METALLIC MULTILAYER COATINGS ON CARBON FIBRES

PAVOL ŠTEFÁNIK, ŠTEFAN KAVECKÝ, PAVOL ŠEBO

The paper deals with the evaluation of structural changes on the surface of galvanically metal coated high strength TORAYCA T300 carbon fibres after annealing at 1123 K.

It was revealed that thin nickel layers ($\sim$ 0.05 μm) during the heat treatment were destroyed and spherical particles of Ni arose. Due to diffusion of Ni from these particles into the carbon fibre the surface notches were created. This effect was not observed when the carbon fibres with both thin Ni layer and galvanically deposited copper layer were annealed. The layers were destroyed and agglomerates of various shapes arose but the surface of the fibres remained smooth. The same behaviour was observed at the annealing of carbon fibres coated only by a copper layer [1].

VIACVRSTVOVÉ KOVOVÉ POVLAKY NA UHLÍKOVÝCH VLÁKNACH

V článku sme hodnotili štruktúrne zmeny na povrchu galvanicky pokovovaných vysokopevných uhlíkových vlákien TORAYCA T300 po žíhaní pri 1123 K .

Zistili sme, že tenké niklové vrstvy ($\sim$ 0,05 μm) sa pri žíhaní rozrušujú a vytvorené sféroidy niklu v dôsledku difúzie Ni do uhlíkových vlákien vytvárajú na povrchu vlákien vruby. Tento efekt sme nepozorovali, keď sa žíhali uhlíkové vlákna s tenkou Ni vrstvou a súčasne galvanicky nanesenou medenou vrstvou. Vrstvy sa rozrušili za vzniku aglomerátov rôznorodého tvaru, pritom povrch vlákien zostával hladký. Rovnako sa správali uhlíkové vlákna po žíhaní, ktoré pokrývala iba medená vrstva [1].

1. Introduction

Carbon fibres possess excellent mechanical properties and very low thermal expansion. They are widely used in polymer composite production because of the reactions between the fibre and polymer which do not lead to the degradation

Ing. P. Štefánik, CSc., Ing. Š. Kavecký, CSc., RNDr. P. Šebo, CSc., Institute of Materials and Machine Mechanics, Slovak Academy of Sciences, Račianska 75, P.O.Box 95, 830 08 Bratislava 38, Slovakia.

of fibre properties. (The application temperatures are mostly under 473 K while carbon fibre oxidation starts over 773 K.) The different situation is in the field of metal matrix composites. The carbon fibres react with many metals to produce carbides (for example Cr, W, Al, Ti, etc.). In some metals carbon is diluted (Ni), and some metals (Cu) are inert in relation to carbon surface and do not wet the carbon. Due to the poor wettability and low adhesion between composite components the transfer of load from the matrix to the fibres is poor and very low values of shear and transverse strengths in the unidirectional composite are obtained.

There are many papers studying the influence of fibre-matrix interface on the mechanical properties of metal matrix composites. As it can be observed from the results, first of all it is necessary to obtain high mechanical properties of the composites in various load directions to optimize the properties of the interface [e.g. 2–4].

The carbon fibres due to unfavourable interaction with many metals should be protected by coatings. Some of these layers have also another functions, e.g. to improve wetting of fibres by metals. Several methods of layer deposition on fibres are used (chemical vapour deposition, physical vapour deposition, sol-gel and others). The galvanic metal coating is a widely used method in which large thicknesses can be obtained, from about several tenths of micrometer up to micrometers what should be enough to produce a matrix of the composite.

Copper is one of the metals that are easily deposited by galvanic method. Copper as the matrix in composites with carbon fibres ensures high electrical and thermal conductivity. The function of carbon fibres is to reduce thermal expansion, density and to increase mechanical properties. The disadvantage is, however, low bonding strength between fibres and copper. Therefore there is a tendency to increase adhesion by adding some metals to copper matrix [2], or to deposit a metal layer or a combination of metal layers, for example copper-iron-copper or copper-nickel-copper [3].

The addition of some elements to copper even in small amount can considerably reduce the thermal conductivity of the material. The large reaction zone at the fibre-matrix interface that can arise due to the fibre-matrix interaction, can deteriorate mechanical properties of the carbon fibre. Therefore, the basic question remains which metal and in what amount to deposit on fibres to improve adhesion of copper to carbon fibre without decreasing copper and carbon fibre properties in the composite.

Nickel can also be relatively simply deposited on carbon fibres but its disadvantage is the interaction with the carbon structure. The literature data show considerable mutual solubility of carbon and nickel at the temperatures above 873 K [5]. Also the interdiffusion coefficients of these elements reach relatively high values [6]. Another paper studied the interaction of carbon and nickel at the elevated temperatures and due to this reaction there is a reduction of mechanical properties of the fibres [7]. A proper way to increase adhesion between the fibre and copper is the deposition of an interlayer with appropriate properties on the fibre surface.

The aim of this study in the system carbon fibre-metal interlayer-copper is to deposit an optimal thickness of metal that reacts with carbon fibre in minimal degree (without loss of mechanical properties of fibre) and on the other hand it is diluted in copper or it builds up intermetallic compounds with copper. The minimal influence of given metal on physical properties (thermal and electrical conductivity) of copper is required. A choice of appropriate metal as coating can be positive even in the case of high affinity of the metal to carbon if this metal diffuses more quickly into copper.

2. Experiment

In our experiments we used high strength carbon fibres TORAYCA T300 with 3000 monofilaments in tow (diameter of a filament is about 7 μm). The fibres were galvanically coated in electrolyte with $NiSO_4$, $NiCl_2$, Na_2SO_4 and H_3BO_3 [8] at the temperature of 333 K in the coating apparatus described by Simančík and Šebo [9]. The thickness of coating nickel layer on carbon fibre was from 0.05 to 1.5 μm (Tab. 1). Some Ni coated tows were then galvanically copper coated from $CuSO_4$ based solution [9]. Thicker Ni coatings allow to increase current at the fibre entry in Cu solution and to deposit thicker Cu layer in one step of galvanic deposition (Fig. 1).

The thickness of thin layers is approximately the same on all carbon fibres in tow. To prepare thicker layers it is necessary to use higher current density that results in the fact that part of the fibres located close to the surface of the tow possesses a bit thicker layer of deposited metal than the fibres inside the tow. The average thickness of coating (Tab. 1) was calculated from weight of one meter long sections of tow and taking into account the densities of fibres and deposited metal.

Table 1. Thicknesses of nickel and copper layers deposited on carbon fibres

Sample	Thickness of Ni layer [μm]	Thickness of Cu layer [μm]
A	0.05	–
B	0.19	–
C	1.50	–
K	0.05	0.8 – 1.2
L	0.19	0.8 – 1.2
M	1.50	2.0 – 4.0

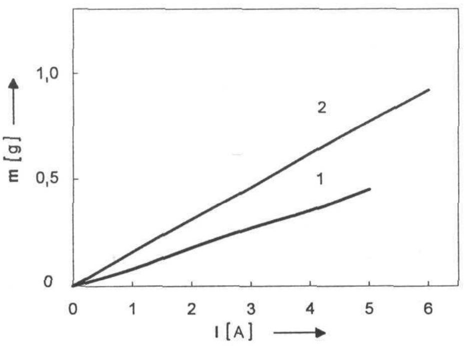

Fig. 1. Dependence of mass (m) of coated copper (on Ni layer with average thickness of 1) 0.05 μm; 2) 0.19 μm), expressed in grams per one meter of fibre tow, on current (I) used at Cu deposition.

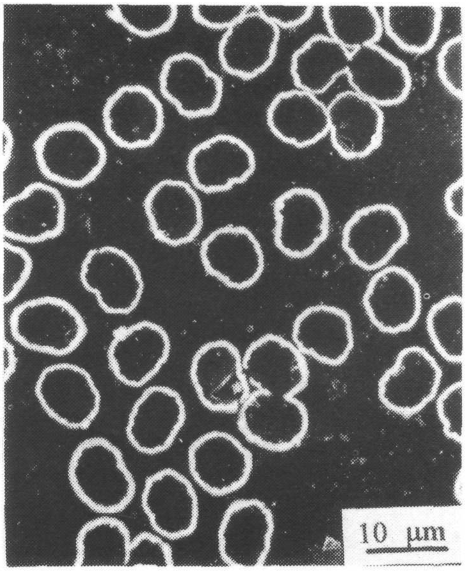

Fig. 2. Cross section of Ni coated carbon fibres (sample K).

It is supposed that all the 3000 filaments passed through coating apparatus. In fact some of the peripheral fibres – from 2 to 4 % – during coating may break away from the tow.

Each fibre in the tow was coated by metal (Fig. 2). The good quality of coating process is documented by Ni layer which follows the folding surface of original carbon fibres (Fig. 3). The structure of the thickest Ni layer was fine-grained (Fig. 4), after Cu coating the surface of fibres was smooth (Fig. 5). The different thickness of Ni and Cu layers were deposited with the purpose to compare their influence on interaction between carbon fibres and metals. The thicker layers allow more accurate study of nickel and copper interaction. To determine the influence of temperature onto the processes running on the fibre surface, all types of tows (uncoated, copper coated, nickel coated and copper and nickel coated) were thermally treated at the temperature 1123 K during 780 s in N_2/H_2 atmosphere. This time and temperature correspond to the parameters of Cu-carbon fibre composite production by diffusion bonding method [9].

The distribution of Ni and Cu in layers across the fibres was measured by the

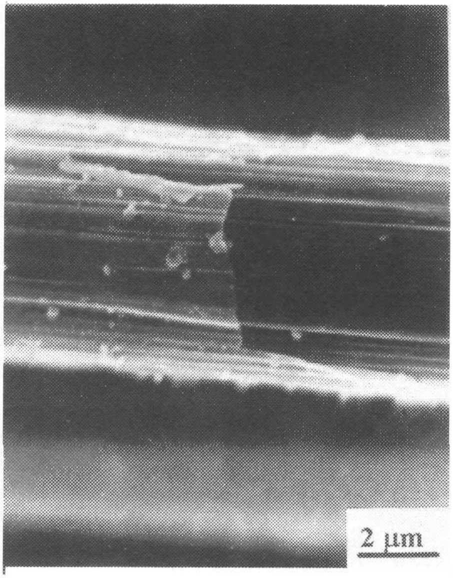

Fig. 3. Surface of carbon fibre with thin Ni layer (sample A).

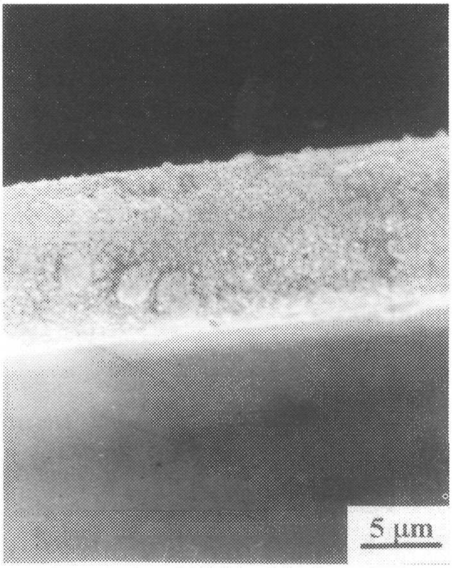

Fig. 4. Surface of carbon fibre with thick Ni layer (sample C).

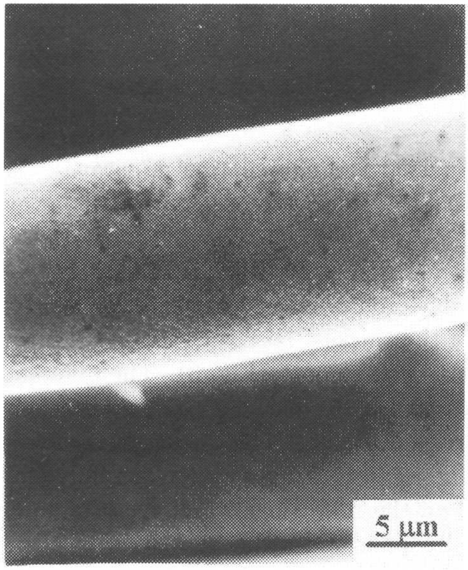

Fig. 5. Surface of carbon fibre with thick Ni and Cu layers (sample M).

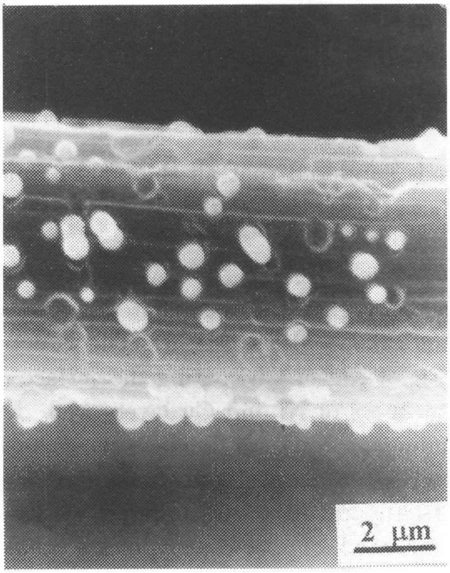

Fig. 6. Surface of carbon fibre with thin Ni layer (sample A) after annealing at 1123 K during 780 s.

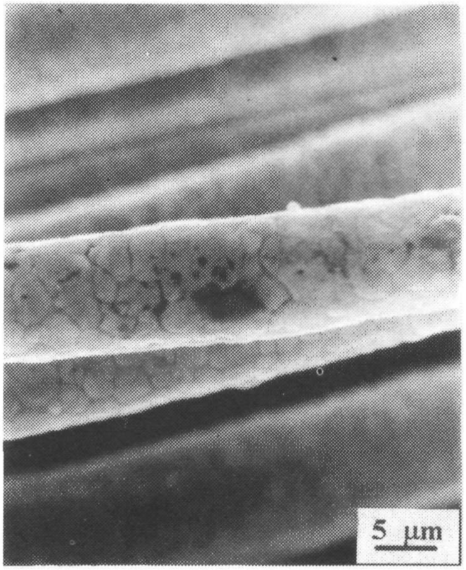

Fig. 7. Surface of carbon fibre with thick Ni layer (sample C) after annealing at 1123 K during 780 s.

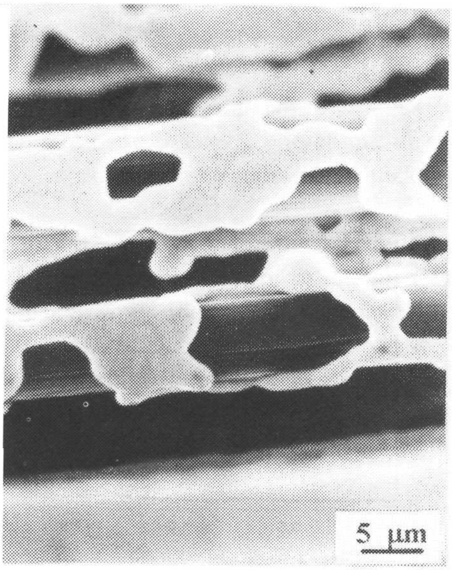

Fig. 8. Surface of carbon fibre with Ni and Cu layers (sample K) after annealing at 1123 K during 780 s.

electron microscope JEM 100 C with the scan apparatus ASID-4D and energy-dispersive spectrometer KEVEX Delta IV.

3. Results and discussion

The behavior of Ni layers of different thickness is dissimilar to each other after annealing at 1123 K. The thin Ni coating on carbon fibres spheroidizes due to low adhesion between Ni and carbon (the spheroidization rate is probably higher than interdiffusion rate). The spheroids fall away from fibre surface. A longer contact of spheroids with carbon fibres causes diffusion of Ni to the fibres. After falling away the notches are created on the fibre surface (Fig. 6). A relatively large decrease of mechanical properties of carbon fibres can be expected. The thick Ni layer aggregates at 1123 K in a different way – the surface is corrugated but the Ni layer itself is not interrupted (Fig. 7).

The different behavior of changes on carbon fibres with thin Ni coating and Cu layer (sample K) represents Fig. 8. On some fibre, the particles of metals agglomerate or they are released from them, the coating on other fibres is almost continuous. An important result is that due to interdiffusion of nickel and copper, a low concentration of nickel close to the carbon fibre exists and the surface of the

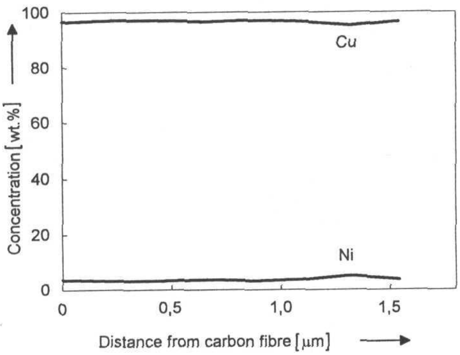

Fig. 9. Distribution of Ni and Cu in bilayer (sample K) after annealing at 1123 K during 780 s.

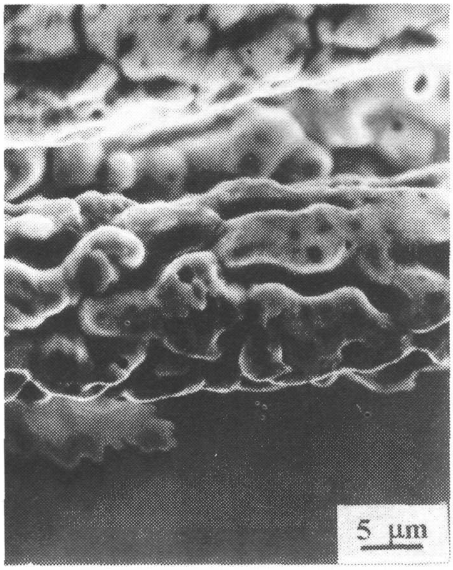

Fig. 10. Surface of carbon fibre with thick Ni and Cu layers (sample M) after annealing at 1123 K during 780 s.

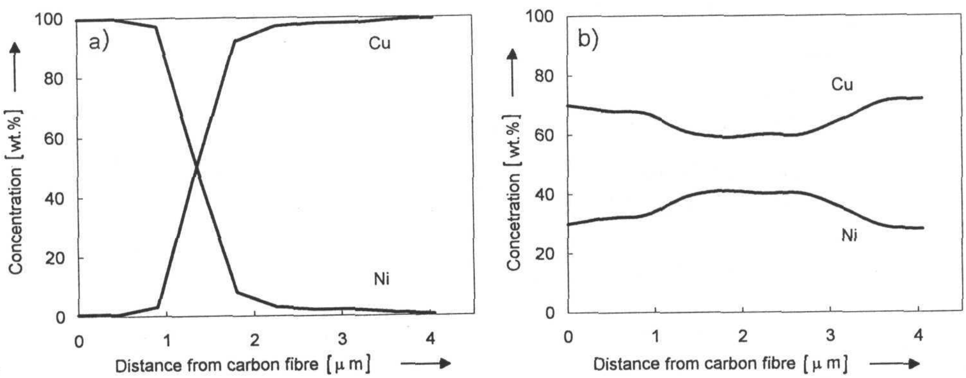

Fig. 11. Distribution of Ni and Cu in bilayer (sample M); a) original fibre b) after annealing at 1123 K during 780 s.

carbon fibre is not defective. The process of spheroidization is similar to the one of the carbon fibres coated only by the copper layer [1]. The uniform distribution of Ni in an annealed layer can be seen in Fig. 9.

The surface changes on sample M after annealing at 1123 K are demonstrated on Fig 10. Large corrugated aggregates that remain near the fibre are remarkable. The line analysis shows a homogeneous distribution of both elements in the metal layer (Fig. 11b). A certain abnormality from the homogeneous composition (the middle part of curves) is due to the fact that during diffusion the shape of the Cu-Ni interface area is not constant and the interdiffusion of copper and nickel is not finished yet.

The present results demonstrate variability of processes running at the interface between carbon fibre-nickel and/or nickel and copper. From practical point of view it is interesting to know that this nickel layer does not form continuous coating at the temperature above 1123 K. Because of that, thin nickel layer does not affect the preparation of composite at these conditions. For example, Ni is wetted by liquid copper and infiltration of continuous nickel coated carbon fibres by liquid copper would be much easier.

4. Conclusion

The results obtained in this work can be summarized as follows:

– Galvanic method is appropriate for deposition of thin Ni layers of the order of tens nanometers that perfectly copy the surface of fibres. This thin coating is fragmented at measured temperature.

– At the beginning of thermal treatment small spheroids are formed due to low adhesion between Ni and carbon fibres. These spheroids are loosed from the fibres leaving craters there.

– Galvanically deposited coating composed of thin nickel and copper layers is at the given temperatures 1123 K disrupted to variously formed agglomerates that fall down from some fibres. No changes on the fibre were observed – the surface stays smooth. The distributions of nickel and copper in metal layer are uniform.

– Galvanically deposited material of the thickest layers of nickel and copper after annealing remains on the fibres and is corrugated.

Acknowledgements. The authors are grateful to the Slovak Grant Agency for Science (grant No 2/1130/95) for partial supporting of this work.

REFERENCES

[1] ŠTEFÁNIK, P.—ŠEBO, P.: J. Mater. Sci. Letters, *12*, 1993, 1083.
[2] LAPIN, J.—DELANNAY, F.: Metall. Mater. Trans. A, *26*, 1995, 2053.
[3] LIU, H.—SHINODA, T.—MISHIMA, Y.—SUZUKI, T.: ISIJ Internat., *29*, 1989, 568.
[4] SUN, S. J.—ZHANG, M. D.: J. Mater. Sci., *26*, 1991, 5762.
[5] BARABÁŠ, O. M.—KOVAL', J. N.: Kristaličeskaja struktura metallov i splavov. Kijev 1986, p. 206.

[6] DUTL, M. V.—SEN, S. K.—BARUA, A. K.: Phys. Status Solidi A, *56*, 1979, 149.
[7] SHIOTA, I.—WATANABE, O.: On the Compatibility of Carbon Fibres in Nickel. In: Proceedings of the International Conference on Composite Materials. Geneva 1975, p. 103.
[8] PLETENEV, S. S.: Nikelirovanie. In: Gaľvaničeskie pokrytija v mašinostrojenii. Vol. *1.*, Moskva 1985, p.105.
[9] SIMANČÍK, F.—ŠEBO, P.: Kov. mater., *29*, 1991, 358.
[10] ŠTEFÁNIK, P.—ŠEBO, P.: Theor. Appl. Fract. Mech., *20*, 1994, 41.
[11] DAMKOHLER, R.—HEUMANN, T.: Phys. Status Solidi A, *73*, 1982, 117.

Rukopis dodaný: 29.9.1995
Rukopis upravený: 15.11.1995