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Increase of boron content in electroless nickel-boron coating by modification of plating conditions

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ABSTRACT

High-boron (7–9 wt%) electroless nickel-coatings were synthesized on mild steel substrates by modification of the plating conditions of a mid-boron (5–6 wt% B) plating bath.
They were fully characterized and compared when possible with the coatings obtained in the usual operating conditions, before and after a heat treatment at 400 °C for 1 h in a protective atmosphere.
The morphology of the coating was similar to mid-boron coatings and left unchanged by heat treatment. Similarly, most properties of the as-deposited coatings were similar for mid and high-boron coatings.
However, the effect of heat treatment was very different on both types of coatings: while mid-boron coatings crystallized fully in the Ni_3B system, high-boron was multiphased. The coatings also presented a difference in terms of hardness behavior with a very important increase for the mid-boron coatings and lesser modification in the case of high boron. The abrasive wear resistance of both kinds of coatings was similar before heat treatment and high-boron coatings had a slightly better behavior after heat treatment. However, the sliding wear behavior of mid-boron coatings is significantly better than that of high-boron electroless nickel.

1. Introduction

Electroless nickel plating is popular as protective coating in several industries, due to the possibility of plating all kinds of substrates and shapes with homogeneous coatings that present a constant thickness and good adhesion [1–7]. The first electroless nickel process was developed in the 1940s by Brenner and Riddel [8] and nickel-boron plating baths were developed approximately 10 years later, very soon after the discovery of the reducing properties of the borohydride ion [9,10].

Electroless nickel-boron coatings differ from their phosphorous-based counterparts by a higher hardness, that can still be increased by a well-chosen heat treatment, higher wear resistance and better adhesion but they usually present a lesser corrosion resistance [1–3,7]. Nickel-boron coatings contain usually a rather limited amount of boron: 0.5 to 3 wt% when amine borane compounds are used as reducing agent [1,2,4,11,12] and up to 7 wt% when sodium (or potassium) borohydride is used [1,2,12–14]. All the properties of the coating are influenced by their boron content, beginning by the structure: the size of crystallites in as-deposited coatings decreases with boron content and coatings with 5 to 6 wt% boron appear X-ray amorphous [15–17]. The hardness of nickel-boron coatings also increases with the amount of incorporated boron [18], while the corrosion resistance seems also to be favorably influenced by higher boron concentrations [18].

Most electroless nickel-boron coatings have a boron content in the 5–7 wt% range and such coatings have been widely investigated [13,14,19–21]. However, the properties of coatings with a higher boron content have not been fully investigated yet and there are still a lot of questions about the properties and behavior of high-boron coatings. Only speculation based on extrapolation of work carried out on nickel-phosphorous can be used to evaluate the properties of high-boron electroless nickel coatings. In this work, electroless nickel-boron coatings with a higher boron content were synthesized and their properties were investigated and compared with those of the 6 wt% boron coatings usually used by our research group to determine the effects of higher boron content. Our aim is to investigate if high-boron electroless nickel coating could provide answer to some needs of the industry by provide better resistance to wear or corrosion, that are the most important features for electroless nickel-boron coatings.

This work is also a rather unique occasion of getting comparable information about other properties than hardness and corrosion resistance because, except in the case of structure, most groups use specific characterization methods (different loads and indenters for hardness, different systems and operating conditions for wear testing, …), which makes the results obtained by various teams extremely difficult to compare [11]. This is even more difficult when heat treatments are taken into account, due to the differences in favorite heat treatments between research groups. In this study, we had the chance to have two coatings made with very similar parameters and to characterize them using a single set of methods and conditions, which allows true

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comparison of the results. This is important for the field because there's truly a lack of comparative work.

2. Materials and methods

2.1. Sample preparation

The coatings were synthesized on mild steel samples (ST 37-DIN 17100 – with a C content <0.17 wt%, Mn < 1.4 wt%, P and S < 0.045 wt%), which is a substrate that is easy to prepare for coating and that can be heat treated without constraints. Coupons with a size of 100 mm × 100 mm × 1 mm were cut and ground with SiC paper (up to 2000 grit) to obtain a repeatable surface roughness (with a R_a close to 0.18 μm). Samples destined for Taber abrasion test were drilled in their center before preparation. After mechanical preparation, the samples were degreased with acetone and etched in 30 vol.% HCl for 1 min before immersion in the plating bath.

The plating bath used in this study is the one developed by Delaunois [22]. It uses nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) as a nickel source, sodium borohydride ($NaBH_4$) as a reducing agent and lead tungstate as a stabilizer ($PbWO_4$). Other components of the bath include sodium hydroxide and ethylene diamine ($NH_2—CH_2—CH_2—NH_2$). Nominal chemical composition of the bath is shown in Table 1. In order to modify the boron content of the plating bath, the process temperature was modified. Coatings were thus synthesized at 95 °C and 96.5 °C. The first temperature is the one used usually for this bath [22–24]. The other one was chosen in order to ensure the highest possible difference in boron content while staying inside the smooth operating range of the plating bath: temperatures lower than 94 °C are accompanied by a sharp decrease of plating rate making them unpractical for experimental and industrial use and the bath destabilizes spontaneously when heated higher than 97 °C [22]. Plating time was chosen to ensure a coating of 15 to 20 μm without replenishment.

To assess the effects of heat treatment on the samples, some samples were treated at 400 °C for 1 h in a 95% Ar–5% H_2 atmosphere at a pressure of 1 bar. This treatment has been studied in previous work and brings maximal hardening to the coatings synthesized at 95 °C [23,25]. The chosen conditions (400 °C, 1 h) are also some of the most popular for all types of electroless nickel coatings [26–32], so they provide a consistent comparison point.

2.2. Characterization methods

The surface and cross section morphology of samples were characterized by digital optical microscopy (with a Hirox 8700 3D optical microscope) and electron microscopy (with a JEOL JSM 5900 LV). The cross section samples were mounted in resin and polished to a mirror finish with SiC paper and diamond paste. The morphology was then revealed by etching (10s) with 10 vol% Nital. Chemistry of the coatings was investigated using acid dissolution and ICP-AES or GDOES analysis to get information about the average and depth profile chemistry respectively. The structure of samples was observed by X-ray diffraction with a Siemens D50 spectrometer in θ–2θ configuration. The measurements were carried out with cobalt Kα radiation (λ Kα = 1.79 Å).

Table 1
Bath chemical composition and operating conditions.

Nickel chloride	24 g/l
Sodium hydroxide	39 g/l
Ethylenediamine $NH_2CH_2CH_2NH_2$	60 ml/l
Lead tungstate	0.021 g/l
Sodium borohydride	0.602 g/l
Bath pH	13.5
Plating time	60 to 70 min
Bath temperature	
Mid-boron coatings	95 °C
High-boron coating	96.5 °C

The hardness of samples was measured by Knoop microindentation on cross section, with a load of 20 gf and a holding time of 20 s and on the free surface of samples with a Vickers indenter and 100 gf load (same holding time). All hardness tests were carried out with a Mitutoyo HM-200 microhardness tester. A Zeiss 119 Surfcom 1400D-3DF apparatus, based on the mechanical stylus method, was used to determine the surface roughness of the nickel-boron coatings. The values of roughness and hardness here presented are the average of ten measurements per sample.

Abrasive wear properties of the coatings were investigated by the Taber method, with a circular abrader (5155 Taber Industries) and an applied load of 1 kg. The abrasive counterparts were CS-17 wheels with a rotating speed of 72 rpm. Taber wear index of each sample was determined from the weight loss and corresponds to the weight loss (in mg) per thousand abrasion cycles [23]. Sliding wear was also investigated by the Pin-on – disc method with a CSM microtribometer (in unlubricated conditions). The coated samples served as the disks and the counterparts were 6 mm diameter alumina balls with hardness of 1400 HV_{100}. The sliding speed and sliding distance were, respectively, 10 cm/s and 100 m. Wear tests were carried out under normal loads of 10 N with sliding distances of 100 m. The specific wear rate (Ws) was calculated following the European Standard EN 1017-13:2008 using the following equation: $Ws = V / F \cdot S$, where V is the volume wear loss; F is the applied load; and S is the sliding distance. The coefficient of friction was determined as the average COF in regime.

The mechanical characterization of the coatings was completed by scratch testing, using the continuous load increase method. The test was carried out with a CSEM scratch tester machine with a diamond Rockwell stylus with a radius of 200 μm. The load varied from 0 to 150 N, with a scratch velocity of 6.75 mm/min and a total scratch length of 10 mm. Critical load and damage were determined by a combination of acoustic emission and post-mortem observation of the scratch with a Hirox KH-8700 Digital microscope.

3. Results

3.1. Morphology, chemistry and structure of the coatings

The average chemistry of the coatings was, for the unmodified bath: 93 wt% nickel, 6 wt% boron and 1 wt% lead, as is usual for the plating bath developed by Delaunois used in typical plating conditions [23]; and for the high temperature bath: 91 wt% nickel, 8 wt% boron and 1 wt% lead. The modification of plating conditions by increasing the temperature allowed us to increase the coating boron content from approximately 6 wt% to approximately 8 wt%, which is a significant increase. The 6 wt% B coatings will be from now on called 'mid-boron coatings' while the 8 wt% B coatings will be called 'high-boron'.

Depth profile chemistry of the coatings is shown on Fig. 1. The difference in boron content between the mid-boron and high-boron coatings is observable on as-plated coatings (Fig. 1a and c) as well as on heat treated samples (Fig. 1b and d). The nickel and boron content of the as-plated coatings do not show any significant evolution across the deposit. The variations in lead content are more easily observable but the scale has been massively enlarged (100 times) to show the lead content curve. Variations of lead content are thus in the range of 0.3 wt%, except for the as-plated high boron sample, where the lead content appears to increase continuously from the interface to the free surface. After heat treatment, the chemistry of mid-boron coatings is left mostly unmodified, with only the possibility of slight lead diffusion inside the coating. However, in the case of high-boron, a surface depletion in boron and enrichment in nickel can be observed in the top 1–2 μm, as well as a leveling of the lead content. This is not due to surface oxidation because the heat treatment was carried out under a protective atmosphere. Moreover, the presence of oxygen, while not shown on Fig. 1, was measured on the surface by GDOES and did not exceed typical oxygen contamination.

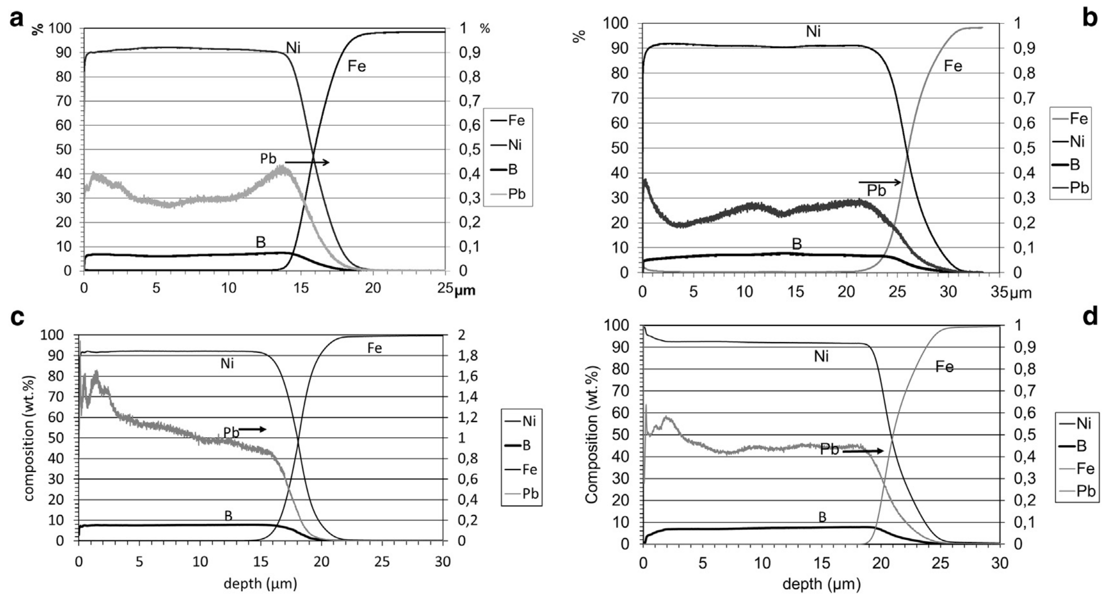

Fig. 1. GDOES depth profile of: a – as-plated Mid-boron coating; b – heat-treated Mid-boron coating; c – as-plated High-boron coating; d - heat-treated High-boron coating. Left axis: Ni, B, Fe. Right axis: Pb. Lead content is enlarged 100 times for better visibility.

Morphology of the coatings is presented in Fig. 2. In cross section (Fig. 2a and b), the difference between mid- and high-boron coatings is very limited. Both coatings present a similar quasi feather-like columnar morphology with columns whose diameter varies (in the 0.1–2 μm range) throughout the coating. The surface morphology of both coatings (Fig. 2c and d) presents the typical cauliflower-like texture of electroless nickel-boron [1,2,7,33,34]. The high-boron coating (Fig. 2b and d) has a more homogeneous morphology than the other, with columns of similar size on the whole coating (the observed relief is linked to substrate roughness). The mid-boron (Fig. 2a and c) presents a wider dispersion in the size of columns, some of which reach 10 μm in diameter on the surface.

After heat treatment (Fig. 3), the morphology of the coatings is conserved and the feather-like features can still be observed on cross section (Fig. 3a and b) while the surface texture keeps the cauliflower-like texture observed in the as-plated condition (Fig. 3c and d).

On a structural point of view, as-plated coatings are very similar. They are X-ray amorphous, as can be seen on Fig. 4 were only a large flat dome centered on the most intense nickel diffraction peak (52.3 °C) is observed for those coatings. This is in accordance with literature and previous results of our group [15–17]. The incorporation of boron in the coating during plating impedes crystallization and, for coatings with >5 wt% boron, the structure appears X-ray amorphous. No difference between the coatings was thus expected. However, after heat treatment, there's a significant difference between mid- and high-boron coatings: mid-boron coatings crystallized fully in the Ni_3B phase, which is expected from the composition of the coating [17,35] (6 wt% of boron equates roughly to 25 at.%). High-boron coatings contained a large amount of Ni_3B phase, as attested by Fig. 3 but they also presented some Ni_2B and Ni phase. The presence of Ni_2B is expected from the average chemistry because this phase has a higher boron content than Ni_3B and is thus formed when boron content exceeds 6 wt% [36–37]. The presence of small amounts of crystalline nickel is linked to the chemical modification observed on the surface of heat treated high-boron samples, were an unexpectedly high nickel concentration is observed in the top 2 μm of the coating.

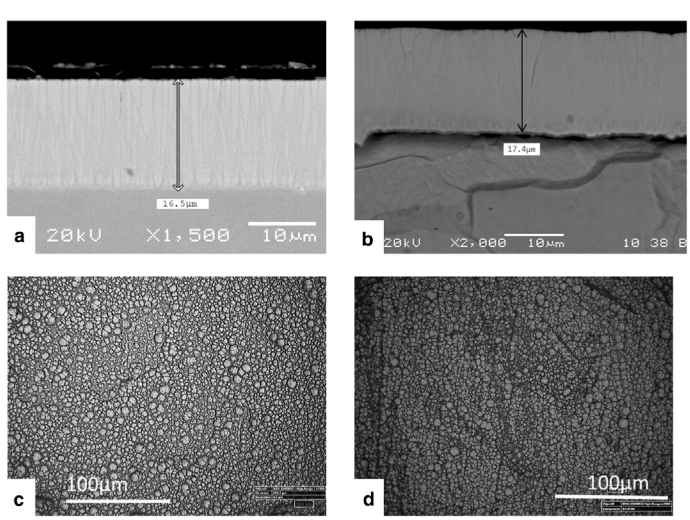

Fig. 2. SEM cross section morphology of: a - mid-boron coating; b - high-boron coating. Optical morphology of the surface of: c- mid-boron coating; d - high-boron coating.

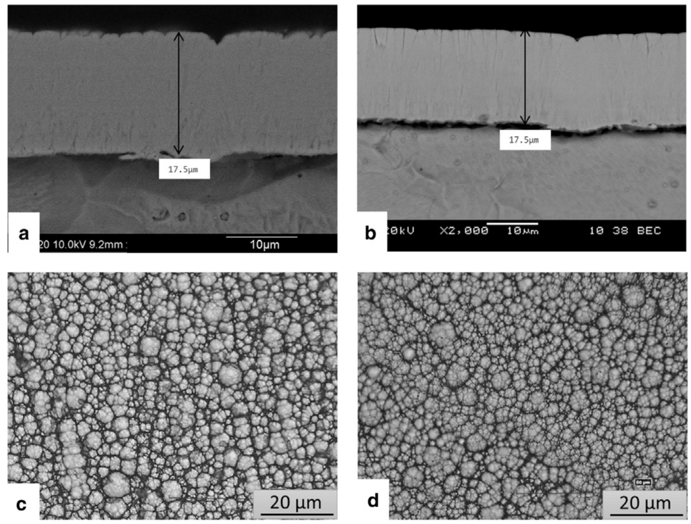

Fig. 3. SEM cross section morphology of: a – heat treated mid-boron coating; b - heat treated high-boron coating. Optical morphology of the surface of: c- heat treated mid-boron coating; d - heat treated high-boron coating.

3.2. Roughness, hardness and wear behavior

Roughness of mid- and high-boron coatings, before and after heat treatment is shown on Fig. 5. The roughness of high-boron coatings is slightly higher than that of mid-boron coatings, in the as-plated and heat treated state. However, the roughness of high-boron coatings (with R_a of 0.21 µm in the as-plated state and 0.24 µm after heat treatment) stays close to that of the substrate that has a R_a of 0.18 ± 0.02 µm before etching. Heat treatment does not affect roughness in a significant manner: all visible modifications stay within the standard deviation of the measurements. More in depth analysis of the roughness parameters reveals that the peak height (R_p) is similar for both kinds of coatings and that the main difference comes from the depth of valleys (R_v) that is larger for high-boron coatings.

In the as-plated state, the hardness of mid- and high-boron coatings is similar, with a value close to 900 hv_{100} for surface measurements, as shown on Fig. 6. This is coherent with previously published results that suggest a plateau in hardness in the as-deposited state for boron content around 7–8 wt% [18] and also with the structural state of the coatings, that is X-ray amorphous nickel in both cases. After heat treatment, the structural state of both coatings is however different and differences in hardness are thus expected. Heat treated mid-boron coatings are formed entirely of nanocrystalline Ni_3B phase after heat treatment [17] while high-boron coatings are a mixture of Ni_3B, tetragonal Ni_2B [38] and Ni, with some nickel near the surface due to superficial segregation, as shown in the previous section. The hardness of pure nickel borides has been reported: Ni_3B has the same structure as cementite [23,39–41] and values of 10.5 GPa have been reported for its hardness [41]. In the case of Ni_2B, the information is contradictory: values of 1500 to 1800 hk have been reported [42,43] but recent research on nickel boronizing showed a hardness close to 1000 hk for a pure Ni2B [44] layer.

Mid-boron coatings, formed only of nanocrystalline [39] Ni_3B presented on cross section a hardness close to 1400 hk_{20} that can be linked to the presence of hard, small grained Ni_3B. The hardness of heat treated high-boron coatings reached 1200 hk_{20}, which is slightly lower but stays acceptable for a nickel-boron coating. Those results are coherent with the findings of Das and Sahoo that suggest a 7.5 wt% B for optimal hardness after heat treatment [37].

The difference between mid and high-boron coatings is more marked in the case of surface hardness, with a value over 1200 hv_{100} for the mid-boron coating and of 950 hv_{100} for the high-boron coating. This difference is linked to the presence of a higher concentration of softer crystalline nickel near the surface of the sample.

Taber wear index of the coatings is shown in Table 2. As-plated coatings presented similar TWIs, with a slightly better abrasive wear resistance for the mid-boron coating. It is difficult to compare this with published results because there are few published studies about abrasion resistance of nickel-boron and most don't mention clearly the

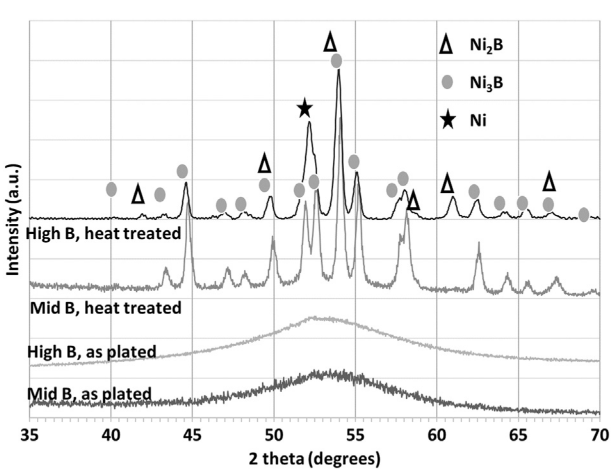

Fig. 4. X-ray diffraction data of mid- and high-boron coatings with and without heat treatment.

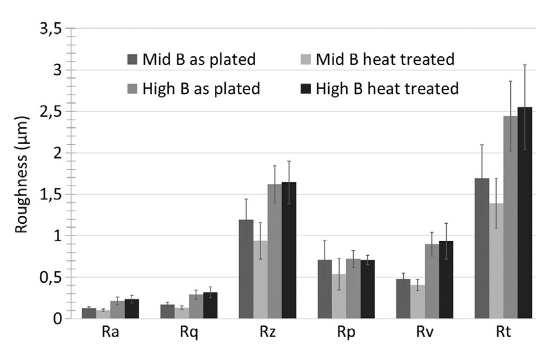

Fig. 5. Roughness parameters of mid- and high-boron coatings with and without heat treatment.

Fig. 6. Surface and cross section hardness of mid- and high-boron coatings with and without heat treatment.

Table 2
Abrasive and sliding wear properties of mid- and high-boron coatings.

	Mid-B as-plated	Mid-B heat-treated	High-B as-plated	High-B heat-treated
TWI	28 ± 3.5	13 ± 1.5	31.1 ± 2	8 ± 1.7
Average friction coefficient	0.684	0.593	0.632	0.579
Wear tracks width (μm)	173 ± 2.82	115 ± 6.02	228 ± 3.53	181 ± 7.21
Specific wear rate Ws (μm^2/N)	0.40	0.12	0.90	0.45

boron content of the coating [11]. However, in accordance with literature [2,3,45], the Taber Wear Index of both coatings decreased after heat treatment.

After heat treatment, the high-boron coating presented a significantly lower TWI than mid-boron. The difference in abrasive wear behavior of the coatings cannot be linked with hardness, as hardness follows an opposite behavior. It may be linked with the presence of softer nickel at the surface of the high-boron coating in the heat-treated state. The better abrasive wear resistance of the high boron coating is a very interesting feature that can be exploited in applications like petrochemical industry, for example for the transport of slurries.

Data from sliding wear tests are shown in Table 2 and Figs. 7 and 8. In regime, the friction coefficient of all coatings lays between 0.5 and 0.8. The friction coefficient of mid-boron coatings is rather unstable, presents significant variations, event after 50 m of sliding test and increases after 50 to 70 m to reach average values close to 0.7 at the end of the test. On the contrary, after the initial decrease, the friction coefficient of high-boron coatings is less prone to variations and stabilizes at 0.55 for the as plated coating and 0.6 for the heat treated one. It is important to note that the friction coefficient of as plated high-boron coatings does not present a marked initial decrease and that the one of heat treated high-boron electroless nickel is very stable after the initial decrease, which can be useful in some applications where stability of the friction is required.

The specific wear rate and width of the wear tracks were also measured. For those parameters, heat treatment brings an improvement of the wear behavior of both kinds of coatings, in accordance with published literature [46,47].

Contrary to the friction coefficient, it's the mid-boron coating that presents the smallest specific wear rate and the narrowest wear tracks, with a specific wear rate as low as 0.12 μm^2/N for the heat-treated mid-boron coating.

The improvement of sliding wear behavior after heat treatment is clearly observable on Fig. 7, with narrower and more regular wear tracks, that are also free of debris for the heat treated coatings (Fig. 7b and d). This is similar to the observations of Krishnaveni et al. [46]. The difference between mid- (Fig. 7a and b) and high- (Fig. 7c and d) boron coatings is also marked. The most noticeable difference is observed between the heat-treated coatings. The specific wear of as-plated high-boron is more than twice that of as-plated mid-boron coating and, while heat treatment improves the wear of both coatings, heat treated high-boron coatings barely reach the level of the as-plated mid-boron.

The marked difference between abrasive and sliding (pin-on-disc) wear behavior of the coatings is due to the fact that abrasive wear is mostly influenced by hardness, which is not so different between mid- and high-boron coatings while sliding wear is also related to cohesive properties of the coatings, that have not been investigated yet.

3.3. Scratch test resistance

Residual scratches are shown on Fig. 9. As can be seen, the damage occurring on all coatings is rather limited. There is no evidence of lack of adhesion or of fragile behavior in any of the coatings in the global views. To assess maximal damage to each type of coating, Fig. 10 presents the end of the residual scratch, where the load reaches 150 N. As-plated mid-boron coatings present low damage and matter accumulation at the edge of the scratch (Fig. 10a and c). A similar behavior is observed for the heat-treated coating (Fig. 10b and d). As-plated high-boron coatings behave in a very ductile manner, still with visible

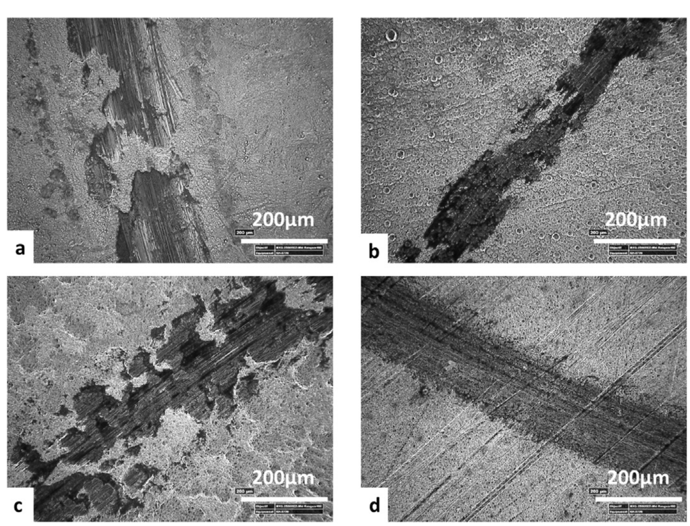

Fig. 7. Sliding wear tracks on: a - as-plated mid-boron coating; b - heat-treated Mid-boron coating; c - as-plated high-boron coating; d - heat-treated high-boron coating.

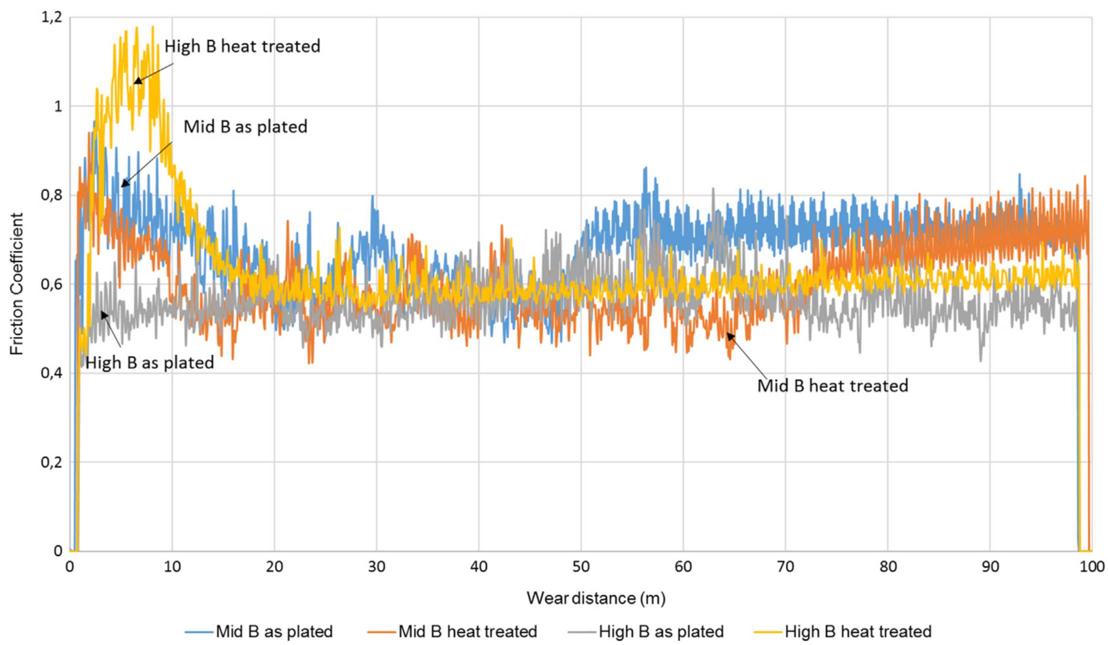

Fig. 8. Evolution of friction with sliding distance for as plated and heat treated electroless nickel-boron coatings.

accumulation of matter at the edges of the scratch (Fig. 10e and g). The behavior of heat-treated high-boron coating is not as favorable, with the presence of marked cracks at the edges of the scratch and matter accumulation (Fig. 10f and h).

Critical loads for the main damage types encountered during scratch testing of electroless nickel-boron coatings (chevron cracks and transverse cracks at the bottom of the scratch) are shown on Fig. 11. First damage occurs around 25–30 N in all cases except heat-treated high-boron coatings that are damaged from the start, in the form of chevron cracks that are later accompanied by transverse cracks. The transverse cracks appear later on as-plated high-boron and heat-treated mid-boron coatings. The mid-boron coatings appear thus to keep a ductile behavior even after heat treatment, which is not the case of the high-boron electroless nickel. Those critical loads confirm that heat treatment decreases adhesion of the coatings. Also, mid-boron coatings present better performance than high-boron.

4. Conclusions

Two kinds of electroless nickel-boron coatings were synthesized from the same plating bath by modifying the temperature: mid-boron electroless nickel with a nickel content of 6 wt% and high-boron electroless nickel with 8 wt% boron. Both kinds of coatings have some similar features but they differ in other properties.

- The superficial morphology of high-boron coatings appears to be more regular as far as the size of columns is concerned. However, the roughness of that type of coatings is higher due to the presence of deeper valleys.
- Boron content is stable throughout both coatings in the as-deposited state but there is a significant diffusion of nickel towards the surface after heat treatment of high-boron coatings.
- The structure of as-deposited coatings is the same in both cases but heat treatment brings significant differences: mid-boron coatings are constituted only of Ni_3B phase while high-boron contain Ni_3B, Ni_2B and nickel, the latter linked to the surface diffusion. This structural difference brings also differences in hardness: mid-boron coatings present a very significant increase of hardness after heat treatment, while that of high-boron coatings is more limited.
- High-boron coatings have better abrasive wear resistance and lower friction coefficient but mid-boron coatings have a better resistance to sliding wear than the others. The effect of heat treatment is similar on both types of coatings: an improvement of the wear properties but the hierarchy between the types of coatings is conserved.

Fig. 9. Residual scratch, from top to bottom: as-plated mid-boron coating; heat-treated mid-boron coating; as-plated high-boron coating; heat-treated high-boron coating.

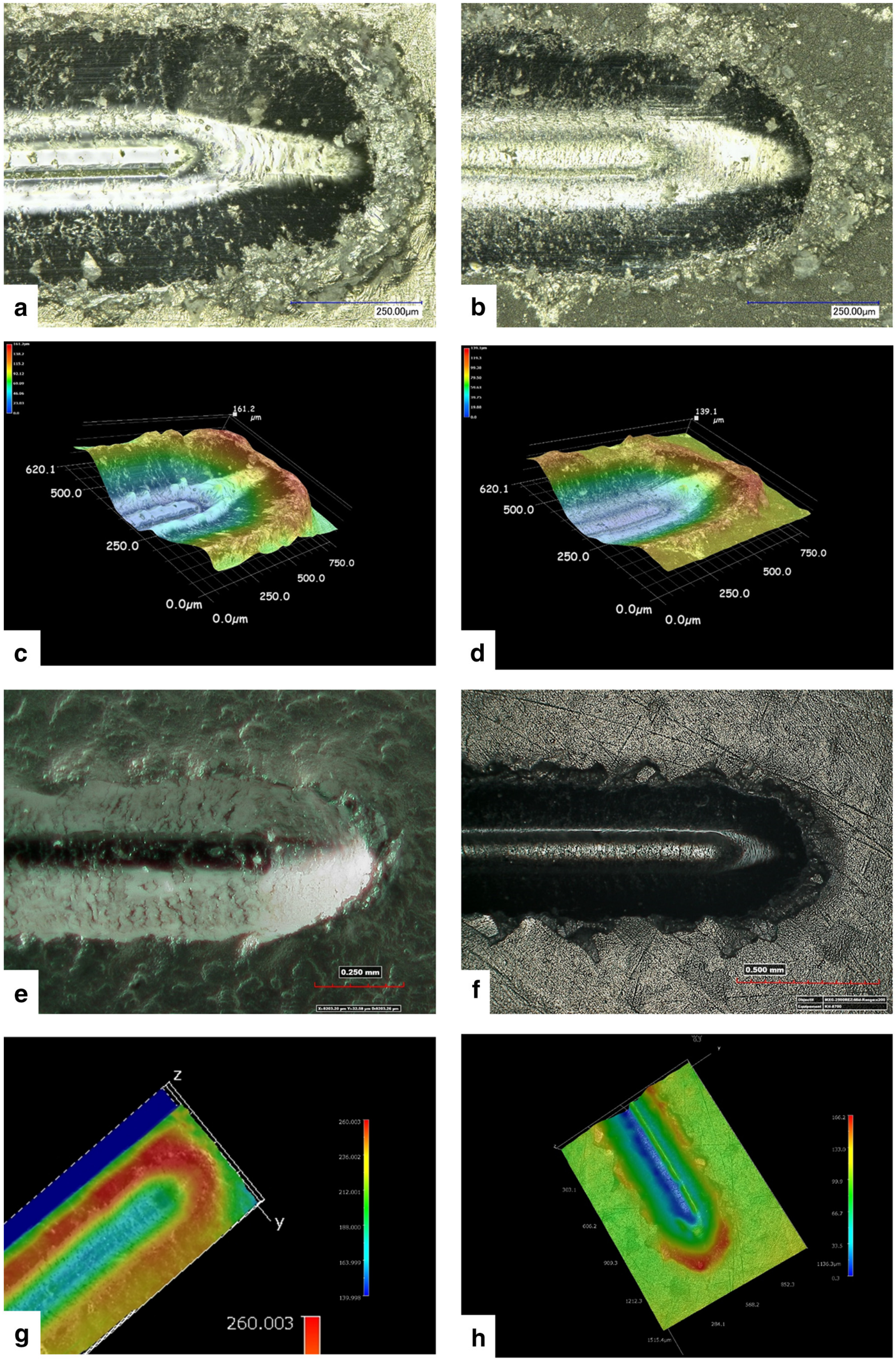

Fig. 10. Detail of the end of residual scratch, optical microscopy and elevation profile: a and c - as-plated mid-boron coating; b and d - heat-treated mid-boron coating; e and g - as-plated high-boron coating; f and h - heat-treated high-boron coating.

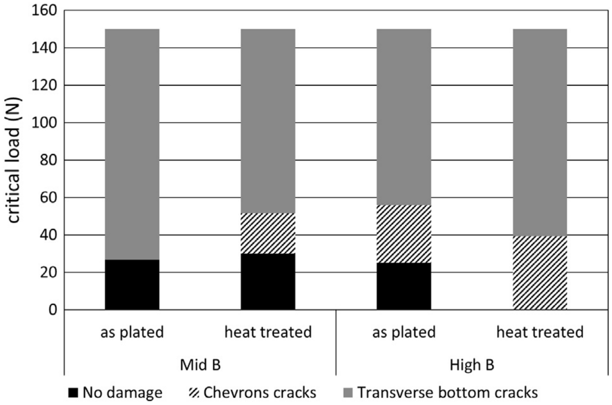

Fig. 11. Critical load for various damage types on electroless nickel-boron coatings with and without heat treatment.

- Scratch resistance of both types of coatings is satisfactory but mid-boron coatings present a slightly better behavior.
- The high boron coating is nearly as good as the mid-boron coating for most features but it has a lower and more stable friction coefficient as well as a better resistance to abrasive wear. The new coating is thus promising for specific wear applications as well as for applications where a stable coefficient of friction is required.

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