

Processing of Carbon Fibers Reinforced Mg Matrix Composites Via Pre-infiltration with Al

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Mg-C composites offer a suitable alternative to Al alloys while allowing for a significant weight reduction, but their production can be impaired by the poor wettability of C substrates by Mg. In this study, a new “liquid” processing route has been investigated. By making use of the well-known effect of a pre-treatment of the C fibers with an aqueous solution of K_2ZrF_6 in favoring spontaneous wetting of C with Al, C yarns have been pre-impregnated with Al and the feasibility of further using them as reinforcements in Mg matrix composites has been assessed. More particularly, it has thus been shown that the, under the thermal conditions involved in the process, C fibers did not suffer damage due to chemical reaction with Al, and also that special care should be taken to control the surface condition of the pre-infiltrated yarns.

Keywords interfacial reactions, Mg/C composites, squeeze casting, wetting

1. Introduction

Mg matrix composites appear as suitable competitors to Al alloys for a wide number of applications, as they allow for a significant weight reduction while exhibiting potentially comparable mechanical properties (Ref 1-3). And a large variety of processing routes have already been considered for their production, including “liquid state” processes such as squeeze casting (Ref 2, 3). These techniques necessitate a very careful control of the wetting behavior (Ref 4) and of the possible interfacial reactions between the reinforcements and the molten metal (Ref 5), along with the solidification process that must not be completed prior to the thorough infiltration of the preform (Ref 2, 5).

In the case of Mg matrix composites with C fibers reinforcements, wetting is more particularly an issue as the wettability of C substrates by Mg alloys is known to be poor (Ref 6-8). As a consequence, a number of processes aiming at

enhancing the wettability of C fibers have already been investigated such as the use of a SiO_2 binder to consolidate the preforms, which would favor wetting by reacting with Mg to form MgO and silicon-rich phases (Ref 9), or the deposition of various coatings on the C fibers, e.g., amorphous SiC (Ref 7), TiN (Ref 10), or BN (Ref 11). Among those, the deposition of a metallic layer on the fibers appears particularly promising since the wetting of a metal on a metallic substrate is known to be usually good (Ref 3, 4, 10).

In this study, an alternative “liquid” processing route has been studied, making use of the known effect of a pre-treatment with an aqueous solution of K_2ZrF_6 in favoring the spontaneous wetting of C substrates by liquid Al (Ref 12-14). Indeed, when coming into contact with the molten Al, the K_2ZrF_6 deposited on the C substrate has been shown to dissolve the superficial alumina layer covering the Al bath following a complex sequence of reactions whose details can be found in Ref 14. This is generally acknowledged as the main cause of the wetting improvement brought about by the K_2ZrF_6 , although some other factors such as the cleaning of the surface of the substrate by the fluorides species or the local increase in temperature due to the heat of reactions might also play a role (Ref 12).

In the presence of Mg, however, the sequence of reactions is modified and the K_2ZrF_6 is consumed to form MgF_2 (Ref 12). As a consequence, a pre-treatment of the C substrate with K_2ZrF_6 does not bring about any improvement of the wetting by Al-based alloys containing Mg (Ref 12) or by Mg-based alloys, as was demonstrated by preliminary tests carried out in our laboratory. Since a spontaneous infiltration of the C reinforcements by liquid Mg alloys could not be obtained by means of a pre-treatment with K_2ZrF_6 , this study aimed at assessing the feasibility of using preforms made of C yarns pre-infiltrated with pure Al (after pre-treatment with K_2ZrF_6) as reinforcing phase for the production of Mg-matrix composites by squeeze casting.

2. Experimental Procedure

C yarns were taken from a C fabric produced by Ten Cate and specifically dedicated to the processing of metal matrix

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composites (MMC), i.e., without a polymeric sizing that could burn when coming into contact with the molten metal, the resulting combustion gases leading in turn to the occurrence of porosity in the composite (Ref 15). These C yarns were first pre-treated by dipping for 2 min in a slightly supersaturated aqueous solution of K_2ZrF_6 at 95 °C, following the discontinuous procedure described in Ref 14, before being dried up at 100 °C and under air for 1 h, so as to eliminate all traces of residual humidity. Second, the pre-treated yarns were dipped in a bath of pure Al molten at 750 °C for 30 s. After this pre-infiltration step, the C yarns were air cooled down to room temperature, and the aluminum was completely solidified.

These pre-infiltrated C yarns were in turn used as preforms in the production of composite samples by squeeze casting, by means of an apparatus that was described in details elsewhere (Ref 5). The preforms were made of a number of pre-infiltrated yarns aligned parallel to each other and set into a copper stand designed in such a way as to allow the molten metal to flow

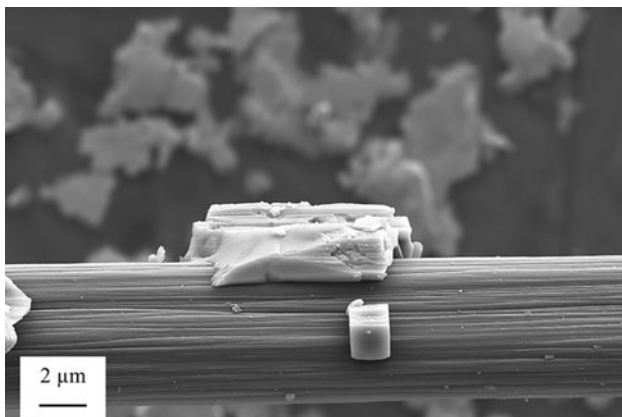
freely and thus infiltrate the preform while keeping it from entering in direct contact with the bottom of the die. Indeed, such a direct contact might cause the solidification to start too

Table 1 Chemical composition of Mg alloy AZ91D (wt.%)

| AZ91D | Al | Zn | Mn | Si | Ni | Fe | Cu | Mg |
|-------|---------|----------|----------|-------|--------|--------|--------|------|
| wt.% | 8.5-9.5 | 0.45-0.9 | 0.17-0.4 | <0.05 | <0.001 | <0.004 | <0.025 | Bal. |



Fig. 2 SEM micrograph showing the cross section of a C yarn spontaneously infiltrated with liquid Al after pre-treatment in an aqueous solution of K_2ZrF_6 . The individual C fibers constituting the yarn appear in black in the Al matrix (bright)



(a)

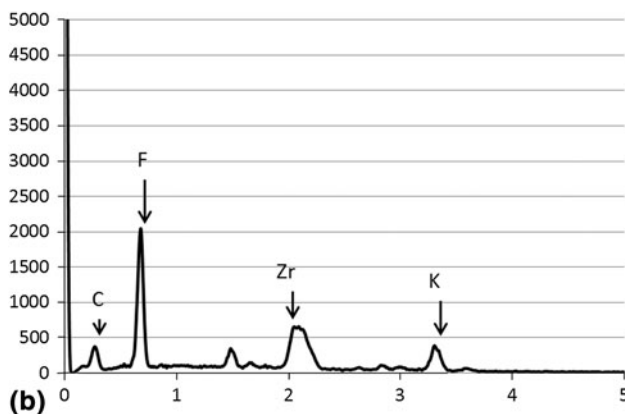
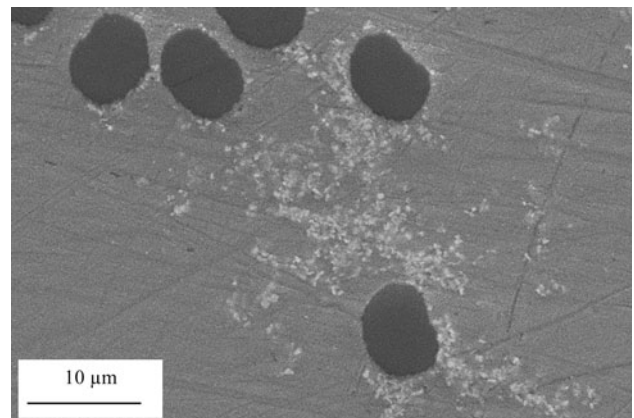
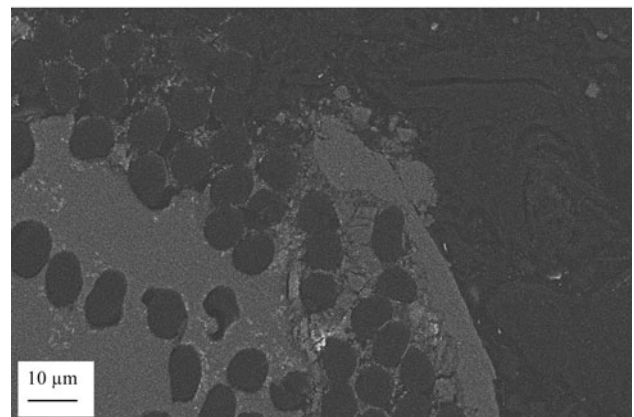


Fig. 1 (a) SEM micrograph of a carbon fiber after pre-treatment in an aqueous solution of K_2ZrF_6 and (b) EDS spectrum corresponding to a crystal of K_2ZrF_6



(a)



(b)

Fig. 3 SEM micrographs of a C yarn infiltrated with Al after pre-treatment in an aqueous solution of K_2ZrF_6 . The small white crystals of $KAlF_4$ and of Al_3Zr result from the decomposition of K_2ZrF_6 , (a) at the core of the yarn and (b) near its surface

early on top of the preform thus preventing a correct infiltration. The preforms were infiltrated with Mg alloy AZ91D, whose composition is given in Table 1, overheated to 780 °C. This alloy is prone to the precipitation of $Mg_{17}Al_{12}$ intermetallics leading to a brittle mechanical behavior (Ref 16), but its excellent castability makes it a good candidate for squeeze casting. The preform was pre-heated up to 400 °C in a furnace under Ar flow, and both the die and the punch were pre-heated up to 350 °C, to prevent the solidification of the liquid metal from taking place too rapidly.

Samples for microstructural examination were characterized by scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). C yarns pre-treated with K_2ZrF_6 were coated with Au/Pd so as to insure for a good evacuation of the electric charges. Al pre-infiltrated C yarns and undeformed C/Al/Mg composite samples, on the other hand, were embedded in conductive resin and polished following standard practices.

Tensile tests were performed with a universal ZWICK 50 kN machine. The tensile specimens were 1.5 mm thick, 6 mm wide, and with an initial gauge length of 22 mm, and their fractured surfaces were also characterized by SEM.

3. Results

3.1 C Yarns Pre-infiltrated with Al

Figure 1(a) shows a SEM micrograph of small K_2ZrF_6 crystals, as identified from the EDS spectrum of Fig. 1(b), deposited on an individual C fiber isolated from a C yarn after treatment in aqueous solution and drying at 100 °C. Dipping of the pre-treated C yarns in a bath of Al molten at 750 °C leads to an excellent and spontaneous infiltration of the yarn by the liquid metal, as can be seen from the SEM micrograph of Fig. 2. Indeed, the molten Al has penetrated everywhere between the individual C fibers constituting the yarn, and down to the very core of the yarn. Figure 3 further shows that small white crystals of $KAlF_4$ and Al_3Zr , resulting from the decomposition of K_2ZrF_6 in good agreement with the reaction scheme proposed in Ref 12-14, are dispersed in the Al and in between the individual C fibers. Moreover, these crystals are not distributed homogeneously inside the pre-impregnated C yarn, but they are present in larger amount in areas closer to the surface of the pre-infiltrated yarn (Fig. 3b).

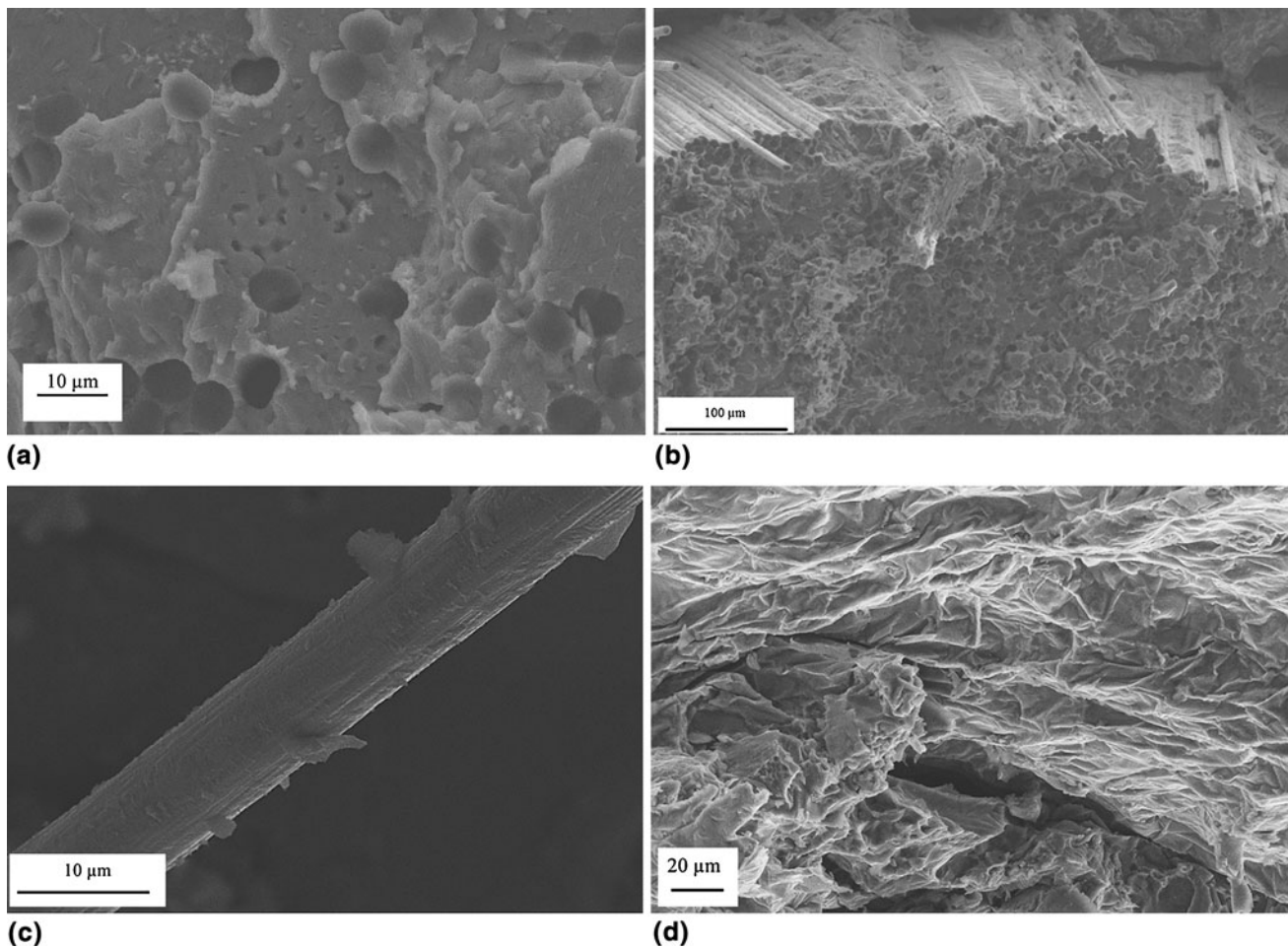


Fig. 4 SEM micrographs from fractured surfaces of C/Al/Mg composites. (a) Outer area of a pre-infiltrated C yarn exhibiting a high density of $KAlF_4$ and Al_3Zr precipitates. (b) Micrograph showing a pre-infiltrated C yarn (in the lower part, with the individual C fibers appearing as black spots in the Al that appears bright) and the AZ91D matrix (in the upper part of the micrograph). Extensive pull-out of the individual C fibers occurs in the outer shell of the pre-infiltrated C yarn but not at its core. (c) SEM micrograph of an individual C fiber that was located in the outer shell of the pre-infiltrated C yarn and that had subsequently been pulled out from the metallic matrix. (d) SEM fractograph of the AZ91D matrix

3.2 C/Al/Mg Composites

C/Al/Mg composite samples obtained by squeeze casting Mg alloy AZ91D into preforms made from C yarns pre-infiltrated with Al were tested under uniaxial tension. Both the Young modulus (with an average value of 9 GPa, i.e., well below the Young modulus of 45 GPa of the AZ91D matrix) and the ultimate tensile strength (ranging between 28 and 78 MPa) exhibit low values. Significant variations from one sample to another are also observed. Both the poor level of the mechanical properties and their variability are clear signs of the existence of important microstructural defects in the C/Al/Mg composites.

A detailed microstructural examination allows for a more precise identification of the weak zones. SEM micrographs of the fractured surfaces can be seen in Fig. 4. First of all, it is worth noting that the outer layers of the pre-infiltrated yarns appear very disturbed, exhibiting both porosities and precipitates

of KAlF_4 and Al_3Zr in significant amounts (Fig. 4a). Furthermore, extensive fibers pull-out occurred in this area (Fig. 4b, c), whereas such pull-out of the individual C fibers was not observed at the core of the pre-infiltrated yarns. This points to the outer shell of the pre-infiltrated C yarns as a particularly weak area in the microstructure of the C/Al/Mg composites. Finally, the AZ91D matrix exhibits a fractured surface typical of the brittle fracture behavior that would normally be expected of this alloy (Ref 16) (Fig. 4d).

A more detailed characterization of the interfacial area between the AZ91D matrix and the pre-infiltrated C yarns was then carried out on undeformed samples, using SEM combined with EDS. This interfacial area seen in Fig. 5(a) exhibits very clear defects in a disturbed zone whose thickness is as high as 50 μm . And both the elemental map and the line scan of Fig. 5(b) and (c) demonstrate a local enrichment of this

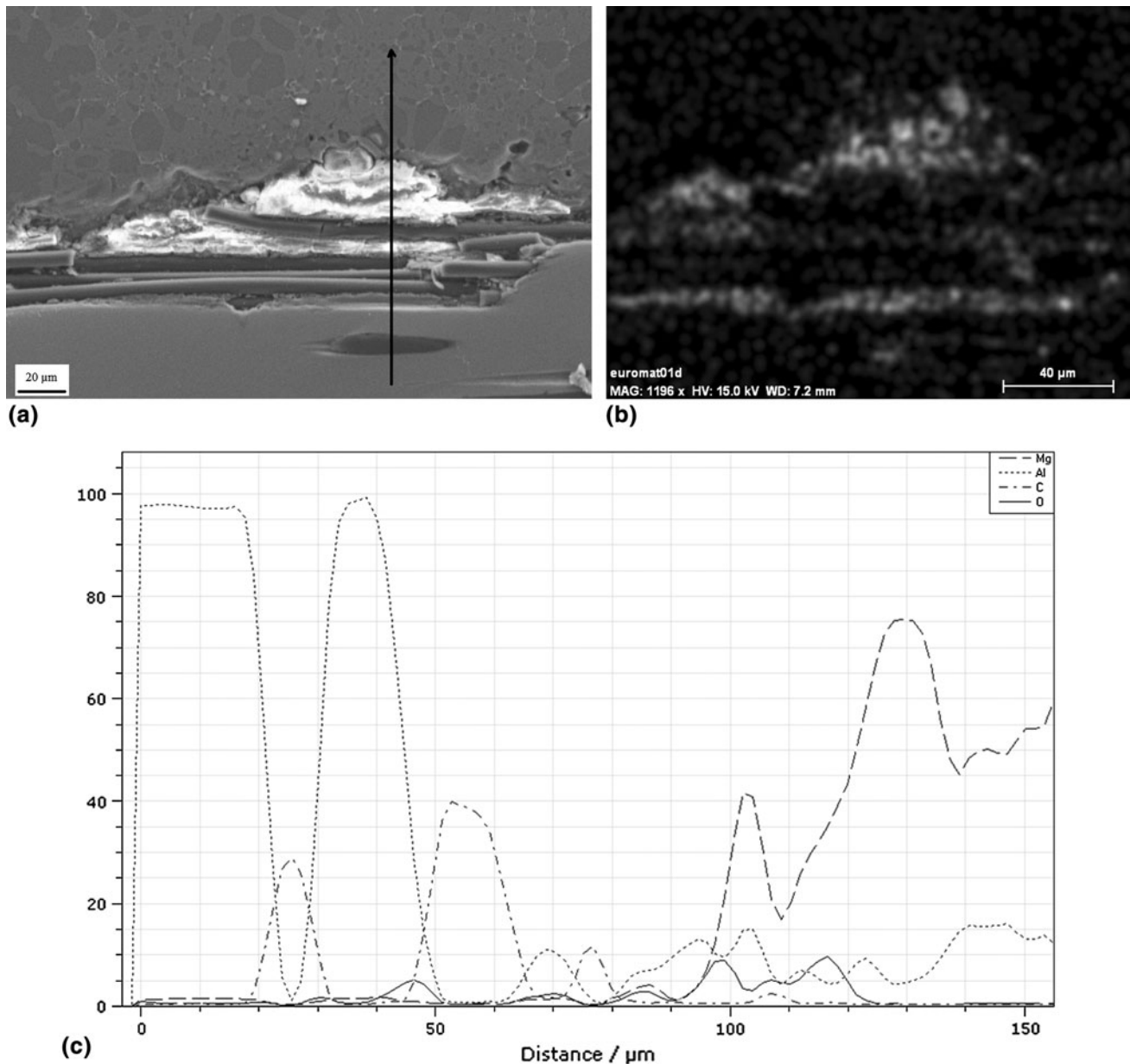


Fig. 5 (a) SEM micrograph, (b) EDS elemental map for oxygen, and (c) EDS line scan taken across the interface between a C yarn pre-infiltrated with Al and the AZ91D matrix

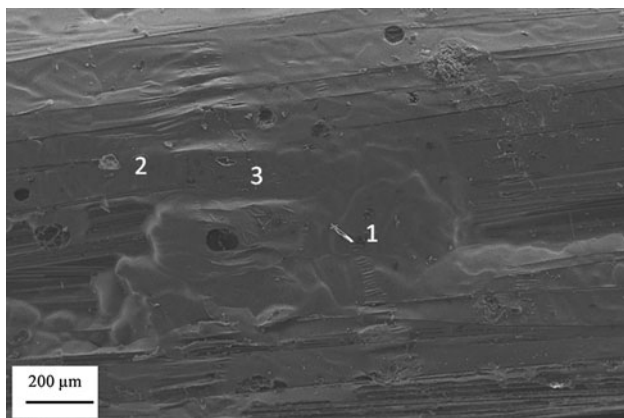
interface with oxygen that is present simultaneously on the Al and the AZ91D sides. This oxygen-rich layer moreover exhibits significant local variations in thickness and morphology. It is also worth noting that a locally higher than normal volume fraction of the $Mg_{17}Al_{12}$ phase can be observed on the AZ91D side of the interface (Fig. 5a), indicating that the outer layers of the pure Al from the pre-infiltrated C yarns partially dissolve into the molten AZ91D during the squeeze casting step.

4. Discussion

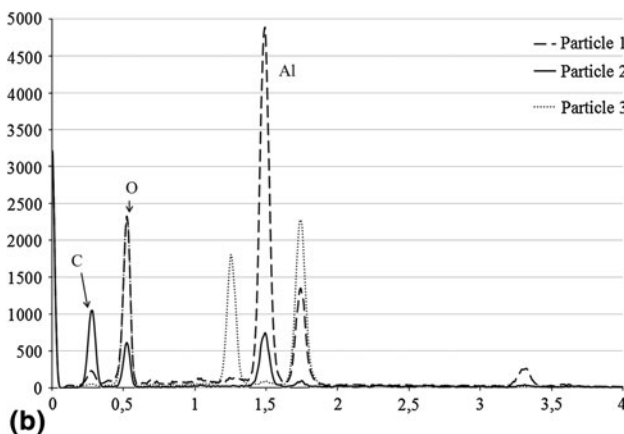
The high tendency of Al to react with C and form carbides such as Al_4C_3 has been widely reported (Ref 8, 17). However, it is worth noting that carbon fibers pulled out of the Al after fracture (Fig. 4c) do not exhibit any damage, contrarily to observations reported by Margueritat-Regenet regarding the elaboration of C/Al composites by a continuous process (Ref 14). It so appears that, if any reaction takes place between the carbon fibers and the Al, this reaction does not reach such an extent as to compromise the fibers integrity under the thermal conditions involved in the composite's elaboration, i.e., dipping the fibers in a bath of molten Al at 750 °C for 30 s followed by air cooling, then pre-heating at 400 °C for 30 min, and squeeze casting with liquid AZ91D overheated up to 780 °C. Causes of

the poor mechanical properties and of their low reproducibility must hence rather be found at the interface between the pre-infiltrated yarns and the AZ91D matrix, i.e., in the thick oxygen-enriched layer and in the high amount of precipitates resulting from the decomposition of K_2ZrF_6 .

Whereas a very thin oxide layer at the interface between the matrix and the reinforcement (typically below 200 nm, Ref 18, 19) might turn not to be detrimental to the mechanical properties of the composite and hence still be acceptable, the very thick and porous oxygen-rich layer observed at the interface between the pre-infiltrated yarns and the AZ91D matrix can be held responsible for the poor mechanical properties of the C/Al/Mg composites. Measures should be taken to suppress it or at the very least to decrease its thickness. Possibly, this layer could result from the reaction of the liquid Mg that would reduce Al oxides present at the surface of the pre-impregnated C yarn (Ref 20), as is indeed confirmed by the occurrence of oxides particles in the SEM micrograph and EDS spectrum of Fig. 6. These particles might have been originally present at the surface of the molten Al during the pre-impregnation, where they could have been picked up by the C yarn upon exiting the Al bath. This might be solved by a proper cleaning of the surface of the Al bath. Moreover, the excess K_2ZrF_6 brought in the system on the pre-treated C yarns had been shown to form a layer at the surface of the Al bath (Ref 14). Cleaning the surface of the bath during the pre-infiltration step might thus also help decreasing the segregation of large amounts of the decomposition products from K_2ZrF_6 near the surface of the pre-impregnated yarn. And, of course, a decrease in the concentration of the aqueous solution of K_2ZrF_6 used for pre-treating the C yarns should also be advised, contrarily to previous works dealing with the direct elaboration of Al/C composites which recommended the use of a solution as concentrated as possible to obtain the most significant improvement in wetting behavior (Ref 12).



(a)



(b)

Fig. 6 (a) SEM micrograph and (b) EDS spectrum of oxides particles on the surface of an Al pre-infiltrated C yarn

5. Conclusions

In this study, C yarns were spontaneously pre-impregnated with Al thanks to a pre-treatment in an aqueous solution of K_2ZrF_6 . And the feasibility of using in turn these pre-infiltrated C yarns as reinforcements in Mg matrix composites produced by squeeze casting has been assessed. It has been shown that under the thermal conditions involved in the elaboration of these C/Al/Mg composites, the C fibers did not undergo any significant damage due to the chemical reactions possibly taking place between C and Al. Furthermore, it has been demonstrated that special care should be taken to keep the surface of these pre-infiltrated C yarns as clean as possible (i) by cleaning the surface of the molten Al bath during the pre-impregnation step so as to avoid pick-up of oxides particles by the exiting yarns and (ii) by keeping the concentration of the K_2ZrF_6 aqueous solution as low as possible while still insuring the spontaneous wetting of the C yarns by the molten Al, contrarily to recommendations made in previous works dealing solely with the production of Al/C composites.

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