Study of Ni-Tio₂ nanocomposite coating prepared by electrochemical deposition

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Advances in materials performance often require the development of composite system. Nanocomposites containing titanium oxide nanoparticles in a nickel matrix have been prepared by means of electrocodeposition process from nickel plating bath an sulphate bath. The nanocomposite coatings were obtained by codeposition of the TiO_2 nanoparticles (mean diameter 21 nm) with nickel during plating process. The surface morphology and microstructure of the nickel matrix was significantly altered due to the presence of titania nanoparticles. In the case of both nickel baths, the Vickers microhardness showed a tendency to increase with the amount of particle incorporation. The corrosion behaviour of the electrodeposited nickel in 0.5M Na₂SO₄ and 0.5M NaCl was studied using electrochemical methods. The corrosion rate calculated by polarization potentiodynamic curves obtained after 30 min and 1 h from immersion in solution is bigger for nanostructured coatings in 0.5M Na₂SO₄ (5.92 µm/year) and a little bit smaller in 0.5M NaCl (3.77 µm/year).

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1. Introduction

Nickel electroplating is an important part of any engineering component. Nanocomposites consisting of ultrafine particles of TiO2 have been reported to be advantageous used widely in many applications area due to their unique physical, chemical and electro-optical properties. Since the mechanical and electrical properties of TiO₂ films are dependent on their composition. crystallinity, surface morphology and total surface area. Over the past few years, metal matrix composite coatings, especially nickel matrix composite coatings containing nano-particles which exhibit excellent properties, such as higher wear and corrosion resistance, higher hardness, and more excellent self lubricating in comparison with single metal coating, have been more widely studied. The coating properties improved with decreasing of codeposited particles size. Corrosion resistance can be affected by microstructure, such as grain size, surface morphology and texture, which is closely related to the electrodeposition parameters, such as current density, pH, electrolyte temperature and particle concentration of the plating bath. Metal matrix composite coating containing alumina (Al₂O₃) and titania (TiO₂) particles has been widely used in industry. Although Ni-TiO2 composites have been reported to be advantageous for high temperature [1], interesting photoelectrochemical and photocatalytical behavior application[2,3,6] relatively little research effort has been dedicated to the electrodeposition of nickel titania composites[2-7]. The electro co-deposition of Ni with second phase nano-particles such as aluminum oxide,

titanium nitride, carbon nanotube (CNTs), diamond, silicon carbide, silicon nitride and zirconium oxide have been studied extensively over the past two decades. A variety of nanosized particles some such investigations with Ni-Al₂O₃ [8-12], Ni-CNTs[13,14], Ni-Si₃N₄[15,16], Ni-diamond [7], Ni-SiC [8-11], Ni-ZrO₂ [14], Ni-TiO₂ [17, 18] have been reported recently. These have the large projected applications for automotive parts, aerospace, printed circuitry and electrical contacts, gold-silver wares and jewelry, musical instruments and trophies, soft metal gaskets, decorative door, light & bathroom fittings [19].

The aim of this work was investigate the electrochemical corrosion behaviour of nanocomposite coatings in nickel matrix with TiO_2 nano-particles (mean diameter 21 nm) were obtained by electrochemical codeposition from a Watts type bath onto cooper substrate. The corrosion behavior of the thus obtained deposits was analyzed by Linear sweep voltametry methods in 0.5M Na₂SO₄ and 0.5M NaCl solution. The microstructure and hardness of electrodeposited Ni-TiO₂ nanonocomposites coatings were also investigated and they will be discussed in this manuscript.

2. Experimental details

Electrodeposited nickel and composite $Ni - TiO_2$ coatings was prepared from a sulphate bath. The detailed composition of the electrolyte and the operating conditions used in this study can be found in Table 1. Analytical grade chemicals and distilled water were used to prepare the electrolyte. The electrolytic bath was stirred by a

mechanical stirrer (250-300 rpm). The temperature of the electrolyte was controlled with a Haake thermostat (model GD1, accuracy ± 1 °C).

The cathode, a copper disc with an area of 2.26 cm², was vertically centered in the electrochemical cell. A cylindrical nickel plate that surrounded the cathode was used as a counter electrode. A saturated calomel electrode (SCE) was used as reference electrode. The copper substrates were mechanically polished with different grade of emery papers (between 800 and 4000), electrochemically degreased in an alkaline bath UNAR EL 63 solution (commercial product from Schering Germany) at 0.2 A dm⁻² for 20-30 seconds and activated at room temperature in a 1N HCl solution. The final step in preparing the substrates was their rinsing with doubly-distilled water and drying under pressured air.

The electrodeposition was carried out galvanostatically using a potentiostat/galvanostat (EG & G PAR model 273A). The thickness of the electrodeposits obtained after 1h were ca. 30 μ m. The pH value of the electrolyte was adjusted and kept to 4 during the electrodeposition with concentrated H₂SO₄ (98 %) solution and NaHCO₃ (purity 99.5%). The obtained deposits were rinsed with doubly-distilled water and dried under pressured air.

 Table 1. The composition of the electrolyte and the working parameters used

| Working parameters | Values | | |
|---|------------------------------------|--|--|
| NiSO ₄ ·6H ₂ O | 0.9 M | | |
| NiCl ₂ ·6H ₂ O | 0.21 M | | |
| H ₃ BO ₃ | 0.48 M | | |
| Sodium dodecyl sulphate (C ₁₂ H ₂₅ SO ₄ Na) | 0.1 gL ⁻¹ | | |
| TiO ₂ | 20 g/l | | |
| Temperature | 50 °C | | |
| Current density | $5 \text{ A} \cdot \text{dm}^{-2}$ | | |
| Time | 60 min | | |
| pH | 4.0 ± 0.2 | | |

The surface morphologies of the electrodeposits were characterized by scanning electron microscopy (SEM Zeiss EVO 50). Grain size and texture were assessed by X-ray diffraction (XRD) technique. X-ray diffraction analyses were performed at room temperature on a Siemens D 500 in order to determine the grain size and the texture of the deposits.

The hardness of the samples was determined with a Vickers microhardness measuring device (Fischer Scope H100) as described in DIN EN ISO14577. The microhardness values are averages of 10 measurements performed on different locations of each sample. The thickness of all coatings is more than ten times the maximum indentation depth of $1\mu m$ in order to reduce effects of the substrates.

EC-Lab complete software was used for the corrosion measurements. A three electrodes arrangement cell was used for these measurements, where the working electrode (WE) was the electrodeposited nickel, a platinum nets was used as auxiliary electrode (CE) and a saturated calomel electrode as reference electrode (RE) (E_0 =0.241 V/SHE). The solution used in the corrosion tests was a 0.5 M Na₂SO₄ electrolyte (pH 2) and 0.5M NaCl (pH 5.5). The corrosions tests were performed at ambient temperature (23±1°C). Potentiodynamic polarization curves (PD) were used initial potential - 600 mV, final potential + 200mV after 30 min and 1 h from the immersion of the Ni deposits in the test solution, at a scan rate of 10 mV/s. The current density for corrosion (i_{corr}) was determined by extrapolating the anodic and cathodic Tafel slopes.

3. Results and discussion

3.1. Morphology and structure of the deposits

Figs. 1a) and 1b) compare the surface structure of pure nickel coating and nanostrucured Ni – TiO₂ composite coatings under a scanning microscope. Embedding of TiO₂ particles in the nickel matrix changes in the grain structure of the pure nickel coating. the surface of a nickel is made up of regular pyramidal crystals with a uniform grain size. The TiO₂ particles codeposited with nickel radically change the structure of the metal. The presence of nanoparticles TiO₂ in composite coatings was evidenced by energy dispersive analysis, EDX (Fig.2). Figure 3 shows XRD pattern of nickel coating (a) and Ni – TiO₂ composite (b) prepared at $5 \text{ A}\cdot\text{dm}^{-2}$.



Fig. 1. SEM surface morphologies of pure nickel electroplated (a) and nanostructured Ni-TiO2 composite coatings (b).





Fig.2. EDX spectrum of $Ni - TiO_2$ composite coatings.

Fig. 3. XRD pattern of nickel coating (a) and $Ni - TiO_2$ composite prepared at $5A \cdot dm^{-2}$ for 1 h.

3.2. Microhardness

The mechanical properties of surface finishing represent an important factor for their implementation in the industrial processes [20, 21]. The mechanical properties evaluated by microhardness measurements are often a method of choice for a straight forward screening because it is relatively inexpensive, easy to use and almost non-destructive [22].

The microhardness of a deposit can be influenced by changes in current density or temperature of the electrolyte. It depends on many factors, but the most important of them is the plating bath composition [23, 24]. Thus, the microhardness values are strongly affected by the presence of impurities, organic substances, or addition agents.

Ten hardness tests were performed for each sample at the maximum indentation depth of 1 μ m. Based upon the averages hardness values obtained and standard deviations, the nickel layers and Ni-TiO₂ are presented in table 2.In the case of both nickel baths, the Vickers microhardness showed a tendency to increase with of particle incorporation.

Table 2. Deposit hardness from a Watts solution for 60 min and $5A \cdot dm^2$

| Coating | Microhardness | S (standard | | |
|-----------------|---------------|-------------|--|--|
| | (Vickers) | deviation) | | |
| Ni | 261.82 | 57.13 | | |
| $Ni - TiO_2 20$ | 672.01 | 71.68 | | |
| g/l | | | | |

3.3. Corrosion behavior Linear sweep voltammetry measurements and Tafel representation

The corrosion investigation of each sample began with monitoring its open circuit potential after immersion into the testing solutions till reaching a relatively stable stationary value.

The performed potentiodynamic diagrams for nanostructured Ni – TiO_2 composite coatings in 0.5M Na₂SO₄ and 0.5M NaCl solution after 30 min and 1 h of immersion are presented in Figs. 4 and 5 respectively. The corrosion potential (Ecorr), corrosion current density (icorr) and polarization resistance (Rp) are determined and summarized in Table 3.

Table 3. Polarization resistance values nanostructured $Ni - TiO_2$ composite coatings calculated from polarizationpotentiodynamic curves obtained after 30 min and 1 h from immersion in solution.

| Solution | | E _{corr} | I _{corr} | β_a | β _c | R _p | Corrosion |
|--------------------------------------|--------|-------------------|-------------------------|------------------------|------------------------|------------------|-----------|
| | Time | (mV)SCE | (μAcm^{-2}) | (mVdec ⁻¹) | (mVdec ⁻¹) | $(k\Omega cm^2)$ | (µm/year) |
| 0.5M Na ₂ SO ₄ | 30 min | -215.9 | 0.55 | 8.72 | 19.57 | 29.93 | 5.92 |
| | 1 h | -149.4 | 0.54 | 3.66 | 6.04 | 18.3 | 5.8 |
| 0.5M NaCl | 30 min | -177.3 | 0.35 | 6.23 | 8.1 | 45 | 3.77 |
| | 1 h | -164 | 0.33 | 7.1 | 9.3 | 53 | 3.55 |



Fig. 6 Comparative potentiodynamic diagram of nanostructured Ni – TiO₂ composite coatings

The corrosion potential is shifted to more negative value for nanostructure coatings in 0.5M Na₂SO₄ (-215.9 mV) for 30 min and positive values for same coatings in NaCl 0.5M (-177.3 mV). From potentiodynamic polarization curves the polarization resistance is 29.93 k Ω cm² in 0.5M Na₂SO₄ and in NaCl 0.5M for 30 min the polarization resistance is 45 k Ω cm² and the corrosion rate (corrosion current) is 0.55 μ Acm⁻² for TiO2–Ni nanocomposite coatings in 0.5M Na₂SO₄. In 0.5M NaCl solution was obtained a little bit smaller value by 0.35 μ Acm⁻² for same nanocomposite coatings.

The corrosion rate of the nickel layers tested in 0.5 M Na₂SO₄ solution indicate almost the same values for the measurements performed after 30 minutes and 1 h respectively. Anyway, for the samples obtained in 0.5M NaCl the corrosion rate is smaller.

4. Conclusions

The SEM micrographs for Ni–TiO₂ deposits indicate that the nanoparticles have a strong influence on the deposit surface morphology. With increasing time for immersion in solution the corrosion potential decreases, this improvement of corrosion resistance could be due to the fine surface structure of composite coating compared with pure nickel coating as well as to the incorporation of TiO₂ nanoparticles into composite coatings.

EIS methods are powerful techniques to investigate the corrosion protection properties of Ni-TiO₂ coatings. The corrosion behaviour depends on the electrodeposition conditions.

From experimental data it was observed that the corrosion rate is is bigger for nanostructured coatings in $0.5M \text{ Na}_2\text{SO}_4$ (5.92 µm/year) and a little bit smaller in 0.5M NaCl (3.77 µm/year).

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