

Electrodeposition and Characterization of Nickel-Titania Nanocomposite Coatings from Gluconate Baths

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Abstract– Ni–TiO₂ Nanocomposites with varying Titania content were electrodeposited on copper substrate employing gluconate electrolyte. The changes in microstructure and corrosion behavior of electrodeposited nickel with respect to Titania addition were studied. The Titania content in the coatings increased with increasing Titania content in the bath and decreased at high current density, the effect of pH shows an increase in Titania up to pH 8. Enhancement in hardness and corrosion resistance were observed due to titania Incorporation in Ni-matrix and also the addition of TiO₂ nanoparticles to the bath, affect the microstructure and the morphology of the nickel matrix as indicated from the X-ray diffraction (XRD) and scanning electron microscope (SEM) results.

Keywords– Ni-TiO₂ Nanocomposite, Electrodeposition, Corrosion Resistance and Polarization Curves

I. INTRODUCTION

Nanocomposites consisting of ultrafine particles of pure metals, ceramics, and organic materials, in an inert metal matrix have attracted extensive attention from science and technology since decades [1–3], due to their beneficial electrical [4,5], optical [5–7], magnetic [8,9] and mechanical [10–13] properties. In order to improve the utilizable properties of nickel layers, the coatings were co-deposited from baths containing metal oxides (TiO₂, Al₂O₃, Sc₂O₃, and NiO), carbide, nitrides or PTFE [14–17]. Such a procedure led to the production of layers with a composite structure, and was characterized by special properties: good catalytic activity, good corrosion resistance, heightened hardness or resistance to high temperatures. Methods available for the preparation of nanocrystalline films include candidates based on chemical solution growth, sol-gel chemistry and slurry spray/brush-coat techniques [18] and occlusion electrodeposition technique [19]. Research related to Ni–TiO₂ composite coatings has demonstrated that the codeposition percentage of nano-titania particles is difficult to be controlled quantitatively, because the particles are frequently agglomerated in the metal-matrix, as well as in the electrolyte due to their significant high surface energy. Given that TiO₂ particles seem to incorporate in a limited extend compare to other ceramic particles, like SiC particles in example [20].

A survey of literature shows that gluconate electrolytes were used to electroplate metals such as nickel [21], copper [22], tin [23] and zinc [24]. Organic additives have been found to affect the electrothrowing power of nickel from sulfate, chloride and Watts's bath. The objective of the present study

is to obtain nickel-titania composite from gluconate bath, in order to determine the dependence of coating characteristics on several electroplating variables and characterizes the obtained coatings by using different techniques such as SEM, EDX, and XRD and examine the coatings hardness and corrosion resistance.

II. EXPERIMENTAL

Solution bath listed in Table 1 used was freshly prepared from Analar chemicals and doubly distilled water. Copper sheet cathode and pure nickel sheet anode both of dimensions 2X2 cm² were used. The copper sheet cathodes were mechanically polished with different grade emery papers and then immersed in pickling solution (300ml H₂SO₄+100ml HNO₃+5ml HCl+595ml doubly distilled water) for 1min, washed with distilled water, rinsed with acetone, dried and finely weighed. The pH was measured using Microprocessor pH/mV/°C Meter (Model CP 5943-45USA) and adjusted by NaOH 20% addition, the temperature was controlled by using hot plate-magnetic stirrer (Philip Harris Ltd). Direct current was supplied by a d.c power supply unit (GP-4303D). The copper cathodes were weighed before and after electrodeposition for a certain period of time and at fixed current density. From the change in weights of the cathodes, the deposited weight was calculated; the composition was examined using the following procedures:

1. The coating layer is stripped using 10% H₂SO₄ solution. The object is then put as anode in an electroplating cell by which the coating layer will be dissolved in the solution, which is then diluted to 250 ml with bi-distilled water.
2. The analysis was done using Atomic absorption Spectrophotometer (Perkinelner3100, Germany).
3. The solution obtained is further diluted by dissolving 5ml in bi- distilled water to 250ml.
4. Nickel standard solutions for the elements to be detected were prepared (1g Ni metal in (1+1) HNO₃. Diluted to 1 L with 1 % (v/v) HNO₃), Ni, Air-Acetylene flame gases, wavelength of 232 nm.
5. The Titania weight was calculated by subtracting the obtained nickel weight from the total deposit weight.

The results are confirmed for some samples with EDX analysis.

The surface of the as-deposited nickel and nickel-titania, on copper substrates was morphologically inspected using scanning electron microscopy (SEM). (JEOL-5410 attached to

an EDX unit), phases of surface and phase changes of the different coated substrates investigated by using an X-Ray Diffractometer (Broker AXS-D8 X-ray diffractometer, ADVANCE, Germany), with a copper target ($Cu_{\lambda} = 1.5406 \text{ \AA}$) and Nickel filter, the obtained coating thickness was measured by taking cross section of the coated layer by using coating thickness /Neophot2-Optical microscope (Germany), Vickers microhardness of the deposits was measured under 50 gm. load microhardness of the specimen material by using a Shimdzu Hardness tester. The electrochemical experiments were performed using A VOLTA LAB 40 (Model PGZ301) with the aid of commercial software (Volta Master 4 version 7.08). A saturated calomel electrode (SCE) and a platinized platinum black were used as the reference and auxiliary electrodes, respectively with different deposited plates as the working electrode and the electrochemical cell was filled by 3.5% NaCl. Volta Master 4 calculates and displays the corrosion rate, Corr. in $\mu\text{m}/\text{year}$: this rate is calculated from the i_{corr} the corrosion current density found, the D density and the M atomic mass and V valence entered in the Tafel dialogue box. The calculation is performed as follows:

$$\text{Corrosion } \mu\text{m}/\text{year} = (i_{\text{corr}} \cdot (\text{A}/\text{cm}^2) \times M \text{ (g)}) / (D \text{ (g}/\text{cm}^3) \times V) \times 3270$$

With: $3270 = 0.01 \times [1 \text{ year (in seconds)} / 96497.8]$ and $96497.8 = 1 \text{ Faraday in Coulombs}$.

Table 1: The bath composition and operating conditions of nickel-titania composite

Nickel sulfate	0.2 mol/L
Boric acid	0.4 mol/L
Ammonium sulfate	0.4 mol/L
Sodium gluconate	0.2 mol/L
Titania(50 nm)	3-7 g/L
Temperature	30-70 ⁰ C
Current density	2.5-7.5 A/dm ²
pH	6-10
Time	10-60 min
Stirring speed	150 rpm

The same bath composition was used for Ni electrodeposition without Titania for comparison.

III. RESULTS AND DISCUSSION

A. Optimization of Nickel-Titania Electrodeposition Parameters

The effect of current density on the coating thickness is illustrated in Fig. 1. It is clear from these results that the thickness is increased with increasing current density up to 6.25 A/dm² and then after that decreased gradually. This may attributed to the fact that, increase in current density results in more rapid deposition of metal matrix and fewer particles are embedded in the coating. Hence, the metal deposition dominates the co-deposition process [25].

From Fig. 2, it is shown that the thickness of the composite is increased with increasing pH up to 8, after that the coating thickness is decreased due to the nickel hydroxide precipitation.

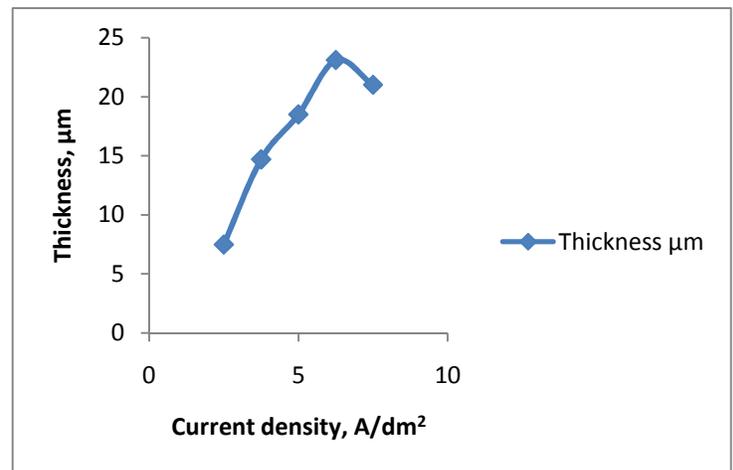


Fig. 1. Effect of current on thickness of the composites from bath containing, 0.2 mol/L NiSO₄.6H₂O, 0.2 mol/L C₆H₁₁NaO₇, TiO₂ 6 g/l, 0.4 mol/L boric acid, 0.4 mol/L Am.Sulfate, pH 8, temperature 25⁰C, time 20 min.

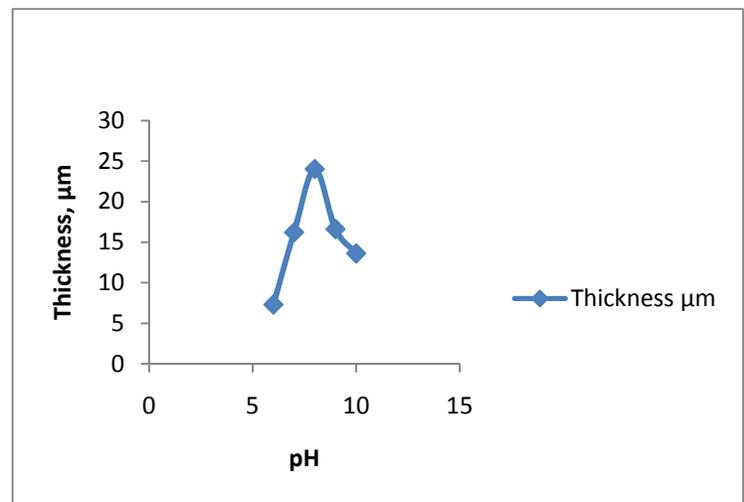


Fig. 2. Effect of pH on thickness of the composites from bath containing, 0.2 mol/L NiSO₄.6H₂O, 0.2 mol/L C₆H₁₁NaO₇, TiO₂ 6 g/L, 0.4 mol/L boric acid, 0.4 mol/L Am.Sulfate, i 6.2 A/dm², temperature 25⁰C, time 20 min.

The effect of plating time in the coating thickness was shown in Fig. 3. These results indicate that the thickness of coating is increased with increasing plating time and this is obeying Faraday's law.

One of the important parameter in the electroplating is the bath temperature. Fig. 4 shows that the coating thickness is increased with the temperature increase up to 60⁰C, after that the hydrogen evolution hinders the composite deposition.

B. Characterization of Nickel-Titania Composites

It is interesting to note that the rate of particle incorporation is higher at low current densities and levels off at higher current densities, Fig (5). This dependence of particle incorporation on the current density is consistent with *Guglielmi's* model [26]. At low current densities the codeposition process is controlled by the particle adsorption and hence the particle incorporation is dominant.

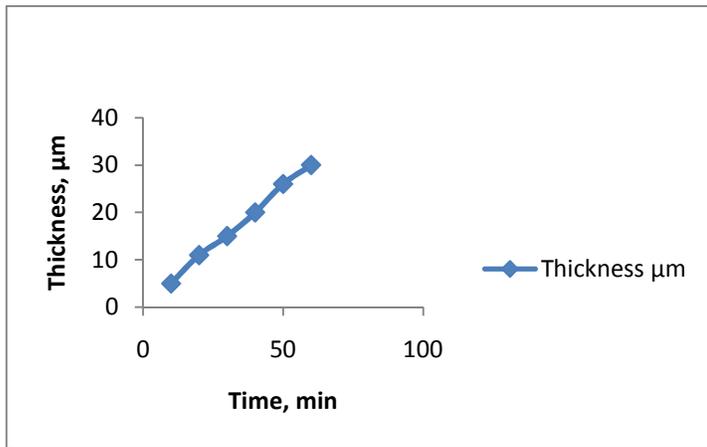


Fig. 3. Effect of time min on thickness of the composites from bath containing, 0.2 mol/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.2 mol/L $\text{C}_6\text{H}_{11}\text{NaO}_7$, TiO_2 6 g/L, 0.4 mol/L boric acid, 0.4 mol/L Am.Sulfate, i 6.2 A/dm^2 , temperature 25°C , pH 8.

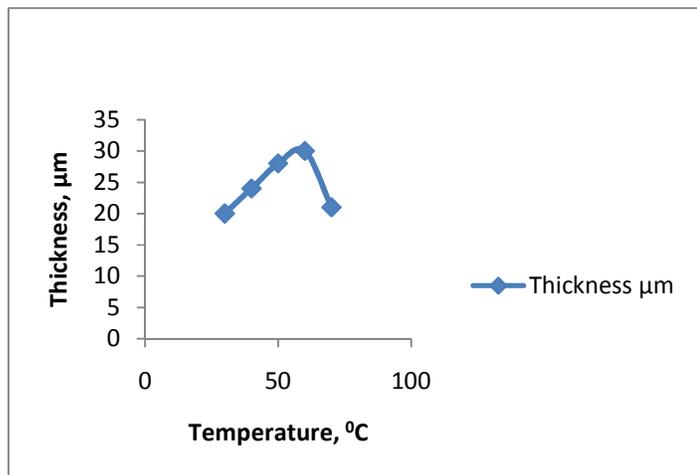


Fig. 4. Effect of temperature, $^\circ\text{C}$ on thickness of the composites from bath containing, 0.2 mol/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.2 mol/L $\text{C}_6\text{H}_{11}\text{NaO}_7$, TiO_2 6 g/L, 0.4 mol/L boric acid, 0.4 mol/L Am.Sulfate, i 6.2 A/dm^2 , time 20 min, pH 8.

EDX Fig. 6-7 show the charts of Ni-TiO₂ composites obtained at current densities 6.25 and 3.75 A/dm^2 , respectively.

X-ray diffraction, Fig (8a, 8b), shows that, the co-deposition of TiO₂ obviously affects the relative intensity corresponding to different crystal faces of nickel, the relative intensity corresponding to crystal face (111) decreases, but the relative intensity of crystal face (200) increases. For composite coatings, the peak of crystal face (220) is not clear; peak of (311) becomes strong with increasing of TiO₂ content. *Erlor et al.* [27] demonstrated that the XRD patterns of nickel nano-composite coatings indicate changes in texture of such coatings which are dependent on the plating current density and the particle content in electrolyte. The average grain size were 42nm. This result is closed to the results obtained by *X. J. Sun and J. G. Li* [28]

The effect of TiO₂ concentration (g/L) on titania content in the composite was shown in Fig (9) and confirmed by the results of EDX Fig (10) in which exhibited an increase in the particle incorporation with increasing particle content of the electrolyte. This behavior can be understood in terms of the

two-step adsorption model of *Guglielmi* [26] which quantitatively describes the influence of particle content in the electrolyte and the current density on the particle incorporation. In the first step the particles become loosely adsorbed on the electrode surface and stay in equilibrium with the particles in solution [29]. The particles are still surrounded by a thin layer of adsorbed ions and solvent molecules governing the interaction between the particles and the electrode. An increase of the particle concentration in the electrolyte causes an increase of the particle adsorption rate. In the second step the shell of adsorbed ions is broken by the electrical field at the interface followed by a strong adsorption of the particles onto the electrode. This result is in agreement with results obtained by *D. Thiemig and A. Bund* [30]. The asymptotic behavior of the particle incorporation with increasing current density can be attributed to the faster deposition of the metal matrix [31].

The effect of pH on Titania content of the composite was shown in Fig. 11 which show that the content of titania increased with pH and decreased after pH 8 due to the formation of $\text{Ni}(\text{OH})_2$, the nickel films from the alkaline bath contained significantly higher amounts of particles, There seems to be a tendency that negatively charged oxide particles are preferentially codeposited in cathodic processes, at least in solutions containing divalent cations. To explain this counter-intuitive behavior were proposed an electrostatic model [32-34] that takes into account the charge distribution on the particle and electrode surface. In the alkaline electrolyte the TiO₂ nanoparticles are negatively charged, whereas in the acidic one they bear a positive charge. Under the condition of the nickel electroplating process, the electrode bears negative excess charges [34]. According to the model negatively charged particles are preferentially attracted by the positive excess charges in the electrolytic part of the electrical double layer of the electrode (EDL). When the particle has come close to the electrode the shell of adsorbed ions on the particle is stripped off within the EDL of the electrode. Finally the particle becomes incorporated into the growing metal layer.

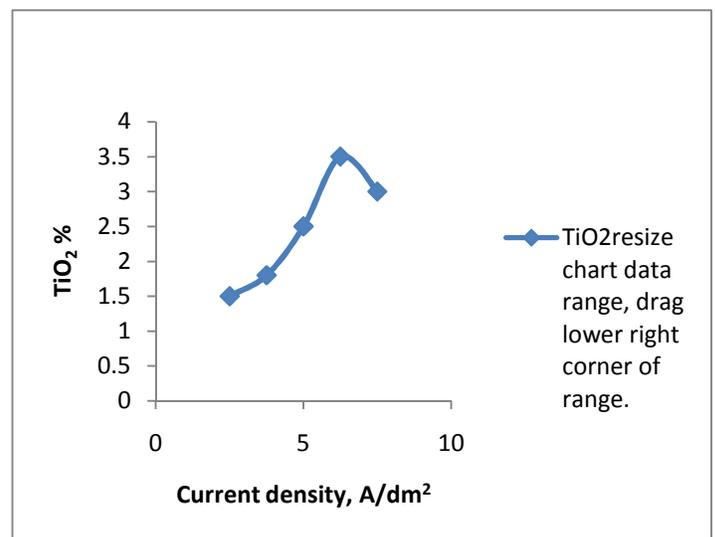


Fig. 5. Effect of current on TiO₂ % in the composites from bath containing, 0.2 mol/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.2 mol/L $\text{C}_6\text{H}_{11}\text{NaO}_7$, TiO_2 6 g/L, 0.4 mol/L boric acid, 0.4 mol/L Am.Sulfate, pH 8, temperature 25°C , time 20 min.

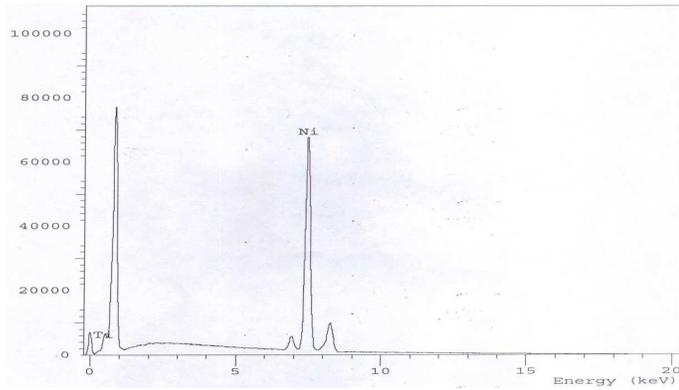


Fig. 6. EDX chart of Ni96.5%-TiO₂ 3.5% composite from bath containing, 0.2 mol/L NiSO₄.6H₂O, 0.2 mol/L C₆H₁₁NaO₇, TiO₂ 6 g/L, 0.4 mol/L boric acid, 0.4 mol/L Am.Sulfate, pH 8,temperature 25°C,time 20 min, i 6.25A d/m².

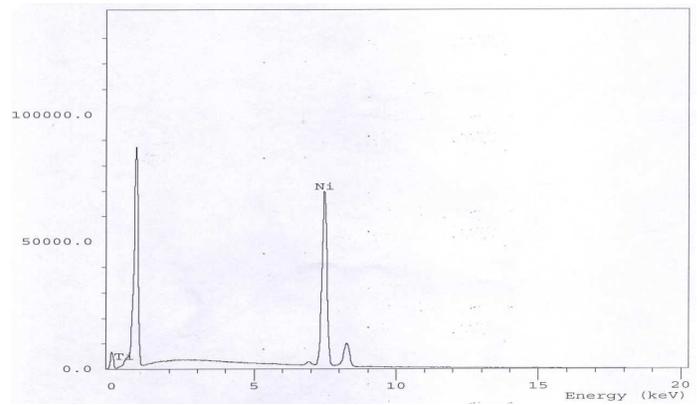


Fig. 7. EDX chart of Ni97.2%- TiO₂ 1.8% composites from bath containing, 0.2 mol/L NiSO₄.6H₂O,0.2 mol/L C₆H₁₁NaO₇, TiO₂ 6 g/L, 0.4 mol/L boric acid, 0.4 mol/L Am.Sulfate, pH 8,temperature 25°C,time 20 min, i 3.75A/dm².

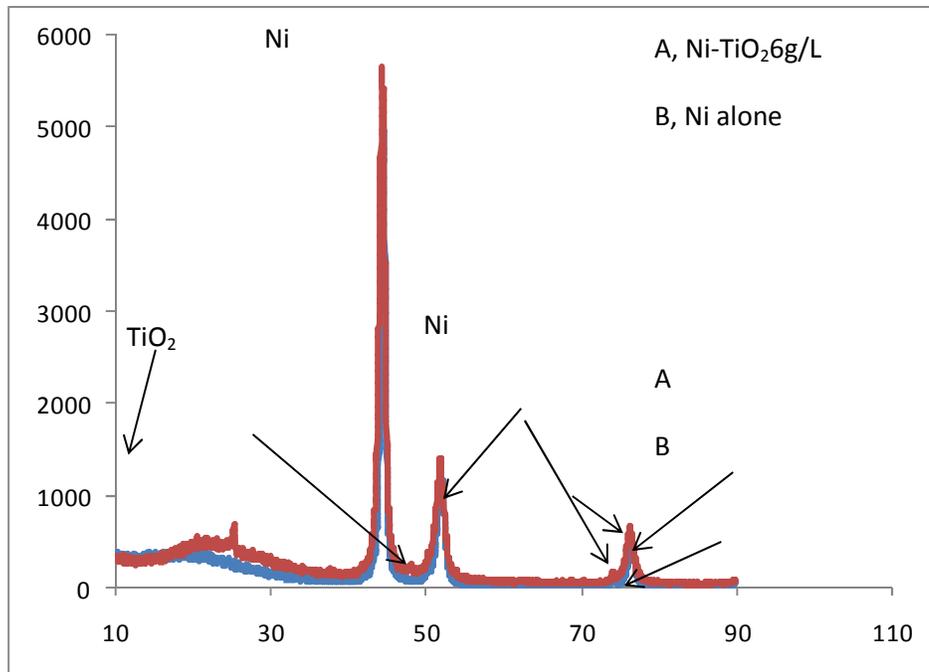


Fig. 8 (a, b). XRD chart of (a) Ni96.5%-TiO₂ 3.5% composite from bath containing, 0.2 mol/L NiSO₄.6H₂O, 0.2 mol/L C₆H₁₁NaO₇, TiO₂ 6 g/l, 0.4 mol/L boric acid, 0.4 mol/L Am.Sulfate, pH 8,temperature 25°C,time 20 min, i 6.25A d/m². (b) Ni obtained from gluconate bath containing, 0.2 mol/L NiSO₄.6H₂O, 0.2 mol/L C₆H₁₁NaO₇, 0.4 mol/L boric acid, 0.4 mol/L Am.Sulfate, pH 8,temperature 25°C,time 20 min, i 2.5 A d/m².

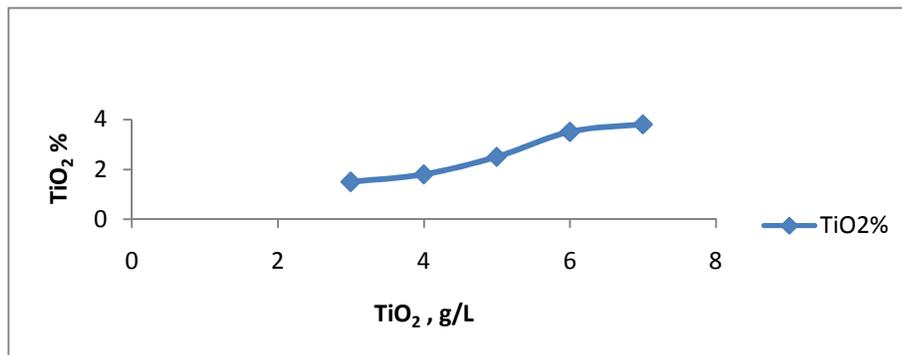


Fig. 9. Effect of TiO₂ g/L on theTiO₂ % from bath containing, 0.2 mol/L NiSO₄.6H₂O, 0.2 mol/L C₆H₁₁NaO₇, 0.4 mol/L boric acid, 0.4 mol/L Am.Sulfate, pH 8, i 6.25 A/dm², temperature 25°C,time 20 min.

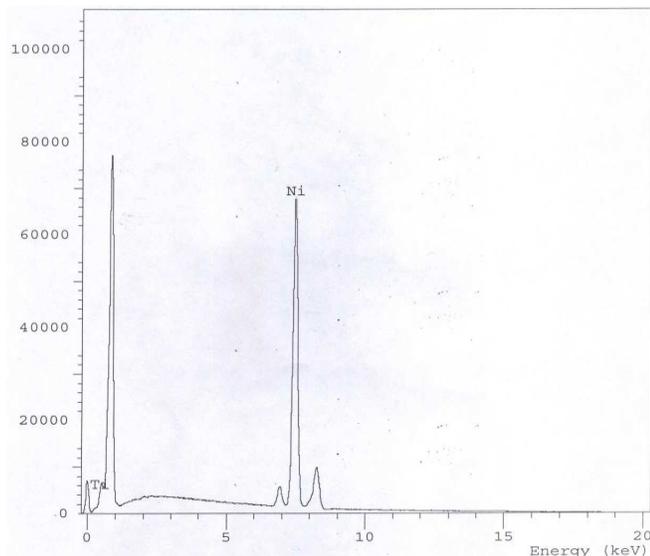


Fig. 10. EDX chart of Ni96.5%-TiO₂ 3.5% composite from bath containing, 0.2 mol/L NiSO₄.6H₂O, 0.2 mol/L C₆H₁₁NaO₇, TiO₂ 6 g/L, 0.4 mol/L boric acid, 0.4 mol/L Am.Sulfate, pH 8, temperature 25°C, time 20 min, i 6.25A d/m².

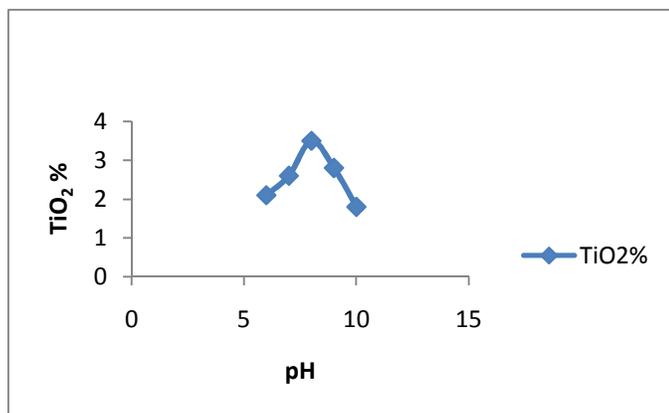


Fig. 11. Effect of pH on TiO₂ % on the composites from bath containing, 0.2 mol/L NiSO₄.6H₂O, 0.2 mol/L C₆H₁₁NaO₇, TiO₂ 6 g/L, 0.4 mol/L boric acid, 0.4 mol/L Am.Sulfate, i 6.2 A/dm², temperature 25°C, time 20 min.

C. Surface Morphology of Ni-TiO₂ Composite Coating

The addition of Titania nanoparticles to the bath obviously affects the surface morphology of the coatings (Fig. 12-13). The Titania particles appear as light spots in the darker nickel matrix. Due to the addition of TiO₂ nanoparticles to the bath the microstructure of the nickel matrix changed from spherical (Fig. 12) to granular (Fig. 13).

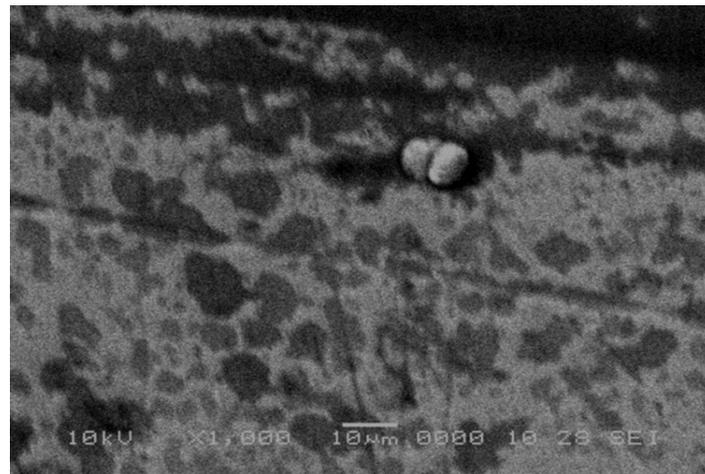


Fig. 12. SEM of nickel deposited from bath containing 0.2 mol/L NiSO₄.6H₂O and 0.2 mol/L C₆H₁₁NaO₇ with 0.4 mol/L boric acid and 0.4 mol/L ammonium sulfate at pH 8, time 20 min and temperature 25°C, current density 2.5 A/dm².

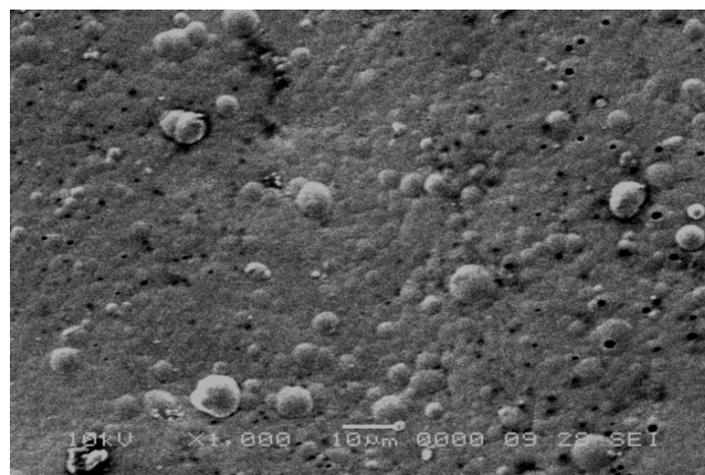


Fig. 13. SEM of Ni96.5%-TiO₂ 3.5% composite coating from bath containing, 0.2 mol/L NiSO₄.6H₂O, 0.2 mol/L C₆H₁₁NaO₇, 6g/L TiO₂, 0.4 mol/L boric acid, 0.4 mol/L Am.Sulfate, pH 8, i 6.25 A/dm², temperature 25°C, time 20 min.

D. Microhardness

The incorporation of TiO₂ in the coating increased the hardness, in the case of TiO₂ 3.5% the observed hardness was 440HV₅₀ instead of 340HV₅₀ in the case of pure Ni coating.

E. Potentiodynamic Polarization Curves

The Corrosion behavior of Ni-TiO₂ composites and Ni deposited from gluconate and copper substrate for comparison is illustrated in Fig (14) and table (2). It can be seen from the curves that a passive region was observed for the composite, indicating that anodic reaction was inhibited to a certain extent with the increase of anodic potential. In addition, it was showed much lower anodic current densities compared within the Ni or copper substrate confirmed by the lower corrosion rate obtained.

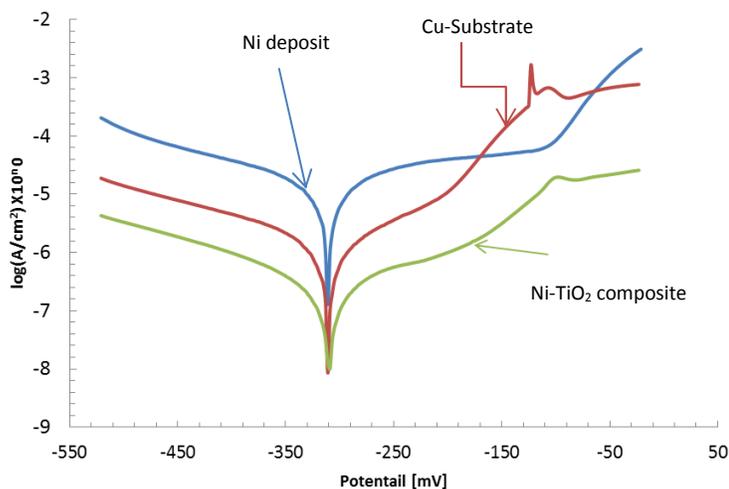


Fig. 14. Potentiodynamic polarization curves of Cu-Substrate, Ni, and Ni-TiO₂ obtained in 3.5% NaCl solutions.

Table 2: Corrosion Data for Cu base, Ni and Ni-TiO₂ obtained from NaCl 3.5% solutions

	E(i=0)) corr. mV	i corr. μA/cm ²	Rp kohm.cm ²	Bet a a mV	Bet a c mV	Corrosio n μm/Y
Cu Bas e	- 315.0	6.2359	1.93	73.4	- 82.7	72.40
Ni- Glu	- 228.7	0.5479	17.83	64.3	- 66.2	6.362
Ni- TiO ₂	- 264.3	120.11	100.77	66.5	- 78.8	1.394

IV. CONCLUSION

In Ni-TiO₂ nano composite, the amount of TiO₂ incorporated is directly increased with increasing the amount of particles present in the bath, however, the applied current density and pH of the electrolytic solution critically affects this amount of incorporation because the particles amount in the deposits increased with increasing current density and pH to certain degree and then decreased (i, 6.25 A/dm² -pH, 8 in this study). The incorporation of TiO₂ nanoparticles affects the structure of Ni-matrix and enhances the hardness and corrosion resistance of the copper substrate and Ni deposited without TiO₂.

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