfaces. Two runs were realized by twisting the sample in order to coat homogeneously the opposite faces. Fig. 1 presents the reactor used. An oxygen microwave plasma was created in a 255 mm diameter quartz tube using a 500 mm diameter applicator. The impedance was matched with two tuner stubs.

Contrary to the direct configuration processes, the samples were located in the deposition chamber far from about 20 cm of the center of the discharge, to place them in the close discharge afterglow. The deposition chamber and the quartz

tube had the same diameter. Trimethylaluminium (TMA) was injected by a ring shape injector located at four centimeters above the substrate holder which was heated up to 800 °C and 100 V RF biased. The TMA gas was carried in the reactor by a flow of argon bubbling through the liquid precursor.

The Si₃N₄–TiB₂ cubic samples, were polished to 1 μm and cleaned with acetone and ethanol with ultrasonic assistance for 5 min. A flow rate of 125 sccm for O₂ and of 3 sccm for TMA and 1 Pa pressure allowed to reach deposition rates of about 250 nm/min. The substrate holder was heated to 800 °C and deposition occurred during 10 min on each side.

The experimental conditions were chosen in order to deposit a stoichiometric film of alumina by limiting the incorporation of impurities like OH groups or reaction by-products.⁹

2.3. Oxidation tests and characterization of the reaction products

The oxidation behaviour was determined on coated and uncoated substrates in flowing oxygen at atmospheric pressure as a function of temperature and time using a Setaram microbalance. The non-isothermal oxidation tests were performed from room temperature up to 1400 °C with a heating rate of 3 °C/min.

In the isothermal oxidation tests at 1350 and 1400 °C for 24 h, the furnace was heated up to the oxidation temperature while the crucible, containing the sample, was kept under protective argon atmosphere in the cold zone with a magnetic device to avoid any preliminary oxidation. When the selected temperature was reached, the sample was moved into the hot zone after the introduction of oxygen.

Microstructural analysis of the surfaces and cross sections of samples, before and after oxidation, were carried out by

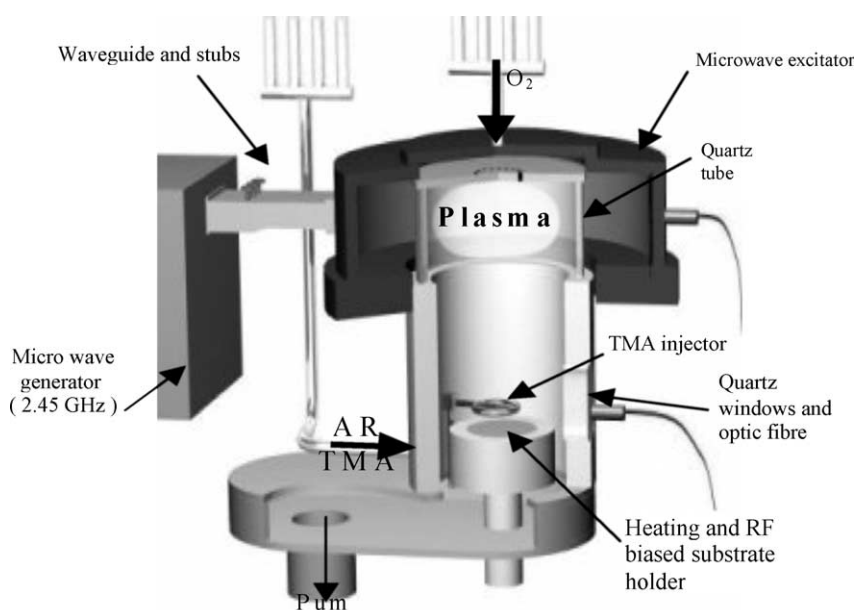


Fig. 1. PECVD reactor.

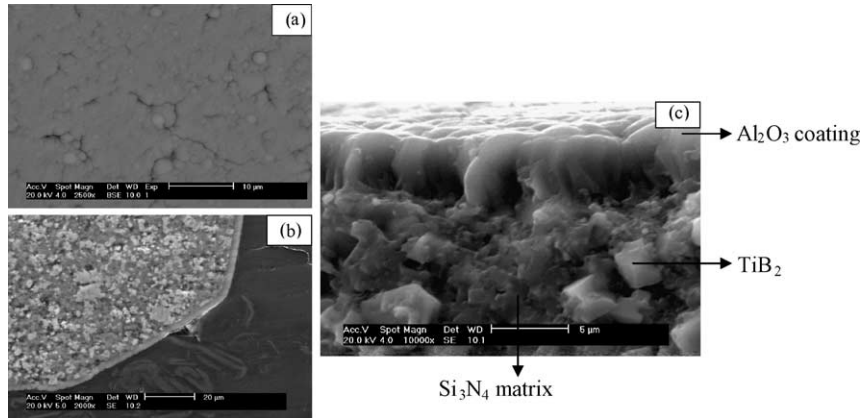


Fig. 2. SEM observations of an Al_2O_3 coated Si_3N_4 - TiB_2 composite: (a) surface, (b) polished cross section, (c) fracture.

SEM (Philips XL 30) and EDS. The nature of the reaction products was determined by XRD.

3. Results

3.1. Characterization of alumina-coated samples before oxidation

The microstructure of an alumina-coated Si_3N_4 - TiB_2 composite sample is shown on Fig. 2. The surface of the Al_2O_3 coating was relatively rough and exhibited microcracks (Fig. 2a) and a cauliflower-like structure (Fig. 2a and c). Its homogeneous thickness was close to $3\ \mu\text{m}$ (Fig. 2b and c). The composite substrate was composed of white TiB_2 grains homogeneously distributed inside a gray Si_3N_4 matrix (Fig. 2b and c).

3.2. Non-isothermal and isothermal oxidation curves

The oxidation behaviour of the Si_3N_4 - TiB_2 ceramic composite with and without coating was both tested in non-isothermal (Fig. 3a) and isothermal (Fig. 3b) conditions.

The non-isothermal oxidation of the uncoated Si_3N_4 - TiB_2 sample started at approximately $600\ ^\circ\text{C}$. Nevertheless, the weight gain slowed down and stopped between $1100\ ^\circ\text{C}$ and $1350\ ^\circ\text{C}$. Above this temperature, the weight gain increased

rapidly (Fig. 3a). The coated sample showed no weight gain up to $1150\ ^\circ\text{C}$. Then, a significant weight gain increase occurred (Fig. 3a).

Isothermal kinetics recorded for 24 h, at 1350 and $1400\ ^\circ\text{C}$, revealed that the presence of the Al_2O_3 coating improved drastically the oxidation resistance and changed the shape of the curves from globally parabolic to logarithmic¹⁰ (Fig. 3b).

3.3. Characterization of alumina-coated samples after oxidation

SEM micrographs, of the uncoated sample surface after non-isothermal oxidation in the temperature range 20 – $1400\ ^\circ\text{C}$ (Fig. 4), showed the formation of a regular network of droplets of glassy phase. Between them, the surface had a micro-porous aspect.

The coated sample, oxidized in the same conditions (Fig. 5), had a glassy phase covering more homogeneously the surface of the composite. An EDS analysis revealed the presence of embedded TiO_2 crystals within the glassy film.

SEM cross sections were made by grinding down one face of the cubic samples treated at 1350 and $1400\ ^\circ\text{C}$ (Fig. 8) in isothermal conditions (24 h). The estimated thickness of the oxidized layer was much smaller in the case of coated specimens. At $1350\ ^\circ\text{C}$, the oxidized thickness decreased from 48 to $12\ \mu\text{m}$ for the uncoated and the coated composite, respectively.

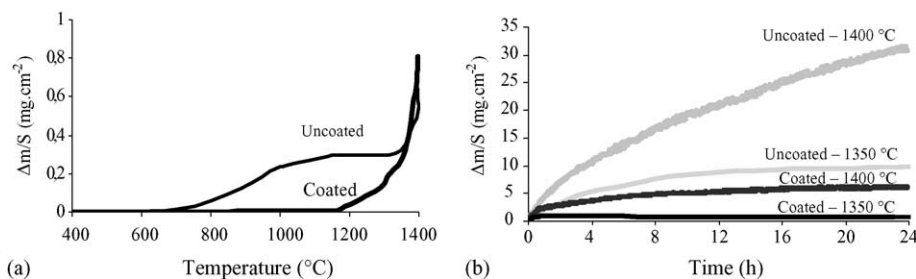


Fig. 3. Oxidation curves in flowing oxygen ($10\ \text{L/h}$) for coated and uncoated Si_3N_4 - TiB_2 samples: (a) non-isothermal conditions and (b) isothermal kinetics for 24 h.

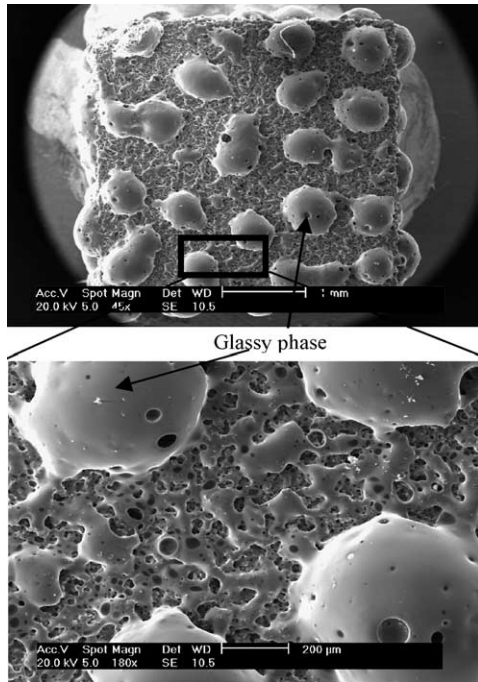


Fig. 4. SEM image of the surface of a non-isothermally oxidized $\text{Si}_3\text{N}_4\text{-TiB}_2$ composite from 20 to 1400°C in 24 h.

Complementary observations had been conducted by following the recession of the non-oxidized core of thin uncoated and coated platelets (approximately 1-mm thick) of composite, after 24 h oxidation, at 1350 and 1400°C . The results shown in Figs. 6 and 7 confirmed the important reduction of reactivity of the coated samples.

The oxidized layer at the surface of non-coated samples contains pores distributed throughout its volume. Conversely, for coated substrates, they are mainly located at the interface

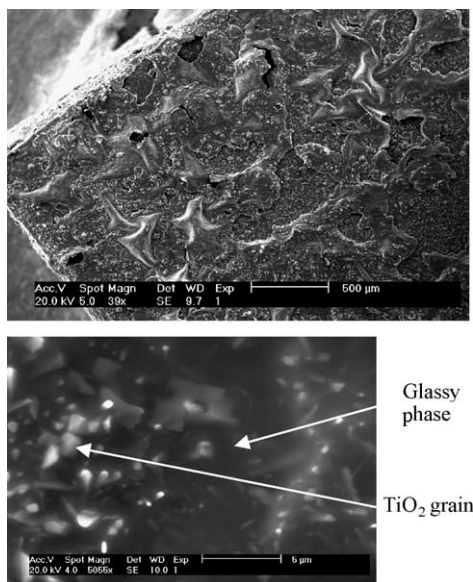


Fig. 5. SEM image of the surface of a non-isothermally oxidized $\text{Si}_3\text{N}_4\text{-TiB}_2$ composite with Al_2O_3 coat from 20 to 1400°C in 24 h.

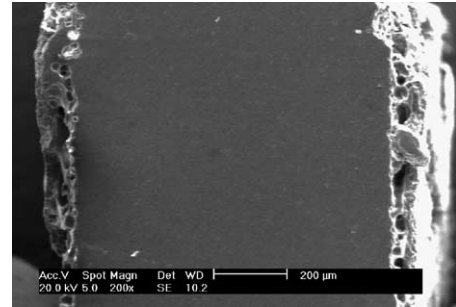


Fig. 6. Uncoated oxidized $\text{Si}_3\text{N}_4\text{-TiB}_2$ platelets at 1350°C , $71\ \mu\text{m}$ recession.

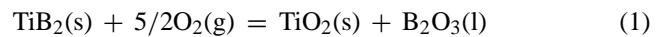
between the oxidized scale and the non-oxidized composite (Fig. 8).

EDS analysis of the coated sample, after 24 h oxidation at 1400°C , revealed two zones (Fig. 9): (1) an internal porous glassy oxide sublayer containing silicon, aluminum and oxygen but no titanium; (2) an external non-porous glassy oxide layer in which TiO_2 crystals were embedded.

4. Discussion

4.1. Oxidation of uncoated $\text{Si}_3\text{N}_4\text{-TiB}_2$ composite

The high-temperature oxidation behaviour of a hot isostatically pressed silicon nitride—35 vol.% titanium diboride ceramic composite has already been studied.⁵ From 600 to 1000°C , the preferential oxidation of the TiB_2 grains occurred according to:



with formation of rutile and boron sesquioxide.

From 1000 to 1300°C , the vaporization of B_2O_3 became important. At 1300°C , it was estimated that 85 wt.% of this oxide had evaporated after 24 h. Also, the superficial Si_3N_4 grains were progressively involved in the oxidation process mainly via a very thin grain boundary film containing silica (and additives), which could react with B_2O_3 to form a borosilicate glass Eq. (2):

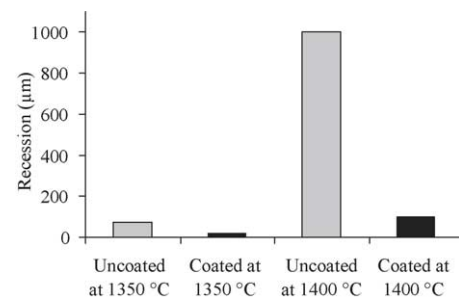
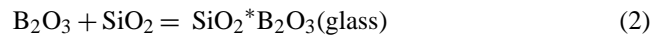


Fig. 7. Recession graphic for uncoated and coated $\text{Si}_3\text{N}_4\text{-TiB}_2$ at 1350 and 1400°C .

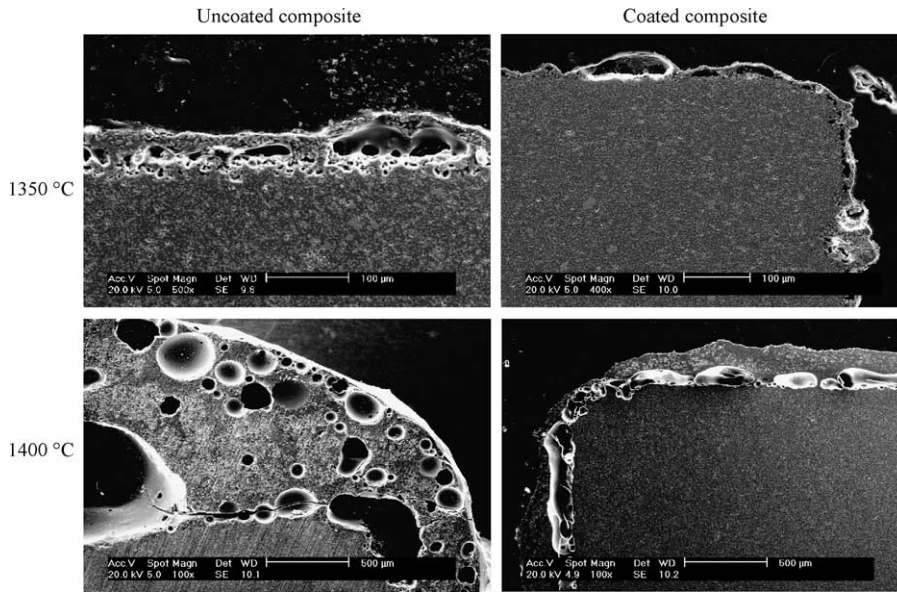
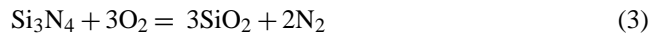


Fig. 8. SEM cross sections of uncoated and coated $\text{Si}_3\text{N}_4\text{-TiB}_2$ samples oxidized for 24 h at 1350 and 1400 °C.

This glass, which covered the surface and embedded the TiO_2 crystals, limited the access of oxygen to the TiB_2 grains and led to logarithmic kinetics by drastic reduction of the effective reactive area. This phenomenon could also explain the presence of a plateau on Fig. 3a for the uncoated composite.

Above 1300 °C, the oxidation rate was rapid during the first hours due to the simultaneous oxidation of TiB_2 Eq. (1)

and Si_3N_4 grains Eq. (3):



and the formation of a low protective oxides film. Indeed, both the TiO_2 crystals and the borosilicate glass droplets originating in a low wetting behaviour (Fig. 4), did not cover

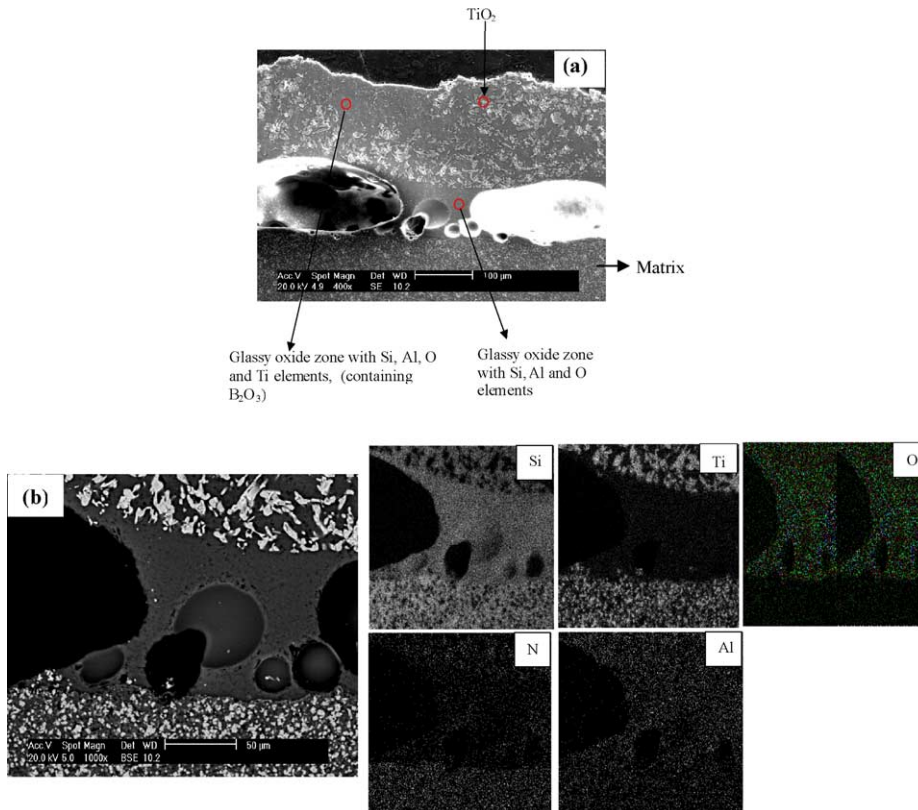


Fig. 9. (a) SEM cross section and (b) EDS maps for different elements, at 1400 °C, 24 h oxidation, of a coated $\text{Si}_3\text{N}_4\text{-TiB}_2$ ceramic composite.

homogeneously the surface of the oxidized composite sample. For longer times, the thickness of the scale increased making the inward migration of oxygen and the outward transport of the gaseous by-products (N_2 and B_2O_3) more difficult, as shown by the formation of bubbles (Fig. 8). As a result, the oxidation rate decreased with time and the overall shape of the kinetics became parabolic.

4.2. Influence of an Al_2O_3 coating on the oxidation behaviour

For the lower temperatures ($T < 1200^\circ C$) the alumina film acted as an efficient diffusion barrier limiting the oxygen access to the surface of the composite. This protective effect resulted in the improvement of the oxidation resistance observed in the non-isothermal tests (Fig. 3a). Above this temperature, the characterization of the reaction products showed that the Al_2O_3 film was progressively consumed. This consumption, becoming rapid above $1300^\circ C$, led to the dispersion of Al in all the volume of the oxidized scale (Fig. 9) and the formation of a high viscosity aluminoborosilicate glassy phase. This phenomenon had two main effects: the suppression of droplets (Fig. 5) and the trapping of the gaseous species (N_2 and B_2O_3) near the inner composite/oxides interface (Figs. 8 and 9). As a consequence, the oxides scale was assuring an improved protection to oxidation thanks to a better coverage of the substrate and a decrease of the inward diffusion rate of the oxygen reactive species and of the outward transport of the gaseous products.

The reduction of the reactivity of the coated samples was exhibited both by the evolution of the shape of the isothermal kinetics and of the thickness of the oxidized scales (Figs. 3b and 8).

By comparing the experimental weight gain and the calculated one based on the substrate recession, an estimation of the quantity of trapped B_2O_3 was obtained (Table 1). In fact, two extreme hypotheses have been put forward:

- either all the oxides formed (TiO_2 B_2O_3 SiO_2) according to Eqs. (1) and (3) were taken into account during the computation of the weight change,
- or only TiO_2 and SiO_2 were considered while B_2O_3 was supposed to evaporate.

In addition, the global composition of the oxidized layer was expressed in weight percent of these oxides.

The percentage of trapped B_2O_3 was derived from the comparison of the experimental weight gain and these two extreme calculated values.

Table 1

Comparison of the recession and estimated quantity of trapped B_2O_3 for uncoated and coated composite platelets, at 1350 and $1400^\circ C$, after 24 h oxidation

	Uncoated $Si_3N_4-TiB_2$	Coated $Si_3N_4-TiB_2$
Recession at $1350^\circ C$	71 μm (7% B_2O_3)	17 μm (4% B_2O_3)
Recession at $1400^\circ C$	Complete (–)	100 μm (12% B_2O_3)

This quantity was rather small and the difference between the results for non-coated and coated samples was not really significant due to the disparity of their thickness. Therefore, the determining factor could be the modification of the physicochemical characteristics (viscosity and transport properties) of the oxidized scale due to the presence of alumina. Consequently, these characteristics are dependent, at a given temperature and time, on the quantity of Al_2O_3 fixed by the initial thickness of the coating. For instance, the calculated global composition in mass of the glass formed at 1350 and $1400^\circ C$, after 24 h, were respectively (19% Al_2O_3 , 79% SiO_2 , 2% B_2O_3) and (4% Al_2O_3 , 90% SiO_2 , 6% B_2O_3). Thus, in order to optimize the performance of this sacrificial protection at high temperature, it would be wise to study the influence of the thickness of the deposited alumina film which is fixing the quantity of Al_2O_3 incorporated in the oxidized scale and by extension its composition.

5. Conclusion

A dense silicon nitride–titanium diboride composite, obtained by hot isostatic pressing, was coated with Al_2O_3 by microwave plasma-enhanced chemical vapor deposition (PECVD). The oxidation behaviour of uncoated and coated cubic samples (4 mm \times 4 mm \times 4 mm) were studied in flowing oxygen up to $1400^\circ C$.

The presence of a 3- μm thick alumina film on the $Si_3N_4-TiB_2$ substrates increased the oxidation resistance both in non-isothermal and isothermal conditions. In non-isothermal conditions, the oxidation of coated specimens started at higher temperature ($1200^\circ C$ against $600^\circ C$ for uncoated ones) as the alumina film acted as a diffusion barrier.

The improvement of the oxidation resistance in isothermal conditions, particularly important at 1350 and $1400^\circ C$, was linked to the interaction of this film with the reaction products (SiO_2 and B_2O_3) leading to the formation of a more viscous aluminoborosilicate layer slowing down the inward diffusion of oxygen and the outward transport of the gaseous by-products (N_2 and B_2O_3).

Therefore, the results were in agreement with previous ones^{1,8} obtained with ternary composites containing an alumina former component. In order to optimize the beneficial effect of the sacrificial alumina coating, it would be interesting to study the influence of its thickness and the induced modification of the glassy phase composition on the viscosity and the transport properties of the oxidized scale.

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