The effect of titanium dioxide coated carbon fibers on the aluminum alloy matrix composite strength

A I Gomzin¹, R F Gallyamova¹,², S N Galyshev³, R M Paramonov¹, N G Zaripov¹ and F F Musin²

¹Department of Material Science and Metal Physics, Ufa State Aviation Technical University, Ufa, Russia
²Ufa Chemistry Institute of RAS, Ufa, Russia
³Institute of Solid State Physics of RAS, Chernogolovka, Moscow distr., Russia

E-mail: andre-gomzi@yandex.ru

Abstract. In this work the possibility of using TiO₂ coating as a barrier between carbon fiber and an aluminum matrix in a Cf/Al composite was studied. Specimens of a composite with a matrix of Al-6Mg alloy were obtained by the method of liquid-phase infiltration under pressure. As a reinforcing component was used continuous uncoated and titanium dioxide coated carbon fibers. TiO₂ coating on carbon fiber preform were prepared by sol–gel method. The protective properties of the coating and the mechanical properties of the composite at three-point bending were evaluated. Microstructural and fractographic analyzes were performed. It was established that the barrier coating made it possible to increase the strength of the composite more than 2.5 times from 250 MPa to 660 MPa.

1. Introduction

Aluminum matrix composites reinforced with carbon fibers has long been interested in many researchers around the world. Due to combining the properties of components (aluminum plasticity and carbon fibers strength with the lightness of both), the Cf/Al composite can become one of the best structural materials for the aerospace, aviation and other industries [1-3]. The mechanical properties of any composite material primarily depend on the properties at the fiber-matrix interface, so at the present time in the manufacture of Cf/Al composites it is not possible to achieve high material strength due to the formation of aluminum carbides [4-6]. Because of the small diameter of carbon fiber, the fabrication of metal matrix composites is possible only by liquid-phase methods, which, in combination with the high reactivity of the carbon-aluminum system, inevitably lead to the formation of carbides.

One way to prevention the formation of carbides is to modify the surface of carbon fiber with protective coatings. With using oxide coatings on composite reinforcing fibers, the final strength usually increases. Considering the positive experience of some researchers using titanium oxide coating on fibers when fabrication a metal matrix composite, an identical coating was chosen for this study [6-8].

In the present paper, TiO₂ coating on carbon fibers was obtained by the sol-gel method which is quite simple and economical. The coated and uncoated carbon fibers were heated in an air atmosphere, after which their mass loss was compared. Aluminum alloy matrix composites reinforced with uncoated fibers and TiO₂-coated fibers and were fabricated by the method of liquid-phase infiltration under pressure. Composites microstructure, bending strength, and fracture behavior were studied.
2. Experimental materials and methods

2.1. Materials
The matrix was an aluminum alloy with 6% magnesium in the composition AMg6. There were also 0.4% Si, 0.4% Fe, 0.1% Cu, 0.6% Mn, 0.2% Zn in the alloy. The choice of an alloy with the presence of magnesium in the composition was due to the suppression of the formation of aluminum carbide at the matrix/carbon fiber interface [9, 10].

The matrix was reinforced with carbon fiber bundles of the UMT430 brand with a tensile strength of 4.5 GPa and an increased modulus of elasticity of 430 GPa (UMATEX Group, Russia).

2.2. Coating
Titanium n-butoxide (Ti(C₄H₉O)₄, 99%, Acros) was used as a source of titanium dioxide. The preparation of sol was carried out according to the following procedure [11]: titanium butoxide was added to the mixture of solutions (butanol, acetic acid, acetylacetone) with stirring. The resulting solution was stirred 1 hour at room temperature. Then a mixture of distilled water and butanol were adding slowly dropwise while vigorously stirring for 1 hour. The prepared sol-gel solution was aged for 3 days to achieve complete hydrolysis.

The coating process involves immersing the carbon fibers in the sol solution. Carbon fibers were aged there for 15 minutes, then slowly removed from the solution and dried at room temperature for 24 hours.

2.3. The fabrication method
Composites reinforced with continuous uncoated and TiO₂-coated carbon fibers were fabricated by one of the varieties of the liquid-phase infiltration method under pressure - the shell molding process. The fabrication technology of the Cf/Al plates was described in [12]. In the present study, the pressure applied during pressing was 70 MPa. The fiber volume fraction was 30%.

2.4. Three-point bending test and characterization
For three-point test plane-parallel samples of composites with dimensions 70x10x2 were prepared. The loading was carried out before the failure of the sample. The maximum strength values were obtained by the following equation:

\[
\sigma_b = \frac{3F_{\text{max}}L}{2bh^2},
\]

where \( F \) is the maximum load preceding failure; \( b \) is specimen width; \( h \) is specimen thickness; \( L \) is the distance between the supports.

The fibers surfaces and the samples fracture surfaces, as well as the microstructure were studied on a scanning electron microscope (SEM, JEOL JSM-6490LV). Determination of the weight loss was conducted using an analytical balance (HR-120, AND company).

3. Results and discussion

3.1. Surface morphology of TiO₂-coating
Using scanning electron microscopy (SEM), images of the surface of the fibers before (figure 1a) and after coating (figure 1b) were obtained. In the initial state, carbon fibers contain many longitudinal strips. After coating, the fiber surface is less banded, individual particles on the surface of different shape are observed.
3.2. Evaluation of coating protective properties
To evaluate the protective properties of coating, the fibers were heated to temperature 600°C and 700°C [11, 13, 14]. Curves of change in fiber mass from the exposure time at various temperatures are presented in figure 2. After 6 hours at a temperature of 600°C, the weight loss of the coated carbon fiber was about 35%, while the mass loss of uncoated carbon fiber was about 67%.

\[\text{Figure 2. Plots of the carbon fibers weight loss the temperature: 600°C (a) and 700°C (b).}\]

At a temperature of 700 °C, the burnout process is accelerated. After 90 minutes of exposure, the weight loss of the coated fiber is about 86%. At the same time, uncoated fiber is completely burned out. Thus, the TiO\(_2\) coating applied by the sol-gel method according to the specified earlier regime significantly slows down of the fiber oxidation process in the studied temperature range. This is a premise for using TiO\(_2\) as a protective coating in the fabrication of Cf/Al composite.

3.3. Microstructure of composites
Typical microstructure of Cf/Al composites in transverse section of the direction of fiber presented in figure 3.
Figure 3. The microstructure of the Cf/Al composites reinforced by uncoated fibers (a) and TiO$_2$-coated fibers (b). The areas with voids are framed by the ovals in Figure (a).

In figure 3a it can be seen that the uncoated fibers composite has areas not infiltrated by aluminum. This is most likely due to the insufficient pressure of infiltration because of the almost complete absence of wetting of the surface of high-modulus carbon fiber by matrix melt.

Under the same fabrication conditions, in the composite with the coated fibers in figure 3b there are no voids. This fact suggests that the TiO$_2$ coating improves wetting with an Al-6Mg melt, which means that less pressure is required to infiltrate the carbon fiber preform with the alloy.

Also in figure 3b, bright inclusions can be observed in the matrix. Using local chemical analysis, it was established that these are particles of titanium oxide that were not in direct contact with the fiber, and which were mentioned earlier in paragraph 3.1. It should also be noted that in the composite with the coated fibers no contacting fibers are observed in the images, which is an additional advantage of using the TiO$_2$ coating.

3.4. Bending test
The average bending strength of the composite with uncoated carbon fibers was 254 MPa, with titanium oxide coated carbon fibers was 667 MPa. In addition, the fracture behavior of the composites correlates with the strength values [4, 5, 15, 16]. The flat fracture surface of the uncoated fibers composite hints at a brittle fracture, and in areas without a matrix, rare individual fibers are pull-out (figure 4a). In the TiO$_2$-coated fibers composite bundle fracture takes precedence, but rare single-fiber fracture is also found here (figure 4b).

Figure 4. Fracture surfaces of the Cf/Al composites reinforced by uncoated fibers (a) and TiO$_2$-coated fibers (b).
Thus, it can be concluded that in the case of using uncoated fibers, brittle fracture with low strength is most likely due to a strong bond at the fiber-matrix interface due to the formation of aluminum carbides [15, 16]. In the case of using TiO$_2$-coated fibers, the bond at the interface is less strong, as evidenced by the results of mechanical tests and the fracture behavior.

4. Conclusion

In this paper, the possibility of using TiO$_2$ coatings as a barrier between carbon fiber and an aluminum matrix was studied and the following conclusions were made:

- Carbon fibers with a TiO$_2$ coating oxidize in air at elevated temperatures much slower than uncoated fibers. So the weight loss of the coated fiber at 600°C (6 hours) and 700°C (1.5 hours) turned out to be about 50% and 15% less respectively. Although the coating on the fibers was fairly uniform, it had a few cracks, which could negatively affect the protective properties. Therefore, by optimizing the mode of deposition of titanium dioxide and getting rid of cracks and other defects, it is possible to further improve the barrier properties and reduce the weight loss of the fiber.
- Under the same conditions of fabrication for infiltration of the entire TiO$_2$-coated carbon fiber preform by aluminum alloy melt, it is necessary to apply less pressure in comparison with the uncoated fibers preform.
- The average bending strength of the uncoated carbon fibers composite was 254 MPa, while the strength of the TiO$_2$ coating carbon fibers composite was more than 2.5 times higher — 667 MPa. These values correlate with the brittle fracture and flat fracture surface for the first case, and with the bundle fracture and the rough fracture surface for the second case. This phenomenon can be explained by a strong bond between the matrix and the fiber, resulting from the formation of aluminum carbides during brittle fracture, and the lower strength of such a bond in the absence of carbides, which does not allow the crack to free propagate in the material.

Acknowledgments

This work was funded by grant of young scientists projects of the Republic of Bashkortostan, project № 10GR.

References

[1] Matsunaga T, Matsuda K, Hatayama T, Shinozaki K and Yoshida M 2007 Fabrication of continuous carbon fiber-reinforced aluminum–magnesium alloy composite wires using ultrasonic infiltration method Composites: Part A 38 1902–11
[2] Yunhe Z and Gaohuia W 2010 Comparative study on the interface and mechanical properties of T700/Al and M40/Al composites Rare Metals 29 (1) 102-7
[3] Asano K 2017 Mechanical properties of aluminum composites reinforced with pan- and pitch-based short carbon fibers Materials Transactions 58 (6) 906-13
[4] Feldhoff A, Pippel E and Woltersdorf J 1997 Interface reactions and fracture behavior of fibre-reinforced Mg/Al alloys J Microsc. 185 122-31
[5] Feldhoff A, Pippel E and Woltersdorf J 2000 Interface Engineering of Carbon Fiber Reinforced Mg–Al Alloys Adv Eng Mater. 2 (8) 471-80
[6] Li S, Qi L, Zhang T, Ju L and Li H 2017 Interfacial microstructure and mechanical properties of Cf/AZ91D composites with TiO$_2$ and PyC fiber coatings Micron 101 170-6
[7] Wen T, Gao J, Shen J and Zhou Z 2001 Preparation and characterization of TiO$_2$ thin films by the sol-gel process J Mater Sci. 36 5923-6
[8] Cunjuan X, Mingliang W, Haowei W and Cong Z 2014 The effect of aluminum content on TiO$_2$-coated carbon fiber reinforced magnesium alloy composites Appl Mech Mater. 488-489 30-5
[9] Revzin B, Fuks D and Pelleg J 1996 Carbide formation in aluminium-carbon fibre-reinforced composites Compos. Sci. Technol. 56 3-10
[10] Pelleg J, Ashkenazi D and Ganor M 2000 The influence of a third element on the interface reactions in metal-matrix composites (MMC) Al-graphite system Mater Sci Eng. A 281 239-47
[11] Hu H, Pang B, Zhu Y and Fu Y 2016 Preparation of titanium dioxide immobilized on carbon fibers annealed in steam ambient and their photocatalytic properties Textile Research Journal 87 1-9
[12] Galyshev S, Gomzin A and Musin F 2019 Aluminum matrix composite reinforced by carbon fibers Mater Today Proc. 11 3249-54
[13] Gadiou R, Serverin S, Gibot P and Vix-Guterl C 2008 The synthesis of SiC and TiC protective coatings for carbon fibers by the reactive replica process J Eur Ceram Soc. 28 2265–74
[14] Xia K, Lu C and Yang Y 2013 Preparation of anti-oxidative SiC/SiO$_2$ coating on carbon fibers from vinyltriethoxysilane by sol–gel method Appl Surf Sci 265 603–9
[15] Vidal-Se’tif M H, Lancin M, Marhic C, Valle R, Raviart J-L, Daux J-C and Rabinovitch M 1999 On the role of brittle interfacial phases on the mechanical properties of carbon fibre reinforced Al-based matrix composites Mater Sci Eng. A 272 321-33
[16] Pei Z, Li K, Gong J, Shi N, Elangovan E and Sun C 2009 Micro-structural and tensile strength analyses on the magnesium matrix composites reinforced with coated carbon fiber J Mater Sci. 44 4124-31