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Formation of nickel layer deposited on carbon fibres by galvanic method

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Abstract

The investigation of coating parameters in quasi-static coating of Ni layer on carbon fibre tow by galvanic method is presented. The tow of fibres was immersed in typical galvanic bath based on $NiSO_4$, $NiCl_2$, Na_2SO_4 and H_3BO_3 whereas the current was supplied to carbon fibres by two leading metal rolls which are parts of continuous coating apparatus. Deposition current of 1 A and/or 1.5 A, electrolyte temperature of 60 °C and the distance from power contacts to the surface of galvanic bath (80 or 130 mm) were applied. The amount and structure of Ni layer deposited during 15, 30, 90, and 180 s exposure times in electrolyte at different immersion depths of tow in the bath were determined.

Key words: galvanic coating, carbon fibres, nickel

1. Introduction

Increasing protection of electronic apparatus against electromagnetic radiation or preparing composites with tailorable conduction is still in the centre of interest of scientific investigations [1–4]. Carbon fibre polymer or metal matrix composites have been explored and used extensively as engineering materials in aerospace, automobiles and sporting goods industry. Their properties depend on properties of carbon fibres which in general exhibit very high mechanical properties, negative axial thermal expansion, and low density. Some types of carbon fibres possess ultra high modulus (about 900 GPa) or ultra high thermal conductivity (up to $1100\,\mathrm{W\,m^{-1}\,K^{-1}}$) [5-9]. One of the important properties of carbon fibre composites is the reduction of the influence of electromagnetic radiation on electronic apparatus. The effective technique to improve the electrical conductivity of plastics and to overcome the electromagnetic interference (EMI) problem is the incorporation of conductive fillers in the polymer matrix [10–13]. Among the various conductive fillers, carbon fibres have been proved to be a good candidate for EMI shielding. However, since the electrical resistivity of a carbon fibre is much higher than that of metal, a larger volume amount of carbon fibres is needed in order to achieve the same shielding effect. Although satisfactory shielding capability could be obtained by adding more carbon fibres, difficulties related to the production of composites with increasing fibre volume fraction seriously arise. The above problems could be solved by applying a thin metallic layer on the surface of carbon fibres [1–3, 14–16].

The processes of continuous deposition of thin metal layer on fibres in the tow are rather complicated. The typical carbon fibre has diameter of about 5–10 μm and there are 1000–12000 fibres in a tow. It is therefore quite important to spread the tow up to individual fibres in order to insure the contact of chemicals with the whole surface of each fibre.

Chemical methods, mainly cementation and electroless deposition, are often used on deposition of metal layers on fibres [3, 16-19]. Electroless plating is a chemical reduction process, which depends upon the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent, and the subsequent deposition of the metal without the use of electrical energy. The surface of fibres is usually activated with palladium which acts as catalyser of chemical reaction. After the deposition of pure metal or metal alloy the concentration of deposited metal ions in solution decreases and it is necessary to refresh the con-

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centration of all treated chemicals. Electroless nickel films have been deposited from solutions at various workloads, pH and temperatures of plating bath with air agitation. Chemical vapour deposition technology is also used for production of metal layers, e.g. nickel, but some chemicals are extremely toxic and the strict safety measures are required.

The galvanic technique is one of the simplest methods of deposition of pure metal or metal alloy layers on different substrates. The concentration of metal ions in solution is practically the same because their decrease due to formation of metal layer on substrate (cathode) is compensated by dissolution of metal anode which can be in plate form. The advantage of many galvanic solutions is their long term stability. The galvanic metal coating is a widely used method providing coatings with thicknesses from nanometric to micrometric range. This is enough to form the matrix of the composite material [5–6, 20–21].

The main objective of this study has been focused on investigations of formation of Ni coatings on carbon fibres by galvanic method. Particular attention has been paid to the early phase of the deposition process as well as to the growth of layer with increasing time and depth of immersion in the galvanic bath. The results will be used for optimisation of laboratory technique for continuous galvanic Ni coating of carbon fibre tow with acceptable plating uniformity and minimal fibre damage.

2. Experiment

HexTow AS4C high strength carbon fibres with the diameter of about 7 μm were used in this work [22]. Sizing free fibres are arranged in tows containing 12 000 monofilaments. C fibres were subjected to galvanic coating in electrolyte containing obvious set of chemicals $NiSO_4$, $NiCl_2$, Na_2SO_4, and H_3BO_3 [23] at the temperature of 60 ℃.

The quasi-static experiments were performed on the coating apparatus described by Simančík and Šebo [24] except for the electroless deposition of nickel. The tow had been placed between the metal rolls and immersed into the bath. The current of 1 A and/or 1.5 A was supplied to carbon fibres by two leading metal rolls at the entrance and the exit from the electrolytic bath. The tow was free of any mechanical tension and spreading of fibres was guaranteed by twisting of the tow. Two distances between the contacts and the electrolyte surface (h) were examined. The length of tow (L) in electrolyte was 400 mm for $h = 80$ mm and/or 300 mm for $h = 130$ mm. Ni layers subjected to analysis were deposited using following sets of parameters presented in Table 1.

Table 1. Deposition parameters

Current (A)	Time of deposition (s)	h (mm)
1.0	15	80
1.0	30	80
1.0	90	80
1.0	180	80
1.5	15	80
1.5	30	80
1.5	60	80
1.5	90	80
1.0	60	130
1.0	90	130

After deposition, the tow was sectioned to 3 pieces with lengths of 50 mm (the first marked 0–50 was just below the electrolyte surface) and amounts of nickel were calculated from weight measurements. Structural observations were performed with field emission scanning electron microscopy (SEM – JEOL 7600 FEG), chemical compositions were analysed using energy dispersive X-ray spectroscopy (OXFORD Inca EDS with X Max detector 50 mm^2). All samples were coated with gold before SEM observations.

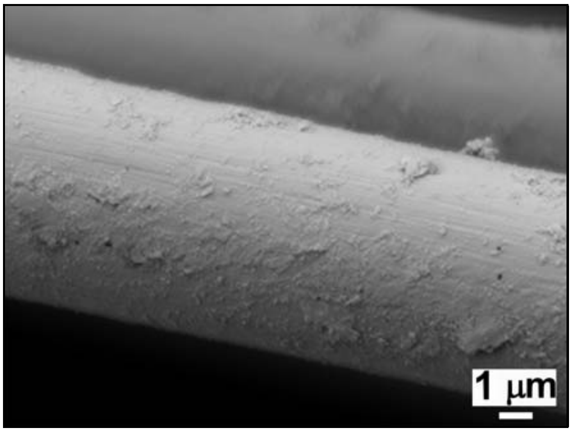

Fig. 1. Secondary electron micrograph of as-received Hex Tow AS4C carbon fibres revealing rough surface morphology with numerous flakes.

3. Results

Typical surface morphology of as-received HexTow AS4C high strength carbon fibre as revealed by scanning electron microscopy is presented in Fig. 1. The surface appears quite rough with numerous surface flakes. No differences in chemical composition between fibre and surface flakes were determined.

The quasi-static deposition experiments were performed in order to understand which parameters are decisive for formation of good quality layer with acceptable rate of Ni layer growth. The effects of time,

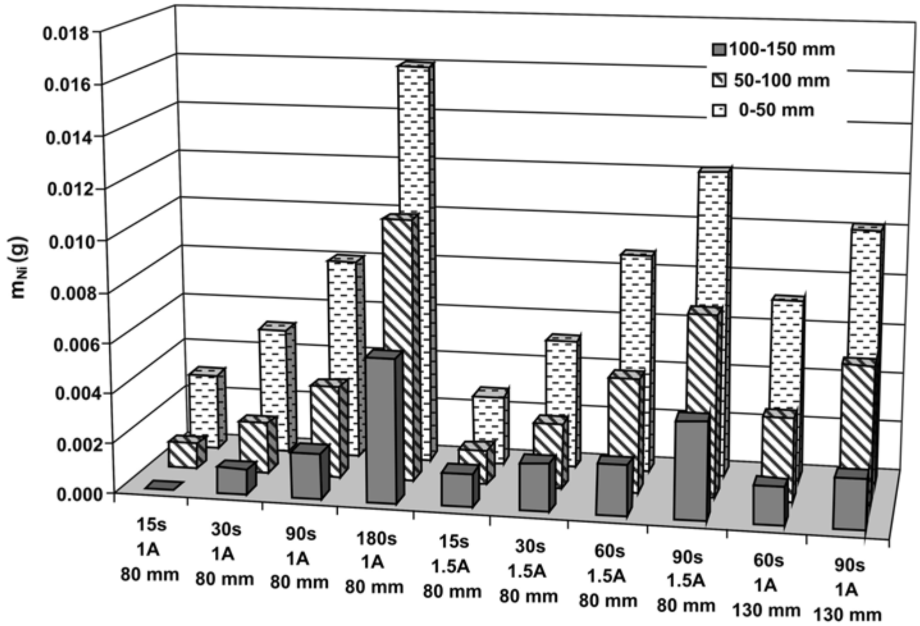

Fig. 2. Dependence of Ni amounts on fibre segments (50 mm) on time, applied current, distance between the electric contact and the surface of electrolyte and depth of immersion of tow.

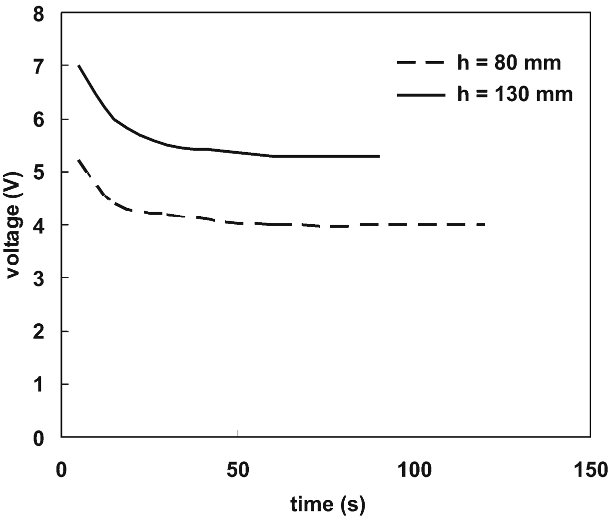

Fig. 3. Dependence of deposition voltage at constant current of 1 A on time and distance (h) between the electrical contact and electrolyte surface.

applied current, distance between the electric contact and the surface of electrolyte and depth of immersion of tow in electrolytic bath on the amounts of deposited nickel is presented in Fig. 2. It can be clearly seen that the substantial amount of nickel is deposited close to electrolyte surface. Longer exposures with 1.5 A current were not possible due to extreme overheating of fibres.

At the beginning of deposition the applied voltage decreased with time for both distances between electrical contact and the electrolyte surface. This is to

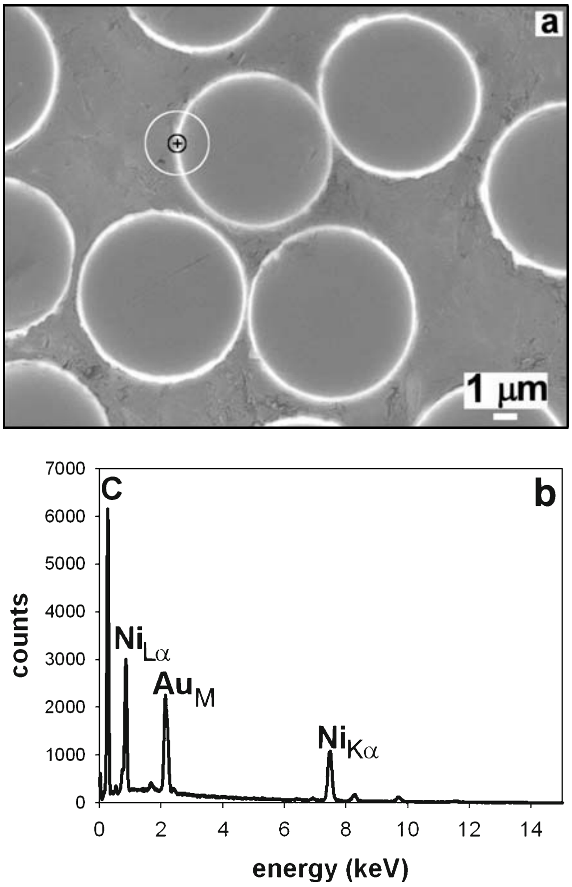

Fig. 4. Secondary electron micrograph of cross sectional view of C fibres Ni coated just below the electrolyte surface using 1 A/180 s deposition parameters (a); EDS spectrum acquired from Ni coating (point +) in Fig. 4a (b).

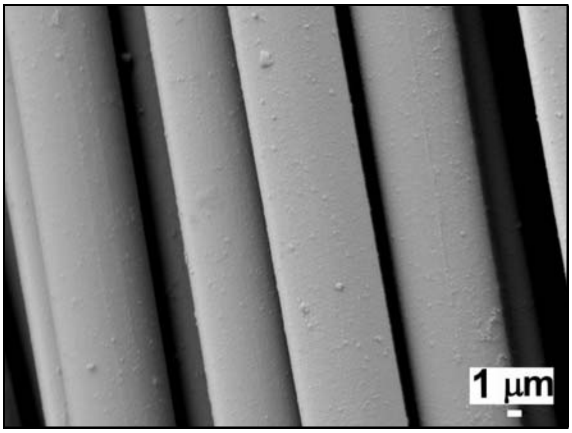

Fig. 5. Secondary electron micrograph of C fibres Ni coated just below the electrolyte surface using 1 A/180 s deposition current and time.

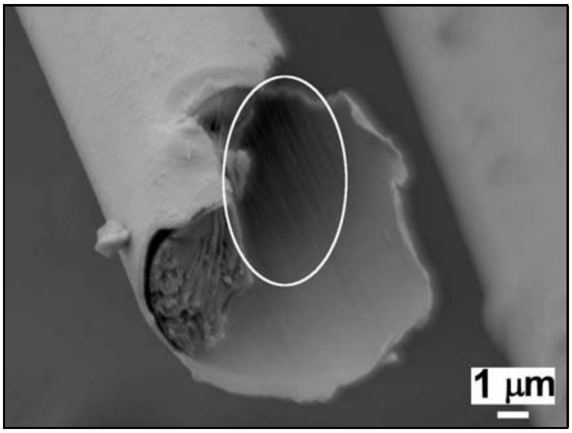

Fig. 6. Secondary electron micrograph revealing Ni coating imprinting the C fibre surface morphology.

be related to the decreased resistance of C fibre due to the deposition of more conductive Ni layer. The time dependence of deposition voltage is presented in Fig. 3.

The quality of Ni coating on carbon fibres is presented in Fig. 4. It is evident that all fibres are coated with thin Ni layer as confirmed with corresponding EDS analysis in Fig. 4b. Black and white circles indicate the diameter of X-ray generation region for the applied accelerating voltage of 15 kV for Ni and C, respectively. The average thickness of the layer is 0.3 µm. The surface of coated fibres is relatively smooth precisely copying the topography of original carbon fibres as shown in Fig. 5.

Ni coatings precisely copy the surface of substrate C fibres as shown in Fig. 6. Moreover, the deposited layers exhibit the character of ductile compact layers as can be seen in Fig. 7. However, only mechanical bonding between C fibre and galvanic Ni coating is formed by presented deposition process.

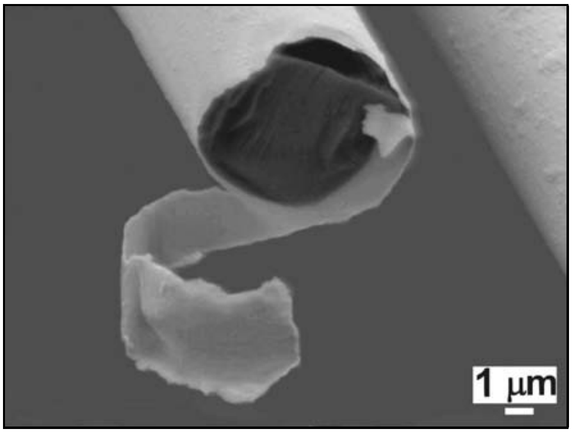

Fig. 7. Secondary electron micrograph of Ni coating exhibiting the behaviour of ductile compact layer.

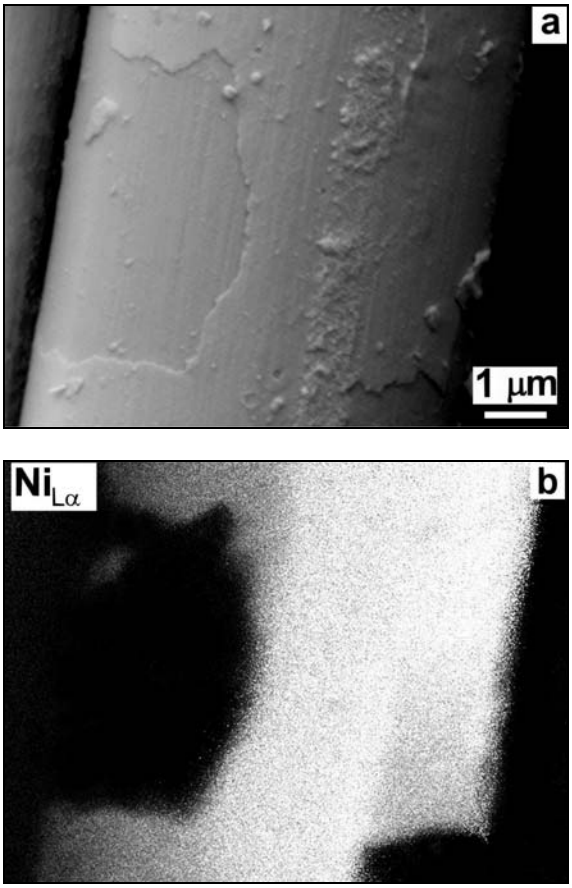

Fig. 8. Secondary electron micrograph of C fibre Ni coated just below the electrolyte surface using 1 A/15 s deposition current and time (a); EDS element map revealing the distribution of Ni on the surface of C fibre shown in Fig. 8a (b).

The initial stages of deposition of Ni after 15 s of exposure in electrolyte with current 1 A just below the electrolyte surface are characterized in Figs. 8 and 9.

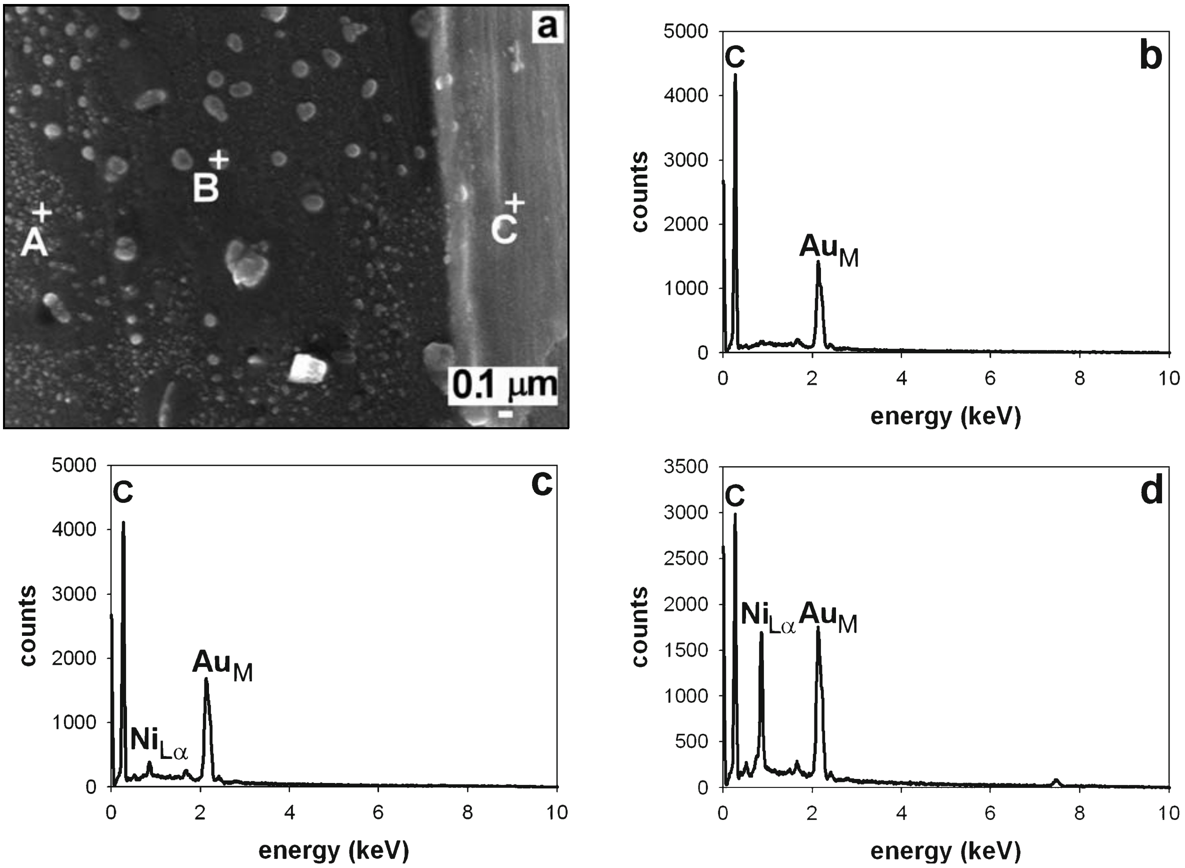

Fig. 9. Secondary electron micrograph of C fibre Ni coated just below the electrolyte surface using 1 A/15 s deposition current and time (a); EDS spectrum acquired from point A in Fig. 9a (b); EDS spectrum acquired from point B in Fig. 9a (c); EDS spectrum acquired from point C in Fig. 9a (d).

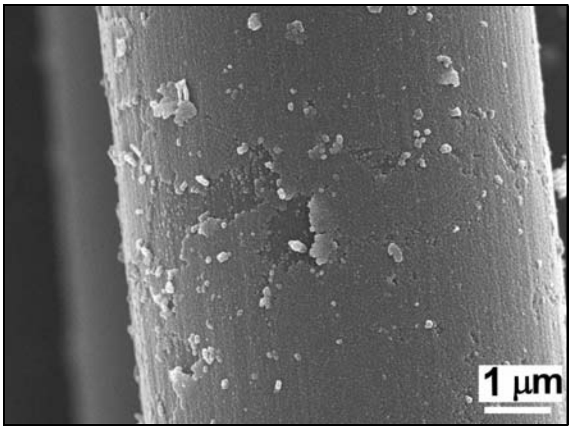

Fig. 10. Secondary electron micrograph of Ni layer deposited 150 mm below the electrolyte surface revealing uncompleted coating (deposition parameters 1 A/180 s).

As can be seen the deposition under these conditions leads to uncompleted coating remaining large Ni free regions at the fibre surface.

As can be seen in Fig. 9, the forming of Ni layer starts with the growth of nucleation nuclei covering successively the whole fibre surface. As the samples had to be coated with gold prior to observation small grains of gold can be distinguished at this magnification at the fibre surface as well.

Similar mechanisms of Ni layer formation were observed on layers in higher depths of galvanic bath. Ni layer shown in Fig. 10 was deposited 150 mm below the surface of galvanic bath using the current of 1 A within 180 s. As can be seen nearly all surface of C fibre is covered with Ni. Only small islands with uncompleted coating can be found. These already contain numerous Ni growth nuclei indicating that the deposition was interrupted close before completion.

The structure of this coating at higher magnification is presented in Fig. 11. As can be seen the thickness of the coating is approximately 0.07 µm. Ni layer is formed by individual grains growing from the C fibre surface throughout the whole layer thickness indicated by white arrows. Smaller grains of sputtered gold indicated by black arrows can be recognised as well.

4. Discussion

The most important factor affecting the quality of Ni layer is the formation of the growth nuclei. Their

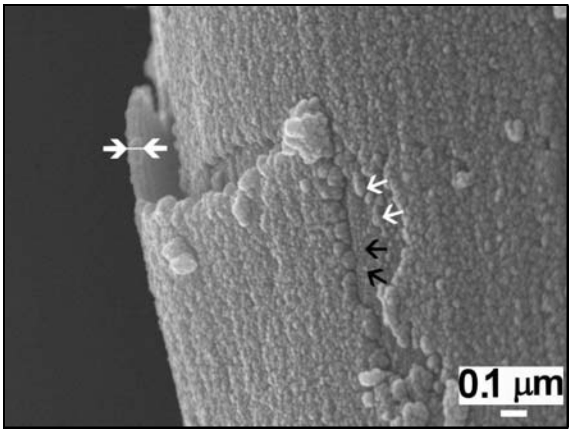

Fig. 11. Secondary electron micrograph revealing the morphology of Ni layer deposited 150 mm below the electrolyte surface (deposition parameters 1 A/180 s).

formation is governed by deposition parameters including values of direct-current, potential and temperature of electrolyte. The highest deposition rates are achieved at high galvanic currents. However, high currents may cause overheating and even burning of fibres between metal leading roll and electrolyte surface. The deposited layers are not uniform at high currents as well. Thus the optimum value of current has to be determined.

It is quite important to keep the potential corresponding to required current within certain ranges to avoid the extreme overheating of fibres, entering as well as exiting the electrolyte. The overheating could lead to burning of fibres or the electrolyte could boil at the fibre surface. On the other hand higher current is required for deposition of higher Ni amounts in galvanic unit and this can be achieved only at higher voltage for given electric resistance. It appears that the Ni coating is preferentially formed close below the electrolyte surface. This leads to the decrease of electric resistance of the fibre tow and also decreased potential at constant current (Fig. 3). Decreasing resistivity near the surface of electrolyte makes the deposition of Ni even in deeper locations possible.

Besides Ni also intense peaks of carbon and gold appear in the presented X-ray spectra. This is because the X-ray generation region, i.e., the volume from which the X-rays are acquired as shown in Fig. 4, is much larger than the thickness of the coating. The qualitative analysis of small particles in Fig. 9a is possible due to the fact that the diameter of the electron beam is only few nanometres when entering the sample, so it can be focused on small surface particles. $\mathrm{Ni}_{\mathrm{L}\alpha}$ line was used to reveal the distribution of Ni at the surface of C fibre in Fig. 8b. This analysis has been performed at lower accelerating voltage (10 kV) in order to support selectively the information related to the fibre surface. Gold particles, generally present on all samples but distinguishable only at high magnification, are generally smaller by an order of magnitude than Ni particles, so they cannot be interchanged.

Proper set of parameters leads to formation of continuous compact Ni layer exhibiting enough plasticity and ductility. This can avoid undesirable cracking by further incorporating of Ni coated fibres into composite matrices.

5. Conclusions

Based on the results achieved within this work, it can be summarized in following conclusions:

– Galvanic deposition of Ni coating on C fibres arranged in tows containing 12 000 monofilaments was presented in this work. Ni layers with acceptable quality in plating uniformity and minimal fibre damage were obtained.

– The most important factors influencing the formation of continuous layer on carbon fibres are exposure time and depth of immersion of carbon fibres in bath.

– The largest thicknesses of Ni layers were obtained using 1 A and/or 1.5 A deposition currents within 180 and/or 90 s of deposition time just below the electrolyte surface, respectively.

– Layers deposited within short deposition times or deep (150 mm) below the electrolyte surface suffered from uncompleted coating.

– Ni coatings precisely copying the surface of substrate C fibres exhibit the behaviour of ductile compact layers. However, only mechanical bonding between C fibre and galvanic Ni coating is formed by presented deposition process.

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