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Fabrication and properties of carbon fibre-reinforced copper composite by controlled three-step electrodeposition

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Fabrication and properties of continuum carbon fibre-reinforced copper materials by controlled three-step electrodeposition are described. The effects of processing parameters, i.e. hot-pressing temperature, pressure and duration, and reinforcement content, on the properties of composites are discussed. An alloying element, nickel, was introduced into the C/Cu interface to enhance the composite strength. Finally, the relatively optimum production parameters (i.e. 30 wt% fibre, 700 °C, 40 min and 10 MPa) are suggested.

1. Introduction

Metals reinforced with carbon fibres are attractive because of their high specific stiffness and strength, high-temperature properties, excellent chemical resistance, and low wear. Advantages can be taken from the high-temperature strength and the self-lubrication property of carbon fibres, and the ductility of the metal matrix, obtaining a composite with superior chemical and physical properties [1]. These composites have been used in airplane, aerospace, sport, and other advanced application, as either structural or functional materials. Many methods have been used to fabricate copper matrix composites reinforced by carbon fibres (e.g. liquid-metal infiltration [2, 3], powder metallurgy [4, 5] and electrodeposition [6, 7]). However, perfect C/Cu metal matrix composites were very difficult to obtain, owing to the high melting point of copper, and the low compatibility between carbon and copper alloys.

In this paper, the preparation of C/Cu composite materials by means of a computerized continuous three-step electrodeposition process is reported, and the effect of fabrication parameters on the properties of the final composite materials are discussed too.

2. Experimental procedure

2.1. Materials

The carbon fibre, PAN(polyacrylonitrile–carbon)-based fibre, was manufactured by ICI plc (APC-2/Hercules Magnamite AS4 carbon fibres). Some selected features are shown in Table I. Different from other carbon fibres, its yield rate was quite high. The carbon fibre was in the form of turbulent-structured graphite.

The chemicals used in the plating process were mainly supplied by Beijing Chemical Reagent Co. The chemical compositions used for copper and nickel deposition are listed in Table II. Electrolytic copper was used as the anode in the deposition of copper, while pure nickel was used as the anode in the deposition of nickel.

2.2. Fabrication of composites

The composite fabrication was carried out in a computerized continuous three-step electrodeposition set. The schematic diagram of the process is shown in Fig. 1. The carbon fibres, after a pretreatment to remove oil, and other contaminants, went through the preliminary electrolytic cell, to obtain a thin layer of copper or copper alloys coating, they were then rinsed, neutralized and were then ready for plating in a secondary cell ready for their use in the modelling cell.

The fibres were aligned either unidirectionally or bidirectionally in the preform. The fibre volume fraction in the composite was controlled by changing the fibre permanence time in the electrolytic cell (i.e. their relative velocity), and the plating current density.

2.3. Mechanical property tests

The strength of composite samples was measured, at room temperature, using an MTS-810 Universal Material Testing Machine. A three-point bending test was performed on each composite sample, in order to compare their strengths. The bending specimens were 4 mm × 3 mm × 30 mm bars. The fibres were aligned in the longitudinal (0°), transverse (90°), or both directions (0°, 90°). Young's moduli of the composites were

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TABLE I Selected features of the carbon fibre used in this study

Physical property	Values
Tensile strength (MPa)	1960
Density (g cm^{-3})	1.75
Average diameter (μm)	6–8
Young's modulus (GPa)	196
Resistivity (μΩ cm)	1.6×10^3

TABLE II Chemical composition of deposited copper and nickel

Deposition	Chemical composition
Cu in basic solution	$CuSO_4 \cdot 5H_2O$ $C_6H_8O_7$ $C_4H_4O_6KNa \cdot 4H_2O$ NaOH
Cu in acid solution	$CuSO_4 \cdot 5H_2O$ H_2SO_4 HCl SH-110 OP-21
Ni	$NiSO_4 \cdot 7H_2O$ $NiCl_2 \cdot 6H_2O$ H_3BO_3 Na_3cit $C_{12}H_{25}SO_3Na$

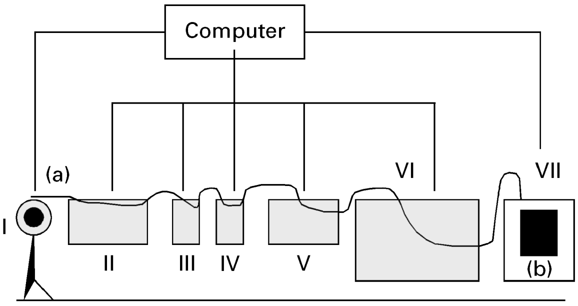

Figure 1 Schematic diagram of the controlled three-step electrodeposition process. (a) Carbon fibres, (b) final composites. I, Fibre reels; II, pretreatment cell; III rinsing cell; IV, neutralizing cell; V, secondary cells; VI, modelling cell; VII, hot-pressing.

also measured, using specimens with the same size as before.

3. Results and discussion

3.1. Hot-pressing

The green body, as obtained from the controlled three-step electrodeposition process, was a porous material, precursor of the composite. In order to obtain the final material, the green body was hot-pressed under vacuum to densify it. The schematic hot-pressing process is shown in Fig. 2.

During the course of hot-pressing, the important process parameters were temperature, time and pressure.

The observed tensile strength values of samples hot-pressed under 10 MPa, for 40 min, at different temperatures, are reported in Fig. 3. When hot-pressed at a temperature below 400 °C, the tensile strength of the resulting composite was very low. At 400 °C, the tensile strength was 150 MPa, i.e. only 18% of the theoretical strength obtained by the mixture rule. With increasing hot-pressing temperature, the tensile strength increased rapidly, and reached its maximum value (about 76% theoretical strength) at 700 °C, then it began to decrease.

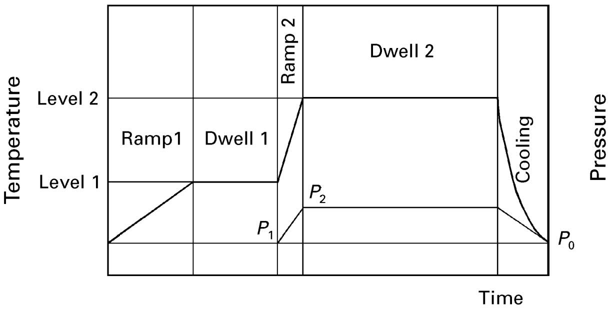

Figure 2 Representation of the behaviour of the hot-pressing treatment parameters.

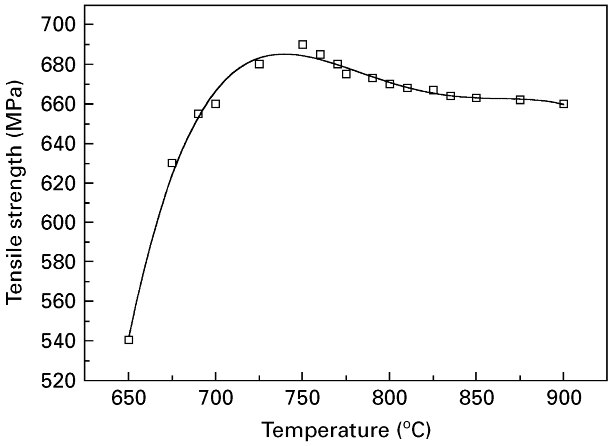

Figure 3 Relationship between tensile strength and hot-pressing temperature (10 MPa, 40 min).

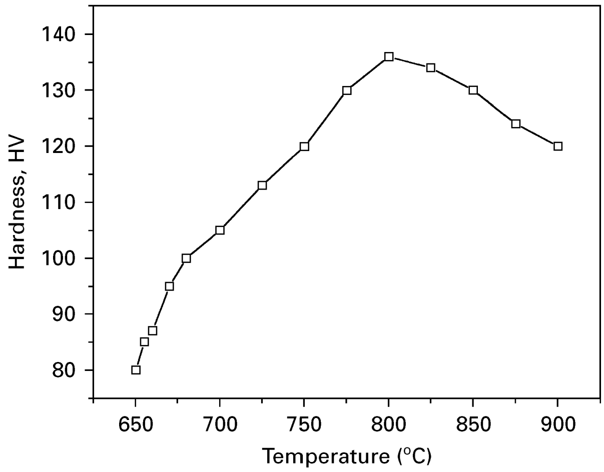

Figure 4 Dependence of the hardness of composite samples on the hot-pressing temperature (10 MPa, 40 min).

However, the hardness behaviour of the composite was quite different, as shown in Fig. 4. It can be easily observed that the hardness decreased with the lowering of the hot-pressing temperature. When the hot-pressing temperature was below 500 °C, the hardness increased rapidly with rising temperature, and then it began to increase more and more slowly, although the tendency remained the same until about 700 °C. Because the material hardness is an index of the densification degree, it could be concluded that the densification process was almost completed at temperatures close to 650 °C.

In fact, because the green body was porous, the hot-pressing treatment was useful to remove pores and crevices contained between different individual coated fibres, and then to densify the composites. At low temperatures (less than 650 °C), the plastic deformation of the green body was not large enough to remove completely pores and crevices, and also the diffusion of atoms was not so active as required to produce penetration of the interface between the coating of neighbouring fibres. The interface between the coatings of different fibres is referred to as a pseudo-interface. In the above situation, the interface between the carbon and the copper was stronger than this pseudo-interface. Therefore, during the tensile tests, the pseudo-interface was damaged first, and the composite material strength was exactly the so-measured strength.

However, the tensile strength of the composite, obtained at a hot-pressing temperature higher than 700 °C, was lower than at 700 °C. This could be explained as an effect of the residual consolidation stress, produced by the thermal expansion mismatch of the components, namely here, the copper substrate and the carbon fibres. The thermal expansion coefficients were $\alpha_f = -0.235 \times 10^{-6}\,°C^{-1}$ for carbon, and $\alpha_m = 16.87 \times 10^{-6}\,°C^{-1}$ for copper. Because the consolidation of the fibres and copper took place at a relatively high temperature, the mismatch in the expansion coefficient would result in the formation of longitudinal and radial residual compressive stresses on the fibre, and correspondingly would affect the tensile strength in the copper matrix. A quantitative estimate of the magnitude of these residual stresses had been made possible by the Schaefer–Christian [8] equation

$$\sigma_m^r = \frac{E_m \Delta\alpha \Delta T}{\left[\left(\frac{E_m V_m}{E_f V_f}\right) + 1\right]} \qquad (1)$$

where E_m, E_f are the Young's moduli, $\Delta\alpha$ is the difference of the thermal expansion coefficients, ΔT is the temperature variation, and V_m and V_f are the volume fractions of matrix and fibre, respectively.

For a 34 wt % C/Cu composite, the residual stresses at 900 °C were almost twice that at 700 °C. Although a purely elastic response of the matrix was assumed in this simple calculation, which is not expected in a real case, it could still give an indication of the magnitude of the difference of residual stresses at different hot-pressing temperatures. So far, it was believed that the lower tensile strength of the composites obtained at a hot-pressing temperature higher than 700 °C was caused by the residual stresses of consolidation, and for the real composite, the damage between the carbon and copper interface resulted from the consolidation of residual stresses.

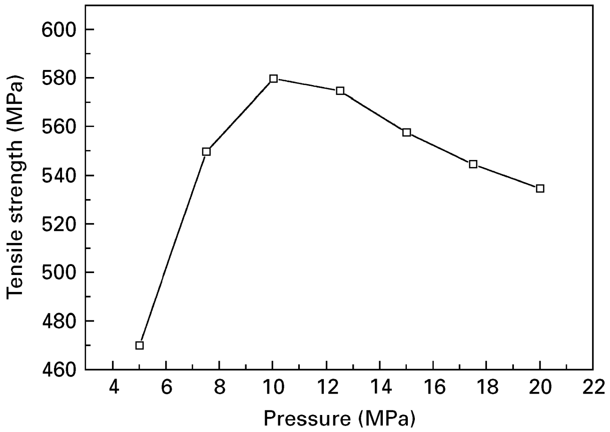

Figure 5 Behaviour of the tensile strength of C/Cu composites with the hot-pressing pressure.

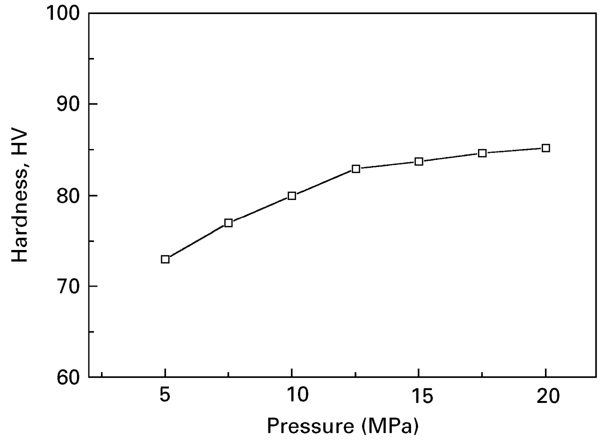

Figure 6 Hardness of C/Cu composites versus the pressure of the hot-pressing process.

3.2. Effects of hot-pressing pressure

The pressure applied during the vacuum hot-pressing process was the most critical parameter for the properties of the final products. The tensile strength and hardness dependence on the pressure is shown in Figs 5 and 6, respectively. One of the effects of pressure is to remove small pores and depress crevices by plastic deformation of the copper substrate. At low pressure (for instance, 5 MPa in this study), the plastic deformation was not sufficient totally to remove the pores, and a netted microstructure resulted in the so-prepared green body. The network was constituted of copper, with pores and fibres in the centre. Consequently, the hardness was poor. When the pressure reached 10 MPa, pores and crevices were almost completely removed or depressed, and then the densification process was completed. However, some problems could occur if the pressure continued to increase. As illustrated in Fig. 5, the composite tensile strength has the highest value at a pressure of 10 MPa, then it decreases with rising of pressure. This phenomenon can be explained by the hypothesis of a partial fracture

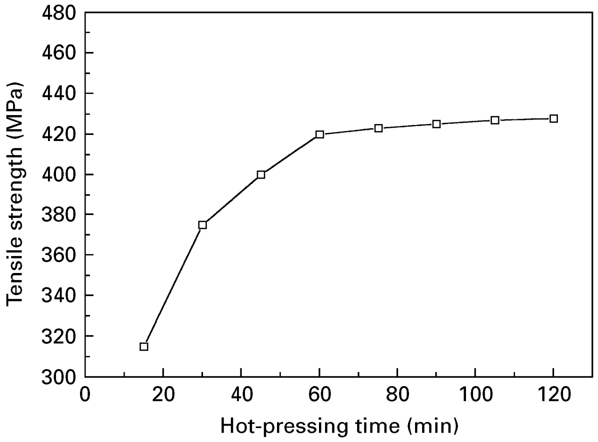

Figure 7 Tensile strength of the C/Cu composites versus the hot-pressing time (700 °C, 10 MPa, $V_f = 0.26$).

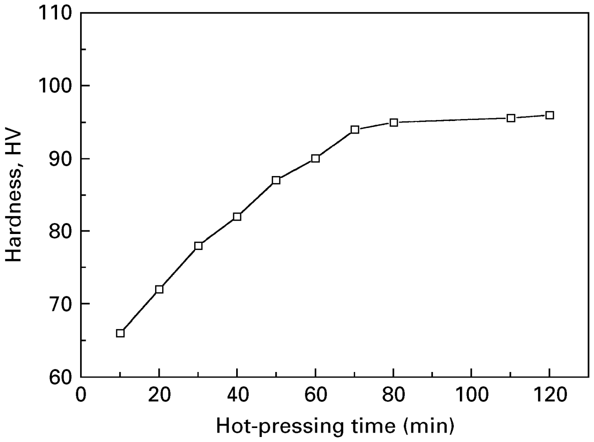

Figure 8 Behaviour of the C/Cu composite hardness with the hot-pressing time (700 °C, 10 MPa, $V_f = 0.26$).

damage of the carbon fibres. In fact, because the copper substrate was more flexible than the carbon fibre, during the hot-pressing, the pressure was offset by the deformation of copper and fibres. Because the carbon fibres were more brittle and the plastic deformation tended to produce a considerable shear stress on the fibres, some of them fractured. The tensile strength of the composite would rise due to the densification process, but also would decrease due to the partial damage of the carbon fibres. In the example studied above, for the combined effects of the two factors, the strength reached the highest value of 590 MPa at a pressure of 10 MPa.

3.3. Effects of hot-pressing time

The hot-pressing time is another important process parameter because it is critical for the material densification, and for the diffusion of atoms throughout the interface. The behaviour of composite tensile strength and hardness with the hot-pressing time is shown, respectively, in Figs 7 and 8 (at 700 °C, 10 MPa, and $V_f = 0.26$). On increasing the hot-pressing time, a trend of data was observed. Under the same temperature and pressure conditions, the duration of the treatment affected the diffusion process. The green body requires some time to densify by means of consecutive plastic deformations and diffusion. Probably, a longer duration can produce a better densification, and therefore a higher tensile strength; however, problems may occur when the hot-pressing treatment is too long. For instance, growth of copper crystals, and damage of fibres (very harmful for the composite tensile strength) were observed. Under the above conditions, the copper crystal size was about 304 nm after 40 min, and about 450 nm after 120 min. Therefore, during the hot-pressing treatment, hardness and tensile strength improved with the hot-pressing time, but a long duration prevented increase of hardness and tensile strength, owing to fibre damage, and growth of copper substrate crystals. The optimum hot-pressing time was about 40 min in this study.

3.4. Effects of fibre volume fraction

Different methods are available to evaluate the relative ratio of the two components in a metal matrix composite. Physical metallurgy, specific gravity, chemical corrosion, and weighing and calculation methods can be used. However, the physical metallurgy and specific gravity methods are easily subject to the influence of pores, micro-crevices, and the degree of densification. Chemical corrosion causes irreversible sample damage. Therefore, here the reinforcement content was determined by the weighing and calculation method.

Generally, the fibre content must be greater than a certain value, V_{min}, because a minimum amount of fibre is required to affect the tensile strength, or reinforce the substrate [9]. As far as the C/Cu composite is concerned, this V_{min} value was 8 wt % (theoretically). Composites with five different V_f values were produced by controlling the residence time of fibres in the electrolytic cells, the plating current, etc. Those composites were hot-pressed in vacuum, at 700 °C, 10 MPa, for 40 min. The fibre volume fraction dependence of the tensile strength is shown in Fig. 9, where σ_b is obtained by the rule of mixtures, and σ_c is the measured value. When V_f was lower than 0.35, the composite tensile strength was linearly proportional to V_f, and it reached the highest point (about 550 MPa, at $V_f = 0.35$), and then began to decrease with increasing V_f. When $V_f = 0.48$, the tensile strength reduced to 400 MPa. With increasing of fibre volume fraction, the tensile strength deviated from the theoretical value more and more severely. When V_f was 0.15, σ_c/σ_b was 0.83, and when V_f was 0.60, σ_c/σ_b was about 0.30. It was observed that a high fibre volume fraction did not necessarily produce high composite tensile strength, because the tensile strength was maximum at a certain value of V_f (about 0.35). The decrease in tensile strength can be explained as follows. With high fibre volume fraction, during the hot-pressing process, the fibres were more likely to deform and to be damaged under the effect of the pressure, because of the extensive contact of neighbouring fibres. Consequently, more defects were left in the composites.

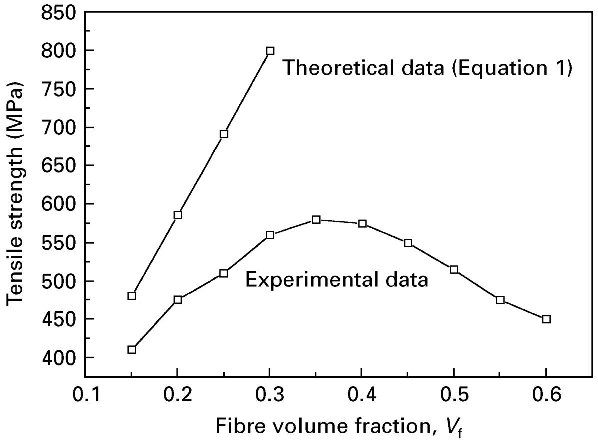

Figure 9 Dependence of the C/Cu composites tensile strength from the fibre volume fraction.

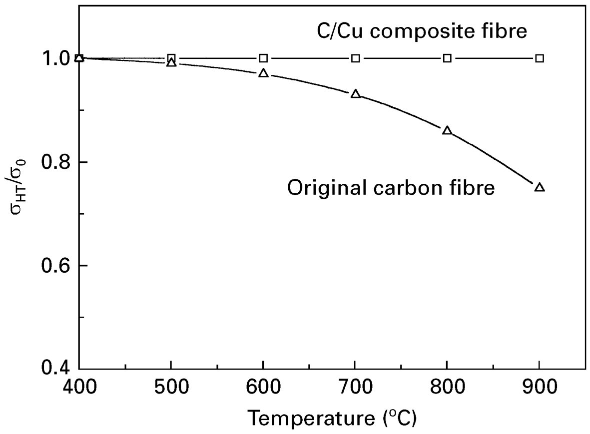

Figure 10 Behaviour of carbon and composite fibre strength versus the annealing temperature.

Although the above composite was produced at relatively optimum conditions (730 °C, 10 MPa, 40 min and $V_f = 0.35$), the tensile strength (680 MPa) was not high enough, and, therefore, alloying elements were added to modify the copper–carbon interface microstructure.

3.5. Effects of alloying elements

The nature of the matrix–reinforcement interface in a composite system is a very important parameter, because of its influence on the behaviour of physical and chemical properties of the material. In order to investigate the character of the copper–carbon interface, carbon and composite fibres were annealed under vacuum (10^{-2} Pa) at different temperatures. The behaviour of strength versus the annealing temperature is shown in Fig. 10. It is obvious that, after heat-treatment, the original carbon fibre and the composite fibre behaviour was quite different. The fracture strength of the carbon fibre decreased, probably, for the partial oxidation process of the fibres in vacuum, as reported by Warren *et al.* [10]. However, the fracture strength of composite fibres after heat treatment remained exactly the same as before the heat treatment. It was believed that the thin copper layer was able to protect the carbon fibres from oxidation reactions.

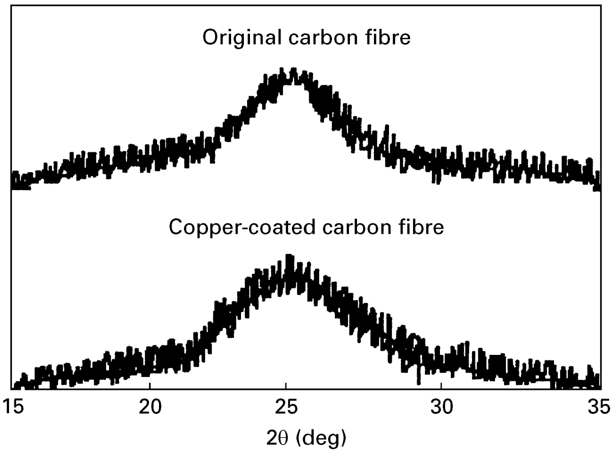

Figure 11 XRD pattern of the interface structure.

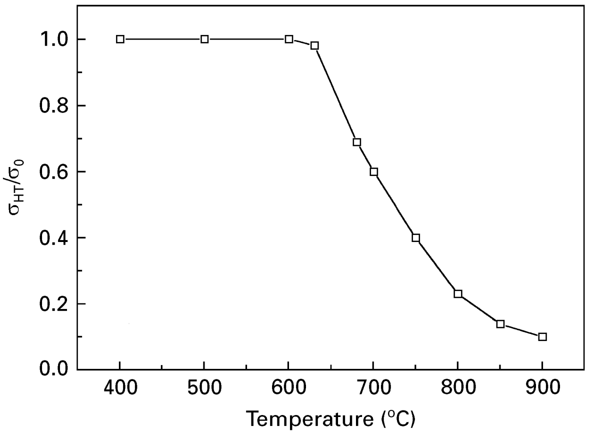

Figure 12 Annealing temperature dependence of the fracture strength of C/Ni composite fibres.

According to the literature data [7], the carbon does not dissolve in copper to form alloys, and the diffusion coefficient of carbon in copper is very low under 1000 °C. Therefore, no diffusion or chemical interaction can occur at the interface, and the carbon–copper bond must have a physical or mechanical nature. The XRD spectrum of the original carbon fibre and that of the same fibre coated by copper are shown in Fig. 11. It is clear that no new phases are contained.

The above conclusions suggest the possibility to enhance the interfacial strength by introducing some alloying elements close to the fibre–metal interface. Using a similar plating process, C/Ni composite fibres were prepared.

Fig. 12 shows the dependence of the strength of C/Ni composite fibres on the annealing temperature. At a temperature higher than 600 °C, the strength decreases with increasing temperature, and it was less than 10% of the original value after annealing for 30 min at 900 °C. Hertman *et al.* [11] reported that, at 900 °C, the solubility of carbon in nickel is about 1 at %. Then a reciprocal diffusion is possible at the C/Ni interface. Moreover, nickel is also a catalyst for the graphitization process [12], and it can catalyse the

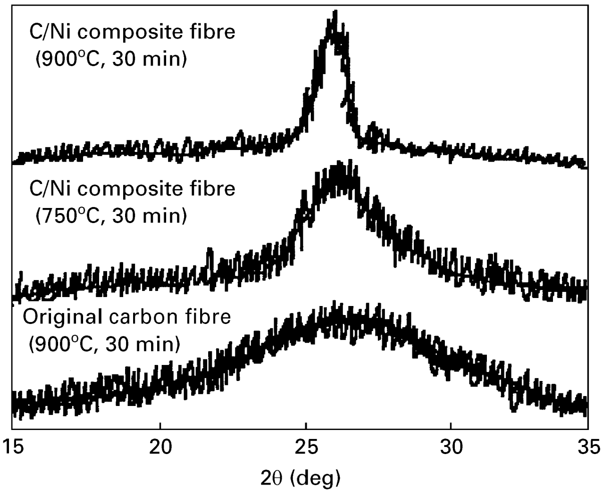

Figure 13 XRD patterns of the C/Ni interface.

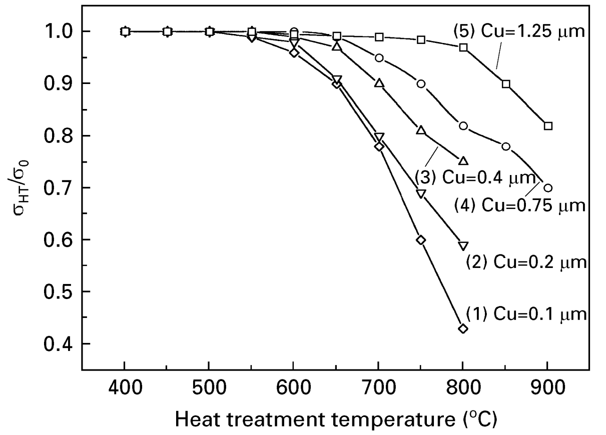

Figure 14 Heat-treatment temperature dependence of fracture strength of the composite fibres.

TABLE III Selected features of C/Cu–Ni composite fibre

No.	Thickness of copper layer (μm)	Thickness of nickel layer (μm)
1	0.1	0.5
2	0.1–0.3	0.5
3	0.3–0.5	0.5
4	0.6–0.9	0.5
5	1.0–1.5	0.5

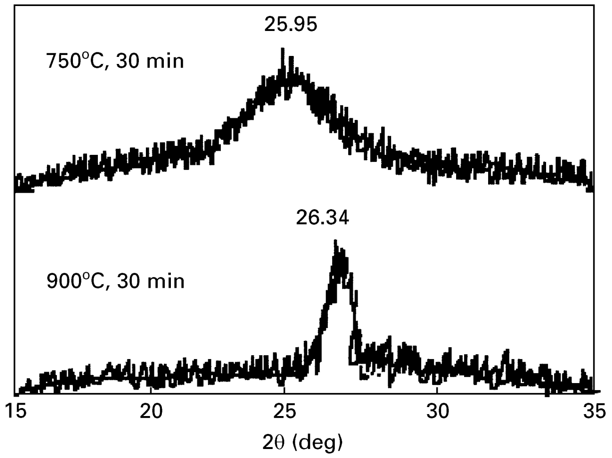

Figure 15 XRD patterns of two samples of sample 3 treated at 750 and 900 °C for 30 min.

transformation of graphite from the turbulent-structure to the laminar structure. The XRD patterns shown in Fig. 13 confirmed this assertion. The X-ray diffraction spectra show that the (0 0 2) peak of the carbon fibres became, after heat treatment, more intense than that observed before treatment, and that of the original carbon fibres. Generally, the distance between the (0 0 2) planes can be used to evaluate the degree of graphitization. The method, established by Maire and Mering [13], was used here to determine the extent of the graphitization reaction

$$g = \frac{3.440 - d_{(0\,0\,2)}}{3.440 - 3.354} \qquad (2)$$

$$d_{(0\,0\,2)} = \frac{\lambda}{2\sin\theta} \qquad (3)$$

where g is a value directly proportional to the degree of graphitization, θ is the diffraction angle, and λ is 0.154 05 nm.

The θ values, 26.037/2 and 25.338/2 at 700 and 900 °C, respectively, were substituted into the above equations, and the obtained g values were 0.24 and 0.76, respectively. Therefore, a higher degree of graphitization was present at higher heat-treatment temperatures.

In fact, the morphology of the carbon fibres used in this study was transition carbon, similar to the turbulent-structured graphite [14]. As stated in the literature, the graphitization is a transformation process from the two-dimensional turbulent-structured characteristic of the original carbon fibres to a three-dimensional crystallized laminar graphite structure. Because of the mismatch between the three-dimensional ordered crystalline structure and the disordered two-dimensional structure, the existing mechanical structure was partially damaged, and the strength decreased.

Apparently, the interface structure of the C/Ni composite was not a purely physical combination, but a diffusion combination. Without the graphitization (caused by the diffusion of nickel atoms inside the carbon fibres), the strength of C/Ni composite fibres should be higher than that of the C/Cu interface. In order to take advantages of the strong C/Ni interface and the high strength of C/Cu fibres, first a thin film of copper was applied on to the fibres, and then they were coated with another layer of nickel. The main features of five C/(Cu–Ni) composite fibres thus prepared are listed in the Table III. The thin layer of copper can prevent the diffusion of nickel atoms into the centre of the carbon. The dependence of the fracture strength of these composite fibres on the annealing temperature is shown in Fig. 14. As expected, the copper layer reduced the nickel diffusion and increased the fracture strength. In addition, a useful piece of information was that a thicker copper film produced a higher transition point of strength. In order to demonstrate the restraint effect of the copper

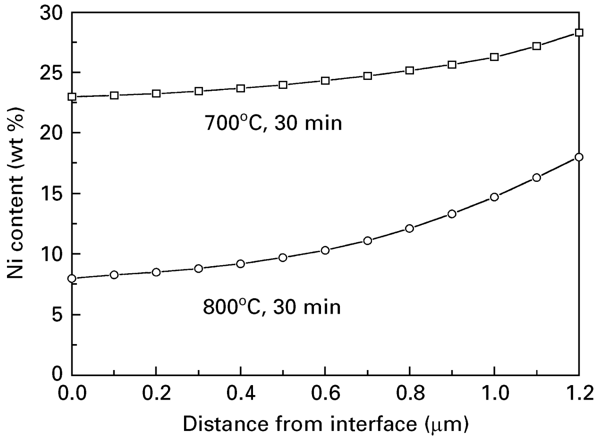

Figure 16 Distribution of nickel in the metal coating.

TABLE IV Selected features of C/Cu–Ni composite material

Physical property	Values
Tensile strength (MPa)	760
Density (g cm^{-3})	6.38
Hardness, (HV)	91
Young's modulus (GPa)	125.8
Resistivity ($\mu\Omega$ cm)	3.0

layer, two samples of composite 3 were treated at 750 and 900 °C for 30 min; their XRD patterns are reported in Fig. 15. The g values obtained from the XRD patterns were 0.11 for 750 °C and 0.69 for 900 °C. The restraint effect of copper to prevent the diffusion of nickel into the carbon fibre, and the reduction of the carbon graphitization were evident. Fig. 16 shows the distributions of nickel in the metal coating.

Therefore, a relatively ideal interface structure of C/Cu can be achieved by introducing a thin layer of nickel into the metal coating. Selected properties of C/(Cu–Ni) composite materials are shown in Table IV.

4. Conclusion

The C/Cu and C/(Cu–Ni) composite systems were produced by a controlled three-step electrodeposition process. During the hot-pressing treatment, the temperature dependence of the composite strength was similar to a dynamic equilibrium, i.e. a high temperature did not necessarily produce high strength. The same effects of the hot-pressing pressure and duration were also observed. The preliminary optimum hot-pressing parameters were 700 °C, 10 MPa, 40 min, and $V_f = 35$ vol %, which were obtained by a trial and error approach. Alloying elements (e.g. nickel) can improve the composite properties, when the coating and alloying operations are properly performed. However, ulterior investigations are required to determine the specific effects of other alloying elements on the composite microstructure and properties.

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