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Structural, Micromechanical and Tribological Characterization of Zn–Ni Coatings: Effect of Sulfate Bath Composition

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Keywords: Zn–Ni coatings, Electrodeposition, Sulfate bath, Sn, Tribological behavior

Abstract: Zn and Zn–Ni alloy coatings were electrode-posed on mild steel from sulfate-based bath containing Sn as additive. The effect of Ni content on the microstructure, morphology, micro hardness and the tribological behavior of these coatings were studied and discussed. Adding Sn in the sulfate bath had a significant effect on the surface morphology, particularly on the Zn–8 wt% Ni coatings. By increasing the Ni concentration from 8 to 14 wt%, the X-ray patterns showed that the phase structure of Zn–Ni alloy coatings was changed from g-phase $\text{Ni}_3\text{Zn}_{22}$ to c-phase $\text{Ni}_5\text{Zn}_{21}$. The plastic deformation and delamination were found to be wear mechanisms for the investigated coatings. While the Zn–14 wt% Ni alloys had the best wear resistance, Zn films had the most severe wear volume loss and the highest friction coefficient.

1. Introduction:

In recent years, the zinc coatings have been found to exhibit a high corrosion resistance to steel components. However, the corrosion protection of Zn coatings is not sufficient due to their high electrode potential with respect to steel [1–3]. For this reason, various investigations tend to improve the zinc deposit's properties. In fact, some research works have investigated the current mode of effect on the zinc electrodeposition. They have found that the use of a pulse current instead of direct current allows the enhancement of the corrosion resistance of the zinc coatings [4–6]. Actually, this improvement is attributed to the refinement of the zinc layers' morphology. According to Wasekar et al. [4], the pulse reverse current increasingly enhances the zinc coatings' corrosion resistance by improving the zinc microstructure and forming a compact corrosion product. Furthermore, the incorporation of an element from the Fe group such as Ni, Co, Fe or Sn is used as an alternative to ensure a better corrosion performance than pure Zn [7–12]. These Zn alloys are recognized by their great corrosion inhibition, thermal stability and mechanical properties in comparison with plated Zn [13–16]. Among Zn alloys, the Zn–Ni films are considered as the most significant ones due to their high corrosion resistance and flexibility along with low hydrogen embrittlement possibility [17]. In the light of the advantages already mentioned, much importance has been paid on the baths used in the Zn–Ni alloy coatings' plating. To begin with, the chloride baths have been widely used and been recently found to be

characterized by their poor deposit distribution on the substrate [18]. Thus, the current alternatives tend to use the sulfate baths. Indeed, several research works are investigating the electrodeposition additives and parameters to be used with these baths to improve the Zn–Ni coatings' properties. In this respect, some studies have been focused on optimizing the parameters of sulfate baths to obtain Zn–Ni coatings with a nanocrystalline structure and investigate the phases formed during the electrodeposition. According to these studies, the current density has a significant effect on the Zn–Ni coatings' properties [19]. Indeed, they have found that the corrosion protection performance increases with the rise of current density. Therefore, the best corrosion resistance corresponds to the Zn–Ni coatings with 18.9 wt% Ni and c-phase $\text{Ni}_5\text{Zn}_{21}$. It is evident that nickel exhibits anomalies in electrodeposition and the increase in current density does not mean further corrosion protection performance. I

In the same context, other researchers have studied the Zn–Ni electrodepositions by varying the bath temperature, stirring speed and $\text{Ni}^{2+}/\text{Zn}^{2+}$ ratio, in order to obtain Zn–Ni coatings with a single c phase [18]. They have deduced that Ni content of coatings has a remarkable effect on the structure, morphology and micro hardness of Zn–Ni coatings. According to them, the Zn–10 wt% Ni coating pre-sent a single phase $\text{Ni}_5\text{Zn}_{21}$ towards 40 °C and 80 mA/cm². Actually, the improvement of the coatings' plating is not limited to the bath parameters, the additives and the use of reverse-pulse are also found as solution. In this context, Feng et al. [20] have also investigated the electrodeposition parameters to obtain a Zn–Ni coating with a single c phase, but have used more complicated alkaline bath containing some additives and DMH as the complexing agent. As a result, they have found that the coatings with 13 or 16 wt% Ni content and single phase c are obtained with nanostructure of about 26 nm grain sizes and the Zn–13 wt% Ni coating present the best corrosion resistance. Yogesha et al.[21] have focused on the optimization of the acid chloride-based bath containing thiamine hydrochloride (THC) as brightener to electrodeposit Zn–Ni coatings. They have deduced that the brightener addition changes the Zn–Ni alloys composition. The wear resistance investigation and improvement of the Zn–Ni alloy coatings have also been of interest to the researchers in order to make these coatings applicable on steel fasteners used for automotive and aerospace industries [22, 23]. Panagopoulos et al. [24] have used a sulfate bath to obtain a Zn–14 wt% Ni nanocrystalline alloys to investigate their tribological behavior. They have shown that the counterpart material has a main effect on the wear mechanism. They have found that a surface delamination is discovered as a chief wear mechanism by using steel pins which got changed due to severe shearing against alumina ball. Additionally, Sriraman et al. [23] have investigated the tribological behavior of the Zn, Zn–Ni, Cd and Cd–Ti coatings. The Zn–Ni coatings are electrodeposited from commercial Zn–Ni plating solutions with commercial additives. Based on these authors' results, Zn–Ni alloys have the highest micro hardness and consequently the superior resistance. Tafreshi et al. [25] have studied the effect of the Zn–Ni alloys' Ni content on the structure and tribological behavior by comparing them with pure Zn layers. Equally important, they have revealed that the micro hardness increases with the increase of the Ni content from 11 to 17 wt% by presenting different intermediate phases (η -phase Ni_3Zn_2 , γ -phase $\text{Ni}_5\text{Zn}_{21}$, β -Zn–Ni). For tribological performance, they found that Zn–14 wt% Ni alloys represented the best wear resistance in terms of wear loss and friction coefficient, whereas, the Zn layer had the worst wear resistance property amongst all the coatings. Despite its diversity, research works on the Zn–Ni alloys that have been electrodeposited via sulfate bath are limited. The limitations mainly concern the analyses of the bath additives and Ni content's effects on the coating microstructure and then its micromechanical and tribological responses.

In the present work, Zn and Zn–Ni coatings with different Ni contents were electrodeposited on mild steel substrate using sulfate-based bath containing Sn as additive. The effects of Sn additive on the coating's microstructures were analyzed and discussed. The evolutions of the structural, micromechanical and tribological properties of Zn–Ni coatings with respect to the Ni con-tents were investigated.

2. Materials and Methods

2.1 Electrodeposition Process

The substrate material used in this study was mild steel. All specimens were machined to the dimensions of 30 9 15 9 20 mm³. The chemical composition of the substrate was as follows: 0.17% C, 1.4% Mn, 0.045% S, 0.045% P and 98.34% Fe. Furthermore, the mild steel samples were mechanically polished with 180, 400 and 1000 grit SiC paper. The substrates were activated in HCl and rinsed with ionized water and ethanol.

For both pure Zinc and Zn–Ni coatings, mild steel substrate was used as a cathode and pure zinc specimen as an anode, within an electrochemical cell. Following each pure Zinc and Zn–Ni electrodeposition, the coated steel specimens were rinsed with distilled water and ethanol. The surface roughness of all the samples were measured via a tactile profilometer.

2.2 Coatings Characterization

The surface microstructure of pure Zn and Zn–Ni alloy coatings were examined with a Scanning Electron Microscope connected with an EDS facility. Moreover, the crystallographic structure of the elaborated coatings was investigated using an X-ray diffractometer (XRD) Brucker–SIEMENS D5000 with Cu α radiation ($= 0.15440$ nm) and a graphite monochromator.

The average crystallite size of the samples was calculated from the peak width at the half maximum of the peak (β), using the Debye–Scherrer equation [13]:

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of the X-ray radiation, Θ is the Bragg angle of the peak, and β is the angular width of the peak at full-width at half maximum (FWHM).

2.3 Hardness and Tribological Testing

Hardness measurements were carried out by Vickers's micro hardness testing machine, using the diagonals method and $P = 1$ daN as applied load for 14 s. The mean value of at least five measurements conducted in different areas of each sample was considered. The tests were developed using a diamond indenter in the shape of a square pyramid with an angle between edges $\alpha' = 136^\circ$. For each test, the hardness H_v and the penetration h of the indenter were calculated from the measured value of the diagonal D footprint using the following expressions [26]:

$$H_v = 1.854 \frac{P}{D^2} \quad (2)$$

$$h = \frac{D}{2 \tan \left(\frac{\alpha'}{2} \right)} \quad (3)$$

To characterize the tribological response of the coatings, a linear alternating motion tribometer was used. This device allowed us to put the coating surface in contact with a 100Cr6 ball counter body (15 mm in diameter, 680 Hv) under an imposed normal force F_n . Besides, the coated substrate was then driven in an alternating and translational movement produced by the combination of a gear motor and a rod/crank system. A force sensor was used to measure the tangential force and a data acquisition system allowed a continuous recording of this effort. The tests were developed for a frequency of 1 Hz, a displacement amplitude of ± 7.5 mm, a maximum cycles number of 5000 and an imposed normal force of 6 N. Namely, five tests were performed for each of the considered coating. At the end of each friction test, the data processing could be traced back to the changes in the friction coefficient evolution with the number of cycles.

Thereafter, the worn surfaces of the coated specimen and the ball counter body were inspected using Scanning Electron Microscope (Philips series XL30) and Optical Microscope (Leica DM 2700 M). At last, surface profile in the transverse direction across the wear scar on the coated specimen was established using a tactile profilometer "SJ- 210". On the basis of this profile, the volume loss due to the wear was calculated.

3. Results and Discussion

3.1 Effect of the Bath Composition on the Microstructure of Zn–Ni Coatings

Zn and Zn–Ni coatings were electrodeposited on mild steel substrate using sulfate-based bath containing Sn as additive. In order to explore the Sn effect on the Ni and Zn–Ni electrodepositions, a preliminary study was conducted. In the first part, we carried out a cyclic voltammetric analysis for which the platinum was used as an anode, the vitreous carbon as a cathode and a saturated calomel electrode (SCE) as a reference electrode. Both solutions used in this work contained $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.8 M (solution1) and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.8 M; SnSO_4 , 8×10^{-5} M (solution2). The curve presented in Fig. 1 shows a typical trend of the voltammograms of pure nickel (Red Curve) and pure nickel with Sn as an additive (Blue Curve) obtained at - 1.2 V and 20 mv/s (scanning speed). Different voltammograms present a peak corresponding to the nickel cation's reduction during the go sweep. At the back sweep, a cross between the flow current and the return current, characteristic of a nucleation and three-dimensional growth, is observed. According to Fig. 1, it is noticed that the Sn promotes the reduction of the Ni and, most important, enhances the nucleation phenomenon. Therefore, the Sn has a significant effect on the Ni electrodeposition, despite its negligible concentration into the bath. In the second part of the preliminary study, typical Zn–Ni coatings were developed with and without Sn as an additive. The microscopic observations of these coatings are presented in Fig. 2 that shows cluster like appearance for both Zn–Ni alloy coatings. Nevertheless, for the Zn–Ni alloys with Sn as an additive, the clusters are more enlarged, mainly due to the three-dimensional growth of the Ni, and therefore promoting nucleation. These electrodepositions were conducted at - 1.2 V, with a non-adjusted pH and without heating. The XRD diagrams of these two types of coatings are shown in Fig. 3. It is observed that the peaks became wider (the value of the angular width of the peak at full-width at half maximum (β) increases) by adding the Sn to the Zn–Ni coatings. This enlargement is due to the reduction of the grain size, which confirms the cyclic voltammetric study and the microscopic observations. From the identification of the phases in these coatings, it is found that the phase $\gamma\text{-(Ni}_5\text{Zn}_{21})$ is well localized in the coatings with Sn addition than those without.

The bath used in the present work is the same as the one used earlier by Panagopoulos et al. [24] to obtain Zn–14 wt% Ni alloys. For the present study, the different concentrations and plating conditions are determined to obtain pure Zinc and Zn–8 wt% Ni alloys coatings. The chemical composition of the electrolyte bath solution as well as the plating conditions are illustrated in Table 1 in which 0.4 M and 0.8 M present the Nickel concentration into the bath for both alloy coatings. The surface microstructures of pure Zn and Zn–Ni alloys coatings are illustrated in Fig. 4. The surface of pure Zn layer presents hexagonal pellets morphology (Fig. 4a). Alloying Zn with Ni is able to change the morphology into a smooth nodular fine-grained structure (Fig. 4b). The indicative areas of the Zn–Ni surface are expanded in order to grasp the grain structure. Figure 4b0 shows a non-uniform surface containing hexagonal pellets with the appearance of nodules. As for Zn alloy coatings with ample amount of Ni, Fig. 4c shows the increase of the cluster's size to obtain surface uniformity with cauliflower morphology. Immediately, EDS analysis on the Zn–Ni coatings alloy shows that Zn–0.4 M Ni presents 8% of Ni in the composition of the alloy. Conversely, it is about 14% of Ni in the Zn–0.8 M Ni alloy coatings. The plating baths are very poor in the order of Sn ions compared to the presence of Zn and Ni ions. In short, the existence of Sn in the layers is undetectable with the EDS technique. On the other hand, Sn has a significant effect on the morphology of the coatings, resulting in the reduction of the alloys' grain size, which appears mainly for Zn–8 wt% Ni alloys. Compared to some research works [19], Zn–8 wt% Ni alloys obtained from a different bath, does not have the same surface morphology. In fact, according to them, the surface morphology seems to be more coarse-grained than that obtained in the present study. This can be explained by the fact that the Sn promotes the Ni nucleation, which in turn results in the grain size reduction [27].

3.2 Phase Structures

The phase structures of Zn and Zn–Ni coatings were determined by using XRD technique as demonstrated in Fig. 5. Accordingly, the main peaks of pure Zn layer are clarified at 2θ of 36, 39 and 43°. Subsequently, the Ni addition to Zn reduces the intensity of the Zn film peaks, giving birth to new peaks. The Zn–8 wt% Ni alloy coating's XRD pattern present three main peaks at about 2θ of 43, 54 and 69° corresponding to the η ($\text{Ni}_3\text{Zn}_{22}$) phase. This phase has an hexagonal close packed (hcp) structure, it is rich in Zn and characterized by being soft and flexible [28]. The increase in the Ni content to 14 wt% lead to the disappearance of this phase into a new γ ($\text{Ni}_5\text{Zn}_{21}$) phase corresponding to the peaks at about 2θ of 44, 62 and 79°. This γ phase presents a body centered cubic (bcc) structure, whose flexibility is lower than the η -phase [18, 25]. Nevertheless, the increase in Ni and the decrease in Zn permits the domination of γ ($\text{Ni}_5\text{Zn}_{21}$) phase over η ($\text{Ni}_3\text{Zn}_{22}$) phase. This domination involves the morphology modification from hexagonal clusters to spherical nodules. The average grain sizes of the coatings that have been measured by Scherrer equation are about 7 μm , 50 nm and 37 nm for the pure Zn, Zn–8 wt% Ni and the Zn–14 wt% Ni, respectively.

3.3 Surface Roughness and Coatings' Thickness

An average roughness (R_a) of $1.6 \pm 0.4 \mu\text{m}$ and $1.4 \pm 0.2 \mu\text{m}$ is detected in the case of pure Zn and Zn–14 wt% Ni coatings, respectively, compared to the Zn–8 wt% Ni coatings which has lesser surface roughness ($0.7 \pm 0.2 \mu\text{m}$). Overall, it seems that the plating time is determined to get 50 μm thickness, whose average for both pure Zinc and Zn–Ni alloy coatings is presented in Table 2.

The optical micrographs of the cross section (Fig. 6) reveals uniform thickness over the whole surface for the different coatings. This figure is obtained after chemical attack (CrO_3 (20 g) and Na_2SO_4 (1.5 g) in 100 ml of distilled water) in order to increase substrate/coating contrast. According to these micrographs, the porosity of the Zn films seems to be inconsiderable. Nonetheless, the level of porosity increases in the case of Zn–Ni alloys. In fact, the porosity into the coatings rises, while increasing the Ni content. This observation can be attributed to the hydrogen release, which is very intense in the Ni containing solutions [29, 30].

3.4 Micro hardness

The micro hardness outcomes are notably illustrated in Fig. 7 showing that the coatings' composition has a significant effect on the hardness. The penetration depth is found to be between 2.5 and 3.5 μm for the different coatings, which is significantly lower than the layer's thickness. It can be seen that the micro hardness of Zn–Ni alloy coatings increases with the rise of their Ni concentration. This supposition is explained by the fact that the hardness of Ni is greater than that of Zn [21] and by the former's ability to decrease the grain size which is a main factor to enhance the hardness. Indeed, the presence of smaller grains impedes the dislocation motion and results in an increase in the micro hardness [31].

3.5 Tribological Behavior

3.5.1 Friction Response

Figure 8 shows the evolution of the friction coefficient of different Zn and Zn–Ni alloy coatings versus the sliding cycles' number. In fact, all Zn–Ni alloy coatings have the same friction coefficient evolution trend. During the running-in stage, a rapid increase in the friction coefficient is observed due to the increase in the contact area between the coating and the steel ball counterpart (Fig. 9). This growth is followed by a decrease in the friction coefficient until stabilization after some sliding cycles. Therefore, the establishment of a transfer film on the steel ball surface and a third body constituting the detached particles have been found to result in this decrease in the friction coefficient in Zn and Zn–8 wt% Ni coatings' case. However, for the Zn–14 wt% Ni alloys, a re-increase in the friction coefficient is noted after about 350 cycles, due to the transfer film loss. The steel ball counter body, which is in direct contact with the hardened coating, results in the increase in the frictional interaction between the contacting bodies. The results in Fig. 8 reveal that after 5000 sliding cycles, the pure Zn coating has the highest friction coefficient. The lowest micro hardness of the Zn film is in the reason behind the increase of the real contact area, and thus the significant elevation of the friction coefficient. Indeed, the Ni content has a significant effect on the friction coefficient that decreases with the increase in Ni content. For both Zn–Ni coatings, the steady values of the friction coefficients are comparable due to their nodular surface morphology.

3.5.2 Wear Response

The optical and SEM micrographs of the Zn–Ni alloy coatings' wear track shows that several wear mechanisms are in motion (Figs. 10, 11). The wear surface of the Zn and Zn–8 wt% Ni coatings are wider than the Zn–14 wt% Ni alloy coatings and seem to be deeper. After 5000 cycles, the width of the worn surface is about 2.5 mm for both Zn and Zn–8 wt% Ni coatings, but it is only about 1.8 mm for Zn–14 wt% Ni alloys.

Figure 10 shows optical micrographs of the worn sur-faces, evolution of the various coatings after 100 and 1000 cycles. Although the wear behavior for both Zn–Ni alloys seems to be similar, it is different from that of pure zinc. This is due to the morphology of the coatings and the presence of the nodules in the alloys. For pure Zn film, after 100 cycles, shear and

delamination are identified as an initial wear mechanism. Furthermore, after 1000 cycles, plowing is located on the edges of the wear track, while the interior is the seat of a plastic deformation (Fig. 10a). For both Zn–Ni alloy coatings (Fig. 10b, c), after 100 cycles, the initial smoothening of the surface layer is activated with material removal pursued by wear debris accumulation. This accumulation is due to the trapping of the debris in the valleys of the nodules. After 1000 cycles, the wear develops and the nodules are clipped with the production of the oxide layers. According to Fig. 10b, c, the nodule crushing is more significant into the Zn–14 wt% Ni alloy wear scars (this is explained by their important size). However, their wear is less developed than the Zn–8 wt% Ni alloys.

By progressing the wear test for Zn and both Zn–Ni coatings (Fig. 11) until reaching 2500 cycles, the center of the wear track for Zn and Zn–8 wt% Ni coatings represents a severe adhesive wear mechanism with a large plastic deformation resulting from the re-deposition of the coatings' torn patches during the advancement of the wear test. By increasing the sliding distance from 2500 to 5000 cycles, similar phenomena are observed. For both cycles' number, wear seems to be more developed for the Zn coatings than for the Zn–8 wt% Ni alloys since the Zn films are less hard than the alloys.

Still in the same vein, by raising the Ni content from 8 to 14 wt%, the wear mechanism seems to be less prominent than pure Zn and Zn–8 wt% Ni. After 2500 sliding cycles, the plastic deformation with the beginning of the shear is observed. In fact, the detached debris already observed during the 100 and 1000 sliding cycles are entrapped between the coating and the steel ball counterpart forming a third-body layer. This layer interact with the underlying coating to form an abraded cracked surface. Then, and after 5000 sliding cycles, a hardened tribolayer with transverse cracks are observed towards the end of the wear test. Therefore, the Zn–14 wt% Ni alloy coatings have better wear resistance than the Zn film and the Zn–8 wt% Ni alloy coatings. Accordingly, this can be explained by the low friction coefficient and the high hardness found for the Zn–14 wt% Ni coatings. According to the Archard theory, wear resistance is proportional to the hardness of the material [32].

The coatings' torn patches analyzed by XRD technique (Fig. 12) shows that the worn surface is composed of pure Zn and zinc oxide layers (ZnO) for the different investigated coatings. Nevertheless, the debris analysis of Zn–Ni alloy films reveal the presence of the intermetallic phase. In fact, while increasing the Ni content, the oxide layers production decreases. As a result, the interaction between the third-body layer and the steel ball counterpart is expected to be relatively soft in the case of Zn–14 wt% Ni coating (Fig. 9). η ($\text{Ni}_3\text{Zn}_{22}$) and the intermetallic phase γ ($\text{Ni}_5\text{Zn}_{21}$) in the case of the Zn–8 wt% Ni and Zn–14 wt% Ni coatings, respectively. The oxidation degree seems to be more significant in the Zn coatings, case than the Zn–Ni alloys case. In fact, while increasing the Ni content, the oxide layers production decreases. As a result, the interaction between the third-body layer and the steel ball counterpart is expected to be relatively soft in the case of Zn–14 wt% Ni coating (Fig. 9).

The wear volume loss of pure Zn coatings and Zn–Ni alloy coatings after 2500 and 5000 sliding cycles are depicted in Fig. 13. It can be seen that the pure Zn coating have a high volume loss if compared to Zn–Ni alloys, for the two considered test durations. By incorporating 8 wt% of Ni to the Zn layer, the wear loss of the Zn–8 wt% Ni alloy coatings decreases slightly compared to that observed in case of pure Zn. Nonetheless, for the Zn–14 wt% Ni alloy coatings, the wear loss decreases to half after 2500 and 5000 sliding cycles. This newly found result may be linked to the micro hardness since the Zn–14 wt% Ni coatings are twice as hard as the Zn

layers. Nevertheless, for all studied coatings, the wear volume loss is slightly affected by the sliding distance.

Therefore, the morphology and the micro hardness of the coatings have a significant effect on their tribological behavior. In fact, according to what have been seen, the tribological behavior of the Zn–Ni alloys at short cycles are practically similar, thanks to their nodular morphology. Nonetheless, during the progression of the wear test, a remarkable difference in terms of the wear mechanisms and volume is observed. This dissimilarity may be related to the reduced size of the nodules and the middling micro hardness of the Zn–8 wt% Ni alloys relative to the Zn–14 wt% Ni coatings. With 14 wt% of Ni in the coatings, the layer becomes harder with a typical nodular morphology. The morphology of these nodules and the micro hardness of these coatings are responsible for the reduced friction coefficient by the decrease of the real contact area. It can be concluded that the particular structure of the Zn–14 wt% Ni coating causes the entrapping of debris in the coating. Consequently, a third-body layer is formed, representing an intimate contact with the counterpart steel ball after removal of the transfer film. This direct contact results in lower wear volume [23].

4. Conclusion

Based on the present study resulting in the electrodeposition of Zn and Zn–Ni alloy coatings on mild steel substrate using sulfate-based bath containing Sn as additive, the following points can be concluded:

- * Sn as additive promotes the Ni nucleation that leads to the grain size reduction.
- * Alloying Zn with Ni permits the change in morphology of the coatings from hexagonal pellets to nodular fine-grained structure. The Zn–14 wt% Ni films show “cauliflower” morphology.
- * The Zn–14 wt% Ni alloys are harder than Zn and Zn–8 wt% Ni films.
- * The stabilized friction coefficient of Zn–14 wt% Ni coatings is found to be more reduced than that of Zn and Zn–8 wt% Ni coatings.
- * For Zn–Ni coatings, the steady values of the friction coefficient are comparable due to their nodular surface morphology.
- * The Zn layers have a significant worn surface that become less and less important by increasing the Ni content.
- * The Zn–14 wt% Ni alloys offer the best wear resistance ability amongst all the studied coatings thanks to its high micro hardness and fine-grained nodular morphology.

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Tables

Table 2. Average thickness of pure Zn and Zn–Ni alloy coatings

Coatings	Zn	Zn–0.4M Ni	Zn–0.8M Ni	Operating conditions	Zn	Zn–0.4M Ni	Zn–0.8M Ni
Bath composition (g/l)				Temperature (°C)	60	60	60
ZnSO ₄ ·7H ₂ O	347.5	347.5	347.5	PH	1.7	3.8	1.7
NiSO ₄ ·6H ₂ O	–	22.37	44.75	Current density (A/dm ²)	3.7	5.5	4.2
SnSO ₄	0.01	0.02	0.01	Plating time (min)	64	50	80
				Electrolyte volume (ml)	250	250	250
				Anode	Zinc	Zinc	Zinc
				Cathode	Mild steel	Mild steel	Mild steel

Table 1: Sulfate baths used for the electroplating of pure Zn and Zn–Ni alloy coatings

	Pure Zn	Zn–8 wt% Ni	Zn–14 wt% Ni
Thickness (μm)	49 ± 2	51 ± 2	53.5 ± 1.5

Figures

Fig. 1 : Cyclic voltammograms of pure nickel (red curve) and pure nickel with Sn as an additive (blue curve) at - 1.2 V (color figure online)

Fig. 2: SEM micrographs of Zn–Ni alloy coatings: a without additive, b with Sn as an additive

Fig. 3: X-ray diffraction patterns of Zn-Ni alloy coatings: a without additive, b with Sn as additive

Fig. 4: SEM micrographs of the coatings' surface: a pure Zn, b and b0 Zn-8 wt% Ni, c Zn-14 wt% Ni

Fig. 5: X-ray diffraction patterns of Zn and Zn–Ni coatings

Fig. 6. Optical micrographs of the coatings' cross section:
a pure Zn, b Zn-8 wt% Ni and c Zn-14 wt% Ni

Fig. 7. Effect of bath composition on micro hardness of Zn and Zn–Ni alloy coatings

Fig. 8. Friction coefficient evolution versus sliding cycle's number of Zn and Zn–Ni alloy coatings

Fig. 9. Optical micrographs of wear scars on both coating and steel ball surfaces within running-in stage and after the friction coefficient stability: a pure Zn, b Zn-8 wt% Ni, c Zn-14 wt% Ni

Fig. 10. Micrographs of wear scars on the coating surface after 100 and 1000 cycles: a pure Zn, b Zn-8 wt% Ni, c Zn-14 wt% Ni

Fig. 11. SEM micrographs giving the wear track morphology on Zn and Zn-Ni alloy coatings surfaces after 2500 and 5000 sliding cycles: a and a' pure Zn, b and b' Zn-8 wt% Ni, c and c' Zn-14 wt% Ni

Fig. 12. X-ray diffraction patterns of pure Zn (a), Zn-8 wt% Ni (b) and Zn-14 wt% Ni (c) coatings' torn patches after 5000 cycles

Fig. 13. Wear volume loss versus sliding cycle numbers for Zn and Zn-Ni coatings