Structural mechanical and corrosion performance of electrodeposited Ni-Nb coatings

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This research paper presents an experimental study that examines the effects of current density on Ni-Nb thin film morphology, structure, mechanical properties, and corrosion resistance. Ni-Nb coatings were effectively deposited onto copper substrates using direct current (DC) electrodeposition technique. The produced films were analyzed using XRD and SEM in order to determine the phase structure and morphology, respectively. Electrochemical measurements were conducted on a Corrtest CS 350 electrochemical workstation at room temperature in a 1M HCl solution. The results indicated that the variations in current density resulted in different Ni-Nb morphologies. For current density of 0.01 A/cm² coatings showed a compact and crack-free. The grains were hemispherical in geometry and acicular. In 1 M of HCl solution Ni-Nb

films confirmed that Nb incorporation into Ni matrice demonstrated improvement in corrosion performance.

(Received November 19, 2024; Accepted February 17, 2025)

Keywords: Electrodeposition, Ni-Nb coatings, Corrosion resistance

1. Introduction

Considering the significant proprieties exhibited by copper (Cu) as excellent electrical and thermal Conductivity, bright formability, attractive Color (Aesthetic Appearance), and alloy ability, Cu widely utilized in many applications; such as building construction, electronic products, transportation, industrial machinery and also medical field. So Cu surface is often under the menace of wear and corrosion, resulting in significant economic and industrial losses. Consequently, Continuous surface treatments are required. A variety of surface treatments such as thermochemical, mechanicals, heat, and coatings are applied. Coatings technology in particular considered one of the best solutions found since it protects and improves the performance and lifetimes of industrial parts.

Electrodeposition in particular is an old, low-cost, simple, and efficient technology, wellknown in surface engineering that allows the production of alloy coatings of high quality and outstanding futures by picking specific electrodeposition parameters. Nickel Ni is a refractory characterized by significant microhardness and promising tribological properties. In a weakly acidic or alkaline milieu, including air, Ni considered an excellent corrosion resistance material, thanks to its easy passivation behavior [1,2] that make it good chose for wide range of industrial application. Despite this, electrodeposited Ni coatings are subject to some limitations when exposed to acid solutions [3].

It was reported in many experiments that the electrodeposited Ni-based alloys could offer better surface performance [4]. Interesting systems include Ni–Co [5], Ni–B [6], Ni–Zn [7], Ni–W[8] and Ni–Fe [9], and Ni-Cu [10] proved optimized micro hardness, wear, and corrosion properties.

As a result of passivation, Nb exhibits a low corrosion rate in all aqueous solutions, compared to Ni [11]. Therefore, Alloying with Nb significantly enhances both corrosion resistance and mechanical properties, making it a compelling choice for improved material performance.

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Ni-Nb successfully deposited with different methods; mechanical alloying [12], High current pulsed electron beam (HCPEB) [13], and electrodeposition [14]. However, very limited studies on electrodeposition of Ni-Nb were reported. *A. Robin, et al* [14] prepared a series of Ni–Nb composite on carbon steel utilizing electrodeposition method. Pure Ni coatings with [110] orientation exhibited smooth surface morphology, however Ni-Nb composite coatings showed a random Ni grain orientation with high surface roughness. Compared to pure Ni layers, Ni–Nb films deposed at 20 and 40 mA cm⁻² showed improved microhardness and enhanced corrosion resistance in NaCl and H₂SO₄ solutions.

In this paper, Ni–Nb composite coatings deposited on copper substrates affect the electrodeposition method. The obtained coating's structural and mechanical properties were studied as a function of current density. Corrosion resistance was also evaluated in a 1M HCl solution. Experimental procedure

2. Experimental

2.1. Deposition process

Copper with a dimension of (2x1) cm was used as a substrate. Niobium Nb elementary powder with 99.94 % purity and an average particle size of 100 µm was used to produce Ni-Nb coating, SEM image of a powder particle of Nb is shown in Figure.1. The powder was milled using a high energy ball mill, Fritsch P7 for 18 h. [15]. Electrodeposition method was used to deposited Ni–Nb coatings. The composition of the bath and the deposition conditions are given in Table 1. Copper samples with 20 mm x 10 mmx 1 mm dimensions served as cathodes. Samples were processed in three steps, (1): mechanical polishing with SiC abrasive paper (120 – 4000) Track by rinsing with distilled water and kept in an acetone solution. (2): degreasing in a solution containing (50 g.l⁻¹ Na₂CO₃ and 15 g.l⁻¹ NaOH) to eliminate greases. (3): pickling in 10% HCl solution to remove oxides trace, and finally (4): washing with bi-distilled water [16].

Ni–Nb coatings were obtained by electrodeposition method varying the current densities from (0.01 to 0.09A.dm⁻²). For the anodes, two nickel sheets (30 mm x 10mm x 4mm dimensions) of commercial purity (99.99%) were used. The cathode (copper) and anode (nickel) were separated by a distance of approximately 10 mm. Bath pH was adjusted by introducing either HCl or NaOH solutions.

Electrolytes	Concentrations	Deposition conditions		
NiSO4·7H2O	52 g/l	Température (⁰ C)	70	
H ₃ BO ₃	24 g/l	Deposition Time (min)	30	
NaCl	40 g/l	pH	3	
C7H5NO3S	0.1 g/l	Current density (A.cm ⁻²)	0.01-0.09	
Nb size of 100 µm	20g/l			

Table 1. Composition of the electrolyte bath and Ni–Nb deposition conditions.

2.2. Material characterization

Ni-Nb coatings' adhesion to the substrates was assessed through the thermal choc, which involved heating samples to 250 °C for 30 minutes and then immersing them in room temperature water. [17]. The morphology of Ni-Nb coatings was thoroughly examined using scanning electron microscopy, (SEM) (FEI QUANTA 200), for structure, and for phases we utilized X-ray diffractometer (XRD, Mini Flex 600, Rigak) with Cu K_{α} radiation (1.5406 A°).

The hardness of Ni-Nb films was assessed using Vickers microhardness (Wilson 402UD Wolpert instrument). A consistent load of 100 Nwas applied over 30 seconds. The average measure was determined based on a minimum of five measurements from different zones in each sample. Using the corr test potentiostat CS350 and the traditional three-electrode system, electrochemical tests were conducted to better understand the wear behavior of Ni-Nb coatings.

The saturated calomel is designated as the reference electrode, the platinum (Pt) serving as the auxiliary electrode, and Ni-Nb coating featuring an exposed area of 1 cm², is utilized as the working electrode. The electrodes were submerged in a 1 M of hydrochloric acid (HCl) solution at room temperature, and the open circuit voltage (Eocp) was tested in the free state after immersing samples in a 1 M of HCl solution for 30 min.

3. Results and discussion

3.1. Ni-Nb coating morphology

According to thermal shock test and visual assessment Ni-Nb coatings demonstrated satisfactory adhesion to substrates (Cu). Figure.2 shows the electrodeposited Ni-Nb composite surface morphology grown at different current densities. SEM images indicated that variations in current density can significantly influence coating morphology. For the lower current density of 0.01 A.cm^2 , all electrodeposited coatings showed compact and crack-free surface, the grains were hemispherical with good distribution on the substrate surface This morphology was observed by *Y*. *Deo et al* [18] for Cu-Ni coating deposited at low current densities.

Increasing current density to 0.03 A.cm⁻², the composite coating surface showed an inhomogeneous granular shape resulting in higher surface roughness.

For current density elevated to 0.05A.cm⁻² the produced Ni-Nb coating exhibited a remarkable changes in the microstructure, where SEM images revealed a remarkable inhomogeneous agglomeration of large spherical grains suggesting an island growth [19], the same shape of spheres was observed in a recent study [20]. The detection of *Stranski–Krastanov* growth mode for this current density could be justified by the insufficient nucleation potential. Ion transport control deposition in bulk solutions, the small nucleation potential, favorites the island growth kinetic regime consequently island shape is probable to dictate. [19].

Furthermore, increasing current density to $I = 0.09 \text{ A.cm}^2$ revealed the return to compact and crack-free that was observed for lower current density (0.01 A.cm⁻²), but with small and refined grains size however, a granular and spherical agglomeration was detected on the top of the coating surface. This densification might be due to the increased applied current creating higher energies of adatoms and higher mobility.



Fig. 1 SEM image of a powder particle of Nb.



Fig. 2. SEM image of Ni-Nb coatings at: a) 0.01A./cm-², b) 0.03A.cm-², c) 0.05A.cm-², d) 0.09A.cm-².

3.2. Ni-Nb coatings grain size

Figure.3 exhibit the effect of current density variation on grain size changes. The grain size was found to have a relation with current density changes. The increase in current density from 0.01 A.cm⁻² to 0.05 A.cm⁻² followed by an increase in grain size from 27.23 nm to 39.64 nm respectively, this increase may be achieved from the decrease in nucleation rate produced from the insufficient over potential [21]. However, further increasing current density to 0.09 A.cm⁻² a refined structure of about 25.64 nm was obtained.



Fig. 3. Grain size of Ni-Nb composite as function of current density.

3.3. Ni-Nb coatings structure

XRD patterns of the electrodeposited Ni-Nb coatings taken at different current densities (I=0.01A, 0.03,0.05, and 0.09) are shown in Figure 4.

The diffraction pattern of Ni-Nb coating deposited at 0.01A showed four main diffraction peaks referred to Ni₃Nb, Ni, Ni_{0.890}Nb_{0.151}, andNi₃₅₇Nb₅ phases; Ni₃Nb at 43.4°, Ni at 44.1°, Ni_{0.890}Nb_{0.151}at 50.46°, and Ni₃₅₇Nb₅ at 74.18°. The crystallographic plans for the corresponding peaks are (012), (111), (002), and (357) respectively. The increase in current density, resulted in remarkable changes in the position of Ni-Nb and Ni peaks, width, intensity, and relative abundances. We can see clearly that the increase in current density affected the Ni-Nb crystallization, and the solid solution formation, that confirmed by SEM images, and the change in grain size.

With increasing current density to 0.03A, Ni peak at $2\Theta = 44.36^{\circ}$ still existed in the XRD pattern but with elevated intensity, Ni₃Nb shifted to higher angle $2\Theta = 74.02^{\circ}$ with (220) orientation.

At I=0.05A we detected the disappear of Ni $_{0.890}$ Nb $_{0.151}$, and NiNb₅ phases, and the appearances of new orientation of (002) at 44.36° and 51.76° respectively and the appearance of Ni₃Nb (220) phase at 74.06° and the amorphous Ni (022) at 76.44°.



Fig. 4. XRD of Ni-Nb composite as function of current density.



Fig. 5. Microhardness of Ni-Nb coatings as function of current density.

3.4. Corrosion performance of Ni-Nb coatings

3.4.1. Electrochemical impedance spectroscopy measurements

Using the impedance technique, corrosion behavior of produced coatings was investigated. Ni-Nb coatings were immersed in a 1 M HCl solution for 30 minutes, impedance spectra were documented as a function of various current densities. Typical impedance spectra of the coatings are shown in Figure 5.

Nyquist impedance plots had a slight decline in semicircle shape. The equivalent circuit diagram consists of Rs, which is the solution resistance (Ω .cm²), representing the resistance of the electrolyte between the counter electrode and the working electrode; Rp is the charge transfer resistance (Ω .cm²); and (CPE) constant phase angle element representing a double-layer electrolytic capacitor is added to suit. The parameters CPE-T (F.cm⁻²) and CPE-P, which represent the CPE constant and the CPE index, respectively, were used to interpret the impedance spectra of the coatings (Fig.6).

It can be noticed from Table 3 that with increasing current densities, Rp decreases. Rp reaches the maximum at a current density of 0.01 A.cm⁻², a significant corrosion resistance was detected as a result.

While an opposite trend is shown essentially by Y0 and charge transfer resistance Rct. For I= 0.01 A.cm $-^2$, the IE is the most elevated, getting 90.04%. Ni and Ni-Nb charge transfer resistance increases can be attributed to the passivation process, in which a thin passive film is formed on the coating's surface. Corrosion-active types originate from the electrolyte due to gradual penetration into the substrate through finer pores and grain boundaries, which later appear as pits on the surface.



Fig. 6. Nyquist plots of Ni-Nb coatings deposited at different current densities in a 1 M of HCl solution.



Fig. 7. Equivalent circuit of Nyquist diagrams.

	Rs (Ω .cm ²)	CPET (F cm ⁻²)10 ⁻³	CPEP (F cm ⁻²)	$Rp(\Omega.cm^2)$	IE (%)
Ni	12.515	4.7146	0.81035	26.482	00
0.01 A/cm2	1.8012	2.7015	0.84481	266.88	90.04
0.03 A/cm2	1.9822	3.5365	0.81702	38.785	31.72
0.05 A/cm2	1.3984	0.87061	0.70818	105.22	74.83
0.09 A/cm2	1.7277	0.56265	0.77047	109.05	75.71

Table 2. Electrical parameters deduced from fitting impedance data.

3.4.2. Polarization measurements

The Tafel polarization curves for Ni and Ni-Nb plotted against the applied current densities are shown in Figure 7. The measurements were performed at room temperature in a 1 M HCl solution. Table 3 provides the appropriate experimental parameters derived from the Tafel linear fit method. The obtained polarization curves of the anodic and cathodic branches were recorded individually at a low scanning speed of 0.5 mV.S⁻¹ on freshly prepared electrodes. The results received from the Tafel curves reveal a strikingly consistent trend with those derived from electrochemical impedance spectroscopy (EIS). We note that the rate of oxygen reduction within the potential range of -0.45 to -0.40 V is unaffected by the increase in current density (from 0.03 to 0.09 A.cm⁻²). Furthermore, a slight increase in the discharge of excess hydrogen was detected for more negative potentials. Commonly, a higher Ecorr and a lower icorr indicate superior corrosion resistance. Consequently, Ni-Nb coatings deposited at a current density of 0.01 A.cm⁻² demonstrate the best corrosion resistance properties.



Fig. 8. Tafel polarization curves of the Ni and Ni-Nb coatings versus the applied current densities in a 1 M HCl solution at room temperature.

Table 3. Polarization measurements o	f Ni-Nb coatings	deposited at various	current density in I	l M HCl.
	,			

J (A/cm ²)	$b_a (mV)$	b _c (mV)	i ₀ (A/cm ²)10 ⁻³	E ₀ (Volts)	Corrosion	IE (%)
					rate(mm/y)	
Ni	166.86	190.68	1.3281	-0.39275	15.58	00
0.01 A/cm ²	63.459	360.04	0.045333	-0.2077	0.53181	96.58
0.03 A/cm ²	203.79	173.4	0.80124	-0.42427	9.3995	39.66
0.05 A/cm ²	173.66	183.03	0.23753	-0.42398	2.7865	82.11
0.09 A/cm^2	245.53	225.77	0.2566	-0.40893	3.0102	82.41

4. Conclusions

Ni-Nb coatings were fabricated through electrodeposition by adjusting the current density between 0.01 and 0.09 A cm⁻². According to the experimental studies, the following insights can be derived (1): Ni-Nb coatings electrodeposited at a current density of 0.01 A.cm⁻² showed compact and crack-free of hemispherical grains. However, increasing current density led to undesired non-homogeneous and increased grain size. (2): The finer grainsize of 27.23 nm corresponds to coating deposited at 0.01 A.dm⁻² delivered the best microhardness of 606 *Hv*. (3): the most desirable corrosion performance was detected to coating with finer grain size and higher mechanical proprieties.

Acknowledgments

The authors are grateful to Dr F. LAKMINE from AbbesLaghrour university, Khenchela, Algeria, and to Physics laboratory of Thin Layers and Applications, Biskra University, BP 145 RP, Biskra, Algeria for their financial support.

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