The K_2ZrF_6 Wetting Process: Effect of Surface Chemistry on the Ability of a SiC-Fiber Preform to be Impregnated by Aluminum

S. SCHAMM, R. FEDOU, J.P. ROCHER, J.M. QUENISSET, and R. NASLAIN

SiC-ceramic materials, either as flat substrates or porous fiber preforms, are spontaneously wetted by aluminum at 700 °C to 800 °C when they have been pretreated with an aqueous solution of K_2ZrF_6. The wetting enhancement effect results from exothermic chemical reactions occurring at the SiC/Al interface. The first phenomenon thought to occur is a disruption of the alumina film covering liquid aluminum due to a reaction of Al_2O_3 with K_2ZrF_6. Then alumina is totally dissolved at low temperatures by potassium/aluminum mixed fluorides, giving rise to a very fluid cryolitic liquid spreading out on the surface of liquid aluminum and to the true SiC/Al interface. Simultaneously, a large evolution of heat occurs, mainly due to the reduction of K_2ZrF_6 by aluminum and the formation of Al_3Zr. The impregnation of 2D-SiC/SiC preforms by aluminum is modeled, and the effect of both the contact angle decrease and local temperature rise on the impregnation of the preforms, e.g., by gravity casting, is established.

I. INTRODUCTION

THE elaboration of aluminum matrix composites (AMCs) according to processing techniques derived from those already used in light alloy casting is made difficult by two main problems: (a) most ceramic fibers (e.g., C- or SiC-based fibers) are poorly wetted by liquid aluminum at the casting temperatures of light alloys (i.e., 700–800 °C), with the result that preforms of complex fiber architectures are only partially infiltrated by the metal; and (b) these fibers react with aluminum above about 500 °C to form a layer of Al_4C_3 crystals lowering the fiber strength, rendering the matrix brittle and increasing the sensitivity of the material to aqueous corrosion.[1,2]

Various solutions have been proposed to enhance the wetting ability of ceramic fibers by liquid aluminum. Generally speaking, they are based on two different approaches: (a) surface treatments of the fibers including coating by metals (Cu, Ag, Ni) or ceramics (Ti-B, Ti-C, Zr-C) as well as treatments by alkali metals (e.g., Na-K/Sn-Mg);[3] and (b) addition of specific alloying elements to aluminum (Li, Ca, Mg).[4,5]

The metal coatings poorly protect the fibers against the attack by aluminum, and the resulting intermetallic compounds ($NiAl_3$) or carbides embrittle the matrix.

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Furthermore, in order to achieve a good wetting of the fibers by aluminum, the coating has to be continuous and thus rather thick (typically about 1 μm), yielding a significant increase in the material density when the volume fraction of fibers is high (usually 0.4 to 0.5). The wetting by liquid aluminum of fibers coated with a ceramic deposit, e.g., a titanium or zirconium carbide, is rarely excellent even under a pressure of a few atmospheres. A Ti-B deposit, which is probably the best ceramic coating in this field, no longer promotes the wetting if it is in contact with the ambient atmosphere prior to the impregnation step. In the alkali metal process, the surface treatment has to be performed in an inert atmosphere. Finally, all of the surface treatment processes are usually limited to the preparation of semiproducts (e.g., composite wires or tapes). Therefore, the elaboration of near net shape parts implies additional and costly steps, such as hot-pressing.

In a similar manner, the impregnation of a porous fiber preform by liquid Al-Li alloys has to be conducted under vacuum (or a low pressure of an inert gas) in order to make easier the penetration of the liquid metal in the pore network and to avoid an excessive oxidation of lithium.

Regarding the drawbacks of the various techniques presented above, the processing of AMCs is usually performed according to a squeeze-casting technique in which a high pressure (about 100 MPa) is applied to the liquid with a piston. Under such conditions, the liquid is forced to flow into the pore network of the preform, the pressure compensating for the absence of wetting and capillary rise of the metal. Furthermore, since pressure is maintained during cooling, it contributes to closing the micropores in the material and yields a matrix of higher microstructural and mechanical quality. However, squeeze-casting would be a costly processing technique for parts of large dimensions, mainly due to the size of the pressing equipment.[6]

A new wetting treatment, which permits the spontaneous impregnation of ceramic porous preforms (made of C- or SiC-based fibers) by liquid aluminum alloys at

low temperatures (*i.e.*, at a temperature slightly above the liquidus), has been proposed by Rocher *et al.*[7] In its principle, it consists of a treatment applied directly to the preform, according to which K_2ZrF_6 microcrystals are precipitated on the fiber surface, from an aqueous solution at a temperature close to the boiling point. After elimination of the solvent by drying, the treated preform can be totally impregnated with a liquid aluminum alloy at about 800 °C by simple gravity casting. The process was successfully applied to various kinds of preforms including 2D-SiC(Nicalon)/SiC(CVI) preforms.[8]

The aim of the present article is to discusss the mechanisms which may be at the origin of the observed wetting enhancement of the ceramic fibers as well as to show the effect of the K_2ZrF_6 treatment on the impregnation ability of the preform by liquid aluminum. The experimental results and thermodynamic calculations that will be used have been presented elsewhere and will be only briefly recalled for the purpose of discussion.[9,10]

II. ORIGIN OF THE WETTING ENHANCEMENT

A. *Experimental Results Recall*

The efficiency of the K_2ZrF_6 process, in terms of wetting improvement, has been established by Rocher *et al.* on the basis of both preform impregnation experiments at laboratory scale and sessile drop experiments.[9,11] Their main results will be recalled and compared to those reported by other authors for the purpose of discussion.

When a preform made of SiC-based fibers* is first

*Nicalon fibers from Nippon Carbon, Tokyo, Japan.

treated with an aqueous K_2ZrF_6 solution at about 80 °C, in order to obtain a deposit of a few milligrams of K_2ZrF_6 per cm^2 after evaporation of the solvent, and then put in contact with the surface of a bath of liquid aluminum in air, the following phenomena are observed: (a) the preform rapidly turns red due to an evolution of heat, and (b) simultaneously, the liquid metal climbs by capillary effect into the preform, the liquid front remaining roughly parallel to the preform-bath contact plane.

Sessile drop experiments were performed under a good vacuum (residual pressure: 10^{-4} to 5.10^{-4} Pa) with planar substrates of graphite coated by CVD (chemical vapor deposition) with a thick deposit of SiC and pure aluminum (chemically etched prior to the experiment in order to remove the majority of the alumina layer). The substrates had been subjected or not to the K_2ZrF_6 surface treatment. The variations of the contact angle θ as a function of both temperature and time are shown in Figures 1 and 2. Data by other authors taken from the literature have been added to the original Rocher *et al.* data for the purpose of discussion.

When the K_2ZrF_6 surface treatment is not applied, the value of θ at the processing temperatures of AMCs, *i.e.*, 700–800 °C, remains very high ($\theta = 160$ deg), a feature which is typical of a nonwetting behavior. It is only by raising temperature at about 900–950 °C that the transition nonwetting/wetting takes place. Conversely, when the SiC substrate has been treated with K_2ZrF_6 prior to the sessile drop experiment, wetting occurs as soon as
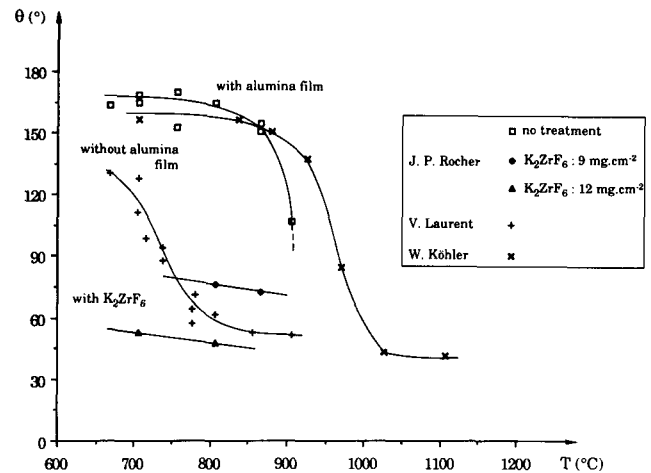

Fig. 1 — Variations of the SiC/Al contact angle (θ) as a function of temperature (T) from sessile drop experiments, according to Refs. 9, 12, and 13.

aluminum melts. Moreover, lower θ values are observed when the amount of K_2ZrF_6 deposited on the substrate is increased ($\theta = 73$ deg and 50 deg when the amount of K_2ZrF_6 is 9 and 12 mg·cm^{-2}, respectively). Finally, the contact angle value remains constant after only a few minutes of contact between the substrate and the liquid.

It is worthy of note that the θ values reported by Rocher *et al.* for substrates treated with K_2ZrF_6 and sessile drop experiments performed at low temperatures (*i.e.*, 700–850 °C) and a few minutes of contact are similar to those measured (after 30 minutes of contact) with SiC single-crystal/pure aluminum couples by (a) Köhler, above 1000 °C and for a residual pressure of 2 to 8.10^{-4} Pa, and (b) Laurent, beyond 800 °C and for a residual pressure of 10^{-4} to 5.10^{-5} Pa.[12,13]

Therefore, K_2ZrF_6 seems to activate both thermally and kinetically the decrease of the contact angle between a SiC substrate and liquid aluminum.
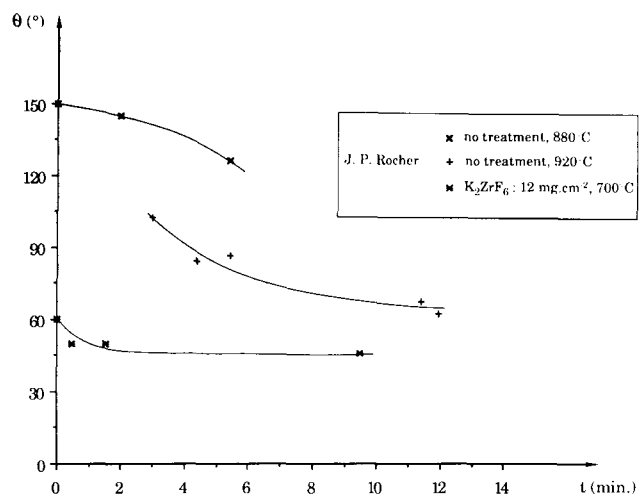

Fig. 2 — Variations of the SiC/Al contact angle (θ) as a function of time (t) from sessile drop experiments, according to Ref. 9.

B. Mechanisms

1. Sessile drop experiment without K_2ZrF_6 treatment

Laurent *et al.* have shown that under particularly clean sessile drop experiment conditions (*i.e.*, $P_{tot} \leq 5.10^{-5}$ Pa; $P_{O_2} \leq 10^{-15}$ Pa; alumina layer separated mechanically from the aluminum sample just before the sessile drop experiment), the thin film of alumina still present on aluminum at the melting point and which prevents the wetting of the SiC substrate from taking place is reduced by aluminum according to the following equation:[14]

$$4Al_l + Al_2O_{3s} \rightleftharpoons 3Al_2O_g \qquad [1]$$

As soon as the true SiC/Al interface has been formed, the variations of the contact angle *vs* time are controlled by the dissolution of SiC in the liquid metal according to the following equation, thought to be the rate-limiting step in the formation of Al_4C_3:

$$4Al_l + 3SiC_s \rightleftharpoons Al_4C_{3s} + 3(Si)_{Al} \qquad [2]$$
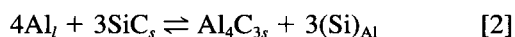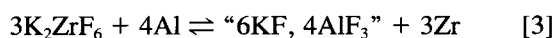
and whose kinetics obey an exponential law with respect to temperature.

As a matter of fact, the sessile drop experiment conditions used by both Rocher[9] and Köhler,[12] *i.e.*, a vacuum corresponding to a higher residual total pressure (one order of magnitude) and oxygen partial pressure, do not modify the general shape of the $\theta = f(T)$ curve, as shown in Figure 1. However, for isothermal contacts of the same durations, (a) the deoxidation process is shifted toward the high temperatures (by about 200 °C) and (b) the slope of the $\theta = f(T)$ curve (related to the thermal dependence of the SiC dissolution in liquid aluminum) is higher at 950 °C than at 750 °C.
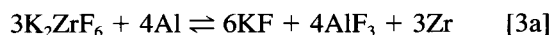
2. Sessile drop experiments and lab-scale preform impregnation with K_2ZrF_6 treatment
#### a. Disruption of the alumina film

Reaction mechanisms related to the interaction between K_2ZrF_6 and liquid aluminum have been already suggested by Lundin[15] and Bushe and Semenov[16] to take into account the wetting enhancement phenomena observed in their processes used to fabricate aluminum-steel bimetallic materials. They proposed the following overall equations:

$$3K_2ZrF_6 + 4Al \rightleftharpoons \text{“6KF, 4AlF}_3\text{”} + 3Zr \qquad [3]$$

or

$$3K_2ZrF_6 + 4Al \rightleftharpoons 6KF + 4AlF_3 + 3Zr \qquad [3a]$$

In the present process, when either (a) liquid aluminum at 800 °C comes in contact with a fibrous preform which has been pretreated with K_2ZrF_6 and preheated at about 650 °C or (b) an aluminum drop/SiC plane substrate (pretreated with K_2ZrF_6) couple is heated at a temperature slightly above the melting point of the metal, the fluoride species are first in contact with alumina present at the metal surface. Therefore, the first reaction which might take place is thought to involve fluoride species and alumina. It could be written, with reference to Eq. [3], as

$$3 \text{“2KF, ZrF}_4\text{”} + 2Al_2O_3 \rightleftharpoons \text{“6KF, 4AlF}_3\text{”} + 3ZrO_2$$

$$[4]$$
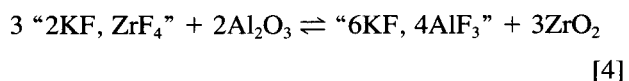
on the basis of the following considerations. As a matter of fact, K_2ZrF_6 undergoes a peritectic melting at a temperature of 592 °C. Thus, it is assumed that K_2ZrF_6, at a temperature corresponding to our experiments, *e.g.*, 700 °C, is totally decomposed into a mixture of a liquid phase and K_3ZrF_7:

$$2 \text{“KF, ZrF}_4\text{”} = x \, L(KF, ZrF_4) + y \, K_3ZrF_7$$
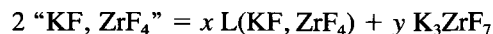
where $L(KF, ZrF_4)$ is the liquid in equilibrium with K_3ZrF_7 at 700 °C in the $KF-ZrF_4$ phase diagram and $x + y = 1$.[17] In the following, this mixture will be referred to as "2KF, ZrF_4." In the same way, it is assumed from the $KF-AlF_3$ phase diagram that "6KF, $4AlF_3$" is a mixture of a liquid phase and K_3AlF_6 at 700 °C:[18]

$$\text{“6KF, 4AlF}_3\text{”} = x' \, L(KF, AlF_3) + y' \, K_3AlF_6$$

where $L(KF, AlF_3)$ is the liquid in equilibrium with K_3AlF_6 at 700 °C and $x' + y' = 1$.

On the basis of a thermodynamic study which has been published elsewhere,[10] the Gibbs free energies of formation of both "2KF, ZrF_4" (-2623.5 kJ·mol^{-1}) and "6KF, $4AlF_3$" (-8154.9 kJ·mol^{-1}) as well as the Gibbs free energy variation corresponding to Eq. [4] were calculated. These calculations have shown that the chemical reaction between alumina and the products of decomposition of K_2ZrF_6 at 700 °C is indeed highly favored, since $\Delta G°[4] = -282.6$ kJ·mol^{-1} at 700 °C.

In order to verify this conclusion, a $3K_2ZrF_6 - 2Al_2O_3$ mixture was prepared in a dry glove box and set in a platinum tube which was then sealed under an atmosphere of dry argon. After heat treatment and cooling, an X-ray diffraction analysis showed that the only crystallized phases in the reaction product were K_3AlF_6, $KAlF_4$, and ZrO_2. This result is in full agreement with the thermodynamic calculations and Eq. [4], since "6KF, $4AlF_3$" gives a $K_3AlF_6 + 3KAlF_4$ mixture after cooling at room temperature.[18]

Conversely, zirconia formed according to Eq. [4] could react immediately with aluminum at 700 °C according to the following equation:

$$3ZrO_2 + 4Al \rightleftharpoons 2Al_2O_3 + 3Zr \qquad [5]$$

since the variation of the Gibbs free energy corresponding to Eq. [5], $\Delta G°[5] = -1.8$ kJ·mol^{-1}, is slightly negative.

Thus, during a first step, the thin alumina film on the surface of liquid aluminum (known to prevent the wetting of the substrate) is disrupted at 700–800 °C as the result of the chemical reactions corresponding to Eqs. [4] and [5], thus allowing the liquid metal to come in contact with the K_2ZrF_6 deposit.

b. Dissolution of the alumina film

In a second step, the alumina film is totally dissolved by the "6KF, $4AlF_3$" mixture formed as a result of the addition of Eqs. [4] and [5]. The corresponding overall equation is another form of Eqs. [3] and [3a], taking into account the physical states at 700 °C of the various species which are involved

$$3 \text{“KF, ZrF}_4\text{”} + 4Al \rightleftharpoons \text{“6KF, 4AlF}_3\text{”} + 3Zr \qquad [3b]$$
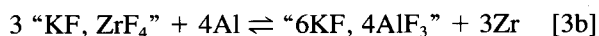
This statement is based on the results of a thermodynamic study of the reciprocal ternary system

KF-AlF$_3$-Al$_2$O$_3$-K$_2$O and related binary systems which have been published in detail elsewhere.[10] From these results, the vertical section "6KF, 4AlF$_3$"-Al$_2$O$_3$ has been calculated and is shown in Figure 3. As a matter of fact, it appears from Figure 3 that for alumina concentrations corresponding to our experiments, i.e., about a few mol Al$_2$O$_3$ pct, the oxide can be totally dissolved for temperatures higher than 520 °C. (This alumina concentration corresponds to a film of alumina 100 Å in thickness and to a K$_2$ZrF$_6$ coating of a few mg · cm^{-2}.)

c. *Local temperature rise*

In a last step, zirconium formed according to Eq. [3b] can further react with aluminum, which is in excess, to lead to the formation of intermetallic compounds, as already shown by Rocher et al.[9,11] according to the following equation:

$$3Zr + 9Al \rightleftharpoons 3Al_3Zr \qquad [6]$$

Reactions [3b] and [6], which probably take place simultaneously, are very exothermic, since ΔH[3b] = −306.4 kJ · mol^{-1} and ΔH[6] = −487.2 kJ · mol^{-1}. This heat evolution yields a local temperature rise either at the fiber/matrix or liquid aluminum drop/substrate interface, which is thought to be particularly significant for preforms due to (a) the high inner pore surface and (b) the important amount of K$_2$ZrF$_6$. In Section III, a model will be presented which allows the calculation of temperature in a porous fiber preform during an impregnation experiment according to the K$_2$ZrF$_6$ process when exothermic reactions (such as those already mentioned) take place. It will be shown that a temperature increase
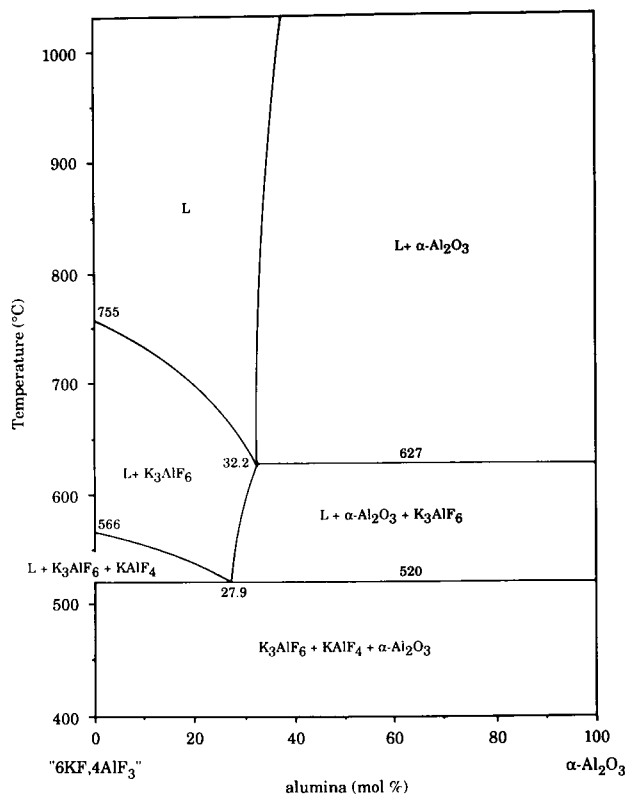

Fig. 3 — The vertical section "6KF, 4AlF$_3$"-α-Al$_2$O$_3$ from the KF-AlF$_3$-Al$_2$O$_3$-K$_2$O ternary reciprocal system, according to Ref. 10.

as high as 150 °C may occur, thus justifying the experimental observations reported in Section II–A.

C. *Discussion*

It clearly appears from Figure 3 that an excess of fluoride mixture "6KF, 4AlF$_3$" coming in contact with a thin layer of solid alumina will yield a homogeneous liquid phase at those temperatures corresponding to preform impregnations. This liquid, formed *in situ* between silicon carbide and liquid aluminum, modifies significantly the wetting ability of the ceramic material.

In a totally different field and processing technique, the influence of K$_2$ZrF$_6$ on the ability of steel sheets to be wetted by liquid aluminum has been reported by Lundin.[15] When a K$_2$ZrF$_6$ powder is poured on the surface of a liquid aluminum bath, it melts and forms a very fluid liquid which spreads out on the entire bath surface (like oil dropped on the surface of water). Furthermore, when this liquid is generated at the interface between a sheet of steel coated with K$_2$ZrF$_6$ and a bath of aluminum in which the sheet was dipped, it is observed that this liquid tends to move up toward the bath surface where it spreads out.

During our impregnation experiments on fiber preforms, performed in air by gravity casting, it was also observed that a fluid liquid resulting from the interaction between the K$_2$ZrF$_6$ treated preform and aluminum had been formed. Due to metal flow, density difference, and surface tension considerations, it was located in the riser of the casting. After cooling, X-ray diffraction analysis showed that the product mainly consisted of a mixture of K$_3$AlF$_6$, KAlF$_4$, and alumina compounds, in agreement with the reaction mechanisms discussed in Section II–B–2.

The molten mixture "6KF, 4AlF$_3$"-Al$_2$O$_3$ considered in our K$_2$ZrF$_6$ process is chemically analogous to the molten cryolitic mixture Na$_3$AlF$_6$-Al$_2$O$_3$ used in the Hall-Héroult process. Thus, since the physical properties of the "6KF, 4AlF$_3$"-Al$_2$O$_3$ molten mixture are not known, we will use below those of the related sodium-based molten mixtures which are well established (given in parentheses).[19]

The "6KF, 4AlF$_3$"-Al$_2$O$_3$ liquid, which is nonmiscible with liquid aluminum and has a lower density (≃2.1 g · cm^{-3} for Na$_3$AlF$_6$-Al$_2$O$_3$ molten mixture and 2.38 g · cm^{-3} for liquid aluminum), will move up toward the free surface of the metal and across the drop of aluminum (in a sessile drop experiment) or the aluminum riser (in gravity casting impregnation) from the SiC/Al interface(s) where it has been formed. The surface tension of liquid aluminum (oxidized, 865 erg · cm^{-2}) is much higher than that of the molten cryolitic mixture (in air, 140 erg · cm^{-2} for Na$_3$AlF$_6$-Al$_2$O$_3$ molten mixture).[19,20] Therefore, to stabilize the system, the "6KF, 4AlF$_3$"-Al$_2$O$_3$ liquid will spread out on the surface of the drop (or of the bath). As a result, the alumina film initially present at the surface of liquid aluminum will be totally dissolved and replaced by a film of cryolitic liquid simultaneously with the formation of the true SiC/Al interface. When the experiments are performed in air, this cryolitic film protects the aluminum bath against any further oxidation.

In conclusion, the formation of the true SiC/Al interface at temperatures close to 800 °C (taking into account the evolution of heat related to exothermic reactions), associated with that of a liquid cryolitic-type phase at the surface of liquid aluminum, seems to justify the low contact angle values which have been measured for SiC substrates pretreated with K_2ZrF_6 (and which are, as a matter of fact, close to those measured by Laurent[13] under very clean conditions at the same temperatures). The same phenomena could also explain the dramatic enhancement of the ability of K_2ZrF_6-pretreated fiber preforms to be impregnated by liquid aluminum.

III. EFFECT OF THE K_2ZrF_6 TREATMENT ON THE IMPREGNATION PARAMETERS OF A POROUS FIBROUS PREFORM

A. Impregnation Modeling

Quenisset et al. have recently modeled, on the basis of a numerical approach, the impregnation of a porous fiber preform by liquid aluminum alloy according to the squeeze-casting process.[21] The aim of their work was to study the effect of various parameters on (a) the maximum impregnation depth, referred to as z_M, and (b) the minimum pressure in the metal at pore entrance necessary to allow the impregnation of the preform at z_M, referred to as P_m. Among the parameters which have been considered were processing parameters (i.e., temperatures of both the liquid metal and porous preform, impregnation rate, etc.) as well as material parameters (i.e., volume fraction, density, specific heat and thermal conductivity for both the reinforcement and the matrix, preform permeability, viscosity and surface tension of the liquid metal, and finally, contact angle between the reinforcement and the liquid alloy).

The modeling was based on the general equations of heat and mass transfers combined with simplified boundary conditions: (a) the preforms are large enough to neglect the edge effect; (b) the interfacial heat transfer is instantaneous; (c) temperatures of the feeding metal (T_{Al}) and of the preform fraction not yet impregnated (T_F) remain constant all along the impregnation; and (d) the effects of gravity are neglected. The model was derived for unidirectional preforms assumed to be of semi-infinite volume and made of a hexagonal packing of cylindrical fibers lying parallel (mode L) or perpendicular (mode T) to the impregnation direction. It was further assumed that impregnation proceeds at constant speed U and stops (at $z = z_M$ from the preform surface) when temperature at the impregnation front reaches the liquidus temperature of the alloy. Finally, the model took into account capillary effect as well as the occurrence of heat sources during impregnation.

B. Impregnation of Porous SiC-Fiber Preforms

The Quenisset[21] modeling was used in the present work to compare the values of the impregnation parameters (mainly, P_m and z_M) of porous SiC preforms, depending on whether they have been pretreated or not with K_2ZrF_6 prior to impregnation.

1. Preform modeling and impregnation conditions

The fiber preforms which were used by Rocher[11] to establish the feasibility of the K_2ZrF_6 process were made of a stack of SiC fabrics* partly densified with SiC ac-

*Nicalon fibers from Nippon Carbon, Tokyo, Japan.

cording to a chemical vapor infiltration (CVI) technique which has been described in detail elsewhere.[22] Their residual open porosity was of the order of 20 pct. Obviously, such materials have a 2D texture with large pores between adjacent fibrous layers. However, since the purpose of our study was simply to emphasize the effect of a K_2ZrF_6 pretreatment on the impregnation ability of a SiC preform with respect to liquid aluminum, we assumed that such preforms could be modeled, in first approximation, as an hexagonal array of SiC fibrous cylinders with the same overall open porosity, i.e., 20 pct $(V_f = 80$ pct). The diameter of these equivalent cylinders, calculated from the mean value of the experimentally determined preform pores sizes and the relation between the pore diameter (D_p) and the cylinder diameter (D_c) in an hexagonal array (i.e., $V_f/(1 - V_f) = D_p/D_c$), was found to be 480 μm, i.e., of the same order of magnitude as that of the SiC-infiltrated tows actually measured on a cross section of the preforms used by Rocher et al. in their impregnation experiments. Moreover, due to the morphology of their pore network, the actual mode of impregnation of these preforms has more common features with mode L than with mode T impregnation. Therefore, we considered only this first mode in our discussion, i.e., the SiC fibrous cylinders lie parallel to the impregnation direction.

The physical characteristics of the equivalent fibrous cylinders and the liquid metal introduced in the calculations were those of the Nicalon fibers and pure aluminum, respectively. The value given to the temperature of the liquid metal was 800 °C (T_{Al}) and that given to the equivalent preform was 650 °C (T_F) at the beginning of the impregnation process. The impregnation rate was assumed to be $U = 0.5$ cm $\cdot$ s^{-1} on the basis of the impregnation rates actually observed for the K_2ZrF_6-treated SiC preforms. Both (a) the exothermicity of reactions [3b] and [6], i.e., 3.3 kJ $\cdot$ cm^{-3} of K_2ZrF_6 associated with an amount $Q = 5$ mg $\cdot$ cm^{-2} of K_2ZrF_6 deposited on the surface of the equivalent SiC cylinders, and (b) the new contact angle due to K_2ZrF_6 $(\theta = 75$ deg) were taken into account. Since the surface tension of aluminum in the presence of the cryolitic liquid film was unknown, that of pure aluminum (i.e., $\sigma = 865 - 0.2(T - 660)$ erg $\cdot$ cm^{-2}, with T in °C) was used for all of the calculations.

2. Results and discussion

The results of the calculations are shown in Table I. It clearly appears that the equivalent preform is impregnated much deeper and with much lower pressures when it has been pretreated with K_2ZrF_6. This dramatic improvement in the impregnation ability of the preform is due, as already mentioned in Section II-B to (a) the occurrence of exothermic reactions related to K_2ZrF_6 and (b) an enhancement of the wetting of SiC by liquid aluminum, i.e., a decrease in the contact angle.

In order to assess the respective contributions of (a)

Table I. Results of the Calculations Performed for a 1D-Model Preform Treated (or Not) with K₂ZrF₆ and Representing in a First Approximation, 2D-SiC/SiC Real Preforms with a Porosity of 20 Percent

Impregnation Parameters	Untreated 1D-Model Preform $\Delta H = 0$ $\theta = 160$ Deg	K₂ZrF₆-Treated 1D-Model Preform $\Delta H = 3.3$ kJ·cm⁻³; $Q = 5$ mg·cm⁻² $\theta = 75$ Deg
z_M (cm)	1	∞ (no solidification of Al)
T (°C) at z_M	660	807
P_z for z (MPa)	0.03 for 1 cm	<0 for 1 cm
		0.004 for 20 cm

and (b), the $z = f(P_z)$ curves, representing the variations of the impregnation depth as a function of the pressure in the metal at the preform surface, were calculated for the following sets of ΔH(kJ·cm⁻³)/Q(mg·cm⁻² of K₂ZrF₆)/θ(deg): (a) 0/0/160; (b) 0/0/75; (c) 3.3/5/160; and (d) 3.3/5/75 (Figure 4). Curve (a) corresponds to the case of the untreated preform and, therefore, is the reference curve; curve (b) takes into account the decrease of θ only; curve (c) takes into account the exothermicity only; and finally, curve (d) corresponds to the K₂ZrF₆-pretreated preform. As shown in this figure, the variation of z as a function of P_z obeys a linear law up to the solidification of the metal in the pore network ($z = z_M$). It is worthy of note that a similar behavior has been experimentally observed by Fukunaga and Goda for a composite made of glass fibers and an aluminum matrix.[23]

A comparison between curves b through d, on the one hand, and the curve a, on the other hand, leads to the following remarks:

(a) Curves (a) and (c): The main effect of the exothermicity of the chemical reactions involved in the K₂ZrF₆ process is to prevent an early solidification of the metal (actually observed at low depths for untreated preforms (a)) as it flows in the preform and thus to allow the impregnation of large size preforms (as far as the required
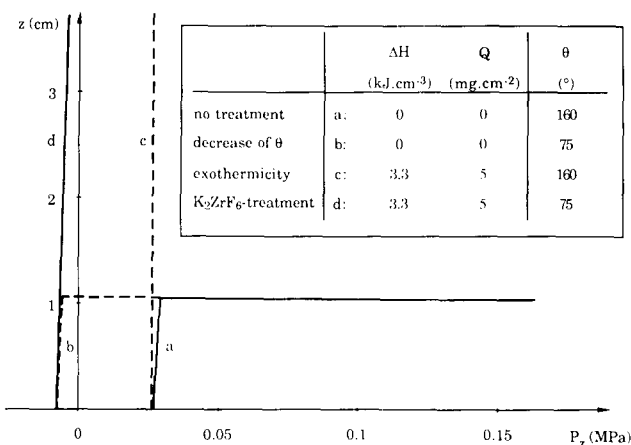
Fig. 4 — Variations of the impregnation depth as a function of the pressure in aluminum for a one-dimensional model preform, $D = 480$ μm.

pressures P_z given by curve (c) are actually applied to the metal). As a matter of fact, the calculations have shown that the heat evolution due to the chemical reactions is large enough to maintain the liquid metal at about its initial temperature (i.e., 800 °C; Table I) as it flows in the slightly colder preform (initial temperature: 650 °C). Thus, the fluidity of the metal, which is directly related to its temperature, is kept constant during the impregnation. Conversely, the effect of the exothermicity of the chemical reactions on P_z, through the decrease in both the surface tension $\sigma(T)$ and viscosity $\mu(T)$ (Eq. [7]) of the liquid metal, is limited.

(b) Curves (a) and (b): The main effect of the contact angle decrease due to K₂ZrF₆ is to lower the value of the pressure P_z which has to be applied to the metal in order to achieve the impregnation of the preform at a given depth z. The pressure field, $P_z - P_a$, between the liquid metal at the preform surface (when the liquid front is at a depth z) and the portion of the preform not yet impregnated (where the pressure is P_a, with $P_a = 100$ kPa for experiments performed in air) results from two contributions. In the following equation, the first term is that of capillary force and the second term is that of frictional force:

$$P_z - P_a = -4V_f(1 - V_f)^{-1}\cos\theta \cdot \sigma(T) \cdot D^{-1} + K^{-1} \cdot U \cdot \int_0^z \mu(T)\,dz \quad [7]$$

(K is the preform permeability proportional to D^2 when V_f is constant). In the mode L considered here for the impregnation, the effects of the capillary forces and frictional forces are of the same order of magnitude. Under this latter condition and taking into account the fact that V_f, σ, D, U, and μ are constant in our calculations, it comes out that the capillary force term depends on $-\cos\theta$ and the frictional force term is constant. Since $-\cos\theta$ is negative for a preform pretreated with K₂ZrF₆ ($\theta = 75$ deg) and positive for an untreated preform ($\theta = 160$ deg), the resulting value of P_z is lower in the former case than in the latter, as shown in Figure 4. This effect on P_z would be more efficient for preforms made of reinforcements smaller in diameter, as illustrated in Figure 5 where the variations of z as a function of P_z were calculated for a new model preform with the following characteristics: (1) presenting the same overall porosity than real 2D-SiC/SiC preforms (i.e., 20 pct) but made of SiC fibrous cylinders only 12.5 μm in diameter (instead of 480 μm for the first model preforms and thus similar to the Nicalon fibers) and (2) supposedly treated or not with the same amount of K₂ZrF₆ (per unit of volume). It is worthy of note that the ability of the preform made of small diameter SiC fibrous cylinders to be impregnated under low pressures depends entirely on the contact angle decrease due to K₂ZrF₆. On the contrary, the contact angle decrease has no influence on the maximum impregnation depth.

(c) Curves (a) and (d): In conclusion, the K₂ZrF₆ process allows the spontaneous impregnation of preforms even of large size (more than a few centimeters) because of the simultaneous effect of contact angle decrease and of heat evolution. It is worthy of note that rather thick 2D-SiC/SiC preforms (thickness: 1 to 1.5 cm) pretreated
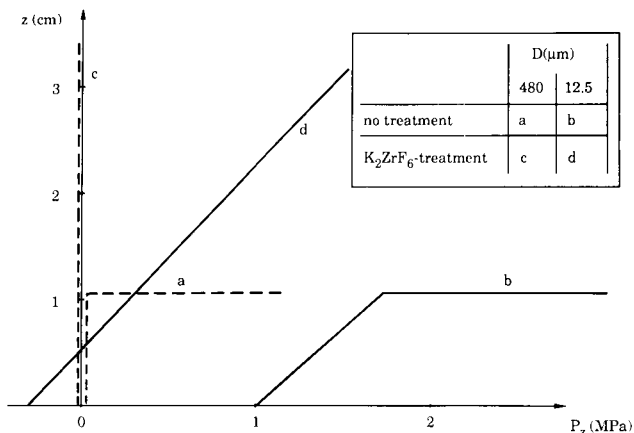
z (cm)

	D(μm)	
	480	12.5
no treatment	a	b
K$_2$ZrF$_6$-treatment	c	d

P_z (MPa)

Fig. 5 — Variations of the impregnation depth as a function of the pressure in aluminum for one-dimensional model preforms, $D = 480$ μm and $D = 12.5$ μm.

with K$_2$ZrF$_6$ have been successfully impregnated by aluminum without any pressure externally applied on the liquid, *i.e.*, by simple gravity casting. Under such a condition, the pressure on the preform is only the metallostatic pressure, *i.e.*, that due to the weight of liquid aluminum (0.03 MPa in our experiments).

The minimum amount of K$_2$ZrF$_6$ necessary to maintain (a) the aluminum at a temperature of 750 °C so that the metal remains fluid as it flows in the preform and (b) the SiC/Al contact angle at a small enough value (75 deg) to lower significantly the external pressure (Figure 4) was calculated for the model preform (for $T_F = 650$ °C and $T_{Al} = 800$ °C). The calculations have established that an amount of 3 mg K$_2$ZrF$_6$ per cm^2 would be sufficient. It is noteworthy that this value (a) corresponds to the maximum amount of K$_2$ZrF$_6$ which could be introduced in the model preform due to the available porosity (20 pct) and (b) is close to that (5 mg · cm^{-2}) actually used for the impregnation of 2-D-SiC/SiC preforms. As a matter of fact, larger K$_2$ZrF$_6$ amounts, that would require preforms of higher porosities, would lead to an excessive overheating of the system ($T > 800$ °C), detrimental to the properties of the composite. In such a case, the temperature of the preform impregnation (T_F) could be lowered.

IV. CONCLUSION

The feasibility of the K$_2$ZrF$_6$ process, already established experimentally by Rocher *et al.*,[11] has been justified theoretically in the present work. This process is based on a very simple procedure and involves products already used in light alloy casting. It has been shown that fiber preforms of rather low porosities and moderate thicknesses could be impregnated, when pretreated with

K$_2$ZrF$_6$, under low pressures, *i.e.*, by gravity casting. It is anticipated that the K$_2$ZrF$_6$ process in squeeze casting will allow the impregnation of large size preforms with pressures much lower than those presently utilized for untreated preforms.

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