

# Nanostructured Nickel Film Deposition on Carbon Fibers for Improving Reinforcement-matrix Interface in Metal Matrix Composites

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The issues in dispersing any form of carbon in metal matrix is the major problem in the field of metal matrix composites with carbon reinforcement (MMCcr). The low wettability of carbon in molten metals and the difference in density are some of the difficulties to obtain a good dispersion of carbon fibers in the matrix and, as a consequence, an improvement of some critical properties for metals in a wide range of application (mechanical properties, electrical properties, optical properties). For this reason, the aim of this work is to obtain a metallic coated carbon fiber to enhance the interaction between the reinforcement and the matrix. Moreover, also the density of carbon fibers could be adjusted depending on the thickness of the coating. Electroless Nickel-Phosphorus Plating (ENP) is one of the candidate to be a coating technique to improve the interaction between the carbon fibers and the metal matrix. Despite of its versatility in terms of complex geometry of the substrate and homogeneity and adhesion of the coating, the presence of the phosphorus in the alloy could create some problems with the metal matrix such as the formation of metal-phosphorus products that can drastically decrease the mechanical properties of the composite. For this reason, in this work, is presented a new way of Electroless Pure Nickel Plating (EPP) without any introduction of phosphorus in the nickel coating. The dependence of the coating thickness and the density of the coated fibers were studied under different plating parameters (temperature of the plating solution, deposition rate and plating solution composition). All the samples were characterized with SEM and XRD and the thickness, density and homogeneity were compared for all the samples obtained.

## 1. Introduction

Nanomaterials are studied, between their applications, to reduce environmental impact deriving from human activities: nanotechnologies can be used, for example, to remove pollutants by direct chemical reaction with pollutant (Ziulli et al. 2002 and Bavasso et al. 2016) and, with a different approach, they can be introduced as improving reinforcement in application such as power source (Fadavi et al. 2015) and electrical distribution (Genova et al. 2015) with a consequent decrease of emissions.

Nanometallic particles were largely studied and used for direct chemical reduction in liquid phase. Nano zerovalent iron, for example, was employed to remove nitrates (Muradova et al 2016; Vilardi and Di Palma 2017) or Cr(VI) from waste waters as reported by Gueye et al (2016). This is possible, theoretically, thanks to the high surface area of nanostructured materials which allows higher reactivity compared with microscale materials. In the field of composites, to enhance the bulk properties by adding fillers in the matrix (Bartolucci et al. 2011), it has become more and more important to improve the fillers-matrix interface. The interesting in surface modification and, in particular, surface nanostructuring is one of the paths to reach a good interaction between the reinforcement and the matrix. In "metal matrix composites with carbon reinforcement" (MMCcr) the low wettability of carbon in most of metals is the reason why this kind of composites is not already used in industrial application despite their potential applications. Therefore, several studies have already been carried out on the importance to modify the fillers surface with a functional coating. (M. Z. Rong, 2006; Arai et al. 2010)

Electroless nickel plating is an autocatalytic reaction that allows to deposit a homogeneous and adherent film on a conductive substrate without using electrical current. This is possible because of a redox reaction between Ni ions and a reductive agent. For this reason, is possible to deposit onto complex geometries regardless the nature of the samples. These features make the technique a good candidate to functionalize the carbon fillers surface and enhance the interaction between the reinforcement and the metal matrix in the step of composite formation. However, depending on the reductive agents, some collateral reduction can occur with the formation of a nickel alloy. The most famous and studied electroless nickel plating solution involves the sodium hypophosphite ( $\text{Na}_2\text{H}_2\text{PO}_2$ ) as reductive agent with the formation of a Ni-P alloy (Fan et al., 2007; Ambat R. et al. 2004; Staia M. et al. 1996; Loto C.A. 2016). The introduction of P in the alloy can represent some limit to use this technique as plating procedure because of the reactivity of P at high temperature. In this work it is presented a new way to obtain a pure nickel coating with the electroless approach onto carbon fibers. In order to avoid the presence of heteroatoms in the alloy, hydrazine was selected as reductive agent. The study of several plating parameters has allowed to optimize the coating rate onto the fibers and to propose a growth mechanism.

## 2. Materials and methods

### 2.1 Experimental

All chemicals were of analytic grade and used without any further purifications. Nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), hydrazine monohydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ), sodium hydroxide (NaOH) and complexing agents (lactic acid and disodium EDTA) were purchased at SIGMA Aldrich. All solutions and cleaning are made with deionized water. Micrograf HT carbon microfibers (CMFs) produced by PROCHIMA (Italy) were selected as substrate. For every depositions, a specific quantity of CMFs was cleaned in acetone for 60 minutes in ultrasonic bath at room temperature to remove impurities then dried in an oven at  $80^\circ\text{C}$ . A quantity of CMFs were added to a small volume of water and place in vigorous stirring. Different volumes of hot plating solution (see composition in Table 1 - Haag S et al. (2006)) were added, at  $85^\circ\text{C}$ . The coating was conducted directly onto the fibers without any sensibilization or activation.

Table 1: Plating solution compositions (mol/L)

Compound	Chemical formula	Role	Concentration
Nickel chloride	$\text{NiCl}_2$	Source of $\text{Ni}^{2+}$	0.08
Hydrazine	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$	Reducing agent	0.4
Lactic acid	$\text{C}_3\text{H}_6\text{O}_3$	Complexing agent	0.15
Disodium EDTA	$\text{Na}_2[\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8]$	Complexing agent	0.016
Sodium hydroxide	NaOH	pH adjusting	0.25

Plating parameters (pH, temperature, time, stirring and plating ratio) were reported in Table 2. For plating ratio ( $P_r$ ) it was considered the volume of plating solution per mass of CMFs.

Table 2: Plating parameters

Parameter	Range
Temperature ( $^\circ\text{C}$ )	85
pH	9.2
Plating time (min)	5 ÷ 15
Stirring (rpm)	400
Plating ratio (ml/g)	50 ÷ 150

A large quantity of deionized water was added, after different plating time, in order to stop the deposition by decreasing the temperature. Then, the coated fibers were filtered, washed with deionized water and dried over-night at  $80^\circ\text{C}$ . The solution were prepared as follows: Ni salt was added in a quantity of water, then the two complexing agents were added once the nickel chloride was completely dissolved. Then the hydrazine was added dropwise, in order to avoid a local chemical concentration of the reducing agent. Then the pH was adjusted to the set value with a solution of NaOH 1M and heated on a magnetic hot plate under vigorous stirring.

## 2.2 Characterizations

X-Ray diffractometry (XRD) was performed with a Philips X'Pert device to confirm the presence of pure nickel on the fibers. The XRD device operated at 40 KV and 40 mA with  $\text{CuK}\alpha_1$  radiation ( $\lambda_{\text{K}\alpha_1} = 1.540598 \text{ \AA}$ ,  $\lambda_{\text{K}\alpha_2} = 1.544426 \text{ \AA}$ ) with a scan range of  $20\text{--}80^\circ$  ( $2\theta$ ), step size of  $0.02^\circ$  and counting time of 2 sec. The variations of density were determined by Micromeritics AccuPyc 1330 helium pycnometer at room temperature. SEM micrographies were performed with a Hitachi S2500 on all the samples as coated to investigate the surface microstructure for the different plating parameters. Compositional analysis were performed with energy dispersive X-ray spectroscopy (EDX) to verify the presence of other elements in the coating.

## 3. Results and Discussion

### 3.1 Microstructural characterization

XRD diffraction have shown that the fibers are coated with pure nickel. In Figure 1 it is reported, as an example, the XRD pattern obtained for the sample coated at 100 mL/g. XRD plots shows the major Ni peaks at  $2\theta$  values of  $44.88^\circ$ ,  $52.29^\circ$  and  $76.77^\circ$  corresponding to the (1 1 1), (2 0 0) and (2 2 0) planes of Ni. The small low-intensity peak at  $25.67^\circ$  confirms the presence of the C in the diffracted sample.

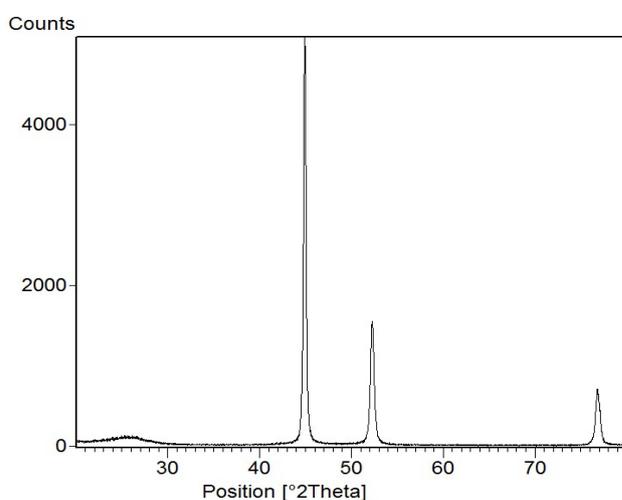


Figure 1: XRD pattern of a CMFs coated with electroless pure nickel plating.

The change in terms of density for the samples obtained with different  $P_r$  is shown in Figure 2. The density gain is directly proportional to the value of  $P_r$ . So, theoretically, a higher volume of solution available for deposition means a higher quantity of nickel deposit onto the fibers surface. The results of XRD and density change confirm that the fibers are theoretically covered by pure Ni onto the surface.

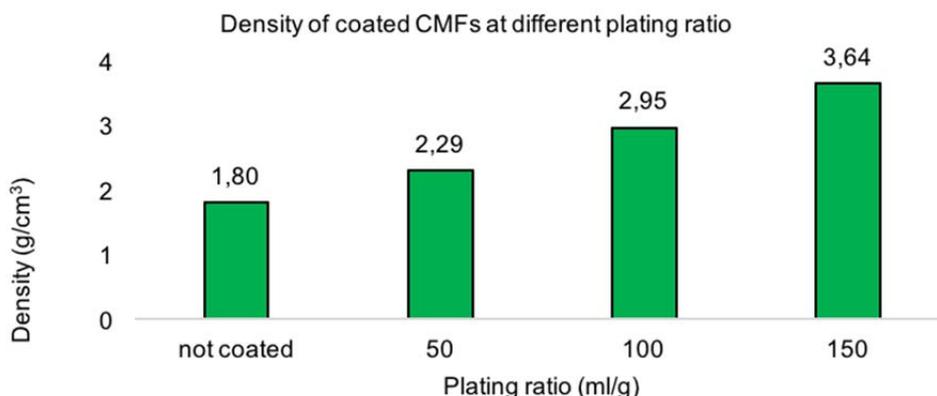


Figure 2: Density measurement vs plating ratio for the samples after 10 minutes of plating deposition.

SEM analysis (Figure 3) show the formation of nickel domains onto the fibers surface. The rate of covering seems not to be affected linearly from the quantity of solution available for the deposition. Contrary to what was expected, a higher volume of plating solution does not mean a higher rate of covering. However, surface microstructure investigations have allowed to identify the optimized plating parameters in terms of homogeneity of nickel coating: in fact, in the sample obtained with a  $P_r$  of 100 mL/g for 10 minutes (Figure 3C), the coating seems to be adherent, continuous and more homogeneous than the other samples.

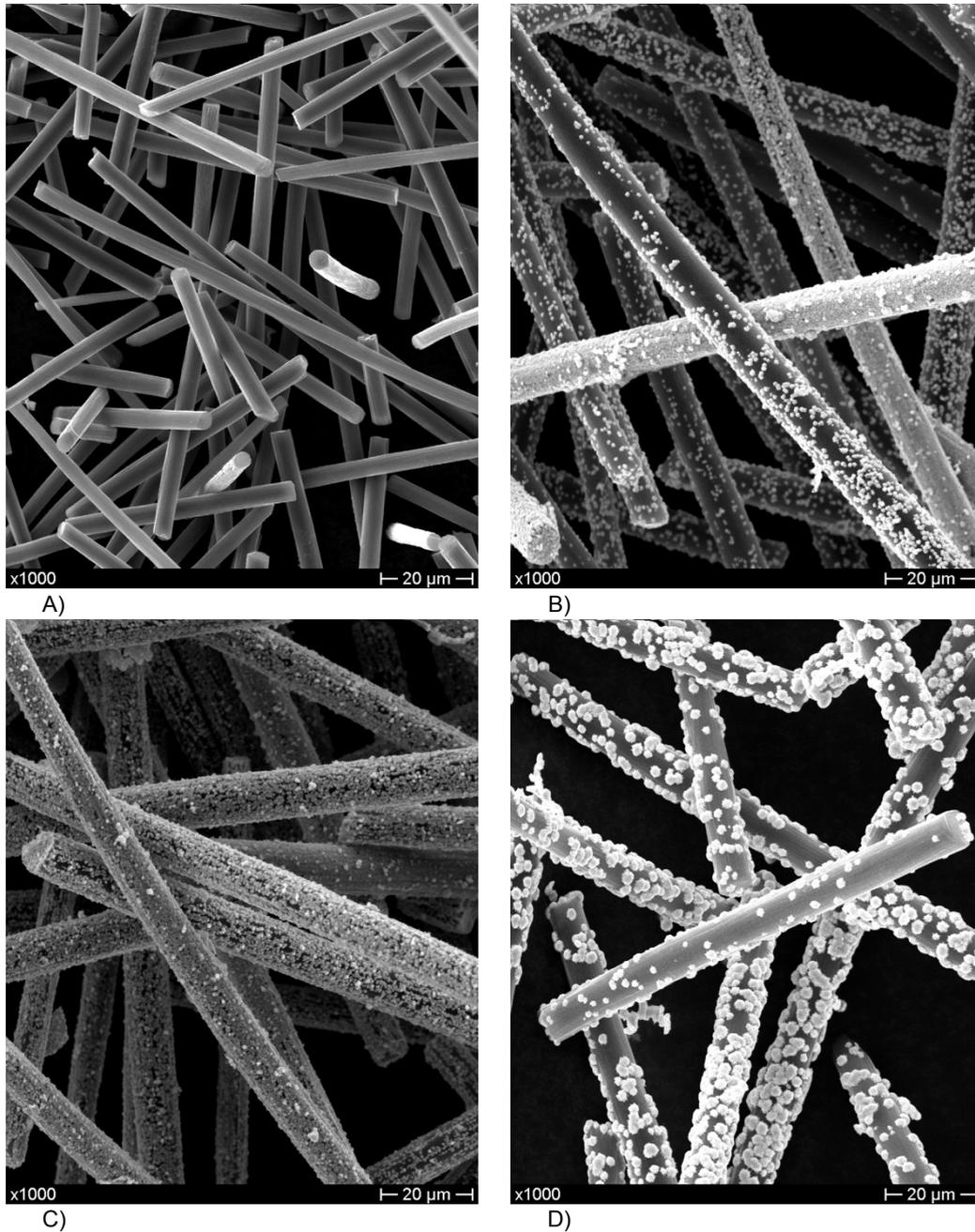


Figure 3: SEM micrographies of CMFs at different plating ratio: A) as received (after cleaning); B) 50 mL/g; C) 100 mL/g; D) 150 mL/g. Plating rate is referred to volume solution per mass of CMFs. All the samples presented in figure were plated for 10 minutes.

In Figure 4A the SEM micrography at higher magnification (10kX) for the sample 100 mL/g shows the nano-structure of the coating. The EDX (Figure 4B) confirms the results obtained from the other characterizations.

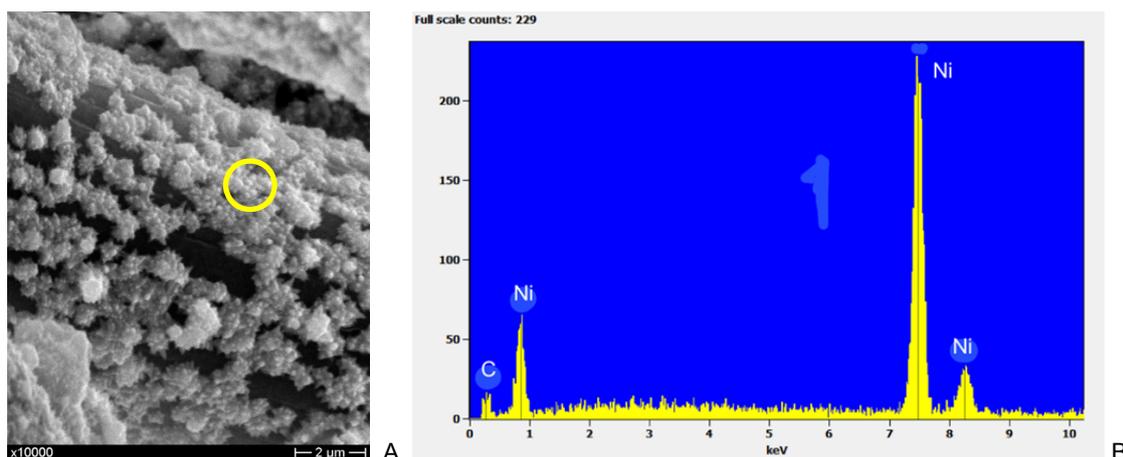
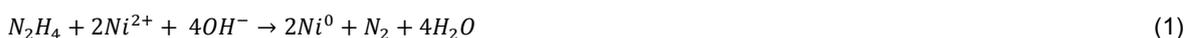


Figure 4: SEM image (A) at higher magnification (10kX) for the sample 100 mL/g with the EDX spectrum (B).

### 3.2 Growth mechanism

The results obtained with SEM micrographies have focused on a particular growth mechanism. In figure 5 is represented the schema for the redox reaction(1):



The substrate plays the role of catalytic surface and promote the exchange and transport of electrons from the reductive agent ( $\text{N}_2\text{H}_4$ ) to the cationic ions. Therefore, the presence of some high-reactivity zone as defects or irregularity in the shape of CMFs can create a zone of nucleation for the nickel. The formation of preferential growth zone seems the reason why the deposition follows a mechanism so defined “by domain”. Furthermore the deposition have a peculiar growth speed: the variation of  $P_r$  has demonstrated that it is possible to deposit a higher quantity of Ni (reference density measurement fig. 2) without cover completely the fiber.

Thus, the covering rate ( $C_r$ ) is dependant, among other things, on quantity of nickel available in solution ( $P_r$ ). According to this theory, the influence of the covering rate should be linearly. However the SEM micrographies have shown a complex growth kinetic that can be explained by considering an anisotropic deposition speed along the axes (fig. 5). In the sample obtained for the plating solution at 150 mL/g the growth along the Z axis is so faster that the domains have no time to coalesce into a film.

On the contrary, for the sample obtained at 100 mL/g the growth along X axis is comparable to the Z axis and results in a nanostructured semi-continuous film of pure nickel.

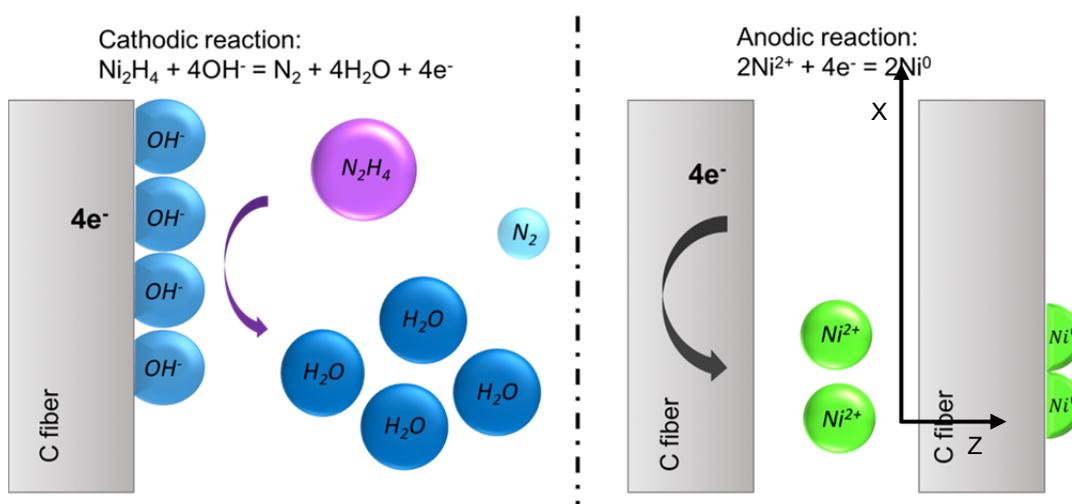


Figure 5: Cathodic and anodic reactions for electroless pure nickel reaction. Growth of nickel domain onto fiber's surface.

#### 4. Conclusions

Nanostructured film deposition onto carbon microfibers was obtained by electroless pure nickel deposition. Different plating parameters were investigated and the plating deposition were optimized in terms of covering rate and microstructure of the coating. All the sample were characterized by microstructural analysis (XRD, SEM, EDX) and this has allowed to propose a growth mechanism confirmed by experimental results.

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