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Effect of metal diffusion barrier on thermal stability of metal-coated carbon fibers

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The thermal stability of carbon fibers coated with different metals was investigated. The fracture strength of metal-coated carbon fibers was measured at room temperature as a function of heat-treatment temperature. It was demonstrated that the fracture strength of the copper-coated carbon fibers (C/Cu) was not affected by heat-treatment at temperatures up to 900°C because of the inert of copper. However, the fracture strength of the carbon fibers coated with an active metal (nickel, iron and chromium) were found to decrease significantly after heat-treatment at temperatures >700°C, owing to graphitization (induced by nickel) of the carbon fibers or a chemical reaction (between fibers and iron or chromium) at the interface. A diffusion barrier layer between the active metal coating and the fibers can reduce the strength loss of the carbon fibers, but the effectiveness of a metal diffusion barrier differed depending significantly on the nature of the introduced metals. It was found that if the diffusing active metal had an adequate solubility in a metal, the latter can effectively hinder the diffusion of the former; if not, the latter can not effectively hinder the diffusion of the former.

1. Introduction

The interface between the fibers and the matrix plays an important role in the mechanical properties of fiber reinforced composites since the stress acting on the matrix is transmitted to the fiber across the interface. By understanding the interface character, it may be possible to tailor interfacial properties and further to tailor the composite performance.

The wettability of the carbon fiber by copper has been shown to be poor [1, 2] so that the interface of carbon fiber reinforced copper (C/Cu) composites is extremely weak [3]. In order to strengthen the interface between the carbon fibers and copper matrix, controllable reaction (diffusion or chemical reaction) at the interface is essential so as to produce dissolution bonding or chemical reaction bonding by adding nickel or iron in copper matrix [4].

In our previous work [5], a series of C/Cu composites were produced by a continuous three-step electrodeposition plus vacuum hot-pressing technique. Briefly, a bundle of fibers was designed to successively go through three plating tanks. Copper coatings were obtained both in the first and in the third tanks. A selected alloying element, nickel, iron or chromium was added into the copper matrix in the second tank where the plating composition can be adjusted depending on the alloying element type (the resulting composites were designated by C/Cu(Ni), C/Cu(Fe) and C/Cu(Cr) composite, respectively). After hot-pressed at 700–750°C under a pressure of 10–20 MPa, a dense composite with modified interface was produced. Our previous works demonstrated that C/Cu(Ni) composite exhibited the largest tensile strength among C/Cu(Fe), C/Cu(Ni), C/Cu(Cr) and C/Cu composites although its interfacial bonding strength was lower than that of C/Cu(Fe) and C/Cu(Cr) composites, indicating that the mechanical compatibility of fiber/metal interface, which involves the influence of the interfacial reaction on the mechanical property of the fiber [6], is another crucial factor influencing the C/Cu composite performance in addition to interfacial bonding strength.

The present paper is intended to provide a deeper insight into the thermal stability of various composite carbon fibers, to show the influence of alloying elements, including nickel, iron and chromium, as well as to correlate this behavior with the properties of the corresponding bulk composites.

2. Experimental procedure

A PAN-based medium-strength carbon yarns (Shanghai Carbon Factory) of 3000 monofilaments (tensile strength 1960 MPa, modulus 196 GPa, average density 1.75 g cm^{-3}, diameter 6–8 μm) were used as the reinforcement. The surface treatment of fibers included desizing, oil clearage, rinsing and drying. The treated fibers were subsequently coated with a single or a duplex coating using the electrodeposition technique. The bath compositions for different coating metals were summarized in Table I. Some carbon fiber bundles were uniformly coated with a single copper or nickel coating, the corresponding composite fibers were denoted

TABLE I Chemical compositions of various plating baths

Metal	Composition	Temperature(°C)	pH
Cu	$CuSO_4 \cdot 5H_2O$ $C_6H_8O_7$ NaOH $C_4H_4O_6KNa \cdot 4H_2O$	25	11-12
Ni	$NiSO_4 \cdot 6H_2O$ $NiCl \cdot 6H_2O$ H_3BO_3 Na_3Cit $C_{12}H_{25}SO_3Na$	25	5-5.5
Fe	$FeSO_4 \cdot 7H_2O$ $(NH_4)_2SO_4$ H_2SO_4 RC stabilizer	25	4.5-5.5
Cr	CrO_3 H_2SO_4 F-S3	45-55	—

as C/Cu and C/Ni, respectively; other bundles were coated with one of the following duplex coatings, including copper (the internal layer)—nickel (the external layer), nickel—copper, copper—chromium, nickel—chromium, copper—iron and nickel—iron, the corresponding composite fibers were referred to as C/Cu-Ni, C/Ni-Cu, C/Cu-Cr, C/Ni-Cr, C/Cu-Fe and C/Ni-Fe, respectively. The typical coating thickness was 0.5 μm unless noted.

Heat-treatment was performed on those coated fibers for 30 min in vacuum (10^{-1}–10^{-2}Pa). The selection of heat-treatment period (30 min) was referred to the hot-pressing time of the practical C-Cu composite system [7] without considering the composition profiles through the metallic coatings. Each composite carbon fiber was heated to a predetermined temperature (500, 600, 700, 800, 900°C) at a heating rate of 30°C min^{-1}. A few samples were examined after the metal coating was etched in acid solutions to observe the surface of the carbon fibers, while the remaining specimens were determined after heat-treatment to obtain the fracture strength values. The mechanical properties (fracture strength) of the heat-treated composite fibers and the corresponding untreated ones were tested at room temperature in a DL-1000B tensile test machine at a cross speed of 1mm min^{-1} and a gauge length of 40 mm, according to the National Standard Testing Method of China GB 3362-82. The ratios of the fracture strength of heat-treated composite fibers to the corresponding untreated ones (σ_{HT}/σ_0) were reported here. At least 10 fiber bundles were tested for each sample group from which the average values and the standard deviations were calculated.

X-ray diffraction (XRD) was performed on a Rigaku D/max-rA diffractometer using CuK_α radiation to determine the crystalline phase (s) at the carbon fiber/metal interface and to evaluate the structural variation of the heat-treated carbon fibers.

3. Results and discussion

3.1. Thermal stability of C/Cu

Fig. 1 shows the ratios of the fracture strength of the heat-treated fibers σ_{HT} to the fracture strength of the untreated (as-coated) ones σ_0 as a function of temperature for C/Cu and uncoated carbon fibers (C). As can be seen from this figure, the fracture strength of C/Cu remained unchanged after treatment at temperatures up to 900°C, indicating that carbon fibers are stable after coating with copper. This resulted from the fact that neither chemical nor diffusion reaction can occur at the copper-carbon fiber interface since carbon and copper can not form a solid solution (according to the Cu-C phase diagram) or a compound (see Fig. 2), which agreed with that obtained by Sun *et al.* [4] and our previous works [5]. The fiber/matrix bonding strength is too low to effectively transfer stress from matrix to fibers, therefore, the C/Cu composite exhibited a fairly low strength [5]. It was noted that the fracture strength of the uncoated carbon fibers was found to decrease slowly at temperatures above 700°C, probably due to the oxidation resulting from the inadequate vacuity. A higher level of the vacuum may prevent the degradation of the carbon fibers, as reported in [8]. Comparison of the strength of the uncoated carbon fibers with C/Cu revealed that oxidation

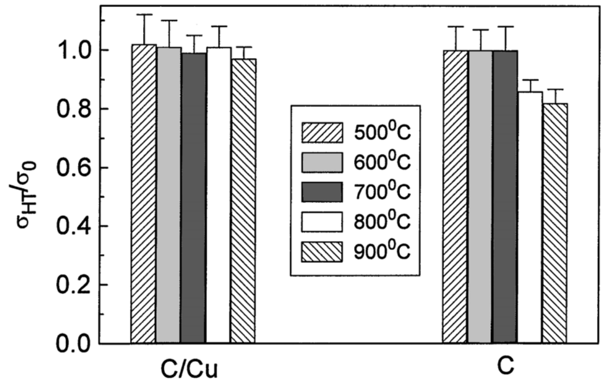

Figure 1 Variations in fiber fracture strength as a function of heat-treatment temperature for C/Cu and uncoated carbon fibers (C).

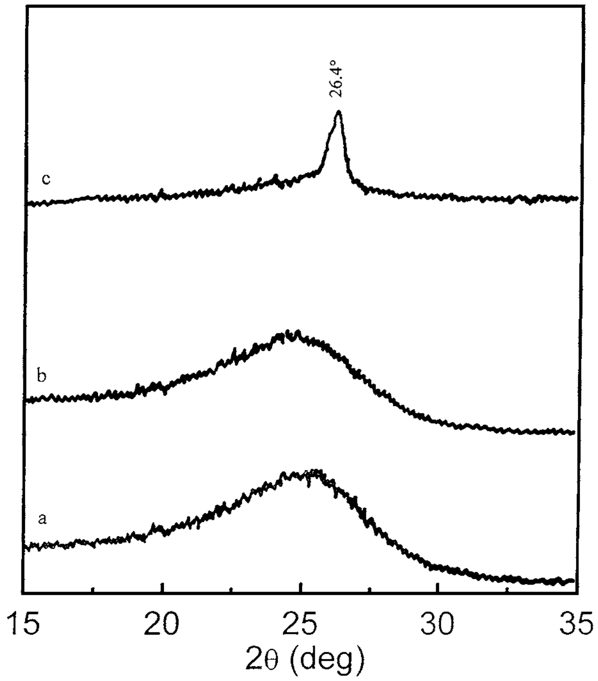

Figure 2 XRD pattern of (a) as-received carbon fibers (b) C/Cu heat-treated at 900°C for 30 min (c) C/Ni heat-treated at 900°C for 30 min.

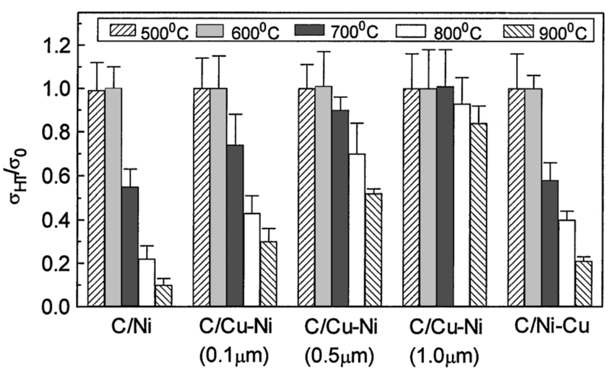

Figure 3 Relationship between the heat-treatment temperature and the fracture strength for C/Cu, C/Cu-Ni (the thickness of internal coating was marked in bracket) and C/Ni-Cu.

of the carbon fibers by atmospheric oxygen at elevated temperatures was alleviated by the introduction of the copper coating.

3.2. Thermal stability of C/Ni, C/Cu-Ni and C/Ni-Cu

Fig. 3 depicts comparison of the fracture strength of C/Ni, C/Cu-Ni (with altering coating thickness) and C/Ni-Cu. It was shown that the strength of C/Ni was virtually unaffected by heat-treatment up to 600°C, beyond that temperature, however, a considerable degradation of the fracture strength occurred. The fracture strength of C/Ni reduced by 55% after heating to 800°C and maintained there for 30 min. Since the effect of a thinner metal coating on the strength of the composite fiber was negligible [8], at least the strength change of the metal coating can be neglected, the reduced strength of the composite fibers corresponded to the strength reduction in carbon fibers. As reported elsewhere [8], there was no chemical reaction at the carbon/nickel interface, nevertheless, XRD detected a sharpened and shifted peak centered at a 2θ of about 26.4° for C/Ni sample heat-treated at 900°C (see Fig. 2), corresponding to (002) basal planes of the carbon fibers; whereas a broad peak was observed for C/Cu. This result reflected partial graphitization of the carbon fibers, due to the diffusion and dissolution of nickel atoms in carbon fibers. A similar result was reported by Jackson and Marjoram [9] by comparing the width of the diffraction arc on a powder crystallogram. Graphitization of the carbon fibers means the transformation of a two-dimensional structure of the original carbon fibers to a three-dimensional graphite structure. This transformation damages the structural continuity of the original carbon fibers and causes the breakage of intercrystalline and transverse bond in carbon structure, and consequently results in reduction in fiber strength [10, 11].

Nickel diffusion and dissolution in carbon fibers was proven to enhance the fiber/matrix bonding, which is beneficial to obtain high performance C/Cu composite. Furthermore, there was a slight solid solubility of carbon in nickel that also could help to achieve good fiber/matrix bonding [12]. However, a great decrease in strength was observed for carbon fibers, which will be detrimental to the overall composite performance, suggesting the mechanical compatibility of the carbon/nickel interface is undesirable. In order to control the strength reduction of the carbon fibers, a barrier layer should be introduced. A copper coating was selected as the barrier layer against nickel diffusion to the carbon fibers. As seen in Fig. 3, the reduction in strength for C/Cu-Ni was much lower in comparison with C/Ni, and the thicker the copper layer, the higher the strength of C/Cu-Ni. This result demonstrates that the diffusion of nickel to the carbon fibers, i.e., the strength loss of the carbon fibers can be adjusted, which is of paramount importance for practical C/Cu composite system.

It is interesting to note that the strength of C/Ni-Cu was also higher than that of C/Ni at temperatures greater than 700°C (Fig. 3). This seems indicate that an inert metal, copper, either as the internal barrier layer or as the external layer, can retard the diffusion of nickel to the carbon fibers. This phenomenon may be attributed to the fact that copper and nickel can form an infinite solid solution (the one had an infinite solubility in another one) and thus the interaction of copper atoms with nickel atoms is more strong than that of nickel atoms with carbon atoms. Anyhow, as derived by comparing the strength values of C/Cu-Ni with that of C/Ni-Cu of identical coating thickness, internal copper coating can more effectively affect nickel-carbon interaction than the external one, which is consistent with prediction.

3.3. Thermal stability of C/Cu-Cr and C/Ni-Cr

It is not easy to directly coat carbon fibers with chromium by the electrodeposition technique. More importantly, it is expected that direct contact of chromium with the carbon fibers will produce severe chemical reaction since chromium is a strongly carbide-forming element. The reaction occurred at the interface can degrade the strength so severely as to render the carbon fibers useless for practical application. Keeping those two considerations in mind, a diffusion barrier layer should be introduced between chromium and the carbon fibers. The choice of the barrier layers was limited by availability of metals which could be easily electrodeposited. Thus nickel and copper were selected. The fracture strength of C/Cu-Cr and C/Ni-Cr was plotted against temperature in Fig. 4. Clearly,

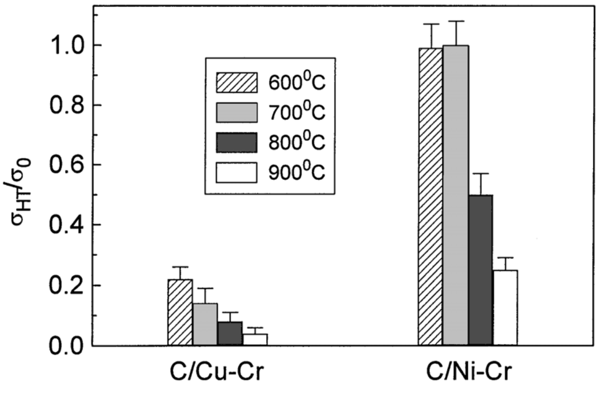

Figure 4 Variations in the fracture strength as a function of heat-treatment temperature for C/Cu-Cr and C/Ni-Cr (the thickness of chromium coating was 0.15 μm.

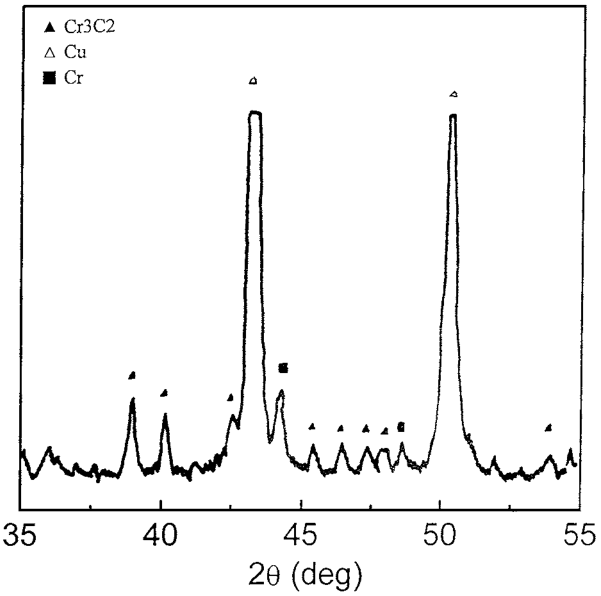

Figure 5 XRD pattern of C/Cu-Cr heat-treated at 900°C for 30 min.

great differences were noted for C/Cu-Cr and C/Ni-Cr. The fracture strength of C/Cu-Cr showed a drastic reduction at temperature as low as 600°C. After heat-treatment at 900°C, only 4% of the strength was maintained. The dramatic reduction in strength was simply due to the chemical reaction occurred at interface, which was confirmed by XRD analysis (see Fig. 5). A chemical reaction product, Cr_3C_2, was detected. This is in good agreement with the prediction from carbon – chromium phase diagram and a previous report [13], in which Cr_3C_2 was found in graphite/copper-chromium alloy interface. Such product layer not only reduces the effective cross-sectional areas of the carbon fibers, but acts as a crack source owing to its brittleness. Furthermore, reaction often generates many cracks on the surfaces of the carbon fibers, may be attributable to the non-uniform growth of the reaction product, as shown in Fig. 6. The remarkable strength loss of the carbon fibers and the presence of a reaction product, Cr_3C_2, were responsible for the lower strength of C/Cu(Cr) composite produced earlier. It can be concluded that chromium can not be added into the copper matrix in practical C/Cu composite system, particularly, when enhancement of the interfacial bonding strength is the sole aim (another aim is to improve the wettability between copper and the carbon fibers in C/Cu composites produced by liquid-metal infiltration technique [14]).

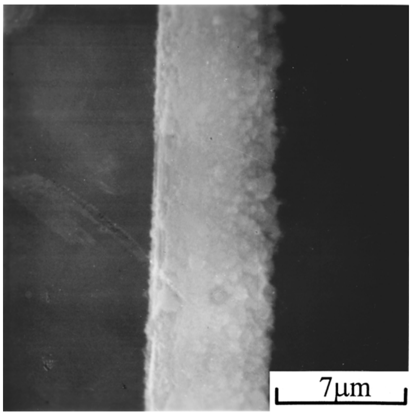

Figure 6 Surface morphology of a carbon fiber heat-treated at 900°C for 30 min (after dissolving the chromium coating).

In the case of C/Ni-Cr, no noticeable reduction in strength was observed up to 700°C, above which the strength began to decrease, as seen in Fig. 4. At 800°C and 900°C, $\sigma_{\mathrm{HT}}/\sigma_0$ was found to be 0.50 and 0.25, respectively, demonstrating the reduction in strength was much smaller when compared to C/Cu-Cr.

It can be deduced that chromium can easily diffuse through a copper coating and induce chromium carbide at the fiber/matrix interface which seriously reduces the strength of the carbon fibers; but chromium can not easily diffuse through a nickel coating. On the basis of the lower strength loss of C/Ni-Cr, nickel appears the better choice for a barrier layer. In other words, nickel can act as an effective diffusion barrier layer for chromium but copper can not.

In order to interpret the observed phenomenon, two phase diagrams for Cu-Cr and Ni-Cr binary alloys were compared [15]. It was found that copper and chromium can neither dissolve each other (in fact, chromium had a solid solubility of about 0.25 at.% in copper at 860°C), nor can form any compounds. For Ni-Cr system, nickel can dissolve some chromium (38 at.% at 900°C for example) and chromium can dissolve some nickel (9 at.% at 900°C). Accordingly, it is reasonable to put forward the following mechanism: If one metal can form a solid solution with another one, i.e., the latter had an adequate solubility in the former, the former can act as the diffusion barrier of the latter resulting from the serious interaction of the two metals. In contrast, if one metal can not form a solid solution with the other one, or exactly, the latter has no solubility or fairly low solubility in the former, the atoms of the latter are likely to be apart from the atoms of the former and have a tendency to migrate and finally segregate on the surface of the carbon fibers, and react with them. Under this circumstance, diffusion of the latter will not be hindered and the former can not behave as the effective diffusion barrier of the latter. It should be stated that reaction between two metals generating an intermetallic compound may also hinder the diffusion of a metal, and, in general, leads to a great decrease in composite performance. That case will not be discussed here.

It is well known that a moderate reaction at the interface can help to improve the fiber/matrix bonding and ameliorates the mechanical properties of a composite, whereas a chemical overreaction at the interface will inevitably cause significant loss in fiber strength and too thick of a reaction product layer, which is deleterious, from the view point of mechanical behavior of the composite. As a result, controlling the degree of the chemical reaction taking place at the interface is very important. Those results suggested that an effective diffusion barrier layer is necessary for a composite system where two constitutes may react. As discussed earlier, the measure to strengthen the fiber/matrix bonding by incorporating chromium into the copper matrix may not be adopted since copper can not effectively hinder the diffusion of chromium to the carbon fibers.

3.4. Thermal stability of C/Cu-Fe and C/Ni-Fe

Although iron is a moderately weak carbide-forming element, incorporation of iron into copper matrix can also improve the interfacial strength of C/Cu composite, which had been confirmed by Sun *et al.* [4]. At the same time, however, addition of iron may result in strength loss for carbon fibers, due to a chemical reaction: $3Fe + C \rightarrow Fe_3C$ [4]. Hence, a suitable diffusion barrier should be embedded. Copper and nickel were also chosen as the barrier layer against iron diffusion, respectively.

Fig. 7 presents the fracture strength of C/Cu-Fe and C/Ni-Fe after thermal treatment at various temperatures. It was clearly evident that after heating to a temperature as low as 500°C, a decrease in the fracture strength of C/Cu-Fe was obviously noted. At a temperature of 600°C, the fracture strength of C/Cu-Fe decreased by 40%, after treatment at 900°C, this composite fiber was found to be completely destroyed (only 6% initial strength was kept). The decrease in strength was mainly caused by the chemical reaction: $3Fe + C \rightarrow Fe_3C$, which was proven by XRD analysis (see Fig. 8).

C/Ni-Fe is more stable as compared to C/Cu-Fe as its strength remained constant up to 700°C, thereafter, it showed a continuous decrease with increasing temperature. At 800°C and 900°C, σ_{HT}/σ_0 for C/Ni-Fe was about 0.70 and 0.30, respectively; whereas for C/Cu-Fe, it was 0.13 and 0.06, respectively. The former was 5 times higher than the latter at both 800°C and 900°C. This indicates that nickel can more effectively inhibit the diffusion of iron to the surface of the carbon fibers in comparison to copper. It was found from Ni-Fe phase diagram [15] that an infinite solid solution can be formed between nickel and iron, but copper can dissolve 2.1 at.% iron at most at approximately 820°C. Combining the strength variations with temperatures for C/Cu-Fe and C/Ni-Fe and phase diagrams of Cu-Fe and Ni-Fe can further confirm the above proposed mechanism that the ability of a metal barrier layer to hinder the diffusion of another metal is dependent on the solubility of the latter in the former. The significant reduction in strength of C/Cu-Fe can explain our previous results that C/Cu(Fe) composite exhibited lower strength than C/Cu(Ni) one under identical fiber volume fraction [5], and indicate that addition of iron to the copper matrix, which is expected to enhance the interfacial bonding strength of C/Cu composite, may be not an optimum method from the view point of C/Cu composite performance.

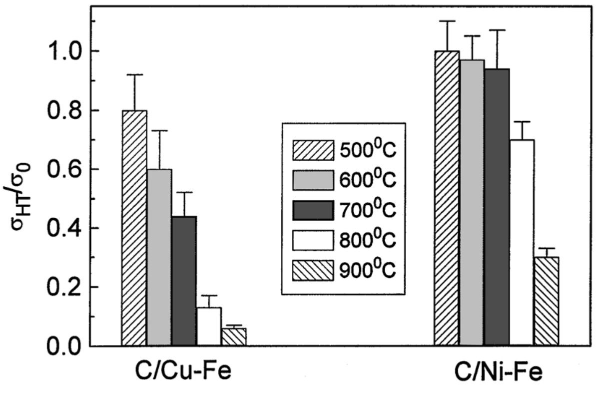

Figure 7 Effect of heat-treatment on the fracture strength of C/Cu-Fe and C/Ni-Fe.

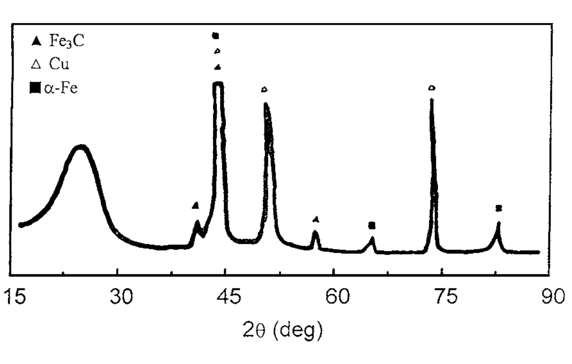

Figure 8 XRD pattern of C/Cu-Fe heat-treated at 900°C for 30 min.

The fact that C/Cu(Ni) composite showed the higher strength than C/Cu, C/Cu(Fe) and C/Cu(Cr) might confirm the proposal that "the ideal case would be to have a system where the matrix and fiber are mutually nonreactive, insoluble and only wetting occurs between them with modest diffusion bonding" [16].

4. Conclusions

(1) The copper-coated carbon fibers (C/Cu) exhibited good thermal stability, its fracture strength at room temperature was not affected by heat-treatment up to 900°C for 30 min in a 10^{-1}–10^{-2}Pa vacuum.

(2) A significant reduction in the fracture strength of C/Ni was noted after heat-treatment at 700°C. The reduction in strength was related to the graphitization of the carbon fibers and was found to increase with increasing temperature. A copper diffusion barrier between the carbon fibers and the nickel coating can reduce the strength loss of the carbon fibers. The thicker the copper coating, the smaller the strength loss of the carbon fibers.

(3) C/Cu-Cr and C/Cu-Fe showed a much greater reduction in room temperature fracture strength when compared to C/Ni-Cr and C/Ni-Fe, respectively, after thermal treatment at identical temperatures. The drastic decrease in strength for C/Cu-Cr and C/Cu-Fe was due to the chemical reaction occurred at the fiber/matrix interface.

(4) The chemical reaction at the fiber/iron and fiber/chromium interfaces could be alleviated by adding a diffusion barrier between them. But the effectiveness of a metal diffusion barrier was dependent on the solubility of the diffusing metal in it. If the diffusing metal had an adequate solubility in a metal, such as nickel in copper, chromium in nickel and iron in nickel, the latter can effectively hinder the diffusion of the former; if not, such as iron in copper and chromium in copper, the latter can not effectively hinder the diffusion of the former.

(5) It is suggested that incorporating nickel into copper matrix is a suitable method to enhance fiber/matrix bonding in practical C/Cu composite system; whereas adding iron or chromium in copper matrix is not appropriate.

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