

## On a thermodynamic approach to the chemical phenomena involved in the formation of a BN interphase by CVD/CVI from a $\text{BF}_3\text{--NH}_3$ precursor

O. Dugne, S. Prouhet, A. Guette and R. Naslain

Laboratoire des Composites Thermostructuraux (UM 47 CNRS-SEP-UB1) Europarc, 3  
Avenue Léonard de Vinci, F-33600-Pessac (France)

C. Bernard

Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques (UA 29 CNRS),  
ENSEEG, INPG, Domaine Universitaire, F-38401 St. Martin d'Hères (France)

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### Abstract

The chemical phenomena involved in the CVD/CVI of BN from  $\text{BF}_3\text{--NH}_3$  mixtures are studied through thermodynamic calculations based on a computer minimization of the total Gibbs free energy of the system for  $1123 < T < 1723$ ,  $P = 0.1, 1$  and  $10$  kPa, and  $0.1 < \alpha = [\text{NH}_3]_{\text{in}}/[\text{BF}_3]_{\text{in}} < 15$ . Various substrate materials, *i.e.* a purely inert substrate, C, SiC,  $\text{SiO}_2$  and SiC– $\text{SiO}_2$  thought to simulate the substrates onto the BN interphase is actually deposited in SiC (ex-PCS) fiber preforms, are considered. C and  $\text{SiO}_2$  are quasi-unreactive whereas SiC-based materials are reactive *vs.* compared with the gas phase. For the former, the  $\text{BF}_3/\text{BN}$  conversion yield is low owing to the stability of  $\text{BF}_3$ . For the latter, it is almost equal to 100% owing to chemical attack of the substrate, but the deposit is a mixture of BN + C and even of BN + C +  $\text{Si}_3\text{N}_4$  (or/and  $\text{Si}_2\text{N}_2\text{O}$ ) for the  $\text{NH}_3$ -rich precursors. The effects of temperature and pressure on the BN yield and substrate attack are studied as well as that of a contamination of the gas phase by oxygen. It is foreseen that a preform made of SiC (ex-PCS) fibers will not be significantly damaged either chemically or mechanically during the infiltration of a BN interphase from  $\text{BF}_3\text{--NH}_3$  if the fiber surface is assumed to be coated uniformly with C,  $\text{SiO}_2$  or C +  $\text{SiO}_2$ .

### 1. Introduction

Boron nitride, prepared by chemical vapor deposition (CVD), is used in different electronic device components, either as thin films or thick coatings, on the basis of its high electrical resistivity, good thermal conductivity and excellent chemical inertia [1].

In a different field, that of advanced thermostructural fibrous composites, the replacement (partial or total) of the pyrocarbon matrix of the carbon–carbon composites by boron nitride (both materials having almost the same turbostratic layered structure), has been suggested in order to improve their oxidation resistance at medium temperatures [2–6]. As an example, Hannache *et al.* have established that C–C/BN composites can be prepared, from a carbon fiber preform, according to a two-step chemical vapor infiltration

(CVI) process involving: (i) the consolidation of the preform with a small amount of pyrocarbon resulting from the *in situ* cracking of methane which acts as a binder; and (ii) the densification of the consolidated, but still porous, two-dimensional C-C preform by boron nitride deposited by CVI from a  $\text{BF}_3\text{-NH}_3$  precursor [2, 3]. In order to optimize the infiltration parameters of carbon-based preforms by BN, these authors have already used a thermodynamic approach for the two  $\text{BF}_3\text{-NH}_3$  and  $\text{BCl}_3\text{-NH}_3$  precursors.

Furthermore, it has been established more recently that the mechanical properties of ceramic matrix composites (CMCs), and more particularly their toughness and failure mode, are directly controlled by the occurrence of a thin layer of a soft material at the fiber-matrix interface, referred to as the interphase. In most CMCs, this interphase is a thin film (thickness less than  $1\text{ }\mu\text{m}$ ) of pyrocarbon formed *in situ* as the result of chemical reactions taking place during the high temperature step of the composite processing. It is thought that the key role played by such an interphase may be related to the turbostatic layered crystal structure of pyrocarbon whose low interlayer shear stress promotes the deflection in mode II, at the fiber-matrix interfaces, of the microcracks resulting from the early failure of the brittle matrix and propagating in mode I. Thus, a pyrocarbon interphase acts in a CMC as a mechanical fuse protecting the brittle fibers against the notch effects arising from the matrix microcracking. Unfortunately, a CMC with a pyrocarbon interphase, *e.g.* a SiC/glass-ceramic composite, may lose its attractive mechanical properties when it is maintained at a high temperature for a long time under an oxidizing atmosphere [7].

It has been shown, as could be expected from simple structural and chemical considerations, that a turbostatic BN interphase deposited (or infiltrated) from a gaseous precursor, is as efficient as its pyrocarbon counterpart from a mechanical standpoint with an improved oxidation resistance at medium temperatures, in many different CMCs [8-17]. However, in most cases the BN interphase is not generated *in situ* as is the pyrocarbon interphase due to a chemical reaction occurring either within or between the components during the composite processing. It has instead to be deposited on the fiber surface prior to embedding the fibers in the matrix.

In the CVI process, where the preform consolidation and the infiltration of both the interphase and matrix materials are preformed in corrosive media (*e.g.* in presence of fluorinated and chlorinated species for the infiltration of BN from  $\text{BF}_3\text{-NH}_3$  and SiC from  $\text{CH}_3\text{SiCl}_3\text{-H}_2$  respectively, as well as hydrogen during the whole process), many chemical reactions involving the thin and vulnerable layer of BN may occur with species from the gas phases. Furthermore, the fibrous substrate on which the BN interphase has to be deposited may itself have a complex chemical composition and may also react with the BN deposit. This is typically the case in preforms made of ex-polycarbosilane fibers (ex-PCS)\* since such fibers are known to: (i) consist

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\*The most commonly used are the Nicalon fibers from Nippon Carbon.

of a nanoscale mixture of SiC and free carbon in an amorphous Si-C-O matrix; and (ii) be coated with a thin layer of silica [18–22]. Finally, in any hot wall CVI furnace, there is usually a low residual partial pressure of oxygen (due to the outgassing of the apparatus) which may result in some contamination of the thin BN interphase either during its deposition from  $\text{BF}_3\text{--NH}_3$  or that of the SiC matrix.

From these considerations, it appeared to us that a detailed experimental study of the chemical phenomena taking place during the processing of, for example, a SiC/BN/SiC composite would have been tremendously time-consuming owing to the complexity and variety of the systems involved. The definition of a representative model system and analytical procedures was in itself quite puzzling due to the fact that most reactions were surface reactions involving fibrous substrates (mean diameter:  $15\text{ }\mu\text{m}$ ) and thin films (with a thickness of less than  $1\text{ }\mu\text{m}$ ). Therefore, it was thought that a thermodynamic approach could be used to assess the main features of the chemical phenomena involved during the infiltration of a BN interphase within a SiC-based fiber preform followed by a SiC densification CVI step. It is worthy of note that a similar approach has been chosen by Benson *et al.* [23] as well as by Cooper and Chyung [24] to study the fiber-matrix interphase in ex-PCS SiC fibers/glass ceramic composites.

The aim of the present work was to study through a thermodynamic approach: (i) the chemistry of the deposition of a BN interphase from a  $\text{BF}_3\text{--NH}_3$  precursor in a wide range of temperature and total pressure compatible with the requirements of CVI; and (ii) the effect of the chemical environment, *i.e.* that of the nature of the substrate (including carbon, SiC,  $\text{SiO}_2$  and SiC/ $\text{SiO}_2$  thought to be representative of the materials seen by a BN interphase in the processing of a SiC (ex-PCS)/SiC composite) as well as that of an eventual contamination of the gas phase by oxygen.

## 2. Thermodynamic approach

The thermodynamic approach, already used for the study of many coupled CVD systems, gives the composition of the gas and condensed phases that would be formed, for a given initial composition of the system, when equilibrium is achieved at a given temperature and total pressure. It is based on the minimization of the total Gibbs free energy taking into account the mass balance [25]. The calculations were performed, using the software SOLGASMIX from Erikson [26], for temperature and total pressure values thought to be compatible with BN CVI, namely  $1123 < T < 1723$  and  $P = 0.1, 1$  and  $10\text{ kPa}$ .

Inasmuch as the aim of the present work was to study the main features of the chemistry of the deposition of BN from a  $\text{BF}_3\text{--NH}_3$  mixture on a substrate made of carbon, SiC,  $\text{SiO}_2$  or SiC/ $\text{SiO}_2$  with a possible contamination of the gas phase by oxygen, the calculations had to be performed in the complex B-N-H-F-Si-C-O multicomponent system. The gaseous and con-

densified species, which have been introduced in the calculations, were selected on the basis of the two following criteria (Table 1): (i) their stability under the temperature and pressure conditions considered here; and (ii) the availability of the thermodynamic data. As a matter of fact, the occurrence at equilibrium of some of them had already been established in published studies on related systems, *i.e.* B–N–H–F–C [2], B–N–H–Cl–O [27], B–N–Cl–Si–H [28], B–N–Cl–Si–C–H [29], Si–C–N–O [30–33] and Si–F–O [34].

The thermodynamic data were mainly taken from JANAF [35]. However, for a few condensed species, namely  $\text{SiB}_3$ ,  $\text{SiB}_6$ , on the one hand, and  $\text{Si}_2\text{N}_2\text{O}$ ,  $\text{Si}_3\text{N}_4$ , on the other hand, the data which have been used are those from Métais [29] and Hendry [36] respectively. Since no data were available for amorphous silica (the modification of silica thought to be present at the ex-PCS SiC fiber/SiC CVI matrix interface), those corresponding to the stable crystalline modification at the temperature considered in the calculations were used.

As far as the initial composition of the system is concerned, the calculations were done for an initial molar ratio  $\alpha = [\text{NH}_3]_{\text{in.}}/[\text{BF}_3]_{\text{in.}}$  ranging from 0.1 to 15. Since in all the calculations  $[\text{BF}_3]_{\text{in.}}$  the number of moles of  $\text{BF}_3$  in the initial gaseous mixture was equal to one, the  $\alpha$ -ratio is also equal to the number of moles of  $\text{NH}_3$  in the initial gas mixture  $[\text{NH}_3]_{\text{in.}}$ . Inasmuch as Hannache *et al.* [2] have shown that the deposition of BN was thermodynamically favored by an excess of  $\text{NH}_3$ , particular attention was given to the results obtained for  $\alpha > 1$ . In order to simulate the effect of the substrate on which the deposition of BN may take place within a preform made of ex-PCS SiC fibers, the calculations were performed successively for initial compositions containing an excess of carbon, silica, silicon carbide or SiC/ $\text{SiO}_2$  mixture as well as for initial compositions consisting only of the  $\text{BF}_3$ – $\text{NH}_3$  mixture. This last composition was regarded as corresponding to the case of a substrate purely inert chemically with respect to the gas phase. Finally, the effect of a possible presence of the gas phase dioxygen was taken into

TABLE 1

Species which have been introduced in the thermodynamic calculations

[BO]	[SiF <sub>2</sub> O]	[BH <sub>2</sub> ]	[CH <sub>4</sub> ]	[SiF <sub>3</sub> ]	<B>
[O <sub>2</sub> ]	[F <sub>2</sub> ]	[BH <sub>3</sub> ]	[C <sub>2</sub> F <sub>2</sub> ]	[SiF <sub>4</sub> ]	<C>
[BO <sub>2</sub> ]	[H <sub>2</sub> O]	[B <sub>2</sub> F <sub>4</sub> ]	[C <sub>2</sub> F <sub>3</sub> N]	[NH <sub>2</sub> ]	<Si>
[B <sub>2</sub> O <sub>2</sub> ]	[NO]	[B <sub>3</sub> H <sub>6</sub> N <sub>3</sub> ]	[C <sub>2</sub> F <sub>4</sub> ]	[NH <sub>3</sub> ]	<B <sub>2</sub> O <sub>3</sub> >
[B <sub>2</sub> O <sub>3</sub> ]	[N <sub>2</sub> ]	[CFN]	[C <sub>2</sub> F <sub>6</sub> ]	[SiH <sub>4</sub> ]	<SiO <sub>2</sub> >
[CH <sub>2</sub> O]	[SiO]	[CF <sub>2</sub> ]	[C <sub>2</sub> H <sub>2</sub> ]	[SiFH <sub>3</sub> ]	<BN>
[H <sub>2</sub> ]	[SiO <sub>2</sub> ]	[CF <sub>2</sub> H <sub>2</sub> ]	[C <sub>2</sub> N <sub>2</sub> ]	[F]	<SiO <sub>2</sub> >
[CO]	[B]	[CF <sub>3</sub> ]	[HF]	[C <sub>2</sub> FH]	<SiB <sub>3</sub> >
[CO <sub>2</sub> ]	[BF]	[CF <sub>3</sub> H]	[SiF <sub>2</sub> H <sub>2</sub> ]	[CFH <sub>3</sub> ]	<SiB <sub>6</sub> >
[C <sub>2</sub> H <sub>4</sub> O]	[BF <sub>2</sub> ]	[CF <sub>4</sub> ]	[SiF <sub>3</sub> H]	[BF <sub>3</sub> ]	<B <sub>4</sub> C>
[Si]	[BF <sub>2</sub> H]	[HCN]	[NF <sub>3</sub> ]		<SiC>
					<Si <sub>3</sub> N <sub>4</sub> >
					<Si <sub>2</sub> N <sub>2</sub> O>

account through calculations run with initial  $\text{BF}_3\text{--NH}_3$  mixtures containing up to 5 mol of oxygen.

In the following, the results of the calculations will be presented as: (i) the mole number at equilibrium, for condensed phases; and (ii) the molar fractions  $X_i = P_i/P$ , where  $P_i$  is the partial pressure of species  $i$  at equilibrium and  $P = \sum P_i$  the total pressure, for the gaseous species. Those species whose relative amounts were less than  $10^{-5}$  (*i.e.* 10 ppm) have been omitted in the figures. Two different kinds of values  $\eta_i$  and  $\gamma_i$  will be used to follow quantitatively the evolution of the system from the initial state to the equilibrium state. The former will be used for the new species (*i.e.* mainly BN) resulting from the chemical reaction. It is defined as the ratio between the mole number of species  $i$  at equilibrium and the initial mole number of the source species from which that species  $i$  has been formed. In the following,  $\eta_i$  will be referred to as thermodynamic or conversion yields. The latter,  $\gamma_i$ , will be used to follow the consumption at equilibrium of a species  $i$  present in the initial composition (*i.e.* a source species such as  $\text{BF}_3$  or a substrate material), due to the chemical reaction. It is defined as the difference between the mole number of that species  $i$  present in the initial composition and the mole number of that species when equilibrium is reached. The  $\gamma_i$  values will be referred to as consumption values. The equations defining the various  $\eta_i$  and  $\gamma_i$  values used in the following are given in Appendix A.

### 3. Results and discussion

Table 2 shows, as an example, the results of the calculations which have been performed for  $T = 1323$  K,  $P = 10$  kPa,  $\alpha = 4.6$  and five different substrates: (i) a purely inert substrate (no substrate material was introduced in the initial composition); (ii) a carbon substrate (with  $\langle \text{C} \rangle_{\text{in.}} = 10$  mol); (iii) a silica substrate (with  $\langle \text{SiO}_2 \rangle_{\text{in.}} = 10$  mol); (iv) a silicon carbide substrate (with  $\langle \text{SiC} \rangle_{\text{in.}} = 10$  mol); and finally (v) a substrate consisting of a mixture of silica and silicon carbide (with  $\langle \text{SiC} \rangle_{\text{in.}} = 8$  and  $\langle \text{SiO}_2 \rangle_{\text{in.}} = 2$  mol). They show that the gaseous species present at equilibrium and originating from the substrate material are only in small amounts for carbon and silica whereas they are present in most significant amounts for the other substrates. Therefore, the former can be considered as quasi-unreactive and the latter as reactive substrates. The corresponding thermodynamic yields  $\eta_i$  and consumption values  $\gamma_i$ , related to both the  $\text{BF}_3$  source species and to the corrosion of the substrate, are listed in Table 3. On the basis of this important feature, the results will be presented and discussed successively for inert or quasi-unreactive substrates, on the one hand, and for reactive substrates, on the other hand.

#### 3.1. Inert and quasi-unreactive substrates

It clearly appears from the example given in Table 2, that the gas phase at equilibrium is made at 99.9 mol% of hydrogen, nitrogen, unreacted  $\text{BF}_3$

TABLE 2

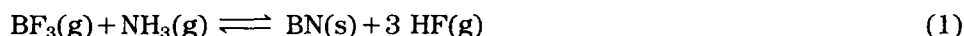
Chemical composition of the gas phase (molar fractions) at equilibrium, calculated for  $\alpha = 4.6$ ;  $T = 1323$  K;  $P = 10$  kPa and various substrate materials representative of the CVI deposition of a BN interphase from a  $\text{BF}_3\text{--NH}_3$  precursor on a SiC (ex-PCS) fiber preform

Species $i$ at equilibrium in the gas phase	Purely inert substrate $X_i$	Carbon <sup>a</sup> substrate $X_i$	Silica <sup>a</sup> substrate $X_i$	SiC <sup>a</sup> substrate $X_i$	SiC–SiO <sub>2</sub> <sup>b</sup> substrate $X_i$
H <sub>2</sub>	$6.6476 \times 10^{-1}$	$6.6431 \times 10^{-1}$	$6.6424 \times 10^{-1}$	$8.1930 \times 10^{-1}$	$8.2116 \times 10^{-1}$
N <sub>2</sub>	$2.2177 \times 10^{-1}$	$2.2178 \times 10^{-1}$	$2.2159 \times 10^{-1}$	$8.7036 \times 10^{-2}$	$7.5611 \times 10^{-2}$
BF <sub>2</sub>	$2.9063 \times 10^{-5}$	$2.9069 \times 10^{-5}$	$2.8437 \times 10^{-5}$	$8.3447 \times 10^{-7}$	$8.9622 \times 10^{-7}$
BF <sub>2</sub> H	$5.2646 \times 10^{-4}$	$5.2639 \times 10^{-4}$	$5.1492 \times 10^{-4}$	$1.6781 \times 10^{-5}$	$1.8044 \times 10^{-5}$
BF <sub>3</sub>	$9.0041 \times 10^{-2}$	$9.0072 \times 10^{-2}$	$8.7133 \times 10^{-2}$	$3.4674 \times 10^{-4}$	$3.7590 \times 10^{-4}$
HF	$2.2879 \times 10^{-2}$	$2.2874 \times 10^{-2}$	$2.2618 \times 10^{-2}$	$3.4066 \times 10^{-3}$	$3.4122 \times 10^{-3}$
NH <sub>3</sub>	$2.9424 \times 10^{-6}$	$2.9396 \times 10^{-6}$	$2.9378 \times 10^{-6}$	$2.5222 \times 10^{-6}$	$2.3588 \times 10^{-6}$
HCN	—	$9.8370 \times 10^{-5}$	—	$6.8435 \times 10^{-5}$	$6.3858 \times 10^{-5}$
CH <sub>4</sub>	—	$2.9861 \times 10^{-4}$	—	$4.5420 \times 10^{-4}$	$4.5627 \times 10^{-4}$
C <sub>2</sub> H <sub>2</sub>	—	$6.5447 \times 10^{-6}$	—	$8.0715 \times 10^{-7}$	$8.0899 \times 10^{-7}$
B <sub>2</sub> O <sub>3</sub>	—	—	$3.5053 \times 10^{-6}$	—	—
H <sub>2</sub> O	—	—	$1.5161 \times 10^{-3}$	—	$5.7033 \times 10^{-6}$
SiF <sub>3</sub> H	—	—	$6.0237 \times 10^{-6}$	$2.4001 \times 10^{-3}$	$2.4065 \times 10^{-3}$
SiF <sub>3</sub>	—	—	$5.8980 \times 10^{-6}$	$1.5885 \times 10^{-3}$	$1.5910 \times 10^{-3}$
SiF <sub>4</sub>	—	—	$2.3367 \times 10^{-3}$	$8.5349 \times 10^{-2}$	$8.5525 \times 10^{-2}$
CO	—	—	—	—	$9.3350 \times 10^{-3}$
SiO	—	—	—	—	$7.8777 \times 10^{-6}$

<sup>a</sup>10 mol.

<sup>b</sup>SiC: 8 mol; SiO<sub>2</sub>: 2 mol in initial composition.

and hydrogen fluoride, when the substrate is purely chemically inert or quasi-unreactive. Both hydrogen and nitrogen result from the thermal decomposition of NH<sub>3</sub> whereas HF is the main product species expected from the overall reaction:



Furthermore, the gas phase at equilibrium also contains trace amounts, *i.e.* less than 0.1 mol%, of boron-containing by-products BF<sub>2</sub> and BF<sub>2</sub>H, which probably result from a slight decomposition of BF<sub>3</sub> as already established by Hannache *et al.* [2]. As shown in Table 3, the conversion yield of BF<sub>3</sub> into BN remains low whatever the nature of the substrate *i.e.*  $\eta_{\text{BN}} = 7.58\%$  for both purely inert and carbon substrates and  $\eta_{\text{BN}} = 8.52\%$  for a silica substrate, owing to the high stability of the BF<sub>3</sub> species.

The use of a carbon substrate instead of a purely inert substrate does not significantly modify the gas-phase composition at equilibrium. However, trace amounts of carbon-containing gaseous corrosion products are present at equilibrium with the following molar fractions: HCN < 100 ppm; CH<sub>4</sub> < 300 ppm and C<sub>2</sub>H<sub>2</sub> < 10 ppm. Therefore, such a substrate can be considered, under CVI conditions, as almost unreactive, its corrosion being very limited, as shown by the low value of  $\gamma_{\text{C}}$  (*i.e.*,  $0.41 \times 10^{-2}$ ).

A slightly more important corrosion of the substrate will be observed at equilibrium, when silica is used since the substrate consumption value

TABLE 3

Chemical composition of the deposit at equilibrium and  $\eta_i$   $\gamma_i$  values, calculated for  $\alpha=4.6$ ;  $T=1323$  K;  $P=10$  kPa and various substrate materials representative of the CVI deposition of a BN interphase from a  $\text{BF}_3\text{-NH}_3$  precursor on a SiC (ex-PCS) fiber preform

Species at equilibrium	Purely inert substrate (mol)	Carbon <sup>a</sup> substrate (mol)	Silica <sup>a</sup> substrate (mol)	SiC <sup>a</sup> substrate (mol)	SiC-SiO <sub>2</sub> <sup>b</sup> substrate (mol)
BN	$7.5899 \times 10^{-2}$	$7.5863 \times 10^{-2}$	$8.5208 \times 10^{-2}$	$9.9695 \times 10^{-1}$	$9.9673 \times 10^{-1}$
C	—	9.9959	—	2.3522	2.3810
SiO <sub>2</sub>	—	—	9.9761	—	1.3764
Si <sub>3</sub> N <sub>4</sub>	—	—	—	0.5358	—
Si <sub>2</sub> N <sub>2</sub> O	—	—	—	—	1.1690
SiC	—	—	—	7.6430	5.5365
B <sub>2</sub> O <sub>3</sub> liq.	—	—	$1.0781 \times 10^{-2}$	—	—
$\gamma\text{-BF}_3$	$8.16 \times 10^{-2}$	$8.53 \times 10^{-2}$	$11.23 \times 10^{-2}$	$99.71 \times 10^{-2}$	$99.68 \times 10^{-2}$
$\gamma\text{-SiC}$	—	—	—	2.357	2.463
$\gamma\text{-SiO}_2$	—	—	$2.39 \times 10^{-2}$	—	0.624
$\gamma\text{-C}$	—	$0.41 \times 10^{-2}$	—	—	—
$\eta\text{-BN}(\%)$	7.58	7.58	8.52	99.69	99.67

<sup>a</sup>10 mol.

<sup>b</sup>SiC: 8 mol; SiO<sub>2</sub>: 2 mol in initial composition.

(for the CVI conditions) corresponding to the example given in Tables 2 and 3, is  $\gamma_{\text{SiO}_2} = 2.39 \times 10^{-2}$ . As a matter of fact, in the presence of an excess of silica more  $\text{BF}_3$  is consumed at equilibrium ( $\gamma_{\text{BF}_3} = 11.23 \times 10^{-2}$  instead of  $8.16 \times 10^{-2}$  for the purely inert substrate or  $8.16 \times 10^{-2}$  for the carbon substrate). One could expect from this feature a higher conversion yield in BN which is not totally the case since some of the boron atoms have reacted with the oxygen atoms of the substrate to give  $\text{B}_2\text{O}_3$ . As a result, the increase in the BN conversion yield is limited to about 1% with respect to the inert or carbon substrates. Finally, the corrosion of the silica substrate is responsible for the occurrence of trace amounts of silicon-containing by-products in the gas phase:  $\text{SiF}_4$  (2300 ppm),  $\text{SiF}_3\text{H}$  (6 ppm) and  $\text{SiF}_3$  (6 ppm) as well as water (1500 ppm).

### 3.1.1. Effect of the $\alpha = [\text{NH}_3]_{\text{in}} / [\text{BF}_3]_{\text{in}}$ ratio

As could be expected, the composition of the system at equilibrium, for given temperature and pressure values, depends on the initial composition *i.e.* on the  $\alpha = [\text{NH}_3]_{\text{in}} / [\text{BF}_3]_{\text{in}}$  values. The variations, as a function of  $\alpha$ , of the molar fractions  $X_i$  of the gaseous species, the mole numbers of the condensed phases and some of the  $\eta_i$  or  $\gamma_i$  thermodynamic ratios are shown in Figs. 1 and 2 for  $T=1323$  K,  $P=10$  kPa, for both the carbon and silica substrate materials. The results of the calculations which were performed for a purely inert substrate are not shown since they are almost identical to those related to the carbon substrate (if one excepts the trace amounts of carbon-containing gaseous by-products, as already mentioned).

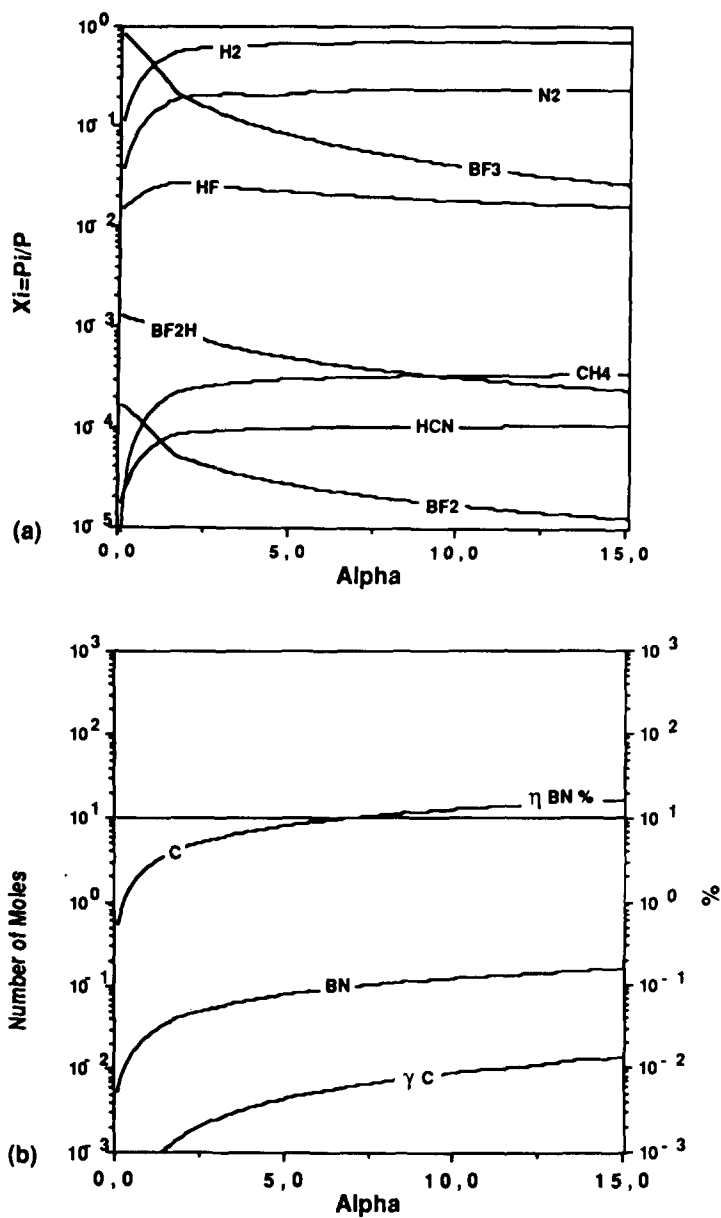


Fig. 1. Variations with  $\alpha$  of (a) the molar fractions  $X_i$  of the gaseous species at equilibrium and (b) the mole numbers of condensed phases at equilibrium and thermodynamic yield or consumption value, calculated for  $T=1323$  K;  $P=10$  kPa and an excess of carbon in the initial composition ( $[BF_3]_{in}=1$  mol;  $\langle C \rangle_{in}=10$  mol)

It clearly appears from Fig. 1(a) that the molar fractions  $X_i$  of hydrogen and nitrogen at equilibrium increase as  $\alpha$  is raised, *i.e.* as the ammonia is more and more in excess with respect to the stoichiometry of the overall



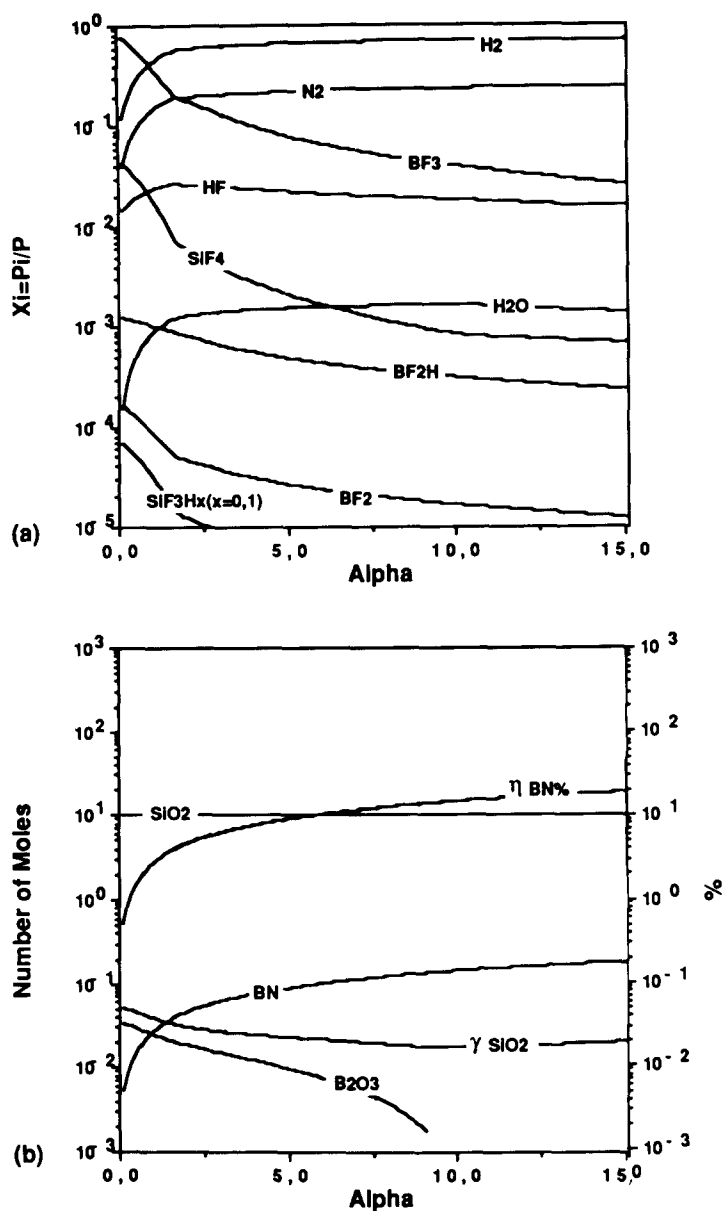


Fig. 2. Variations with  $\alpha$  of (a) the molar fractions  $X_i$  of the gaseous species at equilibrium and (b) the mole numbers of condensed phases at equilibrium and thermodynamic yield or consumption value, calculated for  $T = 1323$  K;  $P = 10$  kPa and an excess of silica in the initial composition ( $[BF_3]_{in} = 1$  mol;  $[SiO_2]_{in} = 10$  mol)

eqn. (3). Simultaneously, and as could have been foreseen on the basis of the law of mass action, the overall reaction corresponding to eqn. (1) is shifted to the right-hand side as evidenced from: (i) the decrease in the

amount of  $\text{BF}_3$  and increase in that of HF (in absolute mole number even it seems to decrease in terms of  $X_i$ ) at equilibrium as  $\alpha$  is raised (*e.g.* for  $\alpha=15$ ,  $\gamma_{\text{BF}_3}=17\times 10^{-2}$  vs.  $8.5\times 10^{-2}$  for  $\alpha=4.6$  in the case of carbon substrate); and (ii) the increase in the conversion yield of  $\text{BF}_3$  into BN as  $\alpha$  is raised (*e.g.*  $\eta_{\text{BN}}=15\%$  for  $\alpha=15$  with respect to  $\eta_{\text{BN}}=7.5\%$  for  $\alpha=4.6$ ) (Fig. 1(b)). Therefore, as already mentioned by Hannache *et al.* [2], an excess of ammonia (with respect to the stoichiometry of eqn. (1) corresponding to  $\alpha=1$ ) has a beneficial effect on the conversion of  $\text{BF}_3$  into BN. However, under CVI conditions, the conversion yield  $\eta_{\text{BN}}$  remains low even for ammonia-rich precursors.

Increasing  $\alpha$ , and thus the amounts of hydrogen and nitrogen resulting from the decomposition of ammonia, favors the corrosion of the carbon substrate as shown by the increase in the amounts of  $\text{CH}_4$  and HCN in the gas phase at equilibrium as well as that of  $\gamma_{\text{C}}$ . However, this chemical attack remains limited, under CVI conditions, even for ammonia-rich precursors (*e.g.*  $\gamma_{\text{C}}\approx 1\times 10^{-2}$  for  $\alpha=15$ ) (Figs. 1(a) and 1(b)).

Conversely, the corrosion of the silica substrate by the gas phase, already mentioned, becomes more and more significant as  $\alpha$  is decreased since it has to be correlated with the formation of a fluorinated silicon species (*i.e.*, mainly  $\text{SiF}_4$ ) from fluorine atoms resulting from the breaking of the B-F bonds. As a matter of fact,  $\gamma_{\text{SiO}_2}$  which is only about  $2.39\times 10^{-2}$  for  $\alpha=15$  reaches a value of about  $5\times 10^{-2}$  for  $\alpha=0.1$ .

### 3.1.2. Effect of temperature and total pressure

The thermal variations of the gas-phase composition at equilibrium, calculated for  $P=10$  kPa and  $\alpha=4.6$ , are shown in Fig. 3 for the conditions simulating a substrate in excess of carbon or silica. The results corresponding to a hypothetical purely inert substrate, very similar to those calculated for the carbon substrate, are not shown as already mentioned.

The  $\text{BF}_3$  molar fraction slowly decreases, whatever the substrate, as the temperature is raised which means that more boron trifluoride is consumed when equilibrium is achieved. As a matter of fact, the  $\text{BF}_3$  consumption value  $\gamma_{\text{BF}_3}$  increases from  $5.6\times 10^{-2}$  to  $17.9\times 10^{-2}$  when the temperature is raised from 1123 to 1723 K but part of the consumed  $\text{BF}_3$  is lost as boron-containing gaseous by-products (*i.e.*  $\text{BF}_2\text{H}$  and  $\text{BF}_2$ ). Moreover, increasing temperature results in a more important corrosion of the substrate material, as shown by the values of  $\gamma_{\text{C}}$  and  $\gamma_{\text{SiO}_2}$  respectively at 1323 K ( $\gamma_{\text{C}}=0.41\times 10^{-2}$  and  $\gamma_{\text{SiO}_2}=2.39\times 10^{-2}$ ) and 1723 K ( $\gamma_{\text{C}}=2.4\times 10^{-2}$  and  $\gamma_{\text{SiO}_2}=8.4\times 10^{-2}$ ). Finally, a temperature increase also results in some changes in the nature of the species originating from a chemical attack of the substrates, *i.e.* the formation of HCN and  $\text{C}_2\text{H}_2$  becomes favored with respect to that of  $\text{CH}_4$  for the carbon substrate whereas the formation of  $\text{SiF}_3$ ,  $\text{SiF}_3\text{H}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{B}_2\text{O}_2$ , BO and  $\text{SiO}_2$  is enhanced compared with that of  $\text{SiF}_4$  and  $\text{H}_2\text{O}$ , for the silica substrate. It is noteworthy that the chemical attack of both substrate materials remains limited even at the highest temperature considered 1723 K (the

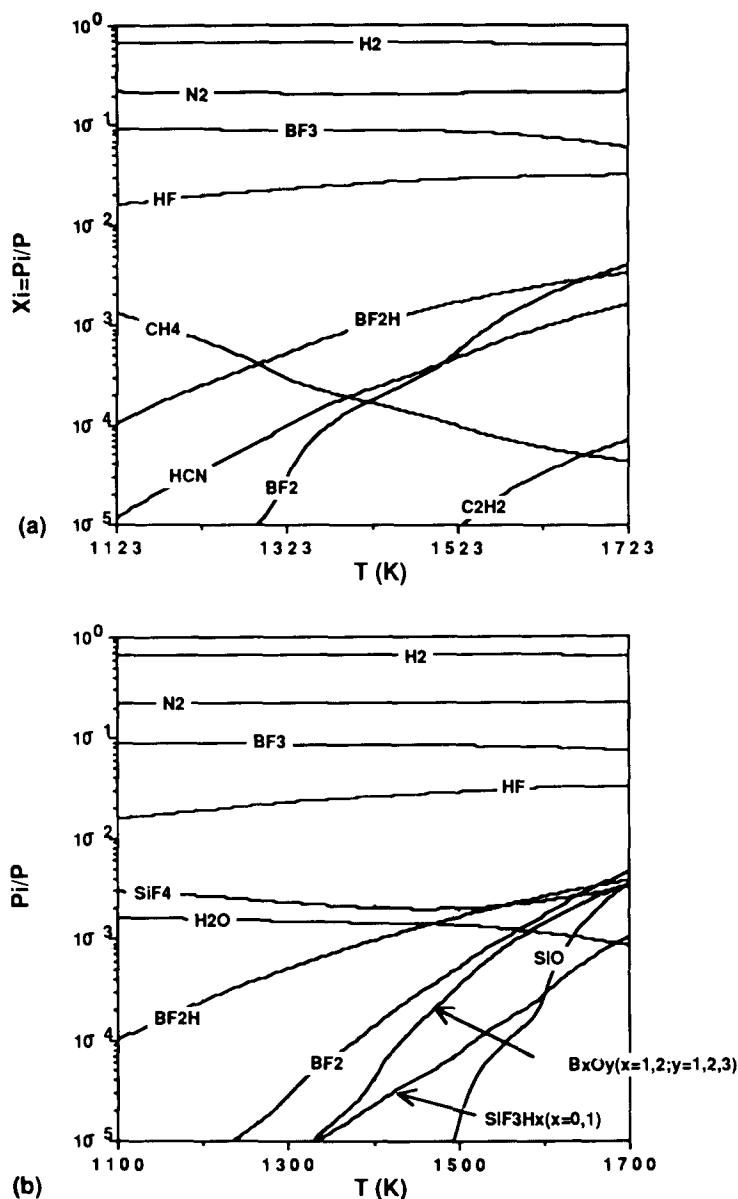


Fig. 3. Thermal variations of the gas phase composition at equilibrium calculated for  $P=10$  kPa an initial composition defined by  $[BF_3]_{in} = 1$  mol and  $\alpha=4.6$  with (a) an excess of carbon ( $\langle C \rangle_{in} = 10$  mol) and (b) an excess of silica ( $\langle SiO_2 \rangle_{in} = 10$  mol).

highest  $X_i$  value for the gaseous species resulting from an attack of the substrates being of the order of  $3 \times 10^{-3}$ .

Under a given total pressure, the  $\eta_{BN}$  thermodynamic yield first increases as the temperature is raised (Fig. 4). It then reaches a maximum before decreasing sharply. Furthermore, the temperature at which this maximum

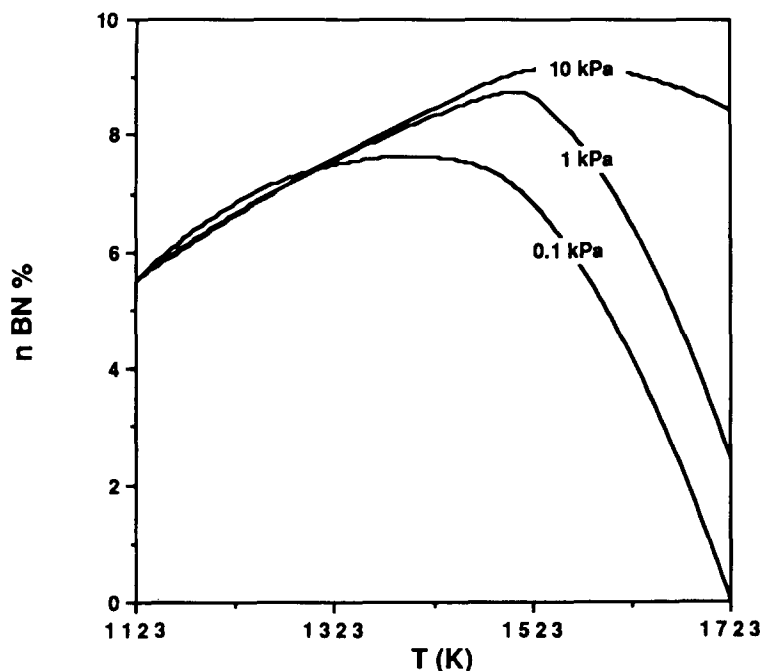


Fig. 4. Thermal variations of the conversion yield of  $\text{BF}_3$  into BN calculated for an initial composition defined by  $[\text{BF}_3]_{\text{in}} = 1$  mol and  $\alpha = 4.6$  in the case of a hypothetical purely inert substrate.

occurs is shifted towards the low temperatures when the total pressure is decreased from 10 to 0.1 kPa. Therefore, the synthesis of BN from  $\text{BF}_3\text{-NH}_3$  is favored, within the 1123–1723 K temperature range and 0.1–10 kPa pressure range considered here, by increasing both the temperature and pressure until a maximum is reached. However, the BN thermodynamic yield remains low (*i.e.* about 9%) under the best conditions.

Finally, the effect of the substrate material (carbon or silica) on the thermal variations of  $\eta_{\text{BN}}$  is shown in Fig. 5 for a total pressure of 10 kPa. For both substrate materials, the BN thermodynamic yield increases (almost linearly) with increasing temperature within the 1123–1500 K range and it decreases when the temperature is further raised beyond the upper limit.

### 3.2. Reactive substrates

A very important chemical attack of the substrate material by the gas phase occurs when an excess of either the pure SiC or the SiC/SiO<sub>2</sub> mixture is introduced into the initial composition of the system, as shown in Tables 2 and 3 for  $T = 1323$  K,  $P = 10$  kPa and  $\alpha = 4.6$ . As a matter of fact, the initial amount of boron trifluoride is almost totally consumed when equilibrium is achieved, the consumption ratio  $\gamma_{\text{BF}_3}$  being equal to  $99.7 \times 10^{-2}$  for both substrate materials (whereas it was also  $8.5 \times 10^{-2}$  for the quasi-unreactive carbon substrate material and  $8.2 \times 10^{-2}$  for the purely inert substrate).

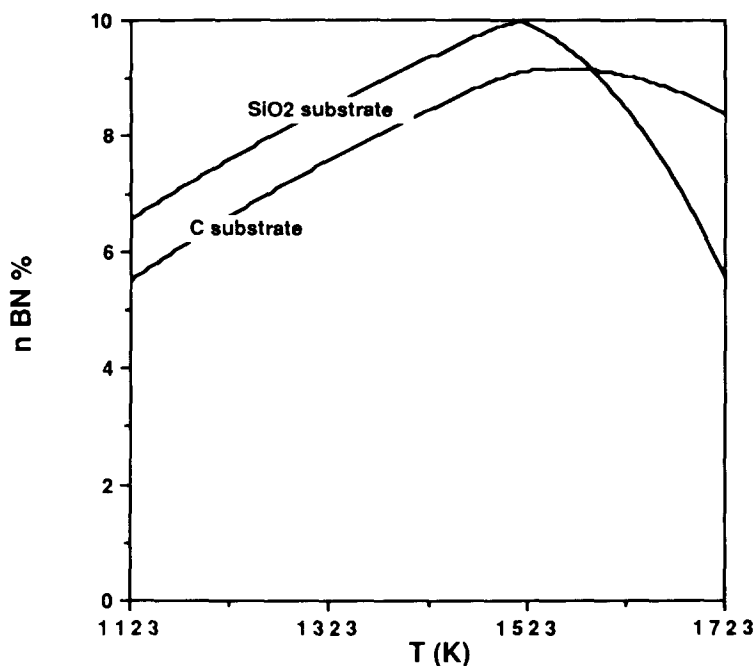
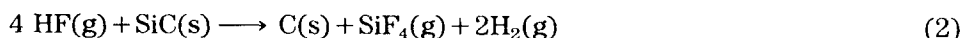
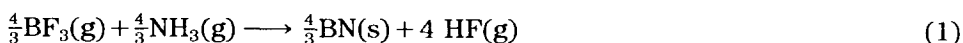


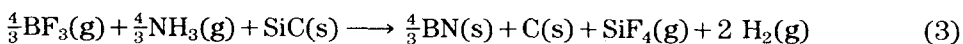
Fig. 5. Thermal variations of the conversion yield of  $\text{BF}_3$  into BN calculated for  $P = 10$  kPa and an initial composition defined by  $[\text{BF}_3]_{\text{in}} = 1$  mol and  $\alpha = 4.6$  with an excess of carbon or silica ( $\langle \text{C} \rangle_{\text{in}} = 10$  mol or  $\langle \text{SiO}_2 \rangle = 10$  mol).

The chemical reactions that take place between the gas phase and the substrate material is also evidenced by the high consumption values, *e.g.*  $\gamma_{\text{SiC}} = 2.36$ . These reactions involving the SiC-based substrate materials result in the formation of new species at equilibrium, *i.e.*  $\text{SiF}_4$  in the gas phase and carbon in the solid (Tables 2 and 3).

On the basis of these results, the following chemical mechanism may be suggested.



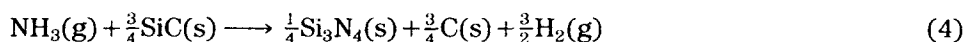
Addition of eqns. (1) and (2) gives



The formation of  $\text{SiF}_4$  (a very stable molecule) and of carbon according to eqn. (2) consumed all the hydrogen fluoride generated according to eqn. (1), with the result that the equilibrium corresponding to eqn. (1) is shifted almost totally to the right-hand side, as shown by the high thermodynamic conversion yield of  $\text{BF}_3$  into BN, *i.e.*  $\eta_{\text{BN}} = 99.7\%$  (with respect to 7.6% for the hypothetical purely inert of carbon substrates).

Furthermore, the chemical attack of the pure SiC substrate material could also be the result of a chemical reaction between SiC and ammonia,

since ammonia is in excess for  $\alpha=4.6$ , according to the following equation



as supported by the occurrence of a significant amount of  $\text{Si}_3\text{N}_4$  at equilibrium (*i.e.* 0.5358 mol, for the example given in Tables 2 and 3). Finally, all the ammonia introduced in the initial composition is not totally consumed by the chemical reactions corresponding to eqns. (3) and (4) since nitrogen which may result from the thermal decomposition of unreacted ammonia according to the following equation.



is observed in significant amounts at equilibrium (*i.e.* 0.72954 mol for the example considered).

In summary, the synthesis of BN from an ammonia-rich  $\text{BF}_3\text{--NH}_3$  mixture (at  $T=1323$  K and  $P=10$  kPa) in the presence of an excess of SiC can be described, at least in a first approximation, on the basis of a chemical mechanism involving eqns. (3)–(5). This mechanism seems validated by Table 4 which permits comparison of the compositions of the system after reaction, derived from the thermodynamic calculations (exact solution) and from eqns. (3)–(5) (the mole number of nitrogen formed according to eqn. (5) being that given by the thermodynamic calculations). The slight differences for BN and  $\text{SiF}_4$  are due to the formation of small amounts of gaseous by-products containing boron (*e.g.*  $\text{BF}_2\text{H}$  and  $\text{BF}_2$ ) or silicon (*e.g.*  $\text{SiF}_3\text{H}$  and  $\text{SiF}_3$ ), as well as to the occurrence of some unreacted  $\text{BF}_3$  at equilibrium.

The thermodynamic calculations when applied to an initial composition containing an excess of silicon carbide and silica (simulating a substrate made of a  $\text{SiC/SiO}_2$  mixture) show that: (i) SiC is severely attacked by the gas phase as already discussed; and (ii) silica undergoes a slightly more important attack than that reported in Section 3.1 when it was introduced

TABLE 4

Compositions obtained after chemical reactions, for a system consisting initially of 1 mol of  $\text{BF}_3$ , 4.6 mol of  $\text{NH}_3$  and 10 mol of SiC, from (i) a chemical mechanism involving eqns. (3)–(5), on the one hand, and (ii) the thermodynamic approach assuming that equilibrium is reached at  $T=1323$  K and  $P=10$  kPa

	SiC consumed (mol)	BN formed (mol)	$\text{Si}_3\text{N}_4$ formed (mol)	Carbon formed (mol)	$\text{SiF}_4$ formed (mol)	Hydrogen formed (mol)	Nitrogen formed (mol)
Eqn. (3)	0.7500	1	—	0.7500	0.7500	1.500	—
Eqn. (4)	1.6074	—	0.5358	1.6074	—	3.2148	—
Eqn. (5)	—	—	—	—	—	2.1886	0.7295 <sup>a</sup>
Total	2.3574	1	0.5358	2.3574	0.7500	6.9034	0.7295 <sup>a</sup>
Thermodynamic calculations	2.3570	0.9969	0.5358	2.3522	0.7154	6.8674	0.7295

<sup>a</sup>Assumed to be equal to that given by the thermodynamic calculations by hypothesis.

alone in the initial composition (the consumption values being 0.624 instead of  $2.39 \times 10^{-2}$ ). Moreover, it appears from Table 3 that  $\text{Si}_3\text{N}_4$  is no longer formed for this particular initial composition (with  $\alpha = 4.6$ ); at least,  $\text{Si}_2\text{N}_2\text{O}$  is formed.

### 3.2.1. Effect of the $\alpha = [\text{NH}_3]_{\text{in.}} / [\text{BF}_3]_{\text{in.}}$ ratio

The variations, as a function of  $\alpha$ , of the composition of the solid obtained at equilibrium ( $T = 1323$  K and  $P = 10$  kPa) from 1 mol of  $\text{BF}_3$  and an excess of substrate material are shown in Fig. 6.

At low  $\alpha$  values (*i.e.*  $\alpha < 1$ ) for the two substrate materials, the condensed phases formed in significant amounts at equilibrium are BN and free carbon whereas, conversely, some silicon carbide is consumed, all these features suggesting that the chemical reaction taking place corresponds mainly to eqn. (3).

Beyond this limit (*i.e.* for  $\alpha > 1$ ) ammonia is in excess. As a result, the substrate material is now attacked by two different gaseous species: (i)  $\text{BF}_3$  mainly according to eqn. (3); and (ii)  $\text{NH}_3$  according to eqn. (4) depending on the nature of the substrate material. As a result, the deposit formed under such conditions will be a mixture of BN, free carbon and either  $\text{Si}_3\text{N}_4$  (for pure SiC) or  $\text{Si}_2\text{N}_2\text{O}$  (for SiC/SiO<sub>2</sub> mixture and if  $\alpha$  is not too high). The occurrence of a ternary BN–C– $\text{Si}_3\text{N}_4$  deposit in equilibrium with SiC is consistent with the mean features of the Si–B–C–N quaternary phase diagram, tentatively drawn by Metais [29] and Ignat *et al.* [17], as shown in Fig. 7. Thus, within this initial composition range, the BN thermodynamic yield  $\eta_{\text{BN}}$  remains constant and equal to almost 100% (since all the available  $\text{BF}_3$  is converted into BN) whereas the consumption value  $\gamma_{\text{SiC}}$  progressively increases as  $\alpha$  is raised, *i.e.* as more substrate material reacts with  $\text{NH}_3$ .

Finally and in the particular case of the SiC/SiO<sub>2</sub> substrate material, for a high enough  $\alpha$  ratio (*i.e.* for  $\alpha \geq 12$ ), all the arbitrary amount of silica introduced in the initial composition is consumed by reaction with the gas phase. Under such conditions,  $\text{Si}_3\text{N}_4$  is formed (eqn. (4)) and the deposit in equilibrium with SiC is made of BN, C,  $\text{Si}_2\text{N}_2\text{O}$  and  $\text{Si}_3\text{N}_4$ . An evolution of this kind was reported previously by Wada *et al.* [33] in the related Si–C–N–O quaternary system.

### 3.2.2. Effect of temperature and total pressure

The thermal variations in the composition of the solid at equilibrium are shown in Fig. 8, for  $P = 10$  kPa,  $\alpha = 4.6$  and an excess of either pure SiC or SiC/SiO<sub>2</sub> substrate material in the initial composition.

When an excess of SiC is introduced into the initial composition, the effect of temperature on the equilibrium composition of the solid is different depending on whether temperature falls below or above a critical value of 1371 K. For  $T < 1371$  K, two chemical phenomena already discussed in Section 3.2.1 take place: (i) the deposition of BN from  $\text{BF}_3$  enhanced by the substrate, which results in a first attack of the substrate by HF (eqn.

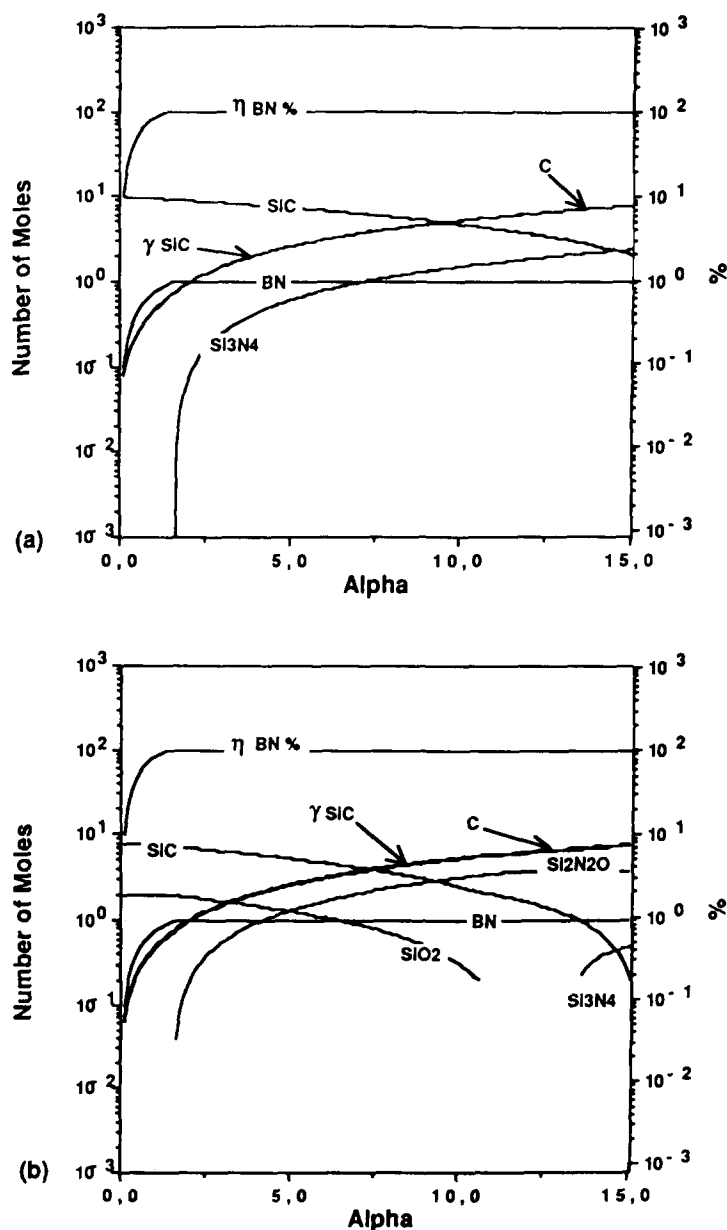


Fig. 6. Variations as a function of  $\alpha$  of the equilibrium composition of the solid formed at 1323 K and 10 kPa from 1 mole of  $\text{BF}_3$ : (a) with 10 mol of SiC and (b) 8 mol of SiC plus 2 mol of  $\text{SiO}_2$  in the initial composition.

(3)); and (ii) another attack of the substrate by ammonia, which is in excess for  $\alpha = 4.6$ , yielding a deposition of  $\text{Si}_3\text{N}_4$  (eqn. (4)). Simultaneously, free carbon is also formed (eqns. (3) and (4)). Within this temperature range, the amount of  $\text{Si}_3\text{N}_4$  (as well as that of carbon) at equilibrium progressively



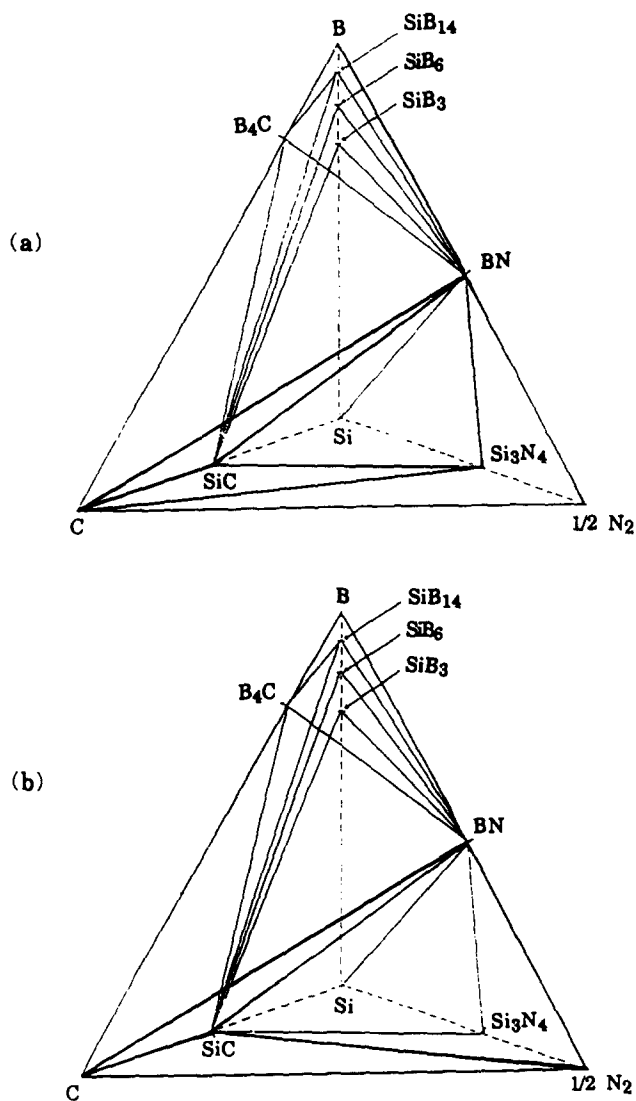


Fig. 7. Main features of the Si-C-B-N phase diagram as calculated by Metals and Bernard (from ref. [17,29]): (a) at 1200 K and 100 kPa; (b) at 1500 K and 10 kPa.

decreases as temperature is raised. Conversely, for  $T > 1371$  K, the SiC substrate material is no longer attacked by ammonia and  $Si_3N_4$  is no longer formed (*i.e.* the reaction mechanism is thought to be limited to reaction (3)). Under such conditions, the deposit is simply made of BN and free carbon in equilibrium with SiC. As the temperature is raised within this temperature range, the mole numbers of both the BN and the free carbon slowly decrease together (eqn. (3)) due to the formation of gaseous by-products. The thermal evolution of the system, from a state where the solid consists of four phases

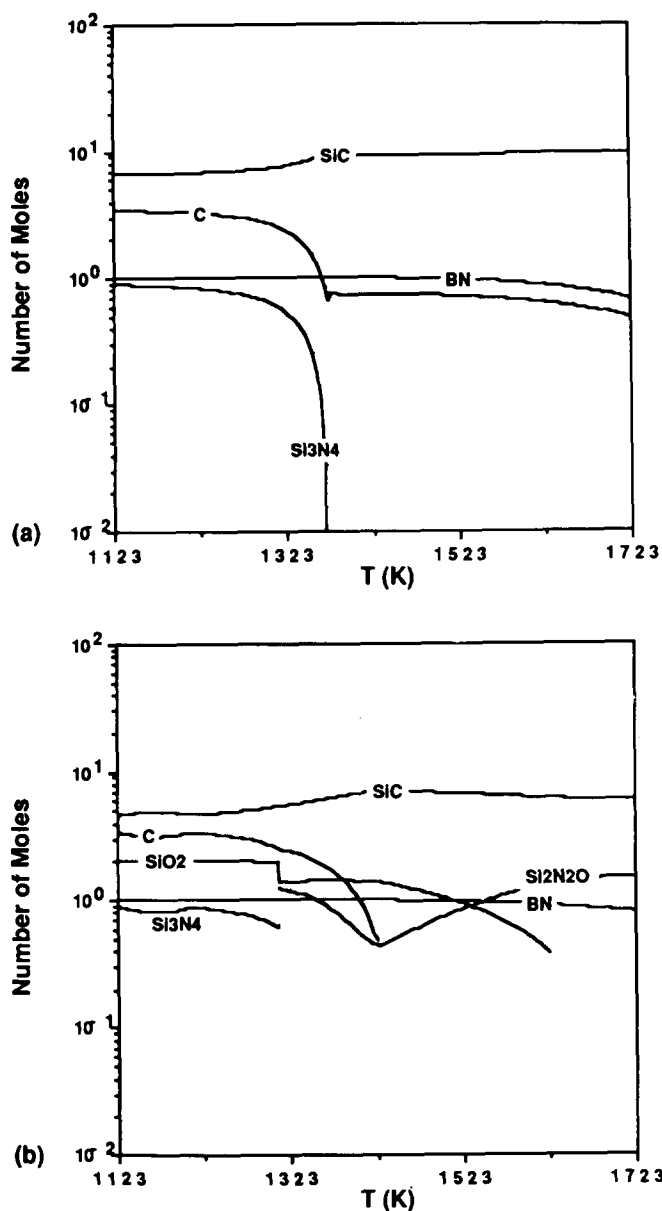


Fig. 8. Thermal variations of the solid composition at equilibrium, calculated for  $P=10$  kPa an initial composition defined by  $[\text{BF}_3]_{\text{in}}=1$  mol and  $\alpha=4.6$  with: (a) an excess of SiC (10 mol) and (b) an excess of SiC/SiO<sub>2</sub> (8 mol of SiC plus 2 mol of SiO<sub>2</sub>).

(i.e. BN,  $\text{Si}_3\text{N}_4$ , SiC and C) to another state where it is made of only three phases (i.e. BN, SiC and C), is consistent with the main features of the Si-C-B-N quaternary phase diagrams tentatively drawn by Metais [29] and Ignat *et al.* [17] (Figs. 7(a) and (b)). When the temperature is raised from

1200 to 1500 K, the point representative of the system composition moves from a four solid phase volume ( $\text{SiC-Si}_3\text{N}_4\text{-BN-C}$ ) to a volume where three solid phases only ( $\text{SiC-BN-C}$ ) are in equilibrium with nitrogen (assuming that the equilibria involving the solid phases are not too significantly modified by pressure in as much as the pressure is not the same for the two diagrams).

The thermal variations in the solid composition at equilibrium are more complex for the system containing an excess of  $\text{SiC/SiO}_2$  in the initial composition (Fig. 8(b)). At low temperatures, *i.e.* for  $1123 < T < 1310$  K, the attack of the substrate is limited to  $\text{SiC}$  and may occur mainly according to eqns. (3) and (4) with the formation of  $\text{BN}$ ,  $\text{Si}_3\text{N}_4$  and free carbon which are in equilibrium with  $\text{SiC}$  and the unreacted  $\text{SiO}_2$ . Conversely, for  $1310 < T < 1700$  K,  $\text{Si}_3\text{N}_4$  is no longer formed. As the temperature is raised, the chemical attack on the substrate due to  $\text{NH}_3$  consumed is mainly  $\text{SiO}_2$  giving rise to the formation of  $\text{Si}_2\text{N}_2\text{O}$ . Within this temperature range, the solid in equilibrium with the gas phase is successively made of: (i)  $\text{SiC-C-BN-Si}_2\text{N}_2\text{O-SiO}_2$ ; (ii)  $\text{SiC-BN-Si}_2\text{N}_2\text{O-SiO}_2$ ; and (iii)  $\text{SiC-BN-Si}_2\text{N}_2\text{O}$ , as the temperature is raised when an arbitrary amount of silica is consumed.

As shown in Fig. 9, a decrease in the total pressure has a strong effect on both the thermodynamic  $\eta_{\text{BN}}$  yield and  $\eta_{\text{SiC}}$  consumption ratio for the initial composition containing an excess of  $\text{SiC}$ . As a matter of fact the  $\text{SiC}$  consumption value decreases, for  $T = 1323$  K and  $\alpha = 4.6$ , from 2.327 to

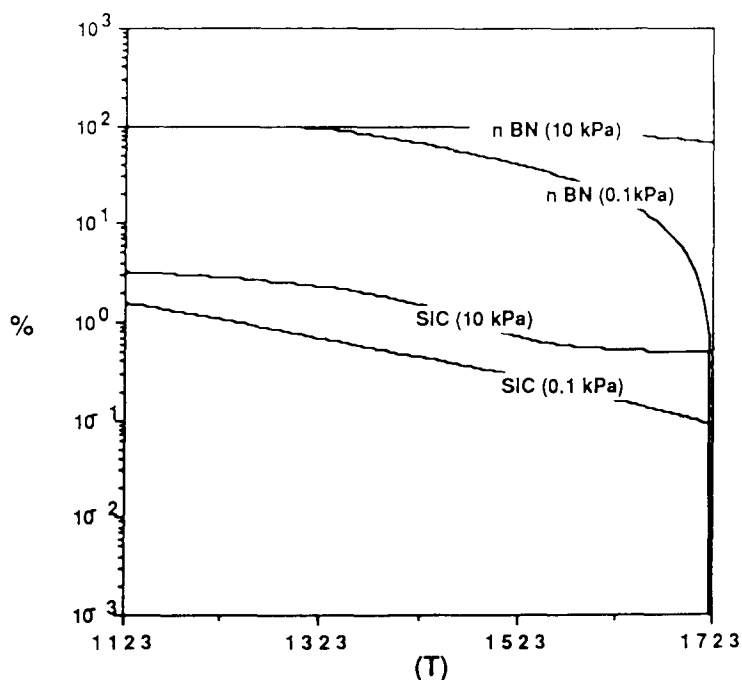


Fig. 9. Thermal variations of the BN thermodynamic yield and substrate consumption value at 10 and 0.1 kPa for an initial system of composition:  $[\text{BF}_3]_{\text{in}} = 1$  mol;  $[\text{NH}_3]_{\text{in}} = 4.6$  mol and  $\langle \text{SiC} \rangle_{\text{in}} = 10$  mol.

0.634 when the total pressure is lowered from 10 to 1 kPa. Since the chemical attack of the substrate by the gas phase is less important when pressure is decreased: (i) the BN thermodynamic yield is lower (93.1% at 0.1 kPa instead of 99.7% at 10 kPa for  $T=1323$  K and  $\alpha=4.6$ ); and (ii) less carbon and  $\text{Si}_3\text{N}_4$  are formed. The effect of lowering the pressure on the BN thermodynamic yield, which remains small at 1323 K, is dramatic at 1723 K ( $\eta_{\text{BN}}=66.5\%$  at 10 kPa and it falls to almost 0 at 0.1 kPa). In a similar manner, decreasing the total pressure results in a less pronounced chemical attack of the substrate material in the system containing an excess of  $\text{SiC}/\text{SiO}_2$  in the initial composition and therefore to lower BN thermodynamic yields.

### 3.3. Effect of a contamination of the gas phase by oxygen

Inasmuch as the occurrence of oxygen as an impurity in the gas phase during the CVI of BN within a fibrous preform may modify the nature of the interfaces, a few calculations were run with oxygen in the initial composition of the system. The results for the different substrate materials are schematically shown in Tables 5 and 6, in terms of: (i) the occurrence of any BN deposit; and (ii) the nature of the oxides, gaseous or solids, formed at equilibrium for  $T=1323$  K,  $P=10$  kPa and  $\alpha=5$ .

The results can be discussed on the basis of the competition that takes place between the various reducing agents. When boron is the only reducing

TABLE 5

Chemical composition of the gas phase (molar fractions) at equilibrium, calculated for one mol of oxygen;  $\alpha=5$ ;  $T=1323$  K;  $P=10$  kPa and various substrate materials representative of the CVI deposition of a BN interphase from a  $\text{BF}_3\text{-NH}_3$  precursor on a SiC (ex-PCS) fiber preform

Species $i$ at equilibrium in the gas phase	Purely inert substrate $X_i$	Carbon <sup>a</sup> substrate $X_i$	Silica <sup>a</sup> substrate $X_i$	SiC <sup>a</sup> substrate $X_i$	SiC-SiO <sub>2</sub> <sup>b</sup> substrate $X_i$
H <sub>2</sub>	$4.8786 \times 10^{-1}$	$5.6685 \times 10^{-1}$	$4.8805 \times 10^{-1}$	$8.2777 \times 10^{-1}$	$8.2777 \times 10^{-1}$
N <sub>2</sub>	$2.2177 \times 10^{-1}$	$1.8924 \times 10^{-1}$	$2.2186 \times 10^{-1}$	$7.5611 \times 10^{-2}$	$7.5611 \times 10^{-2}$
BF <sub>2</sub>	$1.7517 \times 10^{-5}$	$2.5309 \times 10^{-5}$	$1.7249 \times 10^{-5}$	$8.6242 \times 10^{-7}$	$8.6242 \times 10^{-7}$
BF <sub>2</sub> H	$2.7184 \times 10^{-4}$	$4.2336 \times 10^{-4}$	$2.6773 \times 10^{-4}$	$1.7433 \times 10^{-5}$	$1.7433 \times 10^{-5}$
BF <sub>3</sub>	$4.0243 \times 10^{-2}$	$7.0329 \times 10^{-2}$	$3.9428 \times 10^{-2}$	$3.5171 \times 10^{-4}$	$3.5171 \times 10^{-4}$
HF	$1.4533 \times 10^{-1}$	$1.8949 \times 10^{-2}$	$1.4464 \times 10^{-1}$	$3.3607 \times 10^{-3}$	$3.3607 \times 10^{-3}$
NH <sub>3</sub>	$1.8499 \times 10^{-6}$	$2.1403 \times 10^{-6}$	$1.8514 \times 10^{-6}$	$2.3874 \times 10^{-6}$	$2.3874 \times 10^{-6}$
HCN	—	$8.3936 \times 10^{-5}$	—	$6.4114 \times 10^{-5}$	$6.4114 \times 10^{-5}$
CH <sub>4</sub>	—	$2.1742 \times 10^{-4}$	—	$4.6364 \times 10^{-4}$	$4.6364 \times 10^{-4}$
C <sub>2</sub> H <sub>2</sub>	—	$5.5848 \times 10^{-6}$	—	$8.1550 \times 10^{-7}$	$8.1550 \times 10^{-7}$
B <sub>2</sub> O <sub>3</sub>	$3.5053 \times 10^{-6}$	—	$3.5053 \times 10^{-6}$	—	—
H <sub>2</sub> O	$1.0476 \times 10^{-1}$	$6.4867 \times 10^{-5}$	$1.0518 \times 10^{-1}$	$5.7492 \times 10^{-6}$	$5.7492 \times 10^{-6}$
SiF <sub>3</sub> H	—	—	$3.2028 \times 10^{-7}$	$2.2808 \times 10^{-3}$	$2.2808 \times 10^{-3}$
SiF <sub>3</sub>	—	—	$2.7466 \times 10^{-7}$	$1.5018 \times 10^{-3}$	$1.5018 \times 10^{-3}$
SiF <sub>4</sub>	—	—	$8.1179 \times 10^{-4}$	$7.9194 \times 10^{-2}$	$7.9194 \times 10^{-2}$
CO	—	$1.5381 \times 10^{-1}$	—	$9.3350 \times 10^{-3}$	$9.3350 \times 10^{-3}$
SiO	—	—	—	$7.8777 \times 10^{-6}$	$7.8777 \times 10^{-6}$

<sup>a</sup>10 mol.

<sup>b</sup>SiC: 8 mol; SiO<sub>2</sub>: 2 moles in initial composition.

TABLE 6

Chemical composition of the deposit at equilibrium and  $\eta_i \gamma_i$  values, calculated for one mol of oxygen,  $\alpha = 5$ ;  $T = 1323$  K;  $P = 10$  kPa and various substrate materials representative of the CVI deposition of a BN interphase from a  $\text{BF}_3\text{--NH}_3$  precursor on a SiC (ex-PCS) fiber preform

Species at equilibrium	Purely inert substrate (mol)	Carbon <sup>a</sup> substrate (mol)	Silica <sup>a</sup> substrate (mol)	SiC <sup>a</sup> substrate (mol)	SiC–SiO <sub>2</sub> <sup>b</sup> substrate (mol)
BN	0	$8.0146 \times 10^{-2}$	0	$9.9666 \times 10^{-1}$	$9.9666 \times 10^{-1}$
C	—	7.9907	—	3.5968	3.5968
SiO <sub>2</sub>	—	—	9.9908	$2.9811 \times 10^{-1}$	2.2981
Si <sub>3</sub> N <sub>4</sub>	—	—	—	—	—
Si <sub>2</sub> N <sub>2</sub> O	—	—	—	1.3195	1.3195
SiC	—	—	—	6.3143	4.3143
B <sub>2</sub> O <sub>3</sub> (l)	$2.7297 \times 10^{-1}$	—	$2.7765 \times 10^{-1}$	—	—
$\gamma\text{--BF}_3$	$54.64 \times 10^{-2}$	$8.60 \times 10^{-2}$	$55.57 \times 10^{-2}$	$99.68 \times 10^{-2}$	$99.68 \times 10^{-2}$
$\gamma\text{--SiC}$	—	—	—	3.686	3.686
$\gamma\text{--SiO}_2$	—	—	$0.92 \times 10^{-2}$	—	—
$\gamma\text{--C}$	—	2.009	—	—	—
$\eta\text{--BN}(\%)$	0	8.01	0	99.66	99.66

<sup>a</sup>10 mol.

<sup>b</sup>SiC: 8 mol; SiO<sub>2</sub>: 2 mol in initial composition.

agent with hydrogen, *i.e.* for the hypothetical inert or silica substrates, B<sub>2</sub>O<sub>3</sub> is formed at the expense of BN (which may no longer be present at equilibrium when the amount of oxygen is large enough) as well as significant amounts of water. Under such conditions, both reducing agents are active and the occurrence of enough oxygen in the gas phase may preclude the formation of any BN deposit.

On the contrary, when carbon is introduced in excess in the initial composition, it preferentially reacts with oxygen to give mainly carbon monoxide whereas BN is deposited from BF<sub>3</sub> with a thermodynamic yield similar to that reported for the system which did not contain any oxygen. Furthermore, the amount of water at equilibrium is limited. These results show that, as could be expected, carbon is among the three reducing agents (*i.e.* carbon, boron and hydrogen) which have the highest affinity for the oxygen impurity. Under such conditions, the main drawback of oxygen lies in the fact that it yields some corrosion of the substrate material.

Finally, in systems initially containing an excess of SiC-based substrate material (either pure SiC or SiC/SiO<sub>2</sub> mixture), the effect of oxygen is similar to that described for carbon with the exception that pure carbon is now replaced by SiC as a reducing agent (Fig. 10). On the one hand, the oxygen impurity reacts with SiC from the substrate material according to the well known equation (since oxygen is present in a limited amount):



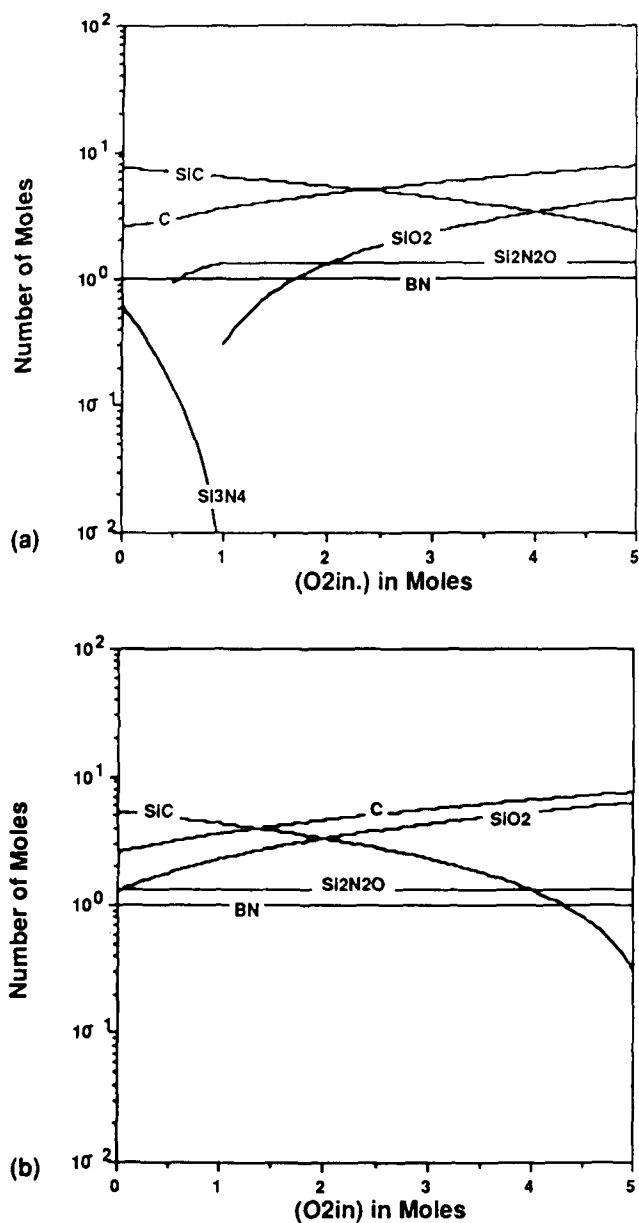


Fig. 10. Effect of oxygen on the composition of the solid at equilibrium calculated for  $T=1323$  K;  $P=10$  kPa;  $\alpha=5$  and an excess of (a) SiC (10 mol) and (b) SiC/SiO<sub>2</sub> (8 moles SiC and 2 mol SiO<sub>2</sub>) introduced in the initial composition.

On the other hand, BN is still deposited from  $BF_3$  with a thermodynamic yield (*i.e.* about 99%) similar to that previously reported for the same system but without any oxygen in the initial gas-phase composition. It is noteworthy that Si<sub>2</sub>N<sub>2</sub>O is formed in the presence of oxygen in the system containing

an excess of pure SiC in its initial composition. The amount of  $\text{Si}_2\text{N}_2\text{O}$  at equilibrium does not depend on that of the oxygen introduced into the initial composition for both substrate materials (except for pure SiC below 1 mol of oxygen).

#### 4. Concluding remarks

Our thermodynamic study has shown that the chemical phenomena that may take place during the deposition of BN from  $\text{BF}_3\text{--NH}_3$  gaseous mixture are very different depending on whether the substrate is quasi-unreactive, *i.e.* made of carbon or silica; or reactive, *i.e.* consisting of a SiC-based material.

For the quasi-unreactive substrates and as already established by Hannache *et al.* [2] the BN deposition occurs mainly according to eqn. (1) with a low yield owing to the high stability of  $\text{BF}_3$  ( $\Delta G_f^0$  (1300 K) =  $-1057.07 \text{ kJ mol}^{-1}$ ) [35]. Furthermore, increasing the  $\alpha$ -ratio only slightly shifts the equilibrium to the right-hand side, as shown in Fig. 1. In the same manner, the BN yield is slightly improved when both the temperature and the total pressure are raised (Fig. 4). However, the  $\eta_{\text{BN}}$  yield remains low (*i.e.* below about 20%) even under the best conditions. In the particular case of a BN interphase which would have to be deposited on either a single filament or a spread tow, one could take advantage of these features by performing the deposition under high temperature, total pressure and  $\alpha$ -ratio conditions. Conversely, when the BN interphase has to be deposited *in situ* on the surface of a fiber located in the pore network of a fibrous preform, the specific requirements of the CVI isothermal/isobaric process preclude any significant increase in both temperature and total pressure [38, 39]. As a matter of fact, the low BN thermodynamic yield which characterizes the CVI of BN from that of  $\text{BF}_3\text{--NH}_3$ , which would be an important drawback for the infiltration of a BN matrix (owing to the long durations required to achieve the full densification of a porous preform), is not a serious disadvantage for the infiltration of a BN interphase whose thickness is of the order of  $1 \mu\text{m}$  only. On the other hand, the fact that almost no chemical attack of the substrate occurs, under such conditions, supports the assumption that the BN interphase deposition from  $\text{BF}_3\text{--NH}_3$  would not result in any significant degradation of the fiber strength.

The chemical phenomena involved in the deposition of BN from a gaseous  $\text{BF}_3\text{--NH}_3$  precursor is dramatically modified when the substrate is made of a SiC-based material. Under such conditions: (i) the BN thermodynamic yield is almost equal to 100% (Fig. 6) due to the formation of the very stable  $\text{SiF}_4$  fluoride ( $\Delta G_f^0$  (1300 K) =  $-1428.3 \text{ kJ mol}^{-1}$ ) according to eqn. (2); but (ii) the deposit is no longer pure BN but consists of a mixture of BN and free carbon, as shown by the overall eqn. (3). Furthermore, if deposition is performed with a  $\text{BF}_3\text{--NH}_3$  precursor rich enough in ammonia, another chemical attack of the substrate will take place with the formation of a new

solid phase (*i.e.*  $\text{Si}_3\text{N}_4$  or  $\text{Si}_2\text{N}_2\text{O}$ ) as shown by eqn. (4). This latter phenomenon could however be suppressed, at least for a pure SiC substrate, if the deposition is performed at a high enough temperature (due to the limited thermal stability of  $\text{Si}_3\text{N}_4$ ) as shown in Fig. 8(a). Thus, the use of a SiC-based substrate has the advantage of improving the BN thermodynamic yield, but also the drawback of resulting in a serious chemical attack of the substrate. One could reasonably assume that the latter would significantly lower the strength of any SiC-based fibrous reinforcement even if the exposure to the gas phase is limited in time.

Finally, the thermodynamic calculations have shown that a contamination of the gas phase by oxygen may modify the chemical phenomena involved in the deposition of a BN interphase from a  $\text{BF}_3\text{--NH}_3$  precursor. In the worst case, *i.e.* that of a  $\text{SiO}_2$ -substrate, the solid deposited may not be any longer BN but  $\text{B}_2\text{O}_3$ . However, when the substrate is made of carbon or SiC, BN is still deposited in the presence of oxygen but again the substrate will be chemically damaged (due to the formation of CO) with a possible lowering of its reinforcing potential if it is fibrous.

The application of the results of the thermodynamic study to the specific case of the infiltration of a BN interphase in a preform made from ex-PCS fibers (*e.g.* Nicalon fibers) is not straightforward owing to their chemical complexity. On the one hand, the fiber seems to be, in the bulk, a nanoscale mixture of  $\beta$ -SiC and free carbon in an amorphous Si-(C,O) continuum, according to the most recent studies [18, 19, 22]. On the other hand, the fiber surface seems to contain free silica and free carbon. However, it is not yet perfectly established whether these two phases are mixed together [19, 20] or alternate *e.g.* as a carbon/silica/carbon sequence [21]. In either case, the result of our thermodynamic calculations suggest that ex-PCS SiC fibers when coated with a  $\text{SiO}_2/\text{C}$  mixture should be a quasi-unreactive substrate with respect to the infiltration of a BN interphase from a  $\text{BF}_3\text{--NH}_3$  precursor (with  $\alpha > 1$ ). As a matter of fact, TEM analyses of the fiber-matrix interfaces in a SiC/BN/SiC composite reported elsewhere gave evidence of the occurrence of a  $\text{SiO}_2/\text{C}$  sublayer sequence between the BN interphase and the ex-PCS SiC fiber [14]. Although this  $\text{SiO}_2/\text{C}$  sequence could have been generated during the CVI deposition of the SiC matrix (several hundreds of hours at approximately 1000 °C) as a result of an intrinsic chemical evolution of the fibers [38], we thought that it might have been present at the beginning of the process (acting actually as substrate for BN), as suggested by the TEM analyses performed on the surface of Nicalon fibers, by Maniette [21]. Therefore, if one assumes that the ex-PCS SiC fibers are uniformly coated with a thin film made of silica and carbon, the BN-interphase deposition treatment should not significantly damage the fibers from a mechanical standpoint. On the contrary, the C-SiO<sub>2</sub> film may not be strictly continuous due to, for example, (i) a non-uniform formation process (SiO<sub>2</sub> is thought to result from a surface oxidation of the fiber whether carbon might be formed by pyrolysis of the organic size or/and surface decomposition of SiC or Si-(C,O)); as well as (ii) local chemical etching. Under such conditions,



the fibers should be considered, at least locally as a reactive substrate (since they contain both SiC and Si-(C,O) species in the bulk. They would be chemically attacked locally by the  $\text{BF}_3\text{-NH}_3$  gaseous mixture, with some lowering of their strength. As already mentioned, ex-PCS SiC fibers contain significant amounts of oxygen in the bulk (*i.e.* 10 at.%) introduced during the stabilization step (to render the green fiber infusible before pyrolysis). It is now accepted that this oxygen is present as a ternary amorphous Si-C-O phase, which has not been taken into account in our calculations, which lack thermodynamic data [18, 19, 22]. We think that its behavior with respect to the gas phase during the deposition of BN from  $\text{BF}_3\text{-NH}_3$ , might not be too different from that of the SiC/SiO<sub>2</sub> mixture actually considered.

Finally, the analyses performed on BNM films deposited on various SiC-based substrates have established that turbostratic BN when deposited at low temperatures from  $\text{BF}_3\text{-NH}_3$ : (i) is not stoichiometric (with the N/B atomic ratio ranging from 0.6 to 0.8); and (ii) contains significant amounts of oxygen (10–15 at.%) [37]. However, both defects are eliminated during the long annealing corresponding to the infiltration of the SiC matrix, as shown by analysis performed on the BN interphase in SiC/BN/SiC composites [14]. As a matter of fact, neither the occurrence of non-stoichiometry in turbostratic BN nor that of an eventual ternary B-N-O species were taken into consideration in the thermodynamic calculations. Furthermore, SIMS analyses of the BN interphase in SiC/BN/SiC composites have established that some fluorine remains trapped, as unidentified species at the fiber/BN interface [38].

From this discussion it appears that the thermodynamic approach to the complex equilibria involved in the deposition of BN on a variety of substrates is a helpful tool in foreseeing the response of the system (at least in its main features), particularly in terms of deposit composition and substrate attack, when the CVD parameters are varied. However, experimental data suggest that the chemical phenomena which actually take place are more complex due to the occurrence of amorphous or imperfectly characterized phases for which no thermodynamic data are presently available. Furthermore, in the CVD of a thin deposit, particularly when it occurs in a pore network (as is the case for the infiltration of an interphase material), a succession of different surface phenomena strongly influenced by the local composition of the gas phase take place in the vicinity of a surface whose local composition may be different from point to point. Obviously such phenomena are difficult to describe in a detailed manner on the basis of the thermodynamic approach alone, whose limitations in such a complex case should not be ignored.

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## Appendix A

The thermodynamic yield corresponding to the conversion of  $\text{BF}_3$  into BN  $\eta_{\text{BN}}$  is that already used by Hannache *et al.* [2]. It is defined as

$$\eta_{\text{BN}} (\%) = 100 \frac{\langle \text{BN} \rangle_{\text{eq.}}}{(\text{BF}_3)_{\text{in.}}} \quad (\text{A1})$$

where  $\langle \text{BN} \rangle_{\text{eq.}}$  and  $[\text{BF}_3]_{\text{in.}}$  are respectively the mole numbers of BN formed at equilibrium and  $\text{BF}_3$  in the initial composition.

The consumption values  $\gamma_i$  are used to characterize the consumption at equilibrium of the species present in the initial composition, *i.e.* the source species  $\text{BF}_3$  and the substrate materials: carbon, SiC or  $\text{SiO}_2$ .

They are defined as

$$\gamma_{\text{BF}_3} = [\text{BF}_3]_{\text{in.}} - [\text{BF}_3]_{\text{eq.}} \quad (\text{A2})$$

$$\gamma_{\text{C}} = \langle \text{C} \rangle_{\text{in.}} - \langle \text{C} \rangle_{\text{eq.}} \quad (\text{A3})$$

$$\gamma_{\text{SiC}} = \langle \text{SiC} \rangle_{\text{in.}} - \langle \text{SiC} \rangle_{\text{eq.}} \quad (\text{A4})$$

$$\gamma_{\text{SiO}_2} = \langle \text{SiO}_2 \rangle_{\text{in.}} - \langle \text{SiO}_2 \rangle_{\text{eq.}} \quad (\text{A5})$$

where  $\langle i \rangle_{\text{in.}}$  and  $\langle i \rangle_{\text{eq.}}$  stand respectively for the mole number of species  $i$  in the initial composition and at equilibrium. Then, the  $\gamma_i$  ratios are different from the  $C_i$  ratios used by Hannache *et al.* to characterize the formation of species  $i$  in small amounts at equilibrium. For carbon and pure SiC substrate materials  $\langle \text{C} \rangle_{\text{in.}}$  and  $\langle \text{SiC} \rangle_{\text{in.}}$  are equal to 10 mol. For the hybrid SiC/ $\text{SiO}_2$  substrate material  $\langle \text{SiC} \rangle_{\text{in.}} = 8$  mol and  $\langle \text{SiO}_2 \rangle_{\text{in.}} = 2$  mol.