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Influence of the anionic part of the stabilizer on electroless nickel-boron plating

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ABSTRACT

Selectivity and smooth operation of electroless nickel plating require that a stabilizing agent is used. It operates by blocking catalytic activity on unwanted germination sites and regulating the activity of the substrate. In the case of alkaline electroless nickel-boron plating systems, which use sodium (or potassium) borohydride as reducing agent, lead and thallium salts are the most popular stabilizers. However, there is little knowledge about the way the stabilizer acts. In this study, 4 different lead-based stabilizers (tungstate, sulphate, nitrate and chloride) have been used, all other things left constant, in electroless nickel-boron plating baths. The thickness, composition, roughness, morphology, hardness and structure of all the obtained coatings have been investigated. Chloride led to thinner deposits and the boron content varied between 5.5 wt.% for lead tungstate and 6.5 wt.% for lead nitrate and lead sulphate, with a lead content between 0.2 and 0.25 wt.%. Coatings obtained with a lead tungstate stabilized bath were thicker, harder and contained less boron and lead than the others. This shows the influence of the anionic part of the stabilizing agent on the plating process.

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Introduction

The principle of electroless deposition has been discovered in the 19th century but the first practical application of the method was reported by Brenner and Riddell in 1946 [1]. The process is based on the reduction of metallic salts by a chemical agent in aqueous solution and uses heat as the only source of energy, thus differing from electroplating that needs an externally applied current. The process can thus be used on all kinds of substrates, including non-conducting materials. A great variety of metals and alloys can be produced by electroless plating but the most popular is nickel. Among nickel coatings, nickel-phosphorous alloys are the most used but nickel-boron deposits that can be synthesized with either amine-borane compounds or borohydride possess very interesting properties, like high hardness and a textured surface that is beneficial to wear applications [2, 3].

Electroless plating is a catalytic reaction that obeys the mixed potential rule: the plating potential is such that the anodic current (oxidation of the reducing agent) is the same as the cathodic current (reduction of the metal). The plating speed is thus greatly influenced by the plating potential, which is in turn a result of the catalytic activity of the substrate and the previously deposited material towards the reaction. The chemical control of the bath must thus be very precise in order to keep constant conditions throughout the plating process.

Electroless plating baths usually contain a nickel salt that provides the metallic ions, a reducing agent, a complexant that allows increasing the amount of metallic salts in solution without precipitation, a pH regulator and a stabilizing agent, all in very precise amounts. The role of the stabilizing agent is very important in the plating bath: it regulates the deposition speed and stops homogeneous germination of metallic

particles in the bath by blocking some of the active sites on the substrate and all the possible states in solution. The most popular stabilizing agents for electroless nickel-boron plating with borohydride compounds are heavy metals salts (lead and thallium), and thiourea is the only alternative [4]. Bath stabilization by lead salts is linked to adsorption of lead ions on the surface of the sample, on the cell walls as well as on any potential germination site like suspended particles. It is possible, by using varying bath loads and measuring lead concentration before and after plating, to measure the amount of lead that adsorbs on the non-reacting surface [5].

While there are several studies on the influence of bath chemistry on the properties of electroless nickel-boron coatings [6–10], most of them study only variations of the amounts of reactive used in the bath, not the nature of those reactive. Delaunois' study, in which 2 distinct stabilizers are used (TlNO_3 and PbWO_4) [8] is thus quite unique in the literature. There is an extensive study of stabilizers action in the electroless nickel-boron plating bath written by Bielinski et al [11] but the authors did not characterize the coatings at all, only the plating ability of the solutions they created. As a result, the knowledge of the effects of stabilizing salts on the coatings are still quite unknown and the literature available for nickel-phosphorous coatings, while it is more abundant [12–14], cannot be used without modifications because the baths operate at very different pH (most nickel-phosphorous bath are slightly acidic, while borohydride-reduced baths are strongly alkaline). However, as it is usual that heavy metals stabilizers are incorporated into the bath, it is truly possible that the choice of a specific salt may influence the plating process and the quality of the coating in a much more important manner than what is usually considered.

In this paper, the anionic part of the stabilizing agent was modified in the electroless plating bath developed by Dr. Delaunois [8], all other things kept constant. As thallium is very toxic, only the lead stabilized baths were thus modified. The compounds used in this study were chosen because either they have been used as stabilizers ($\text{Pb}(\text{NO}_3)_2$ [15], PbWO_4 [(8,5)] or because there are occurrence of similar thallium compounds (PbSO_4 [16], $\text{Pb}(\text{NO}_3)_2$ [8, 16]). Lead chloride was added as a 'neutral' agent because the bath is based on nickel chloride and thus contains already a lot of chloride.

Materials and Methods

The samples used for this study were mild steel sheets (ST 37-DIN 17100 –with a C content <0.17 wt.%, Mn <1.4 wt.%, P and S <0.045 wt.%) with the following dimensions: $25 * 25 * 1$ mm. Before plating, all samples were prepared to ensure reproducible surface condition: grinding with 500 and 1200 MESH silicon carbide abrasive paper; degreasing with acetone; etching in 30 vol.% HCl for 3 minutes and rinse with flowing deionized water before direct immersion in the electroless nickel-boron plating bath for 30 minutes.

The plating bath was based on Delaunois' formulation [8]. It was operated at $95 \pm 1^\circ\text{C}$, with a pH higher than 13 and with constant mechanical agitation (with a magnetic stirrer), in a one-liter cell with controlled heating. The bath load was kept close to $25 \text{ cm}^2 \cdot \text{L}^{-1}$. The composition of all baths is shown in Table 1. To keep the plating conditions as similar as possible between the various baths, the amount of lead ions was kept constant between plating baths and the total amount of stabilizer varied. 4 plating experiments were carried out for each stabilizing agent.

The analysis of samples was carried out by the following methods: the thickness and deposition rate were obtained from the weight gain and from observation of the samples by optical microscopy, with a HIROX KH-8700 digital microscope; the chemistry was measured by glow-discharge optical emission spectroscopy, using a Horiba-Jobin-Yvon apparatus of the last generation. Average values were derived from the values for the whole coating; the roughness was measured with a Zeiss 119 SURFCOM 1400D-3DF apparatus; the morphology was observed, by digital microscopy and by SEM with a Hitachi SU8020 high definition SEM; Vickers microhardness was measured on the surface of samples with a LECO M-400-A hardness tester under a load of 100 g and on polished cross sections with a Mitutoyo HM-200 with a load of 20 g; finally, the structural state of the coatings was investigated with a Siemens D50 θ - 2θ apparatus with $\text{Co } \lambda\text{K}\alpha$ radiation (1.79 \AA).

Results and Discussion

The thickness of all samples is presented in Table 2. The values obtained from the weight gain and from optical measurements

are in the same range. The differences between the values are due to the fact that all coatings were used for the weight gain while the optical measurements are related to one single coating. The plating rate measured with PbWO_4 is the highest, with an extrapolated value of nearly $26 \mu\text{m}/\text{hour}$ while those measured for nitrate and sulphate are slightly lower (close to $24 \mu\text{m}/\text{h}$). The extrapolated plating rate for the chloride stabilized bath is however significantly lower at only $20 \mu\text{m}/\text{h}$. Those values are extrapolated because, in practice, the plating rate will decrease as the deposition slows during the process [5].

All samples contained a similar amount of lead (see Table 2), with a slightly higher lead content for the bath stabilized with nitrate. However, the variations of average lead content are too limited to draw any conclusion from. The boron content of the sample stabilized with tungstate is sensibly lower than that of the other samples, with those stabilized with nitrate and sulphate having the highest content. It was thus not possible to link the average composition of the coatings with the plating rate.

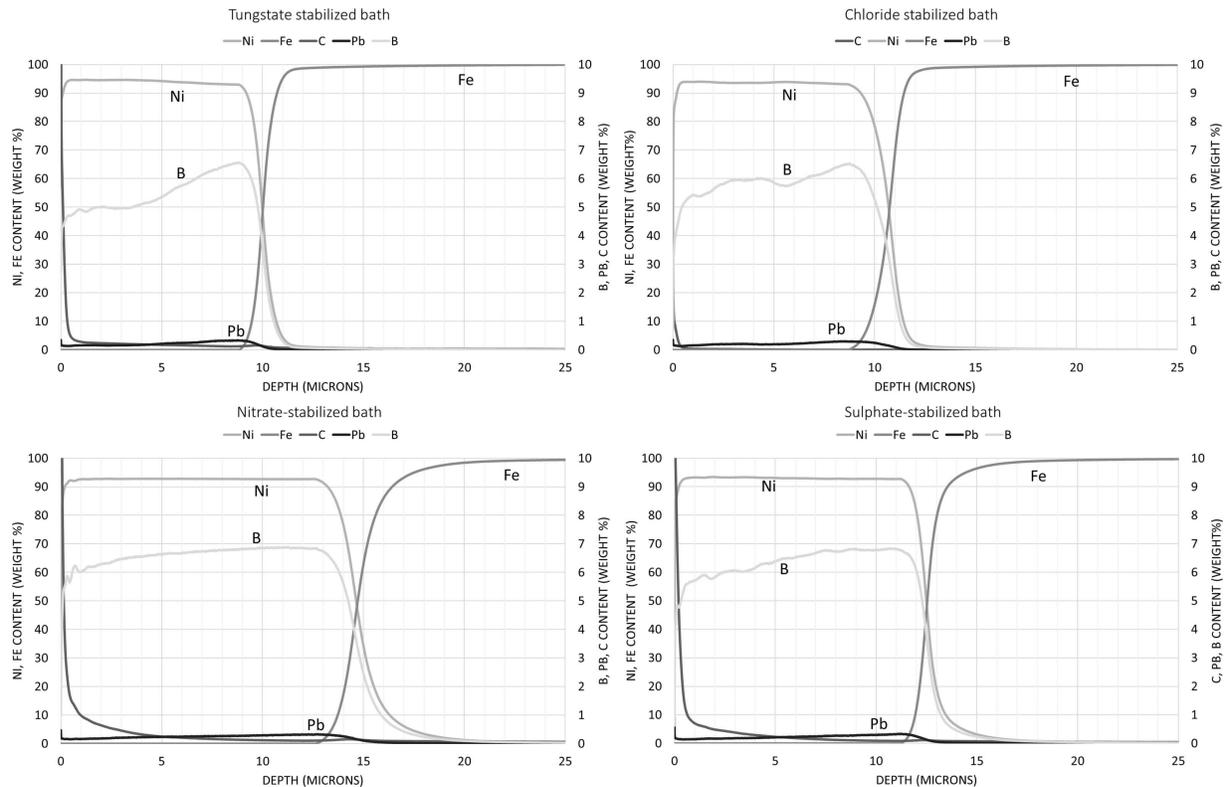
The composition depth profile of samples stabilized with each agent are shown on Fig. 1. While the average lead and boron content of the coatings did not provide a lot of insight about the differences due to the stabilizing agent, the evolution of the amount of various elements in the coating provides interesting information: first, the coatings synthesized with lead nitrate and lead sulphate present similar profiles, like they had similar thicknesses and average composition. For those two stabilizers, the boron content in the coatings is relatively high at the beginning of the plating process and decreases very slowly but steadily, mainly in the case of nitrate, to reach a value close to 6 wt.% at the surface of the coating. The lead content of those two coatings follows a similar pattern, with an initial value close to 0.3 wt.% and a final value at the surface of 0.15 wt.%. The coating stabilized with lead tungstate presents a rather different behaviour: its initial boron content is similar but decreases quickly in the first $5 \mu\text{m}$ to reach a value in the range of 5 wt.% and then stays relatively stable in the coating with only a slight decrease very close to the final surface, that may be linked with superficial roughness. The lead content of the coating follows a similar pattern, with an initial value slightly over 0.3 wt.% and a final value close to 0.15% reached after only $6 \mu\text{m}$. The evolution of the lead and boron content in the coating stabilized with lead chloride resembles the most that of the tungstate stabilized one: the initial lead and boron contents decrease rather quickly. However, in the present case, the lead content stabilizes at 0.2 wt.% rather than 0.15 wt.% like it does for tungstate. Similarly, the boron content stabilizes close to 6 wt.% rather than 5 wt.%. In this case, even if the lead content is globally similar to that of the coating stabilized with lead tungstate, the local content is higher except in the very first microns, which is probably the reason for the slower growth of the coating: the stabilizing action of lead salts is linked to lead adsorption at the growth surface, where some of the lead is then reduced and co-deposited with the nickel and boron [5]. It is thus expected that a higher lead content in a part of the coating is linked with a higher amount of adsorbed lead salts and thus with a slower plating process.

Table 1. Composition of the various plating baths.

Common agents	Stabilizers ($9.56 \cdot 10^{-3}$ g/L lead ions) g/L	
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	24 g/L	PbWO_4 $2.10 \cdot 10^{-2}$
NaOH	39 g/L	$\text{Pb}(\text{NO}_3)_2$ $1.40 \cdot 10^{-2}$
$(\text{NH}_2\text{CH}_2)_2$	60 ml/L	PbSO_4 $1.28 \cdot 10^{-2}$
NaBH_4	0.602 g/L	PbCl_2 $1.53 \cdot 10^{-2}$

Table 2. Thickness, roughness, hardness and composition of the coatings synthesized with varying stabilizing agents.

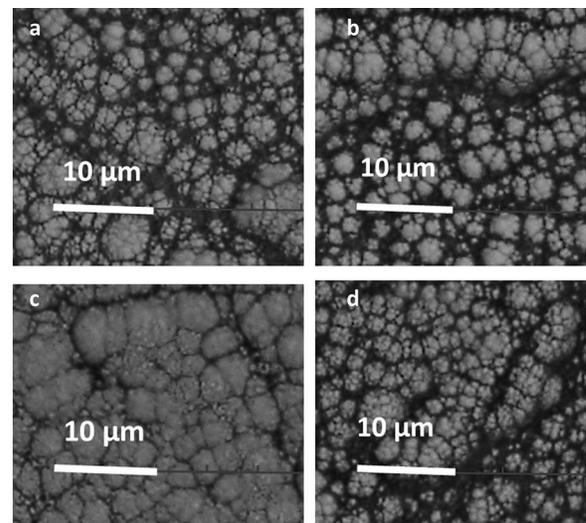
Stabilizer	PbWO ₄	PbCl ₂	Pb(NO ₃) ₂	PbSO ₄
Thickness (from weight gain) (μm)	12.7 ± 1.8	10.2 ± 0.5	11.9 ± 0.1	12.3 ± 0.2
Thickness (from microscopy) (μm)	12.9	10.2	12	12
Roughness (R _a) (μm)	0.42 ± 0.26	0.53 ± 0.03	0.34 ± 0.12	0.48 ± 0.09
Surface hardness (hv ₁₀₀)	760 ± 100	545 ± 70	640 ± 30	700 ± 75
Cross section hardness (hk ₂₀)	815 ± 40	785 ± 25	775 ± 50	765 ± 40
wt.%Ni	94.07	93.64	92.64	92.97
wt.%B	5.41	5.88	6.54	6.27
wt.%Pb	0.210	0.213	0.234	0.215

**Figure 1.** GDOES depth profiles of electroless nickel-boron samples synthesized with lead tungstate, lead chloride, lead nitrate and lead sulphate as stabilizing agent.

The surface morphology of the coatings is presented on Fig. 2. All samples present the typical cauliflower-like morphology of electroless nickel-boron coatings obtained from borohydride reducing agent. However, the texture appears finer on the samples stabilized with lead nitrate (Fig. 1c). This is confirmed by the roughness measurements carried out on the samples (see Table 2): the coating prepared with nitrate has a slightly lower roughness than the 3 other (0.34 μm against more than 0.4 μm). This is probably linked with the higher average lead content of the coating stabilized with nitrate, resulting in a slightly higher lead content at the surface: a higher lead content has been associated with a finer morphology in the coating [17, 18]. The finer morphology induced by this effect leads to a more homogeneous compact aspect of the surface.

The four types of coatings present a columnar morphology on cross section observation, as shown on Fig. 3. There is no obvious difference among the 4 coatings.

The surface and cross-section hardness of all samples is shown in Table 2. Surface hardness of the coatings synthesized with lead chloride as a stabilizer is much lower than that of the

**Figure 2.** Surface morphology of the coated samples synthesized with various stabilizers: a, PbWO₄; b, PbCl₂; c, Pb(NO₃)₂; d, PbSO₄.

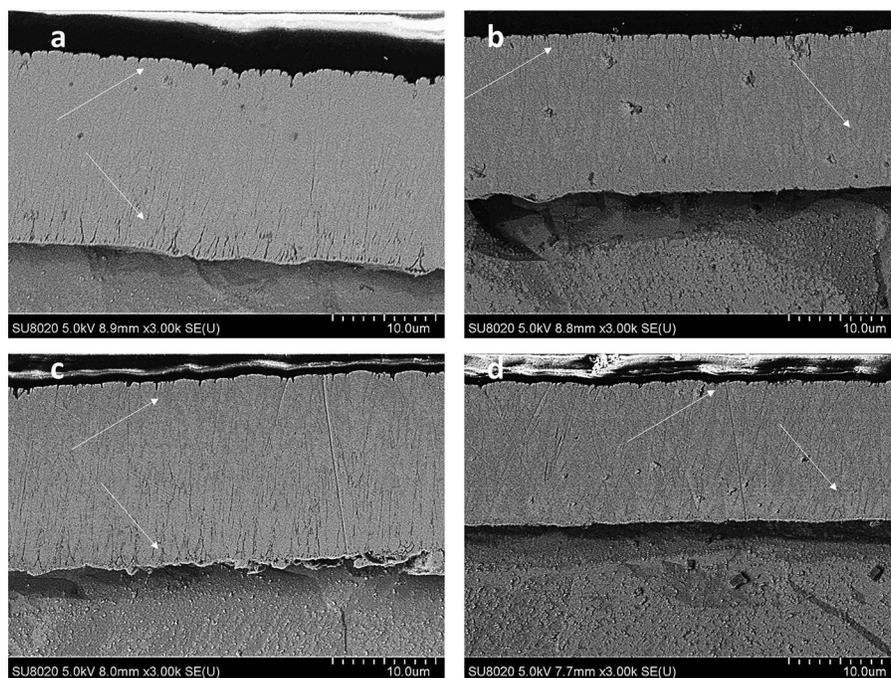


Figure 3. SEM cross section morphology of the coated samples synthesized with various stabilizers: a, PbWO_4 ; b, PbCl_2 ; c, $\text{Pb}(\text{NO}_3)_2$; d, PbSO_4 .

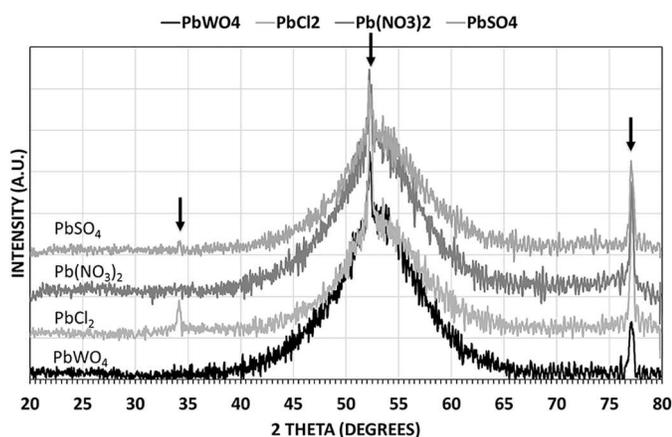


Figure 4. XRD pattern of electroless nickel-boron samples synthesized with lead tungstate, lead chloride, lead nitrate and lead sulphate as stabilizing agent.

other coatings. However, as that precise coating is also thinner than the others, it is possible that the lower hardness is due to the influence of the substrate on the measurement. Surface hardness of the coatings synthesized with nitrate and sulfate are in a similar range (650–700 hv_{100}), confirming the fact that those coatings are very similar, while that of the coating made with lead tungstate is higher. This is confirmed by the cross section measurements that show a higher hardness for the coating synthesized with lead tungstate, even if the difference is less marked, probably because of substrate effects in the surface measurements (the tungstate-stabilized coating used for surface hardness measurement was thicker than the other coatings on which hardness was measured). The hardness of the three other coatings (stabilized with chloride, nitrate and sulphate) is in a close range, between 765 and 785 hv_{20} , which shows that the difference observed for surface hardness in the

case of chloride is linked with thickness effect. All those values are acceptable for electroless nickel-boron coatings. The differences in hardness do not follow the expected behaviour (increase of hardness with increase of boron content) [10]. It is thus probable that the observed differences are also linked with the lead content of the coating that would have an opposite effect to that of boron. However, as it was not possible at the present time to produce coating with a single boron content and varying lead content, we cannot be certain of that.

The X-Ray diffraction patterns of all coatings are similar, as can be seen on Figure 4, with sharp peaks at 34.2° , 52.2° and 77.2° that are due to the substrate (the penetration depth of X-rays in nickel is close to $15\ \mu\text{m}$). This is the reason why those peaks are better defined for the chloride-stabilized coating that is thinner than the others. The part of the pattern directly linked to the coating is the large dome centred on 52° . This dome attests that all coatings are X-ray amorphous, which is expected from electroless nickel-boron coatings with a boron content between 5.5 and 6.5 wt.% [19]. There are no significant differences between the domes obtained for the various coatings. Using different anionic parts of the stabilizers has thus no significant effect on the coating structure.

Conclusions

Electroless nickel-boron coatings were synthesized with four different lead-based stabilizing agents to study the influence of the anionic part of the stabilizing agent on the plating process and the properties of the coating. The thickest coating was obtained with lead tungstate, which is not surprising because the bath composition has been optimized for that particular stabilizer. That coating was also the harder one and contained on average the least lead and boron. The use of either lead nitrate or lead sulphate had similar effects: the coating was slightly thinner, contained more lead and boron than the

tungstate-stabilized one and was also slightly softer. The use of lead chloride led to significantly thinner coatings, with an elevated lead content throughout the coating, a boron content relatively close to that of the tungstate-stabilized coating and a hardness in the same range as the coatings stabilized with nitrate and sulphate.

The use of various stabilizers had no significant effect on the structure as far as can be said from X-ray diffraction patterns, and little effect on the morphology and roughness of the coating, except in the case of lead nitrate, which led to a slightly smoother coating, with more division of the cells on the surface leading to smaller observable features.

In conclusion, it appears that the anionic part of the stabilizing agent may have an influence on the plating process and properties but it is relatively limited.

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