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# **Tensile strength, oxidation resistance and wettability of carbon fibers coated with a TiC layer using a molten salt method**

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## **Abstract**

Titanium carbide (TiC) coating were synthesised on Polyacrylonitrile (PAN)-based carbon fibers by a molten salt method using the molten salt mixture composed of LiCl, KCl and KF as a reaction medium. The surface morphology, tensile strength and oxidation resistance of the uncoated and TiC-coated carbon fibers were investigated. The wettability of these fibers by molten magnesium (Mg) and aluminum (Al) was also examined. TiC coatings obtained have a thickness of approximately 0.05-0.6  $\mu\text{m}$  and are found to be uniform and adherent to the fibres. After being coated with a uniform and continuous TiC layer, the tensile strength of

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the carbon fibers decreases and their oxidation resistance is improved significantly. An increase in the TiC coating thickness leads to the reduction in the tensile strength of the carbon fibers and the improvement of their oxidation resistance. The oxidation activation energy of the carbon fibers increases from 127 to 170 kJ/mol after being coated with a 124 nm thick layer of TiC. Coating of carbon fibers with TiC also induces an increase in the total surface free energy of the carbon fibers, and as a result the wettability of carbon fibers with molten Mg and Al is improved remarkably. TiC coating is found to be stable at 1000 °C in molten Mg. However it is readily decomposed by the molten Al at high temperature, which brings about carbon fibers being attacked by the molten Al and the consequent severe damage of carbon fibers.

**Keywords:** TiC coating; carbon fiber; tensile strength; weight loss; wettability.

## **1. Introduction**

Carbon fiber reinforced metal matrix composites (CfMMCs) possess unique properties, such as high specific strength, high specific modulus, high thermal and electrical conductivity, low expansion coefficient and good self-lubricant [1-3]. These mechanical and physical properties are quite attractive for structural, thermal and electrical applications. However, the development of carbon fiber reinforced metal matrix composites has been hindered by the low oxidation resistance of carbon fibers, poor wetting characteristics of carbon fiber by liquid metal, as well as the chemical reaction between carbon fibers and many metals, which introduce many difficulties in the fabrication and high temperature application of these composites [4]. To promote wetting and simultaneously provide a barrier against excessive interfacial reaction

between the fibers and the matrix metal during the fabrication of the composites, it is necessary to develop a suitable protective coating on the carbon fiber surface [5]. The coating layer must have high enough temperature stability and reasonable strength and adherence to permit good load transfer between fibers and matrix. Among the numerous coatings proposed in the literature, TiC is especially attractive for its stability, low density and excellent wettability by molten Mg and Al [5, 6]. Generally, TiC coating is fabricated by the means of chemical vapor deposition (CVD) or liquid metal transfer agent (LMTA) technique. The CVD method needs special equipment, which is very expensive and time-consuming as well. The presence of chlorine ( $\text{TiCl}_4$  used as titanium source) and the high reaction temperature (above  $1100^\circ\text{C}$ ) may damage carbon fibers in the coating process [7]. The LMTA technique uses a liquid metal medium (Sn) to transport a carbide forming element (Ti) to the carbon fiber surface, whereupon it forms a TiC layer on the carbon fiber. The coated fibres may then be incorporated in an Al alloy matrix by a liquid infiltration process. The major drawback of this technique lies in the contamination of the TiC coating by molten Sn, which further changes the composition and properties of the Al alloy matrix during the fabrication of the composites [8].

To overcome these problems, we proposed a molten salt method in previous papers to synthesize TiC coatings on carbon fibers at a relatively low temperature [9, 10]. This method uses a molten salt medium composed of LiCl-KCl-KF to transport a carbide forming element (Ti or  $\text{TiH}_2$ ) to the surface of each individual filament in the fiber bundle, whereupon it reacts with carbon and forms a uniform and continuous

TiC coating on each carbon fiber filament. After repeatedly washing the mixture of the fibers and salts in distilled water, the salts were dissolved completely in water. The resulting coated carbon fibers are free of residual contamination from the salts.

In this study, TiC coatings were synthesized on carbon fibers by a molten salt method under optimized conditions. The effects of the TiC coating thickness on the tensile strength and oxidation resistance of the carbon fibers were investigated. The wettability and compatibility of the fibers with molten Mg and Al were also studied. The objective of this work is to understand the properties of the TiC-coated carbon fibers and thus to provide theoretical and practical guidance for the development of TiC-coated carbon fibers reinforced metal-matrix composites in the future.

## **2. Experimental**

### **2.1 Preparation of a TiC coating on carbon fibers**

PAN-based carbon fibers with an average diameter of about 7  $\mu$  m, purchased from Jilin Carbon Plant (P.R. China), were used in this work. Before coating, carbon fibers were immersed in acetone for several hours to remove the sizing agent and then dried for use. The molten salt mixture was composed of LiCl, KCl and KF. The molar ratio of titanium (200 mesh, 99.95% purity, Beijing Mountain Technical Development Center for Non-ferrous Metals in China) and carbon fibers in the molten salt was chosen to be Ti : C = 1 : 2. The carbon fibers were placed in an alumina crucible and covered by the mixture of the salts and titanium powders. The crucible was then put into a vertical furnace and heated at 850 °C for 0.5-5 h under a flowing argon atmosphere. After cooling, the product in the crucible was boiled repeatedly in

distilled water to dissolve the salts in order to retrieve the TiC-coated carbon fibers by decanting off the supernatant solution. The coated carbon fibers were then dried at 120 °C for 2 h.

## **2.2 Microstructure characterization**

The phases present in the coated fibers before and after oxidation and on the surface of the samples prepared for testing the wettability between fibers and molten metal (Mg or Al) were identified by an X-ray diffraction (XRD) instrument (Philips X'Pert Pro MPD) using Cu-K<sub>α</sub> radiation ( $\lambda=1.54056 \text{ \AA}$ ). The working voltage and current of the Cu target were 40 kV and 40 mA, respectively. The surface morphologies of the fibers and the samples prepared for testing the wettability of the fibers by molten metal (Mg or Al) were observed using a field emission gun scanning electron microscope (FESEM, NOVA400 NANOSEM). The elemental composition of the surface of the coated carbon fibers was obtained using the energy dispersive X-ray (EDX) analyzer linked to this instrument.

## **2.3 Oxidation resistant tests**

The oxidation resistant properties of carbon fibers with and without TiC coating were studied by isothermal oxidation weight loss technique. Before carrying out the isothermal oxidation test, all the samples were dried at a temperature of 120 °C for a sufficient time until the weight became constant. The samples were put into an electric-resistance furnace and heated under an argon gas flow at a heating rate of 5 K/min up to the desired temperature (200-750 °C), thereafter, the gas flow was switched off and the samples were exposed in static air for varying periods of time.

The weight of the samples before and after heat treated was measured by a high accuracy electronic balance (sensitivity:  $\pm 0.1$  mg), for the calculation of the absolute weight loss and relative weight loss. The relative weight loss was used to indicate the amount of oxidation.

#### **2.4 Tensile strength tests**

The fiber tensile strength was conducted at room temperature using XQ-1C testing machine according to standard test method for tensile strength and Young's modulus for high-modulus single-filament materials (ASTM-D3379). A filament (gauge length = 20 mm) extracted from a tow was fixed on paper frame using a hard resin. The paper frame was carefully cut apart just before application of the load to the filament, and the filament was stretched at a rate of 2.5 mm/min. Before each rupture test, the filament diameter was determined by optical microscope and used for calculation of tensile strength. About 50 filaments for each sample were tested. The tensile strengths of the desized carbon fibers and TiC-coated carbon fibers were also determined after exposure in static air at prescribed temperatures. The average diameter for was determined to be  $7.49 \pm 0.06$   $\mu\text{m}$ .

#### **2.5 Surface free energy analysis**

The surface free energy of the carbon fibers can be determined by measuring the contact angle between the carbon fibers and a variety of liquids, with known polar and dispersive components of their total surface energy. The liquids used included pure water, ethylene glycol, glycerol, diiodomethane, bromonaphthalene etc. [11]. In this paper, a dynamic contact angle measuring instrument and tensiometer (DCAT 21,

Dataphysics, Germany) was used to determine the carbon fibers' contact angles with pure water and diiodomethane by Wilhelmy method, and the Owens-Wendt-Kaelble method was used to evaluate the free surface energy from the measurements. Ten single filaments were tested for each wetting liquid.

## **2.6 Wettability tests**

The wettability of reinforcement by a metal matrix is one of the major factors for the production of metal matrix composites. The wettability is usually measured by the sessile drop method. However, this method is inapplicable in the case of carbon fibers, because this method requires a flat substrate that can hold a complete drop of molten metal [12]. In this study, the wettability measurement process was carried out using the method similar to that reported in literature [5]. The fibers were stacked in alternate layers with Mg granules inside a graphite crucible or with Al granules inside an alumina crucible. The mixture of fibers and Mg or Al was heated under argon protection to 1000 °C for 2 h. The resulting samples were examined by SEM to evaluate the wettability of the fiber by Mg or Al melt.

## **3. Results and discussion**

### **3.1 Morphology of the TiC-coated carbon fibers**

Carbide layers with thickness ranging from 0.05 to 0.6  $\mu\text{m}$  are successfully coated on PAN-based carbon fibers by a molten salt method. X-ray diffraction and SEM/EDX analysis (not shown) of the coated carbon fibers indicate that the carbide coatings are composed of cubic TiC phase. From survey images (Fig. 1a and d) of the TiC-coated carbon fibers prepared at 850 °C for 1 h and 5 h in LiCl-KCl-KF molten



salts, it can be seen clearly that all of the carbon fiber filaments are coated with a TiC layer, indicating a good wettability of the fibers by the molten salts. The TiC coatings synthesized at 850 °C are homogeneous along their length and circumferential directions and no rough defects can be found on the surface of these TiC-coated carbon fibers. The fibers do not appear to become connected by coating “bridges” in any of the above cases. No cracking or peeling of the coating is observed on the surface of these carbon fibers due to differences between the thermal expansion coefficients of the coating and the carbon fiber substrate during cooling. Fig. 1b and e show the cross section of an individual fiber, where there is no breakaway of the coating even after the samples have been cut with scissors, indicating a good adhesion of the coating to the fiber. The thickness of the coating, estimated from the higher magnification image shown in Fig. 1c and f, is about 0.05 and 0.6  $\mu\text{m}$ , respectively, and it can be controlled by adjusting process parameters, such as the molar ratio between Ti powder and the carbon fiber, reaction temperature and reaction time [10].

### **3.2 Tensile strength of the TiC-coated carbon fibers**

It is well known that the mechanical properties of carbon fiber reinforced composites depend not only on the interfacial stress transfer capacity but also on mechanical properties of fibers. Tensile strength of carbon fibers can be greatly influenced by coating, especially ceramic coatings which are usually used to improve the oxidation resistance of carbon fibers at high temperatures [13]. Therefore, it is very significant to test the tensile strength of the coated fibers to evaluate their applicability as reinforcement for composites. In this work, the single filament tensile

tests of the uncoated and TiC-coated fibers were performed at room temperature.

The tensile strength of TiC-coated carbon fibers is strongly dependent on the thickness of coating, as can be seen from Fig. 2. The uncoated carbon fibers show the highest strength. After coated with a 0.06  $\mu\text{m}$  thick TiC layer, the tensile strength of the carbon fibers decreases by 10%. Upon increasing the coating thickness to 0.560  $\mu\text{m}$ , the tensile strength of the TiC-coated carbon fibers decreases to 18% of that of the uncoated carbon fibers. A series of experiments during which the carbon fibers were heat treated in LiCl-KCl-KF molten salt medium in the absence of Ti powders show, that a degradation of the fiber strength by an attack of ions or atoms in the liquid melt on the surface of the carbon fiber or damage due to handling can be excluded. Thus the reduction in the tensile strength of the coated carbon fibers could be explained in terms of differences in the coefficient of thermal expansion and the different mechanical properties of the fiber and coating. Difference in the thermal expansion coefficients of the carbon fibers and coating could cause residual stress at the interface during cooling to room temperature after deposition. The internal residual stress will result in cracks in the coating if the acting load achieves a critical value, in view of the coating having a lower fracture strain than that of the fiber [14]. The cracks will eventually propagate into the fiber under further loading if the bonding between the coating and the fiber is strong enough to withstand the shear stress at the interface [4]. Obviously, these cracks in the coating act as stress raisers which reduce the tensile strength of the fibers. Because the residual stress increases with the increase in the coating thickness, and the acting loads at which cracks form in

the coating and the coated fibers fail decrease with the increasing residual stress, increasing the coating thickness leads to the decrease in the tensile strength of the TiC-coated carbon fibers. Thus the successful application of the TiC-coated carbon fibers in fiber reinforced composites will require the coating thin enough so as not to significantly degrade the fiber strength.

The properties of the coated carbon fibres depend not only on the coating thickness but also on the coating method. Fig. 3 shows the effect of the coating thickness on the normalized tensile strength of the TiC-coated carbon fibers obtained by CVD, by LMTA technique and by a molten salt method used in the present study, respectively. In all cases the normalized tensile strength of the coated carbon fibers decreases with the increasing coating thickness. However, the decrease in strength with coating thickness in the present study is comparable to or much less than that observed with coated fibers synthesized by CVD [15] and LMTA technique [4], indicating that the molten salt method is very promising in terms of preserving the tensile strength of the carbon fibers while obtaining a TiC coating with an appropriate thickness on them.

### **3.3 Oxidation resistance of TiC-coated carbon fibers**

For the production and application of carbon fiber reinforced composites at high temperatures, as is mentioned above, oxidation resistance of carbon fibers is a most important factor and should be taken into consideration. In this study, we investigated the oxidation behavior of the fibers in static air at high temperatures. Fig. 4 presents the relationship between the weight loss of the uncoated and TiC-coated carbon fibers

and the oxidation temperature. The oxidation time in static air was fixed at 10 min. For both the uncoated and TiC-coated carbon fibers, the oxidation weight loss increases with increasing oxidation temperature. However, the oxidation weight loss of the former is higher than that of the latter at any temperature, and the difference is more distinct at higher temperature, revealing that the coated carbon fibers are more stable than the uncoated carbon fibers. Meanwhile, it is noteworthy that the oxidation resistance of the TiC-coated carbon fibers is closely related to the coating thickness. At temperatures above 500 °C the weight loss of the coated carbon fibers decreases with the increase of coating thickness. Fig. 5 shows the weight loss of the uncoated and TiC-coated carbon fibers after oxidation in static air at 550 °C for varying time. With the increase of oxidation time, the weight loss of the uncoated carbon fibers increases rapidly. After being oxidized in air for 40 min, the uncoated carbon fibers lose 32% of their initial weight. In contrast, the TiC-coated carbon fibers have no significant weight loss. When the oxidation time increases to 130 min, the uncoated carbon fibers are oxidized completely, while the TiC-coated carbon fibers with an average thickness of 240 nm lose less than 10% of their initial weight. Overall, the weight loss rate of the TiC-coated carbon fibers is much lower than that of the uncoated carbon fibers, and the difference is enlarged with increasing coating thickness, indicating that the TiC coating improves the oxidation resistance of carbon fibers efficiently. This can be explained by the fact that the TiC coating protects the carbon fibers from direct exposure to air. The carbon fiber is oxidized only when oxygen atoms diffuse from outer surface of the coating into the interface between the

carbon fiber and the coating, and the thicker the TiC coating is, the higher the diffusion resistance will be. Thus increasing the coating thickness leads to an increase of the efficiency as a diffusion barrier and a decrease in the weight loss of the coated carbon fibers as a result. However, the TiC coatings studied here can not completely prevent the oxidation of carbon fibers. While the TiC layer is being oxidized, many channels (pores, microcracks, etc.) form for the transfer of oxygen atoms to the surface of carbon fiber. With the increase of oxidation temperature or oxidation time, the number and size of these passages increase gradually, which result in the increase of the oxidation rate of the TiC-coated carbon fibers.

For the coated carbon materials, the oxidation weight loss is proportional to the time when weight loss is below 70% [16]. According to Arrhenius formula, the oxidation weight loss of fibers satisfies the following equation:

$$\ln\left(\frac{m_0 - m}{m_0}\right) = -\frac{E_a}{RT} + \ln A + \ln t \quad (1)$$

Where  $m_0$  is the initial quantity of the sample,  $m$  is the quantity of the sample at time  $t$ ,  $A$  is the pre-exponential factor,  $E_a$  is the apparent activation energy of the fiber oxidation (kJ/mol),  $T$  is the absolute temperature (K), and  $R$  is the universal gas constant.

The Arrhenius plot is obtained (shown in Fig. 6) according to the weight loss of the uncoated carbon fibers and TiC-coated ones with an average thickness of 124 nm after oxidation at different temperature (550 – 700 °C) for 10 min. The apparent oxidation activation energy of the uncoated carbon fibers and TiC-coated ones can be calculated from the slope of the corresponding fitted line in Fig. 6, which is 127

kJ/mol and 170 kJ/mol, respectively. It is obvious that coating carbon fibers with a TiC layer leads to a 34% increase in their oxidation activation energy, and as a result, the oxidation resistant of the carbon fibers is improved significantly.

To further reveal the influence of oxidation on the tensile strength of the fibers, the tensile strengths of the uncoated and TiC-coated carbon fibers with an average thickness of 124 nm were measured after being oxidized at different temperatures for 10 min in static air, as shown in Fig. 7. At lower temperatures, the tensile strength of the uncoated carbon fibers is larger than that of the TiC-coated ones. As discussed earlier, during applying load on the TiC-coated carbon fibers, cracks are formed gradually in the coating due to the residual stress, which lead to the decrease in their tensile strength. Therefore, uncoated carbon fibers maintain their strength as long as they are not oxidized. When the temperature exceeds 500 °C, the oxidation of the uncoated fibers proceeds quickly and their tensile strength reduces to 15% of their original strength after oxidation at 700 °C for 10 min. In the case of the TiC-coated carbon fibers, the strength degradation starts at 500 °C and up to 700 °C the tensile strength of the coated fibers drops gradually to 62% of their original strength. Moreover, it is worth noting that the TiC-coated carbon fibers exhibit higher strength than that of the uncoated carbon fibers in the temperature range of 600-700°C, in spite of the fact that the tensile strength of the carbon fibers decreases after coated with a TiC layer as shown in Fig. 2.

To achieve more insight into the oxidation behavior of the uncoated and TiC-coated carbon fibers, their surface morphology after oxidation at varying

temperatures for 10 min has been observed by SEM as shown in Fig. 8 and 9. For the uncoated carbon fibers (shown in Fig. 8), there is no distinct change in surface morphology below 500 °C and pits appear on the fiber surface above 550 °C. The number and size of pits increase as the temperature increases. The formation of pits is responsible for the tensile strength decrease. In the case of the TiC-coated carbon fibers (shown in Fig. 9), however, their surface morphology has no obvious variation below 550 °C (shown in Fig. 9a) and many coarse granules present on the coating surface at 650 °C (shown in Fig. 9b), which make the surface appear very rough. Some granules break away from the coating, leaving behind small pores on the fiber surface. As the temperature increases up to 700 °C, there is an apparent increase in the number and size of pores, and cracks are also observed on the fiber surface (shown in Fig. 9c). These pores and cracks are possible channels accessible to transport oxygen atoms, causing the further oxidation and the simultaneous decrease in the tensile strength of the carbon fibers. Fig. 9d shows the hollow shell remaining after conflagration of the carbon core in air at 800°C. The thin and continuous hollow shell replicates the morphology of the initial carbon fiber filament. Further XRD analysis indicates it is mostly composed of rutile type  $\text{TiO}_2$  and a little anatase type  $\text{TiO}_2$ , which are derived from the oxidation of the TiC coating. The above SEM observation indicates that the oxidation proceeds inward from the outer surface of the TiC-coated carbon fibers.

### **3.4 Surface free energy and wettability of the TiC-coated carbon fibers**

Owens-Wendt-Kaelble method [17] for surface free energy analysis assumes surface free energy ( $\gamma_s$ ) is a sum of two components: polar ( $\gamma_s^p$ ) and dispersive ( $\gamma_s^d$ ), and that there is a relation between the three quantities:

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (2)$$

The work of adhesion between the solid and the liquid can be described by means of the Young-Dupré equation:

$$W_a = \gamma_{LV}(1 + \cos\theta) \quad (3)$$

Where  $\gamma_{LV}$  is the liquid–vapour surface free energy,  $\theta$  is the contact angle, and  $W_a$  is the work of adhesion between the solid and the liquid.

However, Owens and Wendt propose the following form of the work of adhesion between interacting solid and liquid.

$$W_a = 2(\gamma_s^d \gamma_{LV}^d)^{0.5} + 2(\gamma_s^p \gamma_{LV}^p)^{0.5} \quad (4)$$

Combining of equation (3) and (4) yields the following equation:

$$\gamma_{LV}(1 + \cos\theta) = 2(\gamma_s^d \gamma_{LV}^d)^{0.5} + 2(\gamma_s^p \gamma_{LV}^p)^{0.5} \quad (5)$$

This equation allows determining the surface free energy of a solid and its components. The surface free energy  $\gamma_s$  is calculated using the adjusted dependence describing the dispersive component of the surface free energy and the polar component of the surface free energy:

$$(\gamma_s^d)^{1/2} = \frac{\gamma_d(\cos\theta_d + 1) - \sqrt{\frac{\gamma_d^p}{\gamma_w^p}} \gamma_w(\cos\theta_w + 1)}{2(\sqrt{\gamma_d^d} - \sqrt{\gamma_d^p \frac{\gamma_w^d}{\gamma_w^p}})} \quad (6)$$



$$(\gamma_s^p)^{1/2} = \frac{\gamma_w(\cos\theta_w + 1) - 2\sqrt{\gamma_s^d\gamma_w^d}}{2\sqrt{\gamma_w^p}} \quad (7)$$

where:  $\gamma_s^d$  – the dispersive component of the test material surface free energy,  $\gamma_s^p$  – the polar component of the test material surface free energy,  $\gamma_d$  – the surface free energy of diiodomethane,  $\gamma_d^d$  – the dispersive component of the surface free energy of diiodomethane,  $\gamma_d^p$  – the polar component of the surface free energy of diiodomethane,  $\gamma_w$  – the surface free energy of water,  $\gamma_w^d$  – the dispersive component of the surface free energy of water,  $\gamma_w^p$  – the polar component of the surface free energy of diiodomethane,  $\theta_d$  – the contact angle of diiodomethane,  $\theta_w$  – the contact angle of water.

Table 1 presents the surface free energies and contact angles of the uncoated and TiC-coated carbon fibers. The deposition of TiC on the carbon fibers causes a decrease in the contact angle between carbon fibers and water or diiodomethane. As a result, the total surface free energy of the TiC-coated fibers is increased by 33% compared with that of the uncoated carbon fibers, and the polar component  $\gamma_s^p$  and dispersive component  $\gamma_s^d$  are increased by 95% and 20% respectively. The increase in the polar component  $\gamma_s^p$  can be attributed to a change in short range polar interactions caused by the TiC coating. To our knowledge, there are few reports on the values of the surface free energy of the TiC-coated carbon fibers. A value for  $\gamma_s^p$  of  $12.9 \times 10^{-3} \text{ N.m}^{-1}$  is obtained for the TiC-coated carbon fibers in this study, which is close to  $10.0 \times 10^{-3} \text{ N.m}^{-1}$  for SiC-coated carbon fibers reported by G. Emig et al. [11]. Higher surface free energy is favorable for increasing the fiber wetting by a matrix and improving the fiber/ matrix adhesion, which enhances a composite's

mechanical performance in various applications [18].

To further investigate the effect of the TiC coating on the wetting and bonding between carbon fibers and molten metals, the wettability tests of both uncoated and TiC-coated carbon fibers by molten Mg and Al were performed as described in section 2.6. For the resulting samples in which uncoated carbon fibers were introduced, the fibers were repulsed without any adherent layer of Mg or Al. No wetting and bonding occurred. However, in the case of the samples in which TiC-coated carbon fibers were introduced, the fibers were completely infiltrated by the molten Mg without applying external pressure and no holes existed between the individual fibers. The TiC-coated carbon fibers remain intact and no degradation has resulted from the infiltrating process, as can be seen in Fig. 10a and b. This suggests that TiC coating does indeed improve the wettability between carbon fibers and molten Mg. Considering the good wettability and the fact that magnesium does not form stable carbides by interfacial reaction in the Mg/TiC system [19], TiC-coated carbon fibers should be suitable reinforcements for Mg matrix composites. Fig. 10c and d show the typical SEM images of the resulting sample composed of TiC-coated carbon fibers and Al matrix. It can be seen that the fibers are cleaved into many parts along the fiber axis after holding 2 h in molten Al at 1000 °C. Further XRD analysis for the sample surface reveals the presence of elementary Al and  $Al_4C_3$  compound. No traces of Ti or any titanium aluminide is identified (not shown). Contreras A et al. [19] have also found the formation of aluminum carbide ( $Al_4C_3$ ) at the interface in their study on TiC wettability by commercial aluminum alloys. They attributed the

formation of  $\text{Al}_4\text{C}_3$  at the interface to the dissociation of TiC in molten aluminum as well as the consequent diffusion of carbon and reaction between carbon and aluminum. These processes are influenced by the temperature and time of the test. In this study, the TiC coating may be readily decomposed by the Al melt, and as a result the surface of the carbon filaments is attacked directly by liquid aluminum, leading to the formation of  $\text{Al}_3\text{C}_4$  and the severe damage of carbon fiber. Decreasing the heat treatment temperature and time may be helpful in protecting the carbon fiber from excessive reaction and achieving good infiltration. This work is still in progress to develop TiC-coated carbon fibers reinforced aluminum matrix composites with good mechanical properties.

#### **4. Conclusion**

TiC coatings of approximately 0.05 to 0.6  $\mu\text{m}$  have been successfully prepared on the surface of the PAN-based carbon fibers by a molten salt method. The coatings are smooth, uniform and adherent to the fibers. This low cost and simple coating method is attractive in terms of preserving the tensile strength of the carbon fibers while obtaining an efficient protection TiC layers on them. Coating carbon fibers with TiC results in the reduction of their tensile strength, and the thicker the TiC coating is, the lower the tensile strength of the fibers becomes. Coating carbon fibers with a 0.06  $\mu\text{m}$  thick layer of TiC results in a 10% decrease in their tensile strength. On the other hand, the uniform and continuous TiC coatings effectively improve the oxidation resistance of carbon fibers. The oxidation activation energy of carbon fibers increases by 34% after being coated with a 124 nm thick TiC layer, and as a result, these coated

carbon fibers exhibit higher tensile strength than that of the uncoated carbon fibers after oxidation at 600-700 °C for 10 min in static air. The oxidation of the TiC-coated carbon fibers appears to start from the pores and microcracks in the coating surface and the TiC hollow shell remains after conflagration of the carbon core. The TiC coating thickness should be optimized so as not to significantly affect the tensile strength of carbon fibers and meanwhile to ensure a good oxidation resistance. The total surface free energy of the carbon fibers increases by 33% after being coated with a TiC layer, which results in a remarkable improvement in the wettability of fibers with molten Mg and Al. The increase of the wetting of carbon fibers by molten Mg and Al is favorable for the significant reduction of the infiltration pressure during the fabrication of the composites. There is no observable chemical interaction between the TiC-coated carbon fibers and molten Mg even though they are exposed to the molten Mg at 1000 °C for 2 h, indicating that the TiC coating is stable in molten Mg. However, the TiC coating is readily decomposed by the molten Al at 1000 °C , and as a result the carbon fibers are readily attacked by the molten Al, leading to the formation of  $\text{Al}_3\text{C}_4$  and the severe damage of carbon fibers. During the development of TiC-coated carbon fibers reinforced Al matrix composites in the future, the infiltration temperature and time should be optimized so as to achieve good infiltration without excessive reaction.

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## Table and Figure captions

Table 1. Surface free energies and contact angles of the uncoated and TiC-coated carbon fibers.

Fig. 1. SEM images of the TiC coated carbon fibers prepared in molten salts at 850 °C for 1 hour (a-c) and 5 hours (d-f) ( (a, d) survey image (b, e) cross section (c, f) high magnification of cross-section).

Fig. 2. Variation of the tensile strength of the TiC-coated carbon fibers synthesized by a molten salt method as a function of the coating thickness.

Fig. 3. Variation of the tensile strength of TiC-coated carbon fibers prepared using CVD method, LMTA technique and a molten salt method in the present study, respectively, as a function of coating thickness.

Fig. 4. Weight loss of uncoated and TiC-coated carbon fibers at different oxidation temperatures.

Fig. 5. Weight loss of uncoated and TiC-coated carbon fibers with increasing of oxidation time at 550 °C.

Fig. 6. Arrhenius plot of oxidation kinetics for the uncoated and TiC-coated carbon fibers.

Fig. 7. Residual tensile strength of the uncoated and TiC-coated carbon fibers after oxidation at different temperatures for 10 min in static air.

Fig. 8. Surface morphology of the uncoated carbon fibers after oxidation at (a) 500 °C, (b) 550 °C, (c) 650 °C, and (d) 700 °C for 10 min in static air.

Fig. 9. Surface morphology of the TiC-coated carbon fibers after oxidation at (a)



550 °C, (b) 650 °C, (c) 700 °C, and (d) 800 °C for 10 min in static air.

Fig. 10. SEM images of the TiC-coated carbon fibers after heat treatment at 1000 °C in molten Mg (a-b) and in molten Al (c-d) for 2 h.

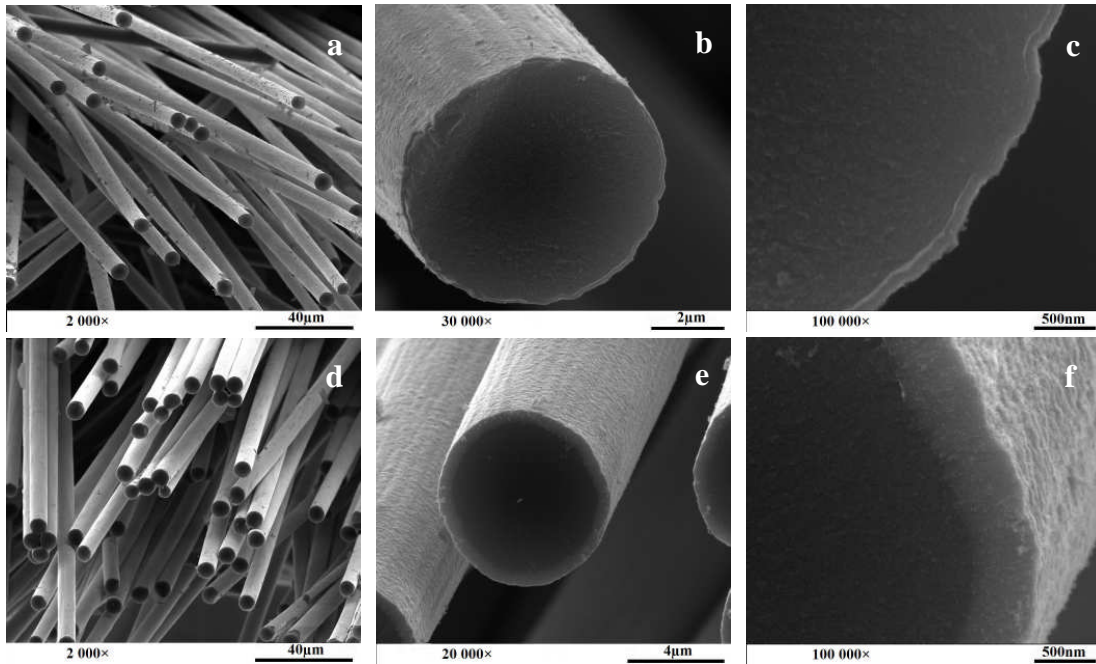


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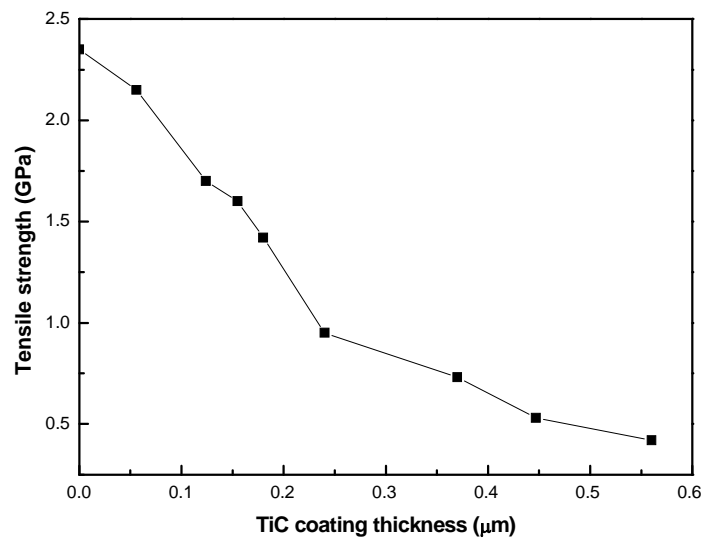


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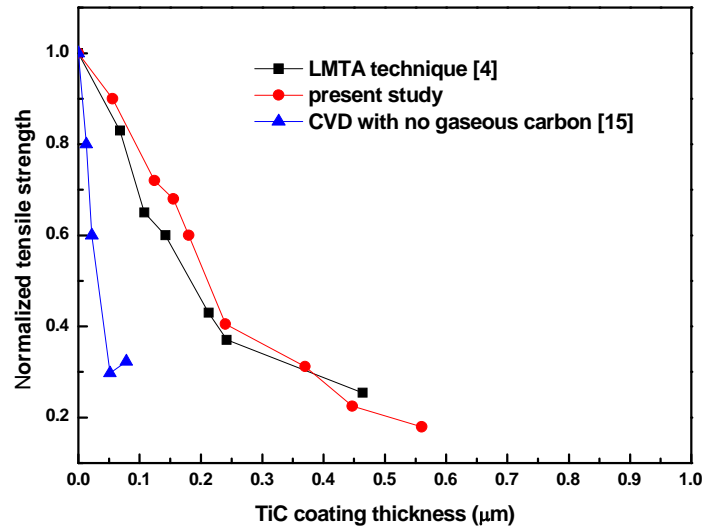


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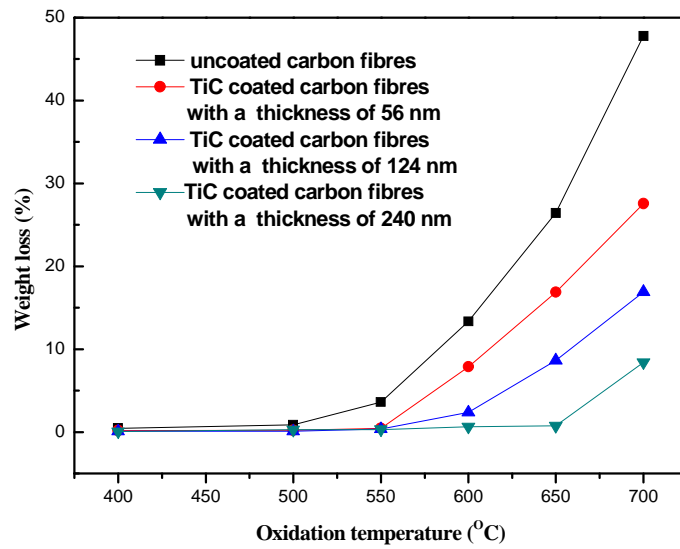


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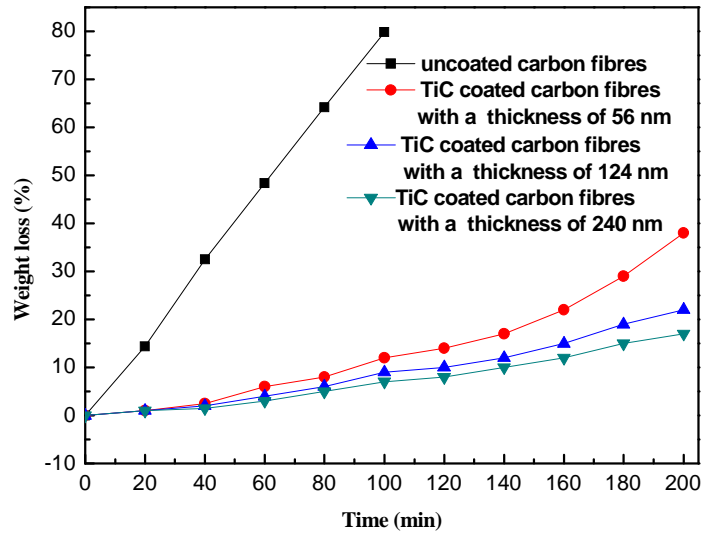


Fig. 5. Weight loss of uncoated and TiC-coated carbon fibers with increasing of oxidation time at 550 °C.

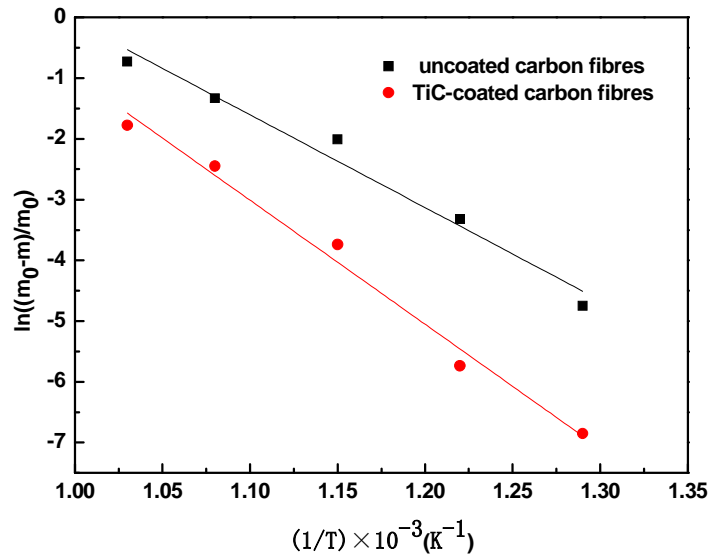


Fig. 6. Arrhenius plot of oxidation kinetics for the uncoated and TiC-coated carbon fibers.

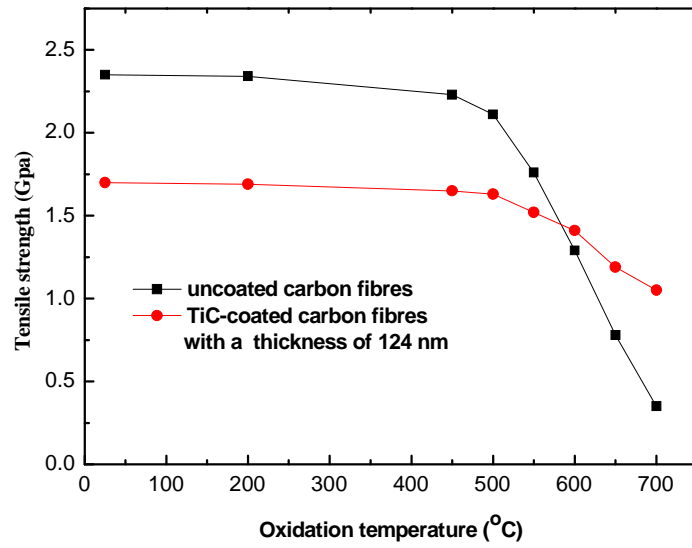


Fig. 7. Residual tensile strength of the uncoated and TiC-coated carbon fibres after oxidation at different temperatures for 10 min in static air.

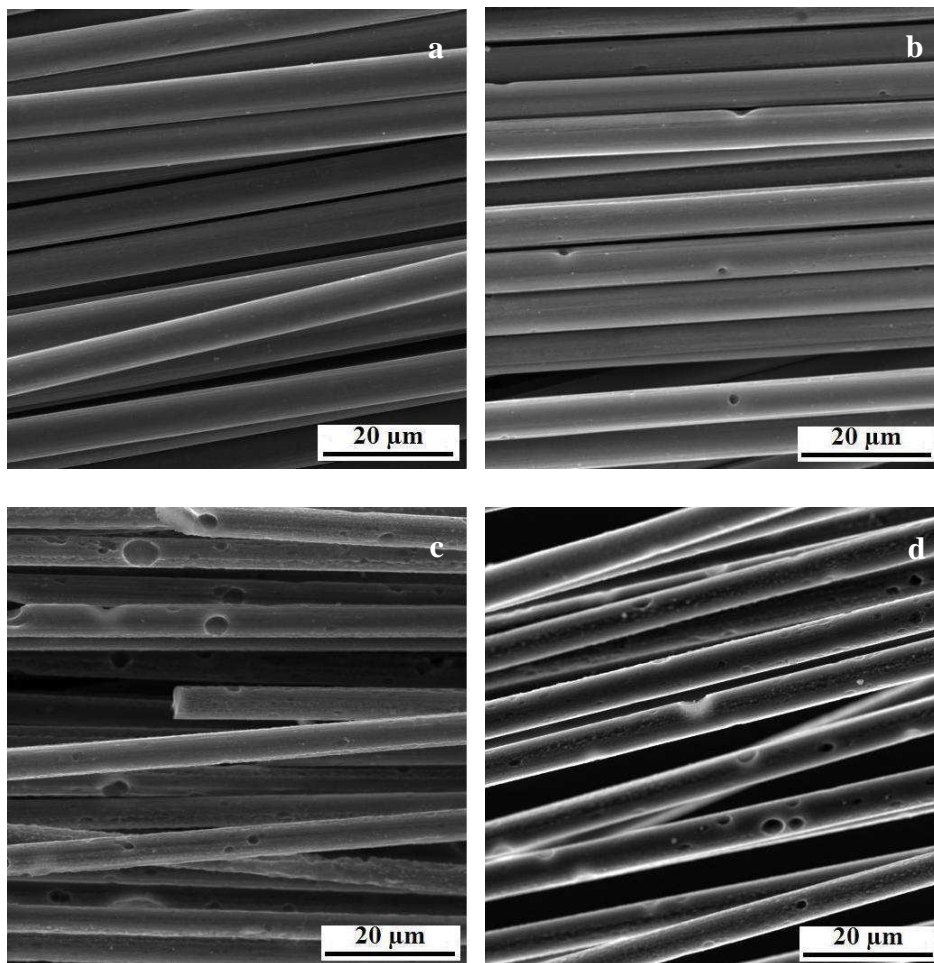


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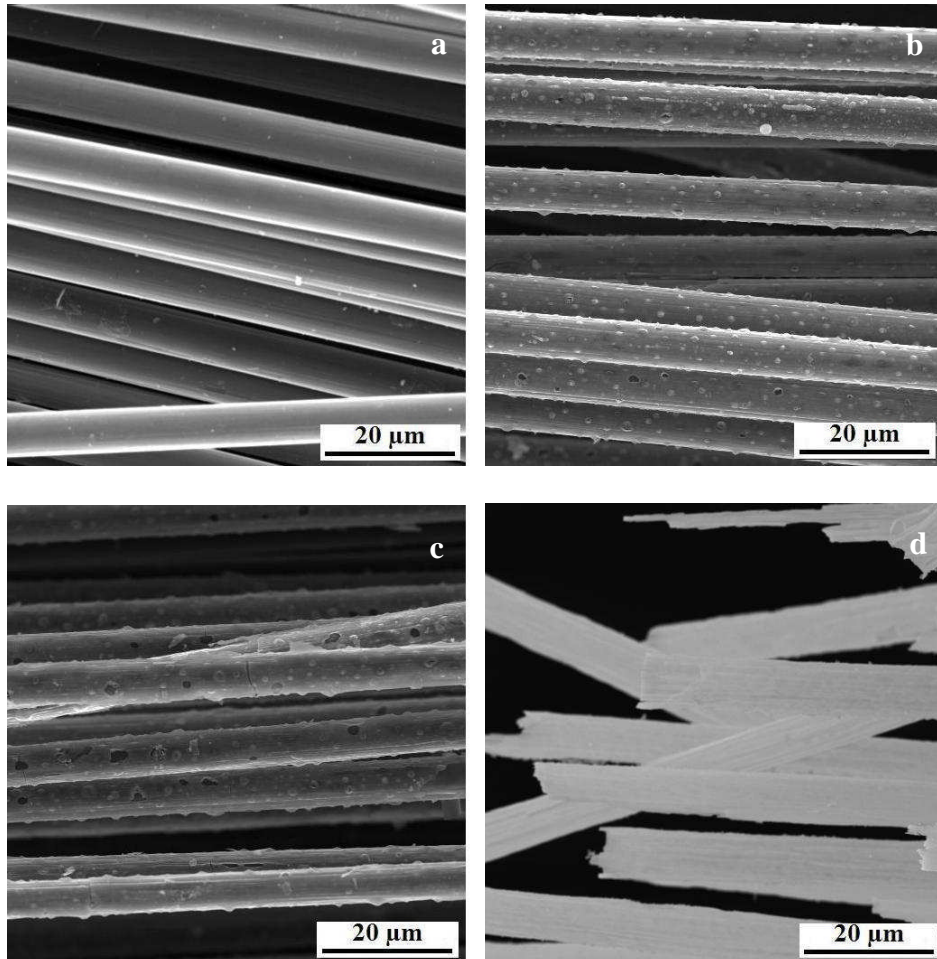


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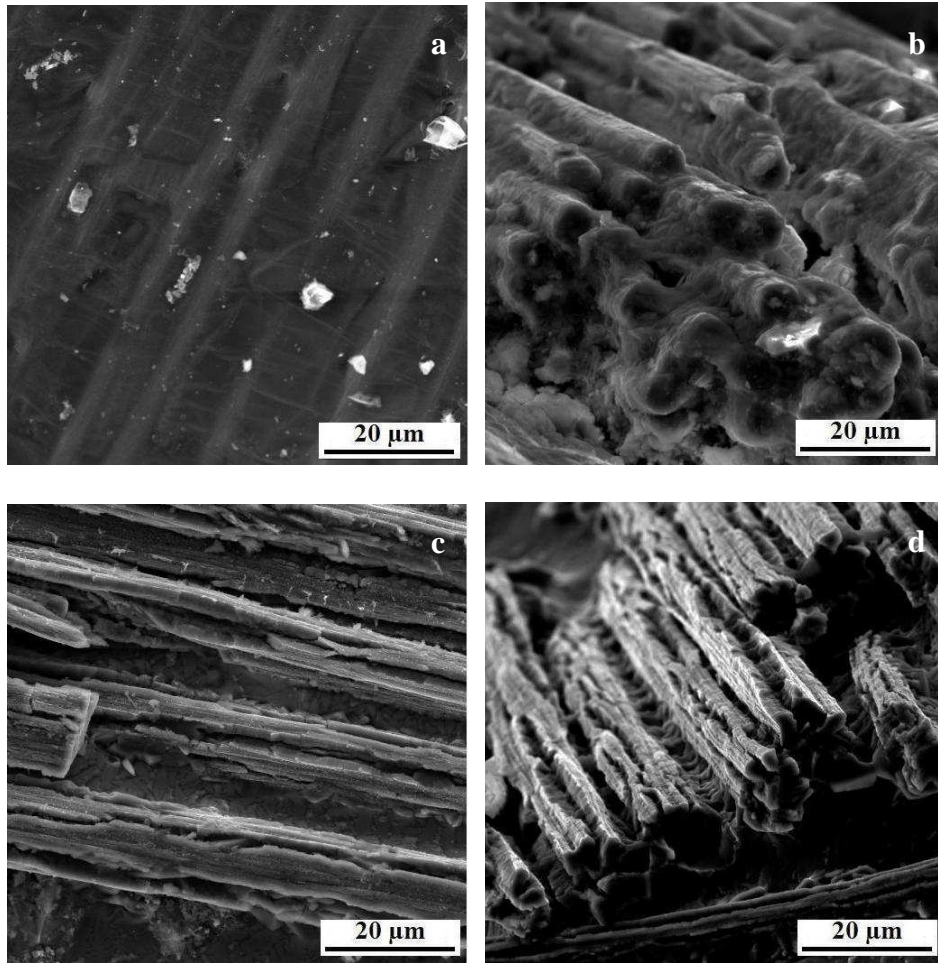


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