

Adhesion study of Nickel over Carbon Fibers

Ravikiran Kamath B

Dept. of Mechanical Engg., NMAMIT
Nitte -574110, Karnataka, India
ravi.nitte@gmail.com

Nithin Kumar

Research Scholar, UVCE
Bangalore-560001, Karnataka, India
nithinmech33@gmail.com

Abstract: The manufacturing of carbon fiber reinforced aluminum matrix composite involves the formation of a brittle intermetallic phase due to the reaction taking place at the fiber-matrix interface at temperatures exceeding 500°C. To avoid this undesired chemical reaction that ultimately results in the degradation of composite properties, the reinforcement is coated with nickel by electroless process. This paper describes the electroless nickel coating process carried out on PAN based short carbon fibers. The resulting fibers are investigated for their metallographic characteristics by optical microscopy.

Keywords: MMCs, carbon fibers, aluminium matrix, interfacial reaction, EN coating, optical microscopy

1. INTRODUCTION

One of the many advantages of composite materials in general is the possibility of tailoring material properties to meet different requirements. The researchers and design experts have perceived their research to emphasis on finding lightweight, environmental friendly, low-cost, high quality, and good performance materials. In accordance with this trend, MMCs have been attracting growing interest among researchers and industrialists [1]. The attributes of MMCs include alterations in tensile and compressive properties, creep, notch resistance, tribological properties as well as intermediate density, thermal expansion and thermal diffusivity. Light weighted aluminium matrix composites have been the focus of much study on account of their outstanding specific properties at room or elevated temperatures [2]. These properties make aluminium matrix composites strong candidates for a wide range of applications in automobile, aerospace and defence industries [3]. Carbon fiber reinforced metal matrix composites are desirable due to their high specific strength, chemical stability, excellent creep resistance, high specific modulus and low coefficient of thermal expansion [4] compared with conventional alloys.

In fiber composites, both the fiber and the matrix retain their original physical and chemical identities. Together they produce a combination of mechanical properties that cannot be achieved with either of the constituents acting alone, due to the presence of an interface between these two constituents.

Interfaces are considered particularly important in the mechanical behaviour of MMCs since they control the load transfer between the matrix and the reinforcement. Their nature depends on the matrix composition, the nature of the reinforcement, the fabrication method and the thermal treatments of the composite. For a carbon fiber reinforced aluminium composite system, it is difficult to obtain a uniform distribution of the carbon fibers in the aluminium matrix and also to control the fabrication process parameters because of poor wettability. This hinders the spontaneous flow of the liquid metal within the interstices of the fibers. Also, it is reported that aluminium and carbon chemically react with each other at the interface to produce the undesirable aluminium carbide [5]. Such chemical interactions result in the formation of detrimental products on the interface and act as damage nucleation sites under stress. This leads to embrittlement of the matrix, degradation of the fibers and appearance of interfacial brittle phases [6]. An interface in fiber reinforced composites is a surface formed by a common boundary of reinforcing fiber and matrix that is in contact with and maintains the bond in between for the transfer of loads. However, this interfacial bond is said to have formed at elevated temperatures. Interfaces with desired better properties can be achieved by modifying the composition of the matrix, coating of the reinforcement, specific treatment to the reinforcement and controlling the process parameters.

2. SHORT CARBON FIBERS

Generally fibers of length less than 2 mm are referred to as short fibers. Their diameter ranges from 6-8 microns. Short carbon fibers provide good process ability, resin compatibility, and translation of mechanical and electrical properties. Compounds containing short carbon fibers provide higher heat distortion temperatures and superior thermal conductivity. Short fibres are long compared to the critical length l_c given by,

$$l_c = d \cdot S_f / S_m \quad \dots 1$$

where, d is the fibre diameter, S_f is the reinforcement strength and S_m is the matrix strength and hence show high strength in composites. These contain reinforcements with an aspect ratio of greater than 5. Short carbon fibers are commonly used as electrically conductive filler for polymers used for electromagnetic interference shielding, antistatic and

refractory insulation purposes. However, they possess low compressive strength compared to tensile strength and have a tendency to become oxidized above 400° C.

2.1 Coating of short fibers

Typically, depositing of metallic coatings around the reinforcements can effectively decrease interfacial reaction as well as address wetting concerns. Over the years, researchers have proposed and successfully employed several metallic coatings for the reinforcements. The toxic nature of chromium and extremely high cost of gold has eliminated them as potential fiber coatings. The two most prominent coatings for carbon fibers are nickel and copper [7]. The formation of intermetallic compounds like Al₃Ni, Ni₃Al₂ creates a strong bond across the fiber matrix interface and plays an instrumental role in improving the wetting of nickel and copper coatings [8]. Compared to other metal coatings, electroless nickel possesses advantages including coating uniformity, corrosion and wear resistance, desirable magnetic and electrical properties.

2.2 Electroless nickel (EN) coating

Electroless coating [9] is an autocatalytic process of depositing the coating with the aid of chemical agents in a bath without the application of external power, via oxidation–reduction reactions in the solution. The term "autocatalytic" means that the nickel deposit resulting from the electrochemical reaction catalyzes the reaction mechanism. A potential is developed when a substrate is immersed in an electroless bath which contains a source of metal ions, reducing agent, complexing agent, stabilizer and other components. Energy is released through charge transfer process. Electroless Nickel coating is a simple, flexible and economical process which increases the overall surface energy of the reinforcement. The technique involves a series of complex chemical reactions among several bath components. Two types of baths are used for depositing alloys-acidic and alkaline. The chemical reduction process involves the reducing agent being oxidized and Ni²⁺ ions being deposited by reduction on the substrate surface. Once the first layer of nickel is deposited, it acts as a catalyst for the process. The operator can precisely control the coating thickness by controlling the immersion time in the EN bath.

2.3 Materials and methods

The reinforcement used in this work is in the form of continuous short PAN based carbon fibers. About 3 kg of fiber is used for the study. The deposition of nickel coating on short carbon fibers by an electroless route is investigated. Fibers of average diameter 6 μm are used in the study. They are cut down to short fiber of length about 1 to 1.5 mm. The electroless coating procedure involves a sequence of

sensitizing, activation and metallization along with swilling and drying at appropriate stages as shown in Figure 1.

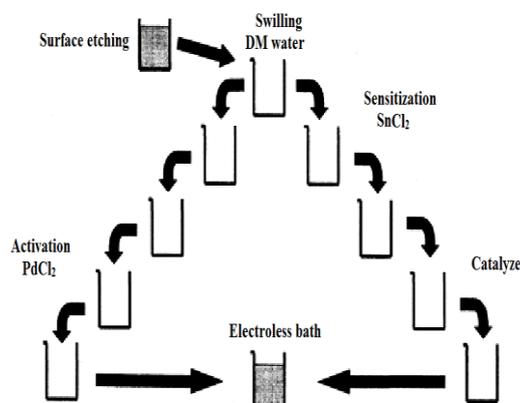
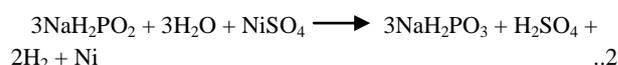


Figure 1 : EN coating route

3. EN BATH COMPONENTS AND EXPERIMENTAL PROCEDURE

In this process no external electrodes are present, but there is electric current (charge transfer) involved. Instead of an anode, the metal is supplied by the metal salt. Instead of a cathode to reduce the metal, a substrate serves as the cathode, while the electrons are provided by a reducing agent. The process takes place only on catalytic surfaces rather than throughout the solution. During the deposition of as-coated electroless nickel films, the growth of the film starts at isolated locations on the substrate. The whole substrate is then covered by lateral growth.

There are a number of possible bath formulations for the electroless deposition of nickel from literature making use of many different reducing agents and under widely different coating conditions. The EN coating bath contains nickel sulphate which is a source of nickel ions. It supplies the nickel ions (Ni²⁺) that are chemically reduced to become the EN coating.



Reduction takes place by means of reducing agent sodium hypophosphite NaH₂PO₂ which supplies electrons for reducing the nickel ion compound to metallic nickel.



where, H₂PO₂⁻ is the hypophosphite ion, HPO₃²⁻ is the orthophosphate ion and H_{abs} is the absorbed atomic hydrogen. The above reaction takes place in the presence of heat from the catalyst.

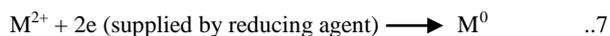


where, Ni^0 is the elemental nickel being deposited on the fibers.



where, OH^- is the hydroxyl ion and P is phosphorus.

Phosphorus is co-deposited with nickel to form a nickel-phosphorus alloy that serves as a natural lubricant to the EN coatings. Typical phosphorus content in the coating ranges from 6 to 12 percent. Higher phosphorus content results in a continuous coating, but with decreased hardness, wear resistance and corrosion resistance in alkaline environments.



This cathodic partial reaction takes place in the presence of a catalyst. Heat energy also affects the rate of deposition. Complexing agents (chelates) control or reduce the free nickel ions available to the reaction. They are a class of additives which help to maintain a stable pH level and prevent the precipitation of nickel salts. After the reduction reaction, the surface quality of coating deteriorates resulting in rough and dark coatings. Sodium citrate helps in checking the coating from becoming porous and dull. Additional requirements are buffers, stabilizers and accelerators. Buffers are substances or combination of substances that are capable of neutralizing both acid and base alike without changing the pH of the solution by much. A measure of the buffer's efficiency is the amount of, say, acid required to change the solution's pH. Clearly, the greater that amount, the better the buffer. Stabilizers or inhibitors adsorb to impurities in the solution and prevent unwanted nickel precipitation and decomposition of the entire bath. Accelerators are added to the bath to increase the plating rate by driving the oxidation of the reducing agent.

In general, deposition requires cleaning, sensitization, catalyzing, activation (acceleration) and metallization. Rinsing or swilling is required between the steps. Prior to coating, to ensure that the substrate is free from any impurities, cleaning is carried out with acetone and then followed by rinsing in distilled water. This helps to achieve effective coating. The coating process begins with the sensitization process where the removal of pyrolytic coatings around the as-received fibers is done in an oven for a small duration. It is followed by the immersion of carbon fibers in a solution of 20 g/l stannous chloride and continuously stirred. The process time is then checked. The fibers will be isolated from the above sensitizer solution and cleaned in distilled water. This process is called as swilling and is done multiple times to ensure that the fibers are free of chemicals. It is followed by neutralization stage where 40 ml of hydrochloric acid is used. It is swilled to clean the fibers in distilled water. This removes any acid traces. In order to have catalytic surfaces, the sensitized fibers are exposed to an aqueous solution constituting of 5 g/l of palladium chloride under ultrasonic agitation. This process, which is called as activation produces the formation of

palladium sites on the fiber surface which allows the subsequent metallization with nickel. This is followed by swilling to make the parts free from palladium chloride and cleaned in distilled water. After this, neutralization process is done with 2.5 ml of hydrochloric acid. It is again swilled to clean the fibers in distilled water. This removes further acid traces. Next is the metallization stage. It involves the immersion of activated fibers in a solution containing 15 g/l of nickel sulphate which is a metallic ion source. The process time, chemical concentration and temperature is checked. Liquid ammonia is used in order to increase the pH from 10 to 12 since at this value the coating will be accurate. Also, sulphuric acid controls the pH value if it goes beyond it and the bath temperature is in the range of 40°C to 50°C. It is subjected to swilling the parts in order to free it from plating chemicals. Then they are cleaned in distilled water. The submerged fibers are then removed from the chemical bath and subjected to drying at a temperature of about 70°C. The temperature and the part surface are checked. Finally, the parts are examined visually for the required thickness.

4. RESULTS

The obtained photographic images of uncoated and nickel coated short PAN based carbon fibers and the surface characteristics of uncoated carbon fibers and the nickel coated carbon fibers as seen under optical microscope Leica ICC50 HD are shown in Figure 2 to Figure 5. In spite of different surface morphology, the electroless nickel films have been deposited on the fiber surface with good adhesion.



Figure 2 : Short uncoated PAN carbon fibers



Figure 3 : Nickel coated carbon fibers



Figure 4 : Optical microscopy image (Uncoated fiber)

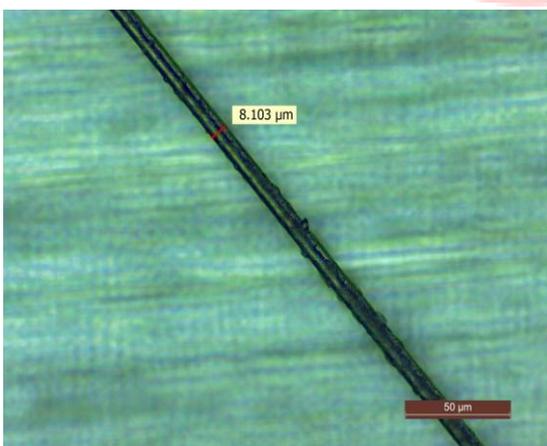


Figure 5 : Optical microscopy image (Nickel coated fiber)

For metals that catalyze the electrochemical reaction (i.e, nickel), a linear relationship between coating thickness and time is obtained as shown in Table 2. As the deposition progresses, islands are formed around the nucleation sites which grow in size until they merge and a continuous film results. The rate of nickel deposition is proportional to the rate at which the nickel complex dissociates to form free nickel

ions. The coating thickness is uniform and homogeneous throughout the fiber circumference regardless of the shape or surface irregularities of the part being coated because the coating is applied without the use of electric current. The rate of deposition is low at temperatures below 65°C and increases with the increase in temperature. Generally the operating temperature is about 90°C, above which the bath tends to become unstable as it becomes difficult to maintain the pH of the solution and therefore, the quality of the coating deteriorates. As the alkalinity of the solutions increases, the nickel content of the deposit increases. Nickel in the deposit increases as pH of the bath increases. If the pH of the solutions is maintained between 12 and 14, the reaction product is principally elemental nickel. The pH should be maintained at higher levels of about 12 to obtain bright coatings.

Table 1. Properties of PAN based Carbon Fibers

Elastic Modulus	Tensile strength	Elongation	Density
220-241 GPa	3450-4830 MPa	1.5-2.2%	1.8 g/cc

Table 2. Time limits for each stage

Sensitization (min)	Activation (min)	Metallization (min)	Coat thickness (micron)
5	5	3	1.8
10	10	6	3.0
15	15	9	5.8
20	20	12	7.4
25	25	15	11.2
30	30	18	13

5. CONCLUSIONS

From the results, it is clear that EN provides a coating that has more uniform thickness. This makes the film an effective corrosion protecting agent. A very bright and smooth electroless deposit of nickel is obtained. From the metallographic study, it is confirmed that the nickel coatings are bonded firmly to the carbon fibers along the length as well as the diameter of the filaments. The images also reveal that the thickness and morphology of the nickel layers is invariably dependent on the metallization conditions in terms of time, bath temperature and pH. Though it is a controlled chemical reaction, the cost of the chemicals required for the process is high. The coating tends to be brittle at times and the coating

rate is a bit slow. From the experimental investigation, it is concluded that maximum coating thickness of 13 microns was observed for 30 minutes of sensitization time, 30 minutes of activation time and 18 minutes of metallization time. It is also concluded that in order to retain the properties the coating thickness has to be maintained within 3 microns.

6. ACKNOWLEDGEMENTS

The authors wish to express their sincere gratitude to Dr. Niranjana N. Chiplunkar, Principal, NMAMIT, Nitte, Dr. K. Subrahmanya Bhat, Professor and Head, Department of Mechanical Engineering, NMAMIT, Nitte and Dr. Srinivasa Pai P., Professor, Department of Mechanical Engineering, NMAMIT, Nitte for their continuous and extended support. The authors acknowledge the kind support and valuable technical assistance given by Mr. Murugan, Managing Director of Balambiga Metal Finishers, Peenya-Bangalore and all those who helped directly or indirectly in carrying out this work.

7. REFERENCES

- [1]. Shehata, F., Elmahallawy, N., Arab, M. & Agwa, M. (2013), "Equal channel angular pressing of Al-SiC composites fabricated by stir casting," *Open Journal of Metal*, vol. 3, pp. 26-33.
- [2]. Lee, W. S., Sue, W. C. & Lin, C. F. (2000), "The effects of temperature and strain rate on the properties of carbon-fiber-reinforced 7075 aluminum alloy metal-matrix composite," *Composites Science and Technology*, vol. 60, pp. 1975-1983.
- [3]. Sozhamannan, G. G., Prabu, S. B. & Venkatagalapathy, V. S. K. (2012), "Effect of processing parameters on metal matrix composites: stir casting process," *Journal of Surface Engineered Materials and Advanced Technology*, vol. 2, pp. 11-15.
- [4]. Rahaman, M. S. A., Ismail, A. F. & Mustafa, A. (2007), "A review of heat treatment on polyacrylonitrile fiber," *Polymer Degradation and Stability*, vol. 92, pp. 1421-1432.
- [5]. Abraham, S., Pai, B. C., Satyanarayana, K. G. & Vaidyan, V. K. (1992), "Copper coating on carbon fibers and their composites with aluminium matrix," *Journal of Materials Science*, vol. 27, pp. 3479-3486.
- [6]. Davidson, A. M. & Regener, D. (2000), "A comparison of aluminium-based metal-matrix composites reinforced with coated and uncoated particulate silicon carbide," *Composites Science and Technology*, vol. 60, pp. 865-869.
- [7]. Byeon, J. H. & Kim, J. W. (2010), "Novel electroless copper deposition on carbon fibers with environmentally friendly processes," *Journal of Colloid and Interface Science*, vol. 348, pp. 649-653.
- [8]. Singh, B. B. & Balasubramanian, M. (2009), "Processing and properties of copper-coated carbon fibre reinforced aluminium alloy composites," *Journal of Materials Processing Technology*, vol. 209, pp. 2104-2110.
- [9]. Njuhovic, E., Witt, A., Kempf, M., Fabris, F. W., Glode, S. & Altstadt, V. (2013), "Influence of the composite surface structure on the peel strength of metallized carbon fibre-reinforced epoxy," *Surface & Coatings Technology*, vol. 232, pp. 319-325.