Improvement of hardness and mechanical properties of electroless nickel-boron deposits by thermochemical treatment

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Abstract: Electroless nickel-boron deposits were synthesised on steel substrate and then submitted to nitrogen based thermochemical treatments. Treatments were carried out between 300 and 600°C, for times up to 10 hours, using conditions very similar to vacuum nitridation or in standard nitriding atmosphere.
Micro- and nanohardness measurement were carried out on the free surface of the sample and on polished cross-sections.
Vacuum nitrided nickel-boron deposits showed a higher hardness than deposits annealed using the same temperature and pressure conditions under argon.
The samples were also investigated by XRD, SEM and optical microscopy to assess the structural and composition changes in the sample during nitridation.

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1. Introduction.

Since the discovery of autocatalytic electroless nickel plating by Brenner and Riddel in 1946 [1], its use has continuously grown because of its useful combination of properties and characteristics. Borohydride reduced coatings have been extensively studied over the last twenty years [2-5], notably because they show a higher hardness than hypophosphite reduced coatings. Their mechanical, electrical and tribological properties are of great interest for applications in the aerospace, automotive, electronic and chemical industries. In the as-deposited state, they are considered to be a mix of amorphous and nanocrystalline phase [6-9]. They present an amount of amorphous phase that increases with the amount of boron in the deposit [10, 11].

The hardness of nickel-boron deposits can be enhanced by crystallization of the coating following a heat treatment in neutral atmosphere. It increases from 650-750 hv_{100} in the as-deposited state to 1200-1300 hv_{100} after optimal heat treatment [6, 7, 13].

Thermochemical treatments are often used to enhance the hardness of metals [14]. Nitridation is a thermochemical process during witch nitrogen is introduced in the metal by diffusion from its surface. The initial introduction of nitrogen in the metal is due to a reaction, such as decomposition and adsorption, between the nitriding environment and the treated surface. This initial reaction is strongly influenced by the composition of the environment and the temperature, while the ulterior diffusion is only influenced by the substrate and the temperature. Four main classes of nitridation processes are used industrially. They differ by the kind of nitriding environment they use : (i) liquid nitridation is performed in a molten salt bath containing cyanide compounds ; (ii) gaseous nitridation is mostly carried out in ammonia based gaseous atmosphere (at ambient pressure) ; (iii) vacuum nitridation uses a reduced pressure and a ammonia or nitrogen-based atmosphere ; (iv) plasma nitridation takes place in a vacuum chamber, under a nitrogen based gaseous flow and uses a glow discharge around the treated part [15-21].

Amongst those, gaseous nitridation is one of the most used processes while the annealing of metals in pure nitrogen atmosphere, although it is the simplest treatment, is not often used because it requires elevated temperature. Nevertheless, it is possible to obtain nitride phases by treatment in pure nitrogen [22].

Nanoindentation is an instrumented hardness measurement method that is mainly used to study ceramics and polymers. The indentation process doesn’t differ from macro and microhardness testing, but the load applied to

the indenter is smaller (generally a few mN). The hardness of the material is then calculated from the displacement of the indenter during loading and unloading [23-25] instead than from the residual size of the indent. Thanks to the smallness of the indents, it is possible to follow the evolution of the hardness over small sections (i.e. coatings) [26]. Other properties of the materials (Young's modulus, elastic recovery) can also be obtained from the nanoindentation results [27-29].

In previous work, we have introduced the use of nitridation treatments for Electroless nickel-boron coatings and compared the hardness of vacuum nitrided coatings and heat treated coatings [30]. In this work, we will focus on the comparison between two different hardness treatments: vacuum nitridation and ammonia nitridation.

2. Experimental details.

2.1. Samples preparation.

Nickel-boron coatings were deposited on a standard commercial carbon steel alloy. The samples are 10 mm thick cylinders with an average diameter of 25 mm. Before plating, the samples were prepared by mechanical polishing and etching in HCl 30% then coated with an acid nickel-phosphorous protective layer. The bath used for the nickel-boron deposition and the sample preparation procedure have been described elsewhere [8]. The bath contains sodium borohydride as a reducer, ethylene diamine as a complexing agent and lead tungstate as a stabilizer.

Vacuum nitridation was performed in a vacuum furnace, under pure nitrogen flow and low vacuum. Temperatures from 300 up to 600°C were used, and times from 2 to 8 hours.

For comparison, classical ammonia nitridation was performed using an industrial process with the following conditions: 10 hours at 540°C in an atmosphere containing 60% NH_3.

2.2. Analyses of the nickel-boron deposits.

The microstructure of the nickel-boron deposits was investigated by X-ray diffraction, with a Siemens D500 X-rays θ–θ apparatus applying Cu K_α (1.5Å). Structure, thickness of the coating and diffusion at the interface were studied using a Philips XL 20 Scanning Electron Microscope. The microhardness of the samples was measured with a LECO M-400-A hardness tester. A Vickers indenter was used to determine the free surface hardness, and a Knoop one (lozenge shaped) for the hardness measured on polished cross-

sections. The nanohardness of the samples was surveyed using a MTS nano-indenter XP with a Berkovitch (tetrahedron shaped) indenter.

3. Results and discussion.

3.1. Thickness and structure of the coatings.

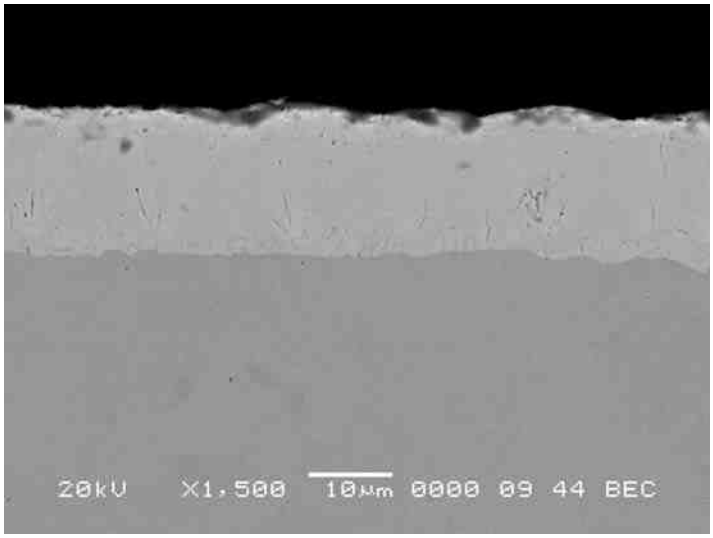

Figure 1: SEM image of a vacuum nitrided nickel-boron deposit on steel substrate.

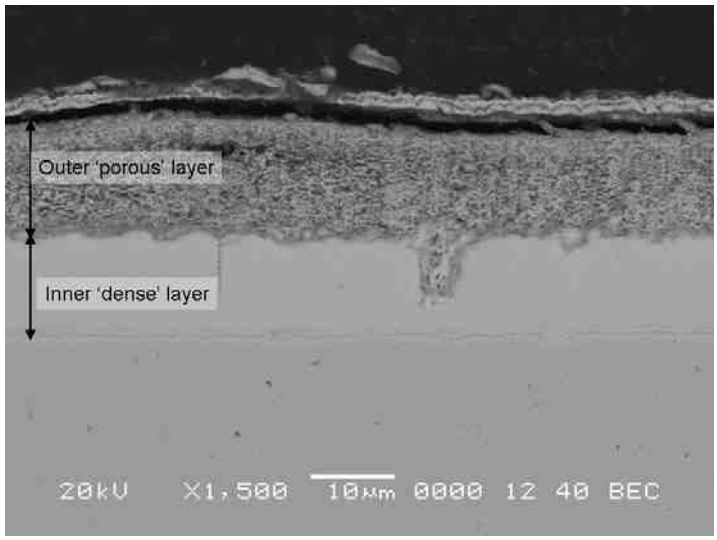

Figure 2: SEM image of an ammonia nitrided nickel-boron deposit on steel substrate.

Thickness and apparent structure of the nitrided coatings were investigated via SEM analysis and optical microscopy. They show an average thickness of 15µm and their structure, columnar in the as-deposited state,

becomes dense after vacuum nitridation (fig. 1). The ammonia nitrided samples show a dual structure. The inner layer is un-columnar and dense, while the outer one is porous (fig.2). The porous outer layer is probably a combination layer such as the “white layer” observed after the nitridation of steel.

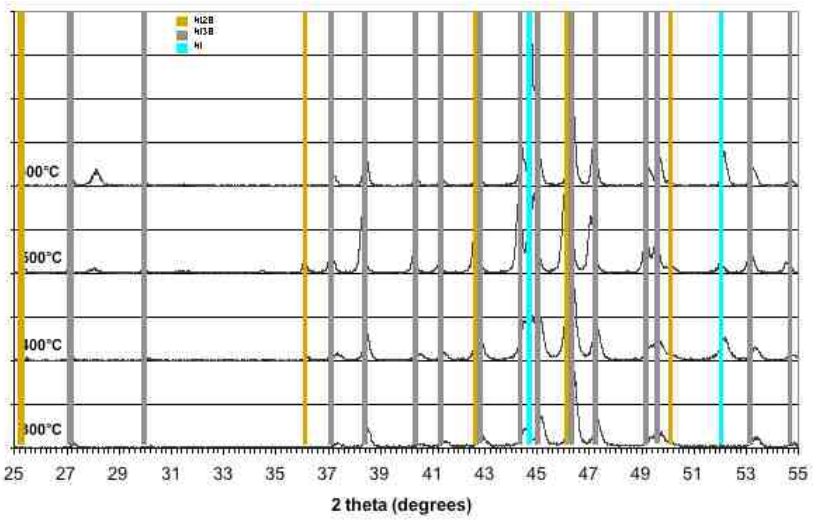

Figure 3: XRD patterns of electroless Ni–B deposits on steel substrate before and after vacuum nitridation.

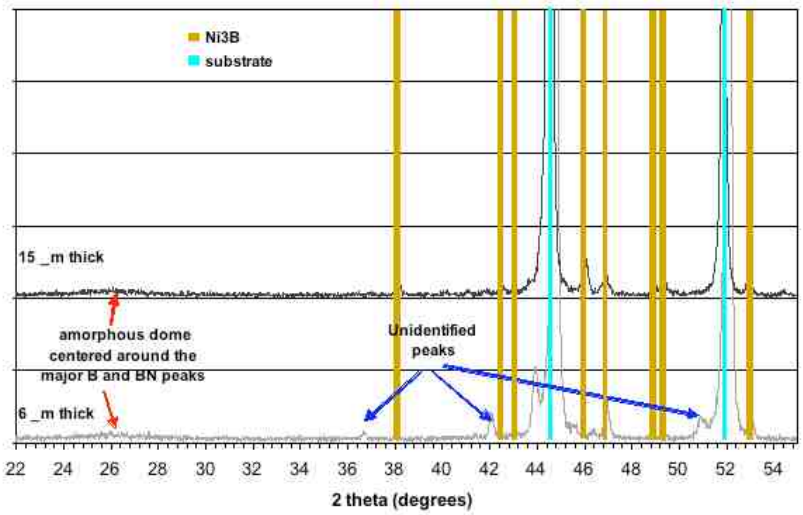

Figure 4: XRD patterns of electroless Ni–B deposits on steel substrate after ammonia nitridation.

X-ray diffraction analyses on vacuum nitrided samples (fig. 3) show the presence of Ni_3B phase for all treatment temperatures, while the intensities of the peaks attributed to the Ni_2B phase reach a maximum for the treatment at 500°C, and those of the peaks attributed to Ni present a continuous increase.

An unidentified peak is observed for temperatures higher than 500°C, at an angle close to 28°.

On ammonia nitrided samples, the only nickel based phase that is detected is Ni_3B (fig.4). The two major peaks observed around 44 and 52° are linked to the steel substrate. A small amorphous dome, centred on 26°, that covers some of the more intense peaks of several boron-based phases such as h-BN (26.764°), BN (rh)(26.176°) and BN (ort) (25.135°), can be seen. Three unidentified peaks at 36.3, 42 and 51° are present for thin samples.

3.2. Diffusion at the interface.

Diffusion at the nickel coating/steel substrate interface was studied via SEM chemical analyses using an energy selective X-ray spectrometer for the identification of the different chemical elements present in the Ni–B deposit, such as Ni, P and Fe. Boron, which is a very light element, cannot be detected due to matrix effects. This analysis (linescan) is performed across the deposit from its external surface to the substrate. Figure 5 shows the superposed linescans obtained for vacuum nitrided (at 600°C) and untreated samples. They do not present any obvious diffusion of iron in the coating or of nickel in the substrate. For ammonia nitrided samples, however, there is an obvious diffusion of nickel into the steel substrate, as can be seen on fig. 6. This difference is probably due to the longer heat treatment (10 h) used in the case of ammonia nitridation.

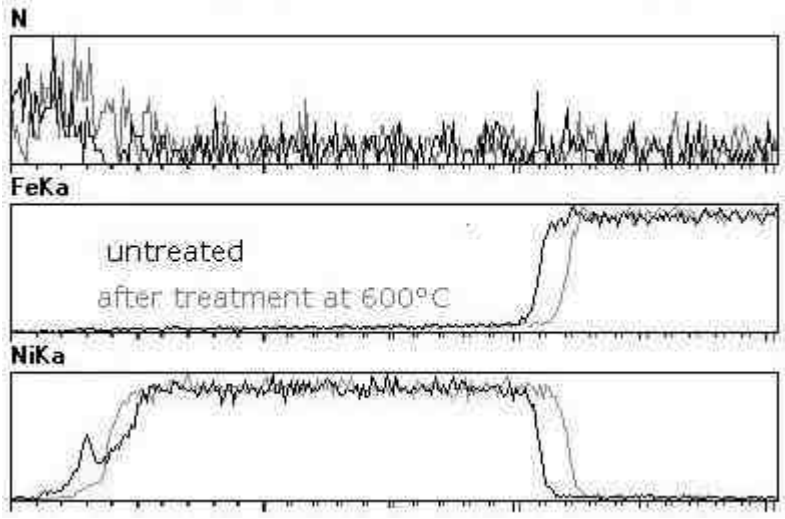

Figure 5: Superposed linescans (qualitative chemical analyses) of an electroless Ni–B deposit before heat treatment (black lines) and after vacuum nitridation at 600°C (grey lines)

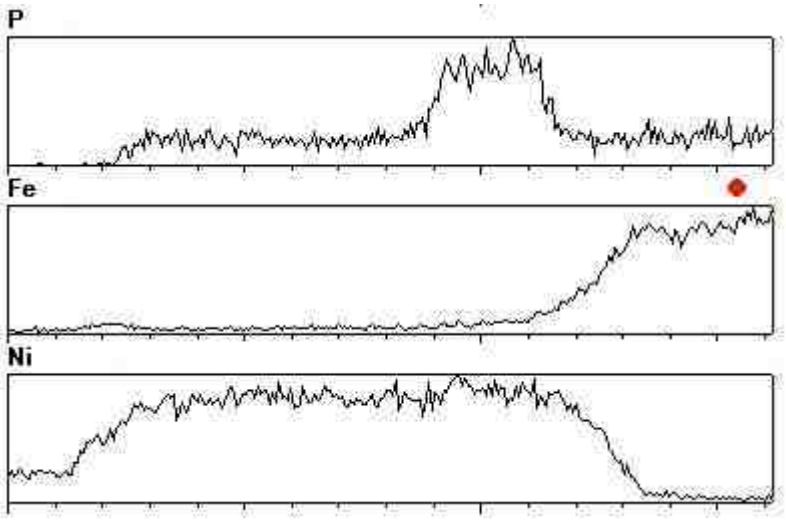

Figure 6: Linescans (qualitative chemical analyses) of an electroless Ni–B deposit after ammonia nitridation at 540°C.

3.3. Comparison of hardness values obtained from various methods.

The hardness of the coatings was measured by means of Knoop microindentation and Berkovitch nano-indentation on polished cross sections, and by Vickers microindentation on the free surface. For each method of measurement, several loads ranging from a few mN to 5N were applied to the sample. The disparity of the loads prevents direct comparison so we used the "zero-load" hardness which is calculated by linear interpolation of the hardness values obtained from different loads using a single method.

The choice of Knoop microhardness tests on cross section was made to avoid any influence of the substrate hardness while measuring the hardness of the coating. The preferential orientation of Knoop indentation parallel to the coating allows better accuracy of the measures. Vickers microhardness measures were carried out on the free surface of the sample to allow the comparison of our results to other published and industrial data (which are mainly non-destructive Vickers microindentations on the surface).

After vacuum nitridation up to 400°C, the Vickers surface microhardness is close to 1200 hv_{100} (see fig.7). It is thus in the same range as after argon-nitrogen treatment at the same temperature [6, 13]. However, for higher temperatures, a continuous increase of the surface hardness, for nitrogen treated samples, up to 1600 hv_{100} is observed. This increase is not predicted by the crystallization of nickel-boron alloys into Ni, Ni_2B and Ni_3B phases. The values obtained from the 3 indentation methods present a similar evolution but their values become more divergent as the measured hardness increases, probably because the experimental error increases with the hardness.

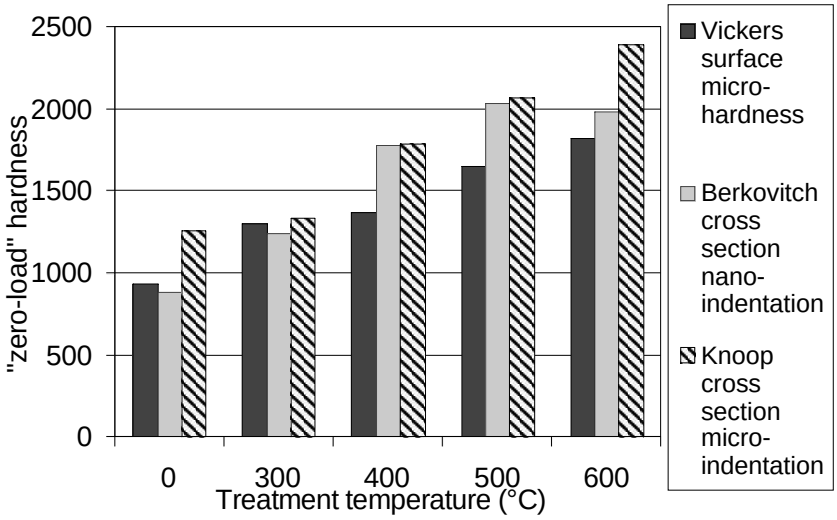

Figure 7: Comparison of the "zero-load" hardness obtained by Vickers and Knoop micro-indentation and Berkovitch nano-indentation, for vacuum nitrided nickel-boron coatings on steel substrate

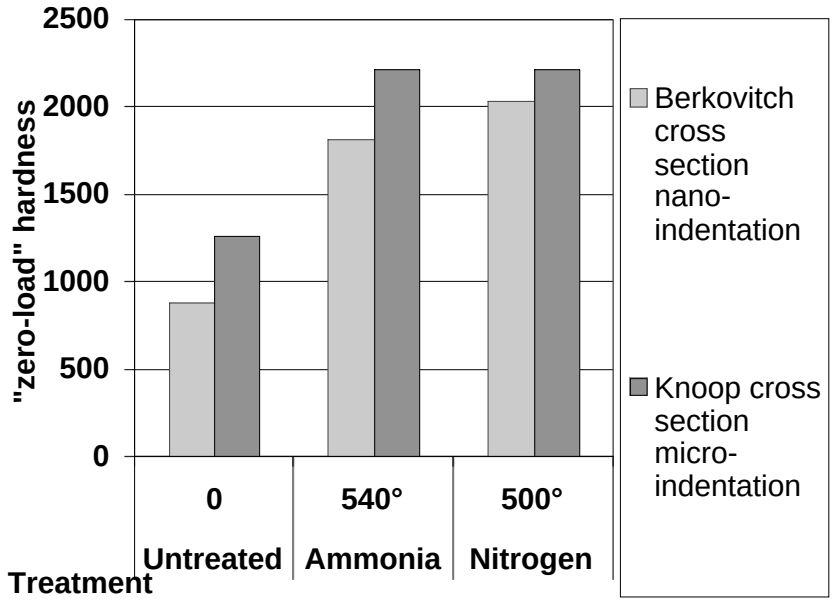

Figure 8: Comparison of the "zero-load" hardness obtained by Knoop micro-indentation and Berkovitch nano-indentation, for untreated, vacuum and ammonia nitrided nickel-boron coatings on steel substrate.

The results from ammonia nitridation (540°C) are compared to those of 500°C vacuum nitridation (fig. 8). The "zero-load" hardness values of the ammonia nitrided coating are less concordant than those obtained for the vacuum nitrided coating. However, the knoop hardness values for ammonia

and vacuum nitrided samples are a nearly perfect match, as can be seen in fig. 9.

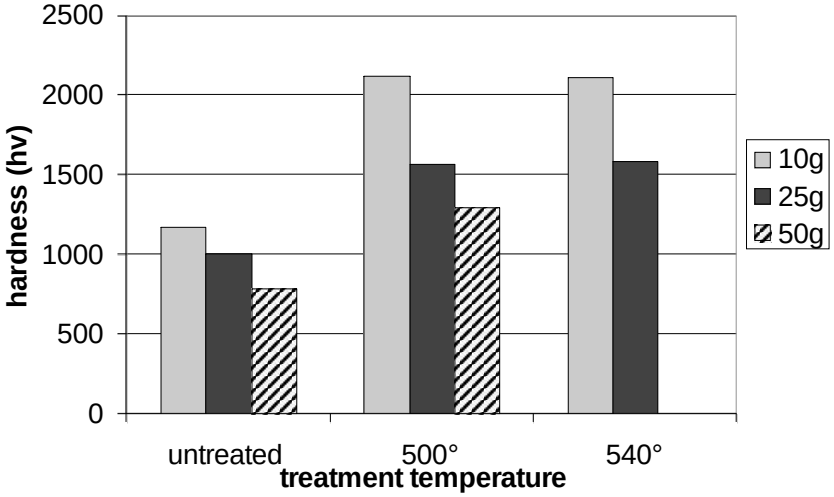

Figure 9: Comparison of the Knoop microhardness values, under various loads, for untreated, vacuum and ammonia nitrided nickel-boron samples.

3.4. Nanoindentation profiles.

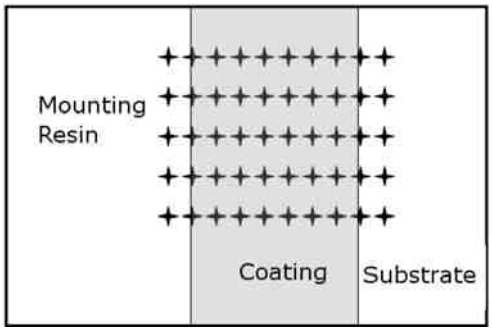

Figure 10: Position of nanoindentation profile tests in the coating.

To obtain the nanoindentation hardness profile of the coating, the samples were indented along 5 rows (each composed of 10 indents) across the coating (fig. 10). Rows are separated by 5 μm, while there is 3 μm between two points of the same row. Knowledge of the hardness profile enables to determine if the coating is homogeneously influenced by the heat treatment.

The hardness of vacuum nitrided nickel-boron coatings on steel substrate is higher near the surface of the coating than near the coating/substrate interface. This hardness increase is thus the consequence of an interaction between the nitrogen atmosphere and the surface of the coating,

and of a diffusion process, that enhance the thermal effect (hardness increase by coating crystallization) (fig. 11).

A comparison between the nanoindentation profile of ammonia nitrided samples and the one obtained from vacuum nitridation at 500°C was made (fig12). These results match near the substrate/coating interface, while the hardness of the ammonia nitrided coating is lower than that of the vacuum nitrided coating near the coating surface. This is explained by the dual structure of the ammonia nitrided coating which is composed of a dense (and hard) inner layer that matches vacuum nitrided coatings, and of a porous outer one.

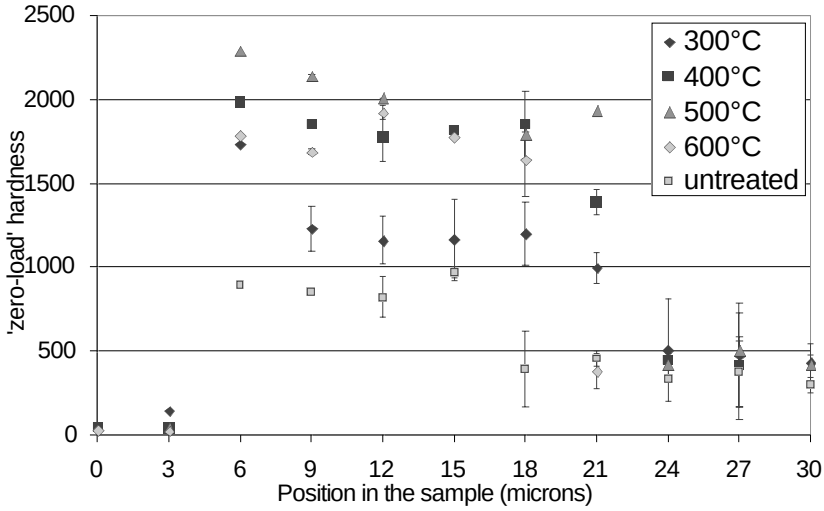

Fig. 11: Nanoindentation profiles on vacuum nitrided nickel-boron deposits on mild steel (left side: mounting resin; centre: coating; right side: substrate)

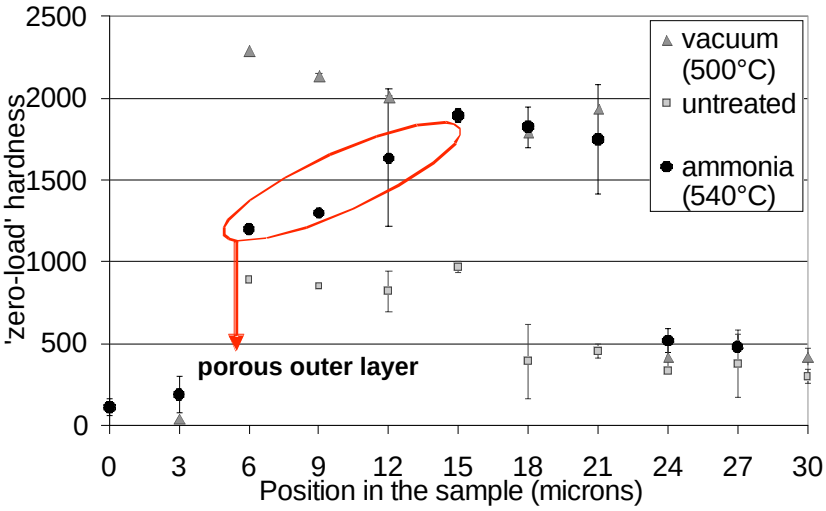

Fig. 12: Nanoindentation profiles on ammonia nitrided treated nickel-boron deposits on mild steel (left side: mounting resin; centre: coating; right side: substrate)

4. Conclusions

Two nitridation treatments were performed on nickel-boron coated steel: (i) a vacuum nitridation treatment, under nitrogen atmosphere, at temperatures from 300 up to 600°C, and (ii) an industrial ammonia nitriding treatment at 540°C, in atmosphere containing 60% ammonia.

After vacuum nitridation, the coating presents a dense uniform aspect. XRD reveals the presence of Ni_2B, Ni_3B and Ni phases, as well as an unidentified peak around 28°. The hardness of vacuum nitrided deposits increases continuously with the increasing of treatment temperature. The hardening mechanism is different than that involved with classical heat treatments in neutral atmosphere that present an hardness decrease over 400°C [9]. Nanoindentation profiles show that the hardness of the coating is higher near the surface, and that the hardening mechanism is due to interactions between the nitriding atmosphere and the coating surface rather than to a thermal crystallization process.

Ammonia nitridation leads to a dual structure of the coating with a dense inner layer that is comparable to the vacuum nitrided nickel-boron coating, and a porous outer one. XRD analyses only reveal the presence of Ni_3B phases; strong peaks are attributed to the substrate and an amorphous dome, seen around 26°, is linked to boron and boron nitride semi-crystallized phases. There is also an important diffusion of nickel into the steel substrate.

Comparison of vacuum and ammonia nitrided samples shows that the properties of the dense layer of the ammonia nitrided coating and the vacuum 500°C nitrided deposit are very similar. The knoop hardness values of those two samples are a nearly perfect match; the hardness profiles match for the inner part of the coating, and the difference observed for the outer part shows that the outer porous layer of ammonia nitrided samples has poorer properties than the dense nitrided layer.

The outer porous layer of ammonia nitrided coating is thought to be similar to the white combination layer observed during nitridation of steel. As for steel, this one must be avoided because its mechanical properties are poorer than those of the rest of the coating.

The vacuum nitridation treatment seems thus to be more adapted to increase nickel-boron coatings' properties. The hardening mechanism is not yet clearly identified but chemical and structural analyses are planned to explain it.

Future works will focus firstly on the hardening mechanism involved in the nitridation of nickel-boron coatings, secondly on the optimisation of the vacuum nitridation treatment, thirdly on the investigation of low temperature

nitridation processes for nickel-boron deposits that provide higher hardness on a larger range of substrates, and lastly on the complete mechanical, tribological and electrochemical characterizations of the nitrided coatings.

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