**PROTECTION AGAINST OXIDATION OF C/SiC COMPOSITES BY CHEMICAL VAPOUR
DEPOSITION OF TITANIUM DIBORIDE : DEPOSITION KINETICS AND OXIDATION
BEHAVIOUR OF FILMS PREPARED FROM $TiCl_4/BCl_3/H_2$ MIXTURES**

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ABSTRACT - TiB_2 coatings were deposited by hydrogen reduction of $TiCl_4$ and BCl_3 . The objective was to correlate process variables with thermodynamic equilibrium calculations, deposition kinetics, coating structure and properties. Particular emphasis was given to obtaining deposits having appropriate oxidation resistance to protect C/SiC composites. Films, obtained at moderate temperature (800°C), acted as self-healing external barriers below the microcracking temperature of the outer SiC coating used as primary oxygen protection.

1.- Introduction

The use of C/SiC composites, as structural materials for aerospace applications at high temperature, involves the development of reliable oxidation protection /1-3/. The current oxidation protection system is based on the use of CVD-SiC coatings, as primary oxygen barriers, coupled with internal inhibitors. Since coatings are normally obtained at elevated temperature, 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 B_2O_3 (m. p. 450°C) which can fill cracks and reduce permeation of oxidants. Unfortunately surface-applied sealants based on B_2O_3 glasses are generally useful for only limited periods due to volatilization (>1300°C). In addition, exposure of borate glasses to ambient moisture produces gradual hydrolysis which results in swelling and crumbling of the glass /2, 3/. Thus the problem common to most composites containing non-oxide components and used in oxidizing, high temperature, non-isothermal environments is how to maintain the presence of a liquid to fill cracks which form in the outer coating.

The main aim of the present work was to test a new oxidation protection system based on the use of an outer layer of titanium diboride able to produce by oxidation a B_2O_3 glass. TiB_2 , which has an exceptional hardness and chemical stability, offers considerable promise for use in highly erosive and corrosive environments /4-7/. Protective layers have been most conveniently obtained by the chemical vapour deposition (CVD) process using the hydrogen reduction of $TiCl_4$ and BCl_3 . Although this reaction has been studied by various researchers /4-12/, we have investigated

its thermodynamics and kinetics in order to determine the lowest deposition temperature possible by use of these reactants. Indeed, such films could also be interesting for tailoring the mechanical properties of fiber reinforced composites through modifications of the fiber-matrix interface /13/. In order to obtain thin homogeneous layers, it is interesting to define the experimental conditions (temperature, pressure...) allowing a control of the deposition rate by the surface reaction, i.e. conditions similar to those used in chemical vapour infiltration (CVI) of the fiber preforms.

In this paper are reported the results concerning the thermodynamic calculations, deposition kinetics and film properties, in particular oxidation resistance. The detailed study of the oxidation protection of the composite or the effect of internal interlayers between the fiber and matrix will be published later.

2.- Experimental

The TiB_2 coatings were deposited according to the reaction:

The deposition runs were performed with the equipment shown schematically in Fig. 1. The hot wall reactor is a vertical graphite tube ($h=130$ mm, $\phi=38$ mm), heated inductively by a 10-30 kHz generator. To help preserve a constant temperature in the furnace reactor, a baffle with exhaust holes was placed at each extremity of the cylinder. The temperature was controlled by a silica-sheathed (Pt/Pt-10%Rh) thermocouple placed under the substrate(s).

$TiCl_4$ (Prolabo, 99.5%), was carried to the reactor by a flow of hydrogen (Prodair, >99.9995%) through an evaporator and a mass flowmeter. The inlet line was heated to prevent recondensation. The other gases BCl_3 (Ucar, 99.9%) and H_2 were metered into the system through mass flowmeters and mixed with $TiCl_4$ before their introduction in the graphite reactor. The vacuum pump of the exhaust system was protected from unreacted and product gases by a liquid nitrogen trap.

Several substrates were used: graphite disks (Vicarb, CWA, $\phi=15$ mm, $h=2$ mm), and alumina or C/SiC (SEPCARBINOX® , SEP BORDEAUX) composite cubes ($5*5*5mm^3$).

Fig.1 : Schematic diagram of C.V.D. equipment.

X-ray diffraction (XRD) was used to identify the deposits and to determine any preferential crystallographic orientation. The deposit morphology was characterized using scanning electron microscopy (SEM), and polished sections were observed by

optical microscopy. The oxidation kinetics of coated and uncoated specimens in pure flowing (5 lh-1) oxygen (Prodair, 99.998%) were determined as a function of temperature using a symmetrical continuous recording thermobalance (MTB 50, Setaram, France). The kinetic curves were obtained by plotting the relative mass gain vs. time. After oxidation the quenched oxide layers were examined by SEM and characterized by XRD.

3.- Equilibrium thermodynamic analysis

The aim of this work was to extend the previous calculations /9,11,12/ towards lower temperatures in order to be able to perform C.V.I. of preforms.

The technique used involves the minimising of the global Gibbs free energy for the Ti-B-Cl-H system. The equilibrium is calculated as a function of the main C.V.D. parameters : temperature, pressure, H/Cl and Ti/B ratios in the reactant gas.

The equilibrium calculations were initially used to obtain CVD phase diagrams as a function of temperature (Fig. 2a) and total pressure (Fig.2b). The only confirmed condensed phases in the investigated CVD conditions are TiB_2 and B. The dotted lines on Fig.2 represent the limits of existence of TiB_2 imposed by the total pressure chosen for the calculation. Boron codeposition areas are decreasing with temperature and pressure.

Fig.2 : C.V.D. phase diagrams based on thermodynamic equilibrium calculation, a) at different temperatures, b) at different pressures.

Detailed information on the equilibrium gas composition of the system as a function of temperature is given in Fig.3. The conditions chosen were : $P=6.69 \cdot 10^3$ Pa, $H/Cl=10$, $Ti/B=0.5$. Species having molar fractions below 10^{-6} were not plotted.

This graph shows that H_2 , BCl_3 , $HBCl_2$, $TiCl_3$, HCl , $TiCl_4$ are the major gaseous species below 1200K. Between 700 and 1200K, the composition of the gas phase is almost constant. But, above this temperature, an important modification of the composition occurs due to the apparition of new species (H , Cl , $TiCl_2$, BH_2 ...). $TiB_2(s)$ appears at 700 K. Complementary calculations have shown that an excess of hydrogen and/or a lower total pressure help the formation of $TiB_2(s)$ at low temperature.

This tendency is quantified by the calculation of the theoretical efficiency. This efficiency is defined as the computed number of moles of TiB_2 deposited at equilibrium, divided by the number of moles which can be formed independently of any kinetic and thermodynamic limitations /9/.

Fig.3 : Equilibrium molar fractions of species present in the C.V.D. system as a function of temperature

Fig.4 shows plots of theoretical efficiency vs. temperature as a function of total pressure ($2.2 \times 10^3 < P < 1.08 \times 10^5$ Pa) or of H/Cl ratio ($1 < H/Cl < 40$). The influence of dilution by hydrogen is more important than that of total pressure. In fact, these results indicate that it is possible to obtain efficiencies close to 1, even at low temperature < 1000 K, provided deposition is conducted at low pressure and with a large excess of hydrogen ($H/Cl > 10$). However, it is necessary to check that reaction kinetics do not prevent deposition at such low temperatures.

Fig.4 : Theoretical efficiency of deposition vs temperature, as a function of : a) total pressure, b) H/Cl ratio.

4. - Results and discussion

4.1.- Deposition kinetics

The deposited weight gain increases linearly with deposition time as shown in Fig.5. This means that the reaction is carried out under steady state and that the deposition rate can be directly derived from the slope of the straight lines. The Arrhenius plot of Fig.6 shows that the temperature dependence of the deposition rate is exponential below 700°C , with an apparent activation energy $E_a 158 \text{ kJ.mol}^{-1}$. Above 700°C , the deposition rate is almost independent of temperature ($E_a 4 \text{ kJ.mol}^{-1}$). As often observed and interpreted in many CVD systems, the surface reaction seems to

limit the deposition rate in the lower temperature range, whereas mass transport becomes the limiting process in the higher temperature region. A confirmation of this interpretation is given in Fig.7 which shows the dependence of deposition on input mass flow rate. A linear increase in growth with input mass flow rate F of reactants ($\text{TiCl}_4 + \text{BCl}_3$) at high temperature and above indicates mass transport limitations in accordance with the corresponding flat curve of the Arrhenius plot (Fig.6).

BESMANN and SPEAR /9/ have also reported such a transition in their experimental conditions. It occurred at far higher temperatures ($\sim 1373\text{K}$), the apparent activation energies for the two rate-limiting mechanisms of mass transport and chemical kinetics being 17 and 170 $\text{kJ}\cdot\text{mol}^{-1}$, respectively.

Fig.5 : Effect of deposition time on weight gain ($\text{Ti/B}=0.5$, $\text{H/Cl}=10$, $F(\text{TiCl}_4 + \text{BCl}_3)=0.5 \text{ l/h}$).

Fig.6 : Arrhenius plot for deposition of TiB_2 $F(\text{TiCl}_4 + \text{BCl}_3)=0.5 \text{ l/h}$.

Fig.7 : Effect of flow rate on weight gain ($\text{Ti/B}=0.5$, $\text{H/Cl}=10$).

4.2.- Main characteristics of coatings

Most of the characterizations were carried out on coatings deposited on graphite substrates.

The deposited layers obtained below 700°C are amorphous, but the results obtained by electron probe microanalysis (EPMA) show that the titanium element is

present in these layers with the same peaks ratios as in crystallized TiB_2 layers. These results also indicate a constant titanium-to-boron ratio across the coating thickness. Therefore, in agreement with the thermodynamic previsions, only single-phase TiB_2 is deposited in the explored experimental parameters domain ($625 < T < 1100^\circ\text{C}$, $2.2 \times 10^3 < P < 2.66 \times 10^4$ Pa, $\text{Ti/B}=0.5$, $\text{H/Cl}=10$). Above 700°C , progressive X-ray detection of the hexagonal crystal structure of TiB_2 occurs. As expected, the crystallite size increases with the increasing deposition temperature. Also, preferred orientations are observed (100,110).

Fig.8 : SEM observation of a TiB_2 coating ($T=800^\circ\text{C}$, $P=6.69 \times 10^4$ Pa, $\text{Ti/B}=0.5$, $\text{H/Cl}=10$, $F(\text{TiCl}_4+\text{BCl}_3)=0.5$ l/h).

SEM observations clearly show the surface morphology to depend on temperature. The coatings deposited below 700°C are rather smooth while those obtained above tend to be rough due to the presence of nodules increasing in size with temperature. At 800°C and above, the surface retains some of this nodular character on which is superimposed a granular texture with faceted surfaces (Fig.8). In general, the crystallized deposits on graphite or C/SiC substrates exhibit intergranular cracks, probably due to the thermal expansion mismatch between the substrate and TiB_2 . In addition, these films tend to separate from the substrate during the preparation of cross sections (by fracture or polishing) prior to metallographic observations.

These results are globally consistent with those reported in the few previous works conducted at temperatures as low as 650°C [4,7].

However, they differ from former findings on the effect of hydrogen. Indeed, it has been shown that coatings prepared in a large excess of hydrogen no longer exhibit a preferred crystallographic orientation, but are incoherent and made up of irregularly shaped, faceted crystallites [8].

4.3.- Oxidation kinetics

In preliminary experiments, the non-isothermal oxidation of $20 \mu\text{m}$ thick TiB_2 coatings deposited on inert Al_2O_3 and oxidizable C/SiC substrates, with the same conditions ($T=800^\circ\text{C}$, $P=3.38 \times 10^3$ Pa, $\text{H/Cl}=10$, $\text{Ti/B}=0.5$, $F(\text{TiCl}_4+\text{BCl}_3)=0.5$ l/h), was studied. The curves of Fig. 9 show that the reaction

becomes noticeable above 500°C and that, for a given temperature, the relative weight gain is higher for the alumina coated sample than for the C/SiC one (m_0 being the initial mass of coating). At 1100°C and above, the weight loss due to the vaporization of B_2O_3 explains why the isothermal kinetic curves (Fig.10 and 11) exhibit a maximum.

Below these temperatures, only the passive behavior is observed and the curves exhibit a parabolic type shape. The protectiveness of the TiB_2 coating below 1100°C is illustrated by Fig.12 which compares the oxidation behavior of coated and uncoated C/SiC samples (here m_0 refers to the initial mass of the C/SiC specimen). In the absence of coating, the C/SiC substrate oxidizes readily. The corresponding weight losses are due to the internal preferential attack of the carbon fibers.

The slight difference in reactivity between Al_2O_3 or C/SiC coated substrates (Fig.10 and 11) may come from a modification of the nature and morphology of the oxidation products.

Fig.9 : Non isothermal oxidation curves for Al_2O_3 and C/SiC samples coated with a $20\ \mu\text{m}$ thick deposit (temperature ramp : $3.5^\circ\text{C}/\text{min}$).

Fig.10 : Oxidation kinetics of TiB_2 coated alumina substrates.

Fig.11 : Oxidation kinetics of TiB_2 coated C/SiC samples.

Fig.12 : Comparison of the oxidation behaviour of coated and uncoated C/SiC substrates.

In fact, no significant difference is observed below 1000°C . As long as the coating is not entirely consumed, it is possible to distinguish on polished cross-sections an internal compact polyphase oxide ($\text{B}_2\text{O}_3 + \text{TiO}_2$) sublayer and an external non-protective porous rutile scale. XRD analysis of the system also indicates that titanium suboxides are present. These observations are in agreement with the few previous data concerning the oxidation of powdered or sintered TiB_2 materials /14-17/.

Above 1000°C, these suboxides are no longer detected and only the porous TiO₂ scale is present on alumina substrates after complete oxidation of the TiB₂ coating. On C/SiC substrates, a dense borosilicate glass layer, embedding rutile grains, is observed at the vicinity of the SiC primary protection coating of the C/SiC composite.

Therefore, the difference in reactivity between the two types of coated substrates, tested in the present work, is probably due to an interaction between the oxidation products of TiB₂ and the SiC coating of the C/SiC composite. Nevertheless, it is not possible to totally exclude a small internal oxidation of the C/SiC substrate. Calculations are in progress in order to evaluate the contribution of the oxidation of each component (C, TiB₂, SiC) to the observed weight change.

5.- Conclusions

Films of titanium diboride are usually deposited by hydrogen reduction of TiCl₄ and BCl₃ at temperatures > 900°C. In the present work, moderate deposition conditions have been explored. The obtained results on various substrates (graphite, alumina and C/SiC composite) reveal the possibility of preparing high quality films in chemical kinetics limitation conditions at temperatures below 700°C.

In addition, it is shown that 20 µm thick TiB₂ coatings, deposited at 800°C on C/SiC composites specimens, can provide self-healing capabilities.

Since they oxidize to form low viscosity B₂O₃ glasses, they are able to seal the cracks present in the CVD SiC coating, acting as primary oxygen barrier.

Complementary work is under way in order to gain a better understanding of the oxidation mechanism and improve the efficiency of this oxidation protection system.

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