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# Type and concentration effects of particulate solid lubricants on the microstructure, friction, and wear of electrodeposited Ni composite coatings

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## Abstract

Nickel–MoS<sub>2</sub> composite coatings were obtained by electrodeposition from a nickel electrolyte containing suspended MoS<sub>2</sub> particles. The coating composition, morphology, crystalline structure, microhardness, and frictional behavior were studied as a function of MoS<sub>2</sub> concentration. The results obtained in this study revealed that the codeposited lubricant particles strongly influenced the composite nickel coating properties. It was found that increasing codeposited MoS<sub>2</sub> decreases the average grain size of nickel crystallites and leads to the formation of clusters which, in turn, lead to rough coatings with a high and variable thickness. The results of tribological response indicated that the reduction of friction coefficient and the improvement of wear resistance were performed until an optimal value of MoS<sub>2</sub> concentration, which provided the best condition that promoted the tribo-layer stability and maintained the matrix integrity. A comparison of tribological and micromechanical properties between the coating containing the optimal fraction of MoS<sub>2</sub> particles and the coating containing nearly the same fraction of graphite particles has been undertaken. Unlike the case of the addition of graphite particles, the microhardness of composite coating has been enhanced with the incorporation of MoS<sub>2</sub> particles. However, the incorporation of graphite particles in the coating induced more effective lubrication and wear resistance.

## Keywords

Electrodeposition, nickel, MoS<sub>2</sub>, graphite, friction, wear

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## Introduction

In order to achieve the technological progress, new metallic coatings with better surface characteristics are still required. Thus, new innovative coatings, with finely dispersed reinforcement particles are synthesized to provide composite coating with excellent properties.<sup>1,2</sup> Although many deposition procedures of composite coatings are being constantly used, the electrodeposition remains one of the most suitable procedures which represents a trade-off between simplicity and economic concerns. Moreover, it is considered as the major deposition technique industrially used for the codeposition of both metal and particles into composite coatings. In fact, the problem of stable suspension of particles in the electrodeposition solution is generally surmounted by the addition of suitable surfactant.<sup>3</sup> This surfactant plays a fundamental role in reducing hydrogen embrittlement in the coatings, minimizing particles agglomeration, and

enhancing particles codeposition.<sup>4</sup> Cetyltrimethyl ammonium bromide and sodium dodecyl sulfate (SDS) are frequently used as surfactant.<sup>5,6</sup>

Tribological coatings with low friction coefficient are highly requested in various industries. They are widely used to control friction and wear, where conventional lubricants cannot afford the desired level of performance and durability under harsh application conditions.<sup>7</sup> Solid lubricants having hexagonal structure as MoS<sub>2</sub> and graphite are widely used

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thanks to their good thermal stability under 400 °C, low cost, and easier incorporation in Ni matrix.<sup>8,9</sup> Graphite is one of the best choices for lubrication in regular atmospheres. In fact, the energy between its hexagonal planes is enormously reduced by the adsorption of humidity, whereas MoS<sub>2</sub> is powerful in high vacuum conditions.<sup>10</sup> On the whole, the addition of MoS<sub>2</sub> or graphite into metallic composite coating allows a low friction characteristic due to the easy shear of the weak interlayer bonds in these materials.<sup>11</sup> These low friction solid lubricants can function similarly to an oil medium by the development of a tribofilm between two sliding surfaces.<sup>12,13</sup>

Nowadays, numerous research works have been developed for the investigation of studying composite coating filled with MoS<sub>2</sub> particles. The most widely studied matrix is nickel, its alloys and compound owing to its high brightness, hardness, and corrosion resistance ability. Actually, tremendous efforts have been made to explore the process aspects of electrolytic codeposition of Ni matrix filled with MoS<sub>2</sub> particles<sup>14,15</sup> and to study the evolution of hydrogen reaction during electro-codeposition.<sup>16,17</sup> Furthermore, several studies have been conducted to minimize the internal stress of Ni–MoS<sub>2</sub> composite coatings<sup>18,19</sup> and others to study the effect of surfactant in the codeposition behavior.<sup>20</sup> The mechanical and tribological behaviors of electroplated Ni-based alloys filled with MoS<sub>2</sub> coating have also been a major concern for various investigations. Cardinal et al.<sup>8</sup> have been interested in the study of the effect of MoS<sub>2</sub> concentration in the tribological behavior of Ni–W alloy coatings. Besides, Fazel et al.<sup>10</sup> have compared the effect of the addition of graphite or MoS<sub>2</sub> solid lubricant particles, at room and elevated temperature, on the tribological properties of Ni–SiC composite coatings. Other research works have focused on the study of the friction, wear, and corrosion behavior of Ni–P electrodeposited coatings filled with MoS<sub>2</sub> particles.<sup>11,21</sup> However, to the best of our knowledge, no research works have documented the effect of MoS<sub>2</sub> concentration on the tribological properties of a pure electrodeposited nickel matrix. Hence, the aim of this work is to perform Ni–MoS<sub>2</sub> composite coatings filled with different concentrations of MoS<sub>2</sub> particles with electrodeposition. At the first step, a study of the microstructural and the tribological behavior of these coatings will be elaborated. In the second step, a comparison of tribological and micromechanical properties between the coating containing the optimal fraction of MoS<sub>2</sub> particles and a coating containing nearly the same fraction of graphite particles will be conducted.

## Materials and methods

### Composite coatings preparation

Ni, Ni–MoS<sub>2</sub> with different concentrations of MoS<sub>2</sub>, and Ni–graphite composite coatings were

electrodeposited using Ni Watt's Bath on mild steel substrate (0.17% C, 1.4% Mn, 0.045% S, 0.045% P, and 98.34% Fe) with dimensions of 30 × 20 × 15 mm<sup>3</sup> and a microhardness of 129 ± 10 Hv. It should be noted that the active surface area was 45 mm<sup>2</sup>; the remaining surfaces were hidden with adhesive tape. To create a good adhesion between substrate and coating, the active surface area of substrate was mechanically polished with abrasive paper (until a surface roughness Ra equal to 0.6 μm), degreased by NaOH solution with pH = 11, and etched by 10% H<sub>2</sub>SO<sub>4</sub> for 1 min. Following the preparation of each step, the substrate was rinsed by distilled water with the intention of completely removing the residuals of each stage. A carbon sheet was used as anode.

The electrochemical bath components consisted of nickel sulfate as Ni source, boric acid, and nickel chloride (all supplied by Sigma Aldrich). The bath composition and operating conditions are presented in Table 1. The plating solution was mixed via magnetic stirrer. Amounts of 0.1, 0.25, 0.5, and 1 g/l of MoS<sub>2</sub> (<2 μm) or 10 g/l of graphite (7–11 μm) particles were added to the electroplating bath. In order to enhance the electrostatic adsorption of suspended particles on the cathode surface, SDS was added to the solution as surfactant. All bath ingredients were agitated for 2 h by magnetic stirring. Subsequently, the sonication process was served for 30 min to provide homogeneous dispersion and prevent the agglomeration of the particles.

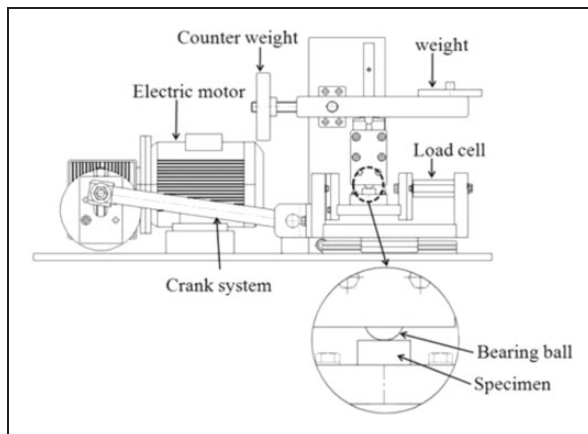
### Characterization techniques

The surface morphologies of the electroplated Ni and Ni–MoS<sub>2</sub> were characterized using atomic absorption to evaluate the MoS<sub>2</sub> weight fraction in the composite coating for each of the considered concentration of particles in the electrochemical bath. At the first step, the mass of the obtained coatings was determined by a balance with a precision equal to 0.01 mg. Therefore, the coated substrate was emerged in a concentrated nitric acid (HNO<sub>3</sub>, 70%), which dissolves the nickel without attacking the steel according to the norm NF A 91 101.<sup>22</sup> After the complete dissolution of Ni, reached when the residual mass was same as that of the substrate before electrodeposition, the steel substrate was extracted and the obtained solution (HNO<sub>3</sub>+nickel) was heated to 100 °C until the full evaporation of HNO<sub>3</sub>. Subsequently, distilled water was added to the solution that was heated to 100 °C in order to remove the residual acid from the sample. After its full evaporation, 50 ml of distilled water was added. Then, the obtained solution was filtered to eliminate the particles. Finally, it was examined by atomic absorption to determine the weight percentage of nickel. Hence, the weight percentage of solid lubricant particles was deduced. The X-ray diffraction (XRD) was used to evaluate the phase compositions of the obtained composite coating. Scanning electron

**Table 1.** Bath composition and operating conditions of Ni-based composite coatings.

		Particle type		
		MoS <sub>2</sub>	Graphite	
Bath composition				
Particles dimensions (μm)		<2	7–11	
Quantity of particles (g/l)		0.1, 0.25, 0.5, and 1	10	
NiSO <sub>4</sub> ·6H <sub>2</sub> O (g/l)		270	270	
NiCl <sub>2</sub> ·6H <sub>2</sub> O (g/l)		50	50	
H <sub>3</sub> BO <sub>3</sub> (g/l)		35	35	
SDS		20 mg/g de MoS <sub>2</sub>	0.2 g/l	
Current density	Bath temperature	pH	Stirring speed	Plating time
4.8 A/dm <sup>2</sup>	50 °C	2	500 r/min	60 min

SDS: sodium dodecyl sulfate.

**Figure 1.** Reciprocating friction and wear apparatus.

microscope (SEM) was used to study the coatings' surface morphologies as well as the wear traces. Furthermore, a cross section of substrate was examined by optical microscope (OM) to find out the thickness of coatings. The roughness of various coatings and wear volume was investigated by tactile profilometer. The surface roughness parameter "Ra" was used for analysis and measured over a tracing length of 12 mm. The microhardness of various coatings was measured by Vickers indentation at a load of 1000 g.

The friction and wear tests were performed by a reciprocating tribometer designed in our laboratory as illustrated in Figure 1. A ball-on-plan contact sliding test was used. The wear tests were carried out at room temperature (25 °C) and with a relative humidity of 55 ± 5%. The high chromium steel (100Cr6) was the material of the counter ball that was 15 mm in diameter with a surface roughness Ra 0.02. Preceding each friction test, the substrate as well as the ball was rinsed with ethanol. The apparatus allows

contact between the steel ball and the coating surface under a constant normal load. Then the tangential cyclic motion was applied to the coated specimen. A load cell located between the coated specimen and its holder allows the measurement of the tangential force. The output of this load cell was continually stored using a data acquisition system. Normal load, tangential motion amplitude, and frequency were adjusted to 6 N, 7.5 mm, and 1 Hz, respectively. Following the friction test, wear tracks were observed by a SEM and worn surfaces of counter ball were observed by OM. The wear volume was measured based on the wear track profile developed by a tactile profilometer over a tracing length of 4 mm perpendicular to the sliding direction.

## Results and discussion

### Characterizations of Ni–MoS<sub>2</sub> coatings

#### Microstructural characterization

- *Weight fraction of MoS<sub>2</sub> particles in composite coatings*

The used concentrations of MoS<sub>2</sub> particles and their corresponding weight percentage in the Ni composite coating are listed in Table 2. The incorporation of MoS<sub>2</sub> particles into the Ni matrix can be explained by the codeposition mechanism of inert particles from electrolyte bath. According to Wasekar et al.<sup>23</sup> and with analogy to Guglielmi's<sup>24</sup> simplified model for composite electrodeposition, during first stage in addition to the metal ions, the adsorption of Ni on the surface of MoS<sub>2</sub> particles occurred. In the second step, the migration of MoS<sub>2</sub> particles with ionic cloud to the cathode surface through diffusion layer took place. Here, these particles were adsorbed, thus losing hydrated shell by electron transfer reaction. Finally, the Ni atoms were incorporated into crystal

**Table 2.** Weight fraction of MoS<sub>2</sub> particles in coatings versus MoS<sub>2</sub> concentration in electrolytic bath.

Concentration of MoS <sub>2</sub> in electrolytic bath (g/l)	MoS <sub>2</sub> weight fraction (wt%)
0	0
0.1	13
0.25	29
0.5	39
1	42

lattice surrounding MoS<sub>2</sub> particles. Thus, the latter were encapsulated in Ni matrix. A higher concentration of MoS<sub>2</sub> particles in plating bath was found to enhance the adsorption rate, leading to a higher volume percentage of the codeposited MoS<sub>2</sub> particles.<sup>25</sup> It is also notable that the incorporation rate of the particles in the Ni matrix was high. This may be related to the semiconducting nature of MoS<sub>2</sub> particles, so they are easily attracted to the cathode surface.

- *Morphologies of coatings*

Figure 2 shows the SEM surface micrographs of Ni–MoS<sub>2</sub> composite coatings, filled with different weight fractions of MoS<sub>2</sub> particles, and their corresponding optical micrographs of cross sections.

The SEM micrograph of pure Ni (Figure 2(a)) coating reveals a regular pyramidal structure with a uniform grain size and smooth surface compared to the surface of Ni matrix filled with MoS<sub>2</sub> particles. The SEM micrographs of Ni–MoS<sub>2</sub> coatings (Figure 2(b) to (e)) revealed the formation of clusters that grew in number as a function of the increase of the MoS<sub>2</sub> content in coatings and led to very rough surfaces. In fact, the formation of clusters is directly related to the semiconductive nature of MoS<sub>2</sub> particles. In fact, when semiconductive particles were added to the electrolytic solution, the electrolytic current concentrated around the adsorbed particles on the cathode. Thus, a nonuniform distribution of current on the electrode surface with adsorbed particles may happen. This indicates that the adsorbed MoS<sub>2</sub> could be the sites for the nucleation of nickel growth and could accelerate the crystal growth at their locations and create many deposit protrusions on the cathode surface. This leads to a nonuniform coating with high and variable thickness (Figures 2(b') to (e')) which becomes higher as a function of the increase in the MoS<sub>2</sub> content.

The XRD patterns of pure Ni and Ni–MoS<sub>2</sub> coatings are shown in Figure 3. The (200) diffraction peak of Ni in the nanocomposite coating has a lower peak intensity and broader peak width than that of the pure Ni coating. This may be attributed to the decrease in

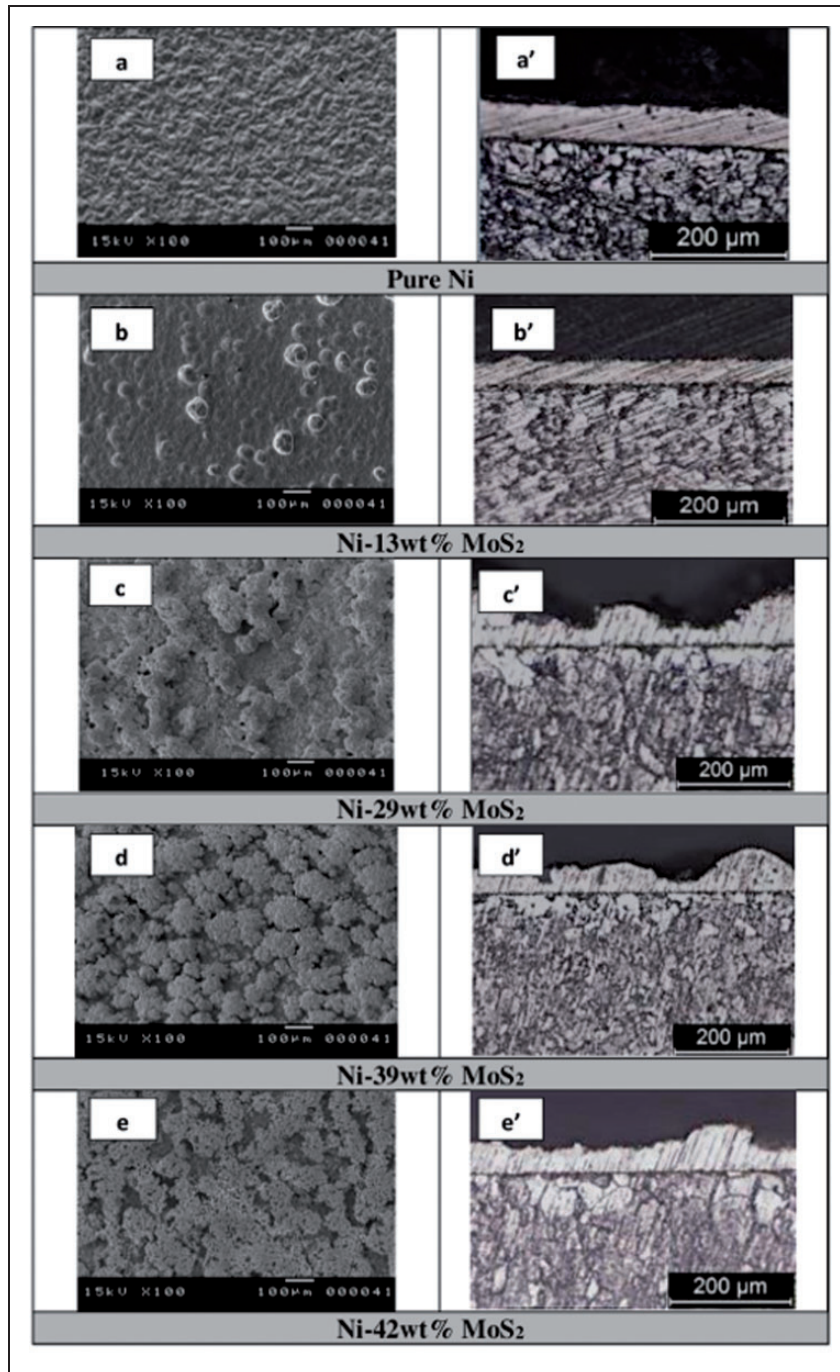
the grain size of the Ni–MoS<sub>2</sub> composite coating with the addition of MoS<sub>2</sub> particles in the plating bath. The particles provided more nucleation sites and accelerated crystal growth, leading to a smaller crystal size for the Ni matrix in the composite coating.<sup>26</sup> This result was confirmed by the calculation of Ni grain size by Debye Scherrer equation. The grain size decreased from 60 nm for pure Ni to 20 nm for Ni–MoS<sub>2</sub> composite coatings. Pure Ni exhibited an intense reflection peak of (200), introducing MoS<sub>2</sub> particles led to the change of the predominant reflection peak to (111). Thus, the (200) plane was changed to predominant diffraction in (111) plane, which is in good agreement with the findings of Srivastava et al.<sup>27</sup> who reported the same results from the incorporation of SiC particles in Ni sulfamate bath. This may be elucidated by the change of surface morphology of the Ni grains. The authors have demonstrated that the incorporation of nano-SiC altered the Ni–Co matrix from a dense spherical smooth surface to rough nodular morphology.

The surface roughness (Ra) as a function of the weight fraction of MoS<sub>2</sub> particles in Ni coatings is presented in Figure 4. The results confirm that the addition of MoS<sub>2</sub> particles in Ni matrix leads to the increase of the surface roughness. Yet, coatings with 29 wt% of MoS<sub>2</sub> particles present the highest level of roughness. Indeed, at a very low concentration of MoS<sub>2</sub> particles (13 wt%), very small dispersed clusters were formed (Figure 2(b)); subsequently, the surface roughness increased but not enormously. While the concentration of MoS<sub>2</sub> particles increased up to 29 wt%, more clusters were formed due to the increase of nucleation sites. However, the nucleation sites remained little, and therefore the individual large clusters grew up and led to a very rough surface. With the increase of the MoS<sub>2</sub> content, the nucleation sites increased and more bonded clusters were formed, leading to much smoother surfaces. The high concentration of MoS<sub>2</sub> in the electrolytic bath led to the formation of denser structures.

#### *Micromechanical and tribological behaviors of Ni–MoS<sub>2</sub> coatings*

- *Microhardness*

The Vickers microhardness test was carried out using a diamond tip microindenter and the value was calculated from indentation widths. However, due to the rough surface of the samples, it was difficult to obtain clear indentation marks. Thus, indentations were carried out on the cross section of the coatings to obtain more trustworthy values of microhardness. As shown in Figure 5, the Ni–MoS<sub>2</sub> coatings at the first stage showed an improvement of microhardness compared to the pure Ni coating. As MoS<sub>2</sub> is much softer than Ni, the microhardness increase of the composite coating must be attributed to other factors, particularly the huge decrease of



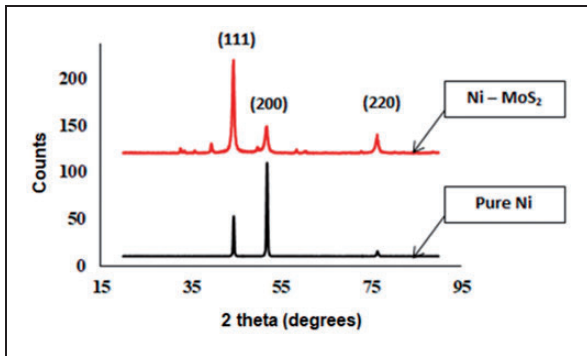
**Figure 2.** SEM micrographs of Ni–MoS<sub>2</sub> composite coatings with different weight fraction of MoS<sub>2</sub>: (a) 0%, (b) 13%, (c) 29%, (d) 39%, (e) 42% and their corresponding cross section optical micrographs: (a') 0%, (b') 13%, (c') 29%, (d') 39%, (e') 42%.

crystal sizes for Ni–MoS<sub>2</sub> coatings, as previously mentioned in the DRX part, where the increased grain boundaries may hinder dislocation mobility. In the second stage, a huge decrease of microhardness was shown for coating containing 42 wt% of MoS<sub>2</sub>, which may be attributed to the deterioration of performance of coating for high weight fraction of MoS<sub>2</sub> particles of coating. Indeed, at this concentration, the particles would smash the continuity and uniformity of the matrix and then result in the weakness of composite coatings.

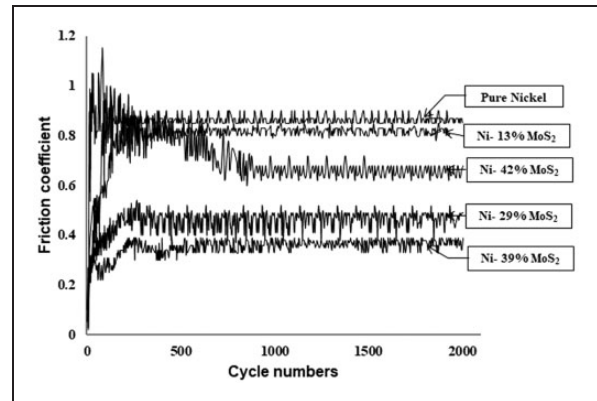
- *Friction coefficient*

Figure 6 shows the friction coefficients versus the cycle numbers produced by the Ni and Ni–MoS<sub>2</sub> coatings with different weight fractions of MoS<sub>2</sub> particles, during 2000 sliding cycles, against the steel ball. For all coatings, the friction coefficient increases with the number of sliding cycles during the running-in stage and stabilizes afterwards to a steady-state value.

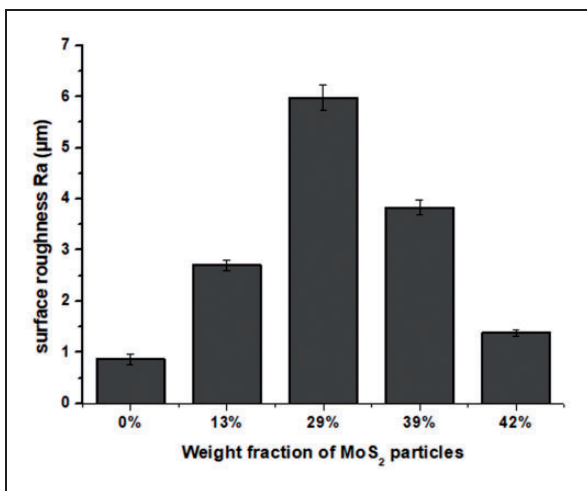
The effect of the MoS<sub>2</sub> weight fraction in the Ni coatings on the stabilized value of the coefficient of



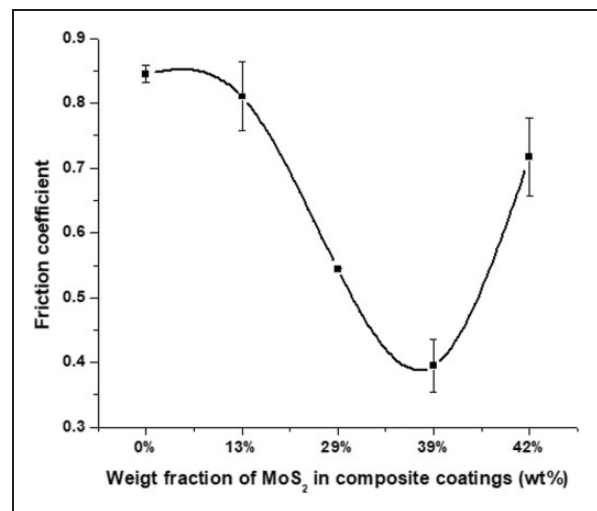
**Figure 3.** XRD of pure Ni and Ni-MoS<sub>2</sub> coating with 13 wt% of MoS<sub>2</sub>.



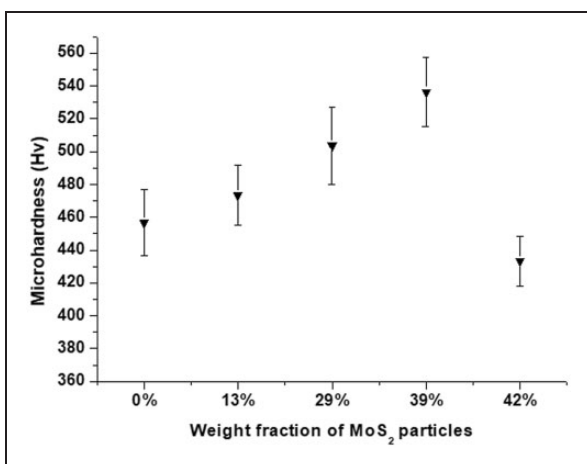
**Figure 6.** Friction coefficient trends of Ni-MoS<sub>2</sub> composite coatings filled with different weight fraction of MoS<sub>2</sub>.



**Figure 4.** Ni-MoS<sub>2</sub> composite coatings roughness versus different weight fraction of MoS<sub>2</sub>.



**Figure 7.** Evolution of stabilized value of friction coefficient versus different weight fraction of MoS<sub>2</sub> in Ni coatings.

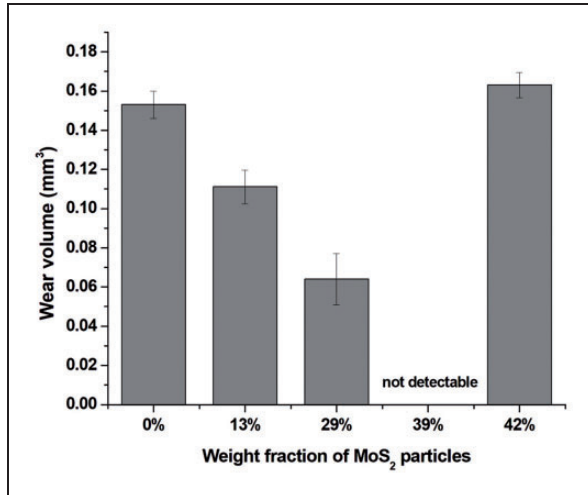


**Figure 5.** Microhardness of Ni-MoS<sub>2</sub> composite coatings with different weight fraction of MoS<sub>2</sub>.

friction (COF) after 2000 sliding cycles is presented in Figure 7. The COF of Ni-MoS<sub>2</sub> composite coatings dropped sharply compared to that of pure nickel coating and decreased from an average value of 0.84–0.37

when Ni coatings had 39 wt% of MoS<sub>2</sub> particles (bath concentration 0.5 g/l). Thus, the incorporation of MoS<sub>2</sub> into the Ni coating lowered the coating friction coefficient by ~60%. Actually, an easy slippage took place between the layers of MoS<sub>2</sub> thanks to its hexagonal structure, and hence the adherence of MoS<sub>2</sub> particles to the worn surface, leading to the formation of solid self-lubricant layer on the wear track. Accordingly, the layer thickness increases with the increase of MoS<sub>2</sub> content and the metal–metal contact is replaced by the MoS<sub>2</sub> film–metal contact.<sup>28</sup> However, when MoS<sub>2</sub> weight fraction attains 42 wt% (bath concentration 1 g/l), the COF enormously reincreases and reaches 0.73. As mentioned above, at this concentration, the particles would smash the continuity and uniformity of the matrix and then result in the weakness and large deformation of composite coatings during the friction test. Subsequently, these coatings were easily detached from the substrate during the friction tests, and consequently the high friction coefficient observed did not correspond to the coating itself but to the substrate

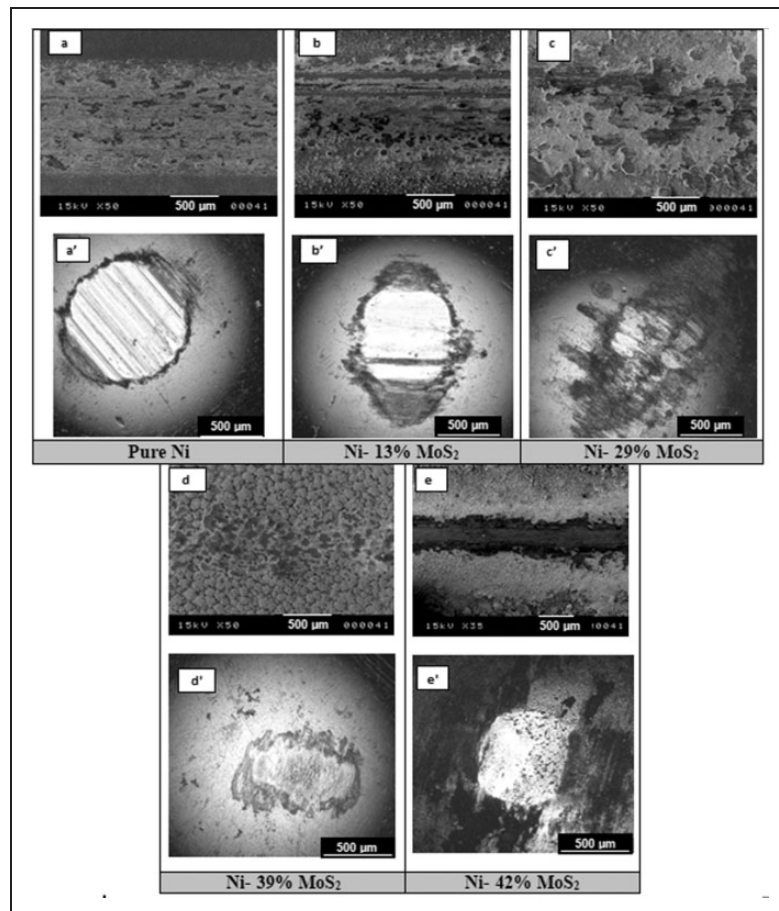
and remains of the coatings. The same result has been found by Cardinal et al.<sup>8</sup> However, He et al.<sup>11</sup> explained the reincrease of COF by the oxidation of coating after exceeding a certain value of concentration of MoS<sub>2</sub> particles.



**Figure 8.** The evolution of wear volume loss with weight fraction of MoS<sub>2</sub> in Ni coatings.

- *Wear behavior*

Figure 8 highlights the evolution of wear volume loss of Ni composite coatings as a function of different MoS<sub>2</sub> weight fractions. Because of the rough surface and the superficial wear, the wear volume loss was not detectable for coatings filled with 39 wt% of MoS<sub>2</sub> particles. It can also be noted that the wear volume decreases until 39 wt% of MoS<sub>2</sub> particles and then increases hugely. The initial reduction of wear volume loss with the increase of the MoS<sub>2</sub> wt% can be related to the ability of MoS<sub>2</sub> particles to develop a layer of soft wear debris on the wear track of the coated sample. Furthermore, on the surface of spherical counterpart, a strongly adherent thin transfer film, mainly composed of MoS<sub>2</sub>, can be developed, resulting in a lower friction between the contacting solids. Beyond 39% of MoS<sub>2</sub> weight fraction, the coating lost its mechanical performances due to the discontinuity of the matrix. Thus, an immense increase of wear volume could be observed. Therefore, 39 wt% of MoS<sub>2</sub> corresponds to the optimal MoS<sub>2</sub> fraction that provides the best condition to promote the solid lubricant layer stability and to maintain the Ni matrix integrity.



**Figure 9.** SEM micrographs of wear track after 2000 sliding cycles of Ni composite coatings filled with different weight fraction of MoS<sub>2</sub>: (a) pure, (b) 13%, (c) 29%, (d) 39%, (e) 42% and their corresponding optical micrographs of the counterbody worn surface: (a') pure, (b') 13%, (c') 29%, (d') 39%, (e') 42%.

**Table 3.** Mechanical and tribological properties of Ni composite coatings filled with 39 wt% of MoS<sub>2</sub> or 38 wt% of graphite particles.

Coatings	Mechanical and tribological properties				
	Surface roughness Ra ( $\mu\text{m}$ )	Microhardness (Hv)	Stabilized COF (after 2000 cycles)	Wear volume ( $\text{mm}^3$ )	Wear track width ( $\mu\text{m}$ )
Pure Ni	$0.86 \pm 0.10$	$456.6 \pm 20.2$	$0.840 \pm 0.013$	$0.158 \pm 0.007$	$1187 \pm 53$
Ni-39 wt% MoS <sub>2</sub>	$3.83 \pm 0.15$	$536.5 \pm 21.1$	$0.390 \pm 0.041$	Not detectable	$698 \pm 48$
Ni-38 wt% graphite	$1.95 \pm 0.23$	$284.4 \pm 24.9$	$0.210 \pm 0.001$	$0.0125 \pm 0.0007$	$343 \pm 74$

COF: coefficient of friction.

Figure 9 illustrates the SEM micrographs of worn surfaces of Ni-MoS<sub>2</sub> composite coatings as well as their corresponding optical micrographs of steel ball worn surfaces after 2000 sliding cycles.

Grooves, scars, and clear adhesive spalling pits along the sliding direction were observed on the wear track of pure Ni coating in Figure 9(a), which indicates that severe adhesive wear occurred. Accordingly, abrasive striations were obvious on the worn surface of counterpart rubbing against pure nickel (Figure 9(a')). The addition of 13 wt% of MoS<sub>2</sub> particles did not have any significant effect on the wear process (Figure 9(b)). The same grooves, scars, and adhesive spalling pits were observed on the wear track. Besides, the same abrasive striations are shown on the worn surface of the counterpart (Figure 9(b')). Thus, the addition of 13 wt% of MoS<sub>2</sub> is not enough to form a continuous third-body layer and to improve the wear resistance of the Ni coating.<sup>28</sup> Thereafter, the increase of MoS<sub>2</sub> weight fraction leads to the decrease in the width of the wear track as well as the radius of worn surface of steel ball sliding against these coatings. When 29 wt% of MoS<sub>2</sub> particles were added, a smoother wear scar with fewer and smaller adhesive craters were obvious (Figure 9(c)) indicating the beginning of formation of a third-body layer on the whole contact track during the sliding process. This result is confirmed by the optical micrograph of the worn surface of counterpart (Figure 9(c')) showing the development of a transfer film that causes a decrease of COF and wear volume. With a further increase to 39 wt% of MoS<sub>2</sub>, the wear track appeared in patches form (Figure 9(d)) and its width was narrower (showing one-quarter of the width of wear track of pure Ni). By the EDS technique, He et al.<sup>11</sup> confirmed that these patches were composed of MoS<sub>2</sub> tribofilm. Therefore, it seems that with 39 wt% fraction of MoS<sub>2</sub>, a self-lubricating Ni-MoS<sub>2</sub> was obtained, and the wear resistance of coating was greatly enhanced as well as a transfer film was observed on the steel ball counterpart (Figure 9(d')). Therefore, the increase of wt% of MoS<sub>2</sub> particles in coatings was proven to lead to an expansion of the transfer film to cover the totality of the worn surface of the counterpart for Ni-39 wt% MoS<sub>2</sub> coating. However, when MoS<sub>2</sub> weight fraction reached 42% (Figure 9(e)), a very wide wear track, greater than the pure nickel wear track width, with

large plastic deformation and, indeed, some areas of massive peelings appeared. This result can be attributed to the huge decrease of microhardness of the corresponding coating. Accordingly, the loss of particles is easily carried out. These snatch particles act as abrasive particles in the contact zones, which, in turn, are considered to harm the transfer film and bring severe abrasive wear.<sup>29</sup> As a result, a discontinuous transfer film appears on the counterpart and a huge denuded zone with abrasive striations was observed in the center of the transfer film of steel ball counterpart rubbing against coating with 42 wt% of MoS<sub>2</sub> particles (Figure 9(e')).

#### Ni-MoS<sub>2</sub> and Ni-graphite coatings: Comparative analysis of micromechanical and tribological properties

The micromechanical and tribological properties of Ni-based coatings filled with nearly the same weight fraction of MoS<sub>2</sub> or graphite are summarized in Table 3. The selected MoS<sub>2</sub> fraction was 39 wt% which is the optimal weight fraction that provides the best tribological behavior for Ni-MoS<sub>2</sub> coatings. For Ni-graphite coating, an almost similar fraction (38 wt%) of graphite microparticles was obtained using an electrolytic bath containing graphite with a concentration of 10 g/l. It can be said that the MoS<sub>2</sub> particles are more easily incorporated into the Ni matrix than graphite particles (almost the same fraction obtained from an electrolytic bath containing 0.5 g/l of MoS<sub>2</sub> particles). In fact, coating with smaller particles (MoS<sub>2</sub> grain size < 2  $\mu\text{m}$ ) exhibited a higher activity than coating with larger particles (graphite grain size 7–11  $\mu\text{m}$ ). This may be attributed to the fact that heavy particles are more difficult to be transported by the Ni ions due to lower effect of their throwing power.<sup>30</sup>

From Table 3, both Ni-MoS<sub>2</sub> and Ni-graphite coating surface morphology were much rougher than those of pure Ni coatings. This high roughness was caused by the formation of agglomerated clusters owing to the conductor or semiconductor nature of particles. However, Ni-MoS<sub>2</sub> coatings present the highest value of roughness. The possible reason for the highest roughness was the small radius of MoS<sub>2</sub> particles, which results in stronger electric field

around the MoS<sub>2</sub> particles. This, in turn, leads to the local increase of deposition current densities during electro-codeposition and the formation of several clusters as well as a very high surface roughness.<sup>30</sup>

The reinforcement types have also an effect on the microhardness of the composites layers. Compared to pure nickel, the microhardness increased with the addition of MoS<sub>2</sub> particles and decreased with the addition of graphite particles. The enhancement of microhardness with the addition of MoS<sub>2</sub> particles is accredited to the grain refining explained previously. Nevertheless, in the case of the addition of graphite particles, the diminution is attributed to the sliding and soft nature of graphite particles. Hence, they are easily deformed under contact stresses. The addition of graphite particles in the composite coatings leads to the decrease of the capability of antiplastic deformation that brings about the smaller microhardness of composite coatings.<sup>28</sup>

A comparison of the tribological behavior of Ni filled with different reinforcement types has been also conducted. In fact, a decrease of COF with the addition of MoS<sub>2</sub> or graphite solid lubricants particles to the nickel coating can be seen. Nevertheless, coatings filled with graphite particles present the lowest COF (~25% of COF of pure Ni and ~50% of COF of Ni–MoS<sub>2</sub> coatings). This can be credited to the formation of tribofilm composed mainly of graphite particles of this coating, thus allowing the reduction of COF. Whereas, for the Ni–MoS<sub>2</sub> coatings, the reason for the higher coefficient was a possible transformation of some particles of MoS<sub>2</sub> to MoO that disrupts layer movement.<sup>11</sup> Therefore, it can be said that the incorporation of graphite particles in the coating induced more effective lubrication.

Since the volume of wear was not detectable for the Ni–MoS<sub>2</sub> coating, due to the high roughness of this type of coating, the widths of the wear tracks were compared for both Ni–MoS<sub>2</sub> and Ni–graphite coatings. The wear tracks widths of Ni composite coatings were enormously reduced compared to the wear track of pure Ni. The incorporation of MoS<sub>2</sub> particles reduced the wear track width by ~45%, while the incorporation of graphite particles decreased the wear track width by ~70%. Hence, it can be concluded that the incorporation of graphite particles in the coating induces more effective wear resistance.

## Conclusions

In this study, the effect of concentration of MoS<sub>2</sub> particles on the microstructure, micromechanical and tribological behavior of electrodeposited Ni–MoS<sub>2</sub> composite coatings was examined. These composite coatings exhibit a surface morphology characterized by the formation of clusters that become more numerous as a function of the increase of the MoS<sub>2</sub> content in coatings. These clusters lead to a smaller grain size of Ni, confirmed by XRD, and to the increase in the

surface roughness. However, at a very high concentration of MoS<sub>2</sub> particles, more bonded clusters were formed, leading to much smoother surfaces. A MoS<sub>2</sub> concentration of 39 wt% has been proved to be optimal to afford a high microhardness and supply a low COF and wear volume.

The micromechanical and tribological properties of Ni-based coatings filled with 39 wt% MoS<sub>2</sub> or 38 wt% graphite were also analyzed and compared. It was found that MoS<sub>2</sub> particles are more easily incorporated into the Ni matrix than graphite particles owing to MoS<sub>2</sub> smaller particles (MoS<sub>2</sub> grain size < 2 μm) which exhibit higher activity than larger particles (graphite grain size 7–11 μm). Compared to pure nickel, the microhardness increased with the addition of MoS<sub>2</sub> particles and decreased with the addition of graphite particles. It was also found that the incorporation of graphite particles in the coating induced more effective lubrication and wear resistance.

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