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Wetting improvement of carbon or silicon carbide by aluminium alloys based on a K_2ZrF_6 surface treatment: application to composite material casting

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A surface treatment with aqueous solutions of K_2ZrF_6 has been carried out to improve, in dramatic manner, the wetting of carbon (or SiC)-base ceramics by liquid light alloys at low temperatures (i.e. within the 700 to 900° C range). The mechanism which is thought to be responsible for the wetting improvement involves two steps: (i) K_2ZrF_6 reacts with aluminium with the formation of K_3AlF_6, other complex fluoride species and intermetallics, (ii) K_3AlF_6 dissolves the alumina thin layer, coating the liquid light alloy and enables the wetting of the ceramics. The mechanism has been worked out from sessile drop experiments, solid state chemistry experiments and composite casting. The K_2ZrF_6 surface treatment appears to be particularly suitable for processing composite materials made of carbon (or SiC) fibrous preforms and aluminium-base matrices according to techniques directly derived from the light alloy foundry.

1. Introduction

During the last decade, the use of aluminium matrix composites (AMC) has been regarded as a way to overcome the main drawbacks of light alloys (i.e. low rigidity as well as low strength, both at room or high temperatures, under static or cyclic loading). As a result, AMCs have been the subject of an important effort of research, particularly in the field of processing [1].

The most suitable techniques for AMC volume production (e.g. in automotive industry) deal with casting processing. One of the advantages of these techniques lies in the fact that the synthesis of the material and its forming to near net shape can be obtained in a single step provided the following two main difficulties are properly solved.

1. Most ceramic fibres (e.g. carbon and silicon fibres) react with liquid aluminium to form aluminium carbide causing a lowering of the fibre strength and an embrittlement of the matrix [2, 3].

2. The ceramic fibres are usually poorly wetted by liquid aluminium at temperatures lower than 950 to 1000° C so that: (i) high pressures are commonly used to infiltrate fibrous ceramic preforms (squeeze casting), or (ii) vigorous stirring is necessary to incorporate short ceramic fibres in liquid or semi-liquid aluminium [4, 5].

Many processes have been suggested to overcome these difficulties [6]. Unfortunately, the most efficient (e.g. Ti–B fibre coating) often significantly raise the AMC production cost and strongly limit any production scale-up. Nevertheless, it has been established recently that at least one of these processes enables the use of common alloy foundry techniques without any sophisticated adjustments. This AMC casting technique is based on a wetting enhancement treatment of the ceramic fibre preform by an aqueous solution of a fluoride salt (i.e. K_2ZrF_6) and has been described in detail elsewhere [7]. The aim of the present paper is to give the fundamentals of the process and to emphasize its efficiency.

2. Basis of the fluoride wetting enhancement treatment

The poor wettability of most ceramics by liquid aluminium and light alloys at low temperatures is thought to be related to the thin layer of alumina which always coats the liquid [8–10]. Therefore, removing this thin layer (i.e. by a chemical reaction taking place near the ceramic surface and resulting in the formation of new species able to dissolve or vaporize alumina) should improve the wetting of ceramic fibrous preforms thus allowing their impregnation by liquid aluminium alloys.

With the purpose of producing AMC by a casting technique, various light alloy foundry fluxes were tested in order to dissolve the alumina layer. Using a flux of K_2TiF_6 (50 wt %)/KBF_4 (50 wt %), carbon fibre preforms were quite successfully impregnated by aluminium–silicon alloys. However, the solubility of these two fluoride salts in common solvents was not found high enough to feed the preforms with a sufficient quantity of fluoride species. Thus other fluorides were investigated with respect to their solubility in water.

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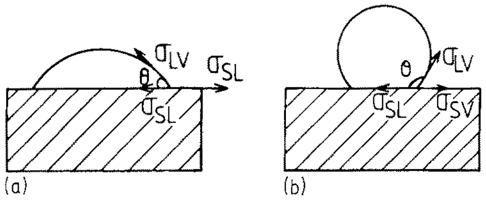

Figure 1 Sessile drop experiments: (a) wetting ($\theta < 90°$); (b) non-wetting ($\theta > 90°$).

Although K_2TiF_6 or K_3TaF_7 led to rather good impregnations, the best results were obtained with K_2ZrF_6, which has a much higher solubility in water (i.e. 25 g/100 cm^3 water at 100° C). Regarding its simplicity, the K_2ZrF_6 pretreatment technique has been integrated into a permanent mould casting process for manufacturing AMC reinforced by either carbon or SiC (e.g. Nicalon-type) fibres.

3. Experimental details

In order to point out the efficiency of the K_2ZrF_6 surface treatment, sessile drop experiments were performed on plan substrates under controlled atmospheres, as illustrated in Figs 1a and b. The substrate is considered to be wetted by the liquid when the contact angle, θ, is less than 90°. This angle is representative of the wettability of the substrate *vis-à-vis* the liquid in a given atmosphere, because θ is related to surface energies by

$$\sigma_{SV} = \sigma_{LV} \cos \theta + \sigma_{SL} \qquad (1)$$

where σ_{SV}, σ_{LV} and σ_{SL} are the surface energies, respectively, between the substrate and the gas phase, the liquid and the gas phase, the substrate and the liquid.

The plan substrates used for the sessile drop experiments were made of graphite cylinders, chemical vapour deposition (CVD)-coated with a thick layer of either pyrocarbon or silicon carbide. Because wetting is a surface phenomenon, the substrate surfaces were analysed with an Auger electron spectroscopy (AES) microprobe. As shown in Fig. 2, the surface of the pyrocarbon-coated substrate is made of carbon only. On the other hand, that of the SiC-coated substrate appears to be made of a thin layer of rather pure silica (i.e. ~6 nm thick) on top of a thick layer of the SiC single-phase main deposit. The identification of both silica and silicon carbide is made on the basis of (i) the shapes of the Auger lines from the *E.N*(*E*) spectra (Fig. 3) and the atomic concentrations calculated from the Auger line intensities according to a method which has been described elsewhere (Fig. 4) [11]. Therefore, in the case of the pyrocarbon-coated substrate, the aluminium drop is directly in contact with carbon, whereas it is actually in contact with silica in the case of the SiC-coated substrate. Even though this extremely thin layer can be dissolved during a wetting experiment, it may modify the wetting mechanism. It is noteworthy that such a thin layer of silica has been observed on Nicalon-type fibres or two-dimensional SiC–SiC preforms (i.e. a stacking of SiC fabrics consolidated by SiC according to a chemical vapour infiltration technique (CVI)).

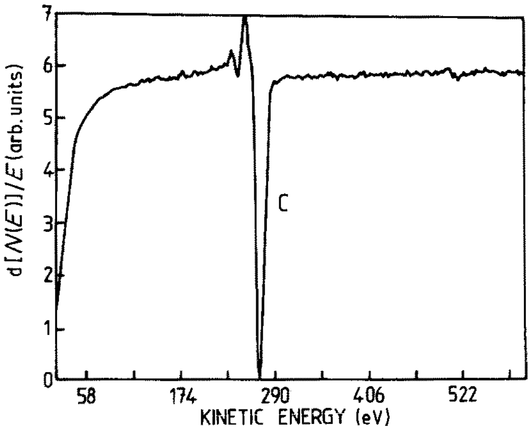

Figure 2 Auger-derived spectrum of the surface of the pyrocarbon-coated substrate.

All sessile drop experiments were performed under a vacuum of 10^{-4} to 5×10^{-4} Pa. The purity of aluminium used for the drops was 99.999 98%. After prior setting of the aluminium pieces on the carbon- or SiC-coated substrate, they were cleaned with an aqueous solution of sodium hydroxide in order to remove most of the alumina, a very thin layer of oxide (i.e. about 2 nm thick), remaining on the aluminium.

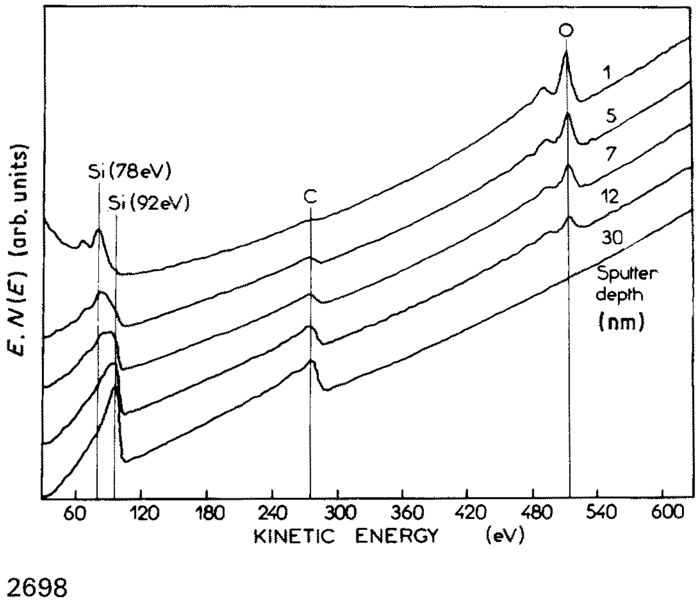

Figure 3 *E.N*(*E*) Auger spectrum obtained after different sputtering times on the surface of SiC CVD-coated carbon substrate. $E_p = 2$ keV.

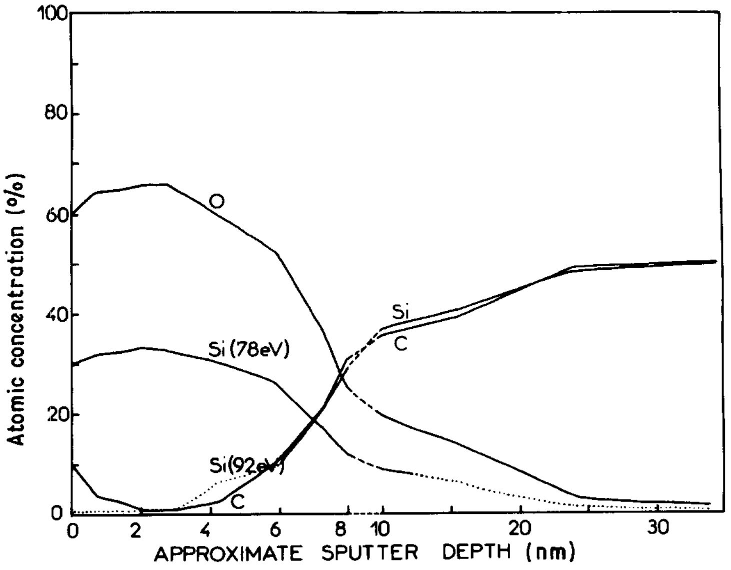

Figure 4 Composition profiles related to the SiC-coated carbon substrate; atomic concentration (%) obtained according to the method described in [11]. $E_p = 2\,\text{keV}$.

The contact angles measured at various temperatures for both C/Al and SiC/Al couples are listed in Table I. Their variations as a function of temperature or time are given in Figs 5 to 7. At 660° C (i.e. just above the melting point of alumina), the contact angle is of the order of 165° for both untreated carbon and silicon carbide surfaces (Fig. 8a). Raising the temperature as well as increasing the contact time led to a lower contact angle. When the aluminium–substrate couple is very quickly heated at high temperatures (i.e. in order to avoid any time dependency), the transition between non-wetting and wetting occurs, respectively, at about 950 and 900° C for the SiC-coated and C-coated substrates. Despite these temperatures being slightly lower than those generally accepted (i.e. within the range 950 to 1050° C), all the present experimental results are in agreement with the data reported previously [8, 12, 13].

In a second step, the contact angles were measured on substrates (coated with either pyrocarbon or SiC) which have been treated with an aqueous solution of K_2ZrF_6 prior to the sessile drop experiment. The variations of the contact angle, as a function of the experimental parameters (i.e. temperature, amount of K_2ZrF_6 deposited on the substrate, and contact time), are given in Table II and lead to the following remarks.

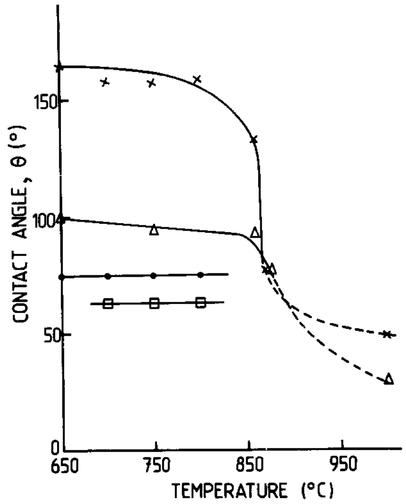

Figure 5 Variation of the contact angle between a pyrocarbon-coated substrate and pure aluminium with temperature. (x) No treatment; (△) slight K_2ZrF_6 treatment; (●) K_2ZrF_6 treatment, $5\,\text{mg}\,\text{cm}^{-2}$; (□) K_2ZrF_6 treatment, $12\,\text{mg}\,\text{cm}^{-2}$.

1. The wetting ability of a pyrocarbon or SiC surface by liquid aluminium is dramatically improved when it has been treated by an aqueous solution of K_2ZrF_6 (the contact angle falling from about 165° to values as low as 50° to 60° at temperatures slightly above the melting point of aluminium) (Figs 5 to 8).

2. The reduction of the contact angle is directly related to the amount of K_2ZrF_6 which has been spread on the substrate surface.

3. For $660 < T < 800°\,\text{C}$, the contact angle is not dependent on temperature.

4. The "apparent" melting point of aluminium is slightly lowered when K_2ZrF_6 is present on the substrate surface (i.e. ~ 647° C compared to 660° C). Such an effect could be due to an exothermic reaction occurring between K_2ZrF_6 and aluminium and resulting in localized temperature increases.

5. At a given temperature, the contact angle measured in the presence of K_2ZrF_6, seems to remain constant with time, thus the fluoride appears to be an accelerator of the evolution kinetics of the contact angle (Fig. 7).

4. Discussion

In order to explain and, eventually, to improve the efficiency of the K_2ZrF_6 surface treatment, the mechanisms according to which K_2ZrF_6 reacts with

TABLE I Variations of the contact angles (deg) between carbon or silicon carbide and pure aluminium with temperature (measurements performed under vacuum in the range 10^{-4} to 5×10^{-4} Pa)

Substrate	Temperature (° C)						
	660	700	750	800	860	900	1000
C	167		157		132 (77 to 870° C)		49
C		158		158			
SiC	161		150		148	104	
SiC		166	167				
SiC		162		162	152		

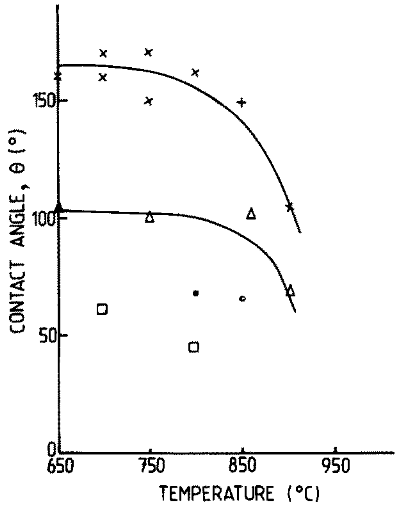

Figure 6 Variation of the contact angle between an SiC-coated substrate and pure aluminium with temperature. (x) No treatment; (△) slight K_2ZrF_6 treatment; (●) K_2ZrF_6 treatment, 9 mg cm^{-2}, (□) K_2ZrF_6 treatment, 12 mg cm^{-2}.

pure aluminium or light alloys were investigated. Because the Al–7Si–0.6 Mg alloy has been mainly used in our experiments on AMC casting, emphasis was on reactions taking place between K_2ZrF_6 and Al–Si alloys.

4.1. Reactions between K_2ZrF_6 and light alloys

As already mentioned elsewhere, reactions taking place at high temperatures between pure aluminium and K_2ZrF_6 can be represented by the following equations [14, 15]

$$3K_2ZrF_6 + 4Al \rightarrow K_3AlF_6 + 3KAlF_4 + 3Zr \qquad (2)$$

$$3Zr + 9Al \rightarrow 3Al_3Zr \qquad (3)$$

This mechanism is supported by the two following experimental results.

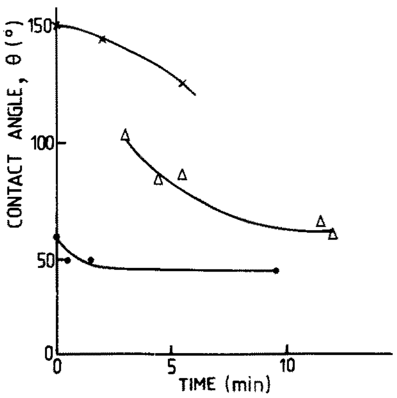

Figure 7 Variation of the contact angle between an SiC-coated substrate and pure aluminium with time. (x) No treatment, 880° C; (△) no treatment, 920° C; (●) K_2ZrF_6 treatment, 12 mg cm^{-2}, 700° C.

1. When aluminium and K_2ZrF_6 powders are mixed in the stoichiometric ratio corresponding to Equation 2 and heated at 700° C (either in air or under vacuum), the X-ray diffraction analysis confirms the occurrence of $KAlF_4$, K_3AlF_6 and Al_3Zr in the reaction products.

2. Similarly, the occurrence of Al_3Zr has been established in AMC reinforced with either carbon or SiC fibres.

When using an Al–Si alloy, either aluminium or silicon is expected to react with K_2ZrF_6. In fact, it has been established that no reaction occurs between K_2ZrF_6 and silicon, on the basis of the X-ray diffraction analysis of the products obtained after heating K_2ZrF_6 + Si or K_2ZrF_6 + Al–7Si mixtures at 700° C (only the three phases $KAlF_4$, K_3AlF_6 and $ZrSi_2$ were identified). Thus, the primary reaction that takes place between K_2ZrF_6 and Al–Si alloy is Reaction 2. Regarding the nature of the intermetallic compound, X-ray diffraction and microprobe analyses performed on Al/C or Al/SiC fibrous composites led to the following conclusions. (i) A Zr–Si intermetallic compound is formed during the impregnation of the fibre preform

TABLE II Contact angles (deg) between C or SiC substrates and pure Al at various temperatures and for different K_2ZrF_6 surface treatments (measurements performed under vacuum in the range 10^{-4} to 5×10^{-4} Pa)

Substrate	Temperature ° C						
	660	700	750	800	860	900	1000
C coated by a thin layer of K_2ZrF_6	100		95		94 (77 to 375° C)		29
C coated by a significant layer of K_2ZrF_6	63		63		63		
C coated by a layer of K_2ZrF_6 (5 mg fluoride cm^{-2})	74	75	75	75			
C coated by a layer of K_2ZrF_6 (12 mg fluoride cm^{-2})		63	63	63			
SiC coated by a thin layer of K_2ZrF_6	103		101		101	68	
SiC coated by a layer of K_2ZrF_6 (3.5 mg fluoride cm^{-2})					131		
SiC coated by a layer of K_2ZrF_6 (9 mg fluoride cm^{-2})				73.5	70		
SiC coated by a layer of K_2ZrF_6 (12 mg fluoride cm^{-2})		61		45			

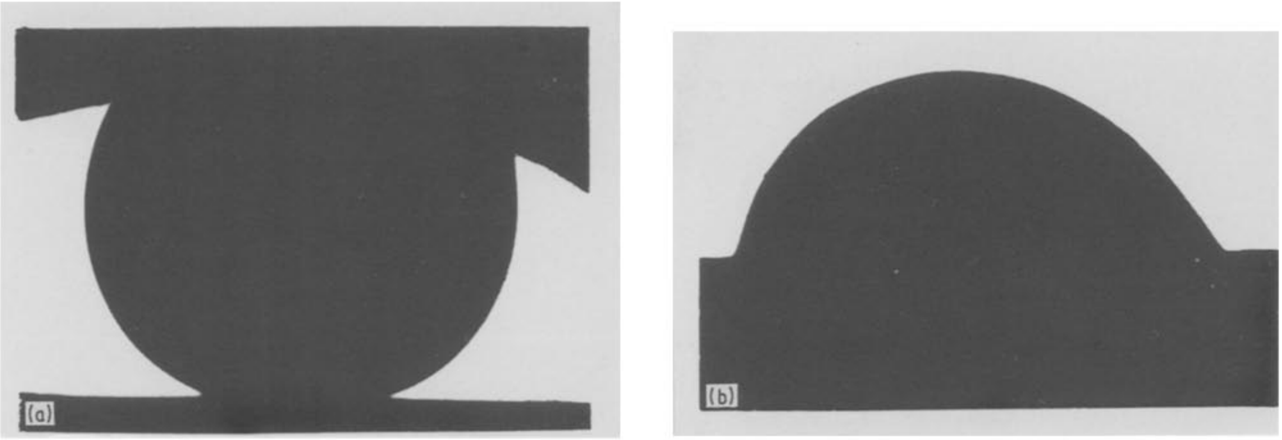

Figure 8 Sessile drop profiles at $T = 660°\text{C}$ and $P = 4 \times 10^{-5}$ Pa for: (a) Al/C (no surface treatment, non-wetting); (b) Al/C (K_2ZrF_6 surface treatment: $12\,\text{mg}\,\text{cm}^{-2}$, wetting).

by the Al–Si alloy, whereas no Al–Zr intermetallic compound (such as Al_3Zr) could be detected, and (ii) zirconium is always associated with silicon, as illustrated in Fig. 9; however the size of the Zr–Si crystals is of the same order as the X-ray microprobe resolution, so that the nature of the zirconium silicide could not be ascertained. On the basis of the experimental data, the following reaction mechanism is suggested:

$$3K_2ZrF_6 + 4Al \rightarrow K_3AlF_6 + 3KAlF_4 + 3Zr \quad (2)$$

$$3Zr + 6Si \rightarrow 3ZrSi_2 \quad (4)$$

Furthermore, in order to forecast what could be the mechanism of the fluoride treatment when Al–Mg alloys are used in preform impregnation experiments, the reactions taking place between K_2ZrF_6 and Mg were investigated. It must be mentioned that Lainer *et al.* [16, 17] have already suggested representation of the reaction between K_2ZrF_6 and magnesium by the following equation

$$K_2ZrF_6 + 2Mg \rightarrow 2MgF_2 + 2KF + Zr \quad (5)$$

Otherwise, the X-ray diffraction analysis of the products obtained after heating at 700° C K_2ZrF_6 and magnesium powders mixed in the stoichiometric ratio corresponding to Reaction 5 establishes the occurrence of three phases $KMgF_3$, MgF_2 and ZrO_2. In fact, ZrO_2 results from the oxidation of zirconium (because the experiment has been performed in air) while $KMgF_3$ is formed by a secondary reaction taking place between MgF_2 and KF. Because MgF_2 is not totally consumed by this secondary reaction, it is thought that KF is either vaporized or reacted with an impurity species (e.g. oxygen or water). On the other hand, when Reaction 5 is performed under vacuum, the only fluoride which is observed in the reaction product is $KMgF_3$ so that the secondary reaction between MgF_2 and KF is thought to be complete. In the absence of reliable data on Zr–Mg intermetallics the occurrence of a secondary reaction, which presumably takes place between magnesium and zirconium, could not be ascertained. In order to establish which one of the two possible reactions (2 or 5) occurs when Al–Mg alloys are used, K_2ZrF_6, aluminium and magnesium powders were mixed and heated up to 700° C. X-ray diffraction analyses show that Reaction 5 occurs first, releasing zirconium which then reacts with aluminium according to Reaction 3. Otherwise, it has been observed that the use of the fluoride pretreatment technique for producing Al–Mg matrix composites is not efficient and leads to poor impregnation of carbon or SiC fibrous preforms. Thus, it seems that Reaction 2 contributes to the wetting improvement whereas the species resulting from Reaction 5 have an impeding effect.

In conclusion, the above analysis (mainly based on X-ray diffraction and microprobe data and which must be verified by complementary investigations) suggests that the reaction of K_2ZrF_6 with either pure aluminium or aluminium-base alloys containing silicon and/or magnesium, leads to an intermetallic compound, on the one hand, and to complex fluorides which have to be eliminated during AMC processing (either by vaporization or by the liquid metal flow through the fibre preform) on the other.

4.2. Origin of the wettability improvement in the K_2ZrF_6 process

From the above analysis, several mechanisms can be suggested to try to explain why a pretreatment with an aqueous solution of K_2ZrF_6 improves the wettability of a pyrocarbon or SiC surface by pure or alloyed liquid aluminium: (1) the alumina thin layer coating the liquid metal is dissolved by the fluorides which are released by the reaction occurring between K_2ZrF_6 and liquid aluminium; (2) the carbon or SiC surface is cleaned and/or activated (e.g. particularly in the case of graphite fibres) by these fluorides: (3) the gas phase involved in the wetting phenomenon is advantageously modified by gaseous fluoride species formed from K_2ZrF_6; and (4) the heat of the reactions that take place is high enough to increase the temperature locally giving rise to a contact angle decrease. Although these four mechanisms can be expected to contribute to some extent to the wettability improvement, (1) is thought to be predominant [8, 9].

4.2.1. Impeding effect of the alumina layer

The following reasons can be suggested to support the wetting improvement related to the dissolution of the alumina layer coating liquid aluminium.

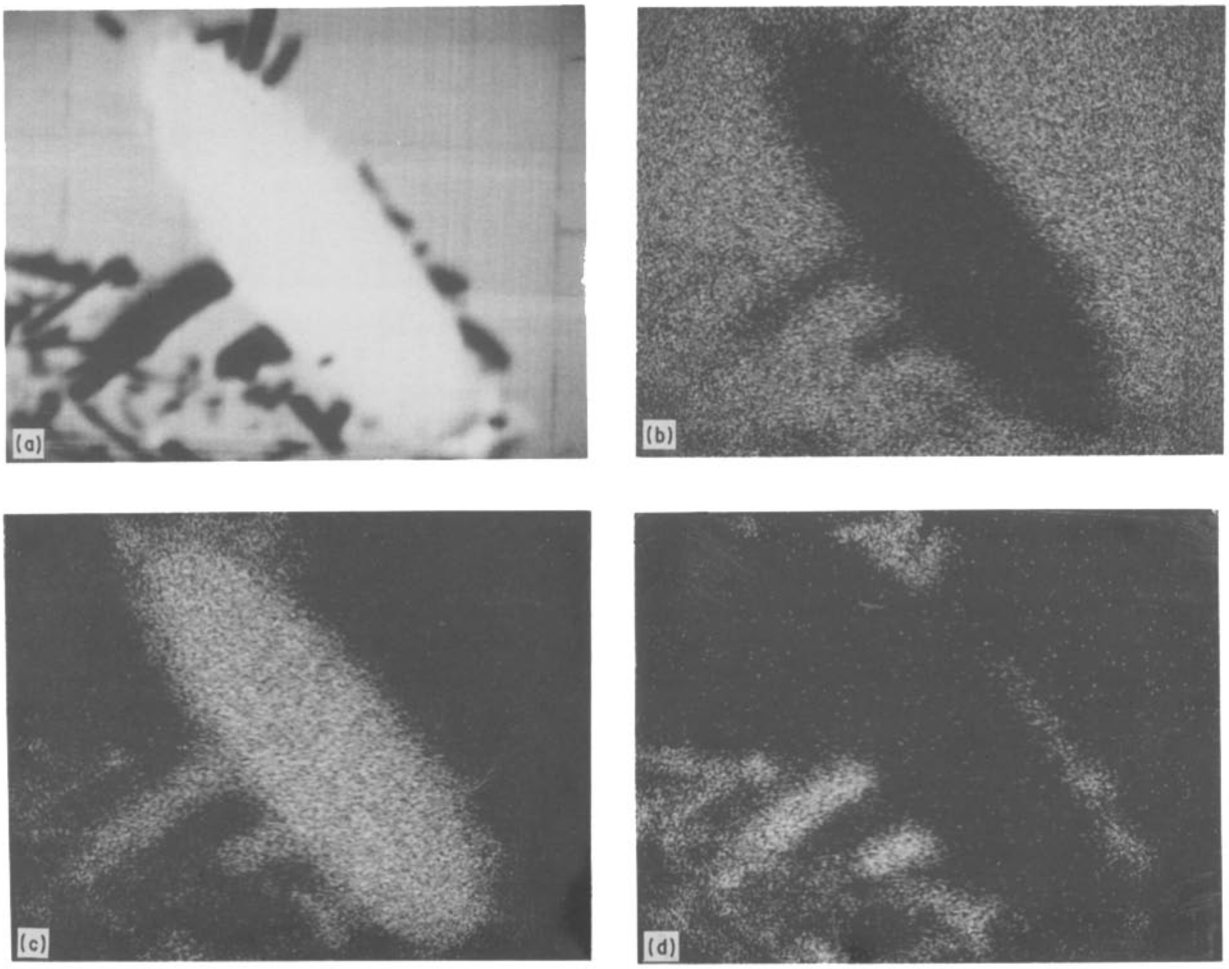

Figure 9 Electronic and X-ray maps recorded from a cross-section of an SiC (Nicalon)/Al–7Si–0.6 Mg composite material: (a) electronic map; (b) X-ray map Al(Al$K\alpha$); (c) X-ray map Si(Si$K\alpha$); (d) X-ray map Zr(Zr$K\alpha$).

1. The contact angle between carbon (or SiC) substrates and liquid aluminium depends on the thickness of the alumina layer as shown by the fact that: (i) it is lower when aluminium has been treated with sodium hydroxide prior to performing the sessile drop experiment (in such a case the thickness of the alumina layer is thought to be of the order of 2 nm), and (ii) at a given temperature, it is lower as oxygen pressure in the gas phase is low.

2. Two types of alloying element are known to modify the ability of a ceramic to be wetted by liquid aluminium [8]: (i) beryllium tends to increase the compactness of the alumina layer rendering more difficult any dislocation of the layer and a direct contact between the aluminium and the substrate (for an Al–0.8 Be alloy on a carbon substrate, θ is about 170° for $700 < T < 900°$ C when for pure aluminium it is 160 at 170° C and 102 at 900° C), (ii) on the other hand, lithium, calcium and to a less extent magnesium, enhance the dislocation of the alumina layer thus decreasing the contact angle (for Al–6Li, $\theta = 29°$ at 640° C).

3. Finally, the analysis of the contact angle values which have been reported for various ceramics shows that: (i) when temperature is low (i.e. $< 800°$ C), all contact angles are nearly the same (in fact they correspond to the aluminium–alumina/ceramic system rather than to the aluminium–ceramic couple), (ii) as soon as the temperature exceeds 850 to 900° C, aluminium reacts with alumina according to the following equation

$$Al_2O_3 + 4Al \rightarrow 3Al_2O \qquad (6)$$

where, at such temperatures, Al_2O is volatile and dislocates the alumina layer, allowing a direct contact between liquid aluminium and the ceramics.

From the above discussion it appears that the alumina layer that coats liquid aluminium appears to be a barrier impeding the wetting phenomenon.

4.2.2. Effect of K_2ZrF_6 on the alumina layer

In order to explain the dramatic wetting improvement due to the K_2ZrF_6 surface treatment which is observed in sessile drop experiments or composite material casting from carbon (or SiC) preforms, two kinds of assumption can be presented.

1. The alumina layer is thin enough to permit a reaction between liquid aluminium and K_2ZrF_6, then the reaction products (i.e. particularly K_3AlF_6) dissolve the alumina layer allowing a direct contact between the liquid metal and the ceramics.

2. The kinetics of thermal decomposition of K_2ZrF_6 is increased at high temperatures leading to the formation of several fluoride species according to the following equations:

$$3K_2ZrF_6 \rightarrow 2K_3ZrF_7 + ZrF_4 \qquad (7)$$

$$ZrF_4 + 2H_2O \rightarrow ZrO_2 + 4HF \nearrow \qquad (8)$$

the latter taking place when the experiment is performed in air. The hydrogen fluoride which is released by Reaction 8 could also react with alumina according to the following equation

$$Al_2O_3 + 6HF \rightarrow 2AlF_3 + 3H_2O \qquad (9)$$

thus dislocating the oxide layer and allowing wetting of the ceramic substrate by liquid aluminium. Assumption 2 is supported by the results of experiments performed in air at 700° C on K_2ZrF_6–Al_2O_3 powder mixtures. On the basis of the Debye–Scherrer pattern, it appeared that the reaction product is made of compounds resulting from the K_2ZrF_6 decomposition. Anyway, alumina completely disappears during such reaction.

However, two arguments lay emphasis on assumption 1: (i) the contact angle measurements were performed under a high vacuum (i.e. 10^{-4} Pa) so that the quantity of water in the gas phase was too small to allow a wetting improvement related to Equations 7 to 9, and (ii) magnesium, when added to the liquid, prevents the reaction between aluminium and K_2ZrF_6 thus rendering the fluoride surface treatment inefficient.

Although a direct reaction between K_2ZrF_6 and alumina could also be expected, the presumable mechanism of the wetting improvement is related to Reaction 2 as already suggested by other investigators in a totally different field [8].

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