Microstructural, morphological, mechanical and tribological characterization of nanocrystalline nickel and Ni-Co electrodeposited coatings

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Abstract
The nanocrystalline nickel and nickel-cobalt coatings were electrodeposited on an A60 steel substrate in a modified Watts bath. The observation of the coatings produced by scanning electron microscopy (SEM) showed that the nickel coatings have a granular structure whereas the Ni-Co alloy deposits have a lens-shaped structure with a considerable increase in the grains size of the Ni-Co alloy deposits. Analysis by profilometer confirms these results where we find that the surface roughness of nano-crystalline nickel coatings is less than that of Ni-Co alloy coatings. The results of XRD showed that the nickel coatings have an fcc phase structure while the Ni-Co coatings have a mixed phase structure hcp + fcc. The study of micro-hardness of the coatings show that this latter follow the Hall Petche effect where nickel deposits which have the small grain size compared to that of the Ni-Co alloy show a higher microhardness to that of Ni-Co coatings. Pin on disk tribometric analysis under unlubricated conditions showed a great improvement of the wear resistance by the addition of cobalt on the nickel coatings, where the friction coefficient and the wear rates are reduced to very significant manner in the Ni-Co coatings compared with nickel coated.

Keywords — Nickel coatings; Ni-Co coatings; Microstructure; Morphology; Micro-hardness; Tribological properties.

I. INTRODUCTION

The electrodeposited nickel coatings are used in a large range of applications to improve the hardness [1], and corrosion resistance [2], and wear resistance of the coated components [3]. In order to improve performances of nickel coatings, different approaches have been applied. Alloying with other elements [4,5], structural refinement using additives (grain size reduction)[6,7], and deposition of composite coatings by dispersing reinforcing particles inside the Ni matrix [8,9]. The alloying of Ni with cobalt is one of the technical commonly used for improve the properties of nanocrystalline nickel coatings. The Ni-Co alloys have been investigated as important engineering materials for several decades due to their unique properties, such as high resilience [10], good corrosion resistance [11], thermal conductivity [12], electro-catalytic activity [13] and their magnetic properties [14]. In this work, we will try to give more value to these alloys coatings, and this by proof of their good tribological properties. For this, a comparison was made between the microstructural and morphological properties of high cobalt content nanocrystalline Ni-Co alloy coating (89% Co) with a nanocrystalline nickel coating produced electrochemically. Thus, a correlation between these properties and the mechanical and tribological properties of these deposits was made.

II. EXPERIMENTAL METHODES AND MATERIALS

A. Substrate preparation
The nanocrystalline nickel and Ni-Co electrodeposited coatings were electrodeposited on an A60 mild steel substrate with an exposed area of 3.14 cm². Before electrodeposition, the substrate was subjected to some surface treatment operations, mechanical polishing with SiC abrasive papers with decreasing grain sizes (80 to 4000), chemical degreasing for 10 min in an alkaline solution of pH 11 by means of an ultrasonic bath, Chemical polishing in a solution of hydrochloric acid (10% by volume) for 30 sec.

B. Electrodeposition of nanocrystalline nickel and Ni-Co alloy coatings
Two electrolytic baths are used in this work. A bath contains NiSO₄ (200 g/l), NiCl₂ (20 g/l) was used for the preparation of nanocrystalline nickel coatings, and a bath contains NiSO₄ (200g/l), NiCl₂ (20g/l), CoSO₄ (200g/l) used for the preparation of Ni-Co alloys coatings with 88% cobalt content. In each bath, boric acid (30 g/l) was added as a buffer to fix the pH at 4.2 ± 0.05 and to limit the alkalization of the solution around the substrate, the saccharine (2 g/l) and BD (0.5 g/l) were added as brighteners to refine crystallites size. A pure nickel disc (purity = 99.99%) provided by SANIAK-BCR Company (Ain-Kbira...
SETIF) was used as a soluble anode, the bath temperature was maintained at 318 K using a thermostatic bath with water circulation, the current density was fixed by 309N Autolab galvanostat-potentiostat at 4A /dm² for a period of 1200 sec to obtain deposits with thicknesses of 20 ± 5 µm.

C. Morphological and microstructural characterization

A JEOL JSM-7001F scanning electron microscope (SEM) (lab. Univ.Sétif DAC-HR-1) was used to characterize morphological and microstructural properties of elaborated deposits, the composition of deposits was determined by electron scattering spectroscopy (EDS) which coupled with SEM. The crystal structure and grain size were characterized by a D8 Avanced Bruker X-ray diffractometer (XRD) (lab.SDM-USTHB), the grain size was calculated according to the Scherrer equation.

D. Mechanical and tribological characterization

The microhardness of the deposits is determined by the use of a Vickers micro-indentener (lab.LPMM Univ.Sétif) under a load of 50 g for a 15 second holding time, five measurements were made at different places in the coating. The tribological behavior of the coatings was studied by the use of a NANOVIA pin on disc tribometer (lab.LMNM Univ.Sétif-1), at room temperature and 34-40% humidity under a load of 3N and with a sliding speed of 5 mm s⁻¹ for a total sliding time of 10 min, an AISI 1040 hard steel ball (Ø = 6mm, hardness HV = 700) was used as a counterpart, the friction coefficient in function of time was automatically calculated during the test, 2D images of wear tracks (50 folds magnification) were taken by Carl Zeiss optical microscope connected with a CCD camera (lab.LPMM Univ.Sétif 1), the wear rate was evaluated by the measurement of the mass lost.

III. RESULTS AND DISCUSSIONS

A. Composition of the coatings

The figure 1 shows the percentage of cobalt \( \frac{[\text{Co}]}{([\text{Co}]+[\text{Ni}])} \) (%) in the electrolyte and in the Ni-Co coating. It is clear that the cobalt percentage in the coating (87%) is higher than that in the bath (47%), this despite that the concentration of Ni²⁺ ions in the bath is greater than that of Co²⁺ ions. This can be explained by the anomalous co-deposition mechanism of Ni-Co alloys, where the less noble element cobalt is deposited preferentially compared to nickel. Several authors working on the co-deposition of Ni-Co alloys noticed the same appearance [14, 15], it is also noted that the thickness of nanocrystalline nickel coatings is about 25 µm, this thickness decreases to about 17 µm in the Ni-Co coatings with 87% cobalt content, which indicated that the deposition rate is reduced by the addition of cobalt in the nickel electrolyte due to the anomalous co-deposition phenomenon.

B. Morphological and structural properties of coatings

The SEM observations of the nanocrystalline nickel and Ni-Co elaborated deposits are shown in Figure 2 a-b, the nanocrystalline nickel is characterized by a smooth surface, while the Ni-Co coatings with high cobalt contents (87% Co) are characterized by a cluster-porous morphology, we also note the appearance of a microscopic porosity in deposits with 87% cobalt content, the change of the smooth surface to cluster-porous morphology is explained by the change of the crystal structure from fcc to hcp phase when we add the cobalt on the nickel coatings as we see in Figure 3, which indicates that the cobalt addition on the nickel coatings has a significant influence on the surface morphology of deposits.

![Figure 1: cobalt proportion in the electrolyte and in the Ni-Co coatings.](image1)

![Figure 2: SEM observations of nanocrystalline coatings: (a) nickel, (b) Ni-Co with 87% cobalt content.](image2)

X ray diffractograms in Figure 3 show that the cobalt content has a great influence on the phases crystal structure of coatings, where we note that the pure nickel deposits are characterized by a fcc phases structure, and with the addition of cobalt in the coatings we notice that the fcc phase is completely disappeared and a new hcp phase which has very good tribological characteristics [16, 17] is appeared. Several authors [18-19] working on the development of Ni-Co arrive at the same results.
C. Microhardness of coatings

The figure 4(a) shows the microhardness of the pure nanocrystalline Ni coating and Ni-Co alloy coating with 87% Co content. And the figure 4(b) shows the grain sizes of the two coatings. The grain size of the deposited coatings was deduced from XRD peak broadening analysis and was calculated using the Scherrer equation: $D = \frac{k\lambda}{\beta \cos \theta}$ [20], where $D$ is the average crystallite size, $\lambda$ is the X-ray wavelength in nanometer (nm) in our case $\lambda \text{CuK}_\alpha = 0.15405$ nm, $\beta$ is the peak width of the diffraction peak profile at half maximum height resulting from small crystallite size in radians and $K$ is a constant related to crystallite shape, normally taken as 0.9.

According to figure 4(a) the microhardness of pure nickel coatings is about 580 HV, it is reduced by the addition of 87% cobalt in the deposits to about 305 HV, which mainly attributed to the increase of the grain size as shown in the figure 4 (b), which indicates that the microhardness of coatings follows the classical Hall-Petch relationship: $H=H_0+kd^{0.5}$ [21]. Where $H_0$ is the constant of hardness, $k$ is constant, and $d$ is the grain diameter. The decrease in microhardness of coatings with the addition of cobalt in the nickel coatings can also be attributed to the appearance of porosity following the addition of cobalt and the formation of the cluster-porous structure as shown in Figure 2.

D. Tribological properties of the coatings

The friction coefficient of nanocrystalline Ni and Ni-Co coatings measured by using of a pin-disc tribometer (without lubrication) is shown in figure 5. It is clear that the friction coefficient of Ni-Co alloy coatings is lower by about five times than that of pure Ni coatings. In addition, the friction coefficients of Ni-Co alloys were much more stable than that of pure Ni deposits (figure 5). Combined with the XRD analysis, we can explain the excellent friction-reduction behavior by the change of crystal structure from fcc to hcp crystal phase, this latter which has very good tribological properties according to several previous studies [16-17,22].

![Figure 3: X-ray diffraction spectrum of Ni and Ni-Co nanocrystalline coatings](image)

![Figure 4: The relationship between the microhardness and the grain size of Ni and Ni-Co coatings.](image)

![Figure 5: Friction coefficient of Ni and Ni-Co coatings.](image)
The addition of high cobalt content in the nickel coatings subjected to the wear constraints, and on the other part, the absence of this bad film in the Ni-Co coatings with high cobalt contents. These results are in good agreement with the study of C. Ma and all [21].

The Figure 7 shows microscopic observations on the wear tracks of pure nickel coating (a) and Ni-Co alloy coating with 87% cobalt content (b), clearly observed the appearance of the tribofilms in the Ni coatings subjected to the wear constraints, and on the other part, the absence of this bad film in the Ni-Co coatings with high cobalt contents. These results are in good agreement with the study of C. Ma, S. C. Wang, C. T. J. Low, L. P. Wang and F. C. Walsh, “Effects of additives on microstructure and properties of electrodeposited nanocrystalline Ni-Co alloy coatings of high cobalt content,” Transactions of the IMF, vol. 92, pp. 191-195, 2014.

The microhardness of nanocrystalline nickel coatings is increased with the increase in the grain size of coatings caused by the addition of high cobalt content, which indicated that the microhardness of deposits follows the Hall-Petch effect.

The Ni-Co alloys deposits have a much lower friction coefficient and higher wear resistance than pure Ni coatings. It was suggested that the hcp crystal structure in the Ni-Co alloys coatings contributed to the remarkable effect of reduction of friction and the very best anti-wear performances.

The Ni-Co coatings with 87% cobalt content have the lowest friction coefficient and the best wear resistance, unfortunately they are characterized by a low microhardness, which requires their hybridization with other components such as hard nano or micro particles of Si-C, Al2O3, ZrO2 ... etc, or the decrease of their grain sizes by the addition of brighteners because their hardnes as we demonstrate in this study following the Hall-Petch effect.

References
