Study on the Kinetics of the Chemical Vapor Deposition Process for the Coating of Carbon Fibers from the Structure of Composites Materials with Metal and Non-Metal Matrix

R Caliman
“Vasile Alecsandri” University of Bacau, Faculty of Engineering, Department of Engineering and Management, Mechatronics, Calea Marasesti 157, Romania
E-mail: rcaliman@ub.ro

Abstract. In order to keep the fibers intact during processing and to produce the desired surface properties, the process by which the composite material is manufactured almost always comprises a process by which the fiber is coated. The coating protects the fiber during the operation in which the fiber is combined with the matrix. Simultaneously, the wetting and binding of the fiber with the matrix is favored; in some cases, the coating is a sacrificial layer, which is destroyed during processing. In general, the structure, composition and morphology of the coating affect the strength of the composite after manufacture. Thus, the Chemical Vapor Deposition (CVD) process and its variants are used for fiber coating. The reaction products diffuse to the surface, producing surface reactions, which lead to the formation of a deposit on the surface of the fiber. The limiting factor in the deposition process may be the reaction kinetics or the diffusion of vapor species to the surface.

1. Introduction
The matrix-reinforcing agent interface plays a key role in the manufacture of composite materials. The quality of the interface determines the structural integrity, the response to the action of the environment and the physical and mechanical properties of the composite material [1-3].

The interface includes the contact area between the matrix and the fibers and the immediately adjacent domain. The nature and strength of the interfacial bond depend on the structure, the surface characteristics of the fibers (roughness, specific surface area, porosity, crystal size, the presence of chemically active functional groups) and the structural characteristics of the matrix (chemical composition, macromolecule conformation) [4-7].

The literature presents different models of adhesion which, alone or combined, provide a satisfactory interpretation of the phenomena at the interface. The adhesion between the matrix and the fibers was explained in terms of mechanical and thermodynamic adhesion, chemical compatibility, by electrostatic attraction forces and based on the phenomenon of macromolecular interdiffusion [8].

The interdependence between maintenance technology and surface phenomena.

From a practical point of view, complex, interdependent correlations between the interactional aspects, properties and compositional microstructure must be analyzed starting from the technology of maintenance and processing of the composite material [9].

In composites obtained by technologies based on the coupling of solid state components (by powder metallurgy, by diffusion), the interfacial effects have a cumulative influence on the properties and do not contribute directly in the different stages of the technological process. The initial stages of
preparation, mixing and preconsolidation of the components in powder form influence the interface through the surface quality of the powders, the adsorbed or deposited layers [10].

In composites obtained by technologies derived from liquid matrix casting processes, the interfacial effects are influenced, to a greater extent and directly, by the following factors: the chemical composition of the matrix, the wetting conditions of the complementary material by the matrix expressed by contact angle, interphase voltage balance, component reactivity, temperature, processing atmosphere, solidification conditions [11].

2. Chemical Vapor Deposition-CVD

Chemical vapor deposition is a well-known advanced technology that consists of the deposition of a solid on a heated surface, as a result of a chemical reaction in the gas phase, which occurs near the surface of the substrate. Figure 1 shows a vertical walled reactor for fiber coating [12].

![Figure 1. Warm wall reactor for carbon fiber coating.](image)

2.1 Kinetics of the CVD process

As a result of the chemical interactions between the matrix and the complementary material, a reaction zone with non-uniform thickness is formed at the interface, with composition and structure determined by the diffusion processes of the elements [13].

Quantitative estimation of the thickness of the reaction layer is difficult, as it depends on specific microstructural parameters (e.g., structural defects interrupt the diffusion circuit, leading to an uneven thickness of the reaction zone), as well as the processing mode and parameters of the composite material [14].

The thickness of the reaction layer - \( x \), has a parabolic increase as a function of time - \( t \), dependence expressed by the equation (1):

\[
x = k \cdot t^{1/2}
\]

where \( k \) is the parabolic growth rate constant of the reaction layer.

When achieving optimal coatings, it is important to predict (or control) the coating speed and coating distribution, as well as the composition and microstructure of the coating.
Coverage speed is a macroscopic parameter. The composition and microstructure of the coating will govern the interaction with the matrix material, during manufacture and after its realization. The presence of grains of irregular shape and size, cracks or inclusions in the coating, will tend to reduce the effectiveness of the coating in the final product [15].

In order to achieve the analytical modeling of the carbon fiber coating phenomena, for their coating a complex analysis of the hot wall reactor was performed, intended for fiber coating. In this analysis, the diffusion equation was numerically integrated along a 2 cm long reactor. Figure 2 shows the profile of the coating arrangement, calculated for the typical conditions in this reactor. According to theoretical estimates, the deposition rate decreases sharply near the reactor outlet. But the actual deposition rates in fiber reactors are variable; the range 1 ÷ 20 μm is considered a common domain.

2.2 Thermal stability of copper coatings on carbon fibers

The performance of metal matrix and fiber reinforced composites is largely controlled by the adhesion between the fibers and the matrix. Interface phenomena are also important in material processing. For example, carbon fiber-reinforced copper matrix composites can be applied as contact materials and substrate for semiconductor devices [16, 17].

Copper poorly moistens the carbon fiber, so the interface of the carbon-copper composite is extremely weak. In order to ensure the possibility for the carbon fiber to take over the maximum load, it is essential to ensure an appropriate interaction between the matrix and the carbon fiber. Increasing the resistance of the interface is generally achieved by two means:
• favoring the reaction of the fiber with the matrix;
• ensuring the dissolution of the fiber in the matrix.

There are studies on increasing the resistance at the interface, on Fe and Ni layers deposited on copper-coated carbon fibers. Iron diffuses through the Cu layer to the carbon fibers, reacting with them and forming Fe₃C (bonds by chemical reaction). In contrast, Ni coating is converted to solid Cu-Ni solution, which is able to dissolve small volumes of carbon fiber (dissolved bonds) [18-21].

By methods that do not involve the use of electric current, it is possible to deposit on the carbon fiber a copper layer with a thickness of several tens of microns. A thicker layer can be deposited by galvanic coating. The compactness of the Cu coating, after heating to high temperatures, becomes...
unstable, starting to exfoliate. This exfoliation of copper occurs due to the surface diffusion process, accompanied by a reduction in surface energy. Therefore, prior oxidation of carbon fiber is recommended.

Oxidation can be performed in air at temperatures of 400 ÷ 700°C for 240 seconds. In order to establish the influence of the prior oxidation process of the fiber, both oxidized fibers and non-oxidized copper fibers were covered (the layer thickness being 0.2 μm). Also, a second set of experiments was performed with oxidized fibers in air, at 600°C and subsequently covered with Cu, by the galvanic method, the thickness of the deposit being 1 μm. Both sets of fibers were then treated up to 1000°C in a hydrogen atmosphere for 600 s.

Microscopic investigations have shown that the limit temperature for exfoliating Cu coating is higher for oxidized carbon fiber at a higher temperature. Oxidation temperatures of 700°C and above lead to a smaller fiber diameter. The coating of Cu on oxidized carbon fibers at this temperature becomes inhomogeneous, generating the appearance of discontinuous bands, after a treatment made at a temperature of 900°C.

In the case of galvanic deposition with a thickness of 1 μm, made on a non-oxidized fiber, it is observed that the Cu coating began to detach from the fiber after an effective treatment at 900°C. After an effective treatment at 1000°C, the coating was partially detached from the fiber. In the case of galvanically coated oxidized fibers, even at 1100°C, the coating is cracked but not spheroidally exfoliated (figure 3).

The limit temperature for a Cu coating on carbon fibers depends on the thickness of the coating (figure 4). The thicker the thickness, the higher the limit temperature.

**Figure 3.** Graphite fiber coated with chemically deposited copper from the vapor phase.

**Figure 4.** SiC coating chemically deposited from vapor phase on C fiber (coating cracks during property testing).

2.3. The efficiency of Ni coatings on carbon fibers

Coatings with Ni by the CVD method, on carbon fibers, lead to obtaining fibers that provide protection against interaction with electromagnetic fields and fields with radio frequencies, when used as polymeric composite materials.

In the case of a polyfilament carbon cable with 12000 filaments, with a diameter of 7 μm/filament, a coating of 20% Ni (mass percentages) can be achieved, resulting in a thickness of less than 1μm. The use, in the form of short fiber of carbon fiber coated with Ni, provides a protection of 75 dB, in the case of polycarbonate composites.
For unidirectionally layered or woven composite structures, Ni-coated conductive fiber embedded in heat-cured resins also provides light protection. Figure 5 shows the efficiency of Ni-coated carbon fiber protection.

![Efficiency of protection against Ni-coated carbon fibers](image)

**Figure 5.** Efficiency of protection against nickel-coated carbon fibers.

3. Conclusions
Experience gained so far shows that there can be large differences between theoretical and real values that have the properties of a composite material. This is especially noticeable when used as polymeric composites.

No change in coating morphology was observed at temperatures up to 400°C. The exfoliation limit value of the Cu coating is determined by the oxidation temperature applied to the carbon fiber: the higher the oxidation temperature, the higher the limit temperature.

An oxidation temperature of 700°C and above accelerated the reaction between atmospheric oxygen and carbon, which led to a change in the appearance of the fiber surface and decreased the fiber diameter.

Another conclusion reached would be that Ni coatings by the CVD method on carbon fibers lead to fibers that provide protection against interaction with electromagnetic fields and radio frequency fields.

4. References
[1] Zang G-H a.o. 2019 Microstructures and mechanical properties of alumina whisker reinforced copper matrix composites prepared by hot-pressing and hot isostatic pressing, *Materials Research Express* 6(11) 116513.
[2] Ashbee K H 1993 *Fundamental Principles of Fiber Reinforced Composites* 2nd edition (Technomic Publishing Company, Lancaster, PA) p 440.
[3] ASM Handbook 2001 *Composites* Vol. 21 (ASM International, Materials Park, OH).
[4] Chawla, K K 1998 *Composite Materials Science and Engineering* 2nd edition (Springer-Verlag, NewYork).
[5] Ayyappadas C a.o. 2017 An investigation on the effect of sintering mode on various properties of copper-graphene metal matrix composite *Advanced Powder Technology* 28(7) 1760-1768.
[6] Hollaway L 1994 *Handbook of Polymer Composites for Engineers* Technomic Publishing Company (Lancaster, PA).
[7] Nayan N a.o. 2017 Processing and characterization of spark plasma sintered copper/carbon nanotube composites *Materials Science and Engineering: A* 682 229-237
[8] Mallick P K 1993 *Fiber-Reinforced Composites*, Materials, Manufacturing and Design 2nd edition (Marcel Dekker, New York).
[9] Peters S T 1998 *Handbook of Composites*, 2nd edition (Springer-Verlag, New York).
[10] Strong A B 2008 *Fundamentals of Composites: Materials, Methods and Applications*, Society of Manufacturing Engineers (Dearborn, Michigan) p 610.
[11] Woishnis W A. 1993 *Engineering Plastics and Composites*, 2nd edition (ASM International, Materials Park, OH).
[12] Caliman R, Olaru I 2006 *An Aluminum Matrix Ni-Ti Fiber-Reinforced Smart Composite*, MOCM 12, vol.1, Romanian Academy, Branch office Iași 35-38.
[13] Samal P K and Newkirk J W 2015 *Metals Handbook*, vol. 7 Powder Metallurgy ASM International p 907.
[14] German R M 2018 *Powder Metallurgy Science* no. 8.
[15] Chawla K K 2005 High-Performance Fiber Reinforcements in Composites *Journal of Minerals, Metals & Materials* 47.
[16] Barrera E V, Lozano K, 2000 New Technologies, New Composites *Journal of Minerals, Metals & Materials* 32.
[17] Suraj R 2001 Metal-Matrix Composites for Space Applications *Journal of Minerals, Metals & Materials*.
[18] Kunze J M, Bampton C C 2001 Challenges to Developing and Producing MMCs for Space Applications *Journal of Minerals, Metals & Materials* 22-25.
[19] Grácio J, Davim JP, Hua Fan Q, Ali N. 2002 New Developments on Tribology: Theoretical Analysis and Application to Industrial Process *Proceedings 8th Portuguese Conference of Tribology* (University of Aveiro).
[20] Marques N, Davim JP 2002 Tribological comparative study of a conventional and composite material to biomedical applications *Key Engineering Materials, Trans Tech Publication Lda* 230/232 487-490.
[21] Marques N, Davim JP. 2001 Tribological comparative study of a conventional and composite material to biomedical applications, *Proc. 10th Meeting of the Portuguese Materials Society and First International Materials Symposium* A 175 (Coimbra, Portugal).