EVALUATION OF ALUMINA AS PROTECTIVE COATING FOR CARBON FIBERS IN ALUMINUM-BASED COMPOSITES

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Abstract
Carbon fiber reinforced aluminum metal matrix composites (C_f/Al-MMCs) have been considered as promising materials for lightweight applications because they offer outstanding mechanical properties combined with low density. Nevertheless, major obstacles in manufacturing of C_f/Al-MMCs are high reactivity and poor wettability of the carbon fibers with molten Al-alloy. Often an undesired formation of carbides (e.g. Al_4C_3) at the fiber-matrix interface is observed. Another issue is the sensitivity of carbon fibers to oxidation especially at temperatures of more than 400°C. In order to solve these problems alumina (Al_2O_3) protective coating was applied on carbon fiber-based high modulus (HM) 2D-textile preforms by means of atomic layer deposition (ALD). The influence of the coating on the carbon fibers was investigated by measurement of the tensile strength with single filaments and by determination of the oxidation behavior using TGA analysis. Alumina coated fibers show an enhancement of tensile strength of up to 700 MPa compared to uncoated fibers. An improved oxidation resistance of coated preforms was verified by TGA analysis. The C_f/Al-MMC using alumina coated HM fibers and alloy 239D as matrix material was prepared via gas pressure infiltration (GPI). Infiltration without alumina protective coating leads to many casting defects (e.g. uninfiltrated areas) and carbide formation at the fiber-matrix interface. Interaction of alloying elements with alumina layer at the fiber-matrix interface is evaluated by TEM analysis.

1. Introduction

Carbon fiber reinforced aluminum metal matrix composites (C_f/Al-MMCs) have been considered as promising material for application in aerospace and automotive tasks. They offer low density, high specific strength, high stiffness and low coefficient of thermal expansion as well as high thermal stability. C_f/Al-MMCs can tolerate much higher loads and offer higher potential of improved mechanical properties compared to light metal without reinforcement or reinforced by short fibers or particles. Nevertheless, major obstacles in manufacturing of C_f/Al-MMCs are high reactivity and poor wettability of the carbon fibers with molten Al-alloy during infiltration. Often an undesired formation of carbides (e.g. Al_4C_3) at the fiber-matrix interface is observed. The formation of carbides is accompanied by fiber degradation and deterioration of its mechanical properties. Therefore an early failure of the composite under load is the consequence. These problems hinder further development of C_f/Al-MMC composites and limit the industrial application. To overcome the problems at the fiber-matrix interface in the C_f/Al system, a protective coating can be applied. According to Feldhoff et al. [1] such a coating must: (i) provide an adequate fiber-matrix adhesion and (ii) act as a diffusion barrier. Moreover Ochiai et al. [2] suggested that the coatings should not exceed a critical thickness because above the critical thickness the crack propagation is enhanced and the fiber strength decreases. Approximately 1% of the fiber diameter is assumed as critical thickness [2]. Different protective layers

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deposited by various technologies are reported in the literature for the use in the C_f/Al system such as electroless and/or electroplating method (Cu, Ni), sol gel (SiC, SiO_2, Al_2O_3) and gas phase method (TiN, SiC, double layers PyC/TiB_2, PyC/SiC and gradient layers C/SiC/Si) [3-17]. So far there are only few reports on alumina (Al_2O_3) protective coatings deposited by gas phase methods with the objective to improve the properties of C_f/Al-MMC. Alumina is an attractive coating material because it works as a diffusion barrier in conjunction with Al-alloys, improves oxidation resistance of carbon fibers, improves the wetting behaviour with Al-melt and exhibits excellent thermal as well as chemical stability. In this work, atomic layer deposition (ALD) is employed for achieving homogeneous coatings within nanometer range at a low deposition temperature.

2. Experimental

2.1. Materials

Carbon fiber-based 2D-textile preforms Torayca (M40J) were used as substrates. The preform is manufactured of rovings where each roving consists of three thousand single filaments of high modulus (HM) carbon fibers. These carbon filaments have a fiber diameter of 5-7 µm, a density of 1.75 g/cm^3, a strain to failure of 1.2%, tensile modulus of 377 GPa, coefficient of thermal expansion of - 0.83*10^{-6} K^{-1} and a tensile strength of 4.4 GPa. Prior to deposition process, sizing on the fibers was removed by thermal treatment at 400°C for 40 min in a vacuum furnace. Additional to the preforms, planar graphite plates (C_{gr}) of 20 mm x 20 mm were also used as substrates for the investigation of the coating structure. As matrix material for the manufacturing of the metal matrix composite a commercial Al-Si alloy 239D was chosen. This alloy contains only small amounts of Cu and Mg to suppress the formation of brittle reaction products at fiber-matrix interface. The chemical composition of the used alloy is summarized in Tab. 1.

Table 1. Composition of the 239D-alloy (in wt.%)

Alloys	Al	Si	Cu	Fe	Mg	Zn	Mn	Ti
239D*	rest	9 – 11	0 – 0.1	0 – 1.0	0.2 – 0.5	0 – 0.15	0 – 0.4	0 – 0.15

** Raffmetal product's spezification (http://www.raffmetal.eu/scarica_file.asp?c=/dati/SearchAlloy/TED/&f=EN43000.pdf)*

2.2. ALD Process

For the deposition of the alumina layer a laboratory-scale showerhead ALD reactor from FHR Anlagenbau GmbH was used. A scheme of the ALD reactor is shown in Fig. 1. The ALD process was carried out at a constant substrate temperature of 220°C using the precursors trimethylaluminum (TMA) and ozone (O_3). The precursor TMA was stored in a bubbler at 17°C and pulsed in the reactor using 100 sccm argon as carrier gas. The ozone delivery was realized by an ozone generator of MKS with 16 wt.% ozone in an oxygen flow of 1000 sccm. Purging was performed by argon at a flow rate of 100 sccm. ALD of Al_2O_3 is characterized by the sequential inlet of the precursors TMA and ozone into the process chamber separated by argon purge gas pulses. During the TMA pulse a monolayer will chemisorb onto the surface. The subsequent Ar purge gas pulse removes residual TMA and by-products from the reactor. The following ozone pulse leads to the oxidation of the chemisorbed monolayer to Al_2O_3. The subsequent Ar purge gas pulse removes excess ozone and by-products from the reactor and an ALD cycle is completed. The layer thickness can be adjusted by repeating this cycle. Details of the applied process parameters for the alumina deposition are given in Tab. 2.

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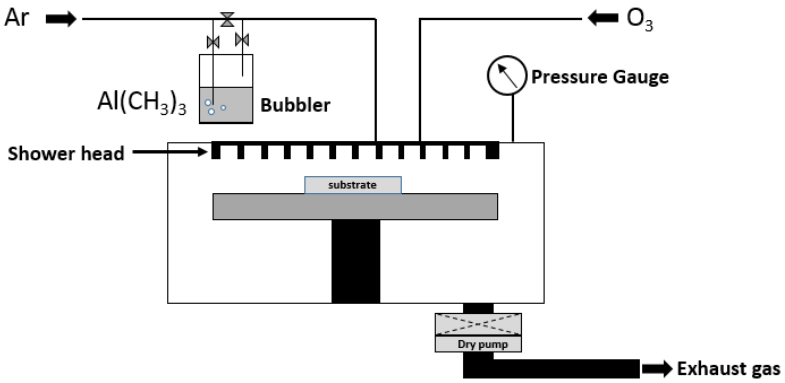

Figure 1. Scheme of showerhead ALD reactor employed for Alumina (Al_2O_3) deposition

Table 2. ALD parameter range for Al_2O_3 layer deposition

Parameter	Range
Substrate temperature,T_s [°C]	220
Pressure, p [kPa]	0.5
TMA pulse time, [s]	0.4 - 2
Purge time after TMA/O_3 pulse, [s]	30 - 120
Ozone pulse time, [s]	2 - 8
Number of ALD cycles	270

2.3. Metal matrix composite fabrication method

Infiltration tests were performed with 239D aluminum alloy as matrix material. The infiltration was performed by gas pressure infiltration (GPI) method as also described in [18]. The process principle of GPI is characterized by four steps. In the first process step (1) the fiber preform, the moulds and the Al-alloy are heated up to the temperature exceeding the melting temperature of the Al-alloy at reduced atmospherical pressure to avoid evaporation of the molten lightmetal (2). After exceeding the melting temperature and initially infiltrating the preform, a high argon gas pressure is applied to improve the infiltration (3). The last step consists of relatively fast cooling under high pressure (4). The main characteristics of the process are shown in Fig. 2.

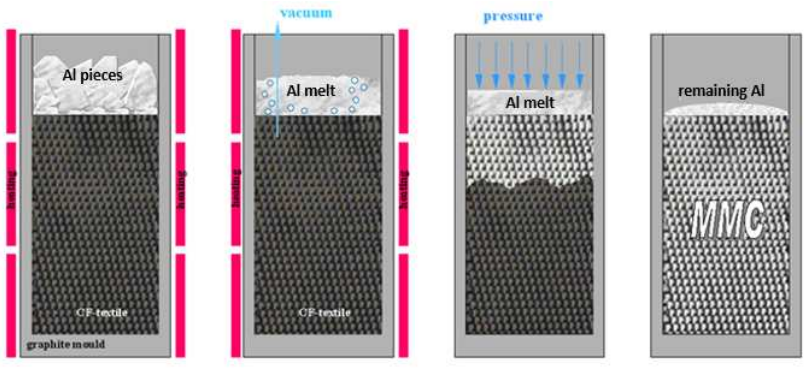

Figure 2. Steps of gas pressure infiltration (GPI) for preparation of C_f/Al-MMC

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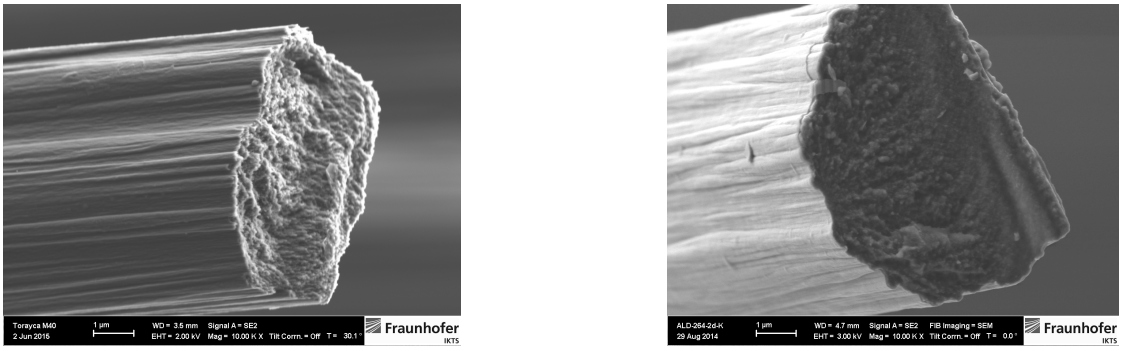
2.4. Analysis Methods

SEM investigations were conducted using a SEM from NVision Carl Zeiss SMT GmbH. The Microstructure of Al_2O_3 coatings was analyzed on planar graphite substrates by X-Ray diffraction (XRD) with glancing incidence technique (XRD-Seifert-FPM 3003TT) under a flat angle of 1°. The oxidation behavior of uncoated and coated fibers was investigated by thermogravimetric analysis (TGA) using a STA 409 (Netzsch-Gerätebau GmbH). The oxidation onset temperature was determined according to DIN 51006 with a tangent procedure. The tensile tests of single fibers were carried out using a Hegewald and Peschke testing machine with a special grip. The test speed was set to 2 mm/min with an applied force of maximal 10 N. Twenty specimens were tested for each coated roving. The tensile strength of single fibers was determined according to ASTM D3379-75 standard. Characterization of the obtained fiber reinforced aluminum metal matrix composite (C_f/Al-MMC) was performed by SEM, elemental mapping and TEM. Samples for TEM were prepared using Focused Ion Beam (FIB) Hitachi FB2100 and then subjected to TEM analysis. In the microscopic investigation STEM Hitachi S5500 and JEOL1200 equipment were used.

3. Result and Discussion

3.1. Coating structure

SEM images of an uncoated and an Al_2O_3-coated M40J single fiber extracted from a 3K roving are shown in Fig. 3a and b. The alumina coating in Fig. 3b covers the fiber surface uniformly. Results of investigations regarding the homogeneity of the deposited Al_2O_3 layers are published elsewhere [19].



a) Uncoated M40J b) Al_2O_3-coated M40J

Figure 3. SEM images of an uncoated and an Al_2O_3-coated M40J single fiber

The microstructure of the deposited Al_2O_3 coatings was investigated by XRD on coated planar graphite substrates. The diffraction pattern reveal no reflections of crystalline phases. The structure remains amorphous even after annealing in a furnace at 720°C for 30 minutes simulating GPI conditions. This result suggests that the structure of Al_2O_3 layer should be unaffected by the thermal conditions during metal matrix composite fabrication with GPI.

3.2. Oxidation behavior and tensile strength of Al_2O_3-coated fibers

As shown in Fig. 4 the oxidation onset for Al_2O_3-coated fibers is approx. 763°C. This onset temperature is higher than for uncoated M40J fibers where the onset temperature is approx. 711°C. The determined onset temperatures for oxidation are much higher for the high modulus M40J fibers

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compared to HTS40 fibers in a previous study [19]. This result is attributed to the different fiber structures. The graphene layers in high modulus fibers are mainly parallel-oriented to the fiber surface. Therefore the oxidation resistance is much higher than for HTS fibers.

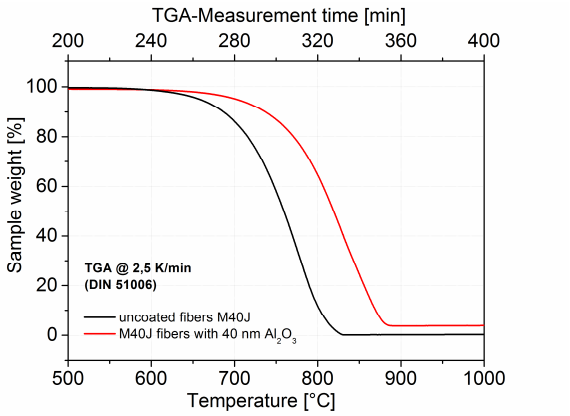
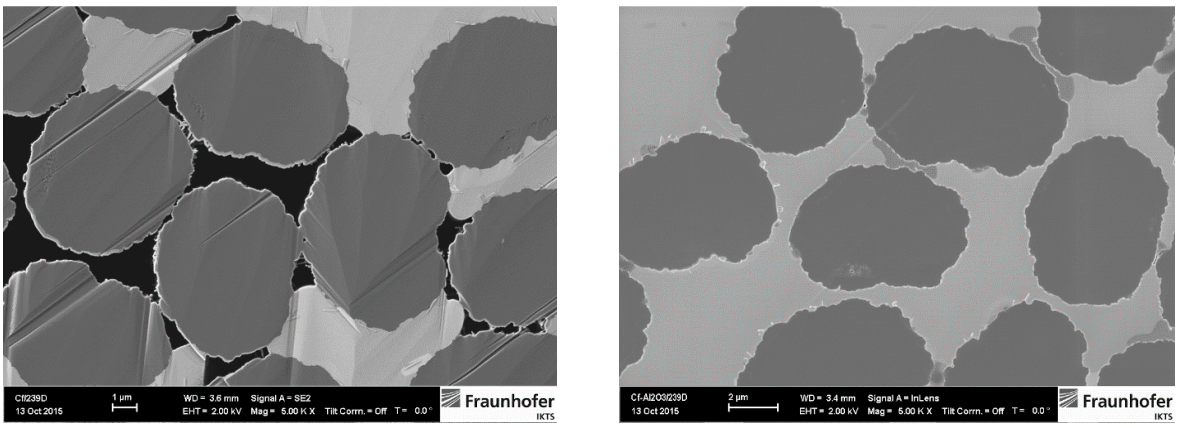


Figure 4. Oxidation behavior of uncoated and Al_2O_3-coated M40J fibers

Contrary to HTS40 fibers in a previous study [19] ultimate tensile strength (UTS) measurements of Al_2O_3-coated M40J single fibers show no loss of UTS compared to uncoated fibers. Al_2O_3 coated M40J single fibers have even a slightly improved UTS of 5.1 ± 0.6 GPa compared to uncoated fibers with an UTS of 4.4 ± 0.7 GPa.

3.3. Infiltration of uncoated and Al_2O_3-coated 2D-textile preforms with 239D-alloy by GPI method and interface analysis

An uncoated M40J textile preform infiltrated with 239D alloy is shown Fig. 5a. Due to a high surface energy of M40J fibers, 239D alloy does not wet the fibers properly and therefore clear casting defects (e.g. uninfiltrated zones) and Al_4C_3 formations are observed. In the case of Al_2O_3-coated M40J textile preform infiltration, a dense composite with very few casting defects is obtained (Fig. 5b). An Al_4C_3 formation at the fiber-matrix is still observed but at a significantly reduced level.



a) b)

Figure 5. 2D (HM) -textile preform infiltrated with 239D by GPI method (720°C, 100 bar, 20 min): a) Uncoated fibers, b) Al_2O_3-coated fibers

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X-Rays elemental mapping of a $C_f(Al_2O_3)$/239D cross-section is shown in Fig. 6. The Al_2O_3 layer seems to remain on the fibers as it is indicated by the O element distribution (Fig. 6a) where O covers the fiber surfaces continuously. However needle-shaped forms are also found eventhough the Al_2O_3 layer covers the fibers continuously. This is a hint that there might be defects in the layer (e.g. cracks). Fig. 6b shows Cu mapping which is homogeneously distributed in the matrix. It shows that there are no precipitations nearby fibers. Eventhough the concentration of Mg is very low in the alloy 239D, which is between 0.2 – 0.5 wt.% (Tab. 1), it seems to precipitate at or react with the Al_2O_3 (Fig. 6c). In the case of Si it is clearly observed that a relatively large amount of brittle Si precipitates nearby/bonded to the fibers (Fig. 6d) which may lower the fiber strength.
A TEM image of the $C_f(Al_2O_3)$/239D interface is shown in Fig. 7a. There, a discontinuity (marked with a red circle) due to a crack or a defect is observed. Furthermore the whole layer seems to be separated from the fiber surface. EDX results of a line scan (Fig. 7b) prove the existence of Mg, Al and O within the layer. According to Rajan et al [20] a spinel $MgAl_2O_4$ formation is assumed which would be formed at low magnesium levels (< 1.5 wt.%) :

$$4Al_2O_{3(s)} + 3Mg_{(l)} \rightarrow 3MgAl_2O_{4(s)} + 2Al_{(l)}, \Delta G°_{627°C} = -13\ kJ/mol$$

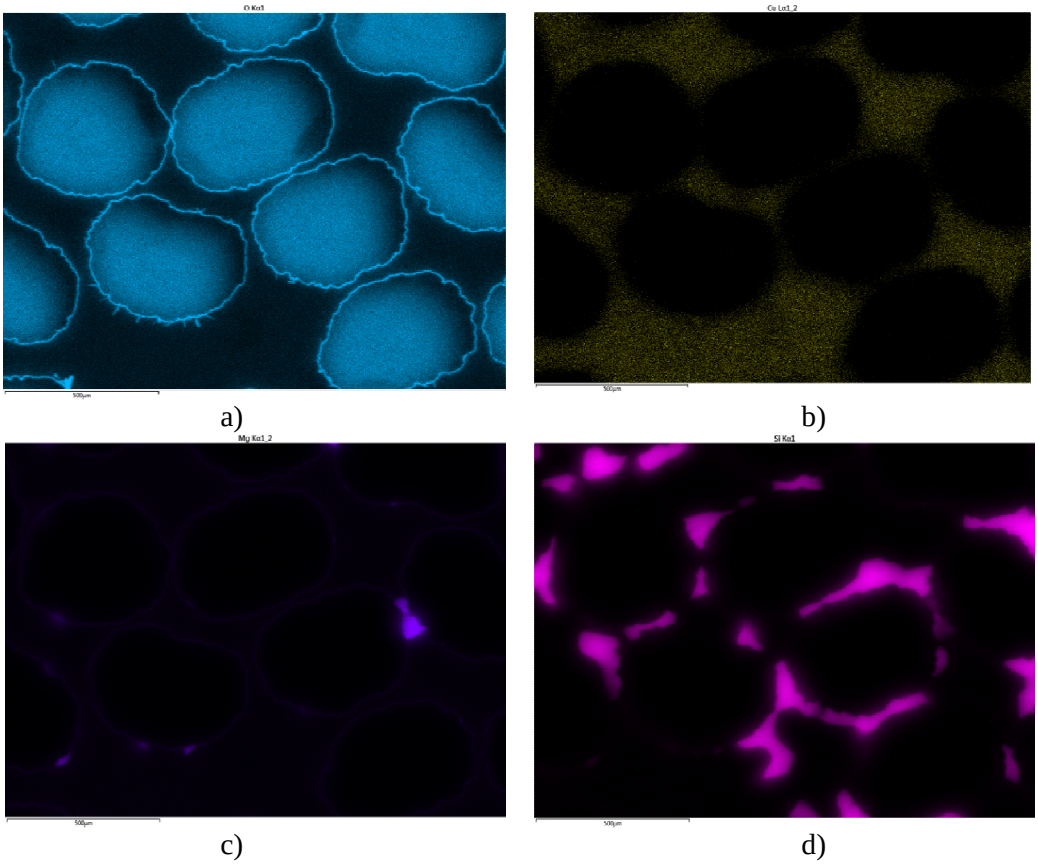

Figure 6. X-Ray elemental mapping of $Cf_{M40J}(Al_2O_3)$/239D composite: a) O, b) Cu, c) Mg, d) Si

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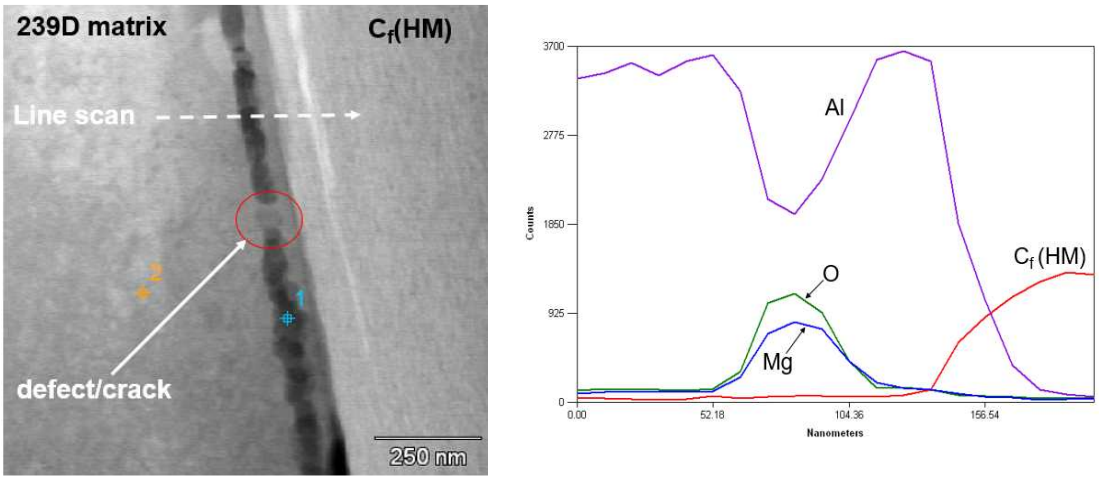

a) b)

Figure 7. Interface analysis of $Cf_{M40J}(Al_2O_3)$/239D system: a) TEM image of interface, b) Chemical composition along line scan perpendicular to the interface

However, a high amount of Al is observed between the carbon fiber and the assumed $MgAl_2O_4$ layer. This Al could originate from the assumed spinel formation or from the diffusion of Al through the assumed spinel $MgAl_2O_4$ layer. These results reveal a degradation of the alumina layer due to a long contact time with metal melt during the GPI process.

4. Conclusions

1. Alumina (Al_2O_3) layer can be deposited homogeneously on complex shaped textile preforms by ALD by proper adjustment of process parameters. The as-deposited alumina coatings are amorphous and remain amorphous after annealing at 720°C for 30 minutes as indicated by XRD analyses.
2. A thin alumina layer (40 nm) improves oxidation resistance significantly without causing an decrease of fiber tensile strength.
3. Al_2O_3-coated textile preforms infiltrated with 239D were dense with very low residual porosity. Alumina layer works properly to improve wettability with 239D-melt. But the alumina layer degrades by the reaction with the alloy component Mg. Formation of spinel $MgAl_2O_4$ is assumed as reason.
4. The fabrication of C_f/Al-MMC requires a proper selection of the matrix alloy because reactions of alloying elements at the fiber-matrix interface play a critical role on the final composite properties.

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