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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.