HOW HEAT TREATMENT CAN GIVE BETTER PROPERTIES TO ELECTROLESS NICKEL-BORON COATINGS

V. Vitry, F. Delaunois, C. Dumortier

Electroless nickel-boron deposits were synthesized on mild steel and submitted to heat treatments under neutral and nitrogen based atmosphere. The properties obtained after these treatments were compared to as deposited nickel-boron coatings. The morphology and structure of the samples were investigated by XRD, SEM and optical microscopy; their composition was studied by ICP, GD-OES and SIMS analysis, and micro and nanoindentation tests were carried out to assess the coatings' hardness. Scratch tests were used to determine the damage mechanisms of the coating.

KEYWORDS: electroless deposition – nickel-boron – nanoindentation – heat treatment

INTRODUCTION

Autocatalytic (Electroless) nickel plating was discovered by Brenner and Riddel in 1946 [1]. This process is based on the aqueous reduction of nickel salts by a chemical agent thus allowing deposition on non-conducting materials and leading to continuous coatings with a constant thickness [2-5]. Nickel boron coatings are obtained when a boron-based agent, such as sodium borohydride is used to reduce the nickel. Those coatings are of great interest and are extensively studied [6-12]. They present, in their as-deposited state, an hardness close to $750hv_{100}$ and are useful in many industries including automotive, electronic and chemical industries because of their good mechanical, chemical and tribological properties [2, 5, 11, 13, 14]. Depending on the amount of boron present, the coatings are considered amorphous, microcrystalline or a mix of the two, the amount of amorphous phases increasing with the amount of boron [2, 7, 15-18].
Heat treatments are often used to enhance the properties of nickel-boron coatings: they allow crystallisation of the amorphous part and, if well designed, lead to nano and microcrystalline structure which are harder than the as-deposited coatings and their hardness can reach $1200hv_{100}$. [2, 17, 19]
Much information can be obtained using nanoindentation: this technique is an instrumented indentation and the loading and unloading curves are recorded during each indent. Moreover, the loads are much smaller than in the case of microindentation (typically a few mN) [20-22]. This technique is often used with a Berkovitch indenter which has the same surface than the Vickers indenter while being easier to manufacture owing its triangle-based pyramid shape. Working with very low loads allows to get very small indents and thus to study the hardness evolution across a relatively thin coating.
Scratch test [23-29] can give information about the "practical adhesion" of coatings as well as the degradation modes of the coatings. It consists in the application of an increasing load to a coating. Modern investigation techniques are used to study the coating's scratch test comportment: acoustic emission, friction coefficient and penetration depth measurements are recorded during the test and microscopic examination is carried out after the test. The critical load of a system which characterizes the adhesive strength of the coating/substrate system is determined from the first adhesive failure. The degradation modes can be identified from observation. However scratch tests cannot be used to predict quantitative wear rates of materials and coatings.

Véronique Vitry, Fabienne Delaunois, Christian Dumortier
Mons Faculty of Engineering, Metallurgy Department, Mons, Belgium

EXPERIMENTAL

Samples preparation

Steel and Aluminium alloy cylinders with a diameter of 25 ± 1 mm and a thickness of 10 ± 1 mm were plated with nickel-boron. Before plating, they were mechanically polished, degreased with acetone and etched in an acid solution. The aluminium samples were subjected to further pre-treatment by double-zincate conversion and acid nickel phosphorous flash deposition.
The deposition bath is based on the reduction by sodium borohydride ($NaBH_4$); the nickel ions source is nickel chloride ($NiCl_2.6H_2O$). The nickel ions are complexed by ethylene diamine (EN) and lead tungstate ($PbWO_4$) is used as a stabilizer. The operation conditions and the installation have been described elsewhere [15].
Classical heat treatments were carried out under neutral gas flow (95%Ar – 5%H_2) at 400°C for 1 hour for steel substrates and at 180°C for 4 hours for aluminium substrates (this temperature was proven by Delaunois et al. to offer a good compromise be-

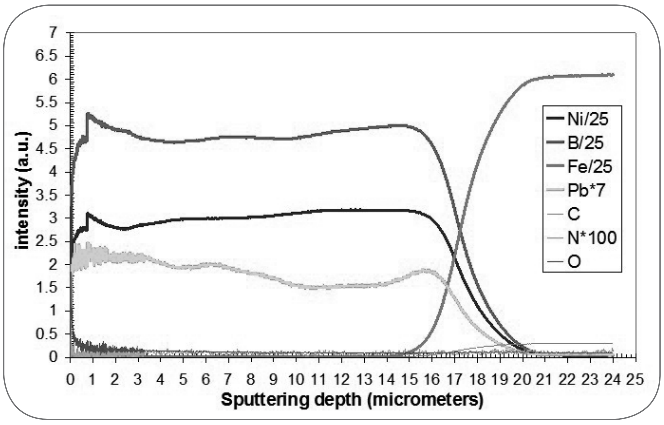

Fig. 1

GD-OES depth profile of an untreated nickel-boron coating on Steel.

Profilo GD-OES nello spessore di un rivestimento nichel-boro non trattato su acciaio.

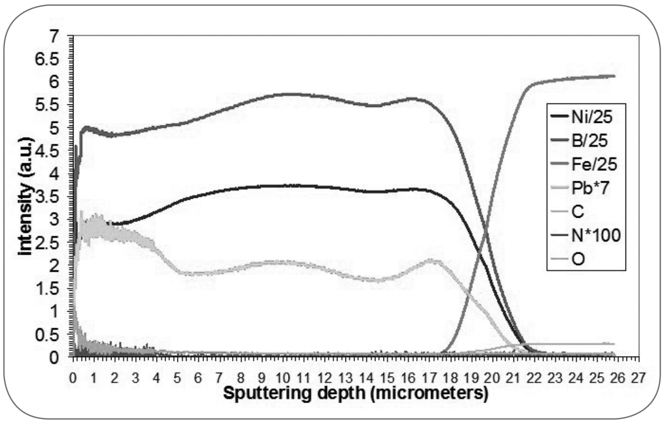

Fig. 2

GD-OES depth profile of a nickel-boron coating on Steel after 1 hour heat treatment at 400°C under neutral atmosphere.

Profilo GD-OES nello spessore di un rivestimento nichel-boro su acciaio dopo 1 ora di trattamento termico a 400°C in atmosfera inerte.

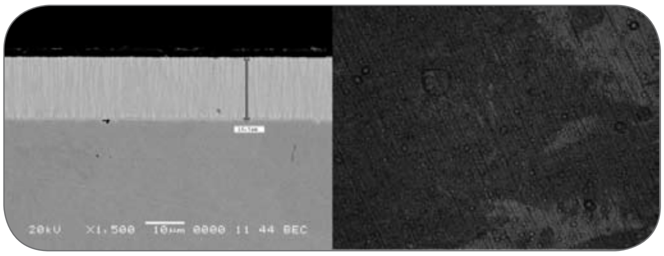

Fig. 3

SEM micrograph of an untreated nickel-boron coating – left: cross section showing the columnar morphology – right: cauliflower-like surface.

Micrografia al SEM di un rivestimento nichel-boro non trattato – sinistra: sezione trasversale che mostra una morfologia colonnare – destra: superficie "a cavolfiore".

tween coating hardening and substrate softening for aluminium substrates [15]). Preliminary test for other treatments were carried out under ammonia and nitrogen-based atmospheres.
Samples prepared for SEM observation and hardness testing were first cut using a Leco Microtom cutting machine with a diamond cutting disk, then mounted in a non-retractable resin and mirror polished.

Samples analysis

Mean chemistry of the samples was investigated after dissolution in concentrated nitric acid by ICP analysis using a Jobin-Yvon apparatus.
Profile analysis was carried out by GD-OES using Jobin-Yvon spectrometer and surface analysis by TOF-SIMS using an ION-TOF IV apparatus.
A Siemens D500 X-rays θ–θ apparatus applying Cu Kα (1,54 Å) radiation was used to study the structure of the samples. Their morphology and thickness were observed using a Philips XL 20 Scanning Electron Microscope.
Microhardness measurements were carried out using a LECO M-400-A, mounted with a Vickers indenter for surface testing and with a Knoop (lozenge-shaped) indenter for cross section testing. A load of 100g was used for Vickers indentation while a load of 50g was used for Knoop hardness testing. The holding time was 20s for both techniques.
Nanohardness was obtained with a MTS nano-indenter XP mounted with a Berkovitch (tetrahedron shaped), using depth controlled indentation in order to obtain indents of similar size. The hardness value at a load of 4000μN was chosen as nanoindentation hardness value.
Scratch tests were performed on selected samples using the continuous load increase method up to 30N with a Microphotonics Micro Scratch Tester (MST), with a load rate of 19.17N/min and an advance rate of 9.58mm/min, resulting in a scratch of 15mm. The tip was a Rockwell C diamond stylus indenter with a radius of 200 μm.

RESULTS AND DISCUSSION

Chemistry of deposits

ICP analysis of as-deposited coatings showed that their average composition is 93 wt. % nickel, 6 wt. % boron and 1 wt. % lead. Heat treatments do not modify the global composition of the coatings.
GD-OES analysis, on steel substrate, allowed us to follow qualitatively the composition into the depth of the coating. In the as-plated state (Fig. 1), the boron and nickel content of the coating don't vary with the depth while the lead content seems to be higher at near the substrate interface then decreases slightly before increasing once more. It means that more lead is deposited at the very beginning of the process and at the end that during the fast "regime" deposition of the coating.
Observation of the interface allows us to predict a good adhesion of the coating because there seems to be a certain amount of interdiffusion with the substrate.
After heat treatment at 400°C for one hour under neutral atmosphere (Fig. 2), the nickel and boron content are quite unmodified while the lead content becomes higher near the free surface of the sample and decreases steeply with depth. The lead seems to diffuse outside the coating. However, the interface between the steel substrate and nickel-boron was not modified by this treatment. Previous work revealed important interdiffusion at the interface after heat treatment in the case of aluminium-silicon alloys (AS7G06) [15].

	Untreated	4h ; 180°C	1h ; 400°C
Knoop microhardness (hk50)	834 ±20	927 ± 30	-
Vickers microhardness (hv100)	854 ± 40	1014 ± 40	1302 ± 40
Berkovitch nanoindentation (4000μN)	823± 155	1140 ± 75	1584 ± 182

Tab. 1

Vickers and Knoop and Berkovitch hardness values of nickel-boron coatings on aluminium alloys.

Valori di durezza Vickers, Knoop e Berkovitch di rivestimenti di nichel-boro su leghe di alluminio.

Positive and negative ions SIMS analysis was carried out on the untreated samples and revealed only the presence of the known constituent of the coating (Nickel, boron, lead) and of the classic surface contamination. The results obtained after neutral atmosphere heat treatment were similar, proving that the coating's chemistry is not much influenced by those treatments.

Structure and morphology of the coatings

In the as-deposited state, the coatings present a columnar morphology and a cauliflower-like surface (which is characteristic of nickel-born coatings [11,15,17]), as can be seen on Fig. 3. Neutral atmosphere heat treatments up to 400°C do not modify those properties.

The structure of untreated samples and samples treated at 180°C revealed they were amorphous (Fig. 4) while crystallization occurred during heat treatment at 400°C. This is expected from the literature and our own previous results [2,15,19,30].

The effect of this crystallization on the mechanical properties of the coating will be discussed later.

Mechanical properties of the coating

Vickers hardness testing on the unprocessed surface of the sample is the standard method to measure hardness of nickel-boron coatings. However, we find it disputable because the surface is unprepared and its smoothness is unwarranted, and because the substrate hardness may significantly influence the results when the applied load is too high. We thus used other hardness testing methods to free ourselves from those potential problems: Knoop microindentation and Berkovitch nanoindentation were used on polished cross-sections. Nanoindentation were converted from GPa into Berkovitch hardness points (equivalent to Vickers values) to facilitate comparison.

Hardness values for untreated samples were close to 825 for all techniques. After heat treatment at 180°C for 4 hours, those values reached 1000, and they were further increased after heat treatment at 400°C. The first increase is caused by short order rearrangement in the coating (the amorphous dome XRD intensity is slightly higher), while the crystallization observed between 180°C and 400°C causes a far greater hardness enhancement and reaches the maximum hardness value for nickel-boron coatings [2,17,19]. It is due to the generation of a high density of grain boundaries inside the coating. The hardness can thus be optimized by the grain-size control: if the grains are allowed to coalesce (i.e. if the heat treatment is too long or the temperature too high), the hardness of the coating will decrease [16.17,31].

It was not possible to obtain a reliable Knoop hardness value after treatment at 400°C because cracking of the coating occurred. This shows the importance of comparing values from different techniques: Nickel boron coatings have a very anisotropic structure, due to their synthesis mode. Vickers hardness is carried out in the growth direction of the coating and any damage occurring during this test will remain unseen because it will take place inside the coating. However, Knoop indentation is made perpendicular to the growth direction of the coating and the subsequent damage is easily observable (Fig. 5). Knoop indentation is thus more reliable. This may also explain why na-

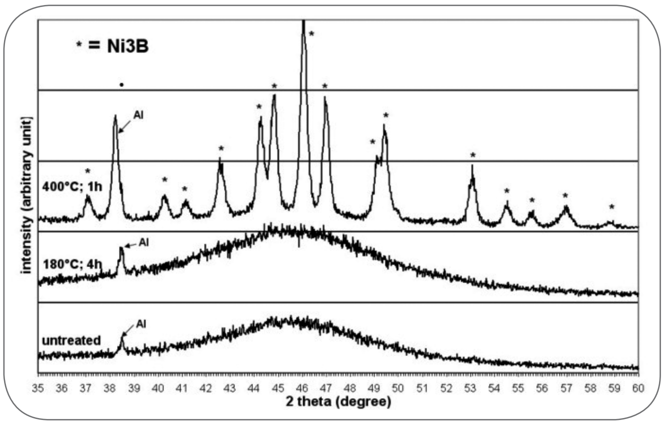

Fig. 4

X-Ray diffraction patterns of Electroless nickel-boron coatings on aluminium substrates with and without heat treatments.

Spettri di diffrazione ai raggi X per i rivestimenti chimici di nichel-boro su substrati di alluminio con e senza trattamenti termici.

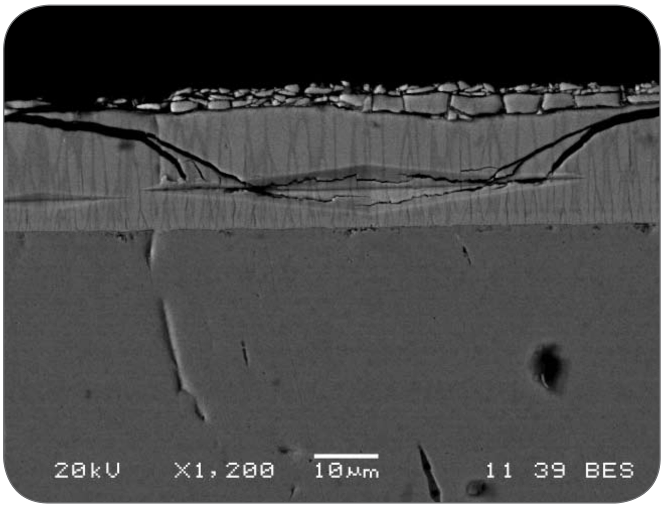

Fig. 5

Cracking of the coating caused by Knoop indentation.

Criccatura del rivestimento causata dall'impronta Knoop.

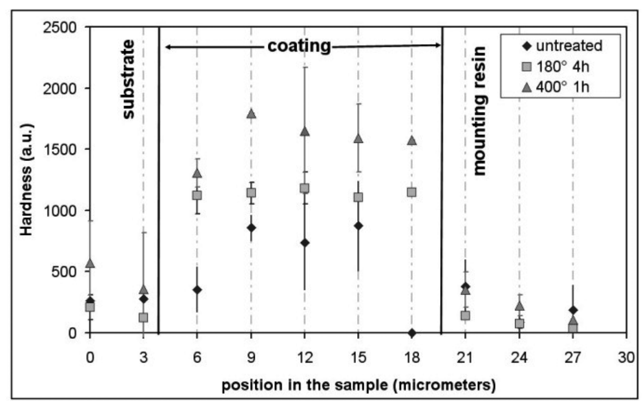

Fig. 6

Nanoindentation profiles on treated and untreated nickel-boron coatings.

Profili di nanodurezza su rivestimenti nichel-boro trattati e non trattati.

noindentation values are so much higher than Vickers values for 400°C treatment: the load applied for the nanoindentation test is too low to generate damage.

The small size of nanoindentation indents allows measuring the hardness of the coating on several points across the coating without any interaction of the indents. We were thus able to draw hardness profiles for nickel-boron coatings (fig. 6). Those profiles showed that the hardness values are not homogeneous across the coating except after heat treatment at 180°C. This is probably due to the fact that as-deposited coatings have important internal stress. Heat treatment at 180°C releases a lot of this stress and the hardness becomes homogeneous. Heat treatment at 400°C however may generate new internal stresses because it is accompanied by important structural modifications. Moreover, as nanoindentation is a very sensitive experimental method it is possible hat part of the values scattering is due to external factors such as roughness of the sample (microscratches in the polished cross section), geometry of the indenter tip, thermal drift and creep.

The usual thickness used for nickel-boron coatings is at least 15-25 micrometers. For coatings of this thickness, scratch tests up to 25N did not reveal any significant damage. We decided thus to work with thinner coatings (with a thickness of 6μm) in order to determine the damage mechanisms observed during scratch test. These tests were only carried out without heat treatment and after heat treatment at 180°C.

The damage mechanisms were the same for both treated (Fig. 8) and untreated (Fig. 7) coatings which is not surprising knowing they present roughly the same structure and morphology. The first failure that was observed is longitudinal cracking on the edges of the coating. Chevron cracks were then observed. Those are cohesive damage. The first adhesive failure is discontinuous ductile perforation of the coating, which is followed, in the case of heat treated samples, by continuous ductile perforation of the coating. To observe this kind of failure is really encouraging because it is a proof of the good adhesion of the coating, which was first suggested by the interface observation by GD-OES. Moreover, this failure was only observed because the coating was so thin.

Effects of alternative post-treatment

Alternative heat treatments are now in their testing phase. They are mainly based on the use of reactive atmospheres. We present hereunder some interesting results we obtained using (i) a treatment under a reduced pressure in a nitrogen-based gas, which will be called "vacuum treatment" in further explanations and (ii) a treatment under an ammonia-based atmosphere, which will be called " ammonia treatment".

SEM cross section micrographs of nickel-boron coatings after "vacuum" and "ammonia" treatments showed an important morphological modification of the coating: it becomes totally dense after "vacuum" treatment and the columnar morphology disappears completely (Fig. 9a), and the coating is composed

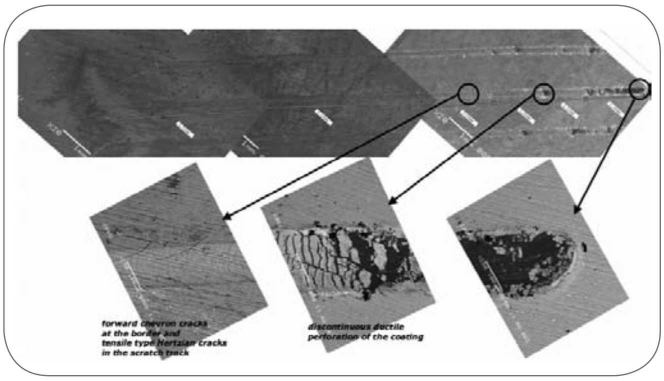

Fig. 7

Micrograph of scratches on 6μm thick nickel-boron coatings (aluminium alloy substrate) without heat treatment.

Micrografia di scalfitture su rivestimenti di nichel-boro dello spessore di 6μm (substrato in lega di alluminio) senza trattamento termico.

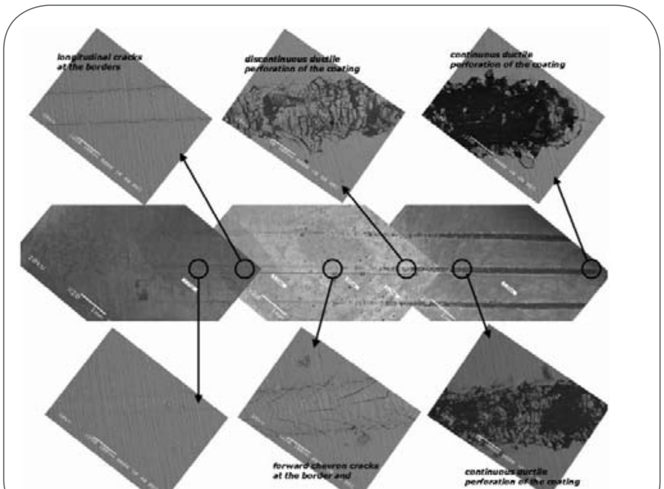

Fig. 8

Micrograph of scratches on 6μm thick nickel-boron coatings (aluminium alloy substrate) after 4 hours at 180°C under 95% Ar + 5% H2 atmosphere.

Micrografia di scalfitture su rivestimenti di nichel-boro dello spessore di 6μm (substrato in lega di alluminio) dopo 4 ore a 180°C in atmosfera 95% Ar + 5% H2.

of 2 distinct layers after "ammonia" treatment (Fig. 9b). The inner layer is dense and resembles the "vacuum" treated coating while the outer layer looks porous.
Knoop hardness measurements were carried out on "vacuum" treated samples and on the dense part of "ammonia" treated samples. Values of 1570 ± 100 hk_{25} and 1630 ± 100 hk_{25} respectively were obtained instead of 1250 ± 100hk_{25} after treatment at 400°C. It shows that the hardness of nickel-boron coatings can be further enhanced by the use of modified heat treatments.
Scratch tests were carried out on "ammonia" treated coatings. Those coatings, while they are plastically deformed, are nearly undamaged after the tests (Fig. 10) which is promising for wear applications.

CONCLUSIONS

As-deposited nickel-boron coatings possess several interesting features: high hardness (~825hv_{100}), good scratch comportment, amorphous structure, columnar morphology and cauliflower-like surface.
Heat treatment influences some of those features, mostly in a positive way:
- The columnar morphology is unmodified by classical heat treatment up to 400°C but is transformed in a dense layer that can be accompanied by a porous outer layer after the alternative treatments we investigated.
- The amorphous structure undergoes crystallization during heat treatment if the temperature is high enough: there is no crystallization for 180°C treatments while crystallization is complete after treatment at 400°C.
- The hardness of the coating is very much influenced by its crystalline state: while low temperature treatment induces a slight increase and an homogenisation of the hardness, the treatment at 400°C leads to an hardness value of 1300hv_{100}. This high values is due to the important grain-boundaries density that is obtained after heat treatment.
- Alternative heat treatment allowed a further hardness increase by a still unidentified mechanism.
- The scratch comportment of nickel-boron coatings is quite unmodified by neutral heat treatments. The comportment after ammonia-based alternative treatment is mainly plastic deformation of the outer layer of the coating, which is very interesting for wear applications.

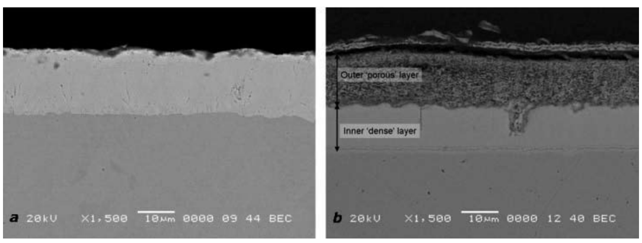

Fig. 9
SEM micrograph of (a) a "vacuum" treated and (b) an "ammonia" treated nickel-boron deposit on steel substrate.
Micrografia al SEM di una deposizione di nichel-boro su substrato di acciaio: a) trattata sotto vuoto e b) trattata in atmosfera di ammoniaca.

- Adhesion of the coating is predicted to be good because of the chemical interaction seen at the coating/substrate interface and of the scratch comportment. Heat treatments don't seem to modify the interface.

REFERENCES

1] A. Brenner, G. Riddel, J. Res. Nat. Bun. Stds. 37 (1946) 31.
2] Riedel A. Electroless nickel plating, Finishing Publication LTD., London, 1991.
3] R. Parkinson, Nickel Institute Technical Papers, 1995.
4] K.H. Krishnan, S. John, K.N Srinivasan, J Praveen, M. Ganesan, P.M.Kavimani : Metal. and mat. Trans., 37A (2006) 1917.
5] P. Bottari, F. Robin, R. Parkinson, Techniques de l'ingénieur M 1567, 2004.
6]T. Watanabe and Y. Tanabe. Transactions of the Japan Institute of Metals, 24 (1983) 396–404.
7] Marie-Aline Clerc, PhD Thesis, Besançon, 1986.
8] P.S. Kumar and P.K Nair, Nanostructured Materials, 5 (1994) 183–198.
9] A. Chiba, H. Haijima, W.C. Wu, Ultrasonics 42 (2004) 617–620
10] A. Mondal, S. Nath, A. Mondal, S. Bandopadhyay, U. Gangopadhyay, H. Saha, Materials Research Bulletin, 39(14-15) (2004) 2187-2192
11] Y.W. Riddle and T.O. Bailer JOM (April 2005) 40-45
12] Qun-li Rao, Gang Bi, Qing-hua Lu, Hao-wei Wang, Xiao-lan Fan, Applied Surface Science 240 (2005) 28–33
13] Y.W. Riddle, C.E.McComas, Proc SAE world congress 2005.
14] L.J.Mayer, Prod. Finish. June 1993, 48
15] F. Delaunois and P. Lienard, Surface and Coatings Technology, 160 (2002) 139–148.
16] Shi Ziyuan, Wang Deqing, and Ding Zhimin, Applied Surface Science, 221 (2004) 32–68.
17] K. Krishnaveni, T.S.N. Sankara Narayanan, and S.K. Seshadri, Surface and Coatings Technology, 190 (2005) 115–121.
18] T.S.N. Sankara Narayanan and S.K. Seshadri, Journal of Alloys and Compounds, 365 (2004) 197–205.
19] C.T. Dervos, J. Novakovic and P. Vassiliou, Materials Letters, 58 (2004) 619–623.
20] K.-H. Lee, O. Takai, Diamond & Related Materials 14 (2005) 1444 – 1450
21] P.-L. Larssont, A. E. Giannakopoulos, E. Soderlund, D. J. Rowcliffe, R. Vestergaard, International journal of Solids Structures Vol. 33, No. 2, (1996) 221-248.

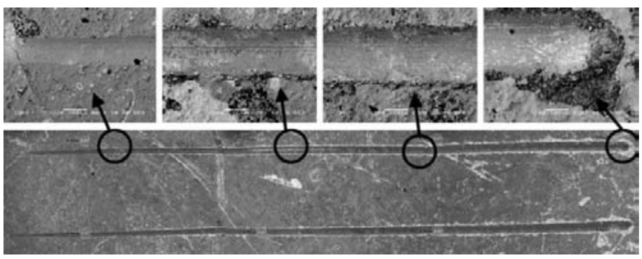

Fig. 10
Scratch test on an "ammonia" treated nickel-boron coating.
Prova di scalfittura su un rivestimento nichel-boro sottoposto a trattamento in atmosfera di ammoniaca.

22] T. Miura, Y. Benino, R. Sato, T. Komatsu, Journal of the European Ceramic Society 23 (2003) 409–416.
23] S.J. Bull, Tribology International Vol. 30, No. 7, (1997) 491-498.
24]S.J. Bull, Wear 233–2351999.412–423
25] Advanced technical ceramics - methods of tests for ceramic coatings - part 3: Determination of adhesion and other mechanical failure modes by scratch test. European standard, European committee for standardization, 1999.
26] Y. Xie, H.M. Hawthorne, Wear 233–235 (1999) 293–305.
27] S. Baba, T. Midorikawa, T. Nakano, Applied Surface Science 144–145 (1999) 344–349.
28] E. Darque-Ceretti, E. felder. Adhésion et adhérence. CNRS édition, Paris, 2003
29] M. Čekada, J. Dolinšek, P. Panjan, Vacuum, 80, (1-3), (2005) 137-140.
30] V. Vitry, F. Delaunois and C. Dumortier, Surface and Coatings Technology, 202, 14 (2008) 3316 - 3324.
31] B. Oraon, G. Majumdar, B. Ghosh, Materials and Design (2007) vol 29 (7) 1412 - 1418.

ABSTRACT

COME IL TRATTAMENTO TERMICO PUÒ MIGLIORARE LE PROPRIETÀ DEI RIVESTIMENTI CHIMICI DI NICHEL-BORO.

Parole chiave: trattamenti termici, rivestimenti, acciaio

Deposizioni chimiche di nichel-boro sono state realizzate su un acciaio dolce e sono state poi sottoposte a trattamenti termici in atmosfera inerte o a base di azoto. Le proprietà ottenute dopo questi trattamenti sono state confrontate con quelle dei rivestimenti nichel-boro di partenza. La morfologia e la struttura dei campioni sono state esaminate mediante XRD, microscopia ottica e SEM; la loro composizione è stata studiata mediante analisi ICP, GD-OES e SIMS; infine sono state eseguite prove di micro- e nano-durezza per valutare la durezza dei rivestimenti. Per determinare i meccanismi di danneggiamento del rivestimento sono stati utilizzati prove di resistenza alla scalfittura.