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TITANIUM DIBORIDE-COATED BORON FIBRE FOR ALUMINIUM MATRIX COMPOSITES*

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Summary

Titanium diboride was deposited by chemical vapour deposition (CVD) from $TiCl_4$ and H_2 gases on a heated boron fibre. A thermodynamic analysis of this deposit was performed. The conditions to limit the formation of gaseous boron compounds were determined. The deposition rate increased with temperature. The CVD was controlled by a diffusion process. The morphologies of the deposits were correlated with the deposition parameters: substrate temperature and the H_2:$TiCl_4$ molar ratio. The diboride deposits exhibited a smooth or a nodular surface. Defects were found to be sensitive to deposition temperature and the duration of the treatment. The CVD conditions which lead to good mechanical properties were determined. The development of B–Al composites required the coating of a TiB_2–B filament with a thin layer of aluminium.

1. Introduction

The fabrication of performant Al–B filament reinforced composite materials sets two problems: that of the chemical compatibility of boron with aluminium (the boron–metal reactivity does not allow the use of uncoated fibres) and that of physical compatibility (fibre–matrix adherence must be as good as possible).

To solve these problems, we protected the boron fibre with a titanium diboride coating, a compound chosen for its good wetting with the molten metal [1, 2].

This paper describes a new TiB_2 chemical vapour deposition (CVD), the characterization of the coating, the CVD conditions necessary to obtain the best mechanical properties of the fibres thus produced, and the preliminary investigations of their use as reinforcing agents in an aluminium matrix.

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2. Titanium diboride coating

The suggested CVD process consists in using the boron of the fibre and titanium as $TiCl_4$ in the gaseous phase.

The growth rate of TiB_2 is controlled by boron diffusion through the coating. This method appears to offer significant advantages over the process consisting in simultaneous reduction of boron trichloride and titanium tetrachloride [3 - 5].

$$TiCl_4 + 2BCl_3 + 5H_2 \longrightarrow TiB_2 + 10HCl$$

The deposition conditions must be perfectly controlled to prevent the deposition of boron and TiB_2 contamination.

2.1. Thermodynamic approach

As well as the main reaction:

$$TiCl_4 + 2B + 2H_2 \longrightarrow TiB_2 + 4HCl$$

we also have various side reactions which lead to the formation of the by-products BCl_3 and $BHCl_2$. This yields a substrate attack and a cracked and not very adherent deposit.

The result of the competition between the two reducing agents boron and hydrogen may be predicted by a thermodynamical approach [6] that postulates that the system is at equilibrium, a hypothesis that is close to reality in the vicinity of the hot substrate [7, 8].

The equilibrium computation included the following gaseous species: $TiCl_4$, $TiCl_3$, BCl_3, $BHCl_2$, HCl, H_2 and the solid species: B, TiB and TiB_2. Thermodynamical data for the species are taken from ref. 9.

At a total pressure of 1 atm and in the presence of excess boron, the calculation of the amount of the solid species and of the composition of the gaseous phase at equilibrium was made with argon as a diluent in the gas mixture, for various temperatures, partial pressures of $TiCl_4$ and ratios R of $[H_2]$ to $[TiCl_4]$ in the initial gas mixture.

The calculated amount of TiB_2 shows that all the titanium in the admitted gas mixture is transformed into TiB_2 and that BCl_3 and $BHCl_2$ occur in all cases.

So as to evaluate the quantity of boron lost in the form of volatile compounds we set the ratio $\rho = 2nTiB_2/(2nTiB_2 + nBCl_3 + nBHCl_2)$ as a function of R for various temperatures and various partial pressures (Fig. 1).

From the curves, it can be deduced that the ratio increases with temperature, with a dilution of $TiCl_4$ by H_2 and with decreasing $TiCl_4$ partial pressure.

2.2. Experimental study

2.2.1. Experimental apparatus

The deposition reactor is shown schematically in Fig. 2. The details of this reactor were given in a previous paper [10].

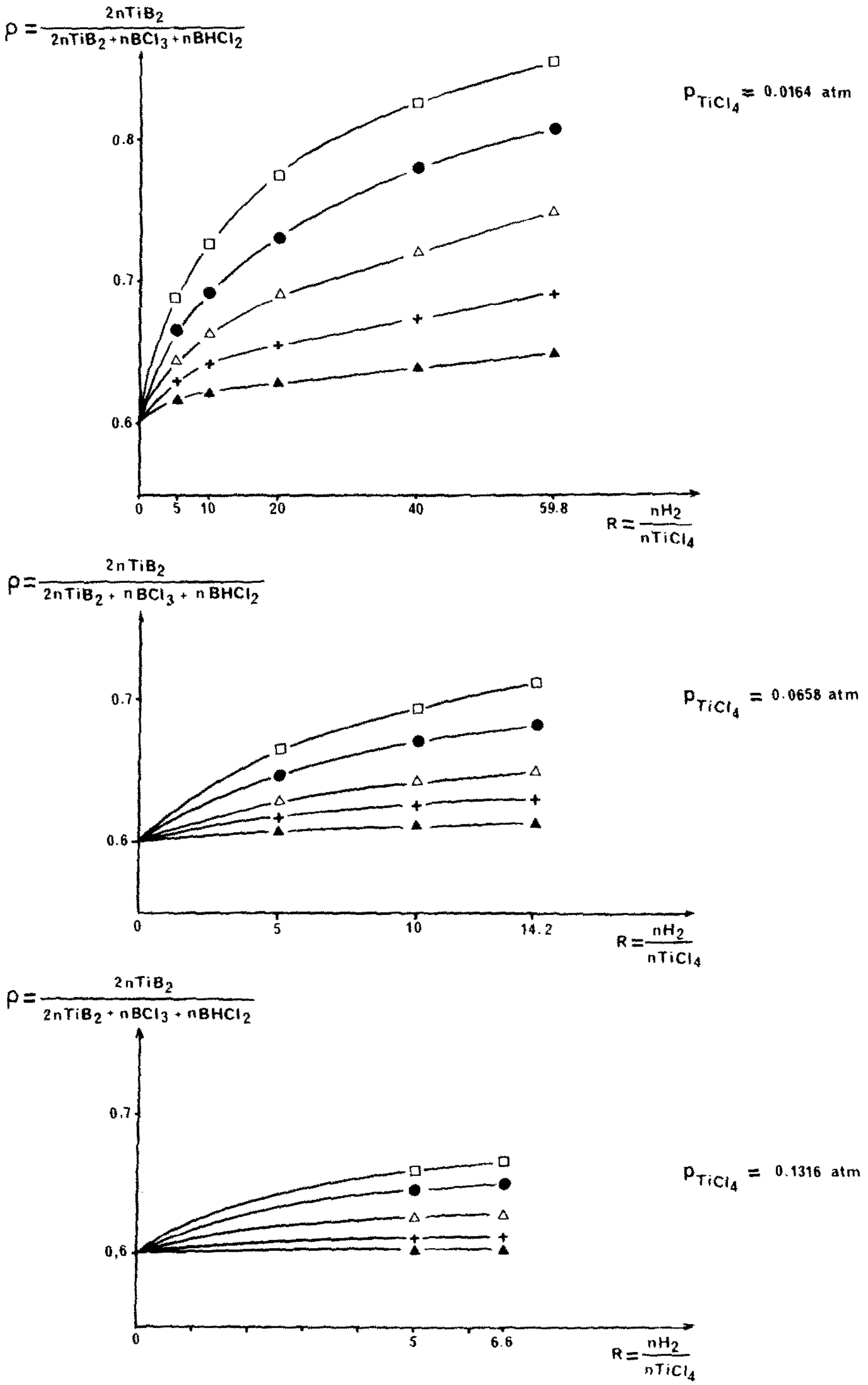

Fig. 1. Yield of boron in condensed TiB_2 with respect to the total boron consumed as a function of the H_2:$TiCl_4$ molar ratio at various temperatures: ▲, 900 K; +, 1000 K; △, 1100 K; ●, 1200 K; □, 1300 K.

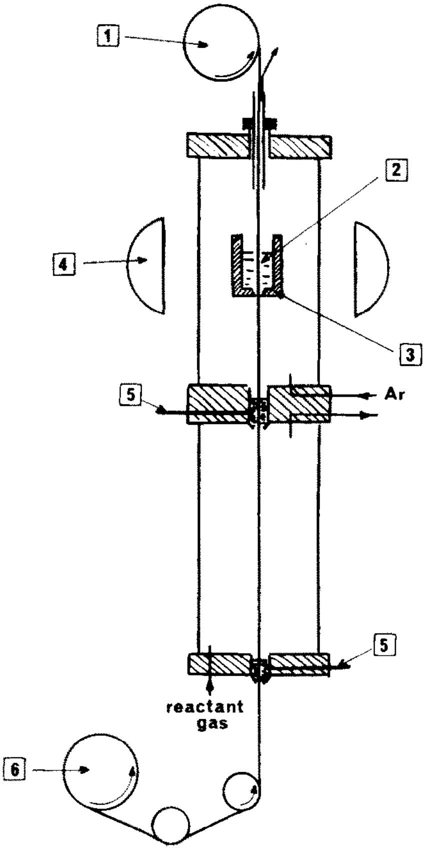

Fig. 2. Schematic diagram of the deposition reactor: 1, drive pulley; 2, molten aluminium; 3, graphite crucible; 4, image furnace with elliptical mirrors and halogen lamps; 5, current leads; 6, spooling and tension pulleys.

The fibre is heated by the passage of an electric current. A second cell is connected in series. Its function is to impregnate the fibre with aluminium. The metal put into a graphite crucible is heated by an image furnace.

CVD is performed at atmospheric pressure. The Ar–H_2 mixture is used as a carrier gas to transfer $TiCl_4$ gas to the cell, the flows of which are controlled by calibrated flowmeters.

2.2.2. Deposition conditions

Taking the thermodynamical study into account, the following parameters were chosen: a $TiCl_4$ partial pressure of 0.0164 atm (vapour pressure at 25 °C); a hydrogen partial pressure of 0.329 atm; an argon partial pressure of 0.654 atm; and a total flow of 500 $cm^3\ min^{-1}$.

We defined the growth rate of the TiB_2 deposit as being the ratio between the increase in the fibre diameter and the time the filament takes to go through the reactor.

We studied the influence of the substrate temperature on the deposition rate and showed that the coating thickness followed a law of the type $x = kt^{0.5}$ where t is the contact time within the temperature range studied (600 - 900 °C) with an activation energy of about 48 kJ mol^{-1}.

2.2.3. *Deposit study*

The purity of the TiB_2 and its characterization were investigated by X-ray diffraction, LEEIXS, XRFS and X-ray microprobe analysis.

Morphology was determined by scanning electron microscopy (SEM). It is dependent on the fibre temperature and on the duration of the treatment. For a deposition time of 2 min and for a temperature lower than 800 °C, the deposit surface is relatively smooth and the coating is completely dense.

For higher temperatures, nodules appear as well as defects in the coating.

2.2.4. *Mechanical properties*

The study of the tensile strength distribution of coated fibres was performed using Weibull's statistics. So as to quantify the contribution of the TiB_2 deposit to the boron fibre properties, we represented the ratio between the average tensile strengths $\overline{\sigma_R}$ of the coated fibre and $\overline{\sigma_{R_0}}$ of the heat-treated fibre in the same conditions (Fig. 3).

For temperatures lower than 700 °C the ratio is greater than 1, which shows the positive role of the high-quality coating (thickness less than 1 μm) which prevents the propagation of surface defects; such an improvement has already been noted for a fibre coated with B_4C [11].

For the temperatures ranging from 700 to 1000 °C, the presence of many defects on the surface and within the fibre decreases the fibre properties.

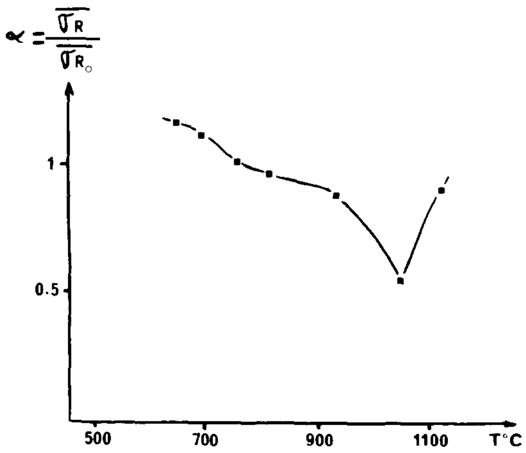

Fig. 3. Relation between relative tensile strength and temperature of the substrate.

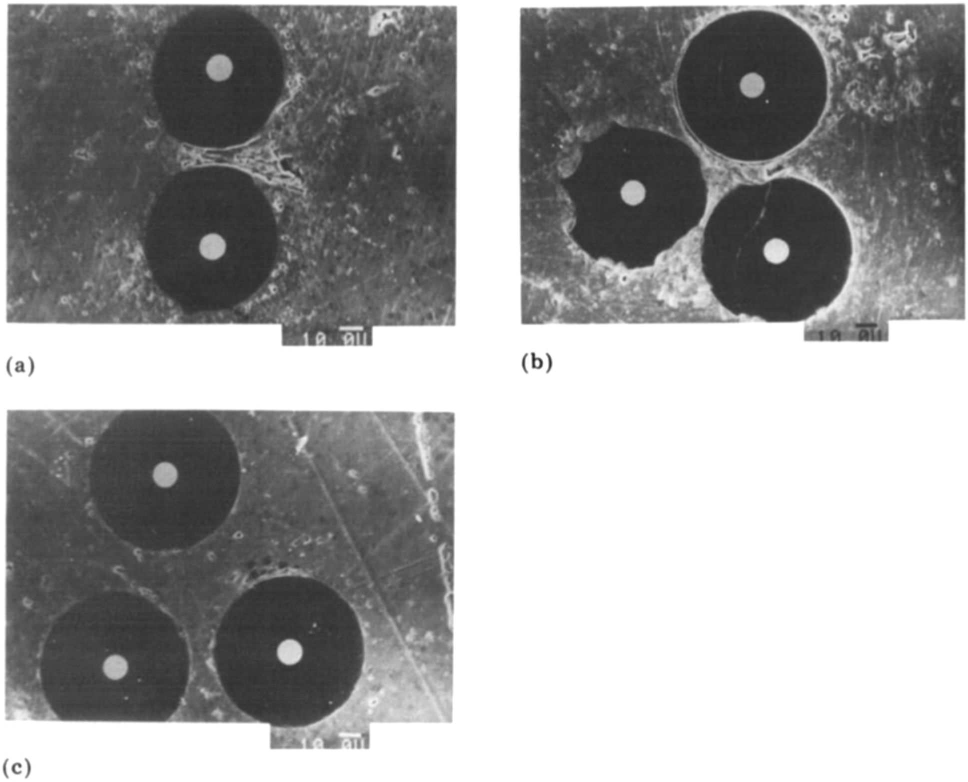

Fig. 4. Scanning electron micrographs of Al–60vol.%B composite: aluminium temperature, 700 °C; treatment time, 5 min. (a) Initial fibre. TiB_2 fibre coated (deposit thickness, 0.4 µm) by (b) BCl_3–$TiCl_4$–H_2 CVD process (800 °C, 20 s) and (c) B–$TiCl_4$–H_2 CVD process (800 °C, 2 min).

At temperatures above 1000 °C, the damage to the boron fibre by heat treatment is so important that the influence of the deposit can be neglected and the ratio α tends to 1.

3. Elaboration of B–Al composites

The coated fibres were introduced into the aluminium matrix by a vacuum infiltration technique. The composite had a fibre volume of approximately 60%.

After cooling, the composite was cut out and its polished surface examined by SEM. This study reveals that wetting is not perfect. Some gaps appear between the fibres and the metal.

The fracture cross section of the composite tested in tension revealed a notable amount of fibre–matrix interfacial failures with fibres pulling out of the specimens.

Good adherence was obtained by using aluminium coated fibres, immediately after the TiB_2 elaboration. The aluminium-layer thickness was about 5 μm and it inhibited the contamination of the fibre by the air.

It was also proved that a TiB_2 thickness less than 1 μm is sufficient to protect the boron fibre in aluminium at 780 °C for 5 min. Figures 4 (a) - (c) show the efficiency of the coating when performed by the suggested CVD method.

4. Conclusions

The deposit of TiB_2 obtained by the suggested CVD method is uniform, dense and adherent; its thickness is perfectly controlled. The mechanical properties of the fibres as coated are stable if the substrate temperature is lower than 700 °C. A 0.4 μm coating is sufficient to protect them from attack by aluminium.

Developing composites necessarily implies the use of fibres as soon as the deposit has formed or the use of aluminium-coated fibres.

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