

The cementation technique for coating carbon fibres

A. G. KULKARNI, B. C. PAI, N. BALASUBRAMANIAN

Materials Science Division, National Aeronautical Laboratory, Bangalore 560017 India

A tow of carbon fibres was coated with copper, nickel and cobalt by the cementation process. Conditions were optimized to obtain continuous, uniform and adherent coatings on three types of carbon fibres. The surface of the carbon fibres was activated by heating in vacuum at 700° C for about 15 min. The fibres were suspended in an aqueous solution of metal (Cu, Ni, Co) salt which also contained glacial acetic acid. To the solution a displacing agent such as Mg, Al, Zn or Fe was added. The metal was displaced from the solution and plated onto carbon. The thickness of the coating was dependent on the metal salt solution concentration and concentration of the surface activator (glacial acetic acid) in the solution. The appearance (dullness or brightness) of the metal coating was dependent on the concentration of the activator and the amount of displacer metal added. Mechanical testing of the single fibres indicated that the strength and modulus of the coated fibres was dependent on the coating thickness. In general, an increase in the coating thickness decreased the mechanical properties of the coated fibres. The coated fibres were introduced into an aluminium matrix successfully by the vacuum-infiltration technique to obtain composites with a uniform distribution of fibres.

1. Introduction

Metal-matrix composites are being studied for use at high temperatures ($> 300^{\circ}\text{C}$) where resin-matrix composites cannot be used. Their other advantages include high toughness, high electrical and thermal conductivity, low susceptibility to thermal shock, the possibility of adapting existing procedures for making, shaping, joining and design of parts, and known durability. To obtain a good composite, the surface characteristics of the fibre must be modified such that the matrix metal can wet the fibre and ensure good bonding. At the same time reactions at the matrix-fibre interface which degrade the composite properties must be minimized. For instance, the use of a silicon carbide coating on boron to protect it from oxidation and to retard interfacial reactions during fabrication or high temperature exposure is well known [1]. In the case of carbon-metal composites, the compatibility problems are due to (i) matrix metal not wetting the fibres except at high temperatures, (ii) formation of carbides at service temperatures and, (iii) dissolution of fibres in the metals. These

factors determine the temperature up to which the composite can be used. A coating on the carbon fibre can promote wetting by the matrix metal and act as a diffusion barrier to the high temperature reactions. A number of methods have been developed to coat the carbon fibres by metals [2–15] and refractory carbides [16–18] and these have been reviewed [19–20]. For instance, C fibre has been coated with Cu, Ni, Co and Pb by electroplating [2–7], with Cu and Ni by electroless plating [8–10], with Al by chemical vapour deposition [11–12], with Ni and Al by physical vapour deposition [8, 12–14], and with Ti by plasma spraying [15].

The present paper describes a simple method to coat carbon fibres using a technique borrowed from extractive metallurgy. This method is known as cementation. The principle of the cementation reaction is the displacement of a noble metal ion from a salt solution by a more reactive metal. (The noble metal has a lower oxidation potential [21] or lower standard half-cell potential). The applicability of the method for coating fibres does not

seem to have been explored so far. In the present work, the cementation technique has been used in a modified form in that glacial acetic acid has been added to the salt solution as an activating agent so that the displaced metal can wet the carbon fibre better. The feasibility of the method has been demonstrated by using three types of carbon fibres. Copper, nickel and cobalt were deposited onto the carbon fibre from the corresponding salt solutions using four displacing agents, Zn, Mg, Al and Fe. In order to obtain uniform, continuous and adherent coatings, the following parameters were investigated and optimized: (1) The metal ion solution concentration; (2) the activation treatment of the fibres; (3) temperature of the solution; (4) time of deposition; (5) effect of the reducing agent; (6) particle size of the reducing agent. The characterization of the coating was done on the basis of metallographic examination and tensile properties of coated fibres.

The coating on the fibres enables their uniform distribution in a metal matrix which would not otherwise wet the fibre in the liquid-infiltration method of producing composites. The coated fibres can be combined with matrix-metal foils and composites produced by hot-pressing. The coated fibres also serve as a model composite for studying interfacial reactions at high temperatures. The present paper, however, will report only the coating techniques and the characterization of coatings.

2. Experimental procedure

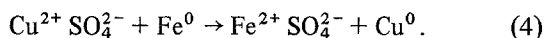
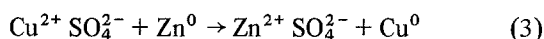
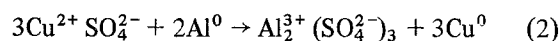
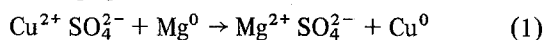
A tow of 1000 filaments, 20 cm long carbon fibres was heat-treated in vacuum (10^{-4} to 10^{-5} Torr) at 700°C for 15 min to remove any coupling agent or moisture and to activate the surface of the carbon fibres. This treatment was found to have little effect on the mechanical properties of the fibres within experimental accuracy. These carbon fibres were then dipped in a known amount of glacial acetic acid to improve further the wettability of the carbon surface with the metal to be coated. Subsequently, metal salt solutions of known amount and concentration were added to the activator bath. The bath was stirred well to disperse the fibres in the solution uniformly. Displacing agents (Mg, Al, Zn and Fe) were added in the form of granules or powder to displace the metal from the solution. The completion of cementation process was detected by the colour change of the solution and of the fibre; at the end, the carbon fibre acquired the colour of the displaced metal

(Ni, Co – metallic white, Cu – red). Copper-coated carbon fibres were treated in an acid stabilizer bath (10% H_2SO_4 + 5% orthophosphoric acid + 2% tartaric acid) for 15 min. The treatment reduced the tarnishing of coated copper. Nickel- and cobalt-coated fibres were not prone to immediate tarnishing. The coated fibres were washed thoroughly with water prior to drying at 60°C .

The concentration of the acetic acid was varied from 0.5 to 15 vol%. Similarly, the concentration of the salt solutions of different metals was also varied, which helped to obtain a varying amount of coating thickness on the carbon fibres (0.5 to $7\ \mu\text{m}$). The uniformity of the coating was studied by examining the individual fibres under the optical microscope. Single fibres were tested in a universal testing machine (Instron) using a gauge length of 2 cm and at a strain-rate of $0.05\ \text{cm}\ \text{min}^{-1}$. In each batch 25 to 30 fibres were tested and the average strength and average modulus were computed.

3. Results and discussion

In the cementation process, Cu, Ni and Co are displaced from the salt solutions by Mg, Zn, Fe and Al. The mechanisms involved have been [22–32]. Briefly, the displacement of, say, copper from copper sulphate solution using different reducing agents can be achieved as follows:



Although extensive literature is available on the use of cementation for the extraction of copper, the application of this process for coating does not seem to have been considered except for one study on the coating of graphite particles [33].

For the coating of carbon fibres using the salt solution and glacial acetic acid, the following mechanism may be suggested. At the end of the cementation reaction the displaced metal ion becomes neutralized. However, for a short initial period, the displaced metal ion (Cu^{2+}) has a positive charge. The carbon fibre after reaction with acids possesses polar surface groups [34–37]. In the present case, the carbon fibre after reaction with the acetic acid has a carboxyl group (R-COOH). This leaves the fibre with a negative charge and the metal ion, with the positive charge, therefore

TABLE I Mechanical properties of uncoated and coated carbon fibres

Sl. no.	Grade of carbon fibre	Metal coating	Diameter of the fibre (μm)	Tensile strength (GPa)	Tensile modulus (GPa)
1.	PAN supplied by Materials Corporation, USA	Uncoated	7.48	2.90	281.21
		Cobalt	7.75	3.69	259.76
		Copper	8.29	2.41	233.90
		Nickel	8.04	3.28	252.77
2.	PAN, Courtaulds Grafil 'A' type	Uncoated	7.35	2.45	231.81
		Cobalt	7.50	2.70	277.25
		Copper	7.50	2.31	288.14
		Nickel	7.50	2.55	250.61
3.	Morganite Modmor	Uncoated	7.70	2.68	250.32
		Cobalt	8.75	3.26	253.37
		Copper	8.75	2.37	212.45
		Nickel	8.50	2.82	245.16

becomes coated on the fibre. The acetic acid also keeps the fibre surface in an activated state so that uniform coating takes place. The experimental conditions are chosen so as to avoid (i) the deposition of copper over the displacing agent, and (ii) the precipitation of free copper (homogeneous nucleation). The aim is to achieve heterogeneous nucleation of copper on the carbon fibre surface and diffusion of metal on the fibre surface. An adherent coating is formed only under these conditions. Since the reaction is controlled by diffusion at the boundary layer, the rate of coating can be increased by raising the temperature of the reaction, as in other rate-processes.

3.1. Copper coating

Three types of carbon fibres, shown in Table I were coated with copper. The carbon fibres were heated to 700°C in vacuum (10^{-4} to 10^{-5} Torr) for 15 min to remove the absorbed layer of gases. An addition of 4.5 vol% glacial acetic acid was found to be optimum as a wetting agent to improve the wetting between the coating solution and the activated carbon surface. Additions of excess glacial acetic acid (more than 4.5 vol%) resulted in (i) slowing down the coating process, (ii) consumption of a larger amount of reducing agent, (iii) a deposit which was not adherent to the surface of the carbon fibre, and (iv) the coating being oxidized to a dull colour. Additions of less than 4.5 vol% acid were not able to activate the fibres uniformly and localized coating resulted.

Mg, Al, Zn and Fe were used as reducing agents. Magnesium reducer gave the fastest deposition as compared to the other reducing agents. The deposited copper was easily oxidized (blackened

end) probably due to the high reactivity of the copper in the nascent form. This could be avoided by dipping of the coated fibre in an acid stabilizer bath as mentioned earlier. The coating was uniform and continuous. Iron as a reducing agent, gave a non-uniform, less adherent, tarnished finish on the carbon surface. This might be due to FeSO_4 being formed during the reduction process, hydrolysed and precipitated as iron hydroxide which might hinder coating. This difficulty could be avoided by increasing the concentration of the acetic acid, but then the problems mentioned in the previous paragraph arose. The cementation reaction was very slow with aluminium as reducer. For the initiation of the reaction, the bath temperature was increased to 90°C or, alternatively, concentrated H_2SO_4 was added. However, the best results were obtained with zinc, which gave a bright, uniform and continuous copper coating on the carbon surface.

Another parameter which was of importance was the particle size of the reducer. Different particle sizes were used in the cementation process. In general, it was found that the larger the size of reducer the slower the cementation process and the deposition was highly localized. Localized deposition was partly overcome by agitation or stirring of the bath; however, the large particles damaged the fibres. On the other hand, finer size particles (less than $100\ \mu\text{m}$) resulted in fast reduction but the reducer metal was also found with the coating. The best results were obtained with a reducer size between 100 and $200\ \mu\text{m}$.

The concentration of the copper ion in the bath was also of importance for uniform coating of fibres. A solution concentration below 0.2 wt% CuSO_4 resulted in only coating the reducer. More

TABLE II Optimum coating parameters for different displacing agents (20 cm length 1000 filament tow is used for coating)

Sl. no.	Properties	Displacing agents						Nickel coating						Cobalt coating					
		Copper coating			Nickel coating			Nickel coating			Cobalt coating			Cobalt coating			Cobalt coating		
		Mg	Al	Fe	Mg	Al	Fe	Mg	Al	Fe	Mg	Al	Fe	Mg	Al	Fe	Mg	Al	Fe
1.	Size of displacing agent (μm)	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500
2.	Temperature for displacement ($^{\circ}\text{C}$)	Room	90	Room	Room	Room	Room	Room	Room	Room	Room	Room	Room	Room	Room	Room	Room	Room	Room
3.	Amount of activator for reaction (%)	4.5	4.5 to 5.0	4.5	4.5	4.5	4	4	4	4	4	4	4	4	4	4	4	4	4
4.	Effect of retained displacing agent	No effect	No effect	Oxidation during drying	Red with black tinge	Red with black tinge	No effect	Bright nickel	White non-uniform coating	No effect	Bright nickel	White non-uniform coating	No effect	Bright nickel	White non-uniform coating	No effect	Bright nickel	White non-uniform coating	No effect
5.	Appearance of coating	Red with black tinge	Red not uniform	Red uniform coating	Red uniform coating	Red uniform coating	Bright nickel	White non-uniform coating	White non-uniform coating	Bright nickel	White non-uniform coating	White non-uniform coating	Bright nickel	White non-uniform coating	White non-uniform coating	Bright nickel	White non-uniform coating	White non-uniform coating	White non-uniform coating
6.	Time required for coating (min)	2	30	5	3	3	3	3	10	3	3	3	3	10	3	3	3	3	3

TABLE III Effect of acid concentration on mechanical and physical properties of Ni-coated Materials Corporation carbon fibres

Sl. no	Acid concentration (ml/20 ml salt solution)	Diameter of carbon fibre (μm)	Tensile strength (GPa)	Tensile modulus (GPa)	Remarks
1.	0	7.48	2.900	281.21	C fibres vacuum heat-treated at 650° C for 30 min
2.	Dipped and dried condition	7.48	2.469	235.20	Heat-treated fibres were dipped in acid and dried
3.	0.5	8.54	2.255	173.64	To the 20 ml salt solution 0.5 ml acid is added
4.	0.8	8.41	2.562	172.32	Fibres were not coated. Reaction ceases
5.	1	8.54	2.856	235.37	All fibres were coated. Reaction is complete
6.	2.0	8.29	2.670	189.50	Large variation in coating thickness

than (100 g CuSO₄/litre) resulted in a thicker non-uniform coating. 20 cm length of 1000 filament carbon tow was coated uniformly with 20 ml (100 g/litre) CuSO₄ solution, 1 ml acetic acid, and zinc as the reducer at room temperature. After consideration of all the parameters discussed above, the best coating process was evolved using the optimum conditions given in Table II.

Table I gives the mechanical properties of the coated and uncoated carbon fibres of different grades. In all cases, it was found that the Cu-coated fibres have a lower strength and modulus compared to the uncoated fibre except in the case of Grafil A. The strength and modulus values of all uncoated carbon fibres matched the manufacturers' data well.

3.2. Nickel coating

An addition of 4 vol% glacial acetic acid was necessary to improve the wetting properties of carbon surface. Less than 4 vol% addition resulted in non-uniform coating and the reaction was incomplete. An excess of acid addition resulted in blackening of the nickel deposit. Table III shows the effect of acid concentration on the reaction and the mechanical properties of coated carbon fibres. The effect of intermittent additions of acid, and the coating method were also studied: the method provided non-uniform, dull and therefore unsatisfactory coating.

Among the reducers (Mg, Al, Zn and Fe) used for the cementation of nickel, Mg was found to be the quickest and yielded the best results. The advantages of using different reducing agents are

listed in Table II. In general, it was observed that with increasing particle size the coating time also increased.

The efficiency of the coating could be varied by increasing the concentration of solution. When the amount of salt solution was increased to 20 ml, all the fibres in the tow were coated. This was confirmed by examination under a microscope of individual fibres taken from the tow. Satisfactory coatings on 20 cm lengths of 1000 filament tows were obtained using 20 ml solution of 40 g/litre NiCl₂ · 6H₂O and, 1 ml acetic acid.

The strength and modulus of the coated fibres were found to vary with the thickness of the coating (Table IV). As the thickness of coating was increased, the strength and modulus values

TABLE IV Variation of strength and modulus with coating thickness (nickel-coated Materials Corporation carbon fibres)

Sl. no.	Diameter of coated fibre (μm)	Tensile strength (GPa)	Tensile modulus (GPa)
1.	7.54	3.648	266.60
2.	8.04	3.280	252.77
3.	8.29	2.850	216.95
4.	8.54	2.856	235.37
5.	8.79	2.648	207.85
6.	9.04	2.503	207.73
7.	9.29	2.330	165.62
8.	9.55	2.140	156.54
9.	9.79	2.090	169.92
10.	10.04	2.300	159.61
11.	10.55	1.730	146.13
12.	11.81	1.003	79.86
13.	13.56	0.685	94.64

decreased. This can be understood from the application of the rule of mixtures to a fibre with a thin coating:

$$\sigma_c = \sigma_f v_f + \sigma_m v_m \quad (5)$$

where σ_c is the strength of the coated fibre, σ_f the average strength of the fibre, σ'_m the stress in the coating at the failure strain of the fibre, and v_f and v_m refer to the volume fractions of the fibre and the metal respectively.

Equation 5 can be re-written as

$$\sigma_c = \sigma_f(1 - v_m) + \sigma_m v_m \quad (6)$$

$$\sigma_f = \sigma_c - (\sigma_c - \sigma_m) v_m \quad (7)$$

The increase in coating thickness corresponds to the increase in v_m and, therefore, the decrease in the strength of the coated fibre. The strength of the coating, σ_m , may also be a decreasing function of coating thickness. Similar considerations also apply to the modulus.

3.3. Cobalt coating

The optimum amount of acetic acid in this case was 2 vol%. A higher amount of acid resulted in slowing down the reaction and cobalt was consumed by the acid. A lesser amount of acid resulted in the coating of the reducing agent. An experiment was done in which the fibre was first dipped in acetic acid and then in metal salt solution, instead of using the two together. This resulted in a non-uniform coating of cobalt. Heating the bath to 90°C accelerated the reaction. Among the reducers attempted (Mg, Al, Zn, Fe), Mg was found to be the best. 20 ml (80 g/litre $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) solution and 2 vol% acetic acid was enough to coat a 20 cm length of 1000 filament carbon fibre. The particle size of the reducer also affected the reaction rate, as observed in previous cases. However, the coating thickness could be varied by varying the concentration of salt solution. Optimum conditions are given in Table II. As in the case of Ni, fibres with a thin coating of Co have higher mechanical properties as compared with uncoated fibres (Table I) for reasons not known at present.

3.4. Microscopy studies

In all the experiments, microscopic examination was used to characterize the coatings and to alter the conditions in order to obtain the best results. The defects in coating could be studied by optical microscopy by mounting the specimens in plastic and by using reflected light. For instance, con-

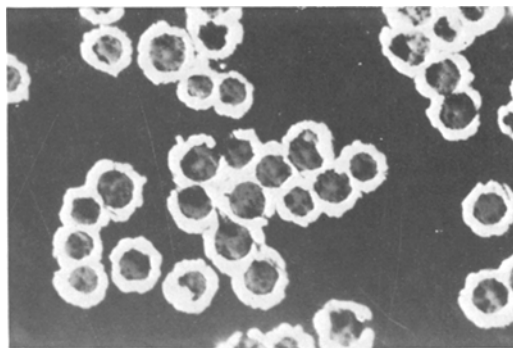


Figure 1 Cross-section of nickel-coated carbon fibre showing cold welding of nickel coating due to non-uniform stirring of the bath. Materials Corporation carbon fibre ($\times 450$).

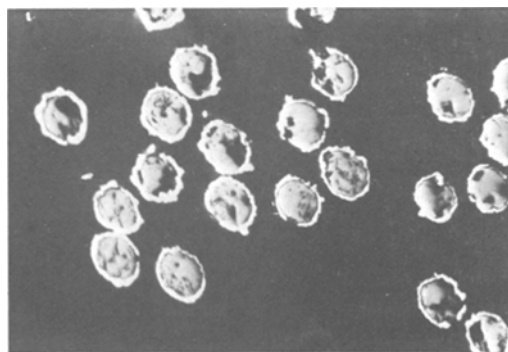


Figure 2 Cross-section of nickel-coated carbon fibres showing uniform coating of the nickel. Cold welding is avoided by stirring the bath ($\times 450$).

ditions leading to the precipitation of metals rather than formation of a film of coating were recognized and avoided. Fig. 1 shows another example of a defect, namely the typical cold welding of coated fibres. This was avoided by the stirring of the bath during coating. The resulting fibre is shown in Fig. 2 where the uniform coating can be seen.

3.5. Composite preparation

The coated fibres were introduced into the aluminium matrix by the vacuum infiltration technique. The uncoated fibres agglomerated during infiltration resulting in poor distribution of the fibres in the composite. However, the coated fibres were distributed more uniformly and gave composites with fewer voids. This is related to the fact that the coating dissolves in the molten metal and a fresh surface of carbon fibres is available for wetting by aluminium. An example is shown in Fig. 3. The composite was prepared by vacuum infiltration of Ni-coated carbon fibres and had a fibre volume fraction of approximately 0.3.

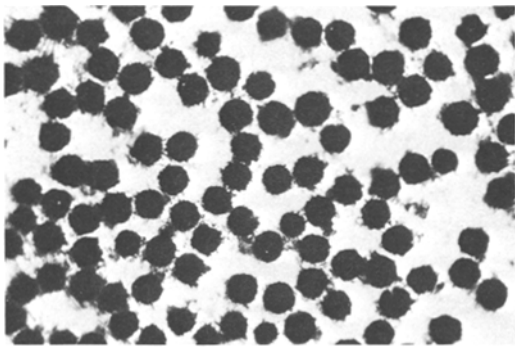


Figure 3 Cross-section of the carbon-aluminum composites (approximately 30 vol% carbon fibre) showing uniform distribution of the fibres in the matrix. Nickel-coated Materials Corporation carbon fibres were introduced.

4. Conclusions

(1) Copper, nickel and cobalt metals can be deposited on the carbon fibre surface by the cementation process.

(2) By controlling the size of the reducer, acid concentration, solution concentration and temperature, uniform and adherent coatings can be obtained.

(3) Cobalt- and nickel-coated carbon fibres have higher tensile strengths and moduli compared to copper-coated carbon fibres.

(4) The coated fibres are introduced into an aluminium matrix by an infiltration technique and are distributed uniformly in the composite.

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