Comparison between the microstructural, morphological, mechanical and tribological characteristics of nanocrystalline Ni and Ni-Co electrodeposited coatings

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Abstract

For improving the wear resistance of steel used commonly in industry, nanocrystalline nickel and nickel-cobalt coatings are electrodeposited on A60 steel substrate in a modified Watts bath. The observation of the coatings produced by scanning electron microscopy (SEM) shows that nickel coatings have a smooth morphology whereas Ni-Co alloy deposits have a lens-shaped morphology with a considerable increase in the grains size of Ni-Co alloy deposits. The results of XRD show that nickel coatings having fcc phase structure while Ni-Co coatings have hcp phase structure. The study of coatings micro-hardness indicates that the latter follows Hall Petche effect where nickel deposits which have the smallest grain size show a higher micro-hardness in comparison with Ni-Co coatings. Pin on disk tribometric analysis under unlubricated conditions illustrates a great improvement of the wear resistance by the addition of cobalt on nickel coatings, where the friction coefficient and the wear rates are significantly reduced in Ni-Co coatings compared with nickel coatings.

Keywords: Ni, Ni-Co, Coating, Microstructure, Morphology, Microhardness, Tribological behavior.

1. Introduction

The electrodeposited nickel coatings are used in a large range of applications to improve the hardness [1], corrosion resistance [2], and wear resistance of the coated substrates [3, 4]. In order to improve the performances of nickel coatings, different approaches have been applied such as alloying with other elements [5, 6], crystallites refinement using additives [7, 8], and deposition of composite coatings by dispersing reinforcing particles inside the Ni matrix [9, 10]. The alloying of Ni with cobalt was one of the most commonly techniques used for improve the properties of nanocrystalline nickel coatings [4-6]. Ni-Co alloys have been investigated as important engineering materials for several decades due to their unique properties, such as high resilience [11], good corrosion resistance [12], thermal conductivity [13], electro-catalytic activity [14] and their magnetic properties [15] .In this work, we will try to give more value to these alloys coatings through improving their good tribological properties, In order to show the engineering feasibility of this coating, it is necessary to electrodeposit Ni–Co alloys onto structural materials such as ordinary steel. This will enable us to apply them as anti-wear coatings for increasing lifetime of the components that are subject to friction forces and wear conditions such as engine cylinders, rolling bearings, motion vectors,...etc.

To prove Ni-Co coatings anti-wear resistance, a comparison is made between the microstructural and morphological properties of high cobalt content nanocrystalline Ni-Co alloy coating (87% Co) with a nanocrystalline nickel coating which are produced electrochemically. Thus, a correlation between these properties with mechanical and tribological properties of these deposits is made.

2. Experimental

2.1. Substrate preparation

The nanocrystalline nickel and Ni-Co electrodeposited coatings are electrodeposited on an A60 mild steel substrate with an exposed area of $3,14cm^2$. Before electrodeposition, the substrate is subjected to some surface treatment operations, mechanical polishing with Si-C abrasive papers with decreasing grain sizes (80 to 4000), chemical degreasing for 10 min in an alkaline solution of pH=11 by using ultrasonic bath, chemical polishing in a solution of hydrochloric acid (10% by volume) for about 30 s. The chemical composition of A60 mild steel used as substrate is given in Table 1.

Element	Fe	P	S	N	Others
Percentage %	99.65	0.028	0.023	0.013	0.286

2.2. Electrodeposition of nanocristallyne Ni and Ni-Co alloy coatings

Two electrolytic baths are used in this work. The first bath contains NiSO4 (200g/l), NiCl2 (20g/l) used for the preparation of nanocrystalline nickel coatings, the second bath contains NiSO4 (200g/l), NiCl2 (20g/l), CoSO4 (200g/l) used for the preparation of Ni-Co alloys coatings with 87% cobalt content. In each bath, boric acid (30g/l) was added as a buffer to fix pH at 4.2±0.05 and to limit the alkalization of the solution around the substrate, saccharine (2g/l) and 2-butyne-1, 4-diol **(BD)** (0.5g/l) which prove their effect in the grain size reduction and in the improvement of coating properties [16-19] are added as brighteners to refine crystallites size. A pure nickel disc (purity = 99.99%) is used as a soluble anode, the bath temperature is maintained at 318K using a thermostatic bath with water circulation. The solution is continuously stirred by a magnetic stirrer bar (6 mm diameter × 30 mm length) at a speed of 200 rpm. In order to obtain deposits of thicknesses 20±5 µm, the current density is fixed at 4A /dm^2 for a period of 1200 s using 309N Autolab galvanostat-potentiostat.

2.3. Morphological and microstrucural characterization

JEOL JSM-7001F scanning electron microscope (SEM) is used to characterize the morphological and microstructural properties of elaborated deposits. The composition of the deposits is determined using electron scattering spectroscopy (EDS) which is coupled with SEM. The coating thicknesses are measured using Taylor Hobson PGI 1240 mechanical profilometer, three measurements are made on each coating. The crystal structure and grain size are characterized by D8 Avanced Bruker X-ray diffractometer (XRD), while the grain size is calculated according to the Scherrer equation.
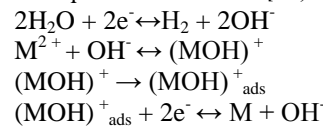
2.4. Mechanical and tribological characterization

The microhardness of the deposits is determined by the use of Tukon 2500 Knoop/Vickers hardness tester under a load of 50 g for a 15 second holding time. Five measurements are taken at different places in the coating. The tribological behavior of the coatings is studied using NANOVIA pin on disc tribometer, at room temperature with 28-34% humidity under a load of 3N and with a sliding speed of 5 mm s^{-1} for a total sliding time of 10 min. AISI 1040 hard steel ball (Ø = 6mm, hardness HV=700) is used as a counterpart. The friction coefficient in function

of time is automatically calculated during the test. Also, images of wear tracks (50 folds magnification) are taken using Carl Zeiss optical microscope connected with a CCD camera, however, the wear rate is evaluated by the measurement of the mass lost using Sartorius precision balance (Readability $\frac{1}{10}$ mg).

3. Results

3.1. Composition of the coatings

Figure 1 shows the percentage of cobalt $\frac{[Co]}{([Co]+[Ni])}$ in the electrolyte and in the Ni-Co coating. It is clear that the cobalt percentage in the coating (87%) is higher than in the bath (47%), this despite that the concentration of Ni^{2+} ions in the bath is greater than that of Co^{2+} 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. A generally accepted explanation for this abnormal phenomenon is the rise of pH at the substrate, this local increase in pH caused by the formation of metal hydroxides Co (OH) and Ni (OH) and their competitive adsorptions [15, 20]. The formation and adsorption of monohydroxides of metal can be expressed as follows [21, 22]:

$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-$

$M^{2+} + OH^- \leftrightarrow (MOH)^+$

$(MOH)^+ \rightarrow (MOH)^+_{ads}$

$(MOH)^+_{ads} + 2e^- \leftrightarrow M + OH^-$

Where M represents the Ni and Co metal atoms and M$_{ads}$ represents adsorbed metal atoms. The adsorption ability of Co(OH)$^+$ was considered to be higher than Ni(OH)$^+$, this can cause enriching deposits by the less noble metal Co. Several authors working on the co-deposition of Ni-Co alloys noticed the same appearance [15, 20], 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 indicates that the deposition rate is reduced by the addition of cobalt in the nickel electrolyte due to the anomalous co-deposition phenomenon.
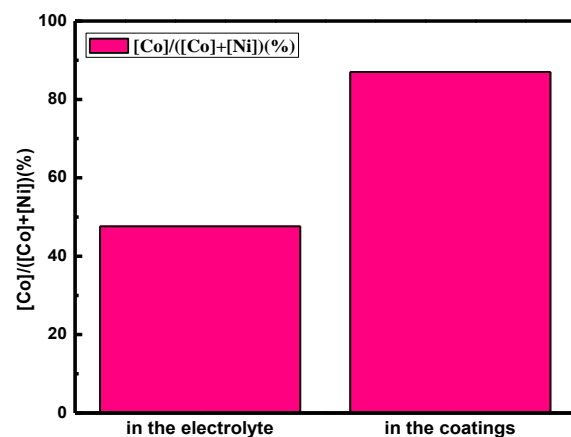
Figure 1: Cobalt proportion in the electrolyte and in the Ni-Co coatings.

3.2. Morphological and microstructural properties of coatings

The SEM observations of the elaborated nanocystalline nickel and Ni-Co deposits are shown in Figure 2a-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 where the appearance of a microscopic porosity in deposits with 87% cobalt content is noticed. 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 the cobalt is added to the nickel coatings as we see in Figure 3. This indicates that the cobalt addition on the nickel coatings has a significant influence on the surface morphology and structure of deposits.
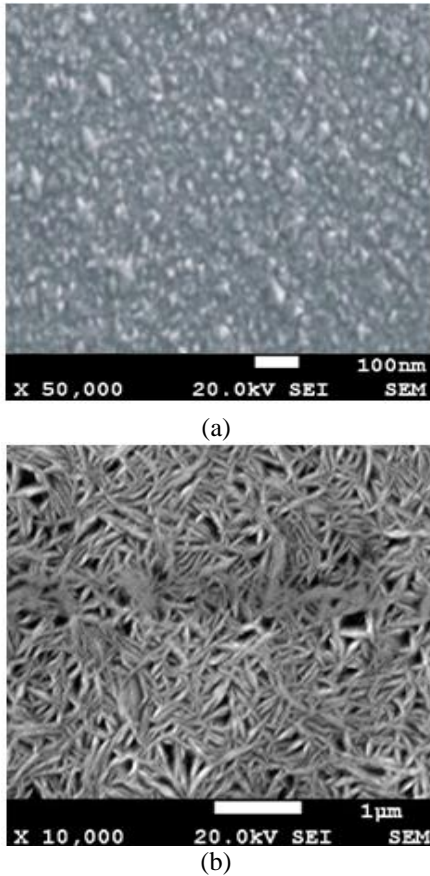

(a)

(b)

Figure 2 : SEM observations of nanocrystalline coatings:
(a)   Pure Ni, (b) Ni-Co with 87% cobalt content.

XRD patterns presented by Figure 3 shows that the cobalt content has a great influence on the coatings crystal structure, where it has been noticed that the pure nickel deposits are characterized by fcc phase structure. But the addition of high cobalt content in the nickel coatings conducted to a complete disappearing of the fcc phase and a new hcp phase which has very good tribological characteristics [23, 24] is appeared. Several authors [25, 26] working on the development of Ni-Co arrive at the same results.
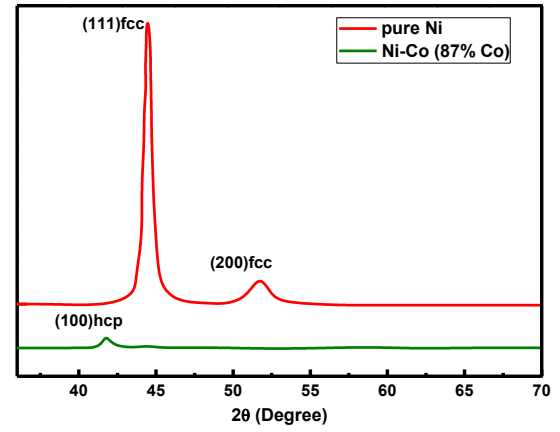

Figure 3: X-ray diffraction spectrum of Ni and Ni-Co nanocrystalline coatings.

3.3. Microhardness of coatings

Figure 4 shows the microhardness of the pure nanocrystalline Ni coating and Ni-Co alloy coating with 87% Co content while Figure 5 shows the grain sizes of the two coatings. The grain size of the deposited coatings is deduced from XRD peak broadening analysis and is calculated using the Scherrer equation [27]:

$$D = k\lambda / (\beta \cos \theta) \qquad (1)$$

where D is the average crystallite size, λ is the X-ray wavelength in nanometer (nm), in our case λ Cu$k\alpha_1$ = 0.15405 nm, β 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 the microhardness of pure nickel coatings is about 580 HV0.05, it is reduced by the addition of 87% cobalt in the deposits to about 305 HV0.05, which mainly attributed to the increase of the grains size as shown in Figure 5. This result indicates that the microhardness of coatings follows the classical Hall-Petch relationship [28]:

$$H = H_0 + kd^{-0.5} \qquad (2)$$

Where H_0 is the constant of hardness, k is constant, and d is the grain diameter. The decrease in microhardness of the coatings with the addition of cobalt in nickel coatings can also be attributed to the appearance of porosity due to the addition of cobalt and the formation of the cluster-porous structure as shown in Figure 2b.
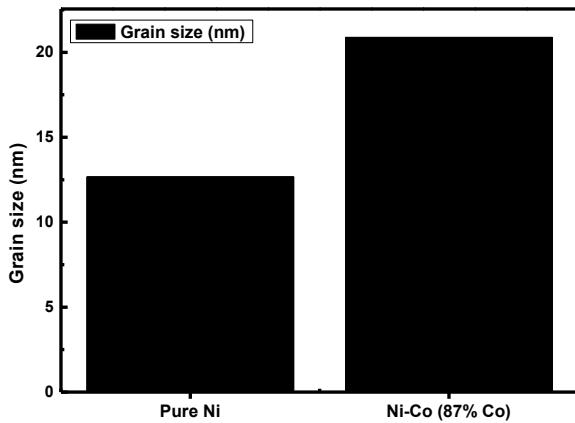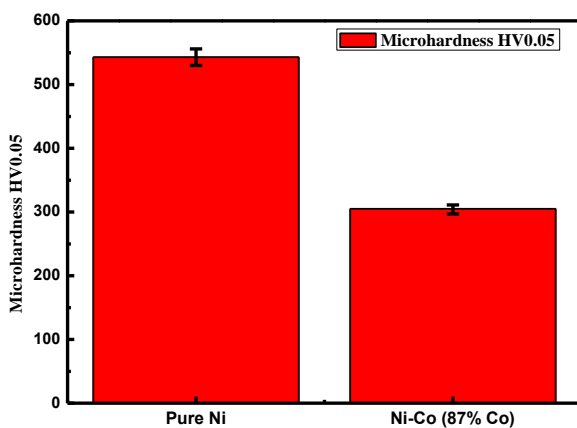
Figure 4: The grain size of Ni and Ni-Co coatings.

Figure 5: The microhardness of Ni and Ni-Co coatings.

3.4. Tribological properties of the coatings

The friction coefficient of nanocristallyne Ni and Ni-Co coatings is measured using a pin-disc tribometer (without lubrication) is shown in Figure 6. 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 are much more stable than that of pure Ni deposits (Figure 6). Combined with the XRD analysis, the excellent friction-reduction behavior can be explained by the change of crystal structure from fcc to hcp crystal phase, this latter has very good tribological properties according to several previous studies [23, 24, 29].
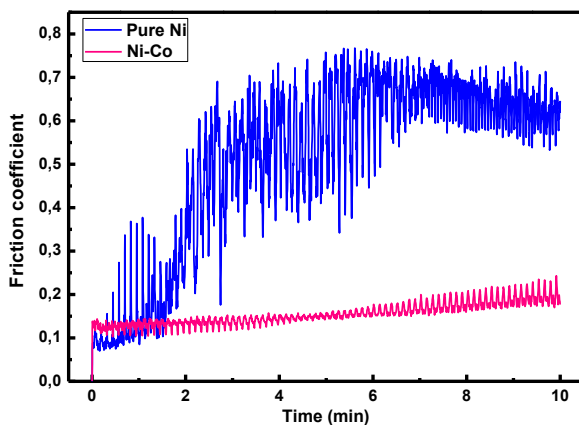

Figure 6: Friction coefficient of Ni and Ni-Co coatings.

In this study, the wear rate is evaluated by the weight loss after pin on disc wear testes for 10 minutes.

$$Weight\ loss\ (\%) = \frac{(mi - mf)}{mi} * 100 \qquad (3)$$

Where m_i and m_f are the initial and the final mass of the sample, respectively. The wear rate of the nanocristallyne Ni and Ni-Co alloy coatings is shown in Figure 7. It is noted in this study that the Ni-Co alloy deposits have the lower wear rate compared to the pure nickel deposits. The pin-disc tribometric analyses without lubrication shows a great improvement of the wear resistance with the addition of 87% Co into the coatings. This despite the decrease in the microhardness of coatings with cobalt addition as we have seen in Figure 5, what contradicts the Archard law [30]:

$$Q = KLN/H \qquad (4)$$

Where Q is the volumic wear rate, L is the total sliding distance; K is the friction coefficient and H the wear surface hardness. This opposite effect to the Archard law is attributed essentially to the formation of the hcp phase in the coatings with high cobalt contents. Also, this effect can be attributed to the wear debris film. A recent study [29] shows the undesirable effect of the formation of tribofilms in the worn surface of pure Ni coatings on the tribological behavior of such coatings, this undesirable film does not appear in the worn surface of Ni-Co coatings with 87% Co as shown Figure 8.
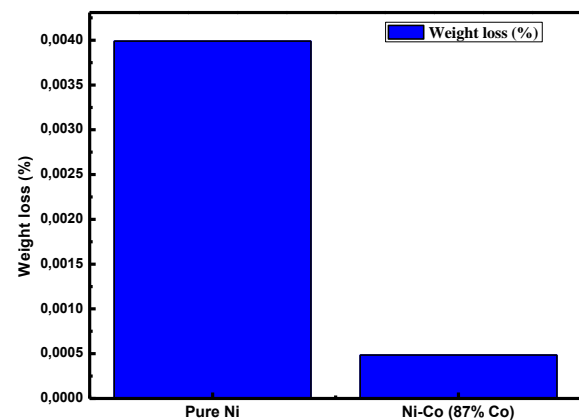

Figure 7: The wear rate of Ni and Ni-Co coatings.

To verify the diversity between the wear behaviour of Ni and Ni–Co coatings, the worn surface morphologies can be used as shown in Figure 8a–b. The appearance of the tribofilms is clearly observed in the worn surface of Ni coatings subjected to the wear constraints which have an fcc crystal structure. The appearance of tribofilms is due to the adhesive wears mechanism of pure nickel coating and the harsh deformation in the sliding track under the compression and shear constraints, which leads to wide wear rate of pure Ni coatings and big tendency for plastic deformation. This led to high formation of asperity spots which guides to high and unstable Ni coatings friction coefficient.

In comparison with pure Ni deposits, there is no tribofilm appearance in the worn surface of Ni-Co coatings with high cobalt contents. When, the worn surface of Ni-Co coatings becomes dense. The worn surface of Ni-Co coating with hcp crystal structure revealed less adhesion wear and smooth surface with smaller smashed spots, just some scars are remarked on the worn surface (Figure 8b). This came out with better wear resistance of Ni-Co alloy coating than Ni coating. That is also the cause behind the friction coefficient of Ni-Co alloy coating that is more stable and about five times lower than of Ni coatings. These results are in good agreement with the study of C. Ma and all [29]. Also, Figure 8a-b shows that the Ni-Co wear scars are much narrower and shallower compared to those of the pure nickel coating, which indicates that the wear rate is lower in the Ni-Co coatings. This observation confirms the obtained results of wear rates verified by the weight loss (Figure 7).
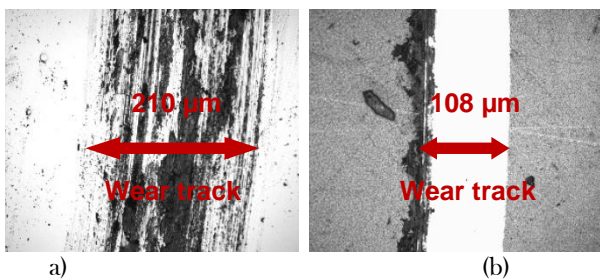

Figure 8: Wear tracks of (a) pure Ni coatings, (b) Ni-Co coatings

4. Conclusion

In this work, the Ni-Co alloys coatings have followed an anomalous codeposition mechanism, where the less noble element cobalt is deposited preferentially compared to nickel.

The addition of high cobalt content in the nickel coatings causes the change of the smooth morphology of nickel coatings to cluster-porous morphology; it also led to the change of the phase crystal structure from fcc to hcp structure.

The microhardness of nanocristallyne nickel coatings is reduced with the increasing 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 much lower friction coefficient and higher wear resistance than pure Ni coatings. It is concluded that the hcp crystal structure in the Ni-Co alloys coatings contributes to the remarkable effect of reduction of friction and to the very good 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, Al_2O_3, ZrO_2 etc, or the decrease of their grain sizes by the addition of additives in the bath because their

hardness as we demonstrate in this study following the Hall-Petche effect.

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