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CARBON-CARBON-TITANIUM CARBIDE COMPOSITE MATERIALS
OBTAINED BY CVI OF POROUS CARBON-CARBON SUBSTRATES

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The *2D-carbon-carbon composites* (2D-CC) are made of layers of woven graphite fiber cloth linked together by carbon. They are used in the space industry as well as in several other fields (e.g. disk brakes or prostheses). However, they have some drawbacks: poor resistance towards air oxidation at high (and even medium) temperatures, strong anisotropy in their mechanical properties (with a tendency to delamination due to weak inter-layer bonding).

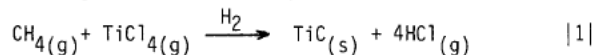
It has been shown recently that part of these drawbacks can be overcome by replacing (partially or totally) the carbon matrix by a refractory material such as SiC. The *CC-SiC composites*, obtained by chemical vapor infiltration (CVI) of porous CC-substrates by SiC, are less anisotropic than the conventional 2D-CC composites, their mechanical properties are much higher and their resistance towards air oxidation remains excellent up to about 1500°C (1-3).

The use of the CC-SiC composites is limited in temperature by the volatility of the SiO₂-protective layer (significant above 1500°C, in air) and the thermal decomposition of SiC (at about 2500°C). For this reason, a program of research is now in progress for replacing SiC by more stable refractory materials. *CC-TiC composites* (prepared by CVI of porous CC-substrates by TiC) will be more particularly considered here. TiC has been chosen, *in a first step*, as a compromise between thermal stability and ease of pro-

cessing (TiC only melts at 3070°C but is more easily CVD-introduced in porous substrates than the more refractory hafnium or tantalum carbides).

THERMODYNAMIC AND EXPERIMENTAL STUDY OF THE CVD OF 2D-CC POROUS SUBSTRATES BY TiC

The CVD of TiC is commonly performed, from CH_4 - TiCl_4 - H_2 gas mixtures according to the overall equation:



As shown elsewhere, such reaction (that usually implies several by-products) can be studied, in a first approximation, by a *thermodynamic approach* (based on the minimization of the total Gibbs free energy) assuming that states close to equilibrium are reached in the vicinity of the substrate. The method gives the composition of both the vapor and condensed phases, at equilibrium, as a function of the initial gas mixture composition, temperature, total pressure and nature of the substrate(4). It has already been used by M. Duccaroir et al. to plot a "*CVD-phase diagram*" for TiC(5).

The thermodynamic calculations have been limited here to those low values of temperature and total pressure which are compatible with the CVD-processing of porous substrates (1,3,6). The main species that may be present at equilibrium are: H_2 , HCl , CH_4 , TiCl_4 , TiCl_3 and TiCl_2 for the vapor phase as well as TiC and C for the deposit. As shown in fig.1, the deposit is made of pure TiC or of a TiC+C mixture depending on the initial composition (a TiCl_4 -excess is usually necessary to give a carbon-free deposit).

The thermodynamic calculations have established that TiC+C deposits are always obtained at 1200K when the initial composition does not contain elemental hydrogen (although CH_4 theoretically contains enough hydrogen to reduce TiCl_4 , as indicated by equation [1]. Thus elemental hydrogen must be added to CH_4 and TiCl_4 (whatever the $\text{CH}_4/\text{TiCl}_4$ ratio), in order to get a carbon-free deposit, at equilibrium.

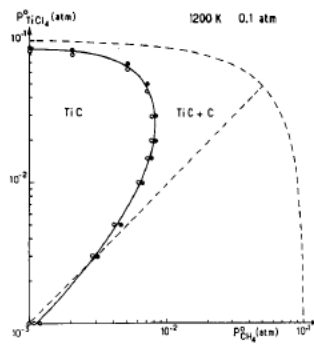


Fig.1-CVD-phase diagram of titanium-carbide

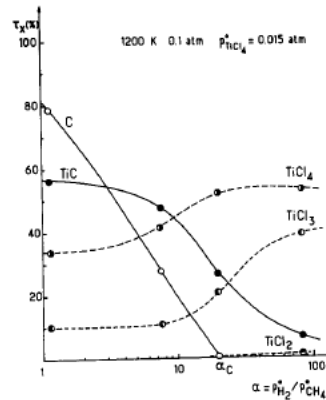


Fig.2-Thermodynamic yields τ_x , as a function of α

Fig.2 gives the percentages τ_x of TiCl_4 which is reacted at equilibrium (to give TiC or titanium sub-chlorides) or remains unreduced, as a function of $\alpha = P_{\text{H}_2} / P_{\text{C}_2\text{H}_4}$ (for $P_{\text{TiCl}_4}^0 = 1.5 \cdot 10^{-2} \text{ atm}$). It appears that at 1200 K, a rather important percentage of TiCl_4 remains unreacted and that TiCl_3 is a significant by-product of the reaction, whatever α . In order to get a carbon-free deposit and to minimize the amounts of TiCl_4 and TiCl_3 , an α value close to $\alpha_c = 20$ has to be used. Under such conditions, the τ_{TiC} theoretical yield is low (27%) and the amount of unreduced TiCl_4 and TiCl_3 is very important. In order to increase τ_{TiC} and decrease both τ_{TiCl_4} and τ_{TiCl_3} , temperature has to be raised; a finding which is not compatible with the CVI of a porous substrate. The results of the thermodynamic calculations have been qualitatively confirmed by experiments run on graphite samples.

As already underlined by F. Christin et al. in the case of the CC-SiC composites, the CVI of a porous substrate by a refractory material (in-depth deposition within the open pores) is much more difficult than the corresponding CVD-overcoating (deposition on the external substrate-surface). In order to favor the former,

the values of the parameters commonly recommended in CVD have to be strongly modified. Thus, the substrate-temperature and the total pressure have to be kept *as low as possible* (to increase the mean life time and the mean free path of the reactant molecules, allowing them to diffuse as far as possible within the pores before reacting). At the same time, the gas flow rates must be rather slow. Under such conditions, the deposition rate is much lower than in CVD and the duration of CVI-runs is usually very important (1,3,6).

On the basis of the thermodynamic study and of the results of experiments run on CC-porous substrates, the most suitable CVI-conditions for TiC were found to be: $900 < T < 1000^{\circ}\text{C}$, $0.025 < p < 0.070 \text{ atm}$. To avoid the appearance of elemental carbon in deposits and to fulfil technical requirements, the initial gas composition was characterized by $p_{\text{TiCl}_4} = 0.015 \text{ atm}$ and $\alpha \sim 20$. As predicted by the thermodynamic study, an important amount of TiCl_3 is formed under such conditions. The porous samples to be CV-infiltrated were located within a graphite susceptor heated, in a vertical silica glass chamber, by an RF coil.

CHARACTERIZATION OF THE CC-TiC COMPOSITES

The substrates were made of carbon fiber (ex-rayon or PAN types) cloth layers linked together by a small amount of pyrocarbon. Their residual open porosity was of the order of 25 to 35 vol.%. The open pores left by the pyrocarbon predensification were mainly of large size ($\sim 100 \mu\text{m}$) and located between the carbon yarns of the cloth layers (the pores of much smaller diameter located between the fibers themselves, within the yarns, being already filled with pyrocarbon or closed).

CC-TiC composites having TiC vol. fractions up to 0.325 and almost no residual open porosity have been obtained by CVI. Fig.3 shows a micrograph of a cross section of a partially densified CC-TiC composite. Microcracks in the TiC-deposit are clearly apparent. They are probably due to the difference in thermal expansion

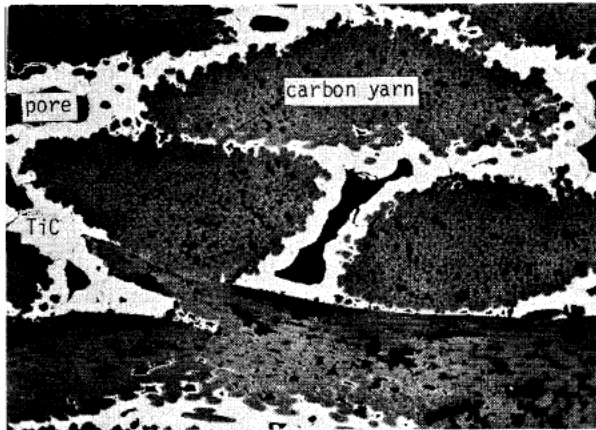


Fig.3-Micrograph of a partially CV-infiltrated CC-TiC composite ($V_{TiC} = 0.20$)

that exists between TiC and the CC-substrates. Microprobe analysis has shown that the deposit is made, within the accuracy limits of such a method, of nearly stoichiometric titanium carbide ($79.7 < Ti\%_{exp.} < 80.5$; $Ti\%_{theor.} = 79.95$).

Compression and shear tests have been performed on samples characterized by increasing V_{TiC} ($0 < V_{TiC} < 0.20$ to 0.30) and thus decreasing residual porosity (since $V_c + V_{TiC} + V_p = 1$ and $V_c = \text{constant}$). They were loaded to failure *in a direction parallel to the fiber cloth layers* (the direction of weakest resistance for a 2D-composite).

Fig.4 shows that the CC-Ti composites are, as expected, *brittle materials* at room temperature whatever V_{TiC} (their mechanical behavior remaining elastic up to failure). As illustrated in fig.5, the ultimate compression stress σ_{\parallel}^R , the Young modulus E_{\parallel} and the shear stress to failure τ_{\parallel}^R linearly increase with increasing V_{TiC} as already found by F.Christin et al. for the related CC-SiC composites (2,3). The highest values of σ_{\parallel}^R , E_{\parallel} and τ_{\parallel}^R obtained for $V_{TiC} = 0.20-0.30$ are significantly greater than those

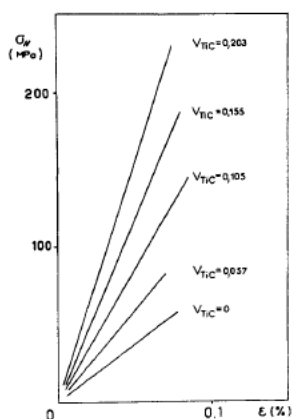


Fig.4-Mechanical behavior (in compression) of CC-TiC composites

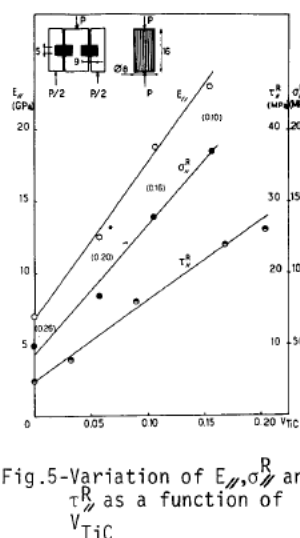


Fig.5-Variation of $E_{//}$, $\sigma_{R//}$ and $\tau_{R//}$ as a function of V_{TiC}

reported for the corresponding CC-composites totally densified with pyrocarbon (3).

The analysis of the samples loaded to failure indicates that failure occurs by interlayer delamination for low V_{TiC} values (the porous C-TiC matrix remaining the weakest point). The tendency to interlayer delamination disappears very rapidly ($V_{TiC} > 0.10$) in the case of the composites made of the rather weak ex-rayon fibers. On the contrary, this tendency partially remains (even for $V_{TiC} \sim 0.25$) in the case of the much stronger ex-PAN fibers. However, in both cases replacing partially the carbon matrix by a TiC-matrix significantly reinforces the strength of the material and the inter layer-cohesion. As expected, the CC-TiC and CC-SiC composites have almost the same mechanical characteristics for a given value of V_{TiC} or V_{SiC} .

Oxidation tests were performed in air on CC-TiC composites having almost no residual open porosity ($V_{TiC} = 0.325$). Fig.6 shows that

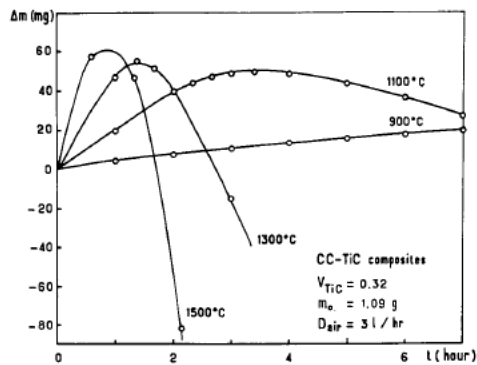


Fig.6-Weight variation of CC-TiC composites during oxidation tests in air

the behavior of the materials remains good for temperatures up to $\sim 1000^\circ\text{C}$, an increase in weight being observed due to the formation of a TiO_2 -layer. At higher temperatures, an important weight loss occurs, probably related to the oxidation of the fibers, oxygen diffusing in the TiC-matrix defects.

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