# Electrolytic co-deposition of a nickel/fluorographite composite layer on polycrystalline copper

Plumier, Fabian; Chassaing, E.; Terwagne, Guy; Delhalle, Joseph; Mekhalif, Zineb

*Published in:*
Applied Surface Science

*Publication date:*
2003

*Document Version*
Peer reviewed version

Link to publication

*Citation for pulished version (HARVARD):*
Plumier, F, Chassaing, E, Terwagne, G, Delhalle, J & Mekhalif, Z 2003, 'Electrolytic co-deposition of a nickel/fluorographite composite layer on polycrystalline copper', *Applied Surface Science*, vol. 212-213, pp. 271-278.

Available online at www.sciencedirect.com

Applied Surface Science 212–213 (2003) 271–278

applied surface science

www.elsevier.com/locate/apsusc

# Electrolytic co-deposition of a nickel/fluorographite composite layer on polycrystalline copper

F. Plumier[a], E. Chassaing[b], G. Terwagne[c], J. Delhalle[a], Z. Mekhalif[a,*]

[a]Laboratoire Interdisciplinaire de Spectroscopie Electronique, Facultés Universitaires Notre-Dame de la Paix,
Rue de Bruxelles 61, B-5000 Namur, Belgium
[b]Centre d'Etudes de Chimie Métallurgique—CNRS, 15 rue Georges Urbain, 94407 Vitry-sur-Seine Cedex, France
[c]Laboratoire d'Analyse par Réaction Nucléaire, Facultés Universitaires Notre-Dame de la Paix,
Rue de Bruxelles 61, B-5000 Namur, Belgium

## Abstract

In this work we report our attempts to prepare uniform and adherent layers of nickel/fluorographite composites by electrolytic co-deposition from a Watts bath on polycrystalline copper substrates. Three parameters have been considered: nature of the surfactant, amount of fluorographite in the electrolytic solution and current density. The best nickel/fluorographite composite layers are obtained with octylphenylpolyoxyethylene glycol as surfactant, 20 g $dm^{-3}$ of fluorographite in the electrolytic solution and 2.5 A $dm^{-2}$ current density. Characterization of the nickel/fluorographite composite layers has been carried out with optical microscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), resonant nuclear reaction analysis (RNRA) and water contact angle measurements.

*PACS:* 81.05.Ni; 81.15.Pq; 81.15.-z; 81.70.Fy; 81.70.Jb

*Keywords:* Metal-matrix composite; Coatings; Nickel; Fluorographite; Electrolytic co-deposition

## 1. Introduction

Electrolytic co-deposition is widely used for producing composites of metallic and non-metallic constituents. By electrolysis of plating solutions in which micron- or sub-micron-size particles are suspended, it is possible to obtain solid materials with improved and/or combined properties which find uses as self-lubricating layers, wear- and corrosion-resistant coatings, materials for electro- and photoelectrocatalysis, energy storage, etc. [1].

Nickel is one of the important metals used in metal-matrix composites prepared by electrodeposition. It is also a metal of choice for electrical contacts [2] which should not only exhibit suitable contact resistance, but also combine good lubrication, wear- and corrosion-resistance properties, hence the interest in metal-matrix composites and their surface properties. Several research papers and patents have reported interesting results on the morphology, hardness, ductility and wear resistance of nickel composites including PTFE and fluorographite $(C_xF_y)_n$ particles of sub-micron size [3–15]. Fluorographite particles are particularly interesting because they are highly hydrophobic, stable at elevated temperature, good lubricants and rather inert chemically. As shown in previous works, the quality of

---

[*] Corresponding author. Tel.: +32-81-725230;
fax: +32-81-724530.
*E-mail address:* zineb.mekhalif@fundp.ac.be (Z. Mekhalif).

0169-4332/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0169-4332(03)00112-0

the composites depend on several parameters such as the composition of the bath, temperature, current density, pH as well as on the nature, concentration, size and morphology of the particles.

In this contribution, the influence of three parameters on the electrodeposition of micron-size (average size 2 μm) fluorographite is studied: the nature of the surfactant, concentration in fluorographite particles and current density. Morphology, particle incorporation, roughness and surface energy are the properties by which the quality of the composite is assessed; they are measured by optical microscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), resonant nuclear reaction analysis (RNRA), profilometry and water contact angle measurements.

## 2. Experimental procedure

### 2.1. Electrodeposition

The electrodeposition set-up is constituted by a double wall cell containing an electrolytic bath with a magnetic stirrer and two electrodes immersed in the bath: a 6 $cm^2$ plate of nickel is used as anode and a 1 $cm^2$ plate of copper constitutes the cathode (substrate). These two electrodes are connected to a generator ensuring a constant current. Moderate agitation with magnetic stirrer was found necessary to maintain all the particles in suspension and to obtain uniform deposits.

The electrolyte is a Watts bath of the following composition: 300 g $dm^{-3}$ nickel(II) sulfatehexahydrate, 35 g $dm^{-3}$ nickel(II) chloride, 40 g $dm^{-3}$ boric acid dissolved in ultra pure water (18.2 MΩ cm). Recirculating water in the beaker maintained the bath temperature at 50 °C. The pH of the bath was adjusted to 3.5 ± 0.1 with $H_2SO_4$. Before electrodeposition, the copper substrate is briefly immersed (~10 s) in a solution $H_2SO_4$ 30% and then copiously rinsed with ultra pure water.

Fluorographite powder was supplied by courtesy of Prof. G.P. Gambaretto (University of Padua). The average size of the particles is 2 μm. This powder is added to the bath in the presence of a surfactant under prolonged stirring to keep the particles in suspension in the electrolytic solution.

### 2.2. Characterization and testing of the coating

The surface morphology of the deposits was examined with optical microscopy and scanning electron microscopy. A SM-4 profilometer was used to assess the roughness of the different surfaces. The measurements are performed on 4 mm long tracks on the sample surface. Contact angles ($\theta_w$) were measured by using a VCA 2500 contact angle meter on $10^{-6}$ $dm^3$ water drops that were allowed to equilibrate in air and at room temperature.

Composition, surface and depth profiles, was obtained by X-ray photoelectron emission spectroscopy. Depth profiling was achieved using argon etching (beam produced at $8.10^{-8}$ Torr, filament current, spot size and energy used were 10 mA, 4 $mm^2$ and 2 kV, respectively). X-ray photoelectron spectra were recorded at a 35° take-off angle relative to the substrate with an SSX-100 spectrometer using the monochromatized Al Kα radiation (1486.6 eV).

The shape of the fluorine profile obtained by XPS combined with argon etching was compared with additional measurements based on the $^{19}F(p, \alpha\gamma)^{16}O$ resonant nuclear reaction of fluorine using proton of 340 keV produced with a 2 mV Tandetron accelerator [16]. This nuclear reaction produces α-particles as well as 5–7 MeV γ-rays emission from excited $^{16}O$. The number of γ-rays detected in a NaI well detector is directly proportional to the fluorine concentration in the sample. The depth profile were obtained by changing the incident energy step by step from 340 keV, the resonant energy, to 550 keV and the distribution is measured down to 2 μm in depth. At each energy step the number of γ-rays were integrated for the same incident charge (5 μC). The absolute fluorine concentration was obtained by measuring the depth profile on a $CaF_2$ standard.

## 3. Results and discussions

### 3.1. Choice of a surfactant on the basis of the surface characteristics of the composite

Since the fluorographite particles are very hydrophobic, addition of a surfactant is essential to disperse these particles in the aqueous electrolytic solution. Two surfactants were considered: polyethylene glycol

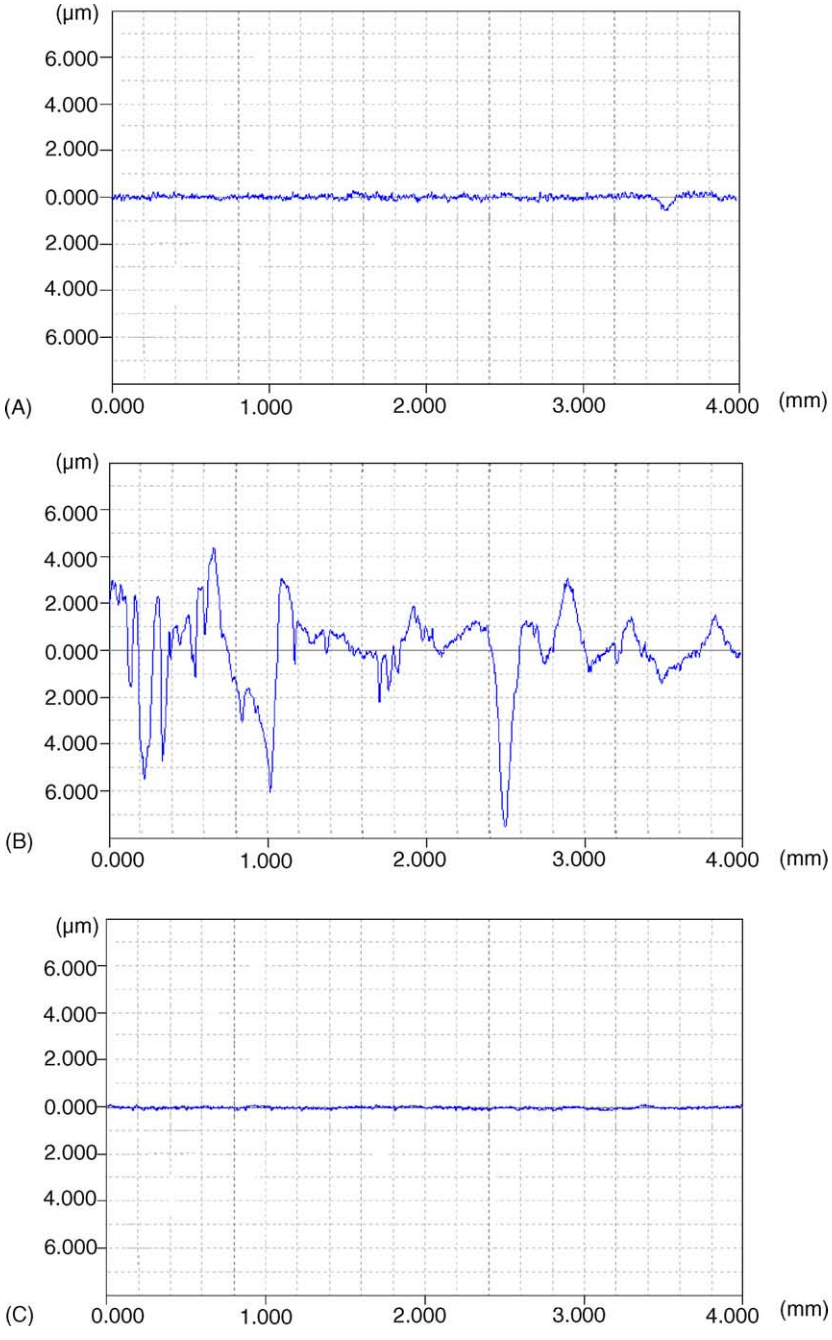

Fig. 1. Roughness analyses. (A) Electrolytic coating of nickel without incorporation of fluorographite particles (reference) (current density = 10 A $dm^{-2}$). (B) Ni–FC composite coating prepared with PEGDE as surfactant (current density = 10 A $dm^{-2}$, concentration in particles = 6.8 g $dm^{-3}$). (C) Ni–FC composite coating prepared with OPPEG as surfactant (current density = 10 A $dm^{-2}$, concentration in particles = 6.8 g $dm^{-3}$).

dodecyl ether (PEGDE) and octylphenylpolyoxyethylene glycol (OPPEG).

Deposits were prepared under a 10 A dm$^{-2}$ current density in an electrolytic solution containing 6.8 g dm$^{-3}$ of fluorographite particles and PEGDE as surfactant. XPS measurements indicate the presence of a very low amount of fluorine on the surface, the relative atomic percentage is less than 1% as compared to the other elements, C (65%), O (24%) and Ni (10%). On the other hand, deposits prepared under the same conditions with OPPEG as surfactant led to following relative atomic percentages: F (25%), C (37%), O (24%) and Ni (14%). These results are reproducible for both types of samples.

Fig. 1A shows representative topographic lines of pure nickel deposits prepared under a 10 A dm$^{-2}$ current density; and of samples previously prepared with PEGDE and OPPEG surfactants is shown in Fig. 1B and C, respectively. The results show that the surface of the composite obtained with OPPEG is smooth (roughness average = 0.05 μm) and very similar to the pure nickel electrodeposit (roughness average = 0.08 μm). The surface of the composite obtained with the other surfactant (PEGDE) is comparatively very rough (roughness average = 1.23 μm).

Average (±3°) water contact angles recorded on the pure nickel deposits and samples prepared with PEGDE and OPPEG surfactants (10 A dm$^{-2}$ current density) are equal to 73, 96 and 103°. In line with their higher content of fluorine, surfaces of the composites electrodeposited with OPPEG are the most hydrophobic. Accordingly, OPPEG will be used in the remaining part of this work devoted to the effects of current density and concentration on the quality of the composite.

### 3.2. Influence of the concentration of fluorographite particles

Electrolytic co-depositions were carried out at an intermediate current density (5 A dm$^{-2}$) in electrolytic solutions containing the OPPEG surfactant. Concentrations of fluorographite particles were varied from 2.5 to 30 g dm$^{-3}$. XPS measurements indicate a steady increase of the surface fluorine content (Fig. 2) which reaches a plateau at 20 g dm$^{-3}$. SEM micrographs (Fig. 3A and B) provide evidence of the fluorographite particles on the surface with sizes of the order of 2–3 μm.

Depth profiles obtained by XPS and resonant nuclear reaction of fluorine, respectively Fig. 4A

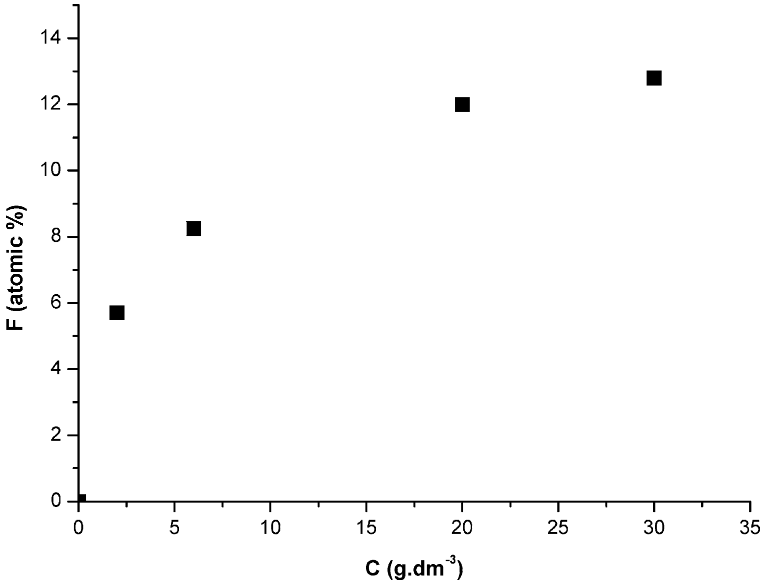

Fig. 2. Effect of concentration on the incorporation rate of fluorographite (current density = 5 A dm$^{-2}$).

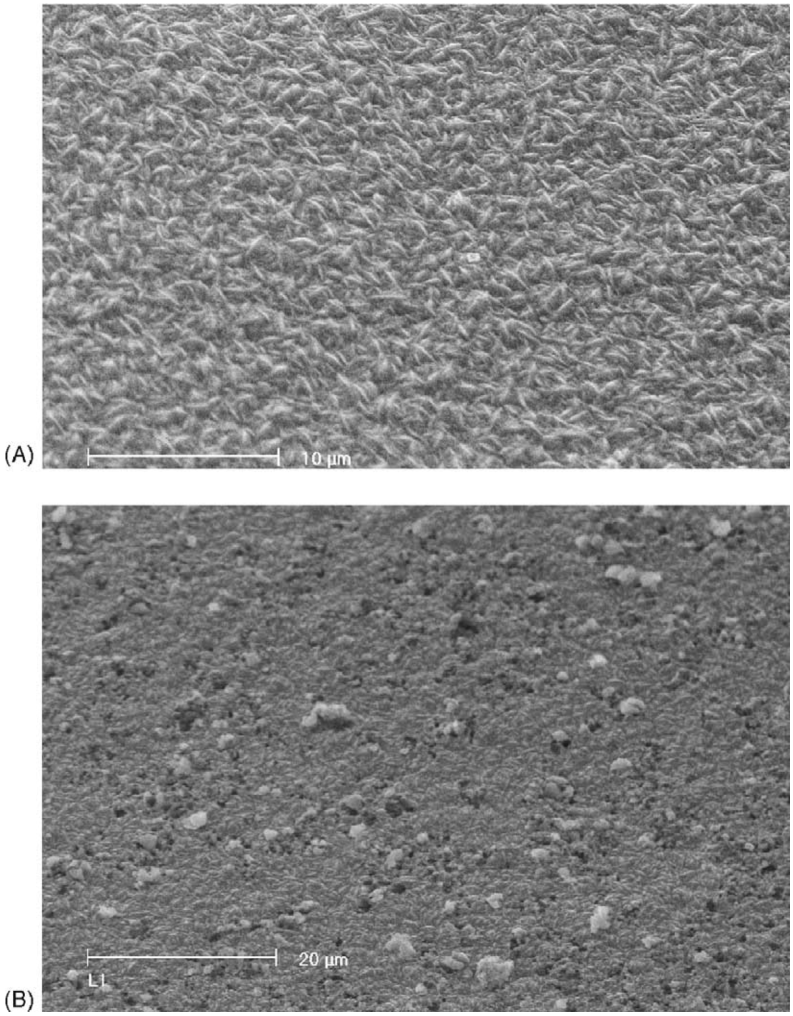

Fig. 3. (A) SEM photomicrographs of Ni coating without incorporation of fluorographite particles (current density = 5.0 A $dm^{-2}$). (B) SEM photomicrographs of Ni–FC composite coatings (current density = 5.0 A $dm^{-2}$, concentration = 20 g $dm^{-3}$ of fluorographite).

and B, suggest that the first layers are richer in fluorographite particles and that the relative atomic percentage of fluorine is nearly constant and close to 8% in the bulk. In absence of precise data on the layer density, the resonant nuclear reaction data can only be qualitative in the sense that it is not possible to transform the abscissa to length scale. Nevertheless, the trends are comparable to XPS results and as such constitute a validation of the trends obtained by both methods. To lower concentrations (results not reported here) correspond lower incorporation of fluorographite particles, hence 20 g $dm^{-3}$ seems to be the most practical concentration to consider for this type of particles.

### *3.3. Influence of the current density*

To assess the effect of plating rate on the quality of the composites, deposits were prepared from an electrolytic solution containing 20 g $dm^{-3}$ of fluorographite particles and OPPEG as surfactant for a series of current densities varying from 2.5 to 20.0 A $dm^{-3}$. The highest relative atomic percentage of fluorine on the surface estimated from XPS data is obtained for a

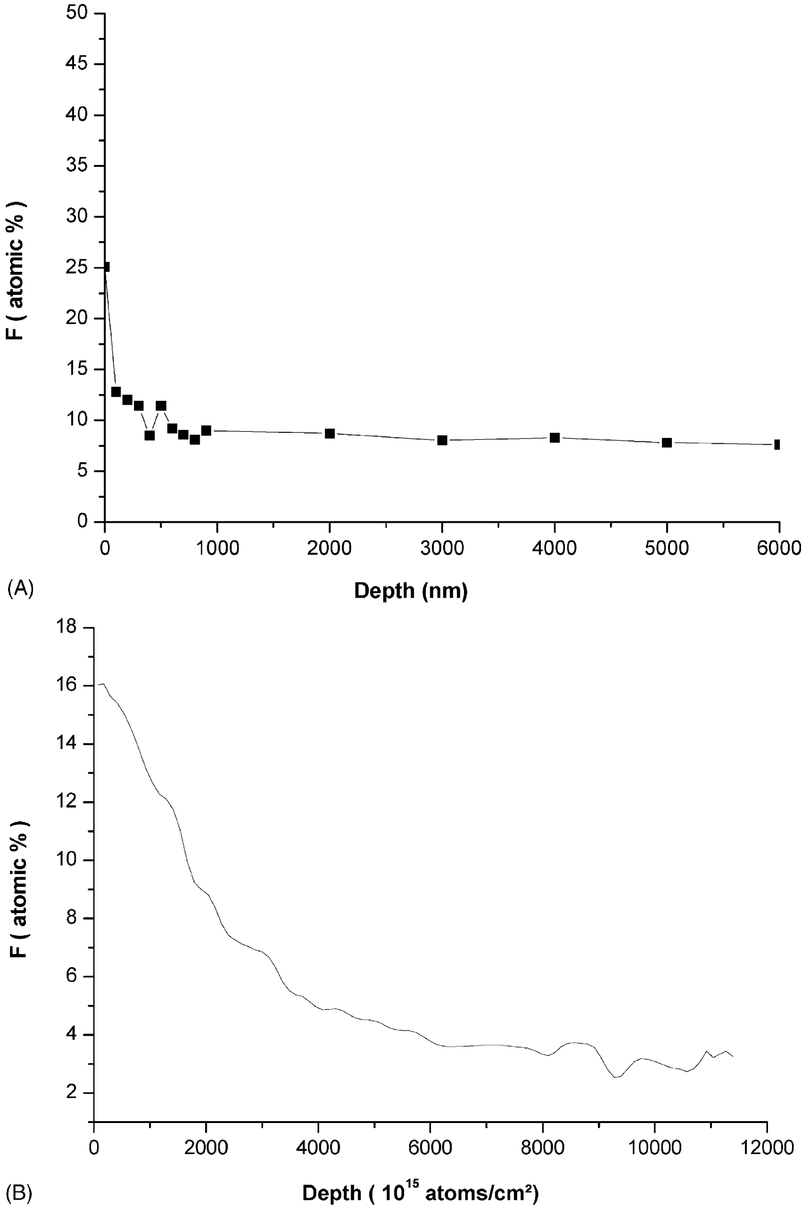

Fig. 4. (A) XPS depth profile of fluorine of a Ni–FC composite coating (concentration = 20 g dm$^{-3}$ of fluorographite, current density = 20 A dm$^{-2}$). (B) RNRA depth profile of fluorine in a Ni–FC composite coating (concentration = 10 g dm$^{-3}$ of fluorographite, current density = 20 A dm$^{-2}$).

current density of 2.5 A dm$^{-2}$ (Fig. 5), but it is not critically dependent on the current density. However, micrographs of samples (A–C) obtained by optical microscopy (Fig. 6) point to significant differences in the surface morphology on the current density, the most homogeneous situation being obtained for lowest current density (2.5 A dm$^{-2}$). This is consistent with previously works reporting that large current densities increase internal stress and favour the occurrence of pits and cracks into the deposits.

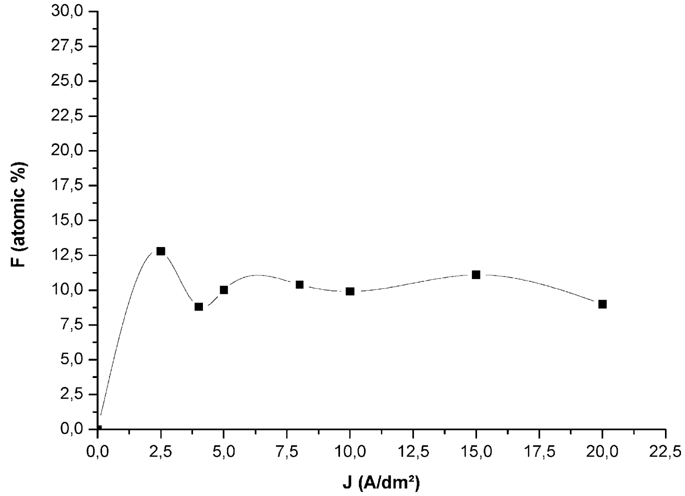

Fig. 5. Effect of current density on the incorporation rate of fluorographite particles (concentration = 20 g $dm^{-3}$ of fluorographite).

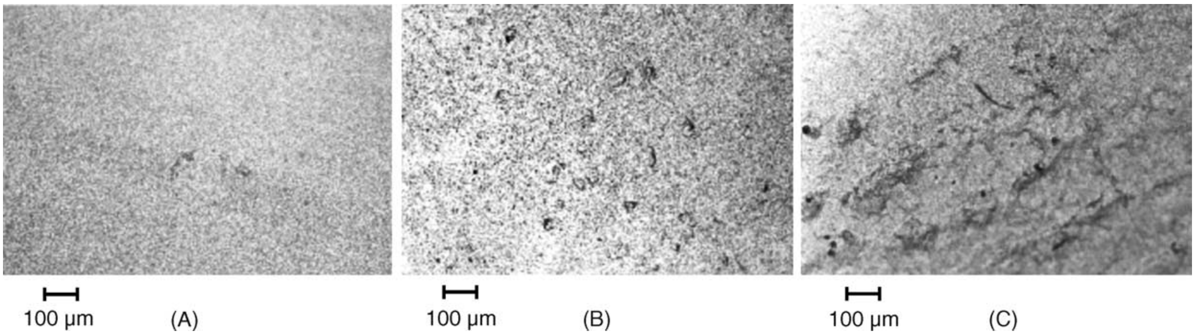

Fig. 6. Micrographs of samples (A–C) prepared under: 2.5, 10 and 20 A $dm^{-2}$, respectively.

## 4. Conclusion

The best nickel/fluorographite composite layers were obtained with octylphenylpolyoxyethylene glycol as surfactant, 20 g $dm^{-3}$ of fluorographite in the electrolytic solution and 2.5 A $dm^{-2}$ current density. With these parameters the highest bulk content in fluorographite particles is achieved, as assessed from XPS measurements on the F 1s level in combination with argon etching. The shape of the concentration profiles have been checked again resonant nuclear reaction analysis. To these parameters correspond also the highest surface fluorine content, the smoothest and most homogeneous surfaces. For such parameters, the water contact angle reaches values greater than 170°. Such values are indicative of a highly hydrophobic surfaces, but also promising for self-lubrification and low friction coefficients. Preliminary results, not reported here, indicate friction coefficient $\mu$ lower than 0.19 as well as interesting contact resistance (<0.01 Ω) for the field of electrical connectors.

## Acknowledgements

The work was supported by the Belgian National Interuniversity Research Program on quantum size effects in nanostructure materials (IUAP P5/01) and the Région Wallanne (SYNATEC Convention no. 0014526).

## References

[1] M. Musiani, Electrochim. Acta 45 (2000) 3397.

[2] (a) C.A. Holden, H.H. Law, C.A. Mattoe, J. Spjeta, J. Plat. Surf. Fin. 76 (1989) 58;
(b) H.H. Law, J. Sapjeta, C.E.D. Chidsey, T.M. Putvinski, J. Electrochem. Soc. 141 (1994) 1977.

[3] E. Pena-Munoz, P. Berçot, A. Grosjean, M. Rezrazi, J. Pagetti, Surf. Coat. Technol. 107 (1998) 85–93.

[4] Bai, Xiajun, Department of Chemistry and Chemical Engineering, Human University, People's Republic of China, Diandu Yu Huanbao 13(4) (1993) 8–10.

[5] A.V. Shkurankov, E.V. Saxin, A.A. Shevyryov, Mater. Res. Bull. 36 (2001) 1551–1560.

[6] N.K. Shresthaa, K. Sakuradaa, M. Masukob, T. Saji 140 (2001) 175–181.

[7] D.F. Susan, K. Barmak, A.-R. Marder, Thin Solid Films 307 (1997) 133–140.

[8] J.V. Shklyanaya, V.N. Belinskii, Vestn. Kiev. Politeckhn. In-Ta. Khim. Mashinostr. I Tekhnol. (18) (1981) 75–79.

[9] J.T. Kim, Composites of metal with carbon fluoride and method of preparation, US Patent 4,716,059 (1987).

[10] E. Zuurdeeg, Process for electro-codepositing inorganic particles and a metal on a surface, US Patent 4,222,828 (1980).

[11] K. Helle, R.C. Groot, A. Kamp, Co-deposition of a metal and fluorocarbon resin particles, US Patent 4,098,654 (1978).

[12] N.L. Weinberg, Fluorinated carbons and uses thereof, US Patent 5,116,592 (1992).

[13] H. Takeuchi, Y. Tsunekawa, M. Okumiya, Composite plating method, US Patent 5,651,872.

[14] A.W. Hothersall, in: Proceedings of the Symposium on Internal Stresses in Metals and Alloys, The Institute of Metals, London, 1948, p. 107.

[15] K.G. Soderberg, A.K. Graham, in: Proc. Am. Electroplat. Soc. 34 (1947) 74.

[16] G. Terwagne, G. Deconninck, Nucl. Instrum. Methods Phys. Res. Sect. B 64 (1992) 153–155.