

## Ni/TiO<sub>2</sub> composite electrocoatings

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**Abstract** Nickel composite coatings have been studied in order to provide increased properties on engineering materials surfaces, such as higher electrical conductivity, wear and corrosion resistance and to decrease the end product manufacturing cost by plating on cheap materials. Adding TiO<sub>2</sub> particles in the bath during the deposition process produced composite coatings. This was tried on electrodeposition from a Watts bath by conventional DC conditions and by pulse plating. The surfaces were studied by SEM, by profilometry and by Vickers' microhardness, and its structure by X-ray diffraction. The incorporation percentage of TiO<sub>2</sub> particles in the metallic matrix was estimated by EDS analysis. Corrosion measurements of the deposits were taken by Tafel curves. The results obtained show that particle incorporation percentage is higher for the Ni/TiO<sub>2</sub> electrodeposits produced by pulse current and the microhardness is significantly increased compared to the electrodeposits produced by DC.

**Keywords** Pulse plating. Nickel. TiO<sub>2</sub>. Composite coatings. Corrosion.

### Recubrimientos electrolíticos compuestos de Ni/TiO<sub>2</sub>

**Resumen** Los electrodeósitos compuestos de níquel confieren mejores propiedades a la superficies de los materiales utilizados en ingeniería, tales como conductividad eléctrica, desgaste y resistencia a la corrosión, y disminuyen el costo del producto manufacturado al utilizarse como recubrimiento de acabado sobre materiales base más económicos. La adición de partículas de TiO<sub>2</sub> al baño durante la electrodeposición da lugar a la formación de recubrimientos compuestos. La electrodeposición se llevó cabo en un baño Watts en condiciones convencionales de corriente continua y por electrodeósito pulsante. Las superficies fueron estudiadas por SEM y microanálisis EDS; se midió su microrrugosidad y microdureza Vickers; y su estructura se analizó mediante Difracción de Rayos X. Las medidas de corrosión de los depósitos se realizaron a partir del trazado de curvas de Tafel. Los resultados muestran que el porcentaje de incorporación de partículas en los recubrimientos Ni/TiO<sub>2</sub> es más elevado y la microdureza es significativamente mayor al realizar la electrodeposición por corriente pulsante en lugar de utilizar corriente continua.

**Palabras clave** Electrodeposición pulsante. Níquel. TiO<sub>2</sub>. Recubrimientos compuestos.

### 1. INTRODUCTION

Composite coatings of a nickel matrix with stable inorganic oxides as fillers may offer the synergistic advantages of the metal matrix which is conductive, corrosion resistant and of the oxide which may enhance the corrosion resistance, optical properties or catalytic properties of the system<sup>[1]</sup>. Also this coating may be employed on a

cheap engineering material, such as steel and increased properties of the system by tailoring the suitability to a new need.

Electrolytic codeposition has been widely investigated as an alternative method for the preparation of metal matrix composite electrocoatings. As electrolytic codeposition is defined the process of incorporation in the metallic matrix of inert particles, homogeneously dispersed

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in the electrolytic bath. TiO<sub>2</sub> particles are employed for the amelioration of optical, electrical and mechanical properties of engineering materials<sup>[2-5]</sup>. Especially, the Ni/TiO<sub>2</sub> composite electrocoatings have been found that they might be used as photocatalysts for the degradation of organic compounds and as surfaces of high hardness<sup>[6 and 7]</sup>.

Both the structure and the properties of composite electrocoatings are influenced by the following parameters: the preparation conditions (composition of the electrolytic bath, pH and temperature of the bath, current density, *J* etc.), the type of the current applied (direct current, D.C., pulse current, P.C.) and the characteristics (type, concentration) of the particles used. Moreover, the properties amelioration depends on the codeposition percentage and the uniform distribution of the particles in the metallic matrix. As far as concerns the type of current applied, it has been proved that the variation of P.C. parameters (pulse frequency, *ν*, and, duty cycle, d.c. =  $[T/(T+T')] \times 100$ , where *T* the deposition time and *T'* the relaxation time) influence significantly the adsorption/desorption phenomena of different chemical species in the catholyte area (cathode/electrolyte interface) leading to the preparation of coatings with improved properties<sup>[8]</sup>.

The work presented in this paper exploits the results obtained from the study of Ni/TiO<sub>2</sub> composite electro coatings prepared under D.C. and P.C. conditions.

## 2. MATERIALS AND EXPERIMENTAL PROCEDURE

The Ni/TiO<sub>2</sub> composite electrocoatings were produced under D.C. and P.C. conditions. The electrolytic bath employed was a Watts type bath (300 g/l of NiSO<sub>4</sub>·7H<sub>2</sub>O, 35 g/l of NiCl<sub>2</sub>·6H<sub>2</sub>O, 40 g/l of H<sub>3</sub>BO<sub>3</sub>) and the powdered TiO<sub>2</sub> to be co deposited was inside the solution. The TiO<sub>2</sub> used was of the anatase type oxide by Merck, with a mean diameter powder of 200-300 nm and concentration in the bath of 20 g/l. The granulometry of the powder was measured by an image analysis computer program under the optical microscope. The anatase powder has also been examined by XRD analysis to identify its crystallography. The deposition was performed on flat brass cylindrical substrates adjusted in a rotated rod (rotation velocity,  $\Omega$ , of 300 rpm) with an active deposition surface of 0.049 dm<sup>2</sup>. The bath temperature was kept constant by a thermostat at

50 °C, the current density was 5 A/dm<sup>2</sup> and the pH of the bath was kept at 4.40. When preparing under P.C. conditions the pulse frequency (*ν*) was 0.1, 1, 10 and 100 Hz and the duty cycle (d.c.) was 10, 50, 90 and 95 %. The deposit final thickness was approximately of 50 μm. The texture of the deposits was determined by XRD (SIEMENS X-ray diffractometer 5000) using a Cu K $\alpha$  X-ray source. Vickers microhardness measurements were carried out on the deposits by employing a load of 40 g for a period of 10 s. The specimen microhardness was evaluated by averaging five experimental runs. Observations of the produced surfaces were based on Scanning Electron Microscopy (SEM), and the particles incorporation percentage was estimated by means of energy dispersive microanalysis (EDS) (JEOL JSM 6100). Corrosion resistance characterization of the deposits was obtained by means of Tafel electrochemical measurements. Potentiodynamic polarization curves were taken on the specimens during their exposure to the electrolyte, which was an aqueous solution of 3.5 % NaCl at room temperature. A three-electrode electrochemical cell configuration was employed having a Saturated Calomel Electrode (SCE) as a reference, and a platinum foil as a counter electrode, the third electrode being the tested specimen. The instrumentation was a CMS100 Gamry potentiostat, computer controlled, with commercial software for the data treatment.

## 3. RESULTS AND DISCUSSION

From the XRD diagrams the preferred textures of the Ni/TiO<sub>2</sub> composite electrodeposits were deduced by data treatment (Table I). In figure 1 a typical XRD diagram is given.

From table I, most of the composite deposits have a mixed texture [211]+[100] but the deposits produced with dc of 50 % have a selective orientation towards the [211] crystallographic axis. Given that the PC preparation conditions in a non-composite environment favour the nickel crystalline development towards the [100] axis<sup>[8 and 9]</sup>, this differentiation may be partly attributed to the presence of TiO<sub>2</sub> nano-particles in the structure. The anatase nano-particles set on nickel crystallite boundaries and on their faces, creating structural defects and thus promoting the development towards the more inhibited textures, such as the [211] one.

The surface morphology of the D.C. and P.C. composite electrodeposits appears in the SEM

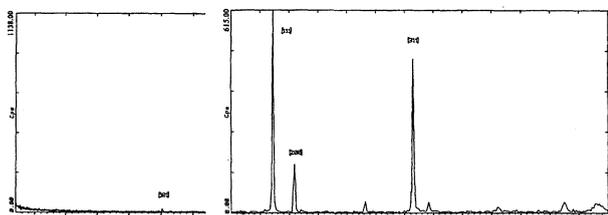
**Table I.** Preferred textures of the Ni/TiO<sub>2</sub> composite electrodeposits depending on the DC parameters

*Tabla I. Texturas preferidas de electrodepositos compuestos de Ni/TiO<sub>2</sub> dependiendo de los parámetros DC*

Texture	[100]			[211]		
v (Hz)	D.C.	10	1	100	10	0.1
d.c. %		10	50	50	50	50

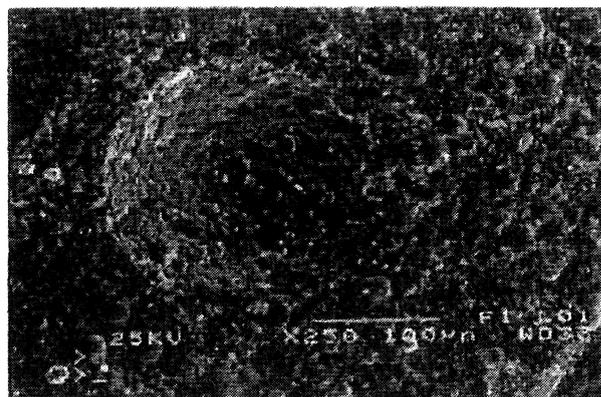
Mixed texture	[211]+[100]							
v (Hz)	100	100	10	10	1	1	0.1	0.1
d.c. %	90	95	90	95	90	95	90	95



**Figure 1.** XRD diagram of a P.C. Ni/TiO<sub>2</sub> composite electrodeposit prepared for n of 100 Hz and d.c. of 50 %. Left side the [101] texture of anatase TiO<sub>2</sub> and on the right side the characteristic nickel textures. The presence of the [311] pseudo-texture is due to the Cu anticathode used instead of Mo, the later that would make the [211] texture apparent.

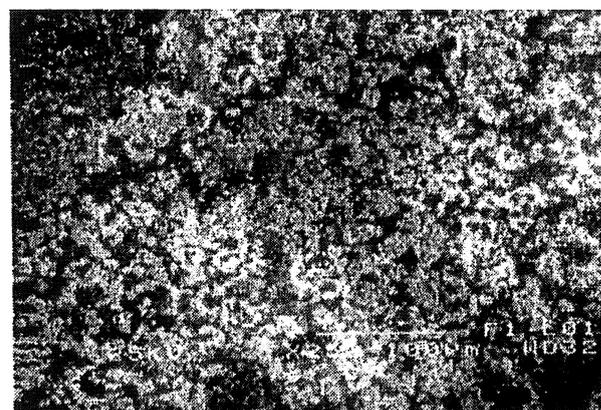
*Figura 1. Diagrama de XRD de un electrodeposito compuesto P.C. de Ni/TiO<sub>2</sub> obtenido a una n de 100 Hz y d.c. de 50 %. Lado izquierdo de la textura [101] de TiO<sub>2</sub> anatase y en el lado derecho las texturas características del níquel. La presencia de la pseudo textura [311] es debida al anticátodo de Cu utilizado en lugar de Mo, este último podría tener la textura aparente [211].*

micrographs of figures 2 and 3, correspondingly. In figure 2 the surface morphology of the D.C. Ni/TiO<sub>2</sub> composite deposit is shown with nickel craters formation and the TiO<sub>2</sub> particles that are mainly deposited on their sides. The SEM micrograph of figure 3 reveals the surface of a P.C. Ni/TiO<sub>2</sub> composite deposit produced by dc of 50 % and n of 10 Hz. The surface of this deposit is ameliorated compared to the previous one and the whitish coloured regions are agglomerates of TiO<sub>2</sub> particles, as EDS analysis has proved (see Fig. 4). The percentage of the TiO<sub>2</sub> particle incorporation in the nickel matrix for the examined deposits, according to the EDS analysis is tabulated in table II. From these data we may conclude that the P.C. composite deposits have higher particle incorporation percentage that the corresponding ones produced under D.C. conditions.



**Figure 2.** SEM micrograph of the D.C. Ni/TiO<sub>2</sub> composite electrodeposit (x250).

*Figura 2. Micrografía SEM de un electrodeposito compuesto de D.C. Ni/TiO<sub>2</sub> (x250).*



**Figure 3.** SEM micrograph of a P.C. Ni/TiO<sub>2</sub> composite electrodeposit (dc of 50 % y n of 10Hz) (x500).

*Figura 3. Micrografía SEM de un electrodeposito compuesto de P.C. Ni/TiO<sub>2</sub>, dc 50 %, y n 10 Hz (x500).*

**Table II.** Incorporation percentages (in w/w %) of particles TiO<sub>2</sub> in the nickel matrix

*Tabla II. Porcentaje incorporado (% en w/w) de partículas de TiO<sub>2</sub> en la matriz de níquel*

v (Hz)	DC	1	10	10	10	100
d.c. %		95	10	50	95	95
% w/w TiO <sub>2</sub>	3.30	5.60	10.00	8.14	6.10	5.63

The performance under corrosion conditions in 3.5 % NaCl solution of the deposits, measured by linear polarization Tafel curves (Fig. 5a-b), shows that the deposits have a very similar corrosion behaviour, independently of the particles incorporation percentage and the type of current

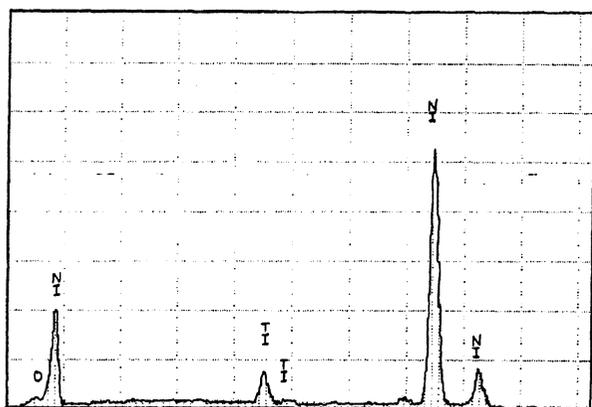


Figure 4. EDS analysis of the P.C. Ni/TiO<sub>2</sub> composite electrodeposit of the figure 3 surface.

Figura 4. Análisis de EDS de un electrodepósito compuesto de P.C. Ni/TiO<sub>2</sub> de la figura 3.

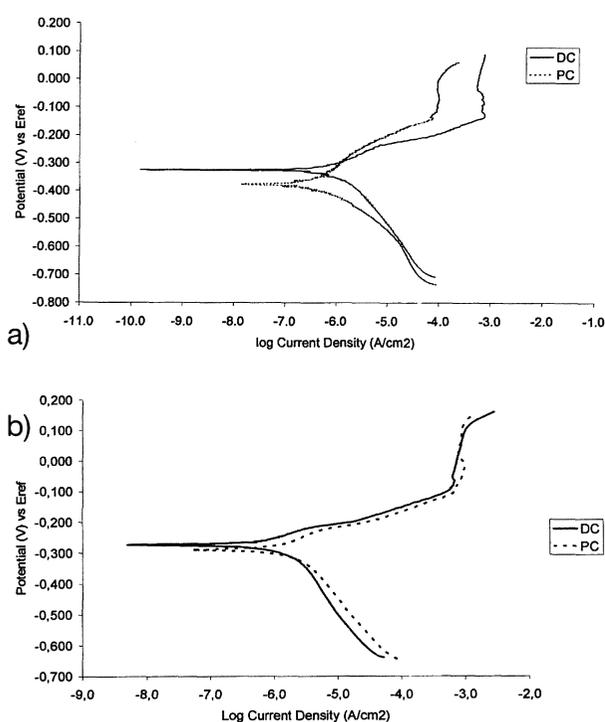


Figure 5. (a) Electrochemical linear polarization Tafel curves for the two types of deposits without TiO<sub>2</sub>, prepared under similar conditions as the composite deposits shown in (b).

Figura 5. (a) Polarización lineal, curvas de Tafel, para dos tipos de depósitos sin TiO<sub>2</sub> preparados en condiciones aparentemente similares como los depósitos mostrados en (b).

applied, i.e. D.C. or P.C. ( $\nu$  of 10 Hz and dc of 50 %). The corrosion rates were 0.006 mm/y for the D.C. composite deposit with 3.3 % w/w of TiO<sub>2</sub> and 0.009 mm/y for the P.C. composite deposit with 8.14 % w/w TiO<sub>2</sub>. These values may be considered as similar and they are attributed to the Ni matrix

and to its passivation. The results from produced deposits with the same preparation conditions as the composites, but without the incorporation of the oxide particles also have similar corrosion rates, i.e. 0.010 mm/y for the direct current one and 0.007 mm/y for the pc prepared surface (Fig. 5b). The incorporated oxide particles do not appear to decrease the corrosion resistance of the composite deposits.

The results of the Vickers microhardness and of the roughness (Ra value) of the Ni/TiO<sub>2</sub> composite electrodeposits in relation to the pulse frequency, for all the d.c. values applied, are presented in figures 6 and 7. The highest measured microhardness value of 830 HV (Fig. 6) is attained by the P.C. produced composite electrodeposit under dc of 95 % and  $\nu$  of 0.1 Hz. The lowest microhardness value (505 HV) is attained by the composite electrodeposit produced under D.C. application.

Additionally, the lowest roughness (Ra of 0.2  $\mu$ m) was exhibited by the P.C. composite deposits produced for D.C. of 90 %,  $\nu$  of 1 Hz and 10 Hz (Fig. 7), while the most rough conditions was met

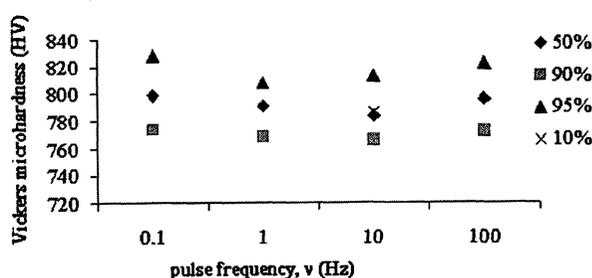


Figure 6. Vickers microhardness variation as a function of pulse frequency,  $\nu$ , for all dc applied.

Figura 6. Variación de la microdureza Vickers en función del pulso de frecuencia,  $\nu$ , para todos los dc aplicados.

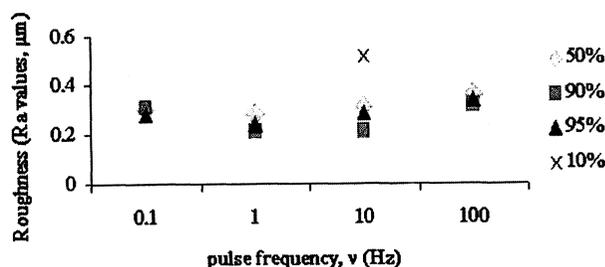


Figure 7. Surface roughness variation (RA value) as a function of pulse frequency,  $\nu$  for all tried d.c.

Figura 7. Variación de la rugosidad superficial (valor Ra) en función de los pulsos de frecuencia,  $\nu$ , para todos los d.c.

macroscopically by the D.C. composite deposit of which the surface roughness could not be measured.

## 5. CONCLUSIONS

From the above experimental data it may be concluded that the codeposition of TiO<sub>2</sub> particles in the Ni matrix can be successfully achieved both under D.C. and P.C. regime. The surface morphology of the P.C. composite deposits is definitely improved (microcrystalline deposits) compared to the one produced by D.C. The incorporation percentage of the TiO<sub>2</sub> particles in the metal matrix for particular values of the P.C. parameters applied is higher for the P.C. deposits and apparently TiO<sub>2</sub> is selectively codeposited at the nickel crystallite edges. Additionally, the crystal growth of the P.C. composite deposits is diversified and the mixed texture [211]+[100] appears to be the most prominent. The preponderance of the [211] texture is attributed to the crystal defects created by the incorporation of TiO<sub>2</sub> particles. This event may explain the microhardness increase and also the surface

roughness decrease of the P.C. composite deposits compared to the D.C. one. Corrosion resistance for both cases (D.C. and P.C. conditions) is excellent and the codeposition of the TiO<sub>2</sub> particles in the metallic matrix does not seem to effect either passivation or creating pores in the nickel matrix.

## REFERENCES

- [1] J.P. CELIS Y J.R. ROOS, *J. Electrochem. Soc.* 124 (1977) 1508-1512.
- [2] L. WENHUA, L. HONG, C. SAO'AN, Z. JIANQING Y C. CHUNAN, *J. Photoch. Photobio. A* 131 (2000) 125-132.
- [3] Y.L. SHI, X.G. ZHANG Y H.L. LI, *Mat. Sci. Eng. A Struct.* 333 (2002) 239-242.
- [4] A. FUJISHIMA Y K. HONDA, *Nature* 37 (1992) 238-241.
- [5] T. DOMOTO, *Japanese Patent* H10-86258 (1998).
- [6] M. ZHOU, N.R. DE TACCONI, K. RAJESHWAR Y W.Y. LIN, *J. Electroanal. Chem.* 402 (1996) 221-224.
- [7] M. ZHOU, N.R. DE TACCONI Y K. RAJESHWAR, *J. Electroanal. Chem.* 421 (1997) 111-120.
- [8] C. KOLLIA, N. SPYRELLIS, J. AMBLARD, M. FROMENT Y G. MAURIN, *J. Appl. Electrochem.* 20 (1990) 1025-1032.
- [9] C.T. DERVOS, C. KOLLIA, S. PSARROU Y P. VASSILIOU, *IEEE T. Compon. Pack. T.* 1 (1999) 1-10.