



# Sur l'élaboration des composites SiC/Al par le procédé au K<sub>2</sub>ZrF<sub>6</sub> bases physico-chimiques et incidence sur la résistance des fibres

Sylvie Schamm-Chardon

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# THÈSE

PRÉSENTÉE A

**L'UNIVERSITÉ DE BORDEAUX I**

POUR OBTENIR LE GRADE DE

**DOCTEUR**

Spécialité : SCIENCES DES MATÉRIAUX

PAR

**Sylvie SCHAMM**

**Ingénieur ENSCPB**

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**SUR L'ÉLABORATION DES COMPOSITES SiC/Al PAR LE PROCÉDÉ AU  $K_2ZrF_6$   
BASES PHYSICO-CHIMIQUES ET INCIDENCE SUR LA RÉSISTANCE DES FIBRES**

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*Soutenue le 7 juillet 1989, devant la commission d'examen :*

|                          |                   |
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| J. GRANNEC .....         |                   |
| R. NASLAIN .....         |                   |

---



*à Jean-Yves*



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de vous-mêmes à vos six enfants, cette thèse  
ne serait pas*

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# **INTRODUCTION GENERALE**

## INTRODUCTION GENERALE

L'idée d'associer des matériaux aux caractéristiques complémentaires au sein d'un même solide, appelé composite, en vue de lui conférer un ensemble de propriétés originales a permis de répondre aux exigences spécifiques des industries aéronautique et aérospatiale que ne pouvaient plus satisfaire les matériaux traditionnels. Depuis, les potentialités de cette technologie ont attiré l'attention et l'intérêt de beaucoup d'autres secteurs d'application tels que l'automobile et même les sports de haute compétition, le choix des constituants du composite pouvant être extrêmement varié. Cependant les composites, matériaux synthétiques qui supposent l'enrobage de l'un des constituants, le renfort, par l'autre, la matrice, sont des matériaux complexes. Aussi, bien que les plus anciens d'entre eux, les composites à matrice organique, aient rapidement connu un développement industriel, l'élaboration et les propriétés de leurs homologues à matrice métallique ou céramique, destinés à des applications respectivement à moyenne et à haute température, posent encore des problèmes tant fondamentaux que technologiques.

L'intérêt de l'approche composite est de permettre d'obtenir des matériaux à caractéristiques mécaniques spécifiques (rapportées à la densité du matériau) plus élevées que celles des métaux et des matières plastiques traditionnels. L'utilisation de renforts fibreux, caractérisés par une résistance à la rupture et un module d'Young élevés et disposés de manière uni- ou multi-directionnelle au sein d'une matrice, confère en plus à ces matériaux un caractère anisotrope, i.e. la possibilité de supporter des contraintes suivant des directions prédéfinies de forte sollicitation. L'emploi d'une matrice métallique plutôt que d'une matrice organique, outre le fait



qu'il permet d'étendre le domaine d'utilisation en température des composites à 350-600°C au lieu de 200°C, leur confère de nouveaux avantages. Ils ont une excellente tenue à l'environnement (absence de vieillissement aux UV, insensibilité à l'humidité) et ne dégazent pas sous vide. Leur résistance et leur rigidité sont plus élevées notamment dans la direction perpendiculaire aux fibres. Ils présentent une bonne conductivité thermique et électrique. Ces avantages justifient le regain d'intérêt que suscitent les matériaux composites à matrice métallique pour leur emploi comme matériaux structuraux dans le domaine aérospatial.

Ce travail concerne les matériaux composites à matrice métallique et plus spécifiquement les problèmes d'élaboration posés par le renforcement des alliages légers (i.e. à base d'aluminium) par des fibres longues de type céramique (SiC, C).

La mise en oeuvre de renforts fibreux au sein d'une matrice d'alliage léger peut se faire de deux manières différentes (1):

- la réalisation de **demi-produits** par imprégnation, généralement en continu, par l'aluminium liquide, des renforts fibreux sous forme de fils, de rubans ou de monocouches suivi de la mise en forme et de la consolidation des demi-produits par compression à chaud.

- l'**imprégnation de préformes** réalisées par tissage multidirectionnel de fibres longues multibrins selon des procédés proches des techniques de la fonderie et du forgeage.

Cependant aux températures d'élaboration des composites (i.e. 700-800°C), proches de la température de fusion de l'aluminium, les fibres de carbure de silicium (ou de carbone) sont mal mouillées par l'aluminium ( $\theta \approx 160^\circ$ ). Le métal ne peut donc pas monter par capillarité entre les brins élémentaires d'une mèche ou dans les pores d'une préforme fibreuse multidirectionnelle. Le mouillage des fibres céramiques par l'aluminium liquide ( $\theta \approx 90^\circ$ ) n'a lieu qu'à des températures plus élevées, de l'ordre de 900-950°C. Eusthatopoulos et coll. ont montré à ce sujet que la

présence d'une pellicule d'alumine à la surface de l'aluminium liquide empêchait le contact direct entre le métal et la céramique aux températures inférieures à 850-900°C et de ce fait retardait, en terme de température, la transition non mouillage-mouillage (2). Envisager l'élaboration des composites aux températures supérieures à 850°C, de façon à favoriser le mouillage, activerait thermiquement la formation du carbure d'aluminium  $\text{Al}_4\text{C}_3$  qui peut avoir lieu dès 500°C par réaction directe entre l'aluminium et le carbone (3). Il en résulterait une dégradation excessive des fibres par dissolution dans l'aluminium, une fragilisation de la matrice et une sensibilité du matériau à la corrosion. Par ailleurs, les propriétés métallurgiques de l'aluminium en souffriraient.

De nombreuses méthodes ont été préconisées pour améliorer la mouillabilité des fibres céramiques par l'aluminium liquide. Elles font appel à deux types de technologies:

(i) le traitement préalable de la surface des fibres tels que le **traitement aux alcalins** (Na/Mg-Sn), les **dépôts métalliques** (Ni, Cu, Ag) et les **dépôts céramiques** (TiC, ZrC, composés Ti-B) (4)

(ii) l'**addition d'éléments d'alliage** spécifiques à l'aluminium (Li) (2,5)

Ces méthodes ont été le plus souvent établies de façon semi-empirique et les publications qui les décrivent (en général des brevets) contiennent peu d'informations sur leurs bases scientifiques. Grâce aux études réalisées sur le mouillage par les métaux liquides du carbone, des carbures et des métaux, il est possible d'expliquer les phénomènes physico-chimiques qui sous-tendent ces procédés (6,7). Dans tous les cas qui vont être cités, on remarquera que, en général, l'amélioration du mouillage est réalisée au détriment d'une fragilisation du composite et/ou du coût de mise en oeuvre.

(i) Les métaux liquides mouillent presque toujours les métaux solides et le degré de mouillabilité est d'autant meilleur que les deux métaux présentent une solubilité mutuelle ou forment un (ou des) composé(s) intermétallique(s) (6,7).

**Le traitement aux alcalins** qui a été essentiellement développé pour les fibres de graphite (à base Rayone ou PAN), consiste à immerger les fibres en continu et sous atmosphère d'argon, successivement dans un bain de Na à 550°C, dans un bain de Sn-2%Mg à 600°C et enfin dans le bain d'aluminium fondu (8). Le sodium formerait des composés d'intercalation avec le graphite (les ions positifs du métal s'insèrent entre les plans graphitiques de la fibre) et l'étain liquide à 600°C dissout le sodium (9). Ainsi, le dépôt intermédiaire du métal alcalin rend possible le mouillage de la fibre de graphite par l'étain. A son tour, l'aluminium liquide dissout le dépôt Na-Sn et mouille la fibre. L'expérience a cependant montré que l'infiltration des mèches par l'aluminium n'est complète qu'en présence de magnésium. Son rôle serait de stabiliser à la surface de la fibre le dépôt Na-Sn, devenu liquide pendant l'imprégnation par l'aluminium, grâce à la précipitation du composé intermétallique à haut point de fusion (772°C) qu'il peut former avec l'étain,  $Mg_2Sn$ . Cependant ni la formation du composé  $Mg_2Sn$ , ni celle de tout autre composé ternaire du type Na-Sn-Mg n'ont encore été démontrées (10). Les composites ainsi obtenus ont des propriétés mécaniques proches de celles théoriquement prévisibles grâce à la loi des mélanges. Malgré tout, la mise en oeuvre du procédé aux alcalins reste délicate (atmosphère contrôlée, produits inflammables).

**Les dépôts métalliques** de Ni, Cu, ou Ag sont en général réalisés par pulvérisation ionique, dépôt électrolytique ou cémentation (4,11-14). Le nickel forme avec l'aluminium des composés intermétalliques stables tel que  $Al_3Ni$ . Mais bien que, en conséquence, le mouillage de la fibre soit excellent, le dépôt de métal et les composés intermétalliques qui se sont formés protègent mal la fibre contre toute attaque par l'aluminium ( $Al_4C_3$ ) et les produits de réaction,  $Al_3Ni$  et  $Al_4C_3$ ,

fragilisent la matrice. Par ailleurs, afin d'obtenir un bon mouillage de la fibre par l'aluminium, un dépôt continu, donc relativement épais (0,5 à 1  $\mu\text{m}$ ), doit être réalisé. Il en résulte une augmentation indésirable de la densité du composite pour les fractions volumiques élevées de fibres. La formation du composé intermétallique  $\text{Al}_3\text{Cu}$  et la forte solubilité de l'argent dans l'aluminium font aussi des revêtements respectivement de cuivre et d'argent des dépôts de choix pour promouvoir le mouillage des fibres céramiques par l'aluminium. Cependant, ces dépôts, de la même façon que le dépôt de nickel, conduisent à une mauvaise protection de la fibre, une fragilisation de la matrice et une densité élevée.

Contrairement aux dépôts métalliques, les **dépôts céramiques** protègent bien les fibres contre l'agression de l'aluminium liquide. Mais l'infiltration de mèches de carbone par du carbure de Ti ou de Zr à partir d'un mélange gazeux réactif ( $\text{H}_2 + \text{CH}_4 + \text{TiCl}_4$  ou  $\text{ZrCl}_4$ ) entre 700 et 1700 °C ne permet qu'une imprégnation partielle des mèches par l'aluminium liquide même en opérant sous une pression de 0,3 kPa bien que les carbures métalliques soient mieux mouillés par les métaux que les carbures covalents ou le carbone grâce à la formation de liaisons métal-métal à travers l'interface. Le plus efficace des revêtements céramiques est le codépôt de titane et de bore obtenu par réduction de vapeurs de  $\text{TiCl}_4$  et  $\text{BCl}_3$  en présence de vapeurs de zinc à 700°C. Ce revêtement qui pourrait être un mélange de Ti, B, TiB ou/et  $\text{TiB}_2$  conduit à une bonne imprégnation des mèches par l'aluminium liquide. Il n'est, en revanche, plus efficace si les fibres sont exposées à l'air avant imprégnation.

Les traitements de surface précédents ne permettent en général que la réalisation de **demi-produits** (élaboration en continu sur mèches longues et sous atmosphère contrôlée). L'élaboration de pièces finies nécessite des opérations supplémentaires de consolidation et de mise en forme dont le coût de mise en oeuvre ne fait qu'accroître le prix de revient du matériau composite.

(ii) L'addition d'éléments très électropositifs tels Mg ou Ca mais surtout Li à l'aluminium permet d'obtenir un bon mouillage de SiC (ou C) bien que ce traitement ait été plutôt préconisé pour les fibres de  $\text{Al}_2\text{O}_3$  (2,5). Les éléments plus électropositifs que l'aluminium se substituent à lui dans la couche d'alumine qui recouvre le métal liquide et diminuent sa compacité. L'aluminium liquide peut alors plus facilement diffuser à travers la couche d'oxyde et mouiller la céramique. Le lithium est particulièrement efficace dans la mesure où il entraîne une dislocation rapide du film d'oxyde (2). Cependant, l'imprégnation de préformes avec les alliages Al-Li ne peut se faire que sous vide de manière à éviter toute oxydation excessive du Li.

Ainsi, les méthodes développées précédemment pour améliorer le mouillage des renforts fibreux ((i) et (ii)), si elles ont fait preuve de leur efficacité au plan chimique, s'avèrent soit d'industrialisation délicate et coûteuse, soit dégradantes au plan mécanique.

Une méthode physique telle que le forgeage liquide (squeeze casting) est un autre moyen de compenser l'absence d'imprégnation spontanée des préformes céramiques par l'aluminium liquide. Elle consiste à appliquer une très forte pression, à l'aide d'un piston, sur le métal liquide qui a été préalablement coulé sur la préforme céramique placée dans un moule. Ainsi, d'une part, l'aluminium entre par force au sein du renfort, d'autre part, il se solidifie rapidement sous l'effet de la très haute pression (environ 100 MPa). En effet, la température de solidification de l'aluminium est augmentée ( $\Delta T$ ) proportionnellement à l'augmentation de la pression ( $\Delta P$ , au dessus de la pression atmosphérique) conformément à l'équation de Clausius-Clapeyron :

$$\Delta T = \frac{T_f(V_l - V_s)}{H_f} \Delta P$$

où  $T_f$ ,  $H_f$ ,  $V_l$ ,  $V_s$  sont respectivement la température de fusion à la pression atmosphérique, la chaleur latente de fusion, le volume spécifique de la phase liquide et le volume spécifique de la phase solide de l'aluminium (15). De plus, le gaz présent au sein de la préforme est chassé lors de l'application de la pression et remplacé par le métal liquide. Dans ce cas, le contact direct du métal sous pression avec les parois du moule de forgeage favorise l'évacuation rapide de la chaleur. Ce mode d'élaboration permet donc, en une seule opération, une imprégnation complète de préformes complexes, quelle que soit leur porosité résiduelle, tout en limitant le temps d'interaction fibre-matrice à haute température et en conduisant à une meilleure qualité métallurgique de l'aluminium. Les pressions utilisées restent cependant élevées. Elles peuvent être une source d'endommagement mécanique pour les préformes les plus rigides. De plus, elles nécessitent l'utilisation de presses de forte capacité lorsqu'il s'agit d'imprégner des pièces de taille significative. Leur mise en oeuvre devient alors coûteuse.

Toute technique simple permettant d'améliorer la mouillabilité du renfort ferait diminuer les pressions à appliquer et contribuerait à la limitation des coûts de production. C'est pour cette raison que J.P. Rocher et al., qui nous ont précédés dans cette étude, ont orienté leurs travaux vers la recherche d'un procédé de prétraitement spécifique qui puisse être utilisé pour des préformes complexes et autorise leur imprégnation par l'aluminium selon des techniques proches de celle utilisées actuellement en fonderie d'alliages légers (16). Le choix a été guidé par "l'idée de rechercher s'il existait, parmi les flux désoxydants déjà utilisés en fonderie d'alliages légers, des espèces chimiques qui seraient susceptibles de promouvoir le mouillage des fibres à base de C ou de SiC par les alliages d'aluminium". Sur ces bases, un procédé original d'élaboration des matériaux composites à matrice d'alliage léger a été développé avec succès et breveté (17). Dans son principe, il consiste à faire précipiter à la surface des fibres qui constituent le

renfort céramique des **microcristaux du fluorure  $K_2ZrF_6$** . Ce dépôt s'effectue en imprégnant la préforme par une solution aqueuse du fluorure portée à ébullition. L'élimination du solvant s'opère ensuite par étuvage à 100°C. La préforme ainsi prétraitée peut alors être installée dans un moule de fonderie. L'ensemble moule-préforme est préchauffé, puis l'aluminium est coulé et pénètre la préforme spontanément par remontée capillaire (principe de la coulée par gravité).

L'intérêt et les avantages de ce procédé, communément appelé **procédé au  $K_2ZrF_6$** , par rapport aux procédés précédemment décrits, résultent du fait qu'il:

- est de mise en oeuvre simple puisqu'il fait appel à des produits déjà rencontrés en fonderie d'aluminium et s'opère à l'air.
- ne nécessite aucune pression (dans le cas de nos préformes de laboratoire) hormis la pression métallostatique.
- s'applique à des préformes poreuses de différentes natures (C, SiC) et de différentes morphologies (tissu, feutre, 2DSiC(Nicalon)/SiC(CVI), 4DC/C).

Ce travail a été motivé par la volonté (i) d'expliquer la nette amélioration de la mouillabilité des préformes céramiques par l'aluminium en présence du fluorure  $K_2ZrF_6$ , (ii) d'étudier la compatibilité chimique entre renfort et fluorure et entre renfort et matrice en présence du fluorure, (iii) de mettre en évidence l'intérêt du procédé dans l'optique d'une transposition industrielle. Les moyens que nous avons utilisés et les résultats obtenus sont présentés dans les trois publications (chapitres I, II et III) et les deux annexes qui constituent le présent mémoire.

Le **premier chapitre** concerne l'établissement du diagramme de phases partiel du système ternaire réciproque  $KF-AlF_3-Al_2O_3-K_2O$  afin de mettre en évidence l'éventuel effet fondant, vis à vis de l'alumine qui recouvre l'aluminium liquide et inhibe le mouillage des céramiques par le métal, des fluorures mis en jeu au cours du procédé au  $K_2ZrF_6$ , i.e. " $6KF,4AlF_3$ ". La mise en cohérence des

résultats du calcul thermodynamique obtenus grâce à la théorie CIS (Conformal Ionic Solution, Annexe I) et des résultats expérimentaux obtenus sur le comportement thermique des mélanges  $K_3AlF_6-Al_2O_3$  a permis de tracer ce diagramme dans un domaine de compositions proches de la section  $K_3AlF_6-Al_2O_3$  (Annexe II) .

Dans le **second chapitre**, nous avons tenté d'expliquer les fondements du procédé au  $K_2ZrF_6$  à partir de considérations thermodynamiques et d'une approche numérique basée sur la modélisation de l'imprégnation de préformes poreuses. En particulier, la section verticale " $6KF, 4AlF_3$ "- $Al_2O_3$  extraite du diagramme de phases du système ternaire réciproque  $KF-AlF_3-Al_2O_3-K_2O$  établi au chapitre I, de même que les grandeurs thermodynamiques - variations d'énergie libre de Gibbs et d'enthalpie - associées aux réactions chimiques mises en jeu dans le procédé ont permis de comprendre l'efficacité du procédé en termes de mouillage. Par ailleurs, l'influence des paramètres physiques associés au procédé au  $K_2ZrF_6$ , i.e. l'exothermicité des réactions chimiques et l'abaissement de l'angle de contact, sur l'aptitude à l'imprégnation de préformes fibreuses (2DSiC(Nicalon)/SiC(CVI)) est étudiée grâce au modèle numérique.

Dans la **dernière partie**, une caractérisation mécanique en traction de monofilaments CVD de carbure de silicium après chaque étape du procédé au  $K_2ZrF_6$ , i.e. dépôt du fluorure, préchauffage à  $650^\circ C$ , incorporation dans l'aluminium, a été effectuée et les résultats ont été analysés de manière statistique sur la base d'une fonction de distribution de Weibull. L'observation des faciès de rupture primaire et de la surface des filaments, de même que les spectrométries X et Auger ont permis de mettre en évidence les causes et les modes de rupture. Ce type d'étude a été un moyen de mettre en évidence les compatibilités chimiques entre renfort, matrice et fluorure.



Cette étude a, en outre, fait l'objet de deux communications publiées:

- l'une dans le cadre des Journées Métallurgiques d'Automne de la Société Française de Métallurgie (Paris, 18-20 octobre 1988) (18)
- l'autre dans le cadre du troisième congrès européen sur les matériaux composites, ECCM3 (Bordeaux, 20-23 Mars 1989) (19).

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## CHAPITRE I

## INTRODUCTION AU CHAPITRE I

Le mauvais mouillage des fibres de SiC ou C par l'aluminium aux températures inférieures à 900°C résulte de la présence d'une pellicule d'alumine à la surface de l'aluminium liquide. A ces températures, la compacité de cette pellicule d'oxyde est telle qu'elle joue le rôle de barrière de diffusion entre le métal et la céramique, les empêchant de réagir.

Le procédé au  $K_2ZrF_6$  a été développé dans l'espoir que les fluorures qu'il met en jeu se comportent comme des flux désoxydants vis-à-vis de l'aluminium. Ces fluorures ont été décrits par Lundin, qui a utilisé un traitement semblable pour favoriser le mouillage de feuillards d'acier par l'aluminium, comme étant les produits de la réaction entre l'aluminium et le fluorure  $K_2ZrF_6$  selon

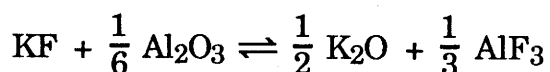


Le processus de mise en oeuvre de cette réaction au travers de la pellicule d'alumine est expliqué au chapitre II.

L'amélioration du mouillage des substrats de SiC et C par l'aluminium, en présence du fluorure  $K_2ZrF_6$ , dès la température de fusion du métal, ayant effectivement été mise en évidence (Thèse J.P. Rocher), nous nous sommes attachés à démontrer l'effet fondant du mélange de fluorures "6KF,4AlF<sub>3</sub>" sur la pellicule d'alumine aux températures inférieures à 900°C. Pour cela, le diagramme de phases du système KF–AlF<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> devait être établi afin d'examiner l'allure des surfaces liquidus dans le domaine de composition, "6KF,4AlF<sub>3</sub>"-quelques % Al<sub>2</sub>O<sub>3</sub> (mol), correspondant aux conditions expérimentales du procédé. Une première approche expérimentale du comportement thermique des mélanges K<sub>3</sub>AlF<sub>6</sub>–Al<sub>2</sub>O<sub>3</sub> (K<sub>3</sub>AlF<sub>6</sub> est un des constituants du mélange "6KF,4AlF<sub>3</sub>") ayant mis en évidence

l'existence d'un nouveau composé,  $\text{Al}_2\text{O}_3\text{-}\beta\text{ (K}_2\text{O. nAl}_2\text{O}_3\text{, n=5,11)}$ , l'étude a dû être étendue au système plus complexe  $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$ . Étant donné le nombre très important de résultats expérimentaux nécessaires pour établir le diagramme de phases d'un tel système, nous avons préféré l'aborder grâce au **calcul thermodynamique**.

Le calcul du diagramme de phases d'un système, basé sur le principe de la minimisation de son énergie libre de Gibbs totale, suppose que soient connues les énergies libres de Gibbs de sa phase liquide et des différents composés solides qu'il contient. Le système  $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$  appartient à la famille des systèmes dits **réciroques** car les espèces qui le constituent vérifient la relation d'échange



En conséquence, il est ternaire et est appelé **système ternaire réciroque**. Grâce à cette particularité, sa phase liquide a pu être modélisée sur la base de la théorie CIS (Conformal Ionic Solution) dont le seul paramètre ajustable,  $Z$ , a pu être fixé en faisant coïncider les résultats du calcul avec les résultats expérimentaux que nous avons obtenus lors de l'étude des mélanges  $\text{K}_3\text{AlF}_6\text{-Al}_2\text{O}_3$ . L'application de la théorie CIS aux systèmes ternaires réciroques est présentée à l'annexe I. Les données thermodynamiques impliquées dans le modèle et nécessaires au calcul du diagramme de phases, i.e. les grandeurs thermodynamiques des sous-systèmes unaires  $\text{KF}$ ,  $\text{AlF}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$  et binaires  $\text{KF-AlF}_3$ ,  $\text{AlF}_3\text{-Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3\text{-K}_2\text{O}$ ,  $\text{K}_2\text{O-KF}$  du système ternaire réciroque, ont été soit retrouvées dans la bibliographie, soit calculées en mettant en cohérence les diagrammes de phases expérimentaux de la bibliographie avec les diagrammes de phases que l'on peut calculer grâce à des modèles. La méthodologie utilisée est présentée à l'annexe II. Finalement, le programme d'optimisation "Mélange 16" mis au point au L.T.P.C.M./Grenoble dans l'équipe de C. Bernard a permis de mener à bien les

calculs de minimisation et de tracer point par point le diagramme de phases du système  $\text{KF}-\text{AlF}_3-\text{Al}_2\text{O}_3-\text{K}_2\text{O}$ . Ce diagramme peut être représenté dans un plan étant donnée la réciprocité du système.

L'utilisation des résultats de ce calcul en ce qui concerne l'allure des courbes liquidus dans la section verticale " $6\text{KF}, 4\text{AlF}_3$ "- $\text{Al}_2\text{O}_3$  est discutée au chapitre II.

Soumis à "Calphad"

**PARTIAL PHASE DIAGRAM  
OF THE TERNARY RECIPROCAL SYSTEM  $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$**

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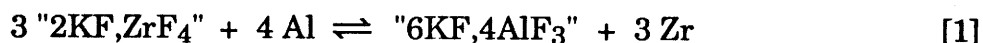
**ABSTRACT**

*A  $\text{K}_2\text{ZrF}_6$  treatment improves the wettability of SiC (or C) fibers by aluminum alloys. A possible mechanism involves the formation of  $\text{K}_3\text{AlF}_6$  followed by the dissolution of the alumina film. DTA analyses of  $\text{K}_3\text{AlF}_6\text{-}\alpha\text{-Al}_2\text{O}_3$  mixtures show that a temperature invariant transition occurs at 1132 K, the solid containing trace amounts of  $\text{KAlF}_4$  and  $\beta$ -alumina at room temperature. Part of the ternary reciprocal system  $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$  is calculated, the Gibbs free energy of the liquid being described according to the CIS theory. The  $\text{K}_3\text{AlF}_6\text{-Al}_2\text{O}_3$  isopleth section is given. It is characterized by a liquidus with a deep minimum at 1132 K and 11.6 wt.% alumina.*



## 1 - INTRODUCTION

The ability of ceramic fibers to be more or less wetted by liquid metals, e.g. light alloys, is a key parameter in the processing of metal matrix composites via liquid routes. It is now well established that both silicon carbide and carbon fibers are not spontaneously wetted by liquid aluminum alloys at the temperatures commonly used in light alloy casting (i.e. 973-1073 K). This drawback has been overcome by applying either a suitable coating to the fibers (e.g. TiC or TiB<sub>2</sub>) or a high pressure to the liquid (squeeze casting). Recently, a new fiber treatment has been suggested by J.P. Rocher et al., which has the advantage of requiring a simple procedure (1,2). In its principle, it consists in immersing the fiber preform in an aqueous solution of K<sub>2</sub>ZrF<sub>6</sub>. After drying, the fiber preform is effectively wetted ( $\theta \approx 70^\circ$ ) by aluminum alloys at a temperature slightly above their liquidus. The chemistry of the process could be related to the following overall equation:



as proposed in a similar way by H. Lundin, who used the treatment to enhance the wetting ability of steel sheets by aluminum, and as discussed in another study of the authors (3,4). The fluorides which are formed could act as fluxes to dissolve the alumina film which covers the liquid and prevents wetting from taking place (5,6). However, the detailed mechanism of the wetting enhancement and the nature of the chemical species involved remains unknown.

The aim of the present contribution was initially to establish the phase diagram of the ternary KF–AlF<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> system with the attention focussed on the liquidus surfaces and invariant points in composition domains of interest for the understanding of the K<sub>2</sub>ZrF<sub>6</sub> fiber treatment. As a matter of fact, in a preliminary experimental approach of the thermal behavior of K<sub>3</sub>AlF<sub>6</sub>– $\alpha$ –Al<sub>2</sub>O<sub>3</sub> mixtures

( $K_3AlF_6$  is one of the fluorides which may result from equation [1]), based on DTA, calorimetric experiments, X-ray and IR analyses, a new phase, i.e.  $\beta$ -alumina ( $K_2O$ ,  $nAl_2O_3$  with  $n = 5, 11$ ) was observed in the solid after cooling at room temperature. Therefore, the study has to be extended to the more complex  $KF-AlF_3-Al_2O_3-K_2O$  ternary reciprocal system. Regarding the amount of work which would have been necessary to establish the phase diagram experimentally, an approach based on thermodynamic calculations was preferred. A statistical model, derived from the Conformal Ionic Solution (CIS) theory, already used for reciprocal molten salt systems (7-9), was chosen to describe the liquid phase and the calculations were performed with the software MELANGE 16 (10).

## 2 - THERMAL BEHAVIOR OF $K_3AlF_6$ - $\alpha$ - $Al_2O_3$ MIXTURES

The fluoride  $K_3AlF_6$  which is one compound of the mixture "6KF,4AlF<sub>3</sub>" (fig.7) was thought to play a key role in the wetting enhancement mechanism (its equivalent for sodium, the cryolite  $Na_3AlF_6$ , is used to dissolve alumina in the electrolytic preparation of aluminum) (4).

Many experimental studies have been devoted to the  $\alpha$ - $Al_2O_3$ - $Na_3AlF_6$  phase diagram which is usually presented as a simple eutectic (with  $T_E=1233-1236$  K and  $X_E = 10-11,5$  wt.%  $\alpha$ -alumina) (fig.1) (11). Similarly, the corresponding  $\alpha$ - $Al_2O_3$ - $Li_3AlF_6$  phase diagram is given as a simple eutectic (with  $T_E = 1048-1058$  K and  $X_E = 0,7-2$  wt.%  $\alpha$ -alumina) (11). Moreover, the general features of the liquidus of the  $\alpha$ - $Al_2O_3$ - $Na_3AlF_6$  system are not strongly modified when  $Li_3AlF_6$  is added, the  $T_E$  and  $X_E$  values being progressively shifted towards those for  $\alpha$ - $Al_2O_3$ - $Li_3AlF_6$  (fig.2) (12). Since, in the same manner, the addition of  $K_3AlF_6$  to  $\alpha$ - $Al_2O_3$ - $Na_3AlF_6$  simply results in a decrease in  $T_E$  and an increase in  $X_E$ , as shown in fig.3, one could reasonably assume that the  $\alpha$ - $Al_2O_3$ - $K_3AlF_6$  system would

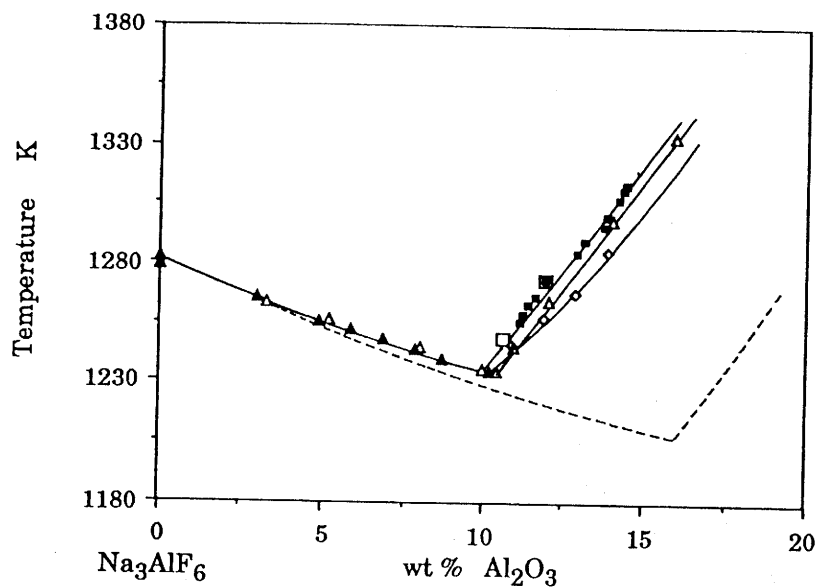


Figure 1:  
Phase diagram of the quasi-binary system  
 $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$  (11)

- Abramov: TA, high cooling rate
- ▲ Fenerty et al.: TA, low cooling rate
- ◇ Fenerty et al.: visual observations
- △ Foster: quenching technique
- Chin et al.: saturation measurements
- Henry et al.: saturation measurements

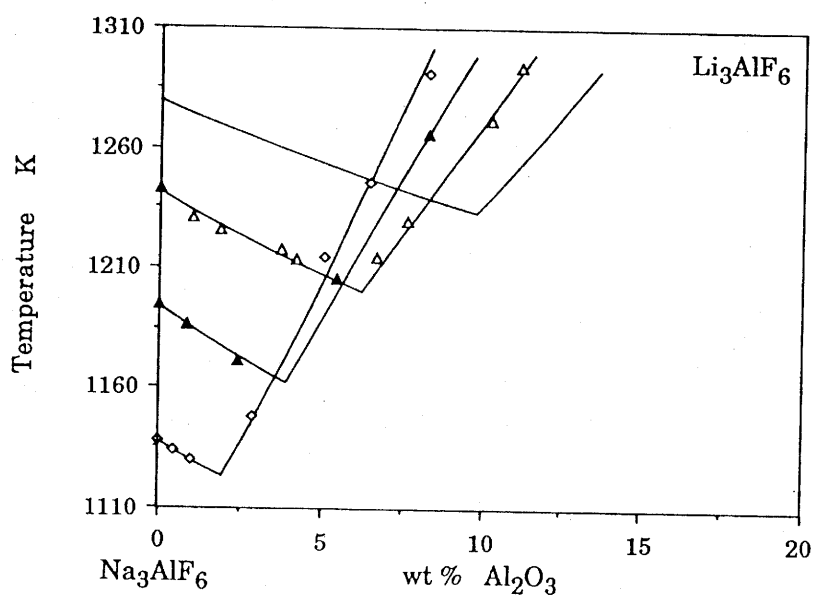


Figure 2:  
Liquidus diagrams for  $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$  with  
 - 0  
 △ 10 wt %  $\text{Li}_3\text{AlF}_6$  given on  
 ▲ 20 alumina-free basis (12)  
 ◇ 30

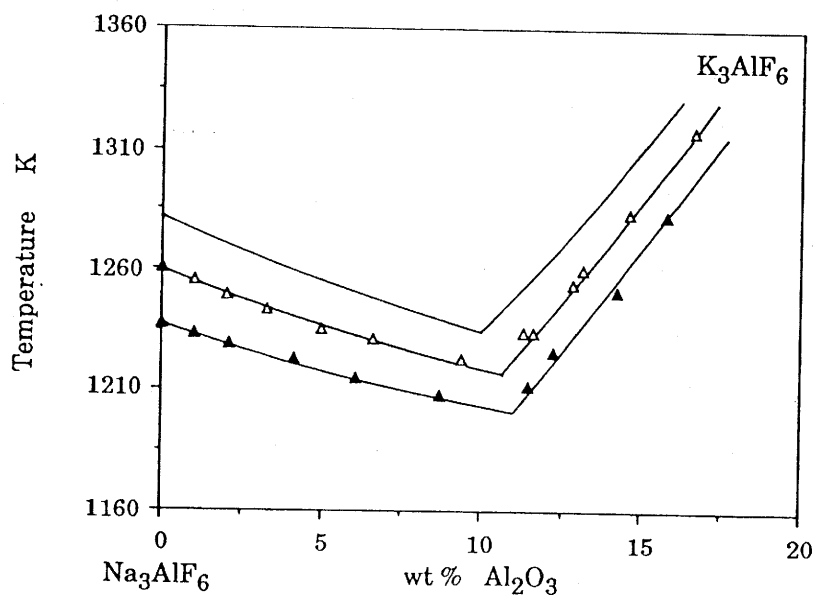


Figure 3:  
Liquidus diagrams for  $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$  with  
 - 0 wt %  $\text{K}_3\text{AlF}_6$  given on  
 △ 10 alumina-free basis (12)  
 ▲ 20

behave as a simple eutectic system with  $T_E (K_3AlF_6) < T_E (Na_3AlF_6)$  and  $X_E (K_3AlF_6) > X_E (Na_3AlF_6)$ .

Several authors have already studied the liquid phase of the  $\alpha-Al_2O_3-K_3AlF_6$  system (13-17). Almost all of them reported a "minimun" on the liquidus curve which falls in the same domains of temperature and composition (i.e. 1083-1113 K and 21-24 wt.% alumina, respectively). Only A.I. Belyaev mentioned somewhat different data (i.e. 1183 K and 14-14,5 wt.% alumina) (14). Finally, the recent study due to R.V. Chernov et al. presented this minimum as an eutectic invariant (17).

Regarding the lack of reliable data in this field, we have in a first step, studied the phase equilibria taking place in the  $\alpha-Al_2O_3-K_3AlF_6$  system on the basis of calorimetric experiments as well as X-ray diffraction (XRD) and infracted (IR) analyses of the solid phases.

## 2.1 - Experimental

Potassium cryolite has been prepared in the solid state according to a chemical reaction corresponding to the following equation :



by heating, at 823 K for 15 hours under an atmosphere of argon, a stoichiometric mixture of potassium and aluminum fluorides. KF was a commercial product, anhydrous and with a low content of cation impurities.  $AlF_3$  was prepared according to a two-step procedure : (i) a treatment in a platinum crucible of  $AlF_3 \cdot nH_2O$  by  $NH_4HF$  followed after grinding by (ii) an annealing treatment of the powder performed in a platinum crucible at 873 K in a stream of gaseous HF (18). The chemical analysis of the potassium cryolite resulted in the following data : K: 32.7; Al: 10.3 and F: 57.0 at.% (vs 30 ; 10 and 60 at. % theor.). Its temperature and enthalpy of melting were found to be 1260 K and  $125 \pm 2.5$  kJ.mol<sup>-1</sup> respectively and

are in a reasonable agreement with the literature ( $T_m(K) = 1268 (19) ; 1269 (20) ; 1273 (21)$  and  $\Delta H_m (kJ.mol^{-1}) = 115.5 (20) ; 122.6 \pm 1.7 (21)$ ).

$\alpha$ -alumina was obtained by heating in air (at 1473K for 16 hours ) a commercial  $\chi$ -alumina powder ( whose total content in cation impurities was less than 10 ppm)

The  $\alpha$ - $Al_2O_3$ - $K_3AlF_6$  samples were prepared according to a two-step procedure : (i) one gram of mixture was prepared from  $\alpha$ - $Al_2O_3$  and  $K_3AlF_6$  powders, in a dry glove box, and then annealed at 1023 K for 24 hours in a platinum crucible, under an atmosphere of dry argon, (ii) after grinding in the dry glove box, 80 mg samples were set in platinum tubes which were sealed under argon with a microtorch.

The thermal analysis experiments were performed with a microcalorimeter designed by L. Rabardel and which is described elsewhere (22). The apparatus was calibrated in both temperature and energy with pure tin and gold. The accuracy of the measurements was thought to be  $\pm 2$  K and 1.5 %  $kJ.mol^{-1}$  respectively. The DTA curves were recorded both during heating and cooling at a rate of 4  $K.min^{-1}$ . Regarding the tendency of the potassium cryolite- $\alpha$ -alumina melts to remain supercooled, only the data obtained on heating will be considered in the following.

The XRD spectra were recorded with a Cu-K $\alpha$  diffractometer according to a conventional procedure. The IR spectra were recorded with a double beam dispersive spectrometer (PE 983) and a data processing computer. The powder samples were first mixed with Nujol and then set within a film cell between two cesium iodide plane crystals.

## 2.2 - Results and discussion

The thermal behaviors of  $\alpha$ - $Al_2O_3$ - $K_3AlF_6$  mixtures containing respectively 0 ; 5.0 ; 15.3 ; 17.9 ; 21.0 ; 23.2 ; 25.0 ; 30.1 and 90.0 wt % alumina were experimentally

studied. The thermal transitions which have been observed suggest, at least in a first approximation, the occurrence of a temperature invariant transition within the whole composition range (fig.4 ; Table 1). The tentative corresponding phase diagram is given in fig.5. It clearly shows the invariant at 1132 K as well as the liquidus curve on the  $K_3AlF_6$  rich side whereas it was not observed on the  $\alpha$ -alumina rich side. It was thought that the slope of the liquidus curve joining the invariant point and the melting point of pure alumina should be very sharp since  $\Delta T = 1195$  K for  $\Delta X = 69$  wt % alumina and consequently : (i) the liquidus could be located at temperatures exceeding the limit of the apparatus (all experiments were limited in temperature at 1300 K) and (ii) the heat of melting could not be detected due to the low fraction of crystals melting per unit of temperature increase. It is noteworthy that N.W.F. Phillips et al. (23) and later on M. Rolin (24) found no thermal deviation on cooling curves corresponding to the primary crystallization of alumina in the  $\alpha-Al_2O_3-Na_3AlF_6$  system, even at a low cooling rate (i.e.  $0.5\text{ K.min}^{-1}$ ).

The Tammann diagram corresponding to the invariant transition has been also plotted in fig.5. From a linear extrapolation of the data (table 1), it appears that the invariant point composition is  $21 \pm 1$  wt.% alumina, a value which is in rather fair agreement with the liquidus curve drawn for the  $K_3AlF_6$ -rich mixtures.

However, the results of the XRD analyses performed on the DTA samples after cooling and grinding (in the dry glove box) show that small amounts of  $\beta$ -alumina and  $KAlF_4$  were present while  $\alpha$ -alumina was not observed for composition ranging from 21 to 30 wt % alumina. The same conclusion could also be drawn for the 17.9 wt % alumina sample (although there is some uncertainty about  $\beta$ -alumina). Furthermore, for 90.0 wt % alumina,  $KAlF_4$  was no longer observed whereas  $\beta$ -alumina was still present and  $\alpha$ -alumina recovered. Finally, the only crystalline phase detected in the 5.0 and 15.3 wt % alumina samples (i.e. on the left of the invariant point) was  $K_3AlF_6$ .

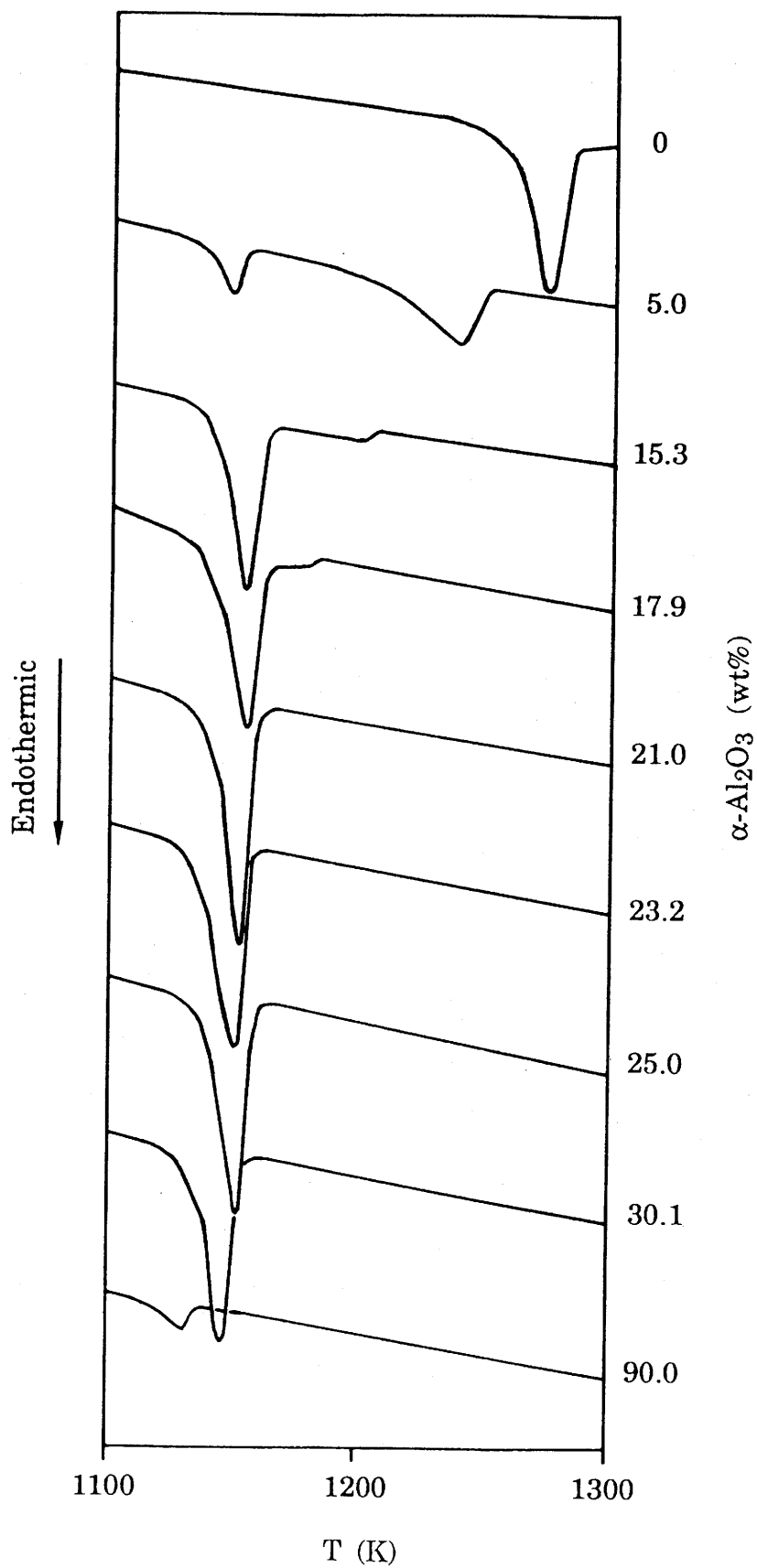


Figure 4: DTA curves of the  $\alpha\text{-Al}_2\text{O}_3\text{-K}_3\text{AlF}_6$  mixtures recorded on heating the samples in sealed platinum tubes

| $\alpha$ -Al <sub>2</sub> O <sub>3</sub> (wt %) | 5.0    | 15.3    | 17.9    | 21.0    | 23.2    | 25.0    | 30.1    | 90.0  |
|-------------------------------------------------|--------|---------|---------|---------|---------|---------|---------|-------|
| T (eutectics) (K)                               | 1131   | 1136    | 1134    | 1133    | 1136    | 1138    | 1131    | 1118  |
| T(liquidus) (K)                                 | 1232   | 1189    | 1167    | -       | -       | -       | -       | -     |
| $\Delta H$ (liquidus) (J.mol <sup>-1</sup> )    | -30740 | -108930 | -121730 | -159050 | -147010 | -138500 | -128240 | -9520 |

Table 1: DTA data for the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-K<sub>3</sub>AlF<sub>6</sub> mixtures



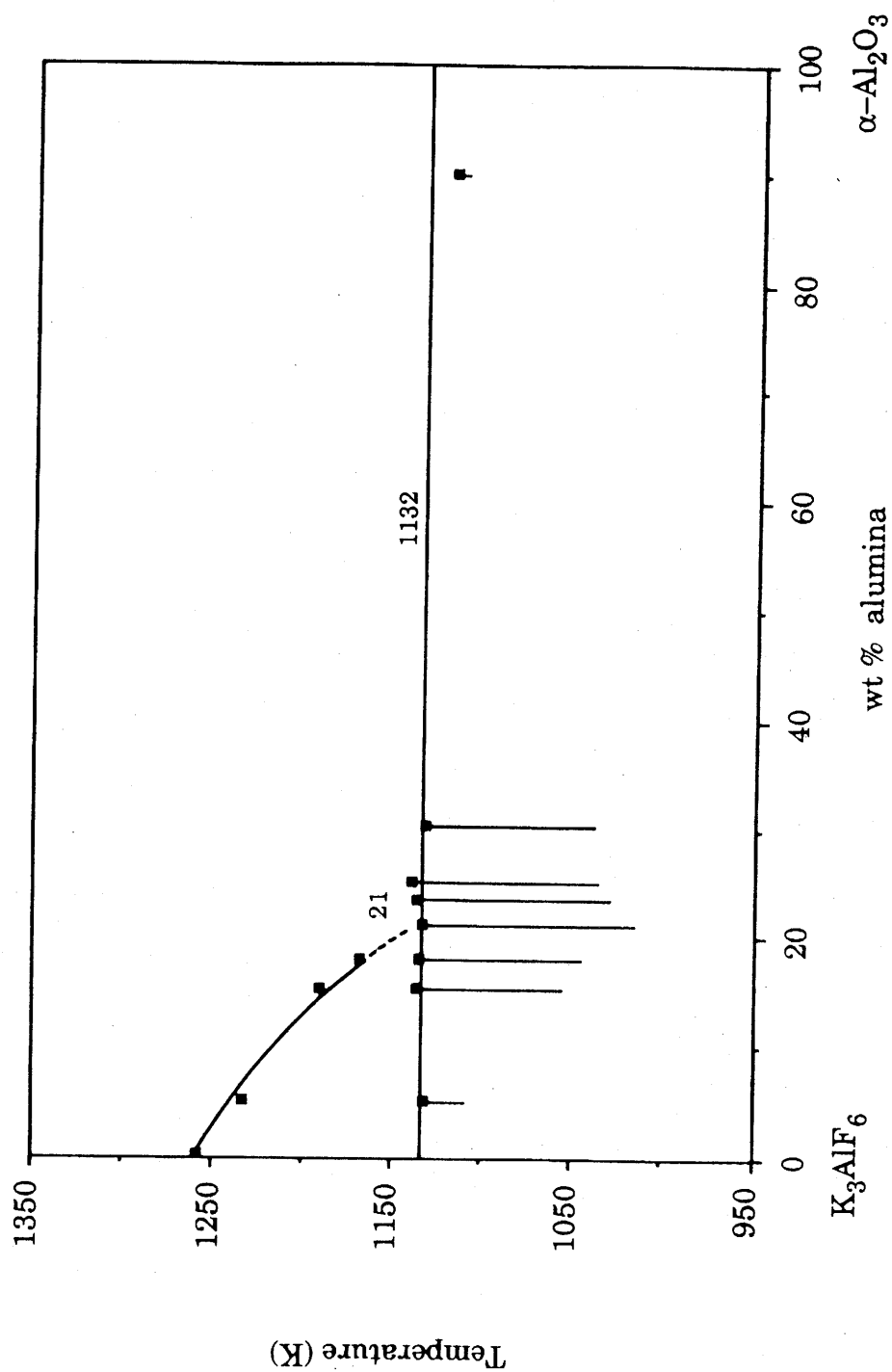


Figure 5: Tentative phase diagram of the  $\text{K}_3\text{AlF}_6$ - $\text{Al}_2\text{O}_3$  system based on DTA data

In the alumina–sodium cryolite system, H. Ginsberg and A. Böhm reported that for alumina concentrations less than 12.5 wt %, the XRD-patterns of samples slowly cooled from 1273 K exhibited only the cryolite lines whereas corundum lines were observed when the alumina concentration was increased. However, for alumina concentrations less than 12.5 wt % and after an aluminum sulfate extraction (to recover the alumina) :  $\beta$ - and  $\gamma$ - aluminas were identified by XRD in the slowly cooled samples while only  $\beta$ -alumina was present in the quenched specimens (25). J. Brynestad et al. also mentioned that  $\beta$ -alumina was present in samples quenched from 1273 K (26). P.A. Foster reported the occurrence, in quenched alumina–sodium cryolite mixtures, of large amounts of what he called a m-alumina (m for mullite-type ) as well as a small amount of zeta-alumina, regardless of the overall alumina content of the mixtures. Moreover, quenching experiments from below the liquidus led to mixtures of m-alumina and corundum for compositions on the high alumina side of the eutectic while only m-alumina was observed for those on the low alumina side (27). It is noteworthy that A. Grant Elliot et al. mentioned later a  $\lambda$ -phase in the  $\text{NaAlO}_2\text{--Al}_2\text{O}_3$  system, with a formula  $\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3$  ( $x = 3\text{--}12$ ), whose XRD pattern is similar to that of m-alumina (28).

The occurrence of  $\beta$ -alumina in the  $\text{K}_3\text{AlF}_6\text{--Al}_2\text{O}_3$  samples submitted to DTA and corresponding to alumina-rich compositions, has been confirmed by IR spectrometry analyses, as shown in fig.6. Starting from pure  $\text{K}_3\text{AlF}_6$  (characterized by two absorption lines at 570 and 390  $\text{cm}^{-1}$  according to (29)), the addition of increasing amounts of alumina gives rise, for  $x \geq 17.9$  wt % alumina, to new sharp IR absorption lines at 1050 ; 860 ; 760 ; 710 ; 600 ; 460 ; 380 and 310  $\text{cm}^{-1}$  different from those of  $\alpha$ -alumina (30) and which have been assigned to potassium  $\beta$ -alumina (on the basis of the IR-spectrum reported for the related sodium phase (31)).

From the results of the XRD and IR data, it thus appears that the  $\alpha\text{-Al}_2\text{O}_3\text{--K}_3\text{AlF}_6$  system does not behave as a true quasi-binary system (at least for  $X > 18\text{--}20$  wt % alumina). The important conclusions which can be drawn from the

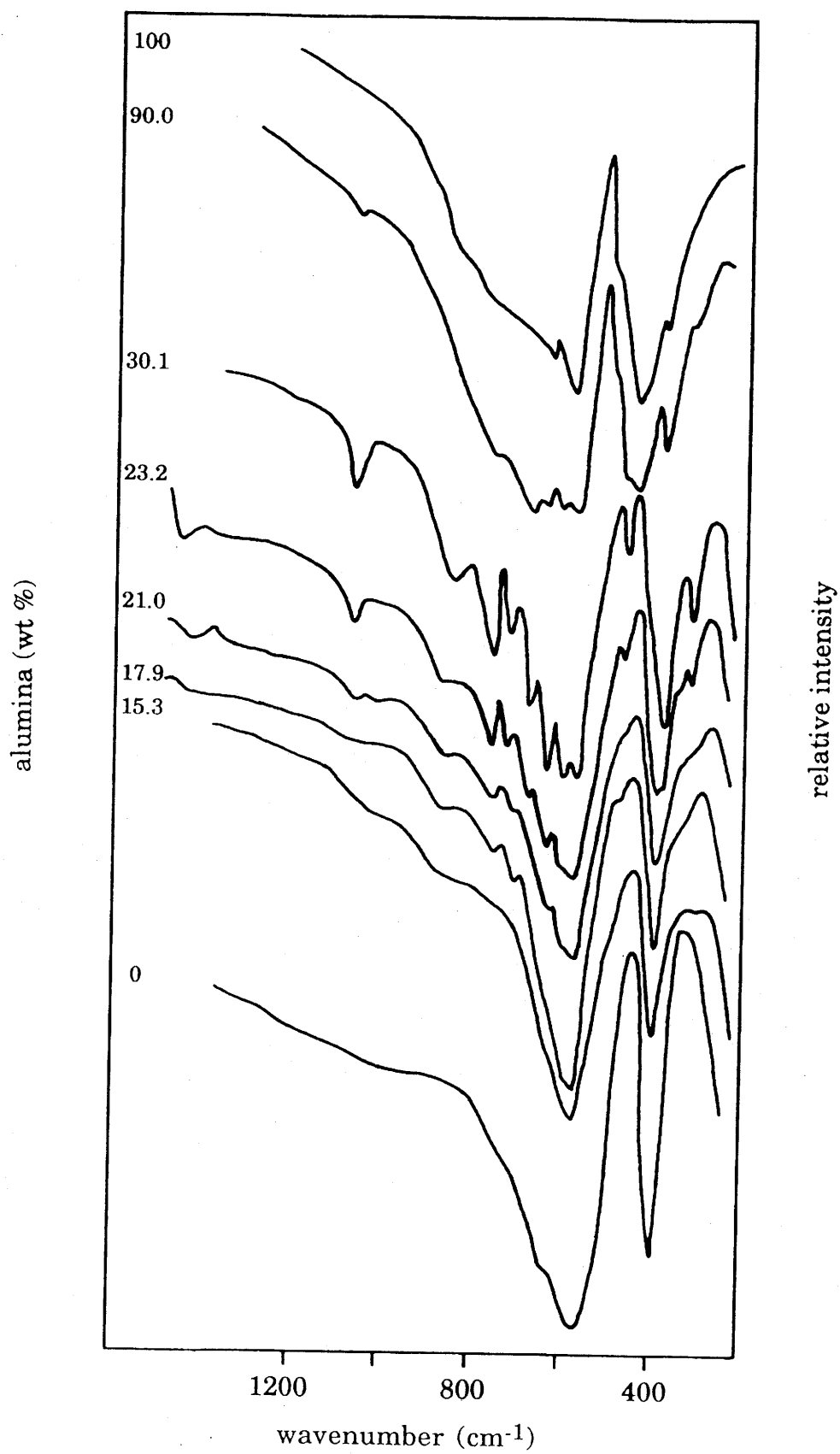


Figure 6: I.R. spectra of the  $K_3AlF_6$ - $\alpha-Al_2O_3$  mixtures

experimental study are : (i) the occurrence of a temperature invariant transition at 1132 K and (ii) that of  $\beta$ -alumina in some of the materials after cooling at room temperature. It is worthy of note that  $\beta$ -alumina type phases have been also mentioned for the related  $\alpha$ - $\text{Al}_2\text{O}_3$ - $\text{Na}_3\text{AlF}_6$  system although it has been generally considered up to now as a true quasi-binary system.

### 3 - PARTIAL CALCULATION OF THE PHASE DIAGRAM OF THE TERNARY RECIPROCAL SYSTEM $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$

On the basis of the identification of  $\beta$ -alumina and  $\text{KAlF}_4$  in the samples submitted to DTA analysis, the study was extended to the more complex system  $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$  ( $\text{K}_3\text{AlF}_6$  and  $\text{KAlF}_4$ , are compounds from the  $\text{KF-AlF}_3$  binary system whereas  $\alpha$ - and  $\beta$ - aluminas belong to the  $\text{Al}_2\text{O}_3\text{-K}_2\text{O}$  binary system ). The calculation of the phase diagram required the knowledge of the Gibbs free energies of the liquid phase and of the various involved compounds. One of the major difficulties of such a calculation lied in the modelling of the liquid phase.

The nature of the chemical species that may be present in the cryolite-alumina molten mixtures has been the subject of different studies (11). On the basis of cryoscopic measurements, S.H.K. Ratkje has established that oxyfluoride species  $\text{Al}_2\text{OF}_{2x}^{4-2x}$  are present besides the previously well-identified  $\text{Na}^+$ ,  $\text{F}^-$ ,  $\text{AlF}_6^{3-}$  and  $\text{AlF}_4^-$  ions in the liquid phase corresponding to NaF-rich compositions in the  $\text{NaF-AlF}_3\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$  system (11). For the related  $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$  system, a similar conclusion has been drawn. In addition, the occurrence of the  $\text{AlOF}_y^{1-y}$  oxyfluoride species has been suggested (32).

Till now, no model has been proposed to describe analytically a liquid phase made of a mixture of oxides and fluorides. However, M. L. Capoor et al. and H. Gaye et al. have described the liquid phase of oxide-based systems in terms of a model assuming the occurrence of  $\text{Mi-O-Mj}$  cells (where  $\text{Mi}$  and  $\text{Mj}$  are the related cations)

while M. Blander, M.L. Saboungi and their coworkers have applied the so-called Conformal Ionic Solution (CIS) to molten salts (7-9, 33, 34).

The CIS theory is suited to systems referred to as reciprocal systems, the simplest being made of two monovalent cations  $A^+$  and  $B^+$  associated with two monovalent anions  $C^-$  and  $D^-$  with the following double exchange equilibrium :



It clearly appeared that the  $KF-AlF_3-Al_2O_3-K_2O$  system could be regarded as a reciprocal system since the four ionic species obey the following double exchange equilibrium :



On the basis of this feature, the CIS theory which is briefly described below was used to : (i) define the composition coordinates and (ii) calculate the Gibbs free energy of the liquid . It is based on the application of the statistical mechanics to molten salts and can be used to predict the main features of the phase diagram from limited experimental data. Its previous application to various ionic systems, e.g.  $Li,K/F,Cl$  (35) ;  $Na,Sr/Cl,NO_3$  ;  $Na,Ba/Cl,NO_3$  ;  $Li,K/Cl,CrO_4$  ;  $Li,K/Br,CrO_4$  ;  $Na,Ba/F,Cl$  (9) as well as to the molten salts used in the Hall-Héroult processing of aluminum (i.e. the  $LiF-NaF-AlF_3$  (36) ;  $LiF-NaF-CaF_2$  ;  $NaF-AlF_3-CaF_2$  and  $LiF-AlF_3-CaF_2$  (37) systems) has led to a good agreement between the experimental and calculated phase diagrams. Moreover, the model has been used to consider composition domains which would have been difficult to study experimentally (9, 37).

### 3.1 - The CIS theory

In the CIS theory, molten salts are assumed to be totally ionized and only anion-cation interactions are taken into account. The model is only suited to

reciprocal molten salt systems involving ions of the same electrical charge, like the  $A^+$ ,  $B^+$ ,  $C^-$ ,  $D^-$  system mentioned above.

The molar Gibbs free energy of the liquid defined relative to the elements A, B, C, D in their standard states can be expressed as a function of temperature, T, and ionic fraction,  $X_A$ ,  $X_B$ ,  $X_C$ ,  $X_D$ , according to the following equation :

$$\Delta G_m = G_m - X_A G_A^\circ - X_B G_B^\circ - X_C G_C^\circ - X_D G_D^\circ \quad [5]$$

which can be rewritten as :

$$\begin{aligned} \Delta G_m = & RT (X_A \ln X_A + X_B \ln X_B + X_C \ln X_C + X_D \ln X_D) \\ & + X_A X_C \Delta G_f^\circ (AC) + X_A X_D \Delta G_f^\circ (AD) + X_B X_C \Delta G_f^\circ (BC) + X_B X_D \Delta G_f^\circ (BD) \\ & + X_A \Delta G^E (AC-AD) + X_B \Delta G^E (BC-BD) + X_C \Delta G^E (AC-BC) + X_D \Delta G^E (AD-BD) \\ & - X_A X_B X_C X_D [\Delta G^\circ (3)]^2 / 2ZRT \end{aligned} \quad [5']$$

The first term of equation [5'] is the entropy of configuration related to the ideal mixing of the ions, the ionic fractions being defined by :

$$X_A = \frac{N_A}{N_A + N_B} = 1 - X_B \quad \text{for the cations} \quad [6]$$

$$X_C = \frac{N_C}{N_C + N_D} = 1 - X_D \quad \text{for the anions} \quad [6']$$

where  $N_A$ ,  $N_B$ ,  $N_C$  and  $N_D$  are the number of moles of ions  $A^+$ ,  $B^+$ ,  $C^-$  and  $D^-$ . The following terms of equation [5'] correspond to the excess Gibbs free energy related to the ion mixing. The contribution of the compounds AC, AD, BC and BD is taken into account through the standard Gibbs free energies of formation of their liquid phases,  $\Delta G_f^\circ$ , whereas that of the binary systems AC-AD; AD-BD; AC-BC and BC-BD is expressed on the basis of the excess Gibbs free energies of the binary mixture of the related salts  $\Delta G^E$ . Finally, the last term of equation [5'] takes into account the fact that ion mixing does not take place in a random manner since the

ions obey the double exchange relation [3].  $\Delta G^\circ(3)$  is the standard molar Gibbs free energy change of the metathetical reaction [3] and  $Z$  is an adjustable parameter.

### 3.2 - Extension of the CIS theory to the $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$ system

The CIS theory has been already empirically extended to reciprocal systems made of ions bearing different electrical charges (which is actually the case for the  $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$  or  $\text{K}^+$ ,  $\text{Al}^{3+}$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$  system) by M.L. Saboungi and M. Blander (9). In equation [5'], the ionic fractions  $X_i$  : (i) should be replaced by the so-called equivalent (ion) fractions  $Y_i$  (that will be defined later on) in the expression of the excess Gibbs free energy of mixing whereas (ii) they are kept in the ideal term. This procedure has been successfully applied by T. Förland to various binary systems (38).

Considering the ternary reciprocal system  $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$  regarded as consisting of the unsymmetrically charged  $\text{K}^+$ ,  $\text{Al}^{3+}$ ,  $\text{O}^{2-}$  and  $\text{F}^-$  ions with the double exchange relation [4], the Gibbs free energy of formation per equivalent of the liquid phase relative to the pure elements K, Al, O, F in their standard states can be expressed according to the following equation :

$$\begin{aligned} \Delta G_m = & RT (N_K \ln X_K + N_{Al} \ln X_{Al} + N_O \ln X_O + N_F \ln X_F) / N \\ & + Y_K Y_F \Delta G_f^\circ (\text{KF}) + Y_{Al} Y_F \Delta G_f^\circ (\text{AlF}_3) / 3 + Y_{Al} Y_O \Delta G_f^\circ (\text{Al}_2\text{O}_3) / 6 + Y_K Y_O \Delta G_f^\circ (\text{K}_2\text{O}) / 2 \\ & + Y_{Al} \Delta G^E (\text{AlF}_3\text{-Al}_2\text{O}_3) + Y_K \Delta G^E (\text{KF-K}_2\text{O}) \\ & + Y_O \Delta G^E (\text{K}_2\text{O-Al}_2\text{O}_3) + Y_F \Delta G^E (\text{KF-AlF}_3) \\ & - Y_K Y_{Al} Y_O Y_F [\Delta G^\circ(4)]^2 / 2ZRT \end{aligned} \quad [7]$$

where  $N_K$ ,  $N_{Al}$ ,  $N_O$  and  $N_F$  are the number of moles of  $\text{K}^+$ ,  $\text{Al}^{3+}$ ,  $\text{O}^{2-}$  and  $\text{F}^-$  ions (with  $N = 3N_{Al} + N_K = 2N_O + N_F$  to satisfy the condition of charge balance), the  $X_i$

and  $Y_i$  fractions being defined by :

$$X_{Al} = \frac{N_{Al}}{N_{Al} + N_K} = 1 - X_K \quad \text{and} \quad X_O = \frac{N_O}{N_O + N_F} = 1 - X_F$$

$$Y_{Al} = \frac{3N_{Al}}{3N_{Al} + N_K} = 1 - Y_K \quad \text{and} \quad Y_O = \frac{2N_O}{2N_O + N_F} = 1 - X_F$$

#### 4 - THERMODYNAMIC DATA AND PARAMETERS

In order to calculate the  $KF-AlF_3-Al_2O_3-K_2O$  phase diagram in the composition domain considered here (i.e. in the vicinity of the  $K_3AlF_6-Al_2O_3$  section), according to the procedure described above, the thermodynamic data for the compounds and related binary systems should be known. Some of them were available but others had to be either set in a coherent basis or even estimated.

##### 4.1 - Thermodynamic data of the compounds

The compounds  $KF$ ,  $AlF_3$ ,  $K_3AlF_6$  and  $KAlF_4$ , on one hand,  $\alpha-Al_2O_3$ ,  $\beta-Al_2O_3$  and  $KAlO_2$  (i.e.  $K_2O \cdot Al_2O_3$ ), on the other hand, were considered in the calculations. Regarding the uncertainty of the nature and composition of  $\beta$ -alumina (which is presented either as stoichiometric compounds  $K_2O \cdot 11Al_2O_3$  ( $\beta$ -phase) and  $K_2O \cdot 5Al_2O_3$  ( $\beta''$ -phase) or as a phase with an extended range of composition  $K_2O \cdot nAl_2O_3$  with  $5 < n < 10$ ), this phase has been treated, in the following, as a compound of formula  $K_2O \cdot 9Al_2O_3$  (39, 40).

The thermodynamic data for  $KF$ ,  $AlF_3$ ,  $K_3AlF_6$ ,  $K_2O$  and  $\alpha-Al_2O_3$  were taken from the last issue of the JANAF (41). However, both the enthalpy and entropy of melting of  $K_2O$  were not available ( $K_2O$  is not stable on heating under a pressure of one atmosphere). Therefore, those of the neighboring  $Na_2O$  compound, which were available, have been taken into account. R.P. Beyer et al. have measured the heat



capacity of  $\text{KAlO}_2$  at constant pressure up to 1400 K, their data have been used here (42). Furthermore, the enthalpy of formation and entropy at 298 K are those which have been estimated by T. B. Lindemer and T. M. Besmann (43).

For  $\beta$ -alumina and  $\text{KAlF}_4$ , no thermodynamic data were available from literature. Their enthalpies of formation and entropies at 298 K were estimated on the basis of  $\Delta G_f^\circ = A + BT$  equations from the related binary phase diagram. The heat capacities were calculated using the Neumann-Kopp rule.

## 4.2 - Binary systems

In the CIS theory, the excess Gibbs free energy of mixing of the binary mixture of the salts  $i$  and  $j$ , i.e. the  $\Delta G^E$  terms in equation [7], is written as :

$$\Delta G^E (i-j) = Y_i Y_j [ a + b (Y_i - Y_j) + c Y_i Y_j ]$$

The parameters  $a$ ,  $b$  and  $c$  were calculated after having set the  $\Delta G_f^\circ$ , the experimental data concerning the binary phase diagram  $i-j$  and the  $\Delta G^E$  in a coherent basis.

### (1) $\text{KF-K}_2\text{O}$ and $\text{AlF}_3\text{-Al}_2\text{O}_3$

These two binary phase diagrams are unknown. Since it was not possible, therefore, to depict accurately the behavior of their liquid phase, they were considered as obeying the law of ideal mixtures with the consequence that  $a = b = c = 0$  in the CIS theory. The  $\text{KF-K}_2\text{O}$  and  $\text{AlF}_3\text{-Al}_2\text{O}_3$  binary edges of the  $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$  phase diagram lie rather far from the  $\text{K}_3\text{AlF}_6\text{-Al}_2\text{O}_3$  section which is of interest here. Thus, it was thought that the above assumption may not have a strong effect on the main features of the liquidus in the vicinity of the  $\text{K}_3\text{AlF}_6\text{-Al}_2\text{O}_3$  section.

(2)  $KF-AlF_3$

The  $KF-AlF_3$  binary phase diagram has been studied experimentally by various authors (44-49). A compilation of the invariants of the diagram is given in table 2. It clearly appears that the data are in good agreement.

Only one study, that of B. Phillips et al., is based on experiments performed on  $AlF_3$ -rich samples heated in sealed tubes (48). However, the melting point of  $AlF_3$  which was given (i.e. 1263K) seems too low. Therefore, the JANAF data have been used to model the behavior of the liquid phase (41).

On the basis of the thermodynamic data calculated for  $KAlF_4$  i.e.  $\Delta H_f^\circ = -2132.82 \text{ kJ. mol}^{-1}$  and  $S^\circ = 125.1 \text{ J.mol}^{-1}.\text{K}^{-1}$  at 298 K and of the following expression for  $\Delta G^E(KF-AlF_3)$  (in  $\text{J.eq}^{-1}$ ):

$$Y_K Y_{Al} [-138100.82 + (39729.43 + 37.79T) (Y_K - Y_{Al}) + 149651.33 Y_K Y_{Al}]$$

the  $KF-AlF_3$  phase diagram has been computed. As shown in fig.7, the calculated phase diagram is coherent with the phase diagram drawn experimentally by B. Phillips et al. (with the discrepancy already mentioned for the  $AlF_3$ -rich compositions).

(3)  $K_2O.Al_2O_3-Al_2O_3$

Only the composition domain ranging from  $K_2O.Al_2O_3$  to pure alumina has been considered in the  $K_2O-Al_2O_3$  binary system. The corresponding phase diagram has been calculated (39) and drawn experimentally in the 1473-1973 K temperature range (40). The two diagrams, although they exhibit the same general features, are characterized by invariant transitions differing in temperature, as shown in table 3.

| Authors         | $T_f$ KF | $T_e X_e$  | $T_f K_3AlF_6$ | $T_e X_e$ | $T_p X_p$ | $T_f AlF_3$ |
|-----------------|----------|------------|----------------|-----------|-----------|-------------|
| Pushin et al.   | 1158     | 1110/0.075 | 1308           | 843/0.40  | -         | -           |
| Fedotiev et al. | 1153     | 1113/0.068 | 1298           | 843/0.45  | 853/0.475 | -           |
| Dergunov        | 1129     | 1093/0.07  | 1285           | -         | -         | -           |
| Barton et al.   | 1129     | -          | 1269           | 833/0.45  | 848/0.45  | -           |
| Phillips et al. | 1129     | 1113/0.07  | 1258           | 833/0.45  | 847/0.5   | 1263        |
| Jenssen         | 1131     | 1093/0.07  | 1273           | 833/0.45  | 853/0.5   | -           |
| Our calculation | 1131     | 1107/0.04  | 1258           | 839/0.455 | 847/0.49  | 2523        |

Table 2: Invariants of the KF-AlF<sub>3</sub> binary phase diagram

$X_e$ ,  $X_p$ : eutectic, peritectic compositions (mole fraction)

$T_f$ ,  $T_e$ ,  $T_p$ : fusion, eutectic, peritectic temperatures (K)

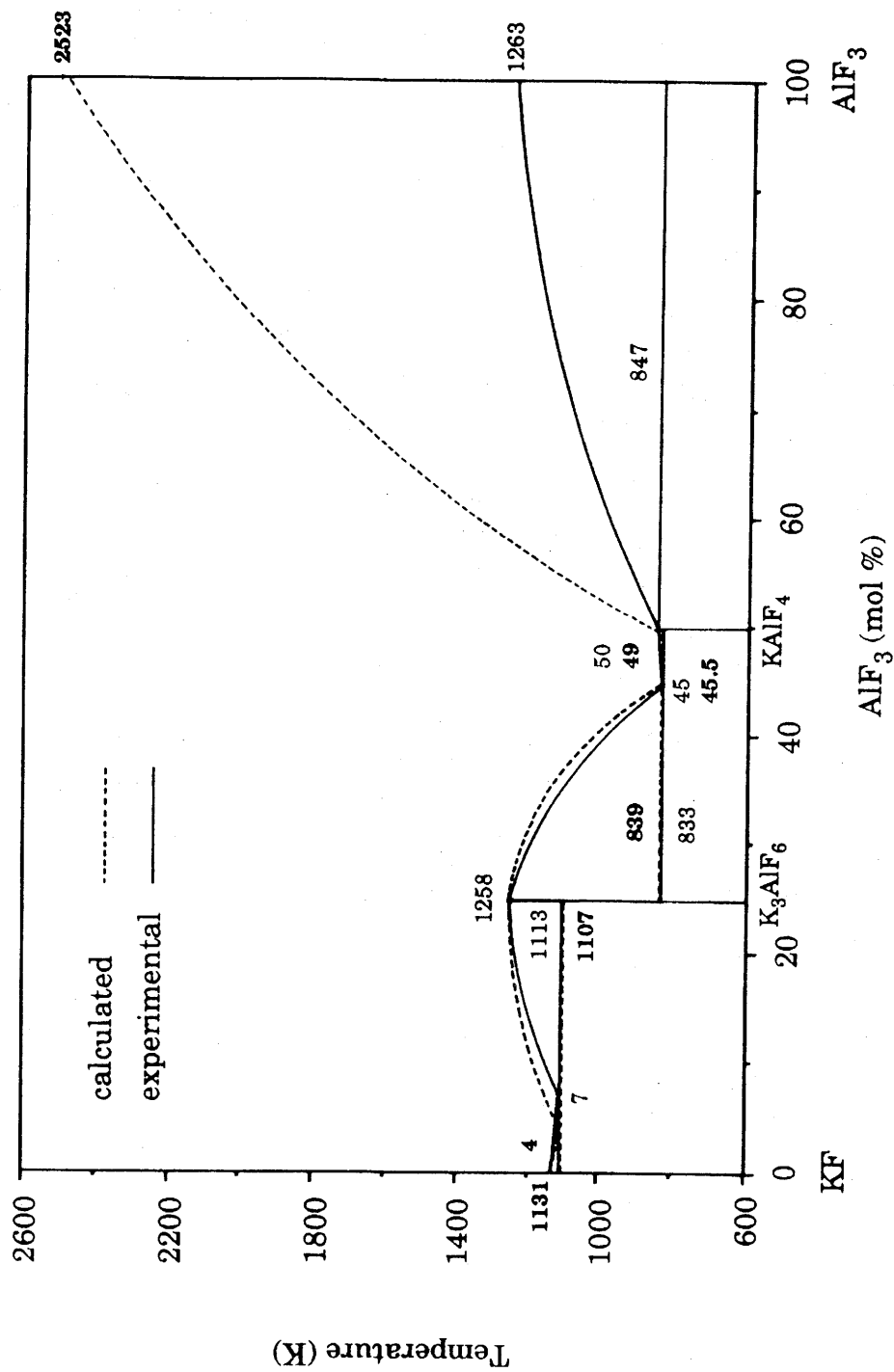


Figure 7: Calculated and experimental (23) phase diagrams of the KF-AlF<sub>3</sub> binary system

| Authors                                                              | $T_f$ KAlO <sub>2</sub> | $T_e/X_e$  | $T_p/X_p$  | $T_f$ Al <sub>2</sub> O <sub>3</sub> |
|----------------------------------------------------------------------|-------------------------|------------|------------|--------------------------------------|
| Eliezer et al.:<br>extended $\beta$ -phase<br>two $\beta$ -compounds | 1968                    | 1905/0.6   | 2150/0.83  | 2327                                 |
|                                                                      | 1968                    | 1843/0.65  | 2150/ -    | 2327                                 |
| Moya et al.                                                          | 2533                    | 1723/0.62  | 2150/ -    | 2327                                 |
| Our calculation                                                      | 1968                    | 1876/0.658 | 2150/0.847 | 2327                                 |

Table 3: Invariants of the K<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> binary phase diagram

$X_e, X_p$ : eutectic, peritectic compositions (mole fraction)  
 $T_f, T_e, T_p$ : fusion, eutectic, peritectic temperatures (K)

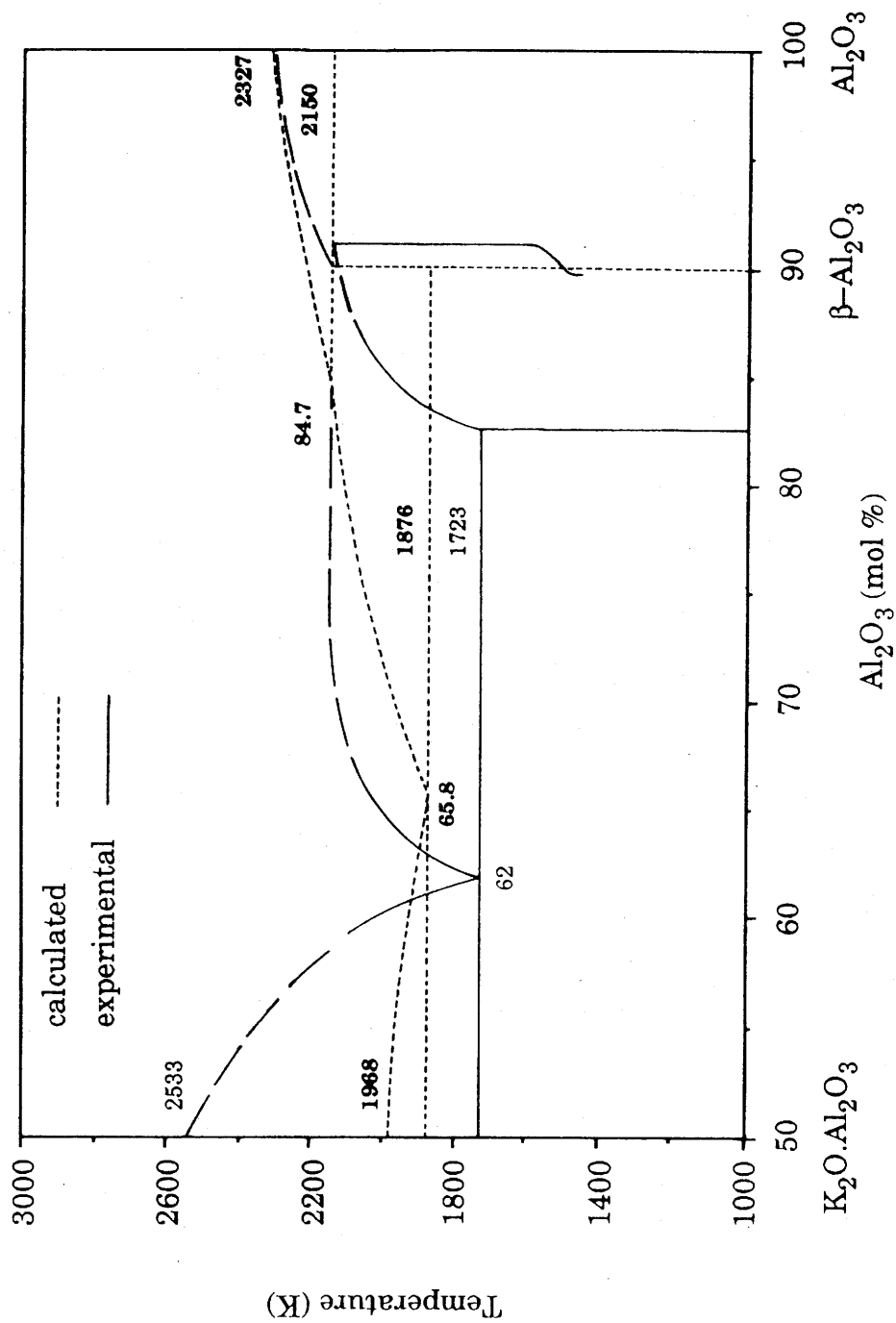


Figure 8: Calculated and experimental (40) phase diagrams of the  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  binary system

On the basis of the thermodynamic data retained for  $K_2O \cdot 9Al_2O_3$  at 298 K i.e.  $\Delta H_f^\circ = -15681.2 \text{ kJ mol}^{-1}$  and  $S^\circ = 593.8 \text{ J.mol}^{-1} \cdot K^{-1}$  and of the following equation used for  $\Delta G^E (K_2O-Al_2O_3)$  in the CIS theory :

$$Y_K Y_{Al} (-128957.14) \text{ in J.eq}^{-1}$$

there is an acceptable compromise between the calculated phase diagram and the diagram drawn experimentally by J.S. Moya et al.(40) (fig.8).

### 4.3 - The liquid phase in the ternary reciprocal $KF-AlF_3-Al_2O_3-K_2O$ system

The only adjustable parameter in [7] is Z. In the CIS theory, the value which is usually taken for Z is 6. However, M.L. Saboungi already mentioned that this value did not lead to a good agreement between calculated and experimental results when  $\Delta G/RT$  (in  $-\Delta G^2/2ZRT$  of the CIS theory) is large with respect to one and thus she suggested to consider Z has an adjustable parameter (9). In the present study,  $\Delta G/RT$  is of the order of 18, this high value justifies the fact that Z has been regarded as an adjustable parameter in our calculations.

To take into account the temperature invariant observed at 1132 K, a Z value of 12.5 has to be retained. It is worthy of note that the calculations were run for a constant pressure (i.e. 1 atm) whereas the experiments were performed at constant volume (i.e. in sealed tubes). It was assumed that the pressure actually reached in such experiments was not high enough to modify significantly the phase diagram, in the condensed state, drawn for  $p = 1 \text{ atm}$ .

## 5 - CALCULATED $KF-AlF_3-Al_2O_3-K_2O$ PHASE DIAGRAM

The phase diagram was calculated, for a composition range close to the  $K_3AlF_6-Al_2O_3$  section, by minimizing the total Gibbs free energy of the system, at a constant pressure of 1 atm and for different temperatures, the composition being

defined with the internal variables  $Y_{Al}$  and  $Y_O$  (with  $Y_K = 1 - Y_{Al}$  and  $Y_F = 1 - Y_O$  as mentioned above). The calculations were run with the software MELANGE 16 (10).

The nature and relative proportion of the phases present at equilibrium thus obtained were used to draw the phase diagram in a plane square where the coordinates are the equivalent fractions  $Y_{Al}$  and  $Y_O$  (fig.9). Due to its reciprocal character (based on equation [4]), the system has only three independent components and the pressure has been fixed (i.e. to 1 atm as said above). Therefore, according to the phase rule the number of degrees of freedom is  $v = 4 - \phi$  ( $\phi$  being the number of phases at equilibrium). Considering the liquidus of the phase diagram : (i) a surface ( $v = 2$ ) represents an equilibrium  $L = S$  (referred to as L+S) , (ii) the intersection of two surfaces, i.e. a line ( $v = 1$ ) represents a three phase equilibrium (referred to as  $L + S_1 + S_2$ ) and finally (iii) the intersection of two lines, i.e. a point ( $v = 0$ ) represents a four phase equilibrium (referred to as  $L + S_1 + S_2 + S_3$ ). The composition, temperature and solid phases at equilibrium corresponding to the various invariant points of fig 9 are listed in table 4.

As shown in fig.9, the part of the phase diagram which has been calculated is self-consistent and has some common features with that experimentally drawn by P.A. Foster for the related  $NaF-AlF_3-Al_2O_3-Na_2O$  system (fig.10) (50). (The outlines of a reciprocal system in equivalent and mole fractions respectively are the same (51)). The main difference lies in the fact that the  $Na_3AlF_6-\alpha-Al_2O_3$  section reported in the literature is generally considered as a quasi-binary section (11) whereas the  $K_3AlF_6-\alpha-Al_2O_3$  section calculated in the present study is not, as already suggested from the experimental data discussed above.

It is worthy of note that the hypothesis according to which the sodium cryolite-alumina system might not exhibit a simple binary eutectic transition but rather a reaction point (of peritectic-type) at the minimum of the two liquidus curves where the three solid phases  $\alpha-Al_2O_3$  ;  $\beta-Al_2O_3$  and  $Na_3AlF_6$  might be in



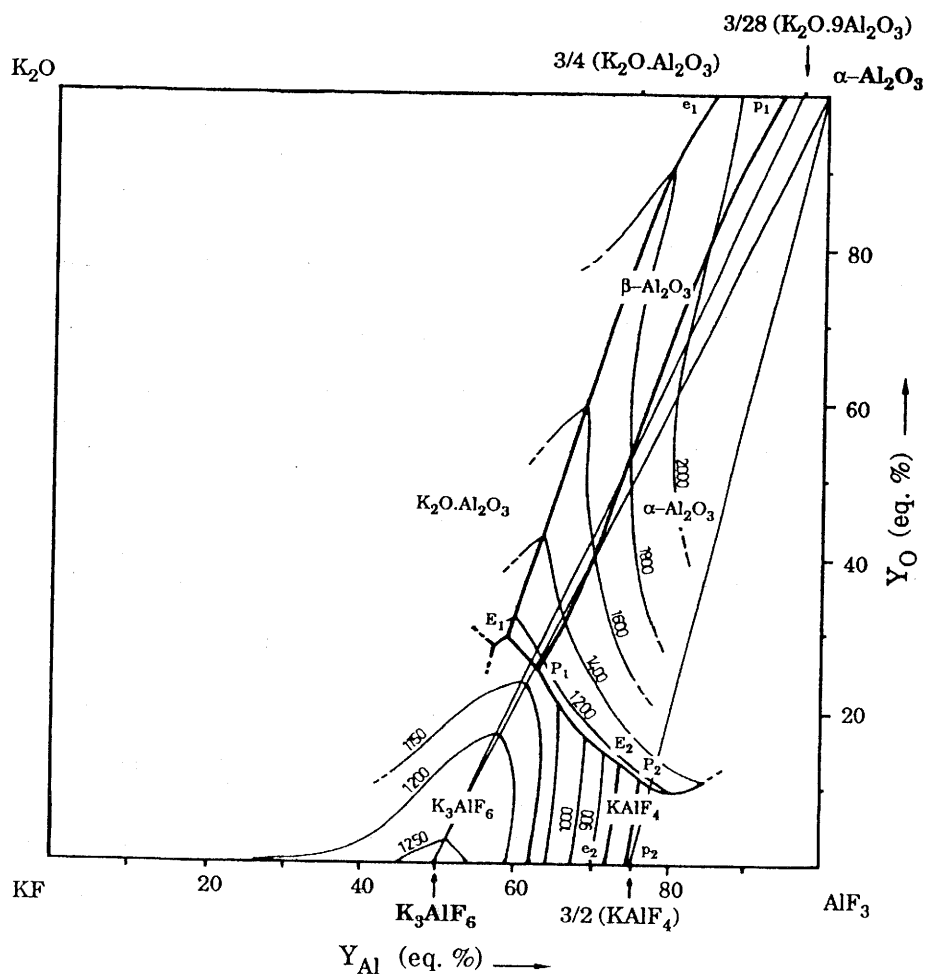


Figure 9:  
Phase diagram of the ternary  
reciprocal system  
 $\text{KF}-\text{AlF}_3-\text{Al}_2\text{O}_3-\text{K}_2\text{O}$   
calculated in the vicinity of  
the  $\text{K}_3\text{AlF}_6$ - $\alpha\text{-Al}_2\text{O}_3$  section

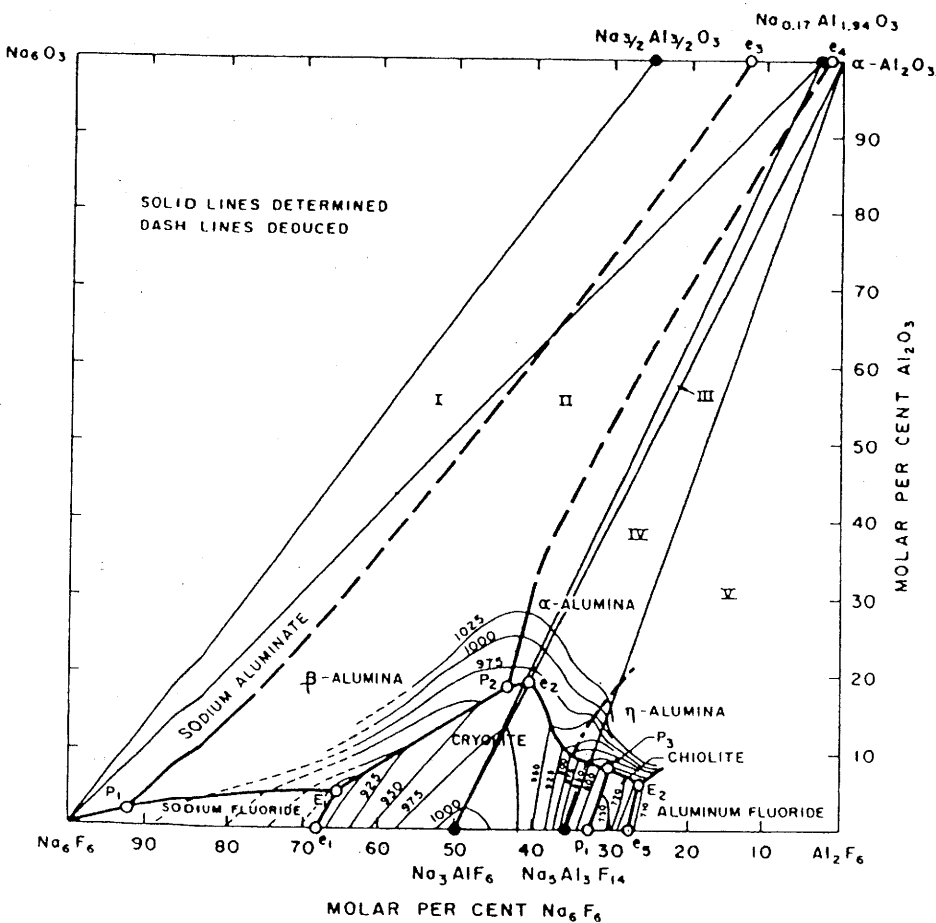


Figure 10:  
Phase diagram of the ternary  
reciprocal system  
 $\text{NaF}-\text{AlF}_3-\text{Al}_2\text{O}_3-\text{Na}_2\text{O}$  (50)

| Point | $Y_{Al}$<br>(eq.%) | $Y_O$ | T(K) | Solid phases                                    |
|-------|--------------------|-------|------|-------------------------------------------------|
| $e_1$ | 85.2               | 100   | 1876 | $KAlO_2$ , $\beta-Al_2O_3$                      |
| $P_1$ | 94.3               | 100   | 2150 | $\beta-Al_2O_3$ , $\alpha-Al_2O_3$              |
| $e_2$ | 71.5               | 0     | 839  | $K_3AlF_6$ , $KAlF_4$                           |
| $P_2$ | 74.2               | 0     | 847  | $KAlF_4$ , $AlF_3$                              |
| $E_1$ | 58.6               | 28.8  | 1110 | $KAlO_2$ , $K_3AlF_6$ , $\beta-Al_2O_3$         |
| $P_1$ | 62.7               | 25.0  | 1132 | $\beta-Al_2O_3$ , $K_3AlF_6$ , $\alpha-Al_2O_3$ |
| $E_2$ | 73.3               | 13.0  | 793  | $\alpha-Al_2O_3$ , $K_3AlF_6$ , $KAlF_4$        |
| $P_2$ | 75.8               | 10.7  | 816  | $\alpha-Al_2O_3$ , $KAlF_4$ , $AlF_3$           |

Table 4: The invariants compositions, temperatures and related equilibrium solid phases

equilibrium with the liquid, has been already discussed by P.A. Foster, on the basis of the study of A.A. Kostjukov and finally was not retained (52, 53).

## 6 - ON THE ISOPLETH SECTION $K_3AlF_6$ - $\alpha$ - $Al_2O_3$

The vertical section  $K_3AlF_6$ - $\alpha$ - $Al_2O_3$  which gives the phase relationships corresponding to the addition of  $\alpha$ -alumina to potassium cryolite has been derived from the calculated phase diagram (fig.9) and is shown in fig.11. Consider the compositions along the line joining A ( $K_3AlF_6$ ) and B( $\alpha$ - $Al_2O_3$ ) in fig.12 (fig.12 is a schematic representation of fig.9 to allow a more convenient definition of the points I, P<sub>1</sub>, K and J) whose liquidus temperatures are given by the crossing of AB with the isothermal lines. The minimum of the corresponding liquidus curve occurs at point I (i.e. at 11.6 wt %  $\alpha$ - $Al_2O_3$  and 1132 K) in fig.12. This minimum lies on the univariant line  $L+K_3AlF_6+\beta$ - $Al_2O_3$  and cannot be regarded as an eutectic point since the  $K_3AlF_6$ - $\alpha$ - $Al_2O_3$  section is not a simple binary system. The reason is that the composition of the primary phase formed from the melt between I and J (J lies at the crossing of the segment AB and the univariant line  $L + \alpha$ - $Al_2O_3 + \beta$ - $Al_2O_3$ , at 21.9 wt %  $\alpha$ - $Al_2O_3$  and 1640 K, fig.12), i.e.  $\beta$ -alumina, is not located in the AB section. The liquids whose compositions lie between the K-cryolite vertex A and the liquidus minimum I give rise to a  $K_3AlF_6$  primary precipitation whereas those whose compositions fall between J and the  $\alpha$ -alumina vertex B give rise to a precipitation of  $\alpha$ -alumina as a primary phase and  $\beta$ -alumina as a secondary phase (the  $\beta$ -alumina vertex C being out of the AB vertical section). These transformations on cooling continue until the liquid becomes saturated both with respect to  $K_3AlF_6$  and  $\alpha$ - $Al_2O_3$  at point K (intersection of AB and CP<sub>1</sub>, from the convex quadrilateral ACBP<sub>1</sub>; at 13.9 wt %  $\alpha$ -alumina and 1132 K), an invariant

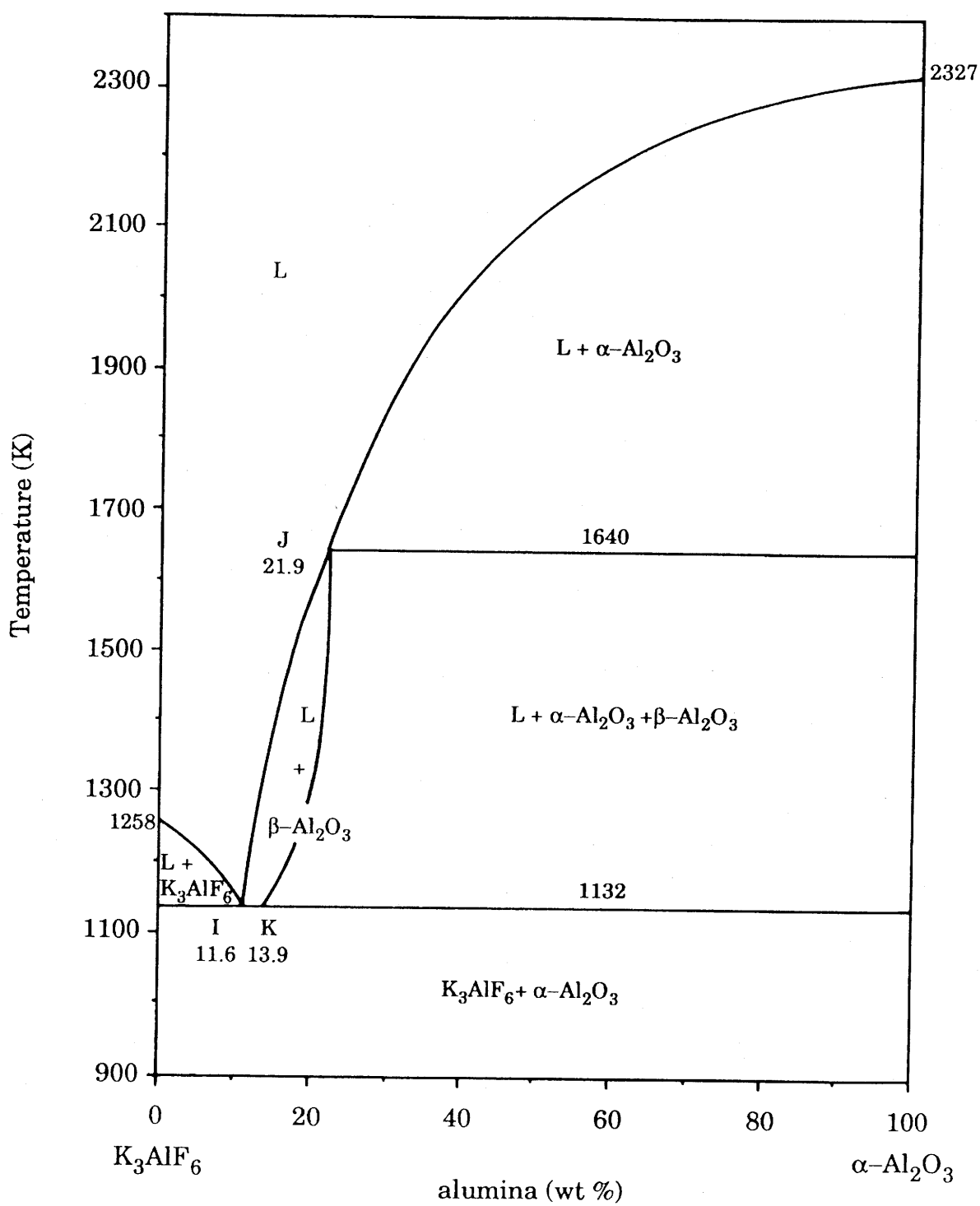


Figure 11: The  $\text{K}_3\text{AlF}_6$ - $\alpha\text{-Al}_2\text{O}_3$  isopleth section of the  
 $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$  phase diagram

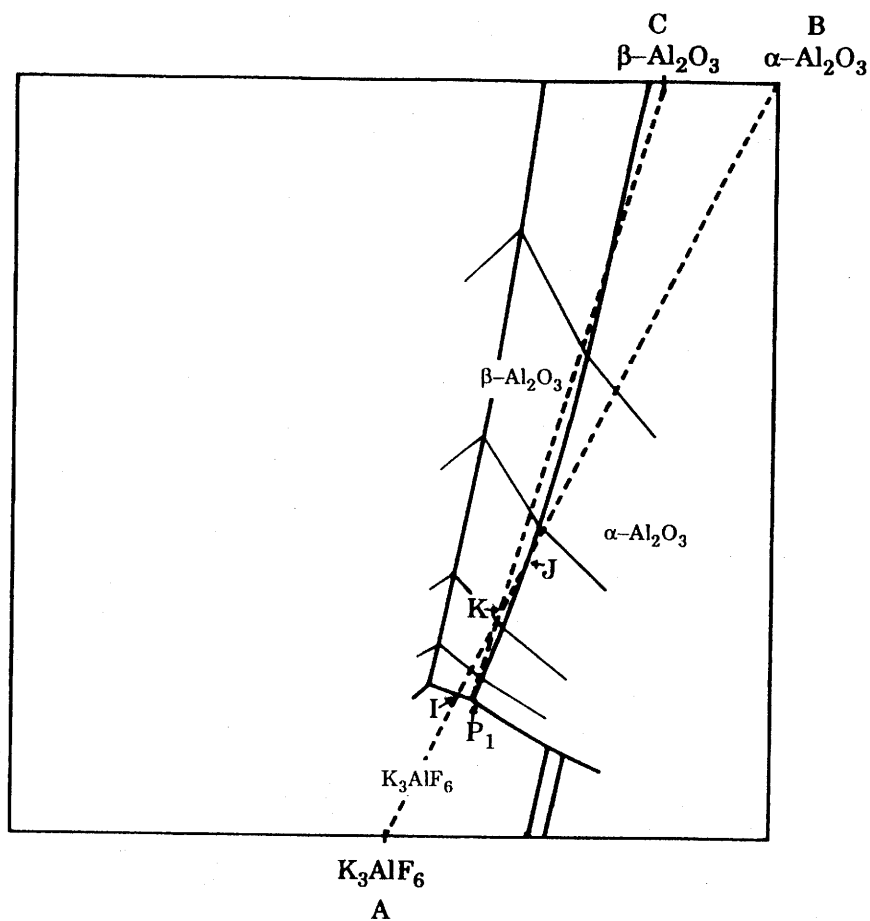


Figure 12: Schematic representation of the diagram of figure 9 to allow a more convenient definition of the points I,  $P_1$ , K and J

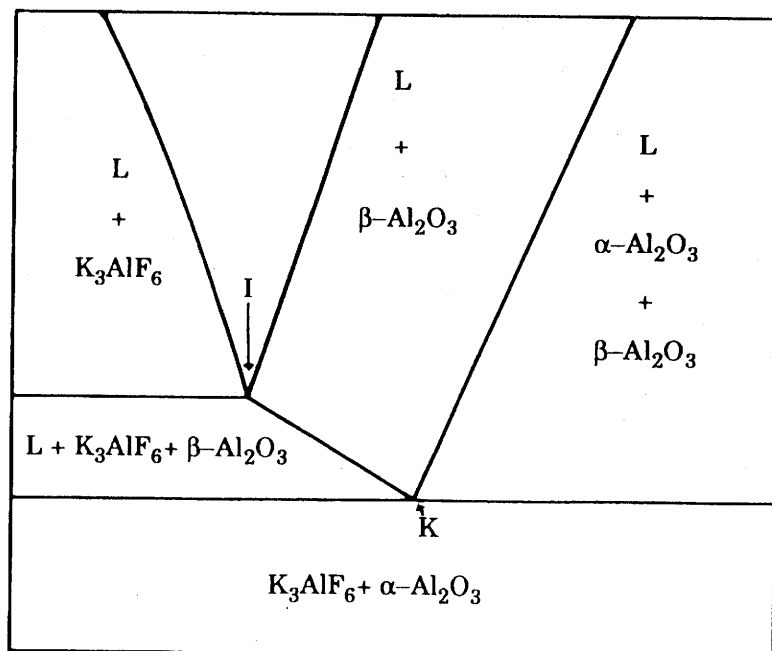
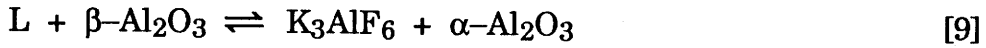


Figure 13: Phase relationship near the minimum of the liquidus in the vertical section  $K_3AlF_6$ - $\alpha-Al_2O_3$  (schematic)

point corresponding to the peritectic-type following transition :



The secondary crystallization of  $\beta$ -alumina for compositions below the minimum of the liquidus I and of  $\text{K}_3\text{AlF}_6$  for compositions between those of points I and K, as shown from fig.12 and 13, could not be evidenced from the calculations due to the fact that  $T_K$  and  $T_I$  were unresolved experimentally (the temperature invariant transition introduced in the calculations was 1132 K).

Thus, the main results of the experimental study can be justified, at least qualitatively, on the basis of fig.11. It appears from the above discussion that the first peak of complex shape observed on the DTA curves on heating (fig.4), for alumina concentrations less than 21 wt %, corresponds to the superposition of transition [9] and of the following transition :



and to the transition [10] only for alumina-rich compositions, whereas the second peak is associated to the end of melting (i.e. to the crossing of the liquidus surface). Therefore, the use of the Tammann drawing which has been made in fig.5 could be, at least formally, questioned.

Futhermore, on the basis of fig.11, it is not surprising that the liquidus could not be observed by DTA for the alumina-rich compositions, as already mentioned, since the temperature of the end of melting raises very rapidly above the  $T_I$ - $T_K$  horizontal line, as soon as the alumina concentration is higher than those corresponding to points I, K (the liquidus temperature being well above the limit of the DTA equipment which has been used).

There is an apparent discrepancy between the calculations and the experimental results for the nature of the solids below the 1132 K invariant

transition. According to the calculations a mixture of  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\text{K}_3\text{AlF}_6$  should be present whereas  $\text{K}_3\text{AlF}_6$ ,  $\beta$ - $\text{Al}_2\text{O}_3$  and  $\text{KAlF}_4$  have been identified by X-ray and IR analyses for alumina concentrations ranging from 17.9 to 30.0 wt %. From the thermodynamic data which have been selected, it appears that although a mixture of  $\text{K}_3\text{AlF}_6$ ,  $\beta$ - $\text{Al}_2\text{O}_3$ ,  $\text{KAlF}_4$  is less stable than a mixture of  $\text{K}_3\text{AlF}_6$ ,  $\alpha$ - $\text{Al}_2\text{O}_3$  of the same composition, the difference in their total Gibbs free energies is very small. This apparent discrepancy could be due to : (i) an insufficient accuracy in the calculations (e.g. related to the thermodynamic data which have been estimated or the assumptions which have been made) and/or (ii) the fact that equilibrium state may not have been reached in the DTA experiments. Thus, a new DTA analysis was performed on a 30.1 alumina wt %  $\text{K}_3\text{AlF}_6$ - $\alpha$ - $\text{Al}_2\text{O}_3$  sample. On cooling, the sample was annealed for 48 hours at 1090 K (and even for 240 hours in a further experiment) and then analyzed by X-ray diffraction and IR spectrometry with the following main results :

(i)  $\alpha$ - $\text{Al}_2\text{O}_3$  was indeed identified from the X-ray diffraction patterns in addition to  $\beta$ - $\text{Al}_2\text{O}_3$ ,  $\text{KAlF}_4$  and  $\text{K}_3\text{AlF}_6$  whereas the number and relative intensities of the diffraction lines of  $\beta$ - $\text{Al}_2\text{O}_3$  and  $\text{KAlF}_4$  were found to have significantly decreased for the sample annealed for 240 hours with respect to those of the sample annealed for only 48 hours.

(ii) similarly the intensities of the main IR absorption lines attributed to  $\beta$ - $\text{Al}_2\text{O}_3$  were observed to have decreased as a function of the annealing time (fig.14).

Therefore, these complementary experimental data suggest that there may exist a transition between the metastable  $\text{K}_3\text{AlF}_6$ - $\text{KAlF}_4$ - $\beta$ - $\text{Al}_2\text{O}_3$  system commonly observed after cooling at room temperature and the stable  $\text{K}_3\text{AlF}_6$ - $\alpha$ - $\text{Al}_2\text{O}_3$  system, characterized by slow kinetics. The slow rate of transition could be the result of : (i) the fact that the transition takes place in the solid state and (ii) the small difference in energy between the two states which has been evidenced from the thermodynamic calculations.

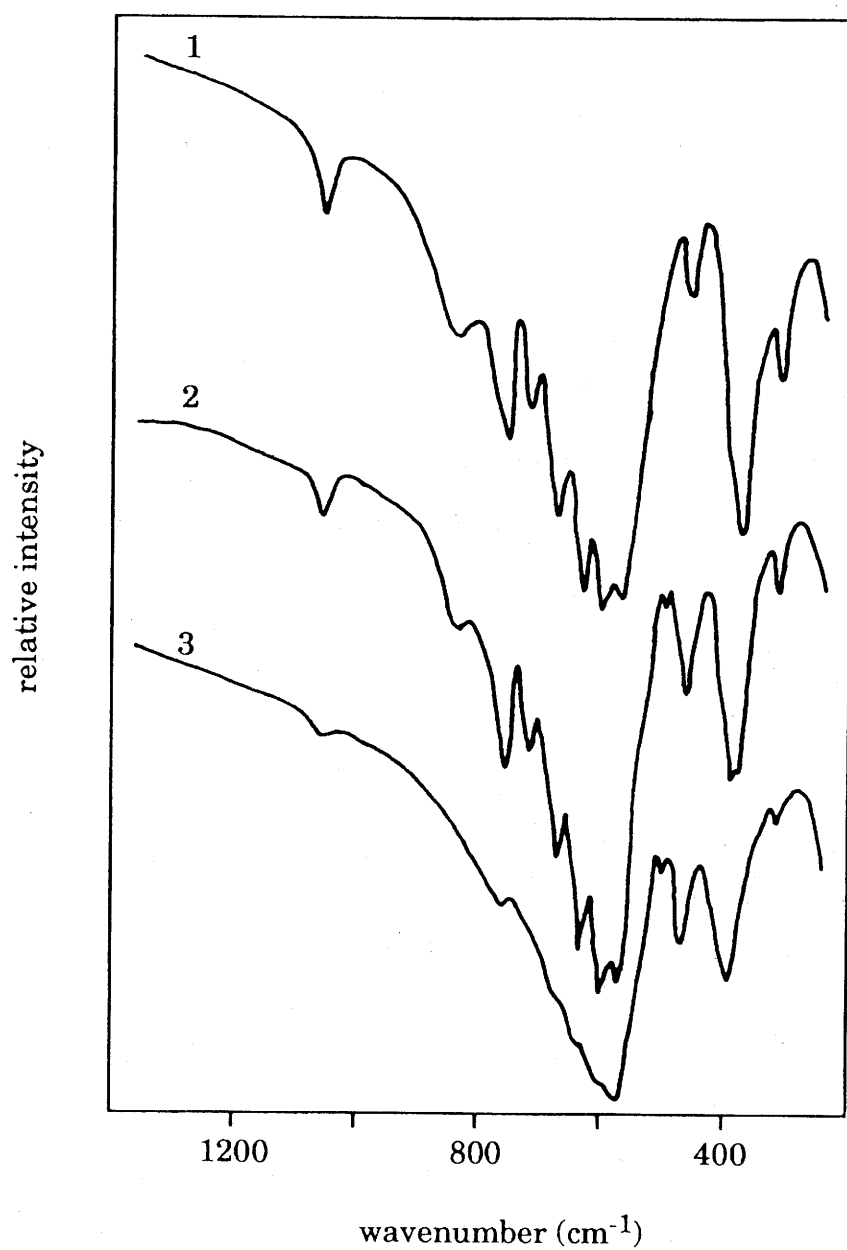


Figure 14 : I.R. spectra of the 30 wt %  $\text{Al}_2\text{O}_3$  samples

1-DTA sample

2-after annealing 48 hours

3-after annealing 240 hours



## 7 - CONCLUSION

The aim of this study was to draw, at least partly, the complex  $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$  phase diagram, from a minimum of experimental data, utilizing an approach based on thermodynamic calculations and the CIS theory for the liquid phase.

The main features of the experimental study have been explained, at least qualitatively, from the calculated phase diagram. The main discrepancies, particularly that concerning the invariant point compositions could be due to : (i) the thermodynamic data which have been selected (some of them had to be estimated) and (ii) the fact that only two of the four edge binary systems were known.

The use of the  $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$  phase diagram, calculated in the present study, for the understanding of the mechanisms of the enhancement of the wetting of SiC(or C) based ceramics by liquid aluminium alloys, will be presented in a detailed manner elsewhere (4).

## ACKNOWLEDGEMENTS

The authors are indebted to professor R. Cohen-Adad for his advices concerning the interpretation of some of the features of the complex  $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$  phase diagram, to J.J. Videau for the IR characterization of the materials and to J.P. Chaminade for his technical assistance.

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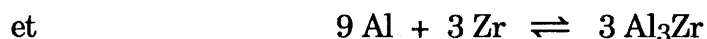
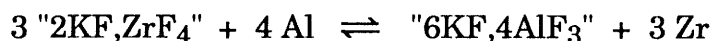
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## CHAPITRE II

## INTRODUCTION AU CHAPITRE II

Afin de mettre en évidence les phénomènes physico-chimiques qui sont impliqués dans le procédé au  $K_2ZrF_6$ , une double analyse a été effectuée. D'une part, l'amélioration du mouillage des préformes céramiques par l'aluminium en présence du fluorure  $K_2ZrF_6$  est interprétée grâce à des considérations thermodynamiques. D'autre part, l'influence des paramètres physiques associés au procédé sur l'aptitude à l'imprégnation de préformes céramiques poreuses est étudiée sur la base d'une approche numérique.

Le calcul des variations d'énergie libre de Gibbs et d'enthalpie des deux réactions principales associées au procédé au  $K_2ZrF_6$ , i.e. :



montre qu'elles sont effectivement favorisées d'un point de vue thermodynamique et qu'elles sont **très exothermiques** (700°C). **L'élévation locale de température** causée par cette source de chaleur a pu être estimée grâce à une approche numérique basée sur la modélisation de l'imprégnation de préformes poreuses appliquée au cas des renforts du type 2D-SiC(Nicalon)/SiC(CVI) imprégnés avec succès par J.P. Rocher et al. La température au sein d'un tel renfort, prétraité par le fluorure, préchauffé à 650°C et sur lequel l'aluminium liquide a été versé, pourrait atteindre environ 800°C. A cette température, l'analyse de la section verticale "6KF,4AlF<sub>3</sub>"-Al<sub>2</sub>O<sub>3</sub>, extraite du diagramme de phases du système ternaire réciproque KF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O présenté au chapitre I, montre que **le mélange de quelques % de Al<sub>2</sub>O<sub>3</sub> (mol) avec "6KF,4AlF<sub>3</sub>" forme une phase liquide homogène très fluide**. L'alumine serait donc dissoute et la phase liquide formée, en s'éloignant de

l'interface Al/SiC vers la surface du métal liquide, rendrait possible le contact réel entre le métal et la céramique vers 800°C. Dans ces conditions, l'aluminium mouille le carbure de silicium.

Grâce au modèle numérique cité précédemment et développé par J. M. Quenisset et al. dans le cas du forgeage liquide appliqué à des préformes unidirectionnelles imprégnées parallèlement ou perpendiculairement à la direction des fibres, l'influence de l'**exothermicité** des réactions chimiques sur la profondeur maximale qu'il est possible d'imprégner, de même que l'influence de l'**abaissement de l'angle de contact** sur les pressions nécessaires à appliquer à l'entrée des préformes pour imprégner jusqu'à la profondeur maximale sont discutées.

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**THE  $K_2ZrF_6$  WETTING PROCESS.  
EFFECT OF SURFACE CHEMISTRY ON THE ABILITY  
OF A SiC-FIBER PREFORM TO BE IMPREGNATED BY ALUMINUM**

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**ABSTRACT**

*SiC-ceramic materials, either as flat substrates or porous fiber preforms are spontaneously wetted by aluminum at 700-800°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 dislocation 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*

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*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 modelled 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.*

**Key-words**     **WETTING, METAL MATRIX COMPOSITE, SILICON CARBIDE, FIBER PREFORM, ALUMINUM,  $K_2ZrF_6$ .**

## 1 - INTRODUCTION

The elaboration of aluminum matrix composites (AMCs) according to processing techniques deriving from those already used in light alloy casting is made difficult by two main problems : (i) 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 (ii) these fibers react with aluminum above about 500°C to form a layer of  $\text{Al}_4\text{C}_3$  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 : (i) 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 (ii) 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 ( $\text{NiAl}_3$ ) or carbides embrittle the matrix. 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  $\mu\text{m}$ ) 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 the

surface treatment processes are usually limited to the preparation of semi-products (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 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 in the pore network of the preform, the pressure compensating the absence of wetting and capillary rise of the metal. Furthermore, since pressure is maintained during cooling, it contributes to close 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 equipments (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<sub>2</sub>ZrF<sub>6</sub> 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 contribution is to discuss 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).

## 2 - ORIGIN OF THE WETTING ENHANCEMENT

### 2.1 - 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). Their main results will be briefly recalled and compared to those reported by other authors, for the purpose of discussion.

When a **preform made of SiC-based fibers\*** is first treated with an aqueous  $K_2ZrF_6$  solution at about 80°C, in order to obtain a deposit of a few mg 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 : (i) the preform rapidly turns red due to an evolution of heat and (ii) simultaneously, the liquid metal climbs by capillary effect in 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 plan substrates of graphite coated by CVD with a

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\* Nicalon fibers from Nippon carbon, Japan.

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 have been submitted or not to the  $K_2ZrF_6$  surface treatment. The variations of the contact angle  $\theta$  as a function of both temperature and time are shown in figures 1 and 2. Data from other authors taken from 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  $\theta$  at the processing temperatures of AMCs, i.e. 700-800°C, remains very high ( $\theta = 160^\circ$ ), a feature which is typical of a non-wetting behavior. It is only by raising temperature at about 900-950°C that the transition non-wetting/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 aluminum melts. Moreover, lower  $\theta$  values are observed when the amount of  $K_2ZrF_6$  deposited on the substrate is increased ( $\theta = 73^\circ$  and  $50^\circ$  when the amount of  $K_2ZrF_6$  is 9 and 12 mg.cm<sup>-2</sup>, 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  $\theta$  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 min of contact) with SiC-single crystal/pure aluminum couples by : (i) Köhler, above 1000°C and for a residual pressure of  $2-8 \cdot 10^{-4}$  Pa and (ii) Laurent, beyond 800°C and for a residual pressure of  $10^{-4} - 5 \cdot 10^{-5}$  Pa (11, 12).

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

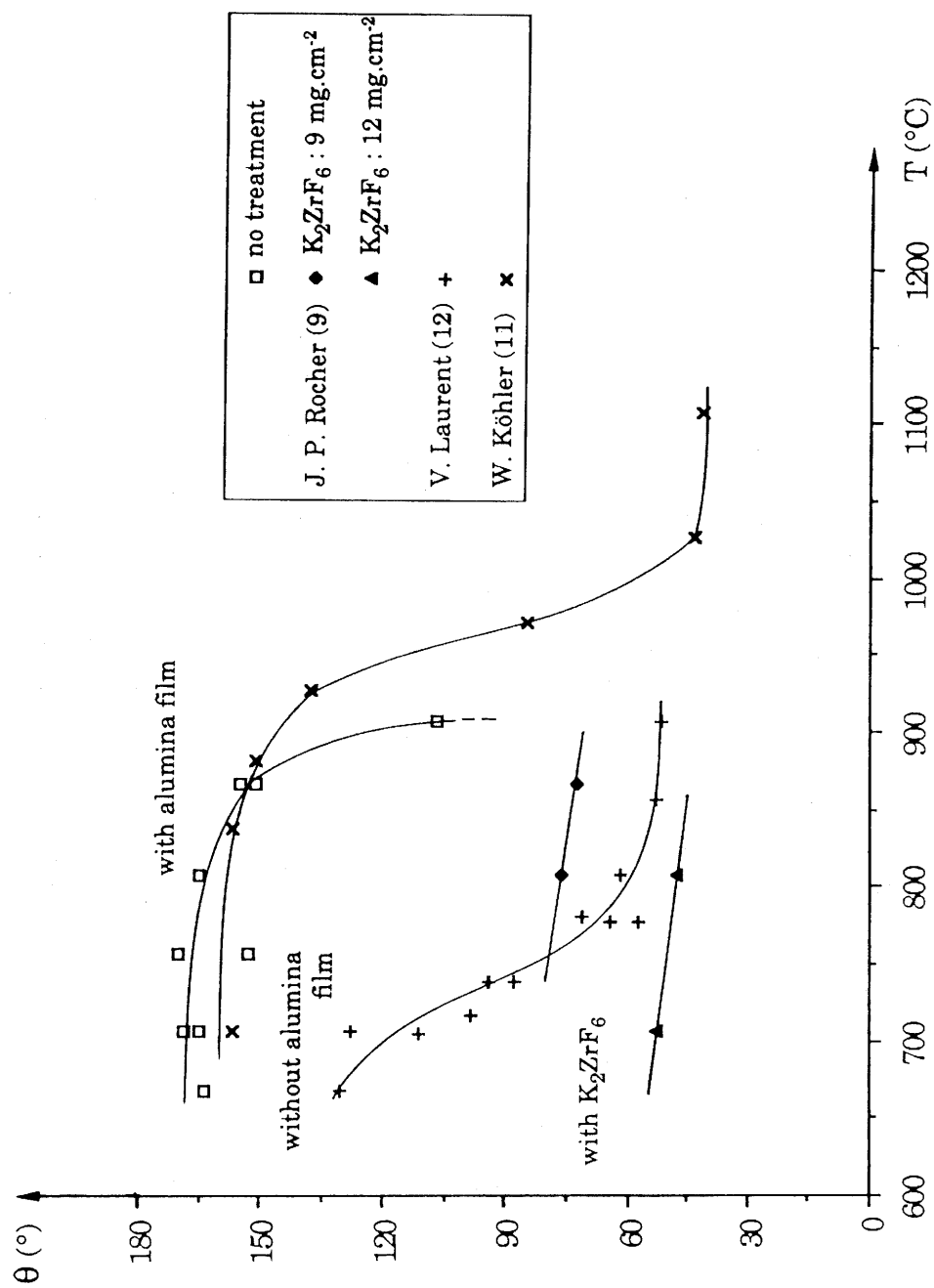


Figure 1 : Variations of the SiC/Al contact angle ( $\theta$ ) as a function of temperature ( $T$ ), from sessile drop experiments

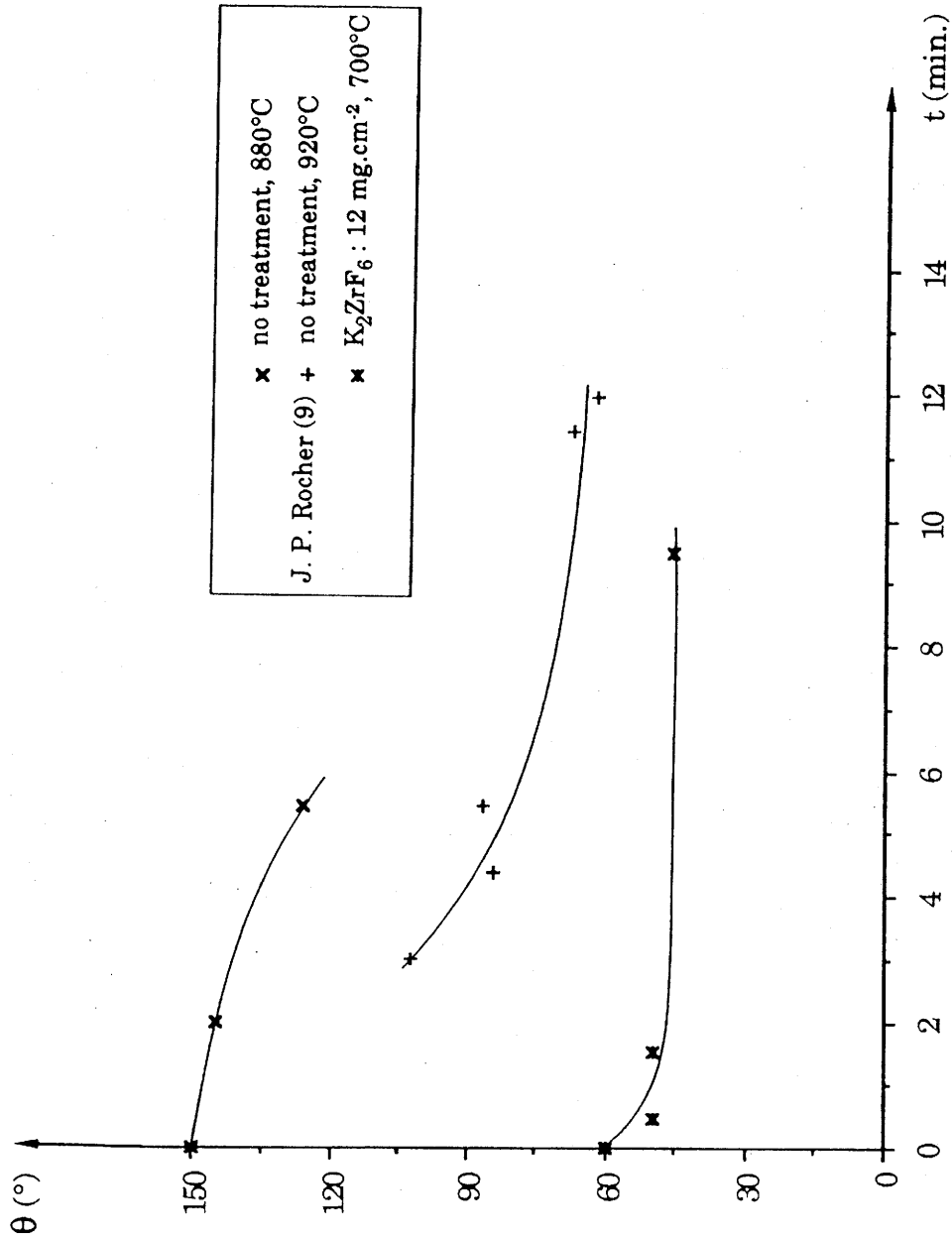
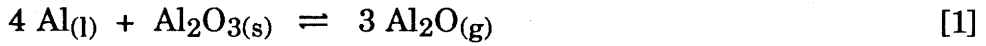


Figure 2 : Variations of the SiC/Al contact angle ( $\theta$ ) as a function of time (t), from sessile drop experiments

## 2.2 - Mechanisms

### 2.2.1 - Sessile drop experiment without $K_2ZrF_6$ treatment

Laurent et al. have shown that under particularly clean sessile drop experiment conditions (i.e.  $P_T \leq 5 \cdot 10^{-5}$  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 (13) :



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  $\text{Al}_4\text{C}_3$  :



and whose kinetics obey an exponential law with respect to temperature.

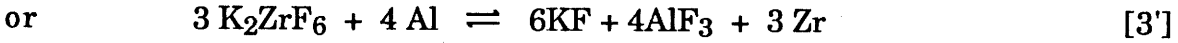
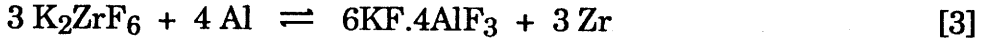
As a matter of fact, the sessile drop experiment conditions used by both Rocher (9) and Köhler (11), i.e. a vacuum corresponding to a higher residual total pressure (one order of magnitude) and oxygen partial pressure, do not modify the general shape of the  $\theta = f(T)$  curve, as shown in figure 1. However, for isothermal contacts of same durations : (i) the deoxidation process is shifted towards the high temperatures (by about 200°C) and (ii) 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.



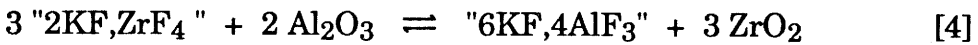
## 2.2.2 - Sessile drop experiments and lab-scale preform impregnation with $K_2ZrF_6$ treatment

### 2.2.2.1 - Dislocation of the alumina film

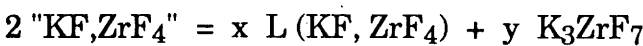
Reaction mechanisms related to the interaction between  $K_2ZrF_6$  and liquid aluminum, have been already suggested by Lundin (14) or Bushe and Semenov (15) to take into account the wetting enhancement phenomena observed in their processes used to fabricate aluminum-steel bimetallic materials. They proposed the following **overall** equations :



In the present process, when either (i) 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 (ii) 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 equation [3] as :



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, as shown in figure 3 (16). 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  $K_3ZrF_7$  :



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  $x + y = 1$ . In the following, this mixture resulting from the

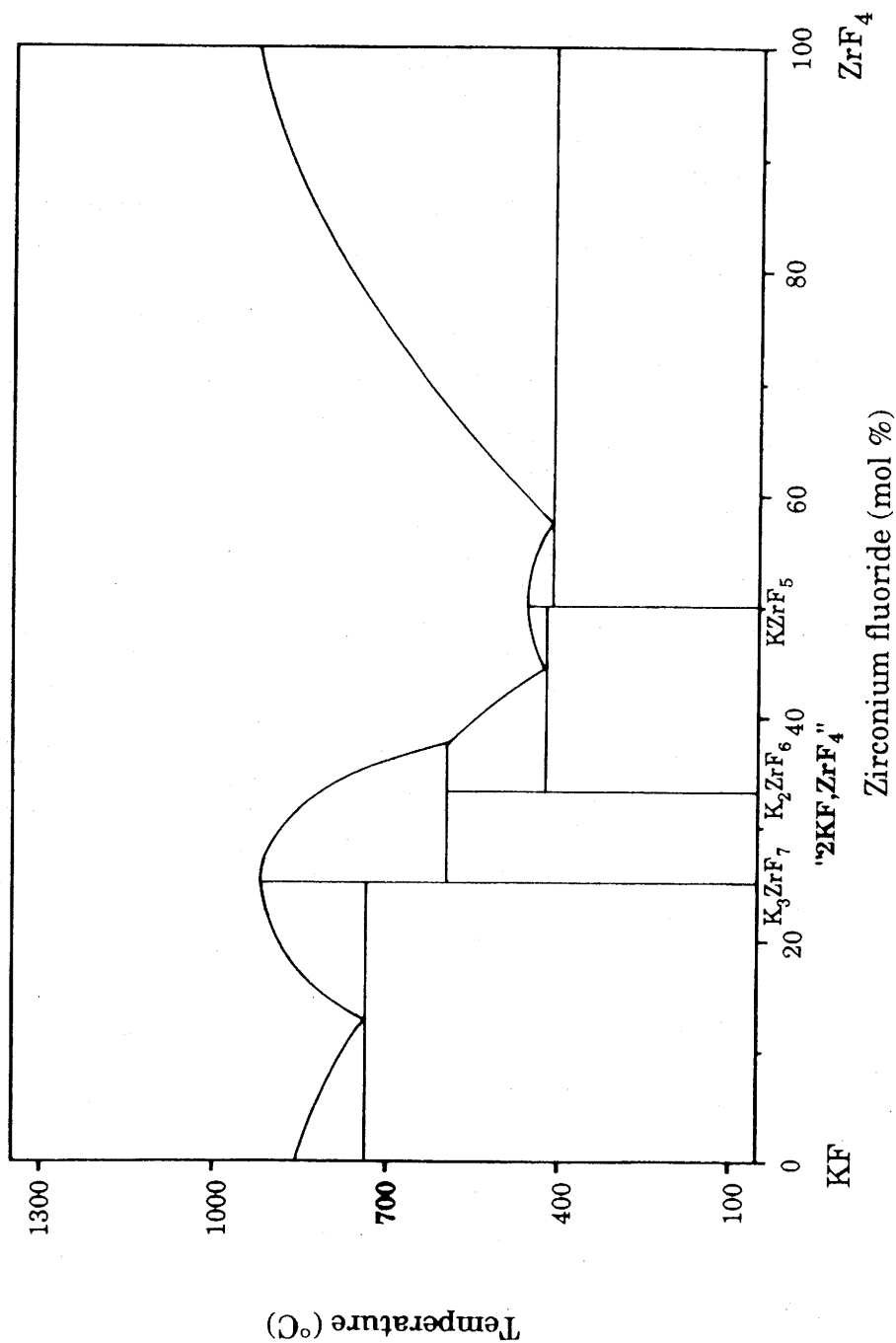
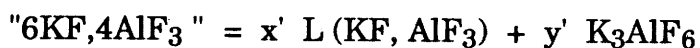


Figure 3: The calculated KF-ZrF<sub>4</sub> binary phase diagram (16)

decomposition of  $K_2ZrF_6$  will be referred to as " $2KF, ZrF_4$ ". In a similar manner, " $6KF, 4AlF_3$ " will be used for the mixture of liquid phase and  $K_3AlF_6$  corresponding to that specific composition (see equations [3] and [4]) at the same temperature in the  $KF-AlF_3$  phase diagram, as shown in figure 4 (10) :

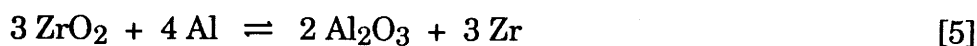


where  $L(KF, AlF_3)$  is the liquid in equilibrium with  $K_3AlF_6$  at  $700^\circ C$  and  $x' + y' = 1$ .

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

In order to verify this conclusion, a  $3 K_2ZrF_6 - 2 Al_2O_3$  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 equation [4] since " $6KF, 4AlF_3$ " gives a  $K_3AlF_6 + 3 KAlF_4$  mixture after cooling at room temperature, as shown in figure 4.

Conversely, zirconia formed according to equation [4] could react immediately with aluminum at  $700^\circ C$  according to the following equation :



since the variation of the Gibbs free energy corresponding to equation [5],  $\Delta G^\circ[5] = -1.8 \text{ kJ.mol}^{-1}$ , 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 **dislocated** at  $700-800^\circ C$

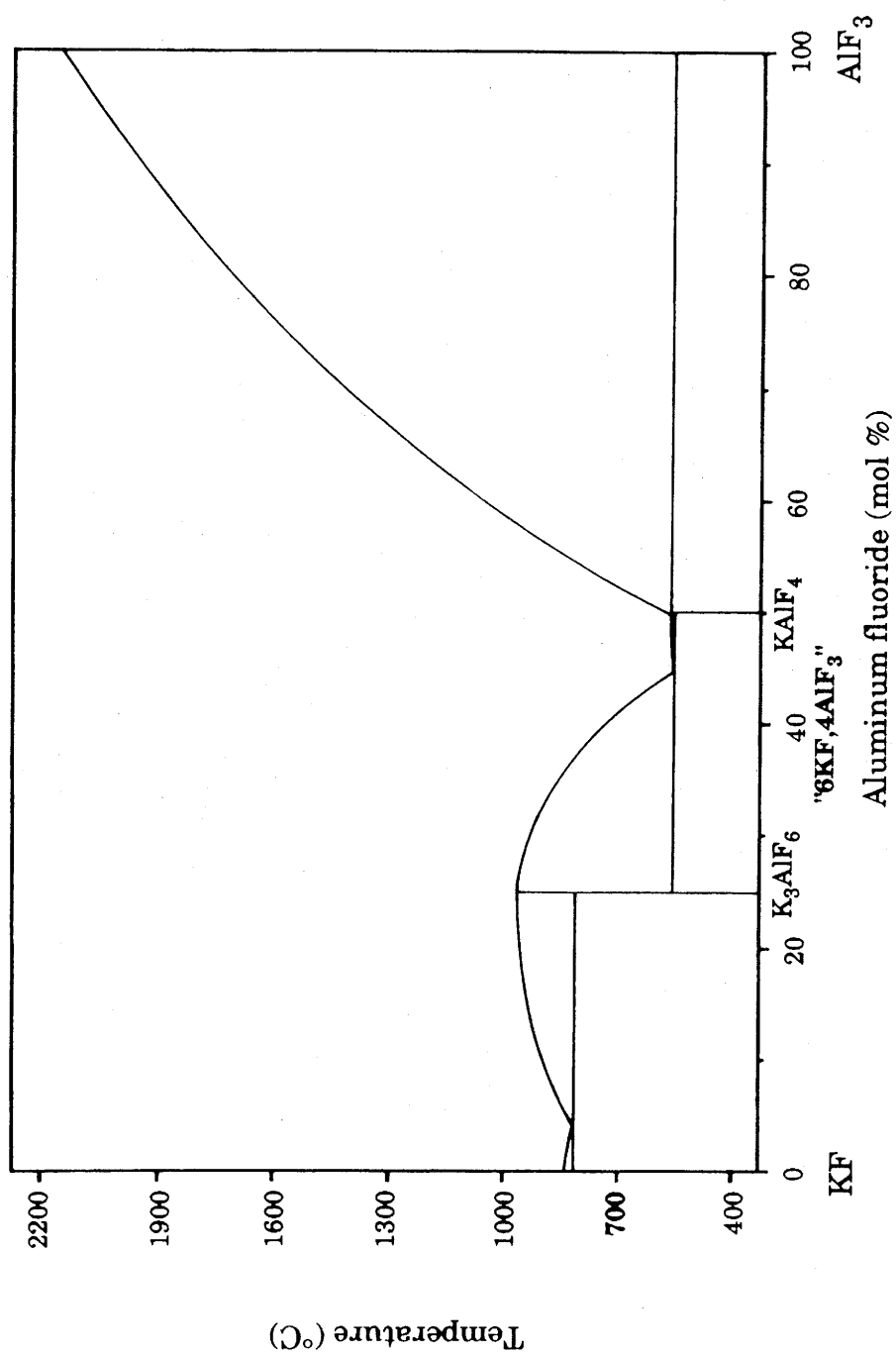
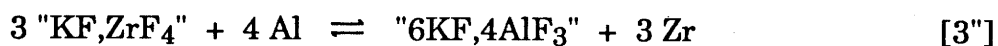


Figure 4: The calculated KF-AlF<sub>3</sub> binary phase diagram (10)

as the result of the chemical reactions corresponding to equations [4] and [5], allowing thus the liquid metal to come in contact with the  $K_2ZrF_6$  deposit.

#### ***2.2.2.2 - Dissolution of the alumina film***

In a second step, the alumina film is **totally dissolved** by the "6KF,4AlF<sub>3</sub>" mixture formed as a result of the addition of equations [4] and [5], i.e. the following overall equation corresponding to another writting of equations [3] and [3'] taking into account the physical states at 700°C of the various species which are involved :



This statement is based on the results of a thermodynamic study of the reciprocal ternary system KF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O and related binary systems, which have been published in details elsewhere (10). From these results, the vertical section "6KF,4AlF<sub>3</sub>"-Al<sub>2</sub>O<sub>3</sub> has been calculated and is shown in figure 5. As a matter of fact, it appears from figure 5 that for alumina concentrations corresponding to our experiments, i.e. about **a few mol. Al<sub>2</sub>O<sub>3</sub> %**, 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<sub>2</sub>ZrF<sub>6</sub> coating of a few mg.cm<sup>-2</sup>).

#### ***2.2.2.3 - Local temperature rise***

In a last step, zirconium formed according to equation [3''] can further react with aluminum which is in excess to lead to the formation of **intermetallic compounds**, according to the following equation :



Reactions [3''] and [6] which might take place simultaneously are very exothermic since  $\Delta H[3''] = - 306.4 \text{ kJ.mol}^{-1}$  and  $\Delta H[6] = - 487.2 \text{ kJ.mol}^{-1}$  respectively. This heat

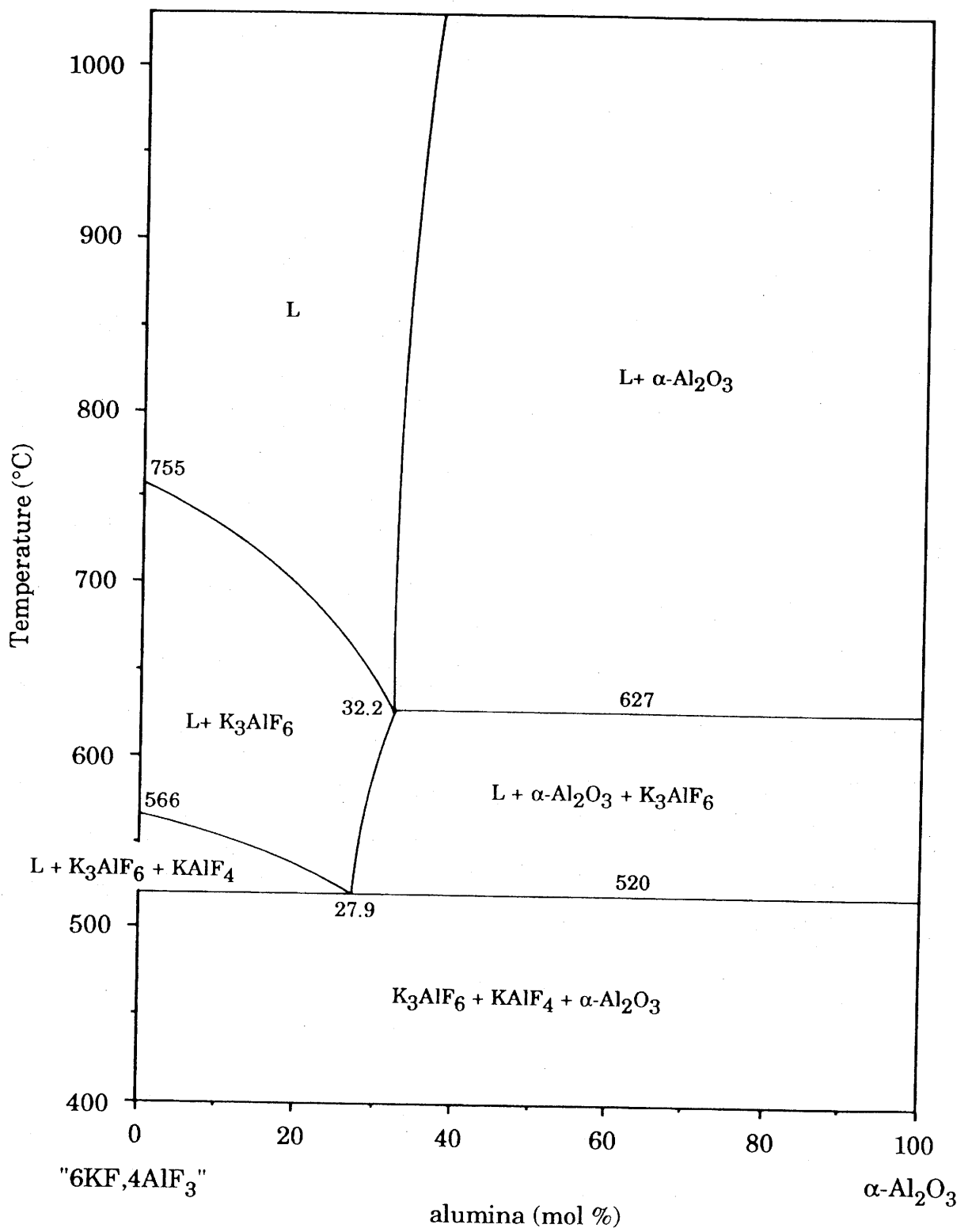


Figure 5 : The vertical section "6KF, 4AlF<sub>3</sub>" - α-Al<sub>2</sub>O<sub>3</sub> from the  
KF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O ternary reciprocal system (10)

evolution yields a **local temperature rise** either at the fiber/matrix or liquid aluminum drop/substrate interfaces which is thought to be particularly significant for preforms due to (i) the high inner pore surface and (ii) the important amount of  $K_2ZrF_6$ . In section 3, a model will be presented allowing the calculation of temperature in a porous fiber preform during an impregnation experiment according to the  $K_2ZrF_6$ -process, when exothermic reactions (such as those already mentioned) take place. It will be shown that a temperature increase as high as  $150^\circ\text{C}$  may occur thus justifying the experimental observations reported in section 2.1.

### 2.3 - Discussion

It clearly appears from figure 5 that an excess of fluoride mixture " $6KF, 4AlF_3$ " coming in contact to 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  $K_2ZrF_6$  on the ability of steel sheets to be wetted by liquid aluminum has been reported by Lundin (14). When a  $K_2ZrF_6$  powder was 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 was generated at the interface between a sheet of steel coated with  $K_2ZrF_6$  and a bath of aluminum in which the sheet was dipped, it was observed that this liquid tends to move up towards 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  $K_2ZrF_6$  treated preform and aluminum has been formed.

Due to metal flow, density difference and surface tension considerations, it was located logically in the dead head of the casting. After cooling, X-ray diffraction analysis showed that the product mainly consists of a mixture of  $K_3AlF_6$ ,  $KAlF_4$  and alumina compounds, in agreement with the reaction mechanisms discussed in sections 2.2.2.

As a matter of fact, the molten mixture " $6KF, 4AlF_3$ "- $Al_2O_3$  considered in our  $K_2ZrF_6$ -process is analogous to the molten **cryolitic mixture**  $Na_3AlF_6$ - $Al_2O_3$ , used in the electrolytic fabrication of aluminum according to the Hall-Héroult process, from a chemical point of view. Thus, since the physical properties of the " $6KF, 4AlF_3$ "- $Al_2O_3$  molten mixture are not known, we will use in the following discussion those of the related sodium-based molten mixtures which are well established (and will be given between parentheses) (17).

The " $6KF, 4AlF_3$ "- $Al_2O_3$  liquid, which is non miscible with liquid aluminum and has a lower density ( $\approx 2.1$  and  $2.38 \text{ g.cm}^{-3}$  respectively) will move up towards the free surface of the metal, across the drop of aluminum (in a sessile drop experiment) or the aluminum dead head (in gravity casting impregnation), from the SiC/Al interface(s) where it has been formed. The surface tension of liquid aluminum (oxidized,  $865 \text{ erg.cm}^{-2}$ ) is higher than the surface tension of the molten cryolitic mixture (in air,  $140 \text{ erg.cm}^{-2}$ ) (17,18). Therefore, as discussed by Carter and Jones, the " $6KF, 4AlF_3$ "- $Al_2O_3$  liquid will spread out on the surface of the drop (or of the bath) (19). 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 whereas the **true SiC/Al interface** is formed. 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  $800^\circ\text{C}$  (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, seem 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 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.

### 3 - EFFECT OF THE $K_2ZrF_6$ TREATMENT ON THE IMPREGNATION PARAMETERS OF A POROUS FIBROUS PREFORM

#### 3.1 - Impregnation modelling

Quenisset et al. have recently modelled, on the basis of a numerical approach, the impregnation of a porous fiber preform by liquid aluminum alloy according to the **squeeze casting** process (20). The aim of their work was to study the effect of various parameters on : (i) the maximum impregnation depth referred to as  $z_M$  and (ii) 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) 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 modelling was based on the general equations of heat and mass transfers combined with simplified boundary conditions. It was derived for **unidirectional preforms** assumed to be of semi infinite volume and made of a **hexagonal packing of cylindrical fibers** lying parallel (longitudinal direction L) or perpendicular (transverse direction 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.

### 3.2 - Impregnation of porous SiC-fiber preforms

The Quenisset modelling was used in 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.

#### 3.2.1 - Preform modelling and impregnation conditions

The fiber preforms which have been used by Rocher (21) to establish the feasibility of the  $K_2ZrF_6$ -process were made of a stack of SiC-fabrics\* partly densified with SiC according to a CVI-technique which has been described in details elsewhere (22). Their residual open porosity was of the order of 20%. 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 modelled, in first approximation, as an **hexagonal array of SiC fibrous cylinders with the same overall open porosity**, i.e. 20%. 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.  $V_f / (1 - V_f) = D_p / D_c$ ,  $V_f=80\%$ ), was found to be 480  $\mu m$ , i.e.

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\* Nicalon fibers from Nippon carbon

of the same order of magnitude than that of the SiC-infiltrated tows actually measured on a cross section of the preforms used by Rocher et al. in their impregnation experiments.

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 and that of the equivalent preform 650°C, at the beginning of the impregnation process. The impregnation rate was assumed to be  $U = 0.5 \text{ cm.s}^{-1}$  on the basis of the impregnation rates actually observed for the  $\text{K}_2\text{ZrF}_6$ -treated SiC-preforms. Both (i) the exothermicity of reactions [3"] and [6], i.e.  $3.3 \text{ kJ.cm}^{-3}$  of  $\text{K}_2\text{ZrF}_6$  associated with an amount  $Q = 5 \text{ mg.cm}^{-2}$  of  $\text{K}_2\text{ZrF}_6$  deposited on the surface of the equivalent SiC-cylinders and (ii) the contact angle decrease due to  $\text{K}_2\text{ZrF}_6$  ( $\theta = 75^\circ$ ), were taken into account. Since the surface tension of aluminum in presence of the cryolitic liquid film was unknown, that of pure aluminum (i.e.  $\sigma = 865 - 0.2 (T - 660) \text{ erg.cm}^{-2}$ , with T in °C) was used for all the calculations.

### 3.2.2 - 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  $\text{K}_2\text{ZrF}_6$ . This dramatic improvement in the impregnation ability of the preform is due, as already mentioned in section 2.2, to (i) the occurrence of **exothermic reactions** related to  $\text{K}_2\text{ZrF}_6$  and (ii) an enhancement of the wetting of SiC by liquid aluminum, i.e. a **decrease in the contact angle**.

In order to assess the respective contribution of (i) and (ii), 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  $\Delta H(\text{kJ.cm}^{-3})/Q(\text{mg.cm}^{-2} \text{ of } \text{K}_2\text{ZrF}_6)/\theta(^{\circ})$  : (a) : 0/0/160 ; (b) : 0/0/75 ; (c) : 3.3/5/160 and

| IMPREGNATION PARAMETERS                                                                                  | UNTREATED 1D-MODEL PREFORM<br>$\Delta H = 0$ $\theta = 160^\circ$ | K <sub>2</sub> ZrF <sub>6</sub> -TREATED 1D-MODEL PREFORM<br>$\Delta H = 3.3 \text{ kJ.cm}^{-3}$ , $Q = 5 \text{ mg.cm}^{-2}$ $\theta = 75^\circ$ |
|----------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|
| MODE-L IMPREGNATION<br><br>z <sub>M</sub> (cm)<br>T (°C) at z <sub>M</sub><br>P <sub>z</sub> for z (MPa) | 1<br><br>660 (aluminum m.p.)<br>0.03 for z = 1 cm                 | $\infty$ (no solidification of Al)<br>807<br><br><0 for z = 1 cm ; 0.004 for z = 20 cm                                                            |
| MODE-T IMPREGNATION<br><br>z <sub>M</sub> (cm)<br>T (°C) at z <sub>M</sub><br>P <sub>z</sub> for z (MPa) | 0.6<br><br>660 (aluminum m.p.)<br>0.13 for z = 0.6 cm             | $\infty$ (no solidification of Al)<br>807<br><br>0.06 for z = 0.6 cm ; 2.4 for z = 20 cm                                                          |

Table 1 : Results of the calculations performed for 1D-model preforms treated (or not) with K<sub>2</sub>ZrF<sub>6</sub> and representing in a first approximation 2D-SiC/SiC real preforms with a porosity of 20%

(d) : 3.3/5/75. As shown in figure 6, the variation of  $z$  as a function of  $P_z$  obey a linear law up to the solidification of the metal in the pore network ( $z = z_M$ ). When the metal is solidified at the impregnation front,  $z$  can no longer increase whatever the pressure. 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 the curves  $b_L$  ;  $b_T$  ;  $c_L$  and  $c_T$ , on the one hand, and the curves  $a_L$  ;  $a_T$ , on the other hand, leads to the following remarks :

(i) The main effect of the **exothermicity of the chemical reactions** involved in the  $K_2ZrF_6$ -process is to prevent an early solidification of the metal (actually observed at low depths for untreated preforms) as it flows in the preform and thus to allow the impregnation of large size preforms (as far as the required pressures  $P_z$  given by curves  $c_L$  and  $c_T$  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.  $800^\circ\text{C}$ ) as it flows in the slightly colder preform (initial temperature :  $650^\circ\text{C}$ ). Thus, the fluidity of the metal, which is directly related to its temperature, is kept constant. Furthermore, since the metal has not to be strongly over-heated, it leads after cooling at room temperature, to a high quality matrix. 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  $\mu(T)$  of the liquid metal, is limited, as shown in figure 6 for  $z < 1$  cm (curves  $c_L$ ,  $c_T$  and  $a_L$ ,  $a_T$ ).

(ii) The main effect of the **contact angle decrease** due to  $K_2ZrF_6$  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  $z$  (curves **a** and **b**). On the contrary, it has no influence on the maximum impregnation depth. The **pressure field**  $P_z - P_a$ , between the liquid metal at the preform surface (when the liquid front is at a depth

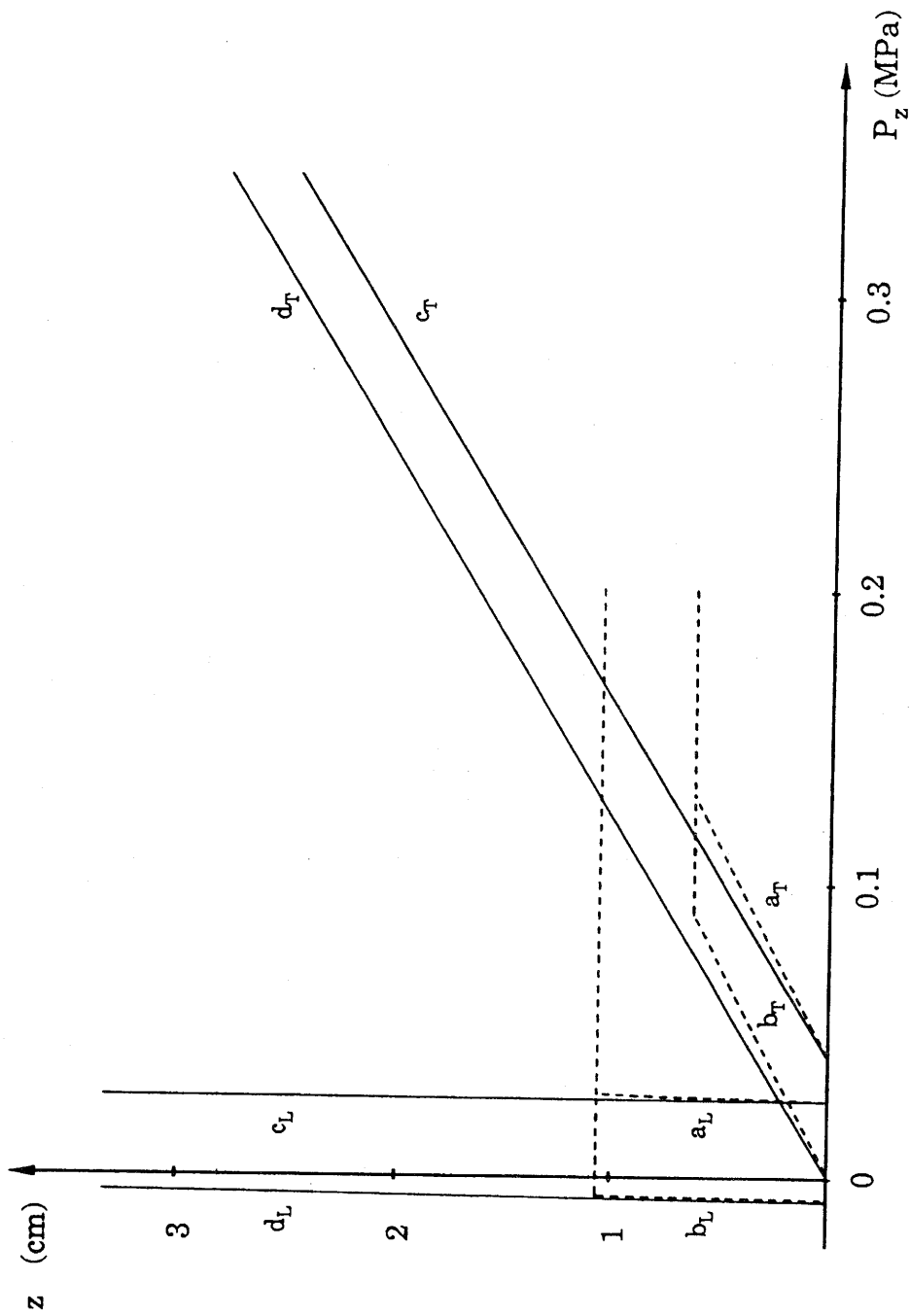


Figure 6 : Variations of the impregnation depth as a function of the pressure in aluminum for one dimensional model preforms ( $D = 480 \text{ } \mu\text{m}$ ). The curves are drawn for different  $\Delta H (\text{kJ} \cdot \text{cm}^{-3}) - \theta (^{\circ})$  values : (a) : 0/160; (b) : 0/75; (c) : 3.3/160; (d) : 3.3/75 and for both mode-L and mode-T impregnations

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 : that of capillary forces, on the one hand, and that of frictional forces, on the other hand. It is given by the following equation :

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

where  $P_\theta$  is a dimensionless parameter which represents the capillary effect (function of both the contact angle and reinforcement volume fraction),  $D$  the diameter of the equivalent fibrous cylinders,  $K$  the preform permeability (proportional to  $D^2$  when  $V_f$  is constant, with a proportionality coefficient different for impregnations in directions L and T) and  $U$  the impregnation rate. Thus, the effect of the contact angle decrease on the pressure field is not straightforward as discussed below.

In **mode T impregnation**, the effect of the capillary forces with respect to that of the frictional forces is small, particularly for large impregnation depths, due to the low transverse permeability of the model preform. Conversely, in **mode L 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  $V_f$ ,  $\sigma$ ,  $D$ ,  $U$  and  $\mu$  are constant in our calculations, it comes out that the capillary force term is proportional to  $-\cos \theta$  and the frictional force term is constant. Since  $-\cos \theta$  is negative for a preform pretreated with  $K_2ZrF_6$  ( $\theta = 75^\circ$ ) and positive for an untreated preform ( $\theta = 160^\circ$ ), the resulting value of  $P_z$  is lower in the former case than in the latter, as shown in figure 6.

As already mentioned, the contact angle decrease due to  $K_2ZrF_6$  does not have any effect on the impregnation depth. As shown in figure 6, the solidification of the liquid metal occurs at the same depth  $z_M$  for (a) and (b). Therefore, for **preforms of large size**, the contact angle decrease has a beneficial effect on the impregnation of the preform only when an evolution of heat occurs simultaneously in order to

maintain liquid the aluminum, which is actually the case in the  $K_2ZrF_6$ -process. Under such conditions, a **spontaneous** impregnation of the preforms is possible in **mode-L** since  $P_z$  is negative (curve  $d_L$ ) whereas this is not the case in mode-T due to the fact that the pressure lowering resulting from the contact angle decrease is too low as shown in figure 6 (curves  $d_T$  and  $c_T$ ). Finally, for **preforms of small size**, the **single** effect of the contact angle decrease will be sufficient for allowing a spontaneous impregnation in mode-L (curves  $b_L$  vs  $a_L$ ).

As far as **2D-SiC/SiC preforms** are concerned, their **actual** mode of impregnation has more common features with mode-L impregnation than with mode-T impregnation, due to the morphology of their pore network. It is worthy of note that rather thick 2D-SiC/SiC preforms (thickness : 1-1.5 cm) pretreated with  $K_2ZrF_6$  have been successfully impregnated by aluminum without any pressure externally applied on the liquid, i.e. by simple gravity casting. Under such 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).

(iii) The **maximum impregnation depth  $z_M$**  depends directly on the temperature field since it is defined as the depth at which the temperature of the liquid front is equal to the melting point of aluminum. Thus, it is function of the reinforcement volume fraction  $V_f$  (both the specific heat and thermal conductivity of the composite depend on  $V_f$ ), the temperatures of both the preform (before impregnation)  $T_F$  and the liquid aluminum  $T_{Al}$  as well as the occurrence of internal heat sources. The variations of  $z_M$  as a function of  $V_f$  were calculated for  $T_F = 650^\circ\text{C}$  ;  $T_{Al} = 800^\circ\text{C}$  and with the hypothesis that no internal heat source is present. They are shown in figure 7 from which it clearly appears that  $z_M$  is small (i.e.  $z_M \leq 1$  cm) for high  $V_f$  values, in the model preform. Therefore, the use of the  $K_2ZrF_6$ -process, which results in exothermic chemical reactions as already discussed, is of particular interest for those preforms characterized by high  $V_f$  values which is indeed the case for the 2D-SiC/SiC preforms studied here ( $V_f = 0.8$ ).



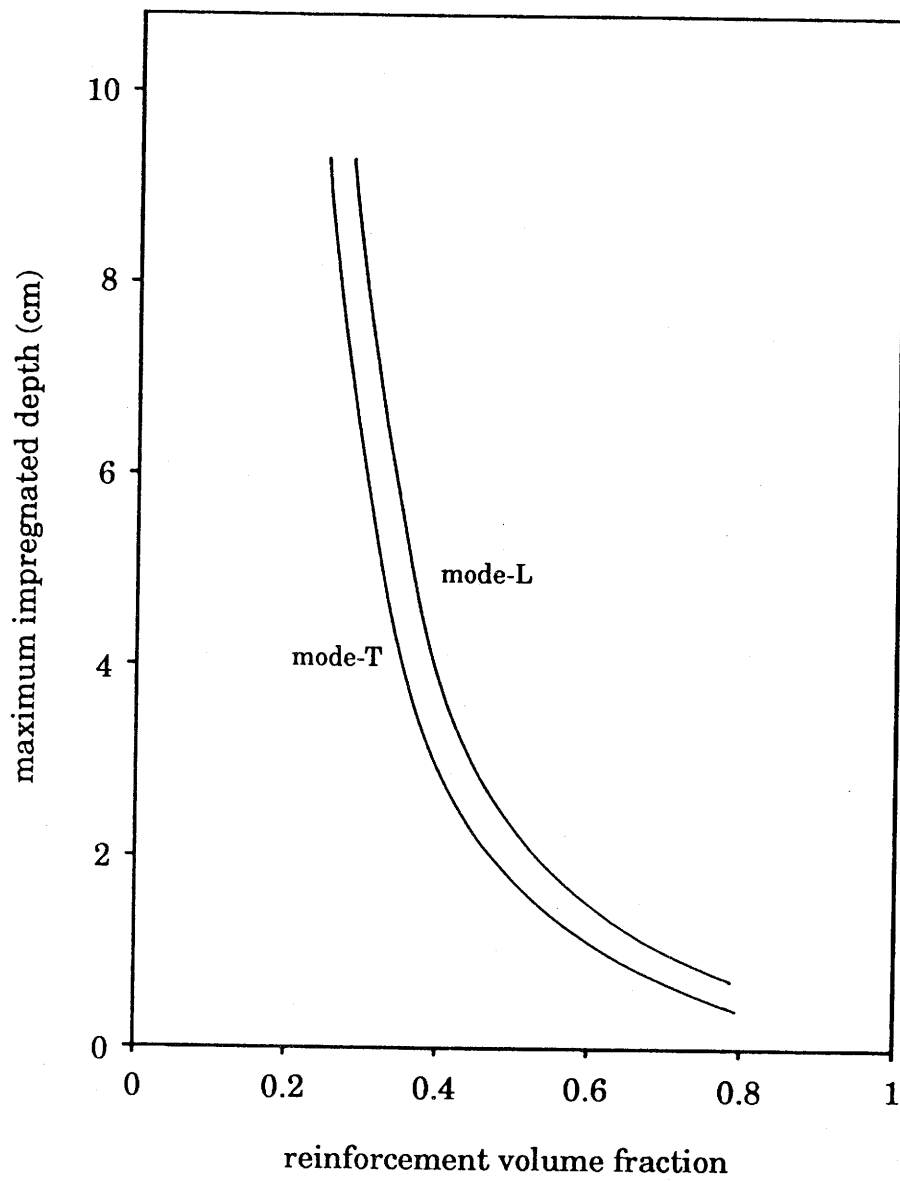


Figure 7 : Variations of the maximum impregnation depth  $z_M$  as a function of the reinforcement volume fraction for 1D-model preforms. The curves are drawn for  $T_F = 650^\circ\text{C}$  ;  $T_{Al} = 800^\circ\text{C}$  and no internal heat source

The **minimum amount of  $K_2ZrF_6$**  necessary to let  $z_M$  reach an infinite value, i.e. to maintain liquid the aluminum as it flows in a preform of infinite thickness, has been calculated for the model preform (for  $T_F = 650^\circ\text{C}$  and  $T_{Al} = 800^\circ\text{C}$ ). The result of the calculations shows that only 0.45 mg of  $K_2ZrF_6$  per  $\text{cm}^2$  would be enough to keep aluminum just above its melting point (i.e.  $660^\circ\text{C}$ ). However and as discussed in section 2.2., such a temperature would not be sufficient to lower significantly the SiC/Al contact angle. A temperature of about  $750^\circ\text{C}$ , at which  $\theta = 75^\circ$  as shown in figure 1, seems to be more appropriate. The calculations have established that an amount of **3 mg  $K_2ZrF_6$  per  $\text{cm}^2$**  would be necessary in order to maintain aluminum at  $750^\circ\text{C}$  as it flows in the model preform (with  $T_F = 650^\circ\text{C}$  and  $T_{Al} = 800^\circ\text{C}$ ). It is noteworthy that this value : (i) corresponds to the maximum amount of  $K_2ZrF_6$  which could be introduced in the model preform due to the available porosity (20%) and (ii) in close to that ( $5 \text{ mg.cm}^{-2}$ ) actually used for the impregnation of 2D-SiC/SiC preforms. As a matter of fact, larger  $K_2ZrF_6$  amounts, that would require preforms of higher porosities, would lead to an excessive overheating of the system ( $T > 800^\circ\text{C}$ ) detrimental to the properties of the composite. In such a case,  $T_F$  could be lowered.

(iv) The variations of  $P_z$  as a function of  $\theta$  is closely related to the **pressure threshold** above which pressure must be set in order to start the impregnation process, as shown in figure 6 (curves  $b_L$ ,  $b_T$  and  $a_L$ ,  $a_T$ ). This pressure threshold is low for the model preforms due to the fact that the capillary force term is proportional to the reciprocal diameter of the fibrous cylinders which is large in the case considered here ( $D = 480 \text{ }\mu\text{m}$ ). This feature is also in agreement with the experimental data obtained for the real 2D-SiC/SiC preforms. On the other hand, the pressure threshold was expected to be much higher for untreated preforms made of **fibers smaller in diameter**. In order to verify this assumption, the variations of  $z$  as a function of  $P_z$  were calculated for a new model preform with the same overall porosity than real 2D-SiC/SiC preforms (i.e. 20%) but made of SiC fibrous cylinders

only **12.5  $\mu\text{m}$  in diameter** (instead of 480  $\mu\text{m}$  for the first model preforms and thus similar to the Nicalon fibers) and supposed to have been treated or not with the same amount of  $\text{K}_2\text{ZrF}_6$  (per unit of volume). The results of the calculations are shown in figure 8 for the two model preforms. It is worthy of note that the ability of the preform made of small diameter fibers to be impregnated under low pressures depends entirely on the contact angle decrease due to  $\text{K}_2\text{ZrF}_6$ .

#### 4 - CONCLUSION

The feasibility of the  $\text{K}_2\text{ZrF}_6$ -process, already established experimentally by Rocher et al. (21) has been justified theoretically in the present work. This process is based on a very simple procedure and products already used in light alloy casting. It has been shown that fiber preforms of rather low porosities and moderate thickness could be impregnated, when pretreated with  $\text{K}_2\text{ZrF}_6$ , under low pressures, i.e. by **gravity casting**. It is anticipated that its use 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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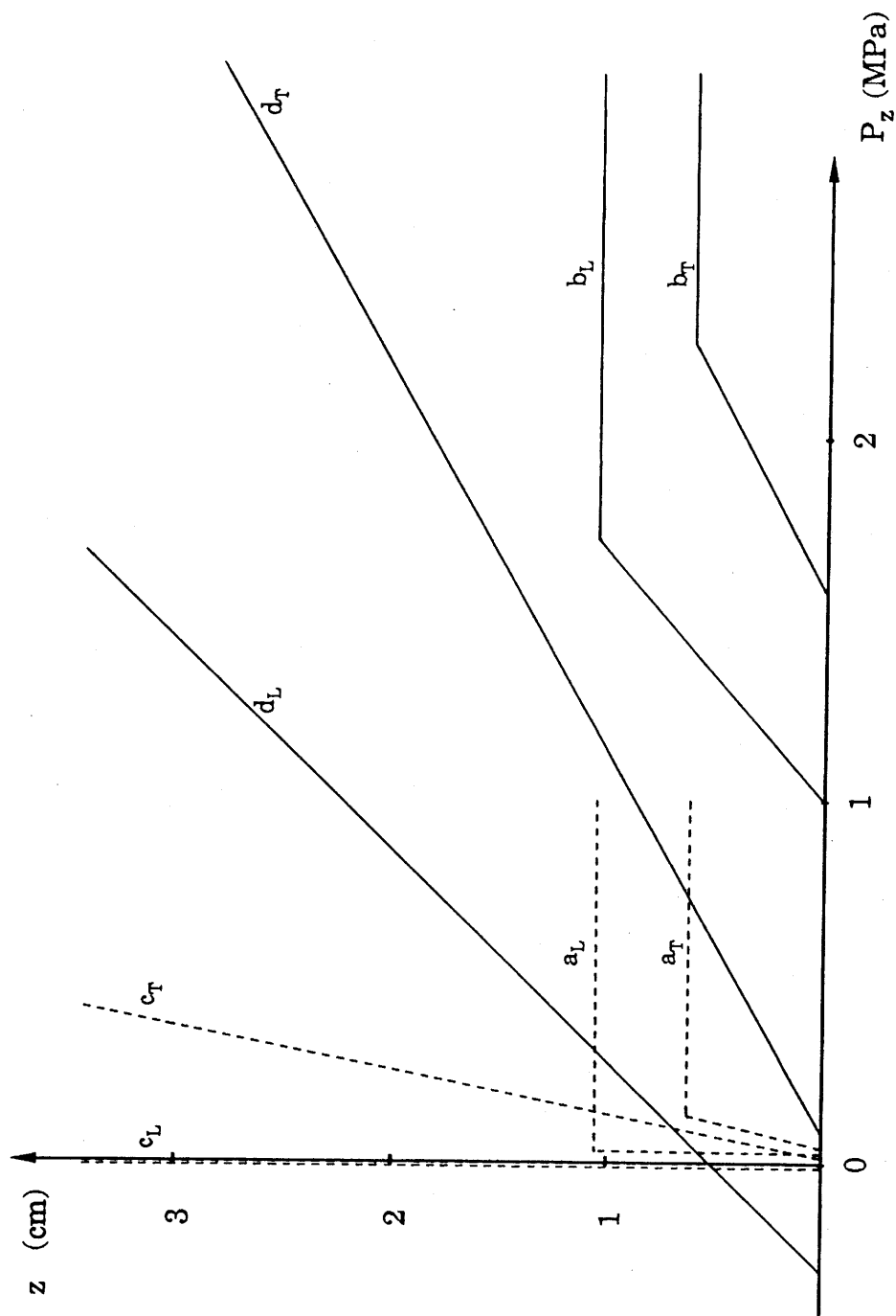


Figure 8 : Variations of the impregnation depth as a function of the pressure in aluminum for one dimensional model preforms :

(a) : untreated,  $D = 480 \mu m$ ; (b) : untreated,  $D = 12.5 \mu m$

(c) : pretreated with  $K_2ZrF_6$ ,  $D = 480 \mu m$  ; (d) : pretreated with  $K_2ZrF_6$ ,  $D = 12.5 \mu m$   
The curves are drawn for both mode-L and mode-T impregnations

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## **CHAPITRE III**

## INTRODUCTION AU CHAPITRE III

Etant donnée la nette amélioration apportée par le procédé au  $K_2ZrF_6$  sur l'aptitude à l'imprégnation de préformes céramiques poreuses par l'aluminium liquide (Chapitre II), il était important, dans la perspective d'une transposition industrielle, de définir la qualité de l'interface fibre-matrice. Cette interface, qui très souvent devient une interphase à cause de l'étendue des réactions chimiques entre fibre et matrice, est en effet l'endroit stratégique du composite où s'effectue le transfert des efforts reçus par la matrice aux fibres.

Pour cela, nous avons choisi d'évaluer l'affaiblissement mécanique de monofilaments SiC-CVD au cours des différentes étapes du procédé, i.e.

- après avoir déposé le fluorure à la surface du monofilament
  - après traitement thermique du filament recouvert de fluorure
  - après incorporation dans l'aluminium du filament traité par le fluorure
- afin de définir la participation de chacune d'elles au processus de fragilisation.

Il est apparu, sur la base de l'analyse statistique de Weibull des résultats de traction, des observations au microscope électronique à balayage des faciès de rupture primaire et de la surface des monofilaments et des analyses X et Auger des produits de réaction, que essentiellement la dernière étape du procédé contribue à l'affaiblissement mécanique des monofilaments. La formation importante de cristaux de **carbure d'aluminium**, au cours de cette étape, est la cause de l'apparition d'entailles initiatrices de rupture à la surface des filaments.

L'étude physico-chimique du mécanisme de l'amélioration du mouillage, présentée au chapitre II, permet de comprendre que le fluorure  $K_2ZrF_6$  intervient de



manière indirecte dans le mécanisme de formation du carbure d'aluminium. Selon un processus exothermique de "nettoyage" de l'interface Al/SiC, il **active la cinétique de formation** du carbure d'aluminium qui résulte de la réaction directe entre le carbure de silicium et l'aluminium.

Soumis à "Composites Science and Technology"

**COMPATIBILITY BETWEEN SiC-FILAMENTS AND ALUMINUM  
IN THE  $K_2ZrF_6$  WETTING PROCESS AND ITS EFFECT ON  
THE FILAMENT FAILURE STRENGTH**

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**ABSTRACT**

*The effect of the various steps of the  $K_2ZrF_6$ -process, used to enhance the wettability of SiC (or C) fibers by liquid aluminum, on the strength of the reinforcement, was studied on model materials. Lots of 45 uncoated SiC-CVD filaments (100  $\mu$ m in diameter) were submitted to three treatments representative of the process : 1) coating with a  $K_2ZrF_6$  layer of variable thickness, 2) annealing of the coated filaments at 650°C in sealed tubes and quenching, and 3) embedding the coated filaments in aluminum by hot pressing. After each step, the filaments were extracted chemically and tensile tested. The UTS data were treated statistically on the basis of a two-parameter Weibull function. Step 1 does not modify the filament strength. Step 2 results in a filament strength loss of about 20% and an increase in the Weibull modulus (from 8 to 20). Zirconium and oxygen were found to be present*

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*(based on AES analyses) at the filament surface but the size of the related critical flaws was too small to make their observation possible by SEM. Step 3 yields a more significant strength loss, depending on the amount of  $K_2ZrF_6$  deposited in step 1, due to the formation of  $Al_4C_3$  related to the chemical reaction between SiC and aluminum. The kinetics of growth of  $Al_4C_3$  is faster than for untreated filaments mainly due to the cleaning effect of fluoride species on the SiC/Al interfaces. Thus, this latter filament strength loss is more an indirect consequence than an intrinsic feature of the process. It could be overcome by utilizing filaments coated with a soft material (e.g. pyrocarbon).*

**Key-words**      $K_2ZrF_6$ -PROCESS, SiC-FILAMENTS, ALUMINUM MATRIX  
COMPOSITES, SiC/Al COMPATIBILITY, FAILURE STRENGTH.

## 1 - INTRODUCTION

It has been shown recently that the impregnation ability of porous preforms made of ceramic fibers (e.g. C or SiC-based Nicalon fibers) by liquid aluminum alloys is significantly improved when the preforms are pretreated with an aqueous solution of  $K_2ZrF_6$  at (or near) its boiling point, according to a very simple procedure (1-2). As a matter of fact, various preforms, with different fiber types and morphologies, e.g. 2D-SiC(Nicalon) preforms consolidated with SiC by chemical vapor infiltration (CVI), have been successfully impregnated by liquid aluminum according to a gravity casting technique, when first pretreated with  $K_2ZrF_6$  (3).

A detailed study of the chemical compatibility between the reinforcement and the matrix is considered as a necessary step in the development of any new metal matrix composite (MMC) in order to assess whether or not the chemical reactions which may occur between the two components during the composite processing result in a fiber strength loss. The chemical reactivity between aluminum and silicon carbide has been already the subject of many studies. The equilibria that may occur in the ternary Al-Si-C system were studied on the basis of thermodynamic calculations (4-6). The analysis and modelling of the Al/SiC interface were performed according to Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), X-ray and UV photoelectron spectroscopies (XPS and UPS) (7-8). The identification of the reaction products formed at the SiC/Al interface was done by X-ray diffraction (XRD) as well as transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (9-10). Finally, the effect of the interfacial chemical reaction on the failure strength of SiC-filaments was assessed through tensile tests (11). It can be concluded from these studies that the interactions occurring during the processing of SiC-Al composites between the reinforcement and the matrix result in the formation of  $Al_4C_3$  and elemental silicon. Under tensile loading, the microcracking of the brittle aluminum carbide

layer surrounding each fiber is responsible for notch effects which may lower the fiber strength.

The aim of the present contribution is to study the chemical reactivity between  $K_2ZrF_6$  and SiC, on the one hand, and that between SiC and aluminum in presence of  $K_2ZrF_6$ , on the other hand, as well as their effect on the reinforcement failure strength in both cases. Within this scope, tensile tests on  $\beta$ -SiC CVD-filaments coupled with a Weibull analysis of the data have been performed after each step of the  $K_2ZrF_6$ -process. Furthermore, the external surfaces of chemically extracted filaments and their failure surfaces were observed by SEM. Finally, the reaction products formed at the SiC-filament/aluminum matrix interface were analysed by SEM, AES and X-ray electron probe (EPMA) microanalyses in order to derive reaction mechanisms.

## 2 - EXPERIMENTAL

### 2.1 - Materials and chemical treatments

The successive steps of the elaboration of a SiC-fiber/aluminum matrix composite according to the  $K_2ZrF_6$ -process have been simulated, utilizing large diameter SiC-CVD filaments<sup>(\*)</sup>, i.e. : 1) precipitation of  $K_2ZrF_6$  microcrystals on the filament surface from a  $K_2ZrF_6$  aqueous solution at a temperature close to its boiling point and drying at 110°C, 2) treatment under vacuum at 650°C for 15 minutes of the coated filaments encapsulated in glass silica tubes (sealed under a residual pressure of 1.2 Pa) and quenching in air at room temperature, and 3) imbedding the filaments in a matrix of aluminum (> 99.5 % in purity) by hot pressing between two foils of metal ( $T = 700^\circ\text{C}$  ;  $t = 5$  min.;  $P = 2$  MPa ; residual pressure in the bag :  $1.3 \cdot 10^{-3}$  Pa) according to a procedure which has been initially designed for

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<sup>(\*)</sup> from SIGMA (FRG)

titanium-matrix composites and described elsewhere (12). Furthermore, for each step, several lots of filaments corresponding to different amounts of  $K_2ZrF_6$  deposited were used. The amount of  $K_2ZrF_6$  deposited was assessed by weighing the filaments before and after the fluoride treatment and expressed as the mass of  $K_2ZrF_6$  deposited per unit of filament surface ( $mg.cm^{-2}$ ).

Within the scope of the present study, **SiC-CVD filaments** were thought to exhibit the following advantages with respect to yarn fibers (e.g. Nicalon fibers) : (i) CVD-filaments<sup>(\*)</sup> are of large and regular diameter, i.e. 100  $\mu m$ , whereas yarn fibers are made of hundreds of filaments whose diameter is small (15  $\mu m$  for Nicalon fibers) and variable both along one given filament (dispersion : 5 %) and from one filament to the other (dispersion : up to 40 %), a feature rendering the deposition of a layer corresponding to a given amount of  $K_2ZrF_6$  per unit of surface much easier for the CVD-filaments, (ii) due to their elaboration by CVD, large diameter SiC-filaments are only made of silicon and carbon (13) whereas yarn fibers spun from polycarbosilane (PCS) and pyrolysed contain a large amount of oxygen (14) and finally, (iii) the failure strength of SiC-CVD filaments is much higher than that of SiC yarn fibers and more uniform (for a 50 mm gauge length, the mean UTS  $\bar{\sigma}$  and Weibull modulus  $m$  are respectively  $\bar{\sigma} = 3500$  MPa and  $m = 8$  for the former and  $\bar{\sigma} = 2000$  MPa and  $m = 4-5$  for the latter). An **uncoated** SiC-CVD filament, referred to as SiC( $\Sigma$ ) and which has been characterized elsewhere (15), was chosen for this study (rather than one from the SCS-i (with  $i = 2, 6, 8$ ) series<sup>(\*\*)</sup> known to have received a thick coating (at least 1  $\mu m$ ) of either pure carbon or a carbon-rich SiC + C mixture). The SiC( $\Sigma$ ) filament has a tungsten core and it is made of a SiC-CVD deposit containing 6 at.% of free silicon (from EPMA data utilizing a SiC single crystal, assumed to be stoichiometric, as a standard). AES depth profiling

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(\*) from SIGMA (FRG)

(\*\*) from AVCO

analyses have shown that the Si/C atomic ratio remains constant near the filament surface (i.e. over at least 2  $\mu\text{m}$ ).

## 2.2 - Mechanical testing

The filaments, after having been submitted to the steps 1, 2 and 3 of the  $\text{K}_2\text{ZrF}_6$ -process mentioned above, were mechanically tested individually in tension (load cell : 500 N ; elongation rate : 1  $\text{mm}\cdot\text{min}^{-1}$ ; pneumatic grips) at room temperature. An average of 45 filaments were tested for each experiment in order to take into account the statistical character of the filament failure. A paper holder, which has been described elsewhere (13), was used to facilitate the filament alignment in the grips, to define accurately the gauge length (40 mm in all the experiments) and to avoid any damaging due to handling.

Before the tensile tests, the filaments were extracted chemically from the materials in which they have been heat treated. The coating of  $\text{K}_2\text{ZrF}_6$  (steps 1 and 2) was dissolved by maintaining the filaments in boiling water. The aluminum matrix (step 3) was dissolved with an aqueous solution of sodium hydroxide. Then, the filaments were dried and their diameter measured according to a laser diffraction procedure (0.95 mW He-Ne laser ;  $\lambda = 0.6328 \mu\text{m}$ ).

In a few tensile tests, the filaments have been embedded in a silicone product in order to recover the filament fragments after rupture and to study by SEM the failure surfaces.

## 2.3 - Statistical treatment of the UTS data

The SiC-CVD filaments are known for their brittleness. Their strength is controlled by their population of defects consisting of (i) intrinsic defects usually of small size and due to processing, and (ii) surface defects often of larger size and due

to handling, mechanical abrasion or chemical reactions with the environment (including the effect of the composite processing technique). As a result, the values of the UTS of SiC-CVD filaments depend on the volume of sample tested and exhibit generally a rather large dispersion. The statistical character of the failure strength of brittle materials is usually taken into account on the basis of a two parameter Weibull distribution function, according to which the probability of failure  $P_R$  of a sample of volume  $V$  loaded at a stress level  $\sigma$  is given by the following equation (16) :

$$P_R = 1 - \exp \left[ -V \left( \frac{\sigma}{\sigma_0} \right)^m \right] \quad [1]$$

where  $\sigma_0$  is a scale factor and  $m$  the so-called Weibull modulus (which is used to characterize the distribution of the UTS values with respect to the mean value). When the sample is a cylinder, which is the case for a CVD-filament, as mentioned above :  $V = \pi d^2 L / 4$  (where  $d$  is the filament diameter and  $L$  the gauge length).

If the gauge length is constant, it can be shown that the variations of  $P_R$  as a function of  $\sigma$  obey the following relation :

$$\text{LnLn } 1/(1-P_R) = m \text{ Ln} \sigma + \text{constant} \quad [2]$$

As a result, if the UTS data obey the Weibull distribution law, the variations of  $\text{LnLn } 1/(1-P_R)$  as a function of  $\text{Ln} \sigma$  must be linear and the slope of the corresponding straight line gives directly the value of  $m$ .

Several estimators can be used to calculate  $P_R$ . Regarding the large number of filaments tested for each lot ( $N = 45$ ), the estimator which has been used, in the present study, was chosen as that given by the following equation :

$$P_R = \frac{i}{N + 1} \quad [3]$$

with  $i = 1, 2, \dots, 45$

Apart the Weibull modulus  $m$ , the other parameters derived from the statistical treatment of the UTS data which have been taken into account are :



$\sigma_{0.5}$ , the median of the UTS values (corresponding to a probability of failure of 50 %),  $\bar{\sigma}$  the arithmetic UTS mean value,  $S$  the standard deviation with respect to  $\bar{\sigma}$ ,  $C_V$  the coefficient of variation defined by  $C_V = S/\bar{\sigma}$  and which is known to depend only on the Weibull modulus  $m$ . The relation between  $C_V$  and  $m$ , which has been used here is that given by Street and Ferte in their study of boron CVD-filaments, i.e. (17):

$$C_V \simeq m^{-0.94} \quad [4]$$

Finally,  $r$  is the correlation factor associated with a given Weibull  $\text{LnLn } 1/(1-P_R) = f(\text{Ln}\sigma)$  plot. The values of the Weibull modulus derived from equations [2] and [4] will be referred to as  $m$  [2] and  $m$  [4] respectively.

It is worthy of note that an overall length of SiC( $\Sigma$ ) filament of about **50 meters** has been used to perform the various experiments described in the present study. In order to take into account the occurrence of possible differences in the characteristics of the material along such a length, the continuous filaments was first cut into segments of equal length (i.e. about 80 mm). Then lots of 45 filaments were prepared in a **random** manner, submitted to the chemical/thermal treatments and finally tensile tested.

### 3 - RESULTS AND DISCUSSION

#### 3.1 - Effects of the $\text{K}_2\text{ZrF}_6$ -process steps on SiC-filaments UTS

Some of the Weibull plots, representative of the effect of the different  $\text{K}_2\text{ZrF}_6$ -process steps on the filament UTS are shown in figure 1 (when several curves have almost the same values of  $\sigma_{0.5}$  and  $m$ , only one among them is represented). It appears that : (i) some of them are almost perfectly linear (corresponding to unimodal Weibull distributions) whereas others are not and will better fit bi-modal distribution as already noticed by Martineau et al. (13) and by Le

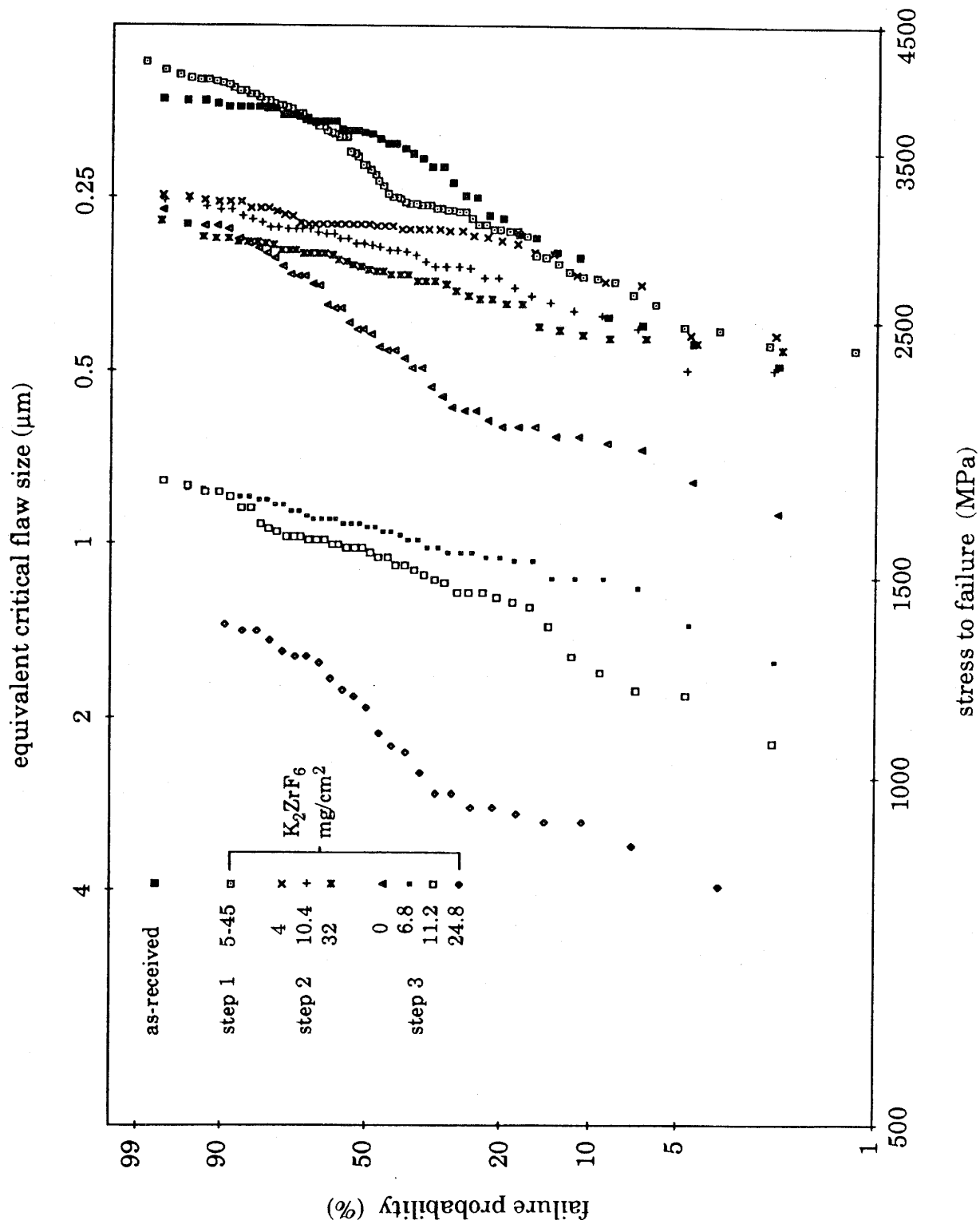


Figure 1 : Weibull plots for SiC( $\Sigma$ )-CVD filaments at different stages of the  $\text{K}_2\text{ZrF}_6$ -process

Petitcorps et al. (15) in their studies of tungsten or carbon core CVD-filaments and (ii) generally speaking, the weibull plots are shifted towards the low UTS side depending on the nature of the treatment which has been applied to the filament. The various parameters derived from the statistical treatment of the UTS data are given in table 1. Finally, the variations of  $\sigma_{0.5}$  measured after the steps 2 and 3, as a function of the amount of  $K_2ZrF_6$  initially deposited on the filament surface, are shown in figure 2.

### 3.2 - Nature and size of the critical defects

As shown in figure 3, the **critical defects**, i.e. the defects which have initiated the filament failure, are mainly located at the filament surface. This result suggests that the strength loss of the filament shown in figures 1 and 2 is due to the chemical interactions between the reinforcement and the products (i.e.  $K_2ZrF_6$ ,  $Al_4C_3$  and aluminum) in which it has been maintained at high temperatures (step 2 and 3). The few failure surfaces which have been observed by SEM exhibit the features typical of brittle materials already reported for other SiC-based fibers (e.g. the Nicalon fibers) (18). Surrounding the critical defect itself (arrows in figures 3 b, c, d), one observes successively : (i) a small mirror zone (slow crack propagation) and then (ii) a mist region and hackles (catastrophic crack propagation) which are located in a plane perpendicular to the fiber and load axis. Therefore, the filaments appear to have failed on **mode I**.

The surface defects, for the filaments submitted to the  $K_2ZrF_6$ -process step 3 (amount of  $K_2ZrF_6$  :  $6.8 \text{ mg.cm}^{-2}$ ), are numerous, rather small in average depth and homogeneously distributed on the filament surface (fig.3b). This feature is in agreement with the high value (i.e. about 16) of the Weibull modulus given in table 1. However, when the amount of  $K_2ZrF_6$  deposited on the filament surface is increased prior to the step 3, i.e.  $11.2 \text{ mg.cm}^{-2}$  for the fractography shown in figure 3c and

| Treatment   | $K_2ZrF_6$<br>(mg/cm <sup>2</sup> ) | $\sigma_{0.5}$<br>(MPa) | $\bar{\sigma}$<br>(MPa) | $\sigma_0$<br>(MPa) | S<br>(MPa) | $C_v$ | r    | m[2] | m[4] | $\bar{d}$<br>( $\mu m$ ) | $\bar{\sigma} a^{1/2}$<br>(MPa.m <sup>1/2</sup> ) |
|-------------|-------------------------------------|-------------------------|-------------------------|---------------------|------------|-------|------|------|------|--------------------------|---------------------------------------------------|
| As-received | -                                   | 3622                    | 3444                    | 1119                | 434        | 0.13  | 0.96 | 8.0  | 9.1  | 100                      | -                                                 |
| Step 1      | 5-45                                | 3405                    | 3376                    | 1127                | 486        | 0.14  | 0.99 | 8.2  | 7.9  | 100                      | -                                                 |
| Step 2      | 0                                   | 3584                    | 3472                    | 1152                | 450        | 0.13  | 0.98 | 8.1  | 8.8  | 100                      | -                                                 |
|             | 1.8                                 | 3079                    | 3047                    | 1910                | 177        | 0.06  | 0.98 | 18.9 | 20.6 | 99.6                     | 1.4                                               |
|             | 4.0                                 | 3026                    | 2989                    | 1821                | 170        | 0.06  | 0.94 | 18.0 | 21.1 | 99.4                     | 1.6                                               |
|             | 6.4                                 | 2837                    | 2764                    | 1641                | 178        | 0.06  | 0.99 | 17.1 | 18.5 | 99.3                     | 1.6                                               |
|             | 10.4                                | 2871                    | 2864                    | 1529                | 223        | 0.08  | 0.99 | 14.3 | 15.1 | 99.3                     | 1.7                                               |
|             | 16.8                                | 2984                    | 2945                    | 1839                | 160        | 0.05  | 0.94 | 19.0 | 22.2 | 99.5                     | 1.5                                               |
|             | 32.0                                | 2771                    | 2748                    | 1637                | 177        | 0.06  | 0.99 | 17.3 | 18.5 | 99.2                     | 1.7                                               |
| Step 3      | 0                                   | 2448                    | 2446                    | 681                 | 383        | 0.16  | 0.98 | 7.0  | 7.2  | 99.4                     | 1.3                                               |
|             | 3.0                                 | 1592                    | 1579                    | 921                 | 105        | 0.07  | 0.98 | 16.6 | 17.8 | 98.4                     | 1.4                                               |
|             | 6.8                                 | 1652                    | 1635                    | 919                 | 115        | 0.07  | 0.99 | 15.6 | 16.8 | 97.8                     | 1.7                                               |
|             | 11.2                                | 1578                    | 1539                    | 613                 | 170        | 0.11  | 0.99 | 9.8  | 10.4 | 97.4                     | 1.8                                               |
|             | 24.8                                | 1096                    | 1108                    | 293                 | 173        | 0.16  | 0.97 | 6.8  | 7.2  | 95.8                     | 1.6                                               |

Table 1: Parameters derived from the Weibull treatment for each step 1, 2 and 3 and for different amounts of  $K_2ZrF_6$  deposited

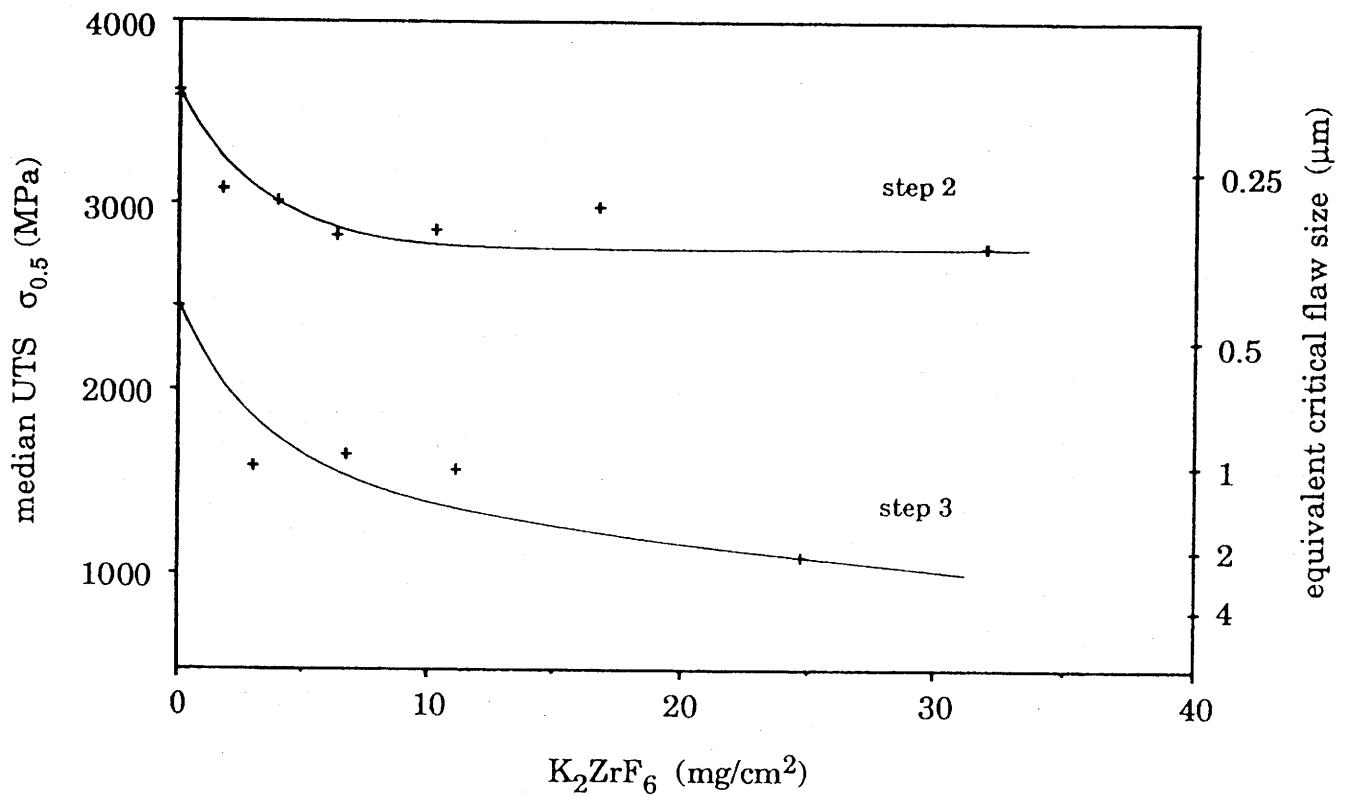
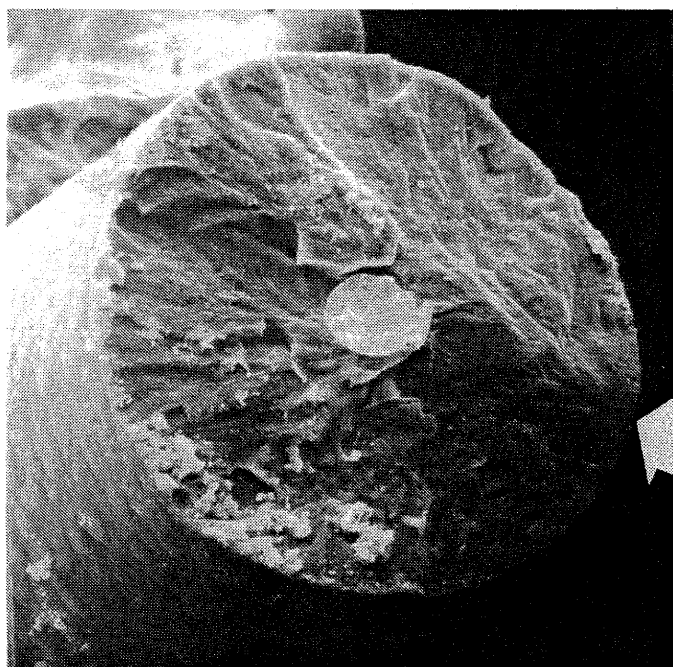
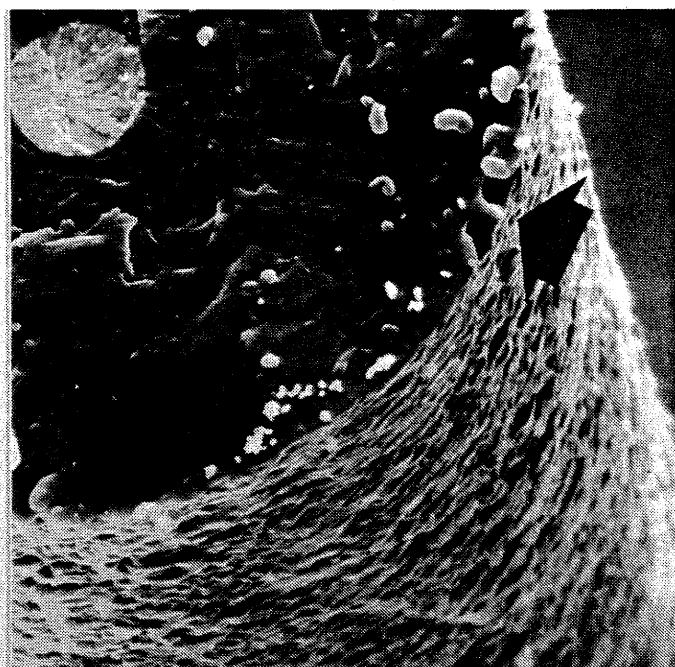


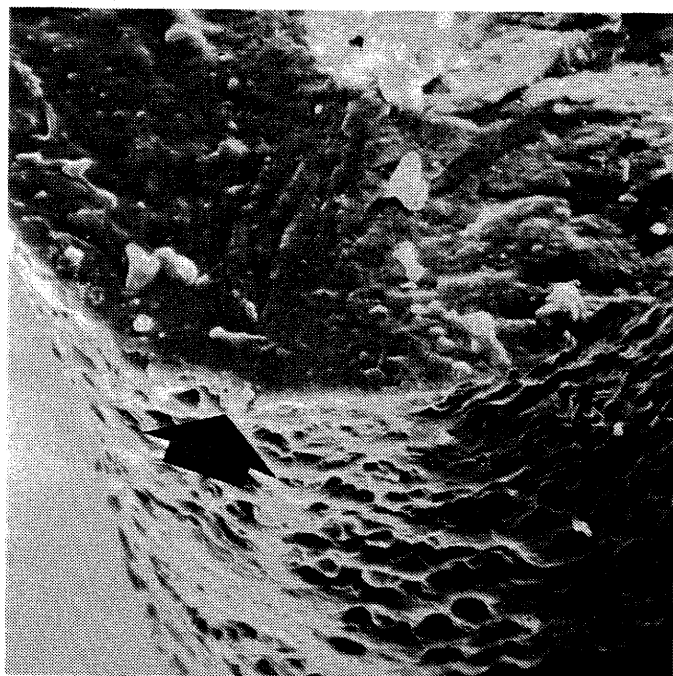
Figure 2 : Variations of the median UTS of SiC( $\Sigma$ )-CVD filaments chemically extracted from  $K_2ZrF_6$  (step 2) or aluminum (step 3) in the  $K_2ZrF_6$ -process



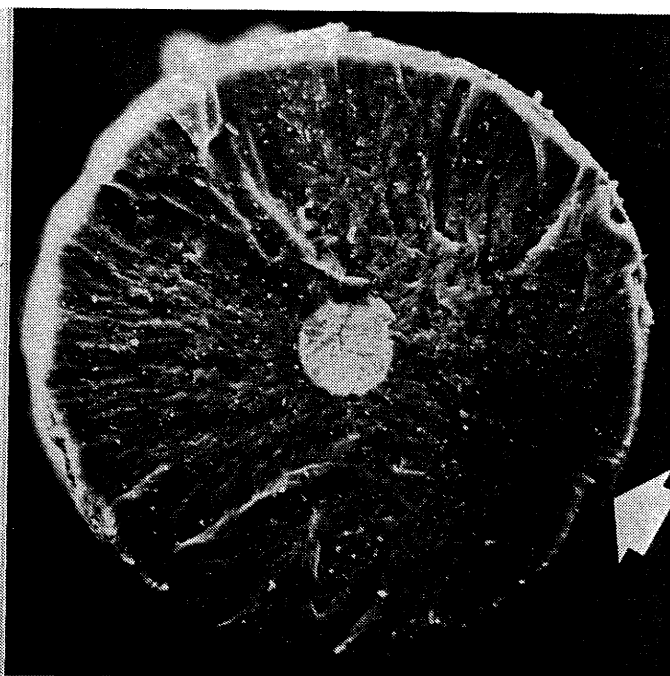
(a) X 700     $\text{—} 10 \mu\text{m}$



(b) X 1200     $\text{—} 10 \mu\text{m}$



(c) X 1200     $\text{—} 10 \mu\text{m}$



(d) X 800     $\text{—} 10 \mu\text{m}$

Figure 3 : SEM fractographic analysis of  $\text{SiC}(\Sigma)$ -filaments after tensile test and for different surface amounts of  $\text{K}_2\text{ZrF}_6$  :

- (a) extracted from  $\text{K}_2\text{ZrF}_6$  after step 2 ;  $\text{K}_2\text{ZrF}_6$  :  $32 \text{ mg.cm}^{-2}$
- (b), (c), (d) extracted from aluminum after step 3 for  $\text{K}_2\text{ZrF}_6$  : 6.8; 11.2 and  $24.8 \text{ mg.cm}^{-2}$  respectively

24.8 mg.cm<sup>-2</sup> for figure 3d, the defects are deeper and distributed in a less homogeneous manner. As a result, the Weibull modulus decreases (9.8 and 6.8, respectively) (table 1).

Although the surface of the filaments which have been submitted only to the step 2 of the K<sub>2</sub>ZrF<sub>6</sub>-process does not exhibit apparent defects (fig.3a), the fact that the corresponding Weibull moduli are high ( $m = 15-20$ ) suggests : (i) that the filament surface has been chemically altered in a similar homogeneous way and (ii) that the surface defects are too small in size to be seen on the SEM micrograph (table 1).

The size of the critical flaw (i.e. the equivalent critical flaw radius  $a_c$ ) could be derived from the UTS value utilizing fracture mechanics, e.g. the critical stress intensity factor in mode I,  $K_{IC}$ , according to the following equation already used by Andersson and Warren in their study of Nicalon-type fibers (14,19) :

$$K_{IC} = 1.12 \sigma (\pi a_c)^{1/2} \simeq 2 \sigma a_c^{1/2} \quad [5]$$

This approach supposes that the value of  $K_{IC}$  is known. Although  $K_{IC}$  can be derived from a detailed fractographic analysis (i.e. by measuring the critical flaw and mirror radii), as recently used by Sawyer et al. for various fibers derived from polymeric precursors (18), this possibility was not exploited here lacking enough reliable fractographic data. Conversely, a value of  $K_{IC} \simeq 3 \text{ MPa.m}^{1/2}$ , given by Andersson and Warren for  $\beta$ -SiC (the SiC modification present in SiC( $\Sigma$ ) filaments) was used, as a first approximation and taking into account the following remark. It is clearly apparent from figure 3 that the surface defects responsible for the filament strength loss are due to a chemical attack. As a matter of fact, this chemical attack results in a decrease in the filament diameter which is very slight for step 2 but significant and variable for step 3 (table 1). Therefore, it is not unrealistic to compare the order of magnitude of the thickness of material consumed by the chemical reaction, defined as  $(\bar{d} - 100)/2$  (where  $\bar{d}$  is the actual mean filament diameter and

100 the initial diameter), to that of the defect critical size ( $a_c$ ). As a matter of fact and as shown in table 1, the product  $\bar{\sigma} [(\bar{d} - 100)/2]^{1/2}$  appears to be constant and equal to  $1.6 \text{ MPa.m}^{1/2}$ . This value would lead to " $K_{IC}$ " value of  $3.2 \text{ MPa.m}^{1/2}$ .

The equivalent critical flaw radius scale derived from that of UTS, on the basis of equation [5] and for  $K_{IC} \simeq 3 \text{ MPa.m}^{1/2}$ , is shown in figures 1 and 2. It is noteworthy that the order of magnitude of the critical flaw size is  $0.3 \mu\text{m}$  for the filaments submitted to step 2. This small value could explain that the defects are not apparent from the SEM micrograph shown in figure 3a.

### 3.3 - Discussion of the effect of step 1 on filament UTS

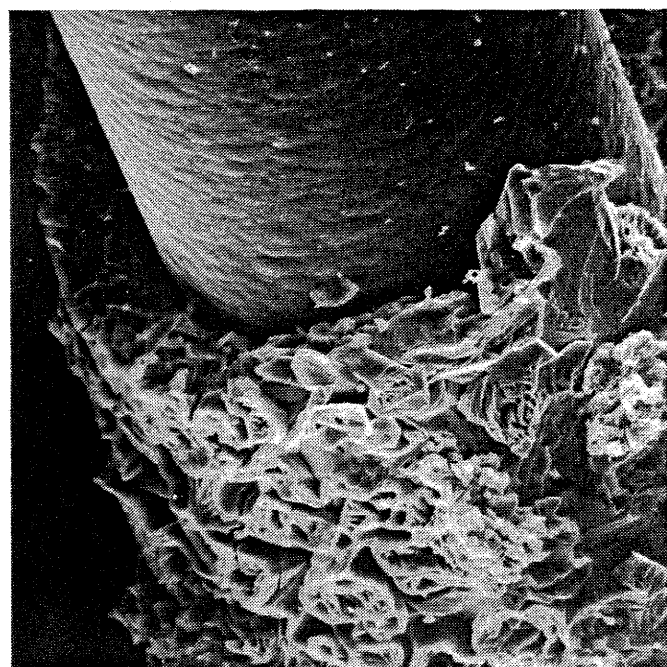
The simple precipitation of  $\text{K}_2\text{ZrF}_6$  microcrystals, from a saturated hot aqueous solution (i.e. at about  $80^\circ\text{C}$ ), on the filament surface does not significantly lower the mean UTS of the filaments, as shown in figure 1 and table 1. Furthermore, the amount of  $\text{K}_2\text{ZrF}_6$  deposited on the filament has no noticeable effect on the UTS value. As a result, the single Weibull plot given in figure 1 is representative of all the data obtained after the step 1 treatment.

As shown in figure 4, for two different surface amounts of  $\text{K}_2\text{ZrF}_6$ , the deposit is not strongly adherent to the filament surface. It has been even partly detached from the substrate (fig.4b) when the filament was broken into small fragments for the purpose of the SEM analysis although it was initially continuous and homogeneous in thickness. At the beginning of the precipitation process (fig.4a), the deposit is not continuous, as could be expected for a nucleation step. The  $\text{K}_2\text{ZrF}_6$  crystals are different in both size and morphology : (i) the smallest crystals are acicular with their long edge parallel to the filament surface whereas (ii) some of the largest ones have a hexagonal habit with the hexagonal axis perpendicular to the filament axis. This growth of hexagonal shaped crystals seems to be later on favored in thicker continuous deposits as they are shown on figure 4c.  $\text{K}_2\text{ZrF}_6$



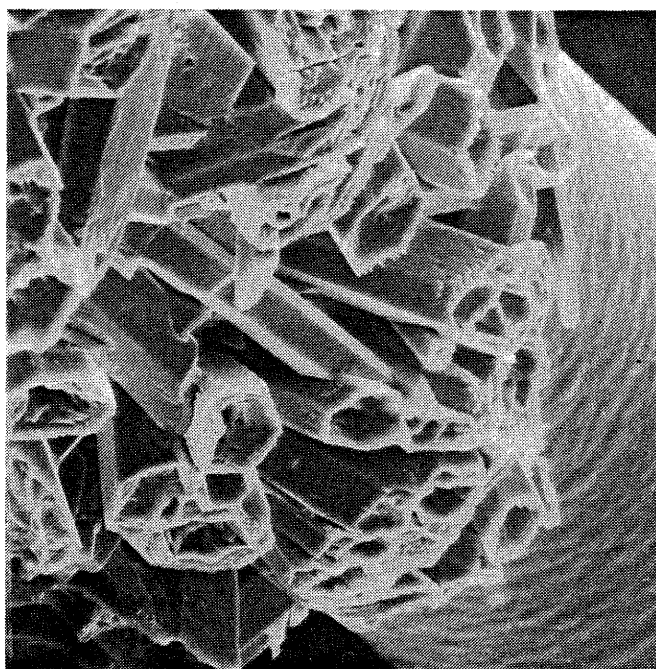


(a) X 700



(b) X 700

└ 10 μm



(c) X 700

Figure 4 : Morphology of the  $\text{K}_2\text{ZrF}_6$  deposited in step 1

(a)  $1 \text{ mg.cm}^{-2}$  of  $\text{K}_2\text{ZrF}_6$

(b)  $11 \text{ mg.cm}^{-2}$  of  $\text{K}_2\text{ZrF}_6$

(c) well-developed  $\text{K}_2\text{ZrF}_6$   
crystals of hexagonal shape

crystallize in the orthorhombic structure and the fact that the parameters  $b$  (11.40 Å) and  $a$  (6.58 Å) are in a ratio of about  $\sqrt{3}$  gives the structure a pseudo-hexagonal character (20).

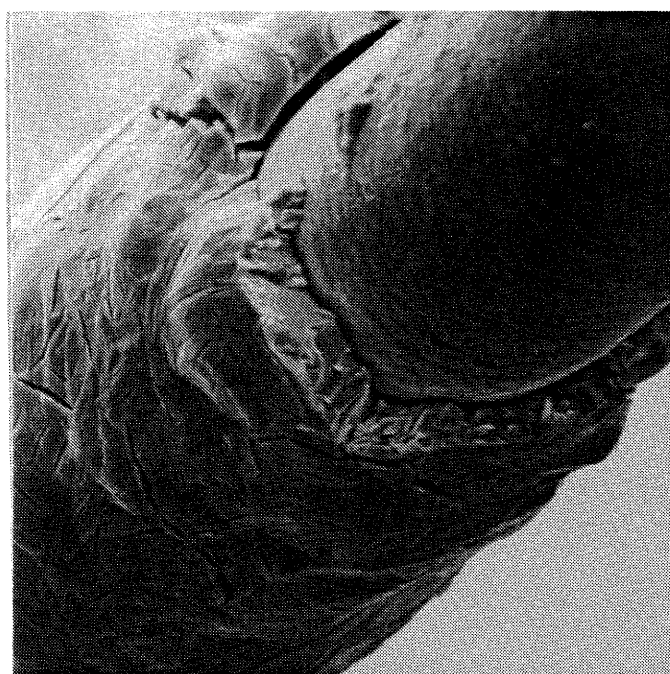
### 3.4- Discussion of the effect of step 2 on filament UTS

The median UTS of filaments, which have been submitted to the step 2 of the  $K_2ZrF_6$ -process, decreases first sharply as a function of the surface amount of fluoride deposited on the filament prior to the heat treatment, **then it remains constant**, at a level of 80 % of the initial value, even for  $K_2ZrF_6$  amounts as large as  $30 \text{ mg.cm}^{-2}$ , as shown in figure 2. Chemical interactions between the filament surface and  $K_2ZrF_6$  during the exposure at  $650^\circ\text{C}$  are thought to be responsible for the filament strength loss.

As shown in figure 5, the  $K_2ZrF_6$  deposit resulting from the step 2 treatment is no longer made of well faceted crystals (fig.4) but appears **to have melted** during the annealing at  $650^\circ\text{C}$  (the molten state appearance being kept by quenching at room temperature). Furthermore and as already mentioned in section 3.3, the deposit is not strongly bonded to the filament surface, a feature which is in agreement with the fact that the strength loss due to this treatment is only limited. The molten state appearance of the deposit is consistent with the related  $KF\text{-}ZrF_4$  phase diagram given by Kaufman (21) according to which  $K_2ZrF_6$  (or  $2 \text{ KF}\cdot\text{ZrF}_4$ ) undergoes at  $590^\circ\text{C}$  a peritectic decomposition :



Assuming that the main features of the phase diagram, which has been established for a pressure of one atmosphere, are kept when the pressure is lowered to 3.7 Pa (the residual pressure in the sealed glass silica tubes), the occurrence of the

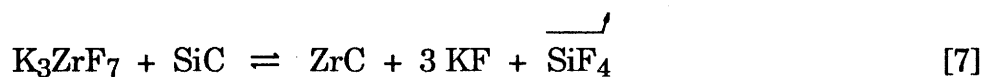


X 450      └ 10  $\mu\text{m}$

Figure 5 : Morphology of the  $\text{K}_2\text{ZrF}_6$  deposit after (i) annealing at  $650^\circ\text{C}$  for 15 min in silica tubes sealed under vacuum (residual pressure : 1.2 MPa) and (ii) quenching at room temperature

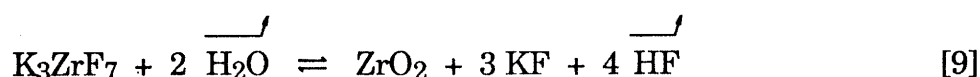
peritectic equilibrium [6] combined with quenching explains the morphology of the deposit shown in figure 5.

The AES depth profile analysis given in figure 6 shows that chemical interactions have taken place during the annealing treatment at the filament surface. As a result, both **oxygen** and **zirconium** are present near the surface. Although a detailed thermodynamic study has not been performed, chemical reactions between SiC or/and Si (the filament contains 6 at % of free silicon), on the one hand, and  $K_3ZrF_7$  or/and the liquid phase resulting from equation [6], on the other hand, could have occurred at 650°C yielding some diffusion of zirconium in the filament. As a matter of fact, the calculation of the Gibbs free energy variation of the two following reactions :



gives rise to  $SiF_4$  equilibrium partial pressures respectively of the order of  $10^{-6}$  and  $10^{-4}$  Pa. These low values support the assumption that reactions [7] and [8] are not well developed in the conditions of our experiments.

The **presence of oxygen** is probably due to different sources of contamination : (i) the initial filament surface contains some oxygen (see insert in fig.6) presumably as  $SiO_2$  which will be dissolved in the fluoride liquid arising from the peritectic equilibrium [6], (ii) some residual water has been undoubtedly encapsulated with the filaments in the sealed silica tube (either as adsorbed species on the silica wall or/and entrapped into the  $K_2ZrF_6$  deposit). This water, whatever its origin, may give rise to the hydrolysis of  $K_3ZrF_7$  at 650°C and the formation of zirconia according to the following equation :



whereas HF may act as a transport agent to extract oxygen from the silica wall of

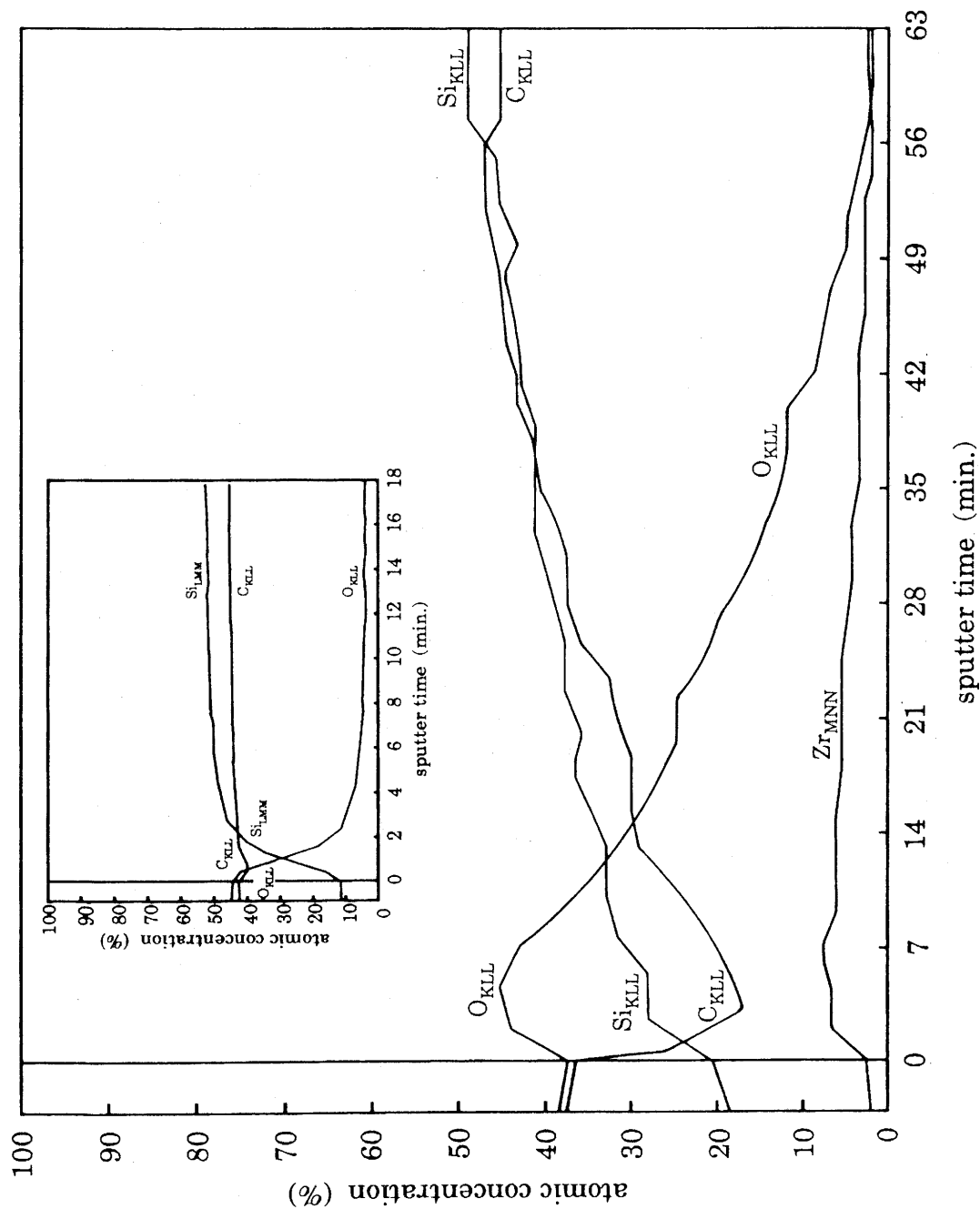
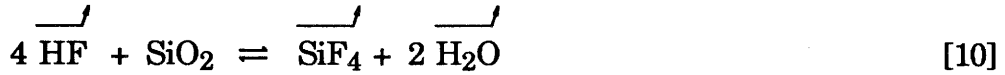


Figure 6 : AES depth profile analysis of silicon, carbon, oxygen and zirconium near the SiC-filament surface for a filament extracted from  $\text{K}_2\text{ZrF}_6$  (step 2).

Insert : AES analysis of the as-received  $\text{SiC}(\Sigma)$  filaments.

Sputter rate : 15 and 2 (insert)  $\text{nm}\cdot\text{min}^{-1}$  (standard :  $\text{Ta}_2\text{O}_5$ )

the tubes :



It thus appears that the interactions that may have occurred between the SiC-filament, the  $\text{K}_2\text{ZrF}_6$  deposit and the silica container during the step 2 of the  $\text{K}_2\text{ZrF}_6$ -process are complex. However, they must have been (i) of relatively low intensity since the resulting filament strength loss is limited, i.e. only about 20% and (ii) homogeneous over the filament surface regarding the increase in Weibull modulus (i.e. from 8 to 20).

### 3.5 - Discussion of the effect of step 3 on filament UTS

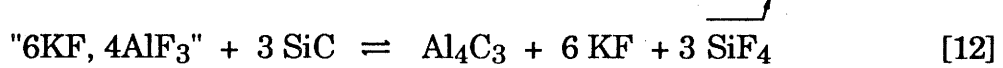
As shown in figure 2 and table 1, the step 3 of the  $\text{K}_2\text{ZrF}_6$ -process results in a filament strength loss which is **more significant** than that observed for the step 2. Moreover, the residual filament strength regularly decreases as the amount of  $\text{K}_2\text{ZrF}_6$  deposited on the filament during step 1 increases. However, it should be mentioned that **untreated** filaments submitted to step 3 undergo a strength loss which is of the order of 30%. Finally, as far as the amount of  $\text{K}_2\text{ZrF}_6$  deposited in step 1 is less than  $10 \text{ mg.cm}^{-2}$  the SiC-filaments have a residual UTS which is still of the order of 50% that of the as-received reinforcement.

The mechanism responsible for the filament strength loss has been identified from experiments performed under very **severe interaction conditions**. Namely, pure liquid aluminum was poured on SiC( $\Sigma$ ) filaments coated with a thick layer of  $\text{K}_2\text{ZrF}_6$  (i.e.  $8 \text{ mg.cm}^{-2}$  corresponding to a thickness of about  $20 \text{ }\mu\text{m}$ ) and the whole maintained at  $800^\circ\text{C}$  for 15 min. After cooling, the aluminum matrix was dissolved in a methanol solution of bromine and the extracted filaments were observed in SEM and analysed by EPMA.

As shown in figure 7 (a, b, c), the surface of the extracted filament is covered with small hexagonal crystals, made of carbon and aluminum combined in an atomic ratio Al/C close to 4/3 (on the basis of EPMA data) and thus identified to the **aluminum carbide**  $\text{Al}_4\text{C}_3$ . The nature of the crystals was confirmed by an AES depth profile analysis performed on the composite before chemical extraction (fig.8). The fact that  $\text{Al}_4\text{C}_3$  is found at the filament surface is in agreement with the conclusions drawn by many authors according to which SiC-based reinforcements react with liquid aluminum to form  $\text{Al}_4\text{C}_3$  crystals having their roots in the reinforcements and silicon which is dissolved in the liquid (22) :



$\text{Al}_4\text{C}_3$  could also result from a reaction between SiC and the mixture of fluorides " $6\text{KF}, 4\text{AlF}_3$ " formed as aluminum reacts with " $2\text{KF}, \text{ZrF}_4$ " during the  $\text{K}_2\text{ZrF}_6$ -process (2), according to the following equation :



In fact, the equilibrium partial pressure of  $\text{SiF}_4$  deduced from the evaluation of the Gibbs free energy variation of reaction [12] ( $700^\circ\text{C}$ ) is very low, i.e.  $10^{-12} \text{ Pa}$ . Therefore, we assume that reaction [12] doesn't proceed.

When in a next step, the  $\text{Al}_4\text{C}_3$ -coated SiC-filament is treated with an aqueous solution of sodium hydroxide, the aluminum carbide crystals are dissolved leaving pits at the filament surface (fig.7d). Therefore, the surface defects, discussed in section 3.1 and which are responsible for the filament strength loss after the step 3, are  **$\text{Al}_4\text{C}_3$  crystal prints in the filament surface** due to chemical reaction [11] and to the NaOH-chemical extraction procedure. These defects act as stress concentrators (notch effect) at the filament surface, their effect on the filament UTS depending on the thickness of the  $\text{Al}_4\text{C}_3$  layer (fig.2).

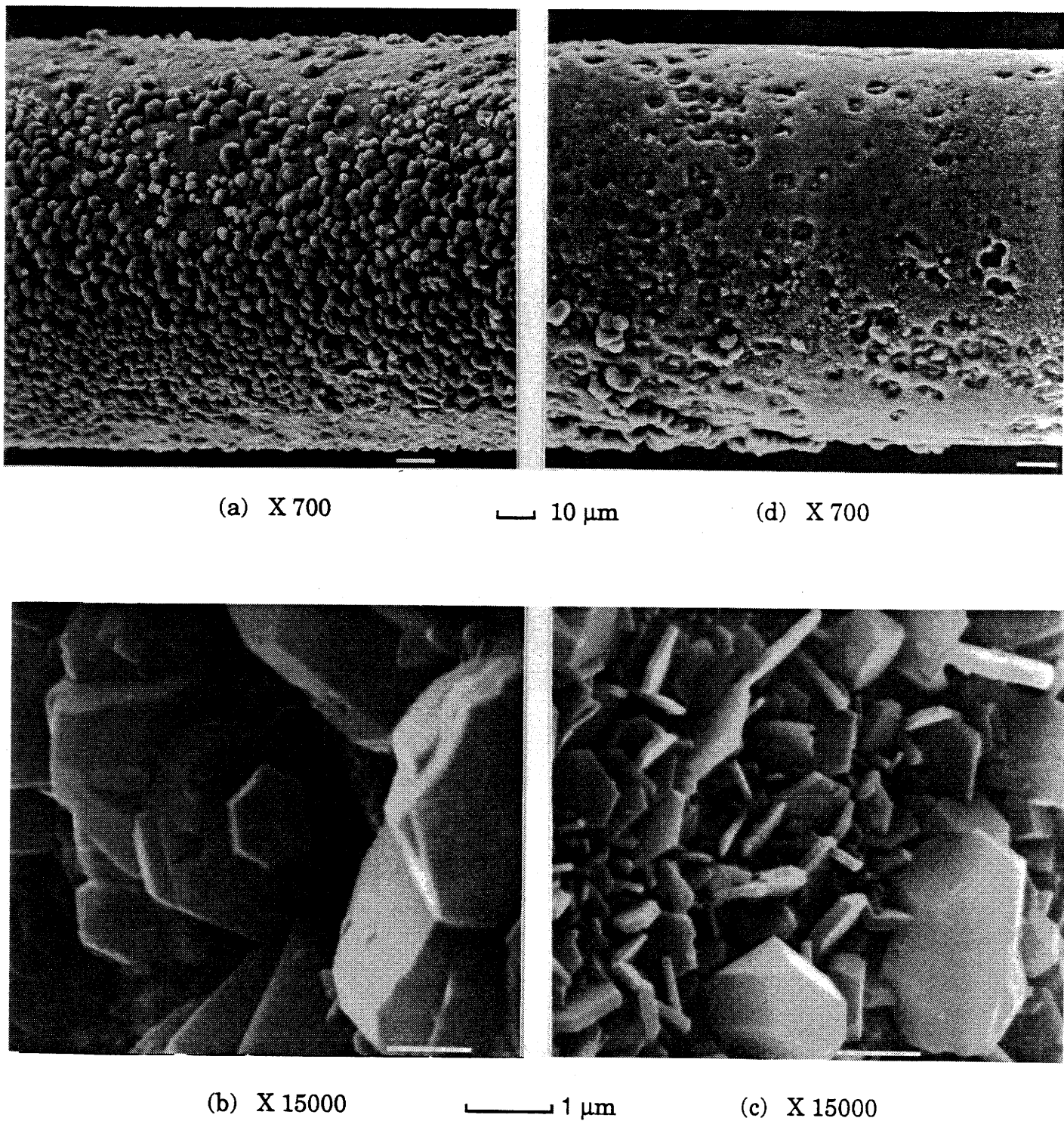


Figure 7 : SEM micrographs of a SiC( $\Sigma$ )-filament coated with  $\text{K}_2\text{ZrF}_6$ , maintained in liquid aluminum for 15 min at  $800^\circ\text{C}$  then treated with: a methanol solution of bromine (a, b, c) and an aqueous solution of sodium hydroxide (d). The crystals are  $\text{Al}_4\text{C}_3$ . Their dissolution in NaOH leaves pits at the filament surface.



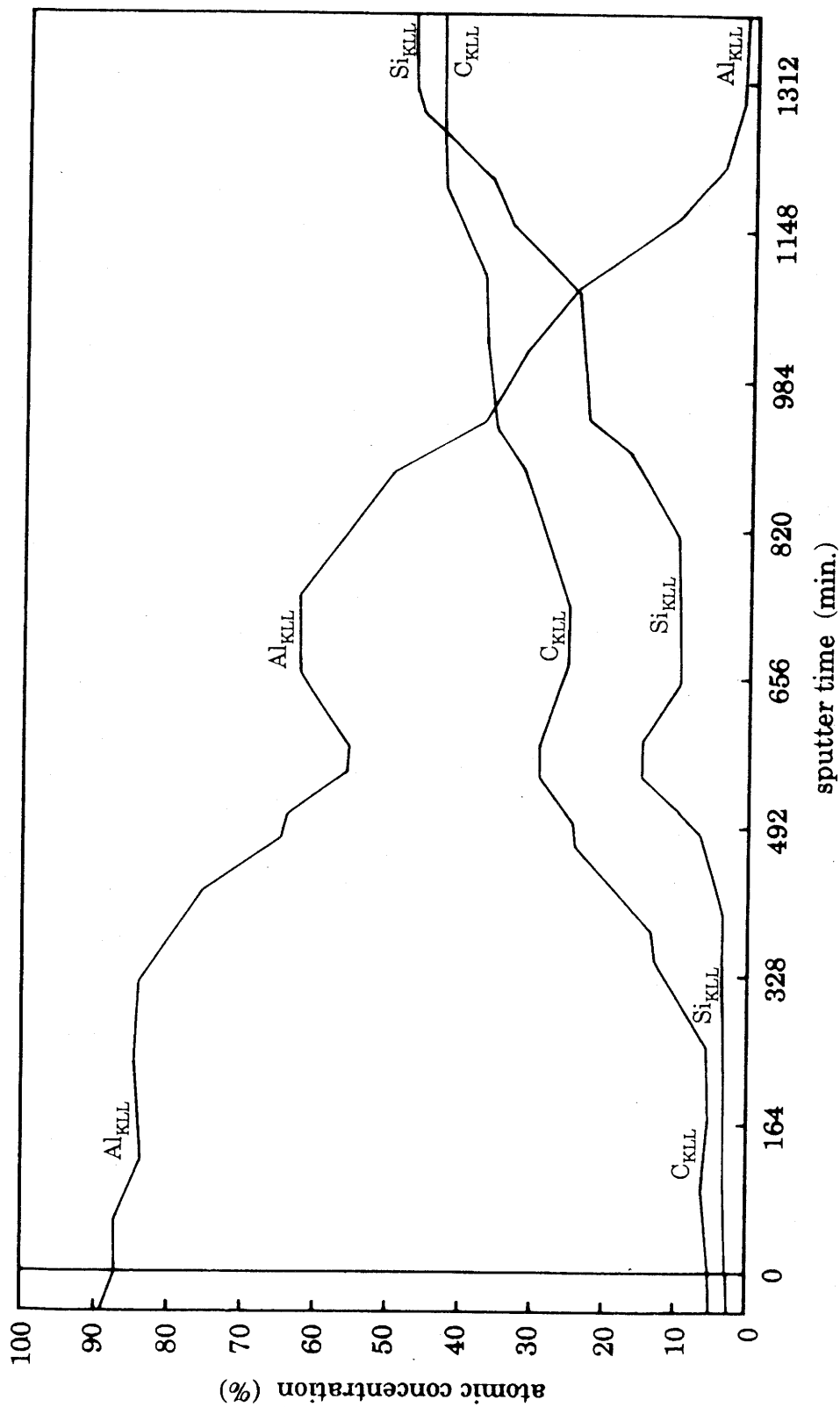


Figure 8 : AES depth profile analysis of silicon, carbon and aluminium near the SiC/Al interface, for a SiC-filament covered with  $\text{K}_2\text{ZrF}_6$  ( $8 \text{ mg/cm}^2$ ) and maintained 15 min in aluminium at  $800^\circ\text{C}$ . Sputter rate :  $25 \text{ nm}\cdot\text{min}^{-1}$  (standard  $\text{Ta}_2\text{O}_5$ )

It is worthy of note that the same experiment performed with **untreated** SiC( $\Sigma$ ) filaments (step 3) results in the formation of less aluminum carbide, as already mentioned, and thus to a lower filament strength loss. Therefore, it seems that the  $K_2ZrF_6$ -process **increases the kinetics of growth of  $Al_4C_3$**  which is anyhow a normal product of the interaction between liquid aluminum and a SiC reinforcement. This activation phenomenon can be explained on the basis of the following features of the  $K_2ZrF_6$ -process, which have been discussed in details elsewhere (2); the  $K_2ZrF_6$ -process : (i) allows a better contact between the SiC reinforcements and liquid aluminum since it enhances their wetting ability and dissolves the alumina film covering the metal (this oxide film may act as a diffusion barrier when no fluoride treatment is applied) and (ii) increases the SiC/Al interface temperature due to the exothermicity of the reactions which are involved.

#### 4 - CONCLUSIONS

It has been shown that the  $K_2ZrF_6$ -process does not significantly lower the failure strength of SiC-reinforcement by itself (the strength loss due to the fluorides species under conditions representative of a casting procedure is of the order of 20% only). On the other hand, it has been observed that the kinetics of growth of  $Al_4C_3$ , which is a normal product of the interaction between SiC and Al, is increased with an additional loss of strength of the reinforcement. This indirect consequence of the  $K_2ZrF_6$  treatment is thought to be mainly related to the cleaning effect of the fluoride species on the SiC/Al interfaces. Obviously, the notch effect due to the failure of the brittle  $Al_4C_3$  layer on the SiC-filament surface, in SiC/Al composites processed according to the  $K_2ZrF_6$ -process, could be : (i) reduced by an optimization of the fluoride layer thickness and casting parameters and (ii) even suppressed by utilizing SiC-filaments coated with a layer of a soft material (e.g. pyrocarbon) acting as a mechanical fuse (23-24). Therefore, in addition to the simplicity of the procedure

according to which it can be used to produce aluminum matrix composites, the  $K_2ZrF_6$ -process does not significantly alter by itself the strength of the reinforcement, under optimized conditions.

## **ACKNOWLEDGEMENTS**

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## **CONCLUSIONS GENERALES**

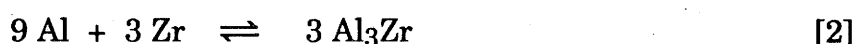
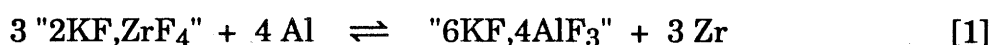
## CONCLUSIONS GENERALES

Ce travail s'inscrivait dans le cadre général des recherches conduites au Laboratoire de Chimie du Solide du CNRS sur les **matériaux composites à matrice d'alliages légers** en vue : (i) de développer des procédés d'élaboration originaux au plan scientifique et technique tout en étant réaliste au plan industriel, (ii) de préciser les interactions physico-chimiques entre fibre et matrice aux températures d'élaboration et d'utilisation du matériau et (iii) de rechercher les corrélations susceptibles d'exister entre le comportement mécanique global du matériau et les aspects physico-chimiques, notamment interfaciaux.

La présente étude fait suite au travail de thèse de J. P. ROCHER qui avait été consacré à la mise au point d'un procédé de prétraitement des renforts fibreux à base de carbone ou de carbure de silicium - **le procédé au  $K_2ZrF_6$**  - en vue d'améliorer leur **aptitude au mouillage** par les alliages d'aluminium et de développer une méthode d'élaboration des composites correspondants qui puisse être aisément transférée au plan industriel. Rappelons que dans son principe, le procédé repose sur une précipitation de microcristaux de  $K_2ZrF_6$ , à partir d'une **solution aqueuse** à température proche de l'ébullition, à la surface des fibres. Ainsi prétraité, le renfort fibreux devient mouillable ( $\theta < 90^\circ$ ) par les alliages d'aluminium (à 700-800°C) et peut être imprégné selon les techniques habituelles de la fonderie des alliages légers (e. g. par coulée par gravité). Enfin, un autre avantage du procédé réside dans le fait qu'il fait appel à des produits qui étaient déjà utilisés comme **flux de désoxydation** et qu'il peut être mis en oeuvre à l'air.

Notre étude, à caractère fondamental, avait pour objectif d'identifier les mécanismes physico-chimiques impliqués dans la mise en oeuvre du procédé au  $K_2ZrF_6$  et d'établir s'ils modifiaient le pouvoir renforçant des fibres de façon significative. Elle nous a permis ainsi : (1) d'expliquer l'efficacité du procédé en termes d'amélioration du mouillage dans le système SiC/Al, (2) de définir la participation du fluorure double  $K_2ZrF_6$  ou/et des produits dérivés à l'affaiblissement mécanique de renforts filamentaires modèles de carbure de silicium et (3) d'attribuer, par une approche numérique, à chacun des paramètres physiques associés au procédé, un rôle spécifique dans l'amélioration de l'aptitude à l'imprégnation par l'aluminium liquide de préformes modèles à base de SiC.

(1) - En ce qui concerne les **bases physico-chimiques** susceptibles de rendre compte de **l'amélioration du mouillage**, nous avons montré que le schéma réactionnel suivant peut être proposé :



Il est en effet très favorisé d'un point de vue thermodynamique puisqu'à 973 K les variations d'enthalpie libre de Gibbs des réactions [1] et [2] sont respectivement - 306,4 et - 487,2 kJ.mol<sup>-1</sup>. Ce schéma réactionnel reprend en partie les mécanismes qui avaient été antérieurement proposés par LUNDIN ainsi que par BUSCHE et SEMENOV pour rendre compte du rôle que pouvait jouer  $K_2ZrF_6$  dans l'élaboration de feuilles bimétalliques acier/aluminium. Nous avons dû, dans l'écriture de la réaction [1], les modifier pour tenir compte du fait qu'aux températures considérées,  $K_2ZrF_6$  est décomposé avec formation d'un liquide et de  $K_3ZrF_7$  (le mélange étant représenté par "2KF,ZrF<sub>4</sub>"). De même, au niveau du second membre, la notation "6KF,4AlF<sub>3</sub>" a été utilisée pour représenter le mélange - liquide +  $K_3AlF_6$  - qui se forme aux



températures considérées (et dont la solidification conduit à  $K_3AlF_6 + KAlF_4$ , après retour à l'ambiante).

Les réactions [1] et [2] sont **très exothermiques** ce qui justifie le rougeoiment qui est observé lorsqu'une préforme fibreuse prétraitée au  $K_2ZrF_6$  est mise en contact avec un bain d'aluminium liquide. Les calculs ont en effet montré qu'une préforme modèle (ayant une porosité de 20% comparable à celle d'une préforme fibreuse 2D-SiC/SiC réelle) ainsi prétraitée et préchauffée à 650°C subissait une **élévation de température de 150°C** lorsqu'elle était imprégnée par de l'aluminium liquide coulé à 800°C.

Par ailleurs, la réaction [1] conduit à la formation de fluorures doubles d'aluminium et de potassium, **en partie liquide**, qui ont la propriété de **dissoudre la couche d'alumine** qui recouvre la surface de l'aluminium liquide et inhibe le mouillage de la céramique par le métal. Pour établir cette importante propriété, nous avons dû, dans un premier temps, procéder à une étude expérimentale des mélanges  $K_3AlF_6-Al_2O_3$  par ATD et diffraction des rayons X et, dans un second temps, calculer une partie du diagramme de phases du **système ternaire réciproque  $KF-AlF_3-Al_2O_3-K_2O$**  (sur la base de la théorie CIS pour décrire la phase liquide). Ce travail nous a permis de tracer la section verticale " $6KF,4AlF_3$ "- $Al_2O_3$  et de montrer que le mélange de fluorures doubles " $6KF,4AlF_3$ " : (i) était susceptible de dissoudre la pellicule d'alumine dès 520°C et (ii) formait avec l'alumine (pour quelques % d'alumine en moles) un **liquide cryolithique homogène et très fluide à 800°C** (comparable à celui, à base de sodium, utilisé dans la fabrication par électrolyse de l'aluminium).

Lors de l'imprégnation d'une préforme fibreuse de SiC, prétraitée par  $K_2ZrF_6$  et préchauffée à 650°C, le liquide cryolithique qui se forme au niveau des interfaces fibre/matrice quitte ces dernières (en raison de sa fluidité et de sa plus faible densité) pour se rassembler à la surface du métal liquide en entraînant avec lui, sous forme dissoute, l'alumine et permet le **contact direct SiC/Al**. Dans ces conditions, nous

avons pu conclure, en nous appuyant notamment sur une étude récente due à V. LAURENT, que la **dissolution du carbure de silicium dans le métal liquide** (étape limitante de la formation de  $\text{Al}_4\text{C}_3$  par réaction entre SiC et l'aluminium liquide) était à l'origine du mouillage du renfort fibreux.

Il apparaît donc qu'au niveau des processus physico-chimiques susceptibles de justifier l'efficacité du procédé au  $\text{K}_2\text{ZrF}_6$  deux phénomènes jouent un rôle particulièrement important : (i) l'**exothermicité** des réactions interfaciales entre  $\text{K}_2\text{ZrF}_6$  et l'aluminium et (ii) la formation de **fluorures doubles  $\text{KF-AlF}_3$  qui dissolvent l'alumine** en formant un liquide cryolithique drainant l'oxygène vers la surface de l'aluminium liquide. L'extraction de l'oxygène permet ensuite la formation des interfaces vraies SiC/Al, l'abaissement de l'angle de contact (qui passe de  $160^\circ$  à  $75^\circ$  en présence de  $\text{K}_2\text{ZrF}_6$  à  $750^\circ\text{C}$ ) étant lié à la formation de  $\text{Al}_4\text{C}_3$ .

(2) - En ce qui concerne l'**affaiblissement mécanique** du renfort qui pourrait résulter de la mise en oeuvre du procédé au  $\text{K}_2\text{ZrF}_6$ , l'étude que nous avons poursuivie sur un **matériau modèle** (filament CVD de SiC de grand diamètre antérieurement étudié au Laboratoire par R. PAILLER, P. MARTINEAU et Y. LE PETITCORPS ) a permis d'identifier la contribution de chacune des étapes du procédé. Il a paru logique d'utiliser comme critère la résistance à rupture en raison de la sensibilité de cette propriété mécanique aux modifications de l'état de surface de l'éprouvette (pouvant résulter, par exemple, d'une réaction chimique interfaciale avec l'aluminium). Toutes les mesures ont fait l'objet d'un **traitement statistique** (loi de distribution de Weibull à deux paramètres) ce qui nous a conduit à tester, pour chaque étape, une quarantaine d'éprouvettes monofilamentaires.

Les résultats de notre étude ont clairement montré que : (i) l'opération de précipitation des cristaux de  $\text{K}_2\text{ZrF}_6$ , à partir de la solution aqueuse à  $80-100^\circ\text{C}$ , à la surface des filaments et (ii) le recuit à  $650^\circ\text{C}$  des filaments prétraités, n'affaiblissaient

que **très légèrement** la résistance à rupture des filaments (20% au plus). En revanche, en présence d'aluminium, le traitement est sensiblement plus dégradant et nous avons pu justifier cet effet et le relier à des causes physico-chimiques.

En effet, l'observation au MEB des faciès de rupture primaire et de la surface des filaments, une fois extraits de la matrice d'aluminium (dissoute par une solution aqueuse de soude), montre que des **piqûres** se sont formées en surface lors du maintien en température (résultant de l'élaboration du composite SiC/Al par compression à chaud). Ces piqures se sont révélées être les empreintes laissées, après dissolution, par des **microcristaux de  $\text{Al}_4\text{C}_3$**  (dissous, comme l'aluminium, par la soude). L'emploi d'un réactif plus sélectif, i.e. d'une solution de méthanol bromé, a permis de dissoudre la matrice d'aluminium tout en conservant les cristaux de  $\text{Al}_4\text{C}_3$  dont la composition a été établie à la fois par microsonde de Castaing et spectrométrie d'électrons Auger. Ainsi, l'affaiblissement de résistance mécanique des filaments résulte d'un **effet d'entaille** exercé sur le filament par les cristaux fragiles de  $\text{Al}_4\text{C}_3$  formés en surface aux dépens de SiC et dont les racines pénètrent, sous la forme de coins, en profondeur. L'affaiblissement de la résistance des fibres de carbone ou de carbure de silicium, dû à une réaction avec l'aluminium, est un phénomène par ailleurs bien établi.

Il est essentiel de noter que le fluorure  $\text{K}_2\text{ZrF}_6$ , ou/et ses produits de réaction avec l'aluminium, n'interviennent **directement que de façon faible** dans l'affaiblissement de la résistance à rupture du renfort. En revanche, sur la base de l'effet de nettoyage de l'interface SiC/Al (i.e. extraction de l'alumine qui la contamine) et de l'effet thermique (lié à l'exothermicité des réactions), les fluorures contribuent à **activer la cinétique de formation de  $\text{Al}_4\text{C}_3$**  et ont, de ce fait, un rôle indirect sur l'affaiblissement mécanique du renfort (la formation de  $\text{Al}_4\text{C}_3$  dans les composites n'ayant pas fait l'objet du traitement au  $\text{K}_2\text{ZrF}_6$  pouvant se trouver ralenti par un effet de barrière dû à l'alumine).

(3) - En ce qui concerne, enfin, **l'amélioration de l'aptitude à l'imprégnation** du renfort fibreux par l'aluminium, liée au procédé au  $K_2ZrF_6$ , nous avons cru approprié de faire appel à une modélisation numérique qui avait été développée par **J. M. QUENISSET** et ses collaborateurs pour les préformes unidirectionnelles. Afin de ne pas trop nous éloigner des préformes 2D-SiC/SiC, élaborées par densification CVI d'un empilement de tissus de fibres Nicalon et qui avaient servi de base à l'étude expérimentale de **J. P. ROCHER**, nous avons défini une **préforme modèle** constituée d'un empilement hexagonal de cylindres fibreux de SiC, ayant la même porosité (i.e. 20%) que les préformes 2D-SiC/SiC. Cette condition a conduit à donner à ces cylindres un diamètre de 480  $\mu m$  qui est bien du même ordre de grandeur que le diamètre des mèches de fibres Nicalon imprégnées de SiC par CVI, dans les préformes réelles. En revanche, il est clair que la préforme modèle ne restitue pas la morphologie effective du réseau de pores des préformes 2D-SiC/SiC. Cette partie de notre étude a donc essentiellement un caractère comparatif.

Sur la base de **l'approche numérique** qui a été développée pour la préforme modèle, supposée avoir été traitée (ou non) par  $K_2ZrF_6$  puis imprégnée par l'aluminium dans des conditions identiques à celles effectivement utilisées pour les préformes 2D-SiC/SiC, il apparaît que les deux principaux phénomènes physico-chimiques i.e. l'exothermicité des réactions [1] et [2] et l'abaissement de l'angle de contact, ont une influence distincte sur les paramètres d'imprégnation :

- d'une part, **l'exothermicité des réactions** permet d'augmenter de manière significative la profondeur de préforme imprégnée, qui peut même dans certains cas devenir infinie. En effet, la chaleur dégagée in situ par les réactions [1] et [2] compense le refroidissement du métal (la température de la préforme est de 650°C seulement), supposé être coulé à 800°C, au fur et à mesure qu'il progresse dans la préforme en évitant sa solidification prématurée. L'apport de chaleur dû à l'exothermicité des réactions [1] et [2] est particulièrement bénéfique pour les

préformes caractérisées par des fractions volumiques élevées de fibres (pour lesquelles le métal se solidifie à une profondeur inférieure au cm quand elles n'ont pas été traitées par  $K_2ZrF_6$ ).

- d'autre part, l'**abaissement de l'angle de contact** permet de diminuer la pression d'imprégnation qu'il est nécessaire d'appliquer au métal pour qu'il atteigne, avant de se solidifier, une profondeur acceptable au sein de la préforme (i.e. quelques cm).

- le calcul a montré, enfin, qu'une **quantité minimale de  $K_2ZrF_6$** , de l'ordre de  $3 \text{ mg.cm}^{-2}$ , était nécessaire pour maintenir l'aluminium à une température, i.e.  $750^\circ\text{C}$ , où il est suffisamment fluide et où l'angle de contact a une valeur suffisamment faible ( $\theta=75^\circ$ ). Il est intéressant de noter que cette quantité correspond au remplissage complet de la porosité de la préforme par  $K_2ZrF_6$  et qu'elle est proche de l'optimum établi expérimentalement ( $5 \text{ mg.cm}^{-2}$ ) pour la préforme réelle. De même, les calculs ont montré qu'il était possible d'identifier des conditions d'imprégnation pour lesquelles : (i) la **profondeur** d'imprégnation devenait **infinie** ou/et (ii) l'imprégnation pouvait se faire sans appliquer **aucune pression extérieure** sur le métal, autre que la pression métallostatique due au métal lui-même (imprégnation spontanée).

En résumé, la présente étude a permis, nous semble-t-il, d'atteindre les objectifs qui lui avaient été fixés dans la mesure où : (i) les bases physico-chimiques justifiant l'efficacité du procédé ont été dégagées et (ii) l'influence du procédé sur le pouvoir renforçant des fibres a été précisée. Le procédé au  $K_2ZrF_6$  apparaît ainsi de **mise en oeuvre particulièrement simple** puisqu'il peut s'opérer à l'air et ne fait appel qu'à des produits déjà utilisés comme flux désoxydant en fonderie d'alliages légers. De plus, il a été prouvé qu'il s'applique à des préformes fibreuses à base de carbure de silicium ou de carbone, de forme complexe, quelle que soit leur porosité. Le procédé, par l'exothermicité des réactions qu'il implique et l'abaissement de l'angle de

contact, permet l'**imprégnation spontanée**, e. g. par coulée par gravité, et complète des préformes. Cependant, il a également pour conséquence d'activer la formation du **carbure d'aluminium** aux interfaces fibre/matrice et, de **manière indirecte**, d'affaiblir ainsi de façon significative le pouvoir renforçant des fibres.

Sans pour autant remettre en cause l'intérêt du procédé au  $K_2ZrF_6$ , une voie permettant d'éviter l'effet négatif qui vient d'être noté, (et qui est intrinsèquement lié à la réactivité des systèmes C/Al et SiC/Al), serait (i) de faire appel à un renfort comportant un **revêtement compliant** (e. g. de pyrocarbone), en partie consommable, qui protégerait le renfort contre l'effet d'entaille dû aux cristaux de  $Al_4C_3$  (des filaments CVD-SiC(C) existent dans le commerce) et (ii) d'envisager un refroidissement rapide (pour minimiser la durée du contact à haute température entre SiC et Al) tel que ceux qui sont mis en oeuvre en **imprégnation par forgeage liquide**. Dans ce dernier cas, on peut penser, sur la base des conclusions de la présente étude, que les pressions de forgeage liquide (qui sont actuellement de 50 à 100 MPa) pourraient être considérablement abaissées.



## **ANNEXE I**

## **APPLICATION DE LA THEORIE CIS (CONFORMAL IONIC SOLUTION) AUX SYSTEMES TERNAIRES RECIPROQUES**

L'étude expérimentale des systèmes polyconstitués est en général très consommatrice de temps. De plus, la difficulté d'une telle étude augmente très rapidement avec le nombre des espèces considérées. Il est donc utile de pouvoir estimer les propriétés thermodynamiques de ces systèmes.

Afin de mieux comprendre le comportement des solutions ionisées qui jouent un rôle essentiel dans certaines technologies, comme par exemple le procédé électrolytique de Hall-Héroult, des concepts généraux et des théories sur les systèmes de sels fondus ont été développés. Ainsi, grâce à la théorie CIS, l'expression analytique de l'énergie libre de Gibbs de mélange de la phase liquide peut être décrite, ce qui permet de calculer à priori le diagramme de phases de tels systèmes (1). La théorie CIS est une théorie de mécanique statistique qui tient compte de façon rigoureuse des interactions électrostatiques entre les ions de même charge constituant un mélange de sels fondus. Elle ne fait intervenir, dans les expressions qui décrivent les propriétés thermodynamiques de ces mélanges, que les données thermodynamiques des sels constituants purs et de leurs mélanges binaires. La théorie CIS et son extension empirique aux systèmes constitués de charges différentes conduit à des diagrammes calculés, en général en très bon accord avec les mesures expérimentales, comme par exemple, ceux des systèmes  $\text{AlF}_3\text{-LiF-NaF}$ ,  $\text{AlF}_3\text{-CaF}_2\text{-LiF}$ ,  $\text{AlF}_3\text{-CaF}_2\text{-NaF}$  et  $\text{CaF}_2\text{-LiF-NaF}$  intervenant dans le procédé électrolytique de Hall-Héroult (2-9).



Blander et Yosim ont appliqué la théorie CIS au plus simple des systèmes ternaires réciproques (10). Un tel système est constitué de deux cations  $A^+$ ,  $B^+$  et de deux anions  $C^-$ ,  $D^-$ , de charge unitaire, auxquels correspondent les sels AC, BC, AD et BD. La théorie CIS est une théorie de perturbation dans laquelle les sels constituants et leurs mélanges sont générés à partir d'un sel "test" hypothétique utilisé comme référence. Reprenons le développement de Blander et Yosim. Soient  $\lambda$  le paramètre de taille caractéristique du sel "test" et  $\lambda_1, \lambda_2, \lambda_3, \lambda_4$  ceux des sels AC, BC, AD et BD respectivement. On définit alors les quatre paramètres de perturbation  $g_i$  tels que :

$$g_i = \frac{\lambda}{\lambda_i} \quad i=1, 2, 3, 4$$

Selon la statistique de Boltzmann, l'intégrale de configuration du sel "test", qui est un arrangement de N cations et N anions de même charge auquel est associé l'énergie potentielle U, s'écrit :

$$Z = \frac{1}{(N!)^2} \int \dots \int \exp(-U/kT) (d\tau)^{2N}$$

$(d\tau)$  = combinaison des éléments de volume des 2N ions

k = constante de Boltzmann

Pour une configuration ionique donnée du sel "test", U peut s'exprimer selon la somme des interactions au sein de paires d'ions (c: cation, a: anion) par la relation :

$$U = \sum_c^N \sum_a^N u_{ca} + \sum_c \sum_{c'} u_{cc'} + \sum_a \sum_{a'} u_{aa'}$$

L'écriture  $c < c'$  et  $a < a'$  signifie que chaque paire cation-cation, anion-anion est prise en compte une seule fois. A cause de la forte tendance locale à la neutralité

électrique, les configurations pour lesquelles deux ions de même signe sont proches voisins sont peu probables et ne contribuent que de façon négligeable à l'intégrale de configuration. Des mesures de diffraction des rayons X et des neutrons sur des sels fondus ont confirmé cette hypothèse. En conséquence, la majeure variation de  $Z$  qui est due à la variation de la taille des ions du sel "test" peut être reliée aux sommes des rayons cation-anion et aux paramètres de perturbation  $g_i$ . Ainsi, dans les configurations les plus probables,  $u_{cc'}$  et  $u_{aa'}$  sont indépendants des  $g_i$ .

Définissons maintenant un mélange d'ions (Conformal Ionic Mixture) tel que l'énergie d'interaction  $u_{ca}$  pour toute paire cation-anion qu'il contient s'exprime sous la forme d'une somme de deux termes : un premier terme  $h_{ca}(r)$ , qui dépend uniquement de la distance entre les centres cation-anion,  $r$ , telles que l'interaction coulombienne, l'interaction ion-multipole, et un second terme  $f_{ca}(g_i r)$  qui dépend de la taille des ions à travers le produit  $g_i r$ , tel que le potentiel répulsif de sphères dures utilisé par Reiss (1). Alors, pour un "mélange ionique conforme" tel que celui des ions  $A^+$ ,  $B^+$ ,  $C^-$  et  $D^-$  :

$$u_{ca} = f_{ca}(g_i r) + h_{ca}(r)$$

$$h_{ca}(r) = h_1(r) = h_2(r) = h_3(r) = h_4(r)$$

où 1, 2, 3 et 4 désignent respectivement les paires AC, BC, AD et BD

$$U_m = \sum_c \sum_a^{N_A N_C} f_{ca}(g_1 r) + \sum_c \sum_a^{N_B N_C} f_{ca}(g_2 r) + \sum_c \sum_a^{N_A N_D} f_{ca}(g_3 r) + \sum_c \sum_a^{N_B N_D} f_{ca}(g_4 r) \\ + \sum_c \sum_a^N h_{ca}(r) + \sum_c \sum_{c'} u_{cc'} + \sum_a \sum_{a'} u_{aa'}$$

et 
$$Z_m = \frac{1}{N_A! N_B! N_C! N_D!} \int \dots \int \exp(-U_m/kT) (d\tau)^{2N}$$

où  $N = N_A + N_B = N_C + N_D$  (condition de neutralité électrique) et  $N_A$ ,  $N_B$ ,  $N_C$ , et  $N_D$  désignent les nombres de moles d'ions  $A^+$ ,  $B^+$ ,  $C^-$  et  $D^-$ . Or l'énergie libre de Gibbs du mélange,  $G_m$ , est liée à la fonction de partition\* par la relation classique :

$$- G_m/kT = \ln Z_m$$

Le développement au deuxième ordre de  $G_m$  autour de la valeur  $\ln Z$  du sel "test" conduit à :

$$\ln Z_m = (\ln Z_m)_{g=1} + \sum_{i=1}^4 \left( \frac{\ln Z_m}{g_i} \right)_{g=1} (g_i - 1) + \sum_{i=1}^4 \sum_{j=1}^4 \frac{1}{2} \left( \frac{\ln Z_m}{g_i g_j} \right)_{g=1} (g_i - 1)(g_j - 1)$$

l'écriture  $( )_{g=1}$  signifie la valeur limite lorsque tous les  $g_i$  approchent l'unité

avec,

$$\begin{aligned} (\ln Z_m)_{g=1} &= \left[ \ln \left( \frac{(N!)^2}{N_A! N_B! N_C! N_D!} \frac{1}{(N!)^2} \int \dots \int \exp(-U_m/kT) (d\tau)^{2N} \right) \right]_{g=1} \\ &= - (N_A \ln X_A + N_B \ln X_B + N_C \ln X_C + N_D \ln X_D) + \ln Z \end{aligned}$$

la formule de Stirling a été utilisée pour le développement des factorielles et les fractions ioniques sont définies par :

$$X_A = \frac{N_A}{N_A + N_B} = \frac{N_A}{N} = 1 - X_B$$

$$X_C = \frac{N_C}{N_C + N_D} = \frac{N_C}{N} = 1 - X_D$$

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\* Rigoureusement, la fonction de partition est le produit de l'intégrale de configuration et de l'intégrale cinétique. Cependant, la partie cinétique sera volontairement ignorée pour la brièveté du calcul étant donné qu'elle s'élimine systématiquement au moment du résultat final où l'on ne prend en compte que la différence entre les valeurs des grandeurs thermodynamiques du mélange et de ses constituants.

De la même façon pour le sel pur i (i=1, 2, 3, 4) :

$$U_i = \sum_c^N \sum_a^N f_{ca}(g_i r) + \sum_c^N \sum_a^N h_{ca}(r) + \sum_c \sum_{c'} u_{cc'} + \sum_a \sum_{a'} u_{aa'}$$

$$Z_i = \frac{1}{(N!)^2} \int \dots \int \exp(-U_i/kT) (d\tau)^{2N}$$

et le développement de l'énergie libre de Gibbs  $G_i$  autour de la valeur du sel "test" est :

$$- G_i/kT = \ln Z_i = \ln Z + \left( \frac{\ln Z_i}{g_i} \right)_{g=1} (g_i-1) + 1/2 \left( \frac{^2 \ln Z_i}{g_i^2} \right)_{g=1} (g_i-1)^2 + \dots$$

De longs calculs de dérivation et de nombreuses simplifications d'écriture conduisent finalement aux expressions suivantes pour les énergies libres de Gibbs par mole de sel pur i,  $G_i$ , et par mole de mélange,  $G_m$  (10) :

$$- G_i/RT = \ln Z + \frac{F}{Z'} (g_i-1) + 1/2 \left[ \frac{1}{Z'} (J + \mathcal{N}K + \mathcal{N}L + \mathcal{N}^2 M) - \left( \frac{F}{Z'} \right)^2 \right] (g_i-1)^2$$

$$- G_m/RT = \ln Z - X_A \ln X_A - X_B \ln X_B - X_C \ln X_C - X_D \ln X_D$$

$$+ \sum_c \sum_a X_c X_a \left\{ \frac{F}{Z'} (g_i-1) + 1/2 \left[ \frac{1}{Z'} (J + \mathcal{N}K + \mathcal{N}L + \mathcal{N}^2 M) - \left( \frac{F}{Z'} \right)^2 \right] (g_i-1)^2 \right\}$$

$$- X_C X_D 1/2 \left[ \frac{1}{Z'} (\mathcal{N}L + \mathcal{N}^2 M) - \left( \frac{F}{Z'} \right)^2 \right] [X_A (g_1-g_3)^2 + X_B (g_2-g_4)^2]$$

$$- X_A X_B 1/2 \left[ \frac{1}{Z'} (\mathcal{N}L + \mathcal{N}^2 M) - \left( \frac{F}{Z'} \right)^2 \right] [X_C (g_1-g_2)^2 + X_D (g_3-g_4)^2]$$

$$+ X_A X_B X_C X_D 1/2 \left[ \frac{\mathcal{N}^2 M}{Z'} - \left( \frac{F}{Z'} \right)^2 \right] (g_1 + g_4 - g_2 - g_3)^2$$

$\mathcal{N}$  désigne le nombre d'Avogadro

$$Z' = (\mathcal{N}!)^2 Z$$

F, J, K, L et M sont des intégrales de la forme :

$$(1/kT) \text{ ou } (1/kT)^2 \int \dots \int \exp(-U_m/kT) (d\tau)^{2N}$$

$$\text{et résultent des dérivations } \left( \frac{Z_i}{g_i} \right)_{g_i=1} \text{ et } \left( \frac{Z_i}{g_i g_j} \right)_{g_i=1}$$

Dans le développement de  $G_m$ , l'expression :

$$\ln Z + \sum_c \sum_a X_c X_a \left\{ \frac{F}{Z} (g_i-1) + 1/2 \left[ \frac{1}{Z} (J + \chi K + \chi L + \chi^2 M) - \left( \frac{F}{Z} \right)^2 \right] (g_i-1)^2 \right\}$$

peut aussi s'écrire :

$$\begin{aligned} \ln Z + \sum_c \sum_a X_c X_a \left\{ -G_i/RT - \ln Z \right\} \\ = \ln Z - \sum_c \sum_a X_c X_a (-G_i/RT) - \ln Z \quad \text{puisque } \sum_c \sum_a X_c X_a = 1 \end{aligned}$$

Par ailleurs, l'expression extrapolée de  $G_m$  dans le cas où le mélange est constitué de deux sels uniquement, par exemple les sels AC et AD, notés 1 et 3 respectivement, est :

$$\begin{aligned} -G_m^{1-3}/RT = & -X_C \ln X_C - X_D \ln X_D - X_C G_1/RT - X_D G_3/RT \\ & - X_C X_D 1/2 \left[ \frac{1}{Z} (\chi L + \chi^2 M) - \left( \frac{F}{Z} \right)^2 \right] (g_1-1)(g_3-1) \end{aligned}$$

que l'on peut aussi écrire :

$$G_m^{1-3} = RT (X_C \ln X_C + X_D \ln X_D) + X_C G_1 + X_D G_3 + \Delta G_{1-3}^E$$

où  $\Delta G_{1-3}^E$  est l'énergie libre de Gibbs d'excès de formation du mélange 1-3 référée aux sels 1 et 3. De la même façon, on pourrait définir  $\Delta G_{1-2}^E$ ,  $\Delta G_{2-4}^E$  et  $\Delta G_{3-4}^E$ .

Compte-tenu de ces deux remarques, l'expression simplifiée de l'énergie libre de Gibbs du mélange des ions  $A^+$ ,  $B^+$ ,  $C^-$  et  $D^-$  devient :

$$G_m = RT (X_A \ln X_A + X_B \ln X_B + X_C \ln X_C + X_D \ln X_D) + \sum_c \sum_a X_c X_a G_i \\ + X_A \Delta G_{1-3}^E + X_B \Delta G_{2-4}^E + X_C \Delta G_{1-2}^E + X_D \Delta G_{3-4}^E \\ - X_A X_B X_C X_D P (g_1 + g_4 - g_2 - g_3)^2$$

avec  $P = 1/2 \left[ \frac{N^2 M}{Z'} - \left( \frac{F}{Z'} \right)^2 \right]$

et rappelons que 1, 2, 3 et 4 désignent les sels AC, BC, AD et BD respectivement.

Seul le dernier terme de cette expression ne peut se déduire de la théorie CIS.

Cependant, par comparaison avec le terme correspondant de la théorie du quasi-réseau (11), il est pris proportionnel à  $\Delta G^2$  (10) où  $\Delta G$  est l'énergie libre de Gibbs standard associée à la relation d'échange :



Le coefficient de proportionnalité est  $-1/2ZRT$ .  $Z$  est le nombre de coordination du quasi-réseau. Ce dernier terme rend compte du mélange non aléatoire des ions dans la solution étant donnée la relation [1].

Alors, puisque :

$$\sum_c \sum_a X_c X_a G_i = X_A X_C G_{AC} + X_A X_D G_{AD} + X_B X_C G_{BC} + X_B X_D G_{BD} \\ = X_A X_C [\Delta G_{AC} + G_A^\circ + G_C^\circ] + X_A X_D [\Delta G_{AD} + G_A^\circ + G_D^\circ] \\ + X_B X_C [\Delta G_{BC} + G_B^\circ + G_C^\circ] + X_B X_D [\Delta G_{BD} + G_B^\circ + G_D^\circ] \\ = \sum_c \sum_a X_c X_a \Delta G_i^\circ + X_A G_A^\circ + X_B G_B^\circ + X_C G_C^\circ + X_D G_D^\circ$$

l'énergie libre de Gibbs de formation par mole de mélange de la phase liquide du système ternaire réciproque AC, BC, AD, BD référée aux éléments simples A, B, C et D pris dans leur état standard s'exprime par la relation :

$$\begin{aligned}
 \Delta G_m &= G_m - X_A G_A^\circ - X_B G_B^\circ - X_C G_C^\circ - X_D G_D^\circ \\
 &= RT (X_A \ln X_A + X_B \ln X_B + X_C \ln X_C + X_D \ln X_D) \\
 &\quad + \sum_c \sum_a X_c X_a \Delta G_i^\circ + X_A \Delta G_{1-3}^E + X_B \Delta G_{2-4}^E + X_C \Delta G_{1-2}^E + X_D \Delta G_{3-4}^E \\
 &\quad - X_A X_B X_C X_D \Delta G[1]^2 / 2ZRT
 \end{aligned}$$

La théorie CIS a été étendue de façon empirique par M. L. Saboungi et M. Blander aux systèmes ternaires réciproques constitués d'ions de charges différentes (4). Comme T. Forland l'avait déjà proposé, avec succès, dans le cas des systèmes binaires, il s'agit de remplacer dans l'expression de l'énergie libre de Gibbs d'excès les fractions ioniques (X) par les fractions d'équivalents (Y), tout en conservant les fractions ioniques dans l'expression du terme de mélange idéal. Soit le système ternaire réciproque  $A_{qC}C_{qA}-A_{qD}D_{qA}-B_{qC}C_{qB}-B_{qD}D_{qB}$  (noté ultérieurement AC-AD-BC-BD) basé sur le mélange des ions  $A^{+qA}$ ,  $B^{+qB}$ ,  $C^{+qC}$ ,  $D^{+qD}$ , et auquel est associé la relation d'échange :

$$(q_A q_C)^{-1} AC + (q_B q_D)^{-1} BD - (q_A q_D)^{-1} AD + (q_B q_C)^{-1} BC \quad [2]$$

Les fractions d'équivalents sont définies par :

$$Y_A = \frac{q_A N_A}{q_A N_A + q_B N_B} = \frac{q_A N_A}{N} = 1 - Y_B$$

$$Y_C = \frac{q_C N_C}{q_C N_C + q_D N_D} = \frac{q_C N_C}{N} = 1 - Y_D$$

où  $N_A, N_B, N_C$  et  $N_D$  sont les nombres de moles d'ions  $A^{+q_A}, B^{+q_B}, C^{-q_C}$  et  $D^{-q_D}$

$N = q_A N_A + q_B N_B = q_C N_C + q_D N_D$  traduit la condition d'électroneutralité

L'énergie libre de Gibbs de formation de la phase liquide contenant  $N$  moles d'équivalents s'exprime selon la relation :

$$N \Delta G_m = RT \sum_c \sum_a N_{ca} \ln a_{ca}$$

où  $\Delta G_m$  est l'énergie libre de Gibbs par mole d'équivalent

$N_{ca}$  est le nombre de moles de l'espèce  $ca$  avec  $ca = AC, AD, BC, BD$

$a_{ca}$  est l'activité de chaque composé, définie selon :

$$a_{AC} = X_A^{q_C} X_C^{q_A} \ln \gamma_{AC}$$

$$a_{AD} = X_A^{q_D} X_D^{q_A} \ln \gamma_{AD}$$

$$a_{BC} = X_B^{q_C} X_C^{q_B} \ln \gamma_{BC}$$

$$a_{BD} = X_B^{q_D} X_D^{q_B} \ln \gamma_{BD}$$

$\gamma_{ca}$  est le coefficient d'activité du composé  $ca$



Donc,

$$\begin{aligned} \Delta G_m = RT/N [ & N_{AC} \ln X_A^{qC} X_C^{qA} + N_{BC} \ln X_B^{qC} X_C^{qB} \\ & + N_{AD} \ln X_A^{qD} X_D^{qA} + N_{BD} \ln X_B^{qD} X_D^{qB} ] + RT/N \sum_c \sum_a N_{ca} \ln \gamma_{ca} \end{aligned}$$

Le premier terme, entropie de configuration du mélange idéal, s'exprime en fonction des fractions ioniques :

$$\begin{aligned} \Delta G_m^{id} &= RT/N [ (q_C N_{AC} + q_D N_{AD}) \ln X_A + (q_C N_{BC} + q_D N_{BD}) \ln X_B \\ &+ (q_A N_{AC} + q_B N_{BC}) \ln X_C + (q_A N_{AD} + q_B N_{BD}) \ln X_D ] \\ &= RT/N (N_A \ln X_A + N_B \ln X_B + N_C \ln X_C + N_D \ln X_D) \end{aligned}$$

et le second terme, énergie libre de Gibbs d'excès du mélange référée aux éléments purs A, B, C et D, s'exprime en fonction des fractions d'équivalents par extrapolation du formalisme de la théorie CIS :

$$\begin{aligned} \Delta G_m^{id} &= \sum_c \sum_a Y_c Y_a \Delta G_{ca}^{\circ} / q_a q_c \\ &+ Y_A \Delta G_{AC-AD}^E + Y_B \Delta G_{BC-BD}^E + Y_C \Delta G_{AC-BC}^E + Y_D \Delta G_{AD-BD}^E \\ &- Y_A Y_B Y_C Y_D \Delta G[2]^2 / 2ZRT \end{aligned}$$

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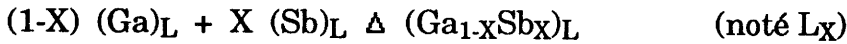
## ANNEXE II

## **ESTIMATION DES GRANDEURS THERMODYNAMIQUES D'UN SYSTEME A PARTIR DE SON DIAGRAMME DE PHASES EXPERIMENTAL**

Un diagramme d'équilibre de phases permet de représenter les domaines de phases stables d'un système pour des conditions données de pression, température et composition. Jusqu'aux années cinquante, les diagrammes de phases ont été essentiellement établis à partir de mesures expérimentales par les métallurgistes ou les céramistes. Parallèlement mais indépendamment, les chimistes mesuraient les grandeurs thermodynamiques de ces phases. Ce n'est que depuis environ quinze ans que l'approche thermodynamique du diagramme de phases a pris son essor. L'état stable d'un système polyconstitué étant associé au minimum de son énergie libre de Gibbs à pression et température constantes, il est possible de calculer à partir des grandeurs thermodynamiques d'un système son diagramme de phases moyennant une description analytique adaptée de ces grandeurs. Ces deux approches du diagramme de phases permettent, une fois mises en cohérence, une description intégrée de l'ensemble des propriétés d'un système.

En dehors des systèmes binaires métalliques les plus usités, le nombre de systèmes pour lesquels il existe à la fois une détermination expérimentale et calculée du diagramme de phases est encore limité. Aussi, lorsque les grandeurs thermodynamiques d'un système ne sont pas disponibles, il est possible de les estimer à partir du diagramme de phases expérimental quand il existe. Les valeurs ainsi obtenues ne sont qu'indicatives et elles devront être confirmées par l'expérience.

Illustrons cette démarche à partir du diagramme de phases expérimental du système binaire Ga-Sb représenté à la figure 1. Ce système est constitué de deux éléments Ga et Sb de structures notées respectivement  $\alpha$  et  $\gamma$ , du composé défini GaSb de structure notée  $\beta$  et enfin d'une phase liquide notée L. Il s'agit de déterminer la variation d'énergie libre de Gibbs qui accompagne la réaction :



Son expression est:

$$\begin{aligned} \Delta G^{L_X} &= G^{L_X} - X G_{\text{Sb}}^{L_X} - (1-X) G_{\text{Ga}}^{L_X} \\ &= RT [X \ln X + (1-X) \ln(1-X)] + \Delta G_{\text{xs}}^{L_X} \end{aligned} \quad [1]$$

où X est la fraction molaire en Sb;  $G_{\text{Sb}}^{L_X}$  et  $G_{\text{Ga}}^{L_X}$  sont les énergies libres de Gibbs de Sb et Ga purs liquides;  $\Delta G_{\text{xs}}^{L_X}$  est l'énergie libre de Gibbs d'excès de formation de la phase liquide; elle peut être modélisée sous la forme :

$$\Delta G_{\text{xs}}^{L_X} = X (1-X) g(X, T) \quad [2]$$

où g est une fonction polynômiale de X et de T.

Le diagramme isobare, isotherme, énergie libre de Gibbs-composition (noté  $\Delta G$ -X) d'un système est un outil pratique pour visualiser et comprendre les problèmes de stabilité et d'énergie des différentes phases en équilibre. Comme il est montré à la figure 2, le diagramme  $\Delta G$ -X du système Ga-Sb, à 800K par exemple, permet de retrouver les limites de phases expérimentales. Etant donné que la grandeur énergie libre de Gibbs ne peut être connue en valeur absolue, seules les variations des énergies libres de Gibbs des différentes phases du système par rapport à une référence qui dans ce cas est commune, à savoir Ga et Sb purs, liquides, sont



indiquées sur ce diagramme. Elles sont définies par les relations :

$$\Delta G^{Lx} = G^{Lx} - X G_{Sb}^{Lx} - (1-X) G_{Ga}^{Lx}$$

$$\Delta G_{Ga}^{L \rightarrow \alpha} = G_{Ga}^{\alpha} - G_{Ga}^L$$

$$\Delta G_{Sb}^{L \rightarrow \gamma} = G_{Sb}^{\gamma} - G_{Sb}^L$$

$$\Delta G_{GaSb}^{L \rightarrow \beta} = G_{GaSb}^{\beta} - 0,5 G_{Ga}^L - 0,5 G_{Sb}^L$$

L'équilibre

$$L_{X_1} \rightleftharpoons (GaSb)_{\beta} \quad [3]$$

observé à 800K sur le diagramme de phases expérimental est illustré sur le diagramme  $\Delta G$ -X par la tangente à la courbe  $\Delta G^{Lx}$  à la composition  $X_1$  menée à partir du point C qui correspond à l'énergie de formation du composé défini  $Ga_{0,5}Sb_{0,5}$  (fig.2). Ce tracé traduit l'égalité des potentiels chimiques des éléments Ga et Sb à 800K dans les deux phases en équilibre. Elle peut s'exprimer par les relations :

$$\overline{\Delta G}_{Ga}^{L_{X_1}} = \overline{\Delta G}_{Ga}^{\beta} \quad [4]$$

$$\overline{\Delta G}_{Sb}^{L_{X_1}} = \overline{\Delta G}_{Sb}^{\beta} \quad [5]$$

En effet, par définition, le potentiel chimique ou énergie libre de Gibbs molaire partielle des éléments Ga et Sb dans une phase  $\delta$  ( $\delta = L_{X_1}, \beta$ ), de composition X, exprimé par rapport aux potentiels chimiques de référence (Ga et Sb purs, liquides) s'écrit:

$$\overline{\Delta G}_{Ga}^{\delta} = \Delta G^{\delta} - X \left( \frac{\partial \Delta G^{\delta}}{\partial X} \right)_{P,T} \quad [6]$$

$$\overline{\Delta G}_{Sb}^{\delta} = \Delta G^{\delta} + (1-X) \left( \frac{\partial \Delta G^{\delta}}{\partial X} \right)_{P,T} \quad [7]$$

Il résulte de ces expressions que l'intersection avec les axes notés (Ga) et (Sb) (fig.2) de la tangente à la courbe  $\Delta G^\delta$  correspond aux potentiels chimiques respectifs  $\overline{\Delta G}_{Ga}^\delta$  et  $\overline{\Delta G}_{Sb}^\delta$ .

La combinaison des équations [1], [2], [4], [5], [6] et [7] conduit à :

$$\overline{\Delta G}_{Ga}^{L_{X_1}} = RT \ln(1-X_1) + X_1^2 g(1-X_1, T) + X_1 (1-X_1) \left( \frac{\partial g}{\partial X} \right)_{X=1-X_1} \quad [8]$$

$$\overline{\Delta G}_{Sb}^{L_{X_1}} = RT \ln X_1 + (1-X_1)^2 g(X_1, T) + X_1 (1-X_1) \left( \frac{\partial g}{\partial X} \right)_{X=X_1} \quad [9]$$

Quand aux variations d'énergie libre de Gibbs associées au passage de Ga et Sb purs, liquides, à Ga et Sb dans un état métastable de structure  $\beta$ , elles peuvent être représentées à l'aide d'une fonction polynômiale de T identique à celles que l'on utilise pour représenter les transitions entre phases stables :

$$\Delta G_{Ga}^{L \rightarrow \beta} = A + B T + \dots \quad [10]$$

$$\Delta G_{Sb}^{L \rightarrow \beta} = A' + B' T + \dots \quad [11]$$

Ainsi, l'égalité des expressions [8] et [10] d'une part et, [9] et [11] d'autre part, qui traduit la condition de l'équilibre [3], fournit deux équations dont les inconnues sont les paramètres de la fonction g et les paramètres A, B, A' et B'. La détermination complète de la fonction  $\Delta G^{Lx}$  suppose donc que l'on écrive et que l'on résolve un système d'équations du type [8,10] et [9,11], dont le nombre doit être égal à celui des inconnues, à partir de l'observation du diagramme de phases expérimental à différentes températures. Dans le cas où il existe des informations expérimentales suffisamment nombreuses, il est maintenant envisageable d'opérer à partir de programmes d'optimisation plus sophistiqués bien que utilisant les mêmes règles de base.



