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2013 J. Phys.: Conf. Ser. 439 012019

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Production and characterization of Ni and Cu composite coatings by electrodeposition reinforced with carbon nanotubes or graphite nanoplatelets

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Abstract. Electrodeposition is well-known as a versatile and economical processing technique to produce metal coatings on conductive substrates. Recently, it has been gaining increasing interest also for the production of tailored composite coatings, containing for instance fluoropolymers or silicon carbide. A more novel approach concerns the use of carbon nanotubes or even graphene, in the form of graphite nano-platelets. The production of Ni- and Cu-based nanocomposites containing carbon nanoreinforcements was carried out by using standard electrodeposition conditions, but with a particular attention to the dispersion of the nanotubes. The obtained coatings were strong and well adherent to the steel substrate, and presented rather well dispersed carbon nanotubes or graphite nanoplatelets, even if some agglomerates could be present in samples obtained from highly concentrated suspensions. In the case of nickel-based composite coatings, the size of nickel grains was reduced, and pin-on-disc tests demonstrated a significant increase in the life of the coating. In the case of copper-based composite coatings, thermal diffusivity measurements demonstrated that the carbon nanomaterial does not reduce the conductivity of the pure copper coating.

1. Introduction

Electrodeposition is nowadays a well-known and low cost technique for the preparation of metallic coatings on a conductive substrate [1]. Many metals can be deposited by this technique, with controlled thickness and properties [2]. Recently, composite coatings started to gain interest, due to the possibility to tailor the behaviour of the deposited film by controlling the composition, thus becoming an interesting alternative to standard deposition methods, like PVD [3,4]. In particular nickel coatings are industrially modified with silicon carbide or other ceramics [5-10], for improving hardness, or fluoropolymers [11-12], for reducing attrition and wear, without modifying mechanical properties of core material like it happens when using traditional or novel MMCs [13-15]. Since the discovery of carbon nanotubes [16], carbon nanostructures are gaining significant interest in the field of materials science, as they present very interesting properties, both mechanical and thermal [17-22]. In recent papers, carbon nanotubes or similar materials have also been used to modify the properties of

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electrodeposited nickel coatings [23-28]. The composite coating seem to have increased properties with respect to un-modified nickel coatings [27,29,30], and they present interesting hardness [25,31] and wear properties [32]. In particular, both Carpenter and co-workers [31] and Khabazian and Sanjabi [25] demonstrated an increase in hardness with the increase of nanotubes. In both cases however the increase in hardness was possible only with pre-treated nanotubes, while untreated nanotubes hardness was not so different than the pure nickel coating. Functionalization was in both cases obtained by oxidation, in order to increase polarity of the nanotubes so that they could disperse easily in water. Regarding wear properties, Carpenter and co-workers [32] observed a significant reduction of wear rate for carbon-containing composites.

Recently, graphene has also gained much interest as a strong reinforcing carbon nanomaterial [33,34]. However, to the authors' knowledge, the deposition of graphene in electroplated coatings has not been widely studied.

In this work, we deposited nickel and copper coatings containing both carbon nanotubes (CNTs) and -COOH modified graphite nanoplatelets (GNPs). Oxidised graphite nanoplatelets are very similar to graphene since they consist of a very limited number of graphene sheets, oxidised on the surface to make them partially compatible with water-based solutions. The coatings were studied in term of the size of nickel crystallites, hardness, wear/frictional properties, thermal conductivity.

2. Experimental

Carbon nanotubes with mean diameter of 13 nm and length between 2.5 and 20 μm were obtained from Sigma Aldrich. Pristine and -COOH functionalized Graphene Nano Platelets (GNPs) were obtained from Cheaptubes USA. The GNPs had diameter of 1-2 μm and a surface area of around 700 m^2/g . The -COOH content in the functionalised ones was declared as 7%.

The solutions used for the electrochemical deposition of nickel were Watt's bath ($\text{NiSO}_4 + \text{NiCl}_2 + \text{H}_3\text{BO}_3$) and Wood's bath ($\text{NiCl}_2 + \text{HCl}$) purchased from Coventia. The solution used for electrodeposition of copper was a self-prepared sulphate bath, containing 0.85 M of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (purchased from Sigma Aldrich) and 0.55 M of H_2SO_4 . Poly acrylic acid (PAA) with mean molecular weight MW 5100, obtained from Sigma Aldrich, was used as dispersing agent.

The homogenous and stable suspensions for the plating solutions were obtained by ultrasonic agitation for 45 minutes with a probe (Sonics VCX750) and magnetic stirring for 16 hours at 200 rpm. To ensure the homogeneity of the baths, gentle magnetic stirring at 100 rpm was done during the deposition process too. A three electrode cell was used for the deposition, and 99.98% pure Ni plates (10 x 2.5 x 1 cm) and 99.99% pure Cu plates (10 x 3 x 0.1 cm) were used as anodes for nickel and copper depositions respectively. In case of wear test samples, the cathode substrates were 42CrMo4 steel while for thermal analysis samples the used substrates were C20 mild steel. The electrochemical deposition for producing the composites was obtained by means of a switching rectifier AF00 by Giussani S.r.l. The deposition was realised at 30 $^\circ\text{C}$ with a controlled pH in the range between 3 and 4.

The compositions of the samples are shown in Table 1. and the aspect of the coating in Figure 1. The N series are the nickel-based coatings, while the C series are the copper-based ones.

Table 1. Composition of coatings.

Sample	CNTs (mg/l)	GNPs (mg/l)	PAA (mg/l)
N0	0	0	0
N1	165	0	140
N2	1000	0	100
N3	0	80	100
C0	0	0	0
C1	1000	0	100
C2	165	0	140
C3	0	65	100
C4	0	190	190



Figure 1. Picture of Ni-coated (left), Cu-coated (middle) and uncoated (right) samples

The morphology of the samples was studied by using Reichert-Jung MeF3 optical microscope (Leica Microsystems S.P.A, Austria) and Hitachi S4000 scanning electron microscope. The microhardness was tested using a LEICA VMHT hardness tester. The wear properties were studied by using a self-made pin on disk apparatus, by using a pin of Co-cemented WC, with 3 mm radius. Surface roughness profiles were also measured by using surface profilometer HOMMEL TESTER T1000. Thermal diffusivity of the samples was measured using a thermal properties analyser FLASH LINE 4010.

3. Results and Discussion

In the first part of this work, the deposition conditions were studied in order to obtain a good and adherent deposit of nickel or copper on the substrate. The chosen substrate was a 42CrMo4 steel for all samples subjected to mechanical testing and a mild steel with 0.2% carbon for thermal tests.

By optical microscopy it was judged the aspect of the deposit, that is shown in Figure 2 for a pure nickel coating (on the left) and a CNT containing one, sample N2 (on the right). A good interface between steel and nickel is observed in both cases and the coating results rather good, without evident defects.

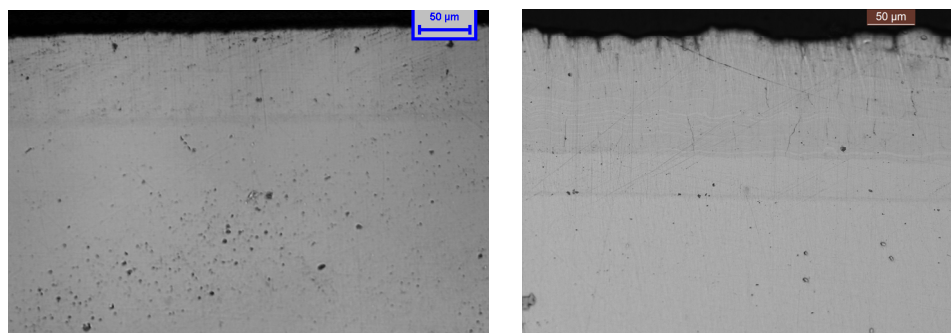


Figure 2. SEM images of pure nickel layer N0 (left) and nickel-CNT composite N2 (right) on steel support.

The realization of CNTs or GNPs containing coating however is much more complicated than the realization of a pure nickel one. In fact, when CNTs or GNPs are added, a significant problem of dispersion of the carbon nanomaterial occurs. While GNPs are functionalized with $-\text{COOH}$ groups, that give some polarity to the surface, increasing their dispersibility in water, CNTs are non-polar, and don't disperse easily in water. Since it was thought not to damage the nanotubes with an acid treatment, pristine nanotubes were used, that were dispersed through the addition of polyacrylic acid (PAA), as suggested in the literature [23]. To break the CNTs agglomeration and homogenise the suspension, ultrasonication was applied for 45 minutes, and afterwards the solution was left overnight under magnetic stirring. Magnetic stirring was also continued during the whole course of deposition, in order to avoid re-agglomeration.

In the case of $-\text{COOH}$ functionalized GNPs, PAA was also added with the same aim, to improve dispersion and avoid re-agglomeration of the carbon nanomaterial. Two SEM images with a larger magnification of the nickel coatings containing CNTs and GNPs are shown in Figure 3. The coatings can present zones with good quality and no defects, on the left, or zones with agglomerates of CNTs or GNPs, as shown on the right.

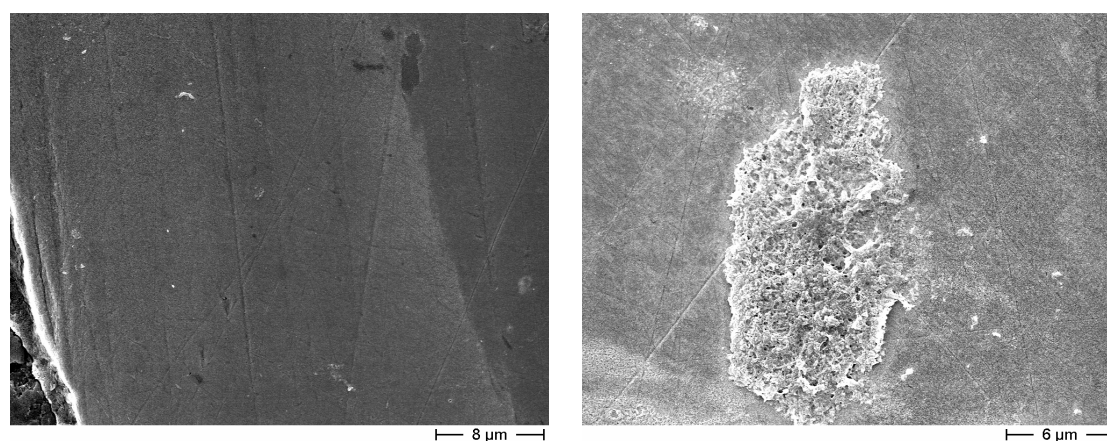


Figure 3. CNTs containing nickel layer with good quality (left); GNPs agglomerate in a nickel layer (right).

In order to measure the size of the nickel or copper crystallites, X-ray diffraction (XRD) was performed and the Scherrer formula was applied,

$$d = K \lambda / b \cos \theta$$

where d is the crystallite size, K is a constant depending on the geometry of the grains, λ is the copper K_{α} wavelength, b is the width of the XRD peaks, and θ is the diffraction angle.

The deposition of pure nickel already gave a rather low grain size, with submicrometric dimension, around 400 nm. The copper grains were a little larger, with a size close to 700 nm. As shown in Table 2, the presence of CNTs or GNPs brought to a significant reduction of nickel grain size, while copper grains were not affected by the presence of carbon nanomaterial.

Table 2. Grain size, calculated by the Scherrer equation, and roughness of nickel and copper-based coatings.

Sample	Grain size (nm)	Roughness Ra (μm)
N0	370	3.43
N1	277	2.27
N2	399	8.96
N3	209	2.08
C0	687	1.58
C1	599	1.99
C2	616	6.46
C3	717	5.52
C4	805	6.12

However, it is important to note that in the case of nickel, samples with too high carbon nanomaterial concentration demonstrated no reduction of grain size. This behaviour suggests that the highest concentrations are not well dispersed and that carbon nanomaterial remains too agglomerated, leaving large bundles of CNTs or GNPs, as the one shown in Figure 2.

With copper deposition instead, carbon nanotubes brings to a slight grain size reduction also in high concentration, while graphite nanoplatelets produce a slight increase of grain size.

The SEM observation of the samples, coupled with XRD, thus suggests that high concentration of nanotubes in nickel brings to a lower quality coating, as also confirmed by roughness measurements, also shown in Table 2. In the case of copper instead, the behaviour is more complicated, probably to interactions between the components of the bath. The most concentrated CNTs containing suspension provide a low roughness coating, while lower concentration of both CNTs and GNPs brings to a much higher roughness of the coating.

Hardness tests, shown in Table 3. were performed on Ni-based coatings, again confirm the previous results. The high concentration CNT-containing suspension brings to a low hardness coating, with HV close to 200. With lower concentration of CNTs or GNPs the hardness is much higher, close to 400 HV, close to the value of the pure nickel hardness. The fact that the composite coating has a lower hardness than the base alloy is due to the presence of low hardness carbon nanomaterial. However, the reduction in grain size of the nickel coating counterbalances the presence of carbon.

Table 3. Hardness values of nickel-based coatings.

Sample	Vickers Microhardness
N0	486
N1	327
N2	212
N3	400

Finally, the wear tests shown in Figure 4. allowed to measure the friction coefficient of the nickel based coating and the rate of removal of the coating. From curve N0 it is possible to observe how the pure nickel behaves. After 200 seconds the coefficient of friction (COF) begins to rise, passing from 0.65-0.7 to around 1.1, where it stabilises, indicating the removal of the coating. The same behaviour, with a faster initial growth, starting immediately, and also with a much higher scatter of the data, is observed for the high concentration CNTs suspension (N2 sample). This is due to the fact that the coating is very rough, and to the presence of many CNTs agglomerates in the coating.

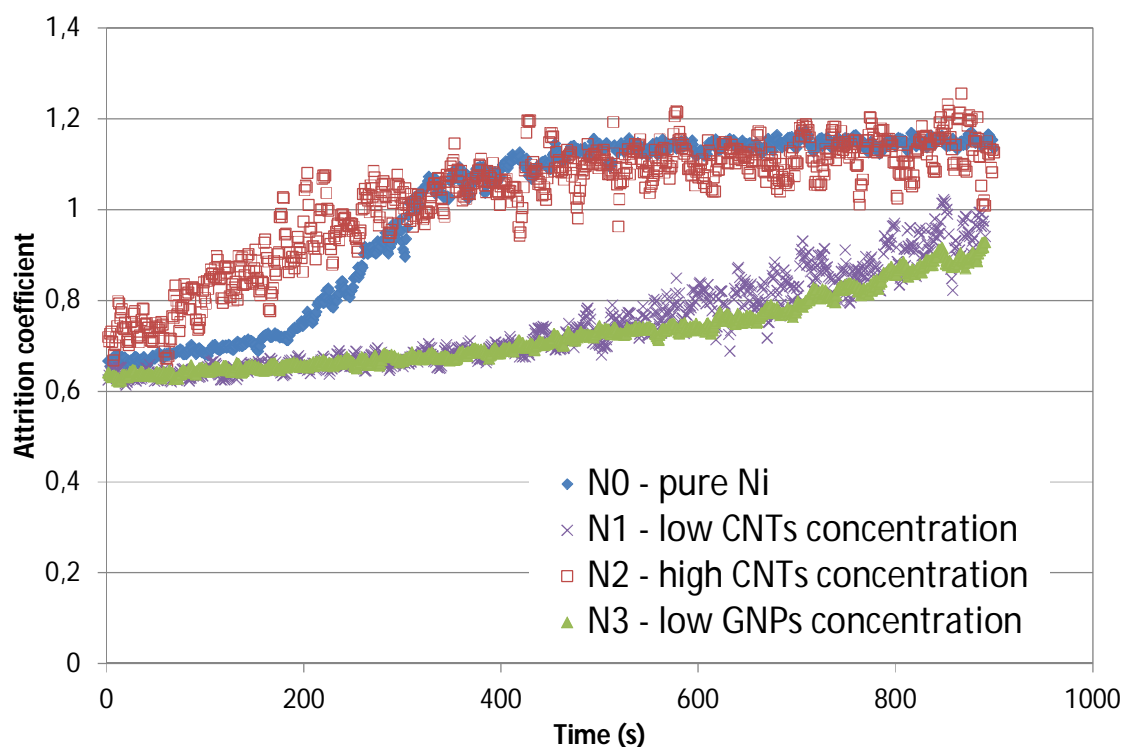


Figure 4. Coefficient of friction behaviour as a function of time for a pin-on-disk test at 5 N weight and 0.1 m/s.

The coatings containing low concentration of CNTs or GNPs (N1 and N3 respectively) instead show a much slower increase of COF. For the first 400 seconds the increase is very marginal, and begins to grow appreciably only after around 600 seconds. After 15 minutes of test, the COF is yet lower than 1 and growing, suggesting that the coating was not yet completely removed by the pin.

Comparing the CNTs and GNPs modified coating, it is possible to note that CNTs containing coatings present more scattered results than GNPs modified ones.

The copper-based samples were submitted to thermal diffusivity measurements, in order to verify if the coating could modify substantially the thermal properties of the support. In Table 4. the results at various temperatures for CNTs and GNPs containing copper coatings are reported.

Table 4. Thermal diffusivity of copper-based coatings.

Sample	40 °C	440 °C	790 °C
support	0.144	0.079	0.048
C0	0.152	0.094	0.06
C2	0.148	0.068	0.044
C3	0.133	0.073	0.044
C4	0.155	0.082	0.047

It is evident from Table 4. that the pure copper coating has a positive effect on the thermal properties of the support at all temperatures. The composite coatings have a more complex behaviour. Close to room temperature the samples obtained with 165 mg/l of CNTs or 190 mg/l of GNPs behave like the pure copper coating, or even slightly better in the case of sample C4. Increasing the temperature the composite coatings show a reduction of thermal diffusivity, probably due to the thermal stresses arising at the interface between the copper matrix and the carbon-based reinforcement. The thermal mismatch is rather high, so that it is possible that some delamination occurs at the interface, increasing the interface thermal resistance.

4. Conclusions

In this work the electrodeposition of composite coatings containing carbon nanotubes or graphite nanoplatelets has been carried out with success using nickel or copper matrices. It was shown that in the case of nickel deposition, the size of the nickel grains is reduced by the presence of the carbon nanoreinforcement, with positive effect on the wear properties, even at the cost of a small reduction of hardness values. In the case of copper deposition, the study shows the feasibility of using these reinforcements to produce well-adherent and solid coatings; regarding thermal properties, probably an increase of dispersion of CNTs or GNPs in the deposition solution is yet needed to fully exploit the exceptional properties of the carbon nanoreinforcement.

5. References

- [1] Dini J W 1993 *Electrodeposition - The Materials Science of Coatings and Substrates* (William Andrew Publishing/Noyes)
- [2] Gómez E, Pollina R and Vallés E 1995 *J. Electroanal. Chem.* **386** 45
- [3] Rosso M, Ugues D, Torres E, Perucca M and Kapranos P 2008 *Int., J. Mater. Forming* **1** 1259
- [4] Lecis N, Ugues D, Previtali B and Demir A G 2012 *Metall. Ital.* **104(6)** 15
- [5] Garcia I, Conde A, Langelaan G, Fransaer J and Celis J P 2003 *Corros. Sci.* **45** 1173
- [6] Srivastava M, William Grips V K and Rajam K S 2007 *Appl. Surf. Sci.* **253** 3814
- [7] Gyftou P, Pavlatou E A and Spyrellis N 2008 *Appl. Surf. Sci.* **254** 591
- [8] Robin A, Pinheiro de Santana J C and Sartori A F 2010 *J. Appl. Electrochem.* **40** 507
- [9] Zanella C, Lekka M and Bonora P L 2009 *J. Appl. Electrochem.* **39** 31
- [10] Sun X J and Li J G 2007 *Tribol. Lett.* **28** 223
- [11] Ivanov V V, Balakai V I, Kurnakova N Yu, Arzumanova A L and Balakai I V 2008 *Russian J. Appl. Chem.* **81** 2169
- [12] Teterina N M and Khaldeev G V 1998 *Prot. Metals* **34** 276

- [13] Chawla N and Chawla K K 2006 *Metal Matrix Composites* (Springer)
- [14] Manfredi D, Pavese M, Biamino S, Fino P and Badini C 2009 *Comp. Sci. Tech.* **69** 1777
- [15] Manfredi D, Pavese M, Biamino S, Antonini A, Fino P and Badini C 2010 *Comp. Part A: Appl. Sci. Manufact.* **41** 639
- [16] Iijima S 1991 *Nature* **354** 56
- [17] Meyyappan M 2004 *Carbon Nanotubes: Science and Applications* (CRC Press)
- [18] Shima H *Materials* **5** 47
- [19] Balandin A A 2011 *Nature Materials* **10** 569
- [20] Shokrieh M M and Rafiee R 2010 *Mech. Comp. Mater.* **46** 155
- [21] Pavese M, Musso S and Pugno N 2010 *J. Nanosci. Nanotech.* **10** 4240
- [22] Castellino M, Tortello M, Bianco S, Musso S, Giorcelli M, Pavese M, Gonnelli R S and Tagliaferro A 2010 *J. Nanosci. Nanotech.* **10** 3828
- [23] Arai S, Endo M and Kaneko N 2004 *Carbon* **42** 641
- [24] An B-G, Li L-X and Li H-X 2008 *Mater. Chem. Phys.* **110** 481
- [25] Khabazian S and Sanjabi S 2011 *Appl. Surf. Sci.* **257** 5850
- [26] Arai S and Endo M 2005 *Electrochem. Commun.* **7** 19
- [27] Guo C, Zuo Y, Zhao X, Zhao J and Xiong J *Surf. Coat. Tech.* **202** 3246
- [28] Wang F, Arai S and Endo M *Electrochem. Commun.* **7** 674
- [29] Dai P-Q, Xu W-C and Huang Q-Y 2008 *Mater. Sci. Eng. A* **483-484** 172
- [30] Jeon Y S, Byun J Y and Oh T S 2008 *J. Phys. Chem. Solids* **69** 1391
- [31] Carpenter C R, Shipway P H and Zhu Y 2011 *Surf. Coat. Technol.* **205** 5059
- [32] Carpenter C R, Shipway P H and Zhu Y 2011 *Wear* **271** 2100
- [33] Choi W, Lahiri I, Seelaboyina R and Kang Y S 2010 *Crit. Rev. Solid State Mater. Sci.* **35** 52
- [34] Young R J, Kinloch I A, Gong L and Novoselov K S 2012 *Comp. Sci. Tech.* **72** 1459