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**Mechanical and wear characterization of electroless nickel mono and bilayers and high boron-mid phosphorous electroless nickel duplex coatings**

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**Abstract**

The mechanical and wear properties of electroless nickel monolayer, bilayers and duplex NiP/NiB coatings were investigated in the as deposited state. Bilayers and duplex coatings, constituted of two layer of 10  $\mu\text{m}$  each, were prepared according to four distinct configurations (NiB/NiP; NiP/NiB; NiB/NiB and NiP/NiP). Single layer coatings from each electroless nickel bath with a thickness of 20  $\mu\text{m}$  were also synthesized and analyzed in this work: mid phosphorous NiP (nickel-phosphorus) and high boron NiB (nickel-boron). The microhardness, roughness and wear resistance of electroless nickel duplex coatings were compared with electroless NiP and NiB coatings of similar thickness. The hardness characteristics of duplex coatings are really influenced by the high hardness of NiB coatings: the hardness of pure NiP coatings was 550 HV while the presence of NiB coating as underlayer allowed to reach 738 HV. SEM observations of the cross-sections of the nickel duplex coatings also reveal that coatings are uniform with proper compatibility between layers.

Key words: Duplex coatings; Electroless nickel; Nickel-phosphorus; Nickel-boron.

## 1. Introduction

Coating technology has been extensively used in the engineering industry as a process that reduces surface reactions such as wear and corrosion and, in addition, promotes better surface finishing. Among of the various deposition methods, electroless plating presents a huge range of interesting properties. Electroless deposition is preferred because it allows producing homogeneous coatings that present good adhesion on various substrate materials with complex geometries [1–8].

Out of the range of electroless deposited films, nickel is the metal with the broadest applications. Spontaneous reduction of nickel was first observed by Wurtz [9-11] in the 19th century. However, the industrial process of electroless nickel plating was discovered in 1946 by Brenner and Riddel [12-14], when they developed a process for plating the inner walls of tubes with nickel using sodium hypophosphite as the reducing agent [15-18]. Electroless nickel-boron plating was developed a few years later, in 1955 [19], just after the discovery of the borohydride ion [20].

Hypophosphite and borohydride have been mainly used as reducing agents for electroless nickel. NiP coatings have been widely used because of their reasonable cost while electroless NiB is somewhat restricted due to its higher cost. However, the remarkable properties obtained by electroless coatings reduced with borohydride explain why these have received much attention, especially in the case of surface finishing of electrical devices [21,22].

Borohydride-reduced electroless nickel coatings also find extensive applications in aerospace, automotive, chemical and electrical industries, especially because of their solderability, high hardness and wear and abrasion resistance [23-29]. In contrast, hypophosphite-reduced electroless nickel coatings find extensive applications in chemical and

automobile industry, hydraulics, as well as oil and gas industries due to their high corrosion resistances [30-35].

Hypophosphite reduced electroless coatings have been used on metal substrates such as firearms, to enhance corrosion resistance. However, these coatings do not possess very high wear resistance and lubricity properties. In addition, NiB coatings have also been used in firearms to enhance wear resistance and lubricity properties. Duplex systems with the corrosion properties of NiP and the wear properties of NiB coatings would be the ideal coatings for these applications [36]. Another application for these duplex systems is the protection of items used in a marine environment, like propellers and hulls that are affected by marine growth and fouling. The nickel boron coating can be applied to reduce friction and increase the hydrodynamic performance of the parts. In addition, NiP coatings can be applied to enhance corrosion properties [37].

As previously mentioned, each class of electroless nickel is known for being particularly suitable for some applications, corrosion resistance for nickel-phosphorous and mechanical and wear applications for nickel-boron. One system that combines both kinds of coatings and improves globally the properties of the coated system was developed several years ago [38-40]. However, none of the previous works compared the duplex coatings with monolayers of similar thickness or with bilayers of a single material, making it impossible to attribute the improved properties to the presence of two layers or to the duplex nature of the coating. In the present research, NiP/NiB, NiB/NiP, NiB/NiB and NiP/NiP duplex coatings were synthesized on mild steel. First, the mechanical and wear characterization of the duplex coatings were evaluated. Next, results for duplex coatings were compared to those for 20  $\mu\text{m}$  thick single coatings obtained from each electroless nickel composition.

## **2. Materials and methods**

### **2.1. Sample preparation**

Specimens of mild steel (ST 37-DIN 17100) were cut to a size of 100mm × 100mm × 1mm. The choice of mild steel substrate is directly linked to its wide range of applications. A hole of 2 mm in diameter was drilled close to one edge of each specimen for convenient handling. The surface of the specimens was polished with emery paper up to 2000 grit. The substrates were prepared for plating by acetone degreasing and etching in a 30 vol.% hydrochloric acid solution. The plates used for the Taber abrasion tests were drilled in their center with a 7 mm diameter tool in order to fit the test equipment.

## 2.2. Electroless Nickel baths

Electroless plating was carried out in a thermostable teflonized cell with a volume of 8L (for 10µm thickness) or 10L (for 20µm thickness), under constant mechanical agitation. The nickel-boron bath operated at  $96.5 \pm 0.5$  °C. The bath parameters and composition were developed by our group and use sodium borohydride ( $\text{NaBH}_4$ ) as a reducer, nickel chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) as a nickel source, ethylenediamine ( $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$ ) as a complexing agent and lead tungstate ( $\text{PbWO}_4$ ) as a stabilizer. The precise composition of this bath is presented in Table I. The increase of plating temperature compared to other works of our group [23-24, 40-43] allowed an increase of the boron content of the coating from 4-6 to 8-9 wt. %. Electroless nickel mid-phosphorous deposition was carried out at  $88 \pm 1$  °C with a commercial bath: Niklad ELV 808A and Niklad ELV 808B from Mc Dermid (7-9 wt. % P). The average composition of the NiB coatings is 8 wt. % B, 0.5 wt. % Pb and 91,5 wt. % Ni and that of NiP is 7 wt. % P and 93 wt.% Ni.

To synthesize bi-layers and duplex samples, (NiB/NiB, NiP/NiP, NiB/NiP and NiP/NiB) two baths were used, one for each layer. After the deposition of the first layer, the samples are stored in a desiccator. The time gap before the second layer was kept between 1 and 6 hours to ensure reproducibility of the surface conditions. The second layer was directly deposited on the sample without any surface preparation or activation. The two layers of every duplex coating were always made on the same day. The different coating configurations are illustrated in Fig. 1.

### 2.3. Characterization methods

The surface and cross section morphology of each sample were observed using a JEOL-SEM 6400 scanning electron microscope and a Hirox 8700 3D optical microscope. Cross sections were mounted in resin, polished with silicon carbide paper and then with diamond paste up to mirror finish before observation.

Instrumented microhardness testing was performed using a four-sided pyramid diamond indenter. Standard Vickers hardness tests were conducted on the surface of samples with a load of 100 gf and a holding time of 20 s, for each coating configuration. A Zeiss 119 Surfcom 1400D-3DF surface roughness measurement apparatus, based on the mechanical stylus method, was used to determine the surface roughness of the nickel coatings. The values of roughness and hardness here presented are the average of ten measurements.

To quantify the abrasive wear characteristics of the coatings, abrasion tests were performed with a circular abrader (5155 Taber Industries) under a load of 1000g. This circular abrasion setup was equipped with CS-17 abrasive rubber wheels with a rotating speed of 72 rpm. The abrasion tests were carried out for 10 sets of 1000 cycles each with weigh characterization after each set. The abrasion results will be presented as the Taber Wear Index (TWI), with the aim of facilitating interpretation. Equation 1 is used to calculate this index.

$$TWI = A/B \quad (1)$$

Where A is the weight lost during the entire test duration (mg) and B the number of wear cycles (of 1000 rotations each) that the sample was submitted to.

A CSEM scratch tester machine with a diamond Rockwell stylus with a radius of 200  $\mu\text{m}$  was used to perform scratch tests. A scratch test is used to estimate the adhesion of the deposits under external solicitations. This method gives a good notion of the deposit adhesion on different substrates. In the present case, this method also gives a good idea of the adhesion

between distinct layers. The linear increasing load method was used in all cases, from 0 to 150N with a scratch velocity of 6.75 mm/min and a scratch distance set to 10 mm. The scratched substrate observed with Hirox KH-8700 Digital Microscope in order to assess the damage features.

### 3. Results and discussion

#### 3.1. Morphology of the coatings

SEM observation of the coatings cross-sections can be seen in Fig. 2. All coated systems presented a thickness in the desired range ( $\sim 20 \mu\text{m}$ ), confirming the reproducibility of the deposition method used in this work. Also, distinction between layers can easily be made for the bilayer and duplex systems. Moreover, the typical columnar morphology of the nickel-boron layers is observed for all such coatings. The cross-sections of nickel-phosphorous, however, appear featureless (except for the delimitation of the layers) because NiP cannot be etched with nital.

The surface morphologies are shown in Fig. 3. Comparing bilayers of the same material (NiB/NiB or NiP/NiP) to monolayers of the same composition, it appears that morphology does not vary significantly. The monolayer and bilayer coatings presented the surface morphologies typical for their type of coating: cauliflower-like texture for NiB and planar aspect, with conservation of the initial surface topography, for NiP. The morphology of duplex coatings is somewhat in between the two electroless nickel types, but with a slight propensity to the cauliflower-like texture. The fact that NiB morphology becomes dominant in duplex coatings can be explained by the very good morphological compliance of NiP, that reproduces perfectly the topology of the substrate. This morphological characteristic should be beneficial for the tribological properties of the duplex coatings, since the NiB surface morphology is known to decrease the friction coefficient in some applications [36].

### 3.2. Roughness

The average values of roughness for all the samples are shown in Table II. The parameters chosen to represent the roughness in this study are Ra (arithmetic average of the height of every point of the surface) and Rp (maximum peak height). Ra is the most used roughness parameter, which facilitates comparisons with other works. Regarding Rp, it represents the height of the highest peak from the mean line. Consequently, the Rp parameter is usually considered for electroless coatings. Since electroless process takes place in solution, peaks have a more important contribution to the deposit initiation and growth than the valleys.

All of the six systems presented very low values of Ra and Rp with limited standard deviation. Regarding the differences between the two types of electroless nickel, nickel-boron (both mono and bilayers) presented higher roughness than similar coatings of nickel-phosphorous. Also, the roughness of the bilayers was higher than that of monolayers. Similarly to morphology, duplex coatings presented intermediate roughness, with Ra and Rp values in between NiP and NiB.

### 3.3. Hardness

Microhardness values are presented in Table III. In view of better characterization of the influence of the two layers, the measurements were carried out on the surface of the samples. The same method was used in the case of single layer coatings for easier comparison. Results indicated that systems coated with electroless NiB are much harder than those protected with NiP. Bilayers and monolayers presented similar hardness. The presence of NiB in the duplex coatings increases significantly the hardness when compared to NiP coatings. In addition, the duplex system where NiB is the top most layer is nearly as hard as NiB. When NiP is on top, the hardness seems to be closer to the hardness of the NiB

monolayer than to that of the NiP monolayer. High hardness is one of the main properties of NiB coatings. Moreover, NiB deposits present high values of the so-called hot hardness; which is the ability to maintain hardness at elevated temperatures. In addition, Zhang et al [38], demonstrated that the hardness of NiP/NiB duplex coatings can be improved with heat treatment.

### 3.4. Wear resistance

Taber Wear Index for all systems is shown in Table III and Fig. 4 shows the weight loss evolution as a function of the number of abrasion cycles. The coatings that were exempt of NiB presented the worst TWI. Another important point is that the use of bilayer coatings improves the abrasive wear resistance of electroless nickel. Indeed, bilayers presented a significantly lower TWI than their respective monolayers. Increase of abrasion resistance for duplex coatings was reported by Sankara Narayanan et al [39]. However, the mechanisms leading to this behavior are still under investigation. The change of behavior observed around 5000 cycles for some coatings is probably related to the interface. Like hardness, wear behavior of duplex coatings can also be improved by heat treatments as shown by Vitry et al [40] after heat treatment at 180 °C.

### 3.5. Scratch test

The critical load ( $L_c$ ) of electroless plated Ni systems, obtained through scratch test, is presented in Table II. These results refer to the first damage and were obtained by a combination of acoustic emission and microscopy observation.

Mono and bilayers of a same material present critical loads in the same range, even though the use of bilayers for nickel-boron seems to increase the critical load for first damage. Nevertheless, the appearance of transversal cracks occurs at the same time for mono and

bilayers NiB systems and seems to be higher for NiP bilayers than for monolayers of the same type.

Regarding duplex coatings, the first damage was certainly influenced by the position of the layers. The low critical load obtained for NiB/NiP suggests a low adhesion of nickel phosphorous on the initial nickel-boron layer while the value obtained in the reverse case (23 N) suggests a good adhesion of nickel-boron on nickel-phosphorous. While the high adhesion of nickel-boron is not surprising, the lower value obtained for the NiB/NiP duplex coating is surprising as the increased roughness and unique texture of nickel-boron seem quite favorable to promote adhesion of an additional layer. The optical micrographs showing the scratched region of the electroless plated Ni specimens are shown in Fig. 5. Mono and bilayers of the same material presented similar damage. The scratched area of the NiP/NiB duplex sample was similar to NiB/NiB bilayers coating. However, the NiB/NiP duplex, with nickel-phosphorous as the top layer, was the only one that presented chipping (regions of coating removal extending laterally from the edges of the groove); as presented in Fig. 6. None of the coatings presented complete failure.

Fig. 7 summarizes the principal failure modes for each coating system as well as the moment that damage appeared. The specimens that comprise electroless NiP had a larger damaged area than the specimens that comprise electroless NiB. As expected from previous results [44], NiB showed a better behavior regarding scratch tests than NiP. NiB presents good adhesion on the steel substrate, on another layer of NiB an also on NiP coatings. However, the NiP coatings presents a less considerable adhesion on the steel substrate and a poor adhesion on NiB coatings.

## Conclusions

Electroless NiP/NiB duplex coatings were prepared using dual baths (hypophosphite mid-phosphorous electroless nickel (7-9 wt. % P) and borohydride-reduced high boron

electroless nickel (7-9 wt. % B)). By producing duplex systems, mechanical and wear properties of electroless coatings have been modified. The duplex coatings present behaviors that are generally intermediate between those of NiP and NiB.

Regarding the morphology, a typical NiB morphology appears to stand out - even when NiP constitutes the top layer of the coating. This can be explained by the very good shape compliance of NiP coatings. SEM observations of the cross-section of the duplex coatings showed that they are uniform with proper compatibility between layers.

1. Roughness characteristics are strongly interconnected with the surface morphology. As expected, NiP coatings are smoother than NiB in similar configurations. The roughness of all coatings presented relatively low values, but the lowest ones were obtained for the systems having NiP as top layer.

2. The hardness of duplex coatings is mainly influenced by the high hardness of NiB even when NiP is the top layer.

3. NiB coatings are more resistant to abrasive wear. Moreover, the duplex coatings presented properties intermediate between NiP and NiB, with better properties for the system with NiB as the top layer.

4. Scratch tests results show that NiB coatings present better adhesion. In the case of duplex coatings, NiB has a good adhesion on NiP but NiP presents poor adhesion of NiB.

As expected, coatings that contain Nickel-boron were harder, presented better wear resistance and had a better scratch teste resistance than the others. Finally, duplex coatings combining NiP and NiB presented, in most cases, an intermediate behavior between the two types of electroless nickel: they tend to present higher values of hardness but with lower resistance to scratch tests. The use of bilayers did not influence hardness and morphology; although it seemed to improve wear resistance.

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Table I – Bath composition and operating conditions of electroless nickel bath.

NiB		NiP	
<b>Nickel chloride</b>	24 g/l	Mc Dermid (7-9 wt. % P)	
<b>Sodium hydroxide</b>	39 g/l		
<b>Ethylenediamine</b>	60 ml/l		
<b>Lead tungstate</b>	0.021 g/l		
<b>sodium borohydride</b>	0.602 g/l		
<b>Bath temperature</b>	96.5±0.5°C	<b>Bath temperature</b>	88±1°C
<b>Bath pH</b>	13.5	<b>Bath pH</b>	5.75
<b>Plating time</b>		<b>Plating time</b>	
<b>for 10µm thickness</b>	32 min	<b>for 10µm thickness</b>	35 min
<b>for 20µm thickness</b>	70 min	<b>for 20µm thickness</b>	70 min

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*Table II: Roughness of electroless mono and bi-layers and of duplex systems.*

	<b>Ra (<math>\mu\text{m}</math>)</b>	<b>Rp (<math>\mu\text{m}</math>)</b>
<b>St37/NiB</b>	0.162+/-0.011	0.366+/-0.017
<b>St37/NiP</b>	0.093+/-0.008	0.208+/-0.013
<b>St37/NiB/ NiB</b>	0.198+/-0.011	0.432+/-0.019
<b>St37/NiP/ NiB</b>	0.119+/-0.001	0.287+/-0.002
<b>St37/NiB/ NiP</b>	0.106+/-0.01	0.247+/-0.018
<b>St37/NiP/ NiP</b>	0.123+/-0.003	0.259+/-0.006

Table III: Hardness, Taber Wear Index (TWI) and critical load for first damage of electroless mono and bi-layers and of duplex systems.

	<b>Hardness (hv<sub>100</sub>)</b>	<b>TWI</b>	<b>Lc (N)</b>
<b>St37/NiB</b>	872.09 +/- 5.5	31.1+/-1.1	25
<b>St37/NiP</b>	551.35 +/- 2.1	35.9+/-0.4	14
<b>St37/NiB/ NiB</b>	875.5 +/- 4.6	27.6+/-2.3	30
<b>St37/NiP/ NiB</b>	860.66 +/- 6.1	27.2+/-0.7	23
<b>St37/NiB/ NiP</b>	738.9 +/- 6.1	28.9+/-1.8	8
<b>St37/NiP/ NiP</b>	549.31 +/- 6.2	34.9+/-2.4	13

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*Fig. 1: Summary of the various NiB/NiP coating systems.*

*Fig. 2: Cross-section morphologies of electroless monolayer, bilayer and duplex coatings.*

*Fig. 3: Surface morphology of electroless monolayer, bilayer and duplex coatings.*

*Fig. 4: Samples weight loss evolution as a function of the number of abrasion cycles.*

*Fig. 5: Observation of the scratch tracks up to 150 N on a 25  $\mu\text{m}$  thick as-deposited electroless nickel-boron coating: (a) NiB (b) NiP (c) St37/NiB/ NiB (d) St37/NiP/ NiB (e) St37/NiB/ NiP (f)St37/NiP/ NiP*

*Fig. 6: Chipping observed in the duplex NiB/NiP coating.*

*Fig. 7: Critical loads for the damage features of the different coating systems.*

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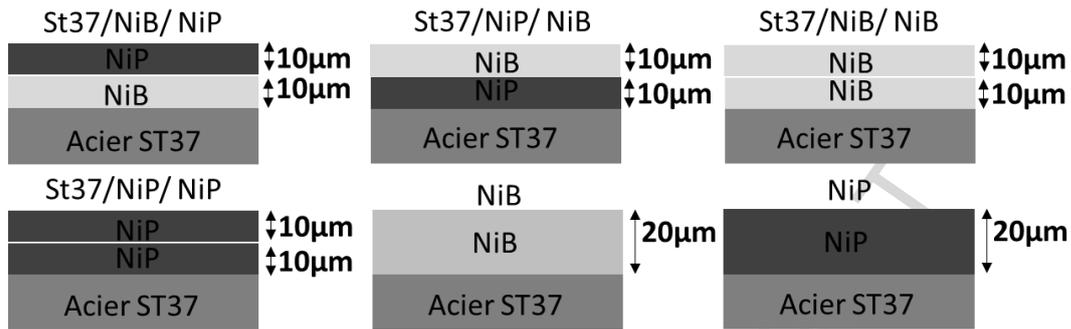


Fig. 1.

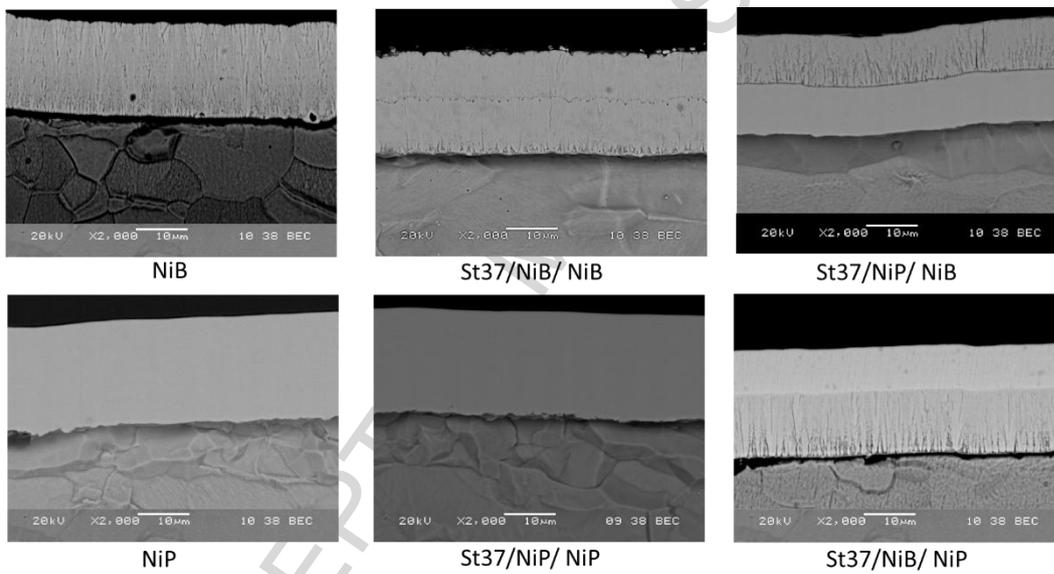


Fig. 2.

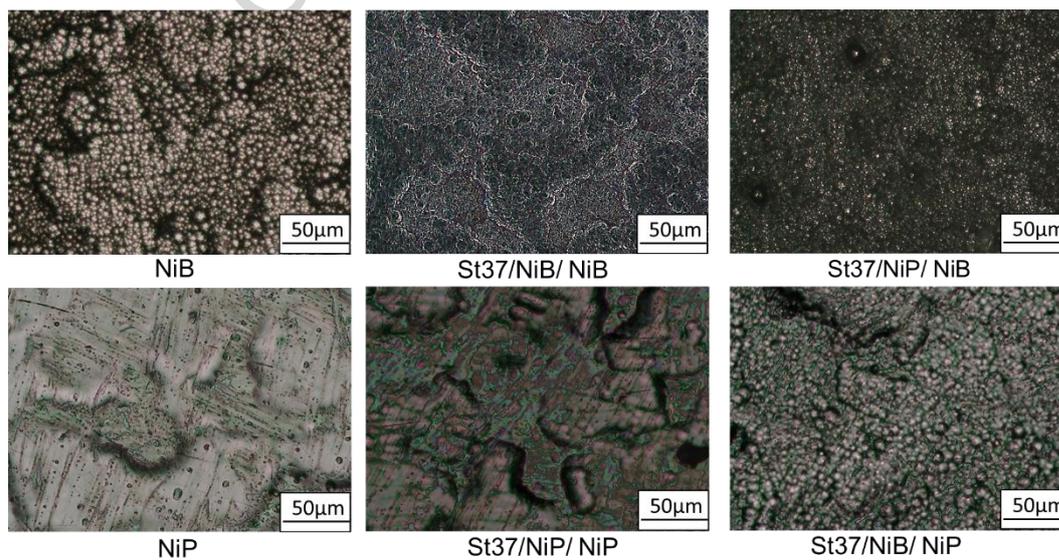


Fig. 3.

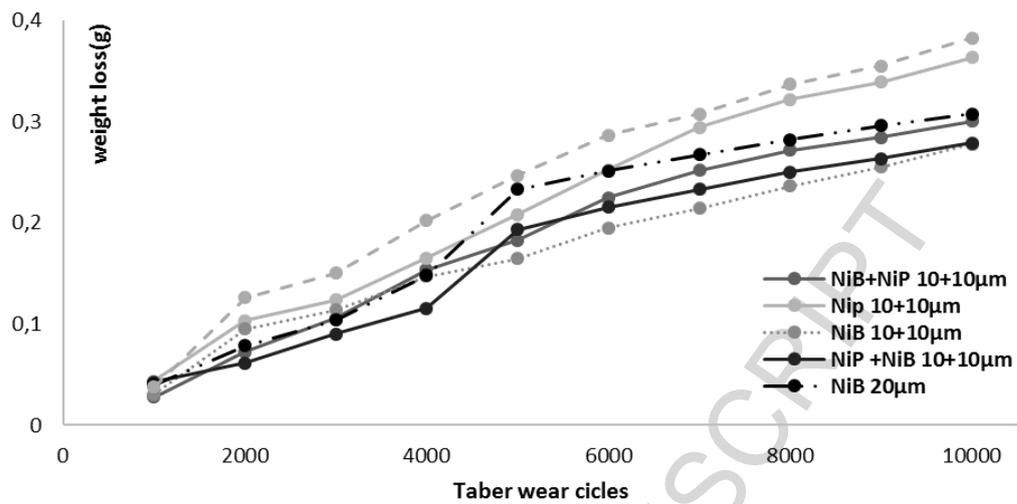


Fig. 4.

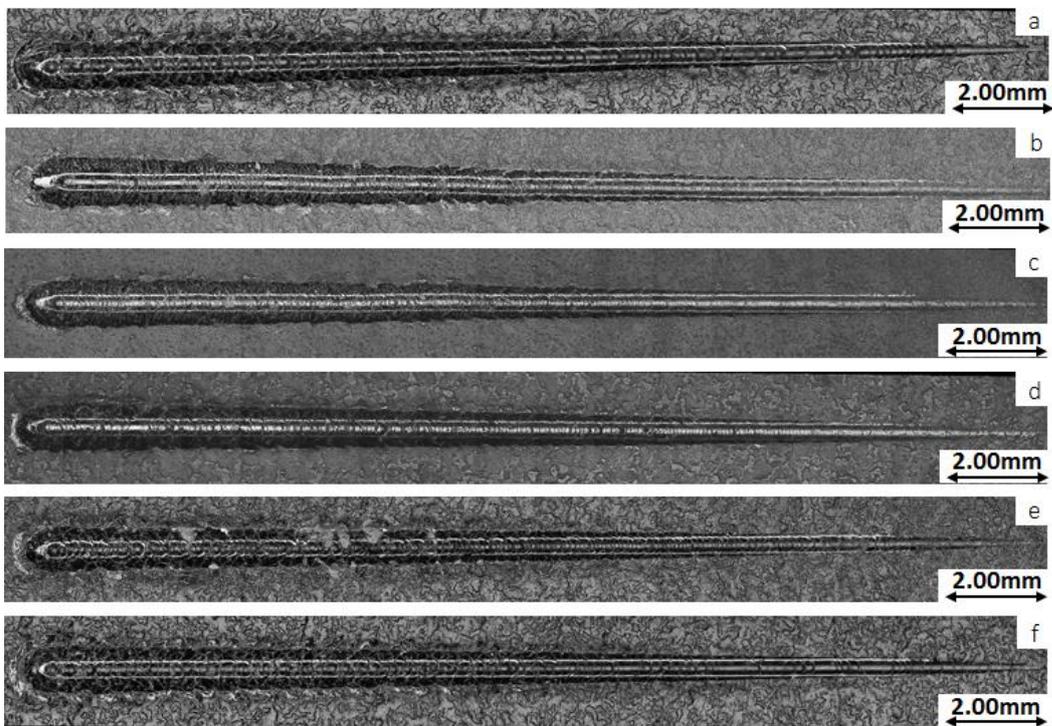


Fig. 5.

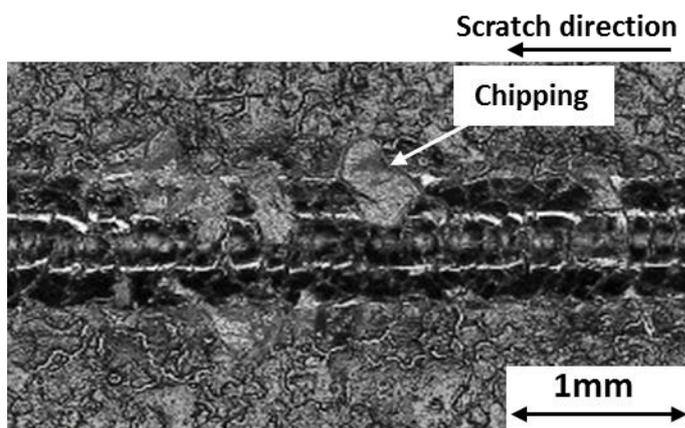


Fig. 6.

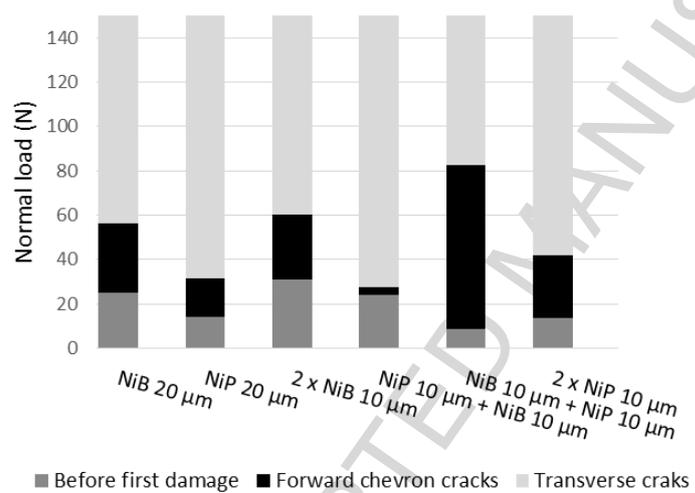


Fig. 7.

## Highlights

- Electroless NiP/NiB duplex coatings present behaviors in between NiP and NiB.
- Duplex coatings present a typical NiB morphology.
- The hardness of duplex coatings is higher than the average between NiP and NiB.
- NiB coatings have good adhesion on NiP. NiP coatings have poor adhesion on NiB.
- Coatings with NiB are harder, presenting better wear resistance and adhesion

ACCEPTED MANUSCRIPT