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

Alfaferi Zainal Abidin[1]*, Michel Wolf[2], Mario Krug[1], Ingolf Endler[1], Martin Knaut[3], M. Höhn[1], Alexander Michaelis[1]

[1]Fraunhofer IKTS
Winterbergstr.28, D-01277, Dresden, Germany
Web page: http://www.ikts.fraunhofer.de

[2]Institute Lightweight Engineering and Polymer Technology, Technical University Dresden
Holbeinstr.3, D-01307, Dresden, Germany
Web page: http://www.tu-dresden.de

[3] Institute of Semiconductor and Microsystems technology Technology, Technical University Dresden
Nöthnitzerstr.64, D-01187, Dresden, Germany
Web page: http://www.tu-dresden.de

*Corresponding author (alfaferi.zainal-abidin@ikts.fraunhofer.de)

Keywords: MMC, Al_2O_3 coating, ALD, carbon fiber, magnesium alloy, GPI

ABSTRACT

There has been a growing interest in carbon fiber-reinforced magnesium alloy metal matrix composites (C_f/MgAl-MMC) for lightweight applications. Especially in automotive and aerospace industries they offer outstanding mechanical properties combined with low density. Nevertheless, major obstacles in manufacturing of C_f/MgAl-MMC are high reactivity and poor wettability of the carbon fibers with molten Mg-Al alloy. Often an undesired formation of carbides (e.g. Al_2MgC_2 and/or Al_4C_3) at the fiber-matrix interface is observed. Another problem is the sensitivity of carbon fibers to the oxidation especially at temperatures of more than 400°C. In order to overcome the major obstacles an alumina protective coating is applied on carbon fiber-based textile preforms. 2D-textile preforms are used which consist of high tenacity (HT) carbon fibers. Atomic layer deposition (ALD) is employed for coating of preforms. The ALD process is performed at a substrate temperature of 220°C and a total pressure of 0.5 kPa using the precursors trimethylaluminum (TMA) and ozone. SEM analysis revealed a conformal and uniform coating with a thickness of 40±3 nm and a good adhesion on carbon fibers. Structure and composition analysis of coated-alumina on planar graphite substrate has revealed an amorphous structure and stoichiometric alumina formation (Al/O atomic ratio ~0.66). The influence of 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. Coated fibers with alumina show a small reduction of the tensile strength of approx. 20%. The TGA results confirm an improvement of oxidation resistance of carbon fibers by alumina coating. The infiltration of the Al_2O_3-coated 2D-textile preform was performed with Mg-Al alloy AZ91 (9 wt.% Al) by gas pressure infiltration (GPI). A dense composite with completely suppressed carbide formation is received. This result confirms that an alumina coating works well as protective layer for carbon fibers in metal matrix composites consisting of Mg-Al alloy with high aluminum content.

1 INTRODUCTION

Magnesium alloys have been utilized in special applications such as in automotive and aerospace industries due to their extraordinary low density (1.74 g/cm^3 instead of 2.7 g/cm^3 for Aluminum), high specific strength, excellent casting behavior, good workability, good weldability and high recycling potential [1]. However, their application is often restricted due to magnesium suffers from several material inherent deficiencies like low stiffness, poor high temperature strength, low wear and creep resistance as well as a high thermal expansion coefficient. Certain improvements were developed in the past. Creep strength at elevated temperatures can be increased by using cost intensive magnesium alloys which contain rare earth elements [2]. Other properties like a low thermal expansion coefficient, a high elastic modulus and a high wear resistance have been realized by particle or fiber-reinforcement [3]. Fiber reinforced magnesium composites (C_f/Mg) have been attracting attention due to their unique properties of high specific strength, high stiffness and very low coefficient of thermal expansion [4]. Nevertheless, the main difficulty for fabricating C_f/Mg composites is that molten magnesium does not wet or bond to carbon fibers and therefore it is impossible to achieve load transfer from the matrix to the fibers. Therefore the achievable volume fraction of fiber in the matrix is limited. In contrast to the C_f/Al system C_f/Mg system is thermodynamically less reactive [5]. This is because the two binary magnesium carbides MgC_2 and Mg_2C_3 are endothermic compounds. Formation of MgC_2 or Mg_2C_3 at MMC processing temperature (approx. 720°C) is unlikely. One way to enhance wettability and to attain suitable fiber-matrix bonding in the C_f/Mg system is alloying magnesium with a carbide-forming element like aluminum. But however appropriate interface properties can be achieved only with small amounts of Al (max. 2 wt. % Al). With higher Al content, formation of carbide becomes stronger and embrittles the carbon fibers and thus early failure of C_f/Mg-Al composite under load is the consequence [6]. To overcome the problems at the fiber-matrix interface in the C_f/Mg-Al system, fiber surface is coated by a material which has a good wettability by molten Mg-Al as well as protects the fibers against chemical attack by the melt during manufacturing. The demands on coating materials are already listed by Feldhoff et al. [6] and Reischer et al. [7]. The layer must: (i) provide an adequate fiber-matrix adhesion and (ii) act as a diffusion barrier. Moreover Ochiai et al. [8] and Shorshorov et al. [9] suggested that the coatings should not exceed a critical thickness. Above the critical thickness the crack propagation is enhanced and the fiber strength decreases. Coating materials deposited on carbon fibers which are applied for Mg-based MMC were titanium nitride (TiN) [2, 10, 11], pyrolitic carbon (PyC) [10, 12], silicon carbide (SiC) [10], yttrium stabilized zirconia (YSZ) [13], silicon dioxide (SiO_2) [14] and boron nitride (BN) [7]. So far there has been very rare report on alumina (Al_2O_3) protective coatings deposited on carbon fibers with the objective to improve the properties of C_f/Mg-Al MMC. Alumina is a promising material to solve the problems at the fiber-matrix interface because it acts as diffusion barrier in conjunction with Al-alloy [15-17], improves oxidation resistance of carbon fibers [18, 19] and promotes wetting and bonding with Al-alloy [15] as well as exhibits an excellent thermal and chemical stability (melting point 2072°C). Different coating technologies for the application of alumina protective coatings were described in literature [15-19]. The main deposition methods were liquid-phase coating (sol-gel technique) and deposition from the gas phase. Both methods allow the deposition of coatings on complex shaped substrates. The sol-gel process is simple and inexpensive but the synthesis needs subsequent annealing steps which might be detrimental to the mechanical properties of coated fibers. Crack formation in the films after annealing could be a result [10]. Furthermore sol-gel processes could lead to the damage of carbon fibers by oxygen-containing precursors or moisture, especially at temperatures exceeding 400°C [19] and they require a careful optimization of many process parameters such as concentration of the coating solution, particle surface charge, viscosity of the sol, wetting behavior of the solution on the fiber and deposition rate. Compared to sol-gel methods a better layer adhesion and oxidation resistance were emphasized as an advantage of gas phase technologies as chemical vapor deposition (CVD). This was evaluated for SiC coatings prepared by sol-gel and CVD routes [20]. But in the case of CVD-Al_2O_3, the high deposition temperature combined with oxygen containing precursors is detrimental for the carbon fibers. Therefore atomic layer deposition (ALD) which is a special variant of CVD is chosen as a promising gas phase technology offering a low deposition temperature (<

400°C) and an excellent coatings conformity. This work is focused on ALD deposition of protective Al_2O_3 coatings on very complex carbon fiber-based textile preforms used as reinforcement material for Mg-Al alloys. Al_2O_3-coated fibers are examined regarding to coating homogeneity, oxidation resistance and tensile strength. Structure and chemical composition of coated alumina layer is analyzed on coated graphite substrate. Finally infiltration behavior of Al_2O_3-coated textile preforms by gas pressure infiltration (GPI) is evaluated.

2 EXPERIMENTAL DETAILS

2.1 Materials

Carbon fiber-based 3D-textile preforms and 24K-rovings were purchased from Toho Tenax, consisting of high tenacity fibers (type HTS40 F13). Single filaments in the 3D-textile preform have diameters of 7 µm, a density of 1.77 g/cm^3, a strain to failure of 1.8%, a tensile modulus of 240 GPa, a coefficient of thermal expansion of $-0.1*10^{-6}$ K^{-1} and a tensile strength of 4.3 GPa. Beside 3D-textile preform, 2D-textile preforms from Torayca (T300) was used. Each fiber bundle/roving in the 2D structure consist of 3K single filament. Each filament has characteristic tensile strength of 3.81 GPa, a tensile modulus of 232 GPa, a density of 1.76 g/cm^3, a strain to failure of 1.76%. The complex 3D-textile preform is used for coating homogeneity evaluation and coated 2D-textile preforms is used for the reinforcement in the Mg-Al matrix. Additional planar graphite plates 20mm x 20mm (C_{gr}) were also coated for chemical composition analysis. Coated rovings are used for the evaluation of tensile strength and oxidation resistance. Prior to deposition process, sizing on the fibers was removed by thermal treatment at 400°C for 40 min in vacuum furnace.

2.2 ALD Process

Alumina layer is deposited in a laboratory-scale shower-head ALD reactor from FHR Anlagenbau GmbH. The ALD process is carried out at a constant substrate temperature of 220°C using the precursors trimethylaluminum (TMA) and ozone (O_3). TMA is delivered using a bubbler at 17°C. Argon at a flow rate of 100 sccm is used to transport TMA vapor into the reactor. Purging is performed by flowing argon at a flow rate of 100 sccm. Ozon in a concentration of approx. 16 % is delivered at a flow rate of 1000 sccm of oxygen gas (O_2). Details of the applied process parameters for the alumina deposition are given in Tab. 1. Scheme of shower-head ALD for alumina deposition is shown in Fig. 1.

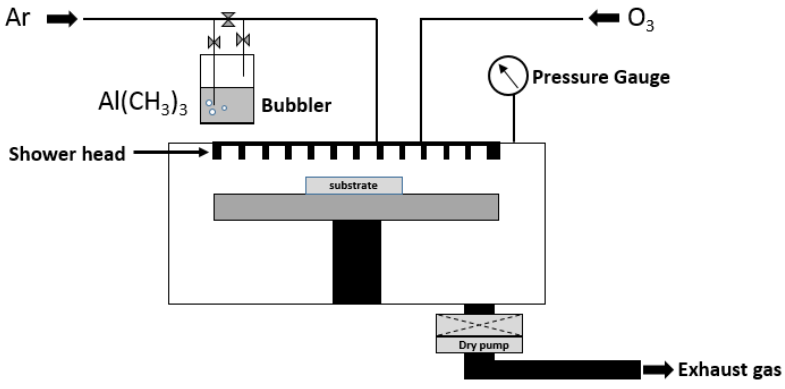


Figure 1: Scheme of shower-head ALD reactor employed for Alumina (Al_2O_3) deposition.

Parameter	Range
Substrate temperature,Ts [°C]	220
Pressure, p [kPa]	0.5
TMA pulse time, s	2
Purge time after TMA/O_3 pulse, s	60 - 120
Ozone pulse time, s	8
Number of ALD cycles	270

Table 1: ALD parameter range for Al_2O_3 layer deposition.

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. The layer thickness can be adjusted by repeating this cycle. Thereby the Al_2O_3 formation mechanism comprises different steps. At first a monolayer of TMA will chemisorb onto the substrate surface during the TMA pulse. During the subsequent Ar purge gas pulse all residual TMA and by-products will be purged away. The following ozone pulse leads to the oxidation of the chemisorbed TMA to Al_2O_3. The subsequent Ar purge gas pulse removes excess ozone and by-products and one ALD cycle is completed. This cycle is repeated as long as the desired layer thickness is obtained.

2.3. Metal matrix composite (MMC) preparation method

The MMC preparation was performed by gas pressure infiltration (GPI) method as described in [21]. The GPI process is generally characterized by four steps (Fig. 2). In the first process step (1) the fiber preform, the moulds and the Mg-alloy are heated up to the temperature exceeding the melting temperature of the Mg-Al. In step 2 vacuum was applied for removing trapped gases. In the following step 3 a high argon gas pressure was applied to accelerate the infiltration. The last step isfast cooling under high pressure.

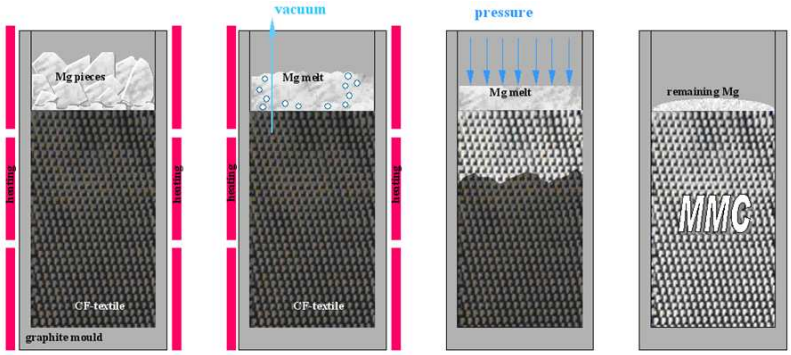


Figure 2: Steps of gas pressure infiltration (GPI) for preparation of C_f/MgAl-MMC.

Commercial magnesium alloy AZ91 was chosen as matrix material to ensure a good compatibility to serial production, especially with regard to automotive and aerospace applications. AZ91 is chemically denoted as Mg9AlZn and has following chemical composition (mass.%): Al – 8.25, Zn – 0.63, Mn – 0.22, Si – 0.035, Cu – 0.003, Fe – 0.014, Be – 0.002, rest Mg [22]. Aluminum in the Mg matrix improves especially mechanical properties and corrosion resistance as well as castability.

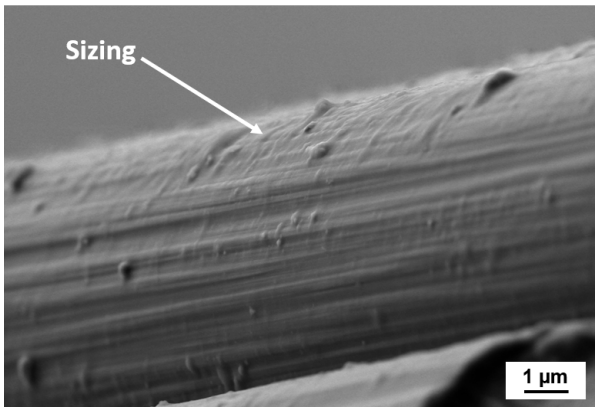
2.4 Analysis Methods

Evaluation of layer thickness and thickness homogeneity over the whole fiber bundle was conducted on cross sections. The samples were embedded in epoxy resin followed by a mechanical polish and afterwards an ion beam preparation using the Broad-Ion-Beam-Technique (BIB).

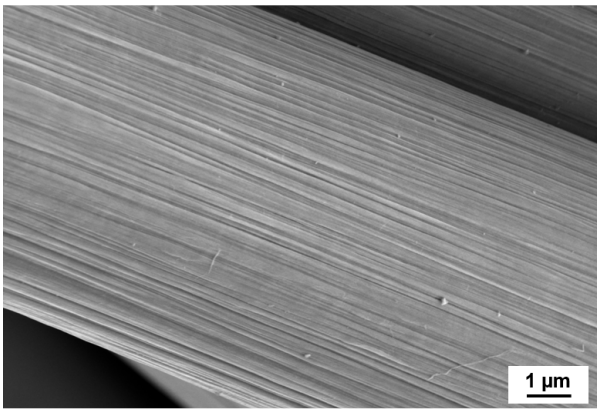
Visualization of the prepared samples was carried out with a SEM from NVision Carl Zeiss SMT GmbH. Additionally fractographs of Al_2O_3-coated fibers were prepared by cutting of coated rovings. The oxidation behavior of uncoated and coated fibers was investigated by STA 409 (Netzsch-Gerätebau GmbH). Fiber bundles with a length of 12 mm were placed in a small ceramic crucible and firstly heated to 100°C at maximal heating rate. After that they were heated to 350°C at 10 K/min followed by a temperature ramp up to 1050°C with a rate of 2.5 K/min. This temperature was kept constant for 30 min. During the entire heating process a flow of synthetic air (80 ml/min) was fed as an oxidation agent. This method was also described from Hackl et al. [23]. The oxidation onset temperature was determined according to DIN 51006 with a tangent analysis. 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 fiber was determined according to ASTM D3379-75 standard. The composition of the coatings was characterized by X-ray photoelectron spectroscopy (XPS). The XPS unit (MultiProbe P, Omicron Nanotechnology GmbH) works with excitation energy Al Kα 1486.6 eV and an exit angle of 45°. Prior to conducting the XPS analysis the layer surface is sputter-cleaned with Ar+ for 2 min with 0.6 keV to remove surface contamination and surface oxide layers. The obtained fiber-reinforced aluminum metal matrix composites (C_f/MgAl-MMC) was cut and the cross section for SEM analysis was prepared by ion beam slope cutting method.

3 RESULTS AND DISCUSSION

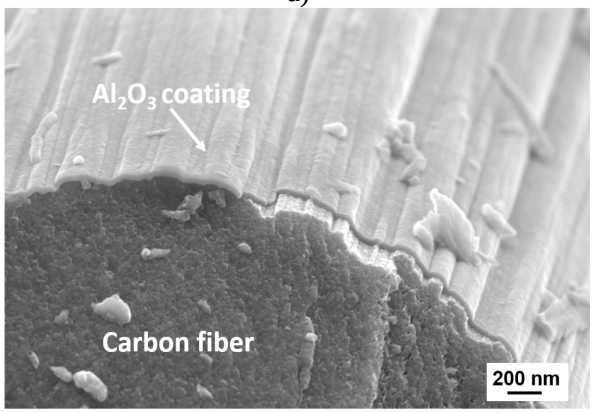
3.1 Homogeneity, morphology and composition of the coating



a)



b)

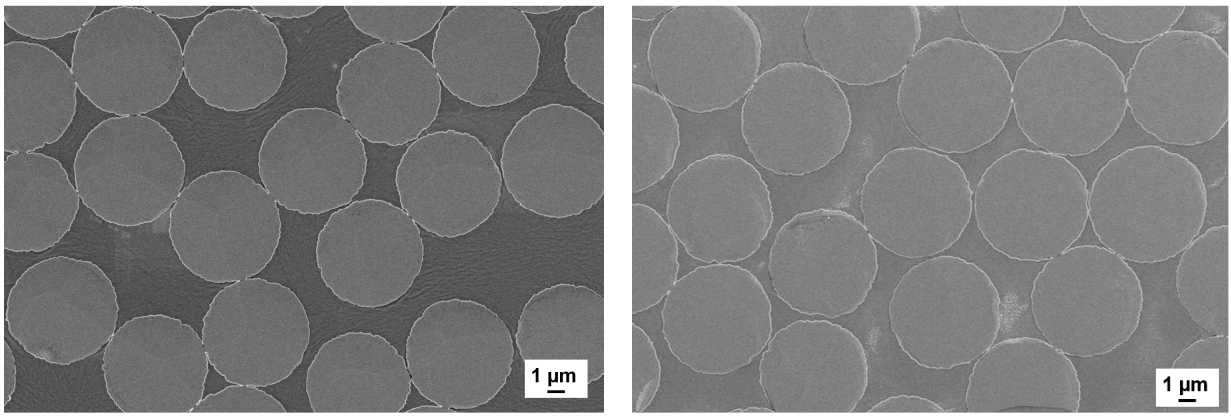


c)

Figure 3: SEM images of HTS40 fibers: a) carbon fiber surface with sizing, b) surface of desized carbon fiber (desized at 400°C in vacuum for 40 min), c) fractograph of Al_2O_3-coated carbon fiber [24].

Fig. 3a shows original carbon fiber surface before thermal treatment. The surface is covered by a polymer sizing (approx. 1.25 wt% of polyurethane base polymer). Prior to ALD-Al_2O_3

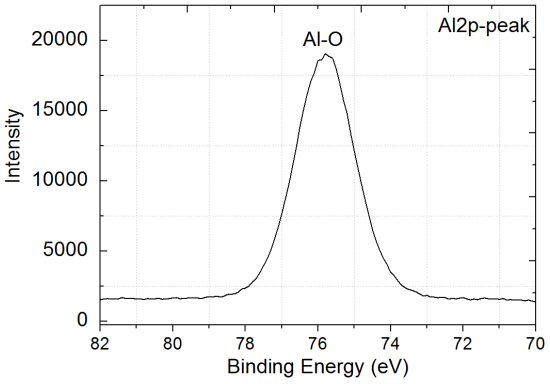
deposition, sizing was removed by thermal treatment at 400°C for 40 min in vacuum furnace. The thermogravimetric analyses (TGA) results have revealed that the applied thermal condition was sufficient to remove the sizing completely. Carbon fiber surface after desizing is shown in Fig 3b. The conditions of the ALD process for coating 3D-textile preforms are described in detail by Krug et al. [24]. As reported in [24], the obtained coating was conformal and covers all of the fiber surface. No flaking of the coatings was observed which indicated that alumina coatings adhere well on the fiber surface (Fig. 3c). The coated fibers shown in Fig. 3c was chosen randomly from the investigated 24K fiber bundle and showed the typical surface morphology of the coated alumina layer. Coating homogeneity evaluation was conducted by means of SEM image evaluation. Average of six values was calculated for center and for perimeter of a 24K fiber bundle each taken from the middle and the perimeter of the 3D-textile preform. In the middle of the 3D-textile preform layer thicknesses of 40.7±2 nm and 41±3 nm were measured at center (Fig. 4a) and perimeter of the fiber bundle, respectively. In the subsequent study a faster ALD deposition process is investigated by reducing Ar purge time from 120 s to 60 s while keeping others parameters constant. The obtained results show that the coating on single fiber is still smooth, uniform and conformal. Coating homogeneity of fibers at perimeter and middle of 24K bundle are 41.3 ± 6 nm and 38.3 ± 4 nm (Fig. 4b), respectively. These results demonstrate that the ALD process can be accelerated by detailed study of the process window.



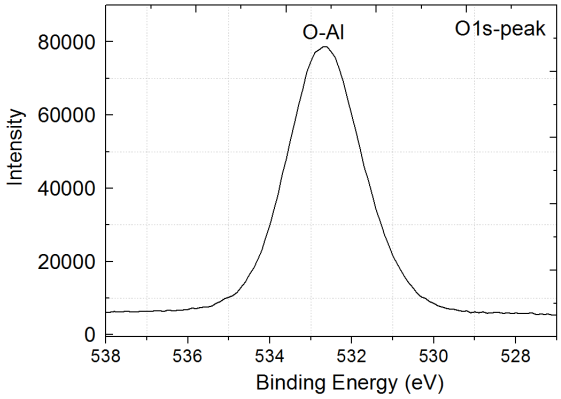
a) b)

Figure 4: SEM images of Al_2O_3 coated fibers inside the 24K fiber bundle prepared with different ALD parameters: a) 2 s TMA/120 s purge/8 s O_3/120 s purge, b) 2 s TMA/60 s purge/8 s O_3/60 s purge.

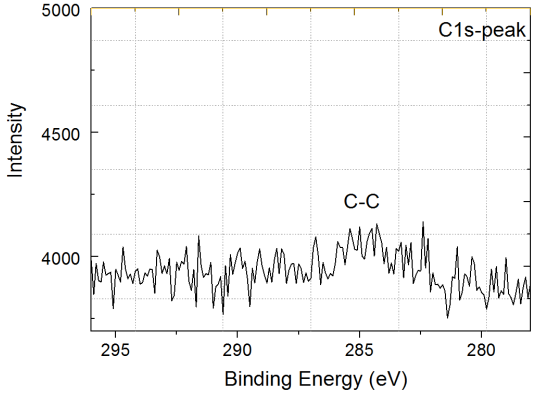
Microstructure analysis of Al_2O_3 coatings coated on planar graphite substrates by X-Ray diffraction (XRD) reveals no reflection of crystalline phase and layer structure remain amorphous even after annealing in the furnace at 720°C for 30 minutes. According to Jakschik et al. [25], ALD- Al_2O_3 layer start to crystallize above 800°C. This result indicates that the structure of alumina layer would remain stable in contact with molten Mg-Al at 720°C during composite fabrication. Further information about layer composition and binding state were received by X -ray photoelectron spectroscopy (XPS). Fig. 5 shows XPS spectra of 40 nm alumina layer coated on graphite substrate under process condition of 2 s TMA/ 120 s Ar purge /8 s O_3/120 s purge. The peaks reveals the presence of Al2p, O1s and C1s peaks at binding energies (BE) of 75.6 eV, 532.3 eV and 285.0 eV which are clearly assigned to Al-O (Fig. 5a) ,O-Al (Fig. 5b) and C-C (Fig. 5c) bonds. The measured binding energies are in good agreement with literature [26] and are comparable with the native aluminum oxide. XPS quantitative analysis indicates that the coated alumina is stoichiometric with Al/O-ratio of 0.67. However a small fraction of carbon impurity (C-C bonds) below 0.5 at.% in the layer is also detected which is visible by a weak peak C1s at a binding energy 285 eV (Fig. 5c). The presence of carbon could be attributed from incomplete desorption of methyl groups after TMA reaction and from graphite substrate itself.



a)



b)



c)

Figure 5: XPS spectra of deposited Al_2O_3 on graphite: a) spectra Al2p, b) spectra O1s, c) spectra C1s.

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

The oxidation behavior of uncoated and Al_2O_3-coated fibers was compared by thermogravimetric analyses (TGA). The oxidation onset temperature is determined according to DIN 51006 with a tangent procedure. Detail procedure of TGA analysis is explained in section 2.3. The results are illustrated in Fig. 6a. For uncoated fibers the onset temperature is approximately 600°C and they are completely burned at a temperature of 680°C to form CO_2 or CO gas. In case of fibers coated with 20 nm alumina the oxidation starts at a temperature of approximately 620°C and fibers are burned completely at 745°C. With increasing thickness of the alumina layer up to 40 nm the onset temperature rises to approximately 635°C. These results show that alumina coatings improve oxidation resistance of carbon fibers significantly which agrees well with the literature [18, 19]. Mechanical properties of carbon fiber-reinforced composites depend not only on interfacial stress transfer capacity but also on mechanical properties of fibers. Therefore it is very important to determine the tensile properties of the coated fibers to evaluate their ability as reinforcement. Influence of alumina coating on the tensile strength of single fiber is shown in Fig. 6b. Al_2O_3-coated single carbon fibers with layer thicknesses of 20 nm and 40 nm show a mean ultimate tensile strength (UTS) of about 3.14 ± 0.46 GPa and 3.27 ± 0.49 GPa compared to 3.85 ± 0.77 GPa for the uncoated carbon fiber. The slightly reduction of tensile strength might be caused by residual stress which is generated as a result of the mismatch in the coefficients of thermal expansion (CTE) between carbon fiber and alumina coating at the interface during cooling to room temperature after deposition. For an Al_2O_3 layer deposited by ALD a CTE of 4.2±0.1 ppm/°C was reported by Miller et al. [27]. The used carbon fibers have a CTE of -0.1 ppm/°C [28] . The internal stress could result in radial cracks and might cause cracking of fibers [29]. Fig. 6b shows that the increase of Al_2O_3 coating thickness did not influence the strength of single fibers significantly. This is a different behavior compared to CVD-coated fibers. CVD coatings lead to a decrease of fiber strength if the coating thickness increases. The decrease of fiber strength is difficult to be avoided as reported in literature [10, 30].

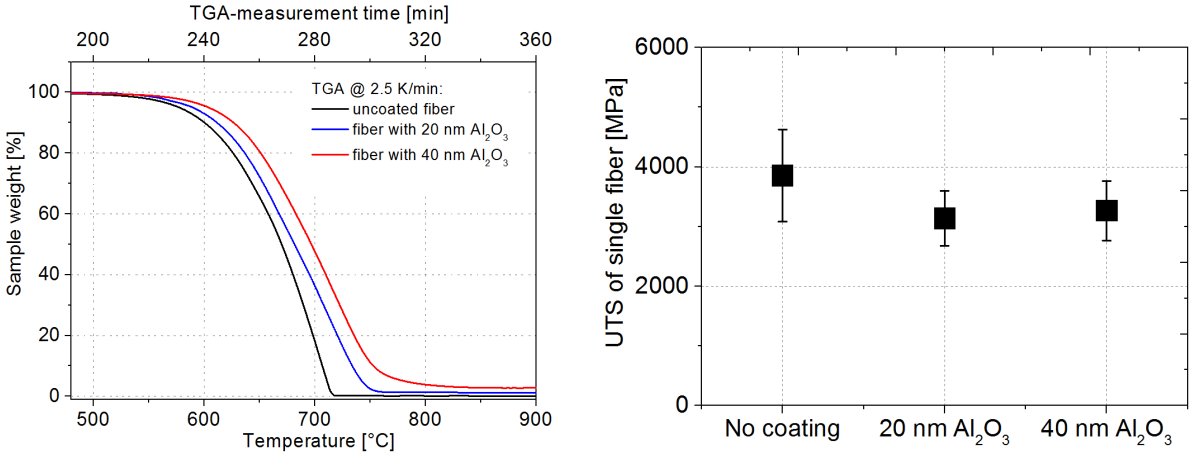
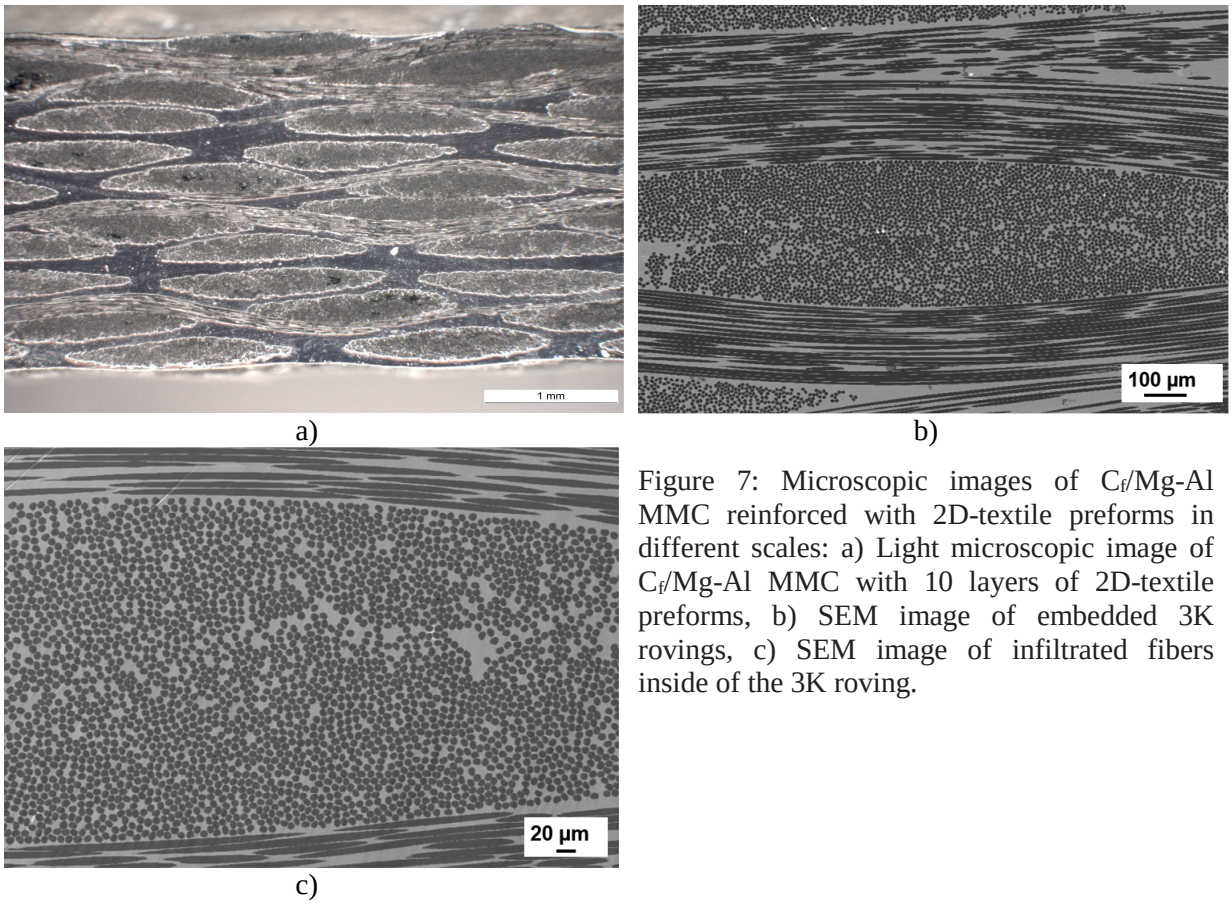


Figure 6: Oxidation behavior and tensile strength of uncoated and Al_2O_3-coated carbon fibers: a) Oxidation behavior measured by TGA, b) Comparison of single fiber tensile strength.

3.3. Analysis of MMC interfacial structure with and without Al_2O_3 protective coating

The uncoated- and Al_2O_3-coated 2D-textile preforms were infiltrated with molten AZ91 by GPI method. The obtained composites were analyzed by SEM to investigate the state of fiber-matrix interface after infiltration. In the GPI process, molten metal infiltrates a fibrous preform and solidifies to form the composite. In the case of Al_2O_3-coated 2D-textile preforms infiltrated with molten AZ91 (720°C, 30 bar) dense composites with very few casting defects and very low residual porosity are received. Fig. 7a shows clearly the stack of 10 layers of Al_2O_3-coated 2D-textile preforms embedded in the AZ91 matrix characterized by light microscopy (fiber volume fraction, $V_f \sim 55\%$). Fig 7b-c show furthermore that the molten AZ91 fills completely the interspaces between the 2D-textile layers (Fig. 7b) and interspaces between carbon fibers in the 3K roving (Fig. 7c). Eventhough the applied pressure is low (30 bar), a dense composite with a good quality of casting is received and thus it indicates that the alumina layer improves wetting with AZ91. The fiber-matrix interfacial structure is shown in Fig. 8a more in detail. After infiltration the alumina layer still exists on the fiber and is stable. As Fig. 8a shows the layer works very well as diffusion barrier and prevents the formation of carbides at fiber-matrix interface. In the case of infiltration without alumina protective coating, casting defects occur. These defects are related to the bad wetting behavior and might act as starting points of cracks. Moreover a strong carbide formation at the fiber-matrix interface is clearly seen as shown in Fig. 8b. The severe reaction at the fiber-matrix interface was due to segregation of aluminum from the AZ91 matrix. The accumulation of aluminum at the fiber-matrix interface starts immediately when rapid solidification begins [32]. The formed carbides at the fiber-matrix interface are the binary carbide Al_4C_3 and/or the ternary carbide Al_2MgC_2 depending on the composition of alloy and applied temperature [33]. At a temperature of 1000 K during GPI Al_2MgC_2 is formed if the Al content of the alloy is lower than 19 wt% and Al_4C_3 develops for an Al content higher than 19 wt% [33]. Both carbides show a hexagonal lattice structure and are rather similar in their appearance of needle-like structures [11]. They can not be distinguished alone by means of their morphology. According to the results obtained by Viala et al. [33] and Feldhoff et al. [11], the carbide shown in Fig. 8b should be ternary Al_2MgC_2 rather than Al_4C_3 carbide. The existence of needle-like Al_2MgC_2 carbide would degrade fiber strength and leads to early failure of the composite. These results demonstrate that an alumina protective layer works well in the C_f/AZ91 system.



a) b) c)

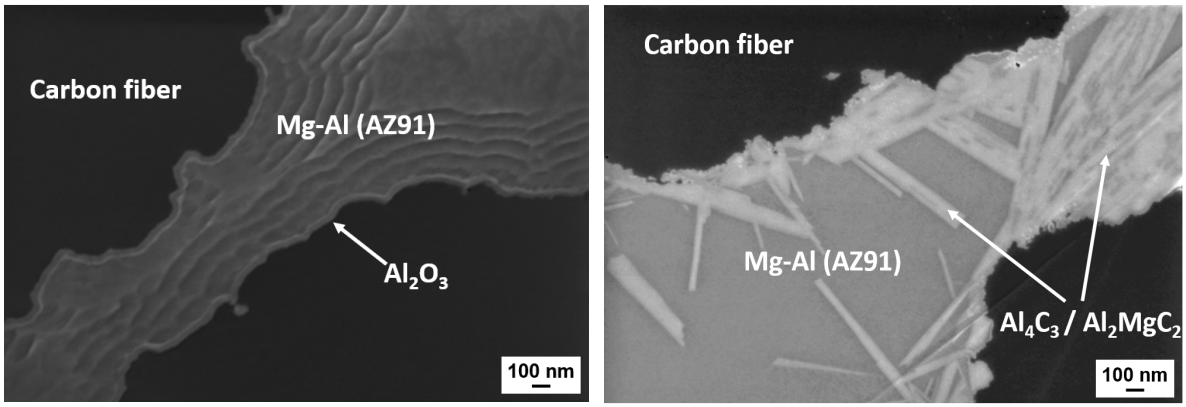
Figure 7: Microscopic images of C_f/Mg-Al MMC reinforced with 2D-textile preforms in different scales: a) Light microscopic image of C_f/Mg-Al MMC with 10 layers of 2D-textile preforms, b) SEM image of embedded 3K rovings, c) SEM image of infiltrated fibers inside of the 3K roving.

Körner et al. [34] and Schmidt [35] reported TiN-coated carbon fibers infiltrated with AZ91 by high pressure infiltration casting (720°C, 100 bar) but however the coating could not protect carbon fibers effectively and carbide formation at the fiber-matrix interface was still observed. Our results have proved that alumina (Al_2O_3) layer could be an alternative to replace Titanium nitride (TiN) as protective coating. Nevertheless, according to Rajan et al. [31] reaction between alumina and magnesium leads to MgO and/or $MgAl_2O_4$ formation:

$$Al_2O_{3(s)} + 3Mg_{(l)} \rightarrow 3MgO_{(s)} + 2Al_{(l)}, \quad \Delta G°_{1000\,K} = -76.63\ kJ/mol \qquad (1)$$

$$4Al_2O_{3(s)} + 3Mg_{(l)} \rightarrow 3MgAl_2O_{4(s)} + 2Al_{(l)}, \quad \Delta G°_{900\,K} = -13\ kJ/mol \qquad (2)$$

Since GPI condition was set at 1000 K, formation of $MgO_{(s)}$ would be favored (reaction 1) than formation of spinel $MgAl_2O_{4\,(s)}$ (reaction 2). Beside $MgO_{(s)}$ formation, there is also release of $Al_{(l)}$ (reaction 2) that dissolves in the AZ91 matrix. This would enrich Al content in the Mg matrix and forms a stable $Al_{12}Mg_{17}$ phase which is normally found nearby fiber-matrix interface. McLeod and Gabryel [36] described that MgO phases are more thermodynamically stable compared to Al_2O_3, therefore Mg tends to reduce Al_2O_3 in order to form MgO.



a) b)

Figure 8: 2D-textile preform infiltrated with AZ91 by GPI method (720°C, 30 bar, 30 min): a) Al_2O_3-coated fiber, b) Uncoated fiber.

When a stable MgO layer is formed on Al_2O_3 layer, it would inhibit further reaction between Al_2O_3 layer and Mg and thus Al_2O_3 layer would be still exist as shown in Fig. 8a. According to reaction 3, $MgAl_2O_{4(s)}$ formation would be proceeded even in solid state as reported by Contreras et al. [37].

$$MgO_{(s)} + Al_2O_{3(s)} \rightarrow MgAl_2O_{4(s)}, \qquad \Delta G°_{900°C} = -44\ kJ/mol \qquad (3)$$

Investigation of MgO and/or $MgAl_2O_4$ formation at the fiber-matrix interface is under investigation and will be reported later. The results of this work show that Al_2O_3 coating improves bonding and wetting behavior as well as prevents undesirable reactions at fiber-matrix interface. Therefore preferable mechanical properties of C_f/AZ91-MMC can be expected.

4. CONCLUSIONS

1. Alumina thin layer (Al_2O_3) can be deposited homogeneously on complex shaped 2D-/3D-textile preforms by adjusting pulse times, temperature and pressure for the ALD process. The as-deposited alumina coatings are amorphous. After annealing at 720°C for 30 minutes no reflections of crystalline phases were observed. The chemical composition analysis by XPS indicates that the coated alumina is stoichiometric with Al/O-ratio of 0.67.
2. Oxidation resistance of alumina-coated carbon fibers is improved by increasing alumina layer thickness. The loss in fiber strength by ALD coating with alumina is low compared to CVD coatings. One reason is the low deposition temperature.
4. Coated Al_2O_3-coated textile preforms infiltrated with molten AZ91 are dense composites with very low residual porosity. The Al_2O_3 layer is stable and works very well as diffusion barrier. Furthermore alumina coating improves significantly the wetting and bonding between the carbon fibers and MgAl alloy.

ACKNOWLEDGEMENTS

Part of investigations in this study was obtained during joint research project between Germany and Poland, sponsored by the DFG (DFG EN 302/2-1 and MI 509/15-1).

REFERENCES

[1] K.U. Kainer, F. von buch, *The current state of technology and potential for further development of Magnesium applications*, Magnesium-Alloys and Technology, (Eds: K. U. Kainer), Wiley-vch Verlag, Weinheim, 2003.

[2] C. Körner, W. Schäff, M. Ottmüller, R.F. Singer, Carbon long fiber reinforced magnesium alloys, *Advanced Engineering Materials*, **2**, 2000, pp. 327-337.
[3] Ch. Fritze, *Fibre-reinforced magnesium composites*, Magnesium-Alloys and Technology, (Eds: K. U. Kainer), Wiley-vch Verlag, Weinheim, 2003.
[4] W.A. Ferrando, Review of corrosion and corrosion control of magnesium alloys and composites, *Journal of Material Engineering*, **11**, 1989, pp. 299-313.
[5] A. Feldhoff, E. Pippel, J. Wolsterdorf, Interface Engineering of Carbon-Fiber Reinforced Mg-Al Alloys, *Advanced Engineering Materials*, 2, 2000, pp. 471-480.
[6] A. Feldhoff, E. Pippel, J. Wolsterdorf, Interface Engineering of Carbon-Fiber Reinforced Mg-Al Alloys, *Advanced Engineering Materials*, **2**, 2000, pp. 471-480.
[7] F. Reischer, E. Pippel, J. Woltersdorf, S. Stöckel, G. Marx, *Carbon fibre-reinforced magnesium: Improvement of bending strength by nanodesign of boron nitride interlayers*, Materials Chemistry and Physics, **104**, 2007, pp. 83-87.
[8] S. Ochiai, Y. Murakami, Tensile strength of composites with brittle reaction zones at interfaces, Journal of Materials Science, **14**, 1979, pp. 831-840.
[9] M.Kh. Shorshorov, L.M. Ustinov, A.M. Zirlin, V.I. Olefirenko, L.V. Vinogradov, Brittle interface layers and tensile strength of metal matrix-fibre composites, *Journal of Materials Science*, **14**, 1979, pp. 1850-1861.
[10] D. Wurm, Einfluss einer Faserbeschichtung auf die Eigenschaften von Kohlenstofflangfaserverstärkten Magnesiumlegierungen, *PhD. Thesis, Friedrich Alexander University of Erlangen-Nürnberg, 1998*.
[11] A. Feldhoff, E. Pippel, J. Wolsterdorf, TiN coatings in C/Mg-Al composites: microstructure, nanochemistry and function, *Philosophical Magazine A*, **80**, 2000, pp. 659 - 672.
[12] AA. Dörner-Reisel, Y. Nishida, V. Klemm, K. Nestler, G. Marx, E. Müller, Investigation of interfacial interaction between uncoated and coated carbon fibres and the magnesium alloy AZ91, *Analytical and Bioanalytical Chemistry*, **374**, 2002, pp. 635 - 638.
[13] W.G. Wang, B.L. Xiao, Z.Y. Ma, Evolution of interfacial nanostructures and stress states in Mg matrix composites reinforced with coated continuous carbon fibers, *Composites science and technology*, **72**, 2012, pp. 152-158.
[14] A. Olszowka-Myalska, A. Botor-Probierz, Studies of the AZ91 magnesium alloy/SiO_2 coated carbon fibres composite microstructure, *IOP Conf. Series: Materials Science* and *Engineering*, **7**, 2010, pp. 012022.
[15] Q.Zeng, Fabrication of Al_2O_3-coated Carbon Fiber-Reinforced Al-Matrix Composites, *Journal of Applied Polymer Science*, **70**, 1998, pp. 177-183.
[16] Y.Tang, Y. Deng, K. Zhang, L. Liu, Y. Wu, W. Hu, Improvement of interface between Al and short carbon fibers by α-Al_2O_3 coatings deposited by sol-gel technology, *Ceramic International*, **34**, 2008, pp. 1787-1790.
[17] Y.Tang, L. Liu, W. Li, B. Shen, W. Hu, Interface characteristics and mechanical properties of short carbon fibers/Al composites with different coatings, *Applied surface science*, **255**, 2009, pp. 4393-4400.
[18] A.K. Roy, S. Schulze, M. Hietschold, W.A. Goedel, Oxidation protection of carbon fibers by coating with alumina and/or titania using atomic layer deposition, *Carbon*, **50**, 2012, pp. 761-770.
[19] A.K. Roy, W. Baumann, S. Schulze, M. Hietschold, T. Mäder, D.J. Nestler, B. Wielage, W.A. Goedel, Atomic Layer deposition of Alumina onto Carbon Fibers, Journal of the American Ceramic Society, **94**, 2011, pp. 2014-2022.
[20] Y.-Q. Wang, Z.-M. Wang, J.-Y. Yang, F.-Q. Zhang, B.-L. Zhow, SiC coating on carbon fibres by a solution coating process, *Composite Manufacturing*, **6**, 1995, pp. 103-106.
[21] W. Hufenbach, M. Gude, A. Czulak, F. Engelmann, Study of manufacture of CF/Al-MMC with aid of the gas pressure infiltration method, *Composites*, 10, 2010, pp. 213-217.
[22] L. Cizek, M. Greger, L.A. Dobrzanski, I. Juricka, R. Kocich, L. Pawlica, T. Tanski, Mechanical properties of magnesium alloy AZ91 at elevated temperatures, *Journal of Achievement in Materials and Manufacturing Engineering*, **18**, 2006, pp. 203-206.

[23] G. Hackl, H. Gerhard, N. Popovska, Coating of carbon short fibers with thin ceramic layers by chemical vapor deposition, *Thin Solid Films*, **513**, 2006, pp. 217-222.
[24] M. Krug, A.Z. Abidin, M. Höhn, I. Endler, N. Sobczak and A. Michaelis, Al_2O_3 protective coatings on carbon fiber-based 3D-textile preforms prepared by ALD for application in metallic composite material, *Proceeding of 13th AUTEX World Textile Conference, Dresden, Germany, May 22-24, 2013*, paper 125, 2013.
[25] S. Jakschik, U. Schroeder, T. Hecht, M. Gutsche, H. Seidl, J.W. Bartha, Crystallization behavior of thin ALD-Al_2O_3 films, *Thin solid film*, **425**, 2003, pp. 216-220.
[26] C. Hinnen, D. Imbert, J.M. Siffre, P. Marcus, An in situ XPS study of sputter-deposited aluminium thin films on graphite, *Applied Surface Science*, **78**, 1994, pp. 219-231.
[27] D.C. Miller, R.R. Foster, S.H. Jen, J. A. Bertrand, S. J. Cunningham, A.S. Morris, Y. C. Lee, S.M. George, M. L. Dunn, Thermo-mechanical properties of alumina films created using the atomic layer deposition technique, *Sensors and Actuators A*, **164**, 2010, pp. 58-67.
[28] Toho Tenax Product data sheet, Toho Tenax Europe GmbH, Version 05, 30.9.2014.
[29] K.K. Chawla, *Composite Materials*, Springer verlag, New York, 1987, pp. 12
[30] Y.Q. Wang, Z.M. Wang, B.L. Zhou, C.X. Shi, Strength degradation of SiC-coated carbon fibres, *Journal of Materials Science Letters*, **12**, 1993, pp. 817-818.
[31] T.P.D. Rajan, R.M. Pillai, B. C. Pai, Review: Reinforcement coatings and interfaces in aluminium metal matrix composites, *Journal of Materials Science*, **33**, 1998, pp. 3491-3503.
[32] M. Song, G. Wu, W. Yang, W. Jia, Z. Xia, G. Chen, Mechanical properties of Cf/Mg composites fabricated by pressure infiltration method, *Journal of Material Science and Technology*, **26**, 2010, pp. 931-935.
[33] J.C. Viala, G. Claveyrolas, F. Bosselet, J. Bouix, The chemical behavior of carbon fibres in magnesium base Mg-Al alloys, *Journal of Materials Science*, **35**, 2000, pp. 1813-1825.
[34] C. Körner, W. Schäff, M. Ottmüller, R.F. Singer, Carbon long fiber reinforced magnesium alloys, *Advanced Engineering Materials*, **2**, 2000, pp. 327-337.
[35] S. Schmidt, Beschichtung kohlenstofffasern durch chemische gasphasenabscheidung (CVD), *PhD. Thesis, Friedrich Alexander University of Erlangen-Nürnberg*, 2004.
[36] A.D. Mc Leod, C.M. Gabryel, Kinetics of the growth of Spinel,MgAl2O4, on Alumina Particulate in Aluminum Alloys Containing Magnesium, *Metallurgical Transactions A*, **23a**, 1992, pp. 1279-1283.
[37] A. Contreras, E. Bedolla, R. Perez, Interfacial phenomena in wettability of TiC by Al-Mg alloys, *Acta Materialia*, **52**, 2004, pp. 985-994.