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Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Inorganic salts stabilizers effect in electroless nickel-boron plating: Stabilization mechanism and microstructure modification

L. Bonin*, V. Vitry, F. Delaunois

Metallurgy Lab, UMONS, 20 place du Parc, 7000 Mons, Belgium



ARTICLE INFO

Keywords:

Coating materials
Electroless plating
Nickel-boron
Stabilizer

ABSTRACT

Electroless nickel-boron coatings present exceptional wear and corrosion resistance, but the presence of toxic heavy metals like Pb or Tl in most plating baths and the coatings synthesized using them impedes their wide-spread use. In this study, several candidates potential as stabilizing agent were investigated (Pb^{2+} , Ti^{3+} , V^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Cu^{2+} , Zn^{2+} , Ge^{4+} , Zr^{4+} , Nb^{5+} , Mo^{5+} , Ce^{3+} , Ag^{1+} , In^{3+} , Sn^{2+} , W^{6+} and Bi^{3+}). The investigation was based on the fact that stabilizers can stop the deposition in high concentration, once stabilizers also act as inhibitors depending on the concentrations—four distinct groups were observed. In group 1: Cu^{2+} , Zn^{2+} , Ge^{4+} , Ce^{3+} , Zr^{4+} , In^{3+} , Sn^{2+} and Bi^{3+} , the solution is not decomposed until the end of deposition time (1 h) a deposition take place. Group 2: Ti^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Nb^{5+} and W^{6+} causes bath decomposition in less than 5 min. In Group 3: Mo^{5+} , Ag^{1+} and V^{3+} the solution decompose in less than 1 min due to the presence of surface activators. Last, group 4: Pb^{2+} and Tl^{1+} , are toxic stabilizers already studied in the literature. This paper presents a simple way to preselect metallic ions that can act as a stabilizing agent in electroless nickel-boron plating. The method includes 3 aspects: The redox potential of the cation, the catalytic activity for hydrogenation and the atomic size of the metal. Besides, two green stabilizers were identified: $\text{Bi}_2(\text{WO}_4)_3$ and SnCl_2 that act as a stabilizer for concentrations of 10^{-5} mol/L and 10^{-3} mol/L respectively.

1. Introduction

Electroless nickel plating is a popular surface treatment method that consists in the deposition of a layer of nickel on a substrate by chemical reduction of nickel ions from an aqueous solution, without recourse to any external current source [1,2]. The method is very efficient for non-conductive substrates and complex shapes because it is entirely free of edge effect, contrary to electroplating [1,2]. Among electroless nickel plating methods, electroless nickel-boron presents excellent potential as an alternative to several other metallic coatings, such as electroplated nickel and hard chrome, notably due to its excellent wear resistance and high hardness [2–4].

The electroless nickel-boron plating process has been developed in 1950 [5] but has long stayed less popular than electroless nickel-phosphorus deposition due to the lower stability of the nickel-boron plating baths [1]. There is thus still a lack of fundamental studies about the process, even if electroless nickel-boron coatings based on sodium borohydride as a reducing agent have been studied on a more practical point of view (development of bath compositions [6–12] and characterization of the coatings [8,10,13–23]) and commercially available for decades [24–28].

Stabilization is a crucial part of the electroless plating process: due to the spontaneous nature of the plating reaction, it is necessary that reaction is favoured on the substrate - which is made possible by the intrinsic or synthetic catalytic activity of the substrate and deposited material [1,2,29] – and impeded everywhere else, which includes all other immersed surfaces and the bulk of the solution, which is the primary role of the stabilizing agent. The stabilization of electroless plating is still not fully understood. This catalytic regulation is based on additions of minimal amounts of compounds belonging to one of the four following classes: compounds of group IV elements, oxygen-containing anions, heavy metal cations and unsaturated organic acids (such as maleic and citric acid).

In the case of electroless nickel-boron, the most efficient reducing agent is sodium borohydride, and its efficiency is much higher than that of sodium hypophosphite, that is used for nickel-phosphorus coatings [3,15]. This means that the need for stabilization is increased compared to electroless nickel-phosphorus plating baths. For this reason, the range of stabilizers used in electroless nickel-boron coatings is somewhat limited and Tl and Pb, being the most efficient, have been used for a long time with little alternative [1,2,12].

The recent environmental laws (ELV, RoHS and WEEE in the USA

* Corresponding author.

E-mail address: Luiza.Bonin@ugent.be (L. Bonin).<https://doi.org/10.1016/j.surfcoat.2020.126276>

Received 8 June 2020; Received in revised form 27 July 2020; Accepted 8 August 2020

Available online 10 August 2020

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and the REACH directive in Europe) significantly limit the use of toxic heavy metals such as Pb and Tl in electroless nickel coatings. The issue is even more critical for electroless nickel-boron than for electroless nickel-phosphorus because the incorporation of stabilizer in the coating happens to a greater extent in the first, with reported Tl content up to 5–6 wt% [12]. It is thus essential to find suitable alternatives to those cations as stabilizers for electroless nickel-boron plating.

A few studies were carried out, that lead to the development of promising bath formulations [30–33] but this had to be carried out in a trial and error way because there's no actual data in the literature about the stabilizing abilities of compounds in the electroless nickel-boron process when borohydride is used as a reducing agent, except a single paper from 1990 [34] whose conclusions cannot be used any more in today's environmental and health protection minded world.

This paper, based on experimental work carried out to seek for lead and Tl replacement, aims to develop a theory about the effect of various metallic salts, when used as stabilizers, on the morphology and properties of ENB.

The first part of the paper will present the effect of additions of several metallic cations on the stability of electroless plating baths and their ability to form coatings with sufficient efficiency. The focus will then be shifted on the understanding of stabilization of the plating bath by this type of compounds: a reverse engineering method is used to create a theory about electroless inorganic stabilizers. Until today, there is no theory about why one element presents stabilizing properties in an electroless plating bath. There are a few works focused on a specific stabilizer [35–37], but there is no theory that predicts if an element can or cannot stabilize an electroless bath.

2. Materials and methods

2.1. Electroless NiB bath

As the present study focuses mostly on the plating process and the effect of plating bath chemistry on the coating, the substrate material was chosen to be as simple and easy to plate as possible. For this reason, mild steel St 37 (AISI 1045) was used. Specimens were cut in a size of 25 mm × 50 mm × 1 mm. After cutting, substrate specimens were ground up to 1200grade SiC paper to ensure a reproducible surface state. Cleaning of the samples was realized with distilled water followed by acetone. Just before starting deposition, the specimens were subjected to a pickling treatment with 35 vol% hydrochloric acid for 3 min and rinsed with distilled water.

The starting bath composition for electroless NiB was the composition developed by Delaunois et al. [38], presented in Table 1, composed by sodium borohydride (NaBH₄ - 99.9%) as reducing agent, nickel chloride hexahydrate (NiCl₂·6H₂O - 99%) as nickel source, ethylenediamine (NH₂-CH₂-CH₂-NH₂ - 99%) as complexing agent and sodium hydroxide (NaOH) as pH regulator. In Delaunois's baths, lead tungstate is used as a stabilizer. Due to the small amount of stabilizer needed in the plating solution, a moderately concentrated solution containing the stabilizer is added in the bath in small amounts. Traditional lead stabilized formulation use an aqueous NaOH solution to dissolve PbWO₄. In this work, all the solutions use demineralized water as a solvent and contain only the respective stabilizer.

Table 1

Bath composition of sodium borohydride reduced electroless nickel bath [38].

Chemical	Concentration
Nickel chloride	24 g/L
Sodium hydroxide	39 g/L
Ethylenediamine NH ₂ CH ₂ CH ₂ NH ₂	60 ml/L
Sodium borohydride	0.602 g/l
Stabilizer (PbWO ₄)	0.021 g/L

The concentration of all the components used in the baths was kept fixed for this study, except for the stabilizer. The deposition time was kept constant (1 h). After the deposition, the samples were taken out of the electroless nickel bath, washed in distilled water and dried in air. The temperature (95 ± 1 °C) and agitation (300 rpm) were regulated by a hot plate with magnetic stirring.

2.2. Inorganic substitute selection

This work has focused only on inorganic replacer candidates due to the preference of industry for these components in the bath recyclability. Seventeen different inorganic salts were tested. In all the cases, the anionic part was one of the four anions (WO₄, SO₄, Cl, or NO₃) studied before [33], where the work has proved that the anionic part of the salts has little influence in the properties of the coatings. The tested cations were Ti³⁺, V³⁺, Mn²⁺, Fe³⁺, Co²⁺, Cu²⁺, Zn²⁺, Ge⁴⁺, Zr⁴⁺, Nb⁵⁺, Mo⁵⁺, Ag¹⁺, In³⁺, Sn²⁺, W⁶⁺ and Bi³⁺.

2.3. Deposition rate with concentration variation

The deposition rate test was used to determine the effect of the stabilizer on the plating rate, for different concentrations, in order mainly to assess the stabilizing ability of the various cations and the optimal concentration for those that present an effect. 1 L of the plating solution described above with different stabilizer concentrations and mild steel specimens with a total area of 25 cm² was used. The samples were weighed, before and after deposition, on an analytical balance with a precision of 0.1 mg. The deposition rate R (μm/h) was calculated assuming 8.3 g/cm³ as the density of NiB alloy (it corresponds to the density of an alloy with a B content of approximately 6%) [39].

2.4. Coatings characterization

When a cation presented stabilizing ability, the coatings obtained with the concentrations closest to the optimum were observed on the surface and in cross-section by SEM. Electroless nickel-boron coatings observation was carried out with a Hitachi SU8020 scanning electron microscope. The cross-section morphology was examined after polishing with silicon carbide paper and diamond paste up to mirror finish. The composition of coatings after 5, 30 and 60 min of deposition was analyzed by ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometry) after dissolution of samples in aqua regia.

3. Experimental results and discussion

3.1. Inorganic substitute selection

The most effective stabilizers can be divided into four groups: compounds of group IV elements, oxygen-containing anions, heavy metal cations and unsaturated organic acids, such as maleic and citric acid. Besides, some classes of surfactants, dispersants and emulsifying agents can be used.

Starting research with all of these candidates would not be possible. This work has thus focused only on inorganic replacer candidates due to the preference of industry for these components in the bath recyclability. Among inorganic candidates, selenium and tellurium compounds are expensive due to the low concentration of these metals in the earth's crust and to their use in photovoltaic cells market. Also, both can form toxic compounds [40]. The two remaining options in terms of potential stabilizers are thus oxygen-containing anions and heavy metal cations.

The choice of heavy metal cations was made with the future properties of the coatings in mind: the chance to have a coating that presents similar properties increases when stabilizers are from the same family. To better understand the mechanisms of stabilization by metal cations, several cations were studied, some as possible stabilizers but others as a

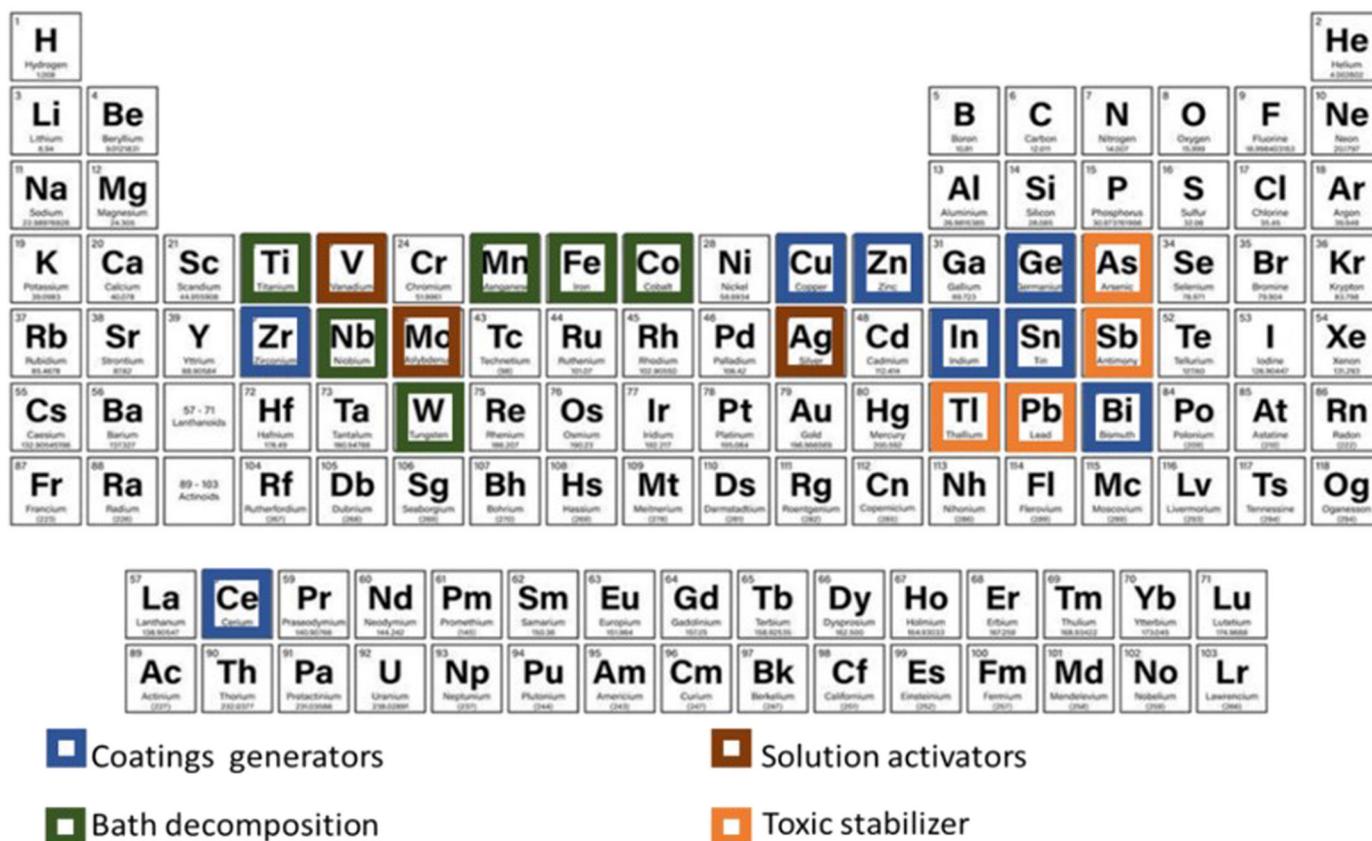


Fig. 1. Elements tested as NiB stabilizer: in blue elements that enable a coating formation (coatings generators); in green elements that cause bath decomposition in less than 5 min; in brown, the solution activators, elements that instantly decompose the bath; and in orange the toxic stabilizer elements recognized as a stabilizer in the literature but toxic. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

comparison point. Fig. 1 presents the cations that were tested, as well as the four toxic stabilizers found in the literature.

Four distinct groups can be observed in Fig. 1: group one, represented in blue, is the group where the solution is not decomposed until the end of deposition time (1 h) and, for which weight gain of the sample is observed, which suggests that a coating is formed. The second group, shown in green, is the group that causes bath decomposition: the addition of those metallic cations in the bath generates a completely dark solution in less than 5 min. The third group, represented in brown, is formed by solution activators for which the solution decomposes in less than 1 min. And the last one, shown in orange, is formed by stabilizers already studied in the literature. In our case, due to the toxicity of those compounds, only lead was tested for comparison.

3.2. Stability characterization and discussion of the characteristics of stabilizing elements

As described before, group one (blue) can keep the solution from breaking down during the one-hour plating process. Besides, the samples immersed in the solution presented a weight gain. However, this information is not sufficient to prove the stabilizing properties of these elements. Different tests can be used to determine the stabilizing properties of a compound. The method chosen here is the evolution of the deposition rate with stabilizer concentration. This method was selected because it is the test that generates the most significant variations for heavy metal stabilizers. Stabilizers such as Pb and Tl have a minimal effect on the steady-state potential of electroless nickel bath, even at stabilizer concentrations that significantly reduce the plating rate. For example, Malory et al. [41] noticed that when the lead concentration in an electroless nickel bath increased from 1 ppm to 10 ppm, the mixed potential of the working electrode changed from

–625 mV to –609 mV respectively. On the other hand, for the same changes in Pb concentrations, the plating rate decreased from 15 $\mu\text{m}/\text{h}$ to less than 2 $\mu\text{m}/\text{h}$. The plating rate test is thus susceptible.

The deposition rate study was performed for the eight elements of group one, as well as for lead to help interpretation. Deposition rate versus concentration of metallic salts is presented in Fig. 2. Metallic salts concentration in the solution varied from 10^{-9} to 10^{-1} mol/L. All the presented results are the average of two tests.

This test was based on the correlation between the stabilizer concentration and the plating rate. In the case of elements with significant stabilization properties, the deposition should completely stop (plating rate equals to zero) for high stabilizer concentrations. Also, a peak, with superior thickness can be expected. On the other hand, elements that never stop the deposition are considered as not having any stabilizing properties.

Cerium, zinc and zirconium do not present complete bath inhibition (plating rate did not go down to zero). Also, variations in the concentration of these elements did not show any influence on the plating rate. Consequently, we can conclude that Ce, Zn and Zr are neutral cations for electroless nickel boron plating.

Indium, germanium, copper, bismuth and tin caused the complete inhibition of electroless NiB bath at high concentrations. Besides, all of these elements presented a plating rate peak, a concentration where the optimum between stabilization and deposition is reached.

The deposition rates stayed in the 0–7.72 $\mu\text{m}/\text{h}$ range in the case of InCl_3 . The plating rate increases in the range from 10^{-9} to 10^{-4} mol/L, with the plating rate peak at 10^{-4} mol/L. For concentrations higher than 10^{-4} mol/L, the plating rate started to decrease, and the complete inhibition was reached at 10^{-2} mol/L. This shows that In(III) has stabilizer properties for the present NiB electroless plating bath.

In the case of GeCl_4 , the deposition rates were in the range of

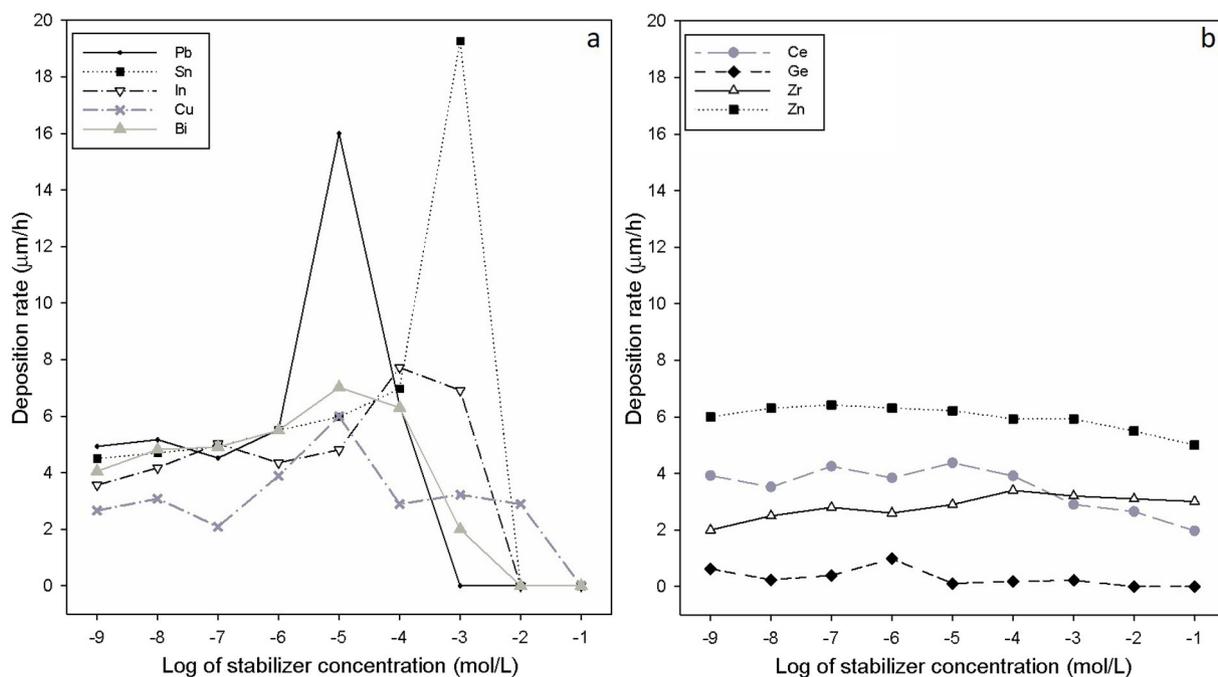


Fig. 2. Effect cations concentration on deposition rate of electroless NiB: (a) concentration influences the deposition rate Pb, In, Cu, Bi, and Sn; (b) concentration does not influence the deposition rate Ce, Ge, Zr and Zn.

0–0.98 $\mu\text{m/h}$. The plating rate increases in the range from 10^{-9} to 10^{-6} mol/L, with the plating rate peak at 10^{-6} mol/L. Concentrations higher than 10^{-6} mol/L lead to plating rate decrease, and the complete inhibition is reached at 10^{-2} mol/L. This shows that Ge(IV) has stabilizer properties for the present NiB electroless plating bath. However, the deposit thickness after 1 h of deposition is too low for practical applications.

CuCl_2 presented deposition rates in the range of 0–5.99 $\mu\text{m/h}$. The increase of plating rate is observed in the interval between 10^{-9} to 10^{-5} mol/L, with a deposition peak at 10^{-5} mol/L. The decrease is seen after the maximum, and the complete inhibition is reached for 10^{-1} mol/L. This shows that Cu(II) has stabilizer properties for the present NiB electroless plating bath. However, the complete inhibition is obtained at very high concentration. Chen et al. [37] studied the role of Cu^{2+} as an additive in an electroless nickel-phosphorus. They showed that Cu cation is principally co-deposited and are thus not real stabilizing agents, although stable bath can be obtained in specific concentrations.

The deposition rates were in the range of 0–7.16 $\mu\text{m/h}$ for $\text{Bi}_2(\text{WO}_4)_3$. The plating rate increases in the range from 10^{-9} to 10^{-5} mol/L, with a peak at 10^{-5} mol/L. For concentrations of $\text{Bi}_2(\text{WO}_4)_3$ higher than 10^{-5} mol/L, the plating rate starts to decrease, and the plating rate of 0 $\mu\text{m/h}$ is reached at 10^{-2} mol/L. This shows that Bi(III) has stabilizer properties for the present NiB electroless plating bath.

Tin cations presented the more significant range in the deposition rate of 0–19.17 $\mu\text{m/h}$ for SnCl_2 . The plating rate increases in the range from 10^{-9} to 10^{-3} mol/L, with a peak at 10^{-3} mol/L. For concentrations higher than 10^{-3} mol/L, the plating rate drops directly to 0 $\mu\text{m/h}$ at 10^{-2} mol/L. This shows that Sn(II) also presents stabilizer properties for the present NiB electroless plating bath.

The traditional lead stabilizer presented depositions rate in the range of 0–16.17 $\mu\text{m/h}$ for PbWO_4 . Almost no variation is observed in the plating rate is found from 10^{-9} to 10^{-6} mol/L, a fast increase is observed from 10^{-6} to 10^{-5} mol/L with the peak at 10^{-5} mol/L. For concentrations higher than 10^{-5} mol/L, the plating rate drops directly to 6 $\mu\text{m/h}$ at 10^{-4} mol/L and 0 $\mu\text{m/h}$ for concentrations higher or equal to 10^{-3} mol/L. This proves once more the Pb(II) stabilization properties

for the present NiB electroless plating bath.

The enhancement of nickel deposition at low stabilizer concentration is most probably linked to the decrease of the amount of nickel reduced spontaneously in the solution and not on the substrate. The reduction in the deposition rate with high elements concentrations can be attributed to a decrease in the number of catalytic sites on the surface, limiting the catalytic reaction and consequently, the deposition.

3.3. Discussion of stabilizing effect of heavy metal cations

The discussion in the literature about stabilizers is rather weak, with only a few works. Also, those are usually focused on the ability of additives to stabilize the bath or to accelerate the rate of deposition. A theory that explains why some elements can stabilize the bath has not been previously published, to the extent of our knowledge.

This work, after the characterization of 19 metal cations and the analysis of others presented in the literature, proposes that the stabilizing properties of an element are once again a mix between thermodynamic and catalytic activity, that principally depends on three factors:

- The redox potential of the metal cation/metal pair,
- The catalytic activity of the metal,
- The atomic size of the metal.

The redox potential of stabilizers was vastly discussed in this work, as the first reaction in an electroless bath stabilized by heavy metal cations is a displacement reaction. Heavy metal ions such as Pb^{2+} stabilize the plating bath by depositing on the active metal surface through displacement reaction. The reaction initiation is an immense challenge for the solution stabilization, as it is at that time that the solution has the highest concentration of reducing agent. In the present study, the substrate was always mild steel, so metal cations that have a redox potential lower to that of iron ($\text{Fe}^{2+} + 2e \rightarrow \text{Fe} = -0.41$) will not be able to present a displacement reaction with the substrate. All the effective stabilizers characterized in this work have a redox potential superior to iron, and the values are shown in Table 2.

This fact shows that the initiation process will be different for

Table 2
Redox potential for stabilizers proposed in this work.

Reaction	E° (V)
$Fe^{2+} + 2e \rightarrow Fe$	-0.410
$Tl^+ + e \rightarrow Tl$	-0.340
$In^{3+} + 3e \rightarrow In$	-0.340
$Ni^{2+} + 2e \rightarrow Ni$	-0.257
$Sn^{2+} + 2e \rightarrow Sn$	-0.140
$Pb^{2+} + 2e \rightarrow Pb$	-0.126
$Bi^{3+} + 3e \rightarrow Bi$	0.293
$Cu^{2+} + 2e \rightarrow Cu$	0.337

different substrates, and the optimal stabilizer concentration can be affected by this. However, stabilizing elements can stabilize the bath without the initial displacement reaction due to the catalytic properties.

The stabilization mechanism for heavy metal cations is generally explained by the fact that the presence of a stabilizer adsorbed on the substrate will block part of the catalytic sites and decrease the number of free positions for the reaction to take place. As shown by Malory et al. [41], modifications in the stabilizing agent generate only small changes in the mixed potential. However, they made significant variations in the deposition rate. The changes are caused by the decrease of the available catalytic sites. A catalyst substance, when added to a chemical reaction, does not affect the thermodynamics of that reaction but increases the rate of reaction.

However, not all the elements that can be adsorbed on the substrate will block the catalytic sites. Elements should have a low (to null) catalytic activity. Transition metals, for example, are good metal catalysts because they readily give and take electrons from other molecules. On the other hand, post-transition metal and metalloids are weak catalytic elements and can block the catalytic sites. Not coincidentally, all the elements with proved stabilizing characteristics have weak catalytic activity.

Sodium borohydride oxidation occurs due to the catalytic hydrogen adsorption on the surface. Different metals have different metal-hydrogen binding energy [42,43]. In the case of stabilizers, the metal-hydrogen bonding energy is always small, and the oxidation of borohydride does not take place. The Sabatier principle organizes the metal-hydrogen bonding energy in volcano plots. Balandin volcano plots (Fig. 3 [44]) for metal-hydrogen bonding energy show the logarithm of current exchange densities for cathodic hydrogen evolution vs the bonding adsorption strength of intermediate metal-hydrogen bonds formed during the reaction itself. What is interesting to note from this data is that inside of the blue circle, all the elements present really low bonding adsorption strength with hydrogen (coupled with low hydrogen evolution rates on those metal surfaces). Not coincidentally, this group is formed by the elements described as a stabilizer for electroless NiB, except for Zn. Zinc is a metal from d group. However, it is not a transition metal, as the d-orbital is filled in the case of zinc. This explains the poor catalytic behaviour of zinc (which has shown a neutral effect in the stabilization study) is the low redox potential of Zn ($Zn^{2+} + 2e \rightarrow Zn = -0.763$ V) that does not allow the displacement reaction with iron.

Other interesting information obtained from this graph is the second group, inside the red circle: all the elements are known as autocatalytic and can be synthesized in coating form by electroless deposition.

The third influent factor is the atomic size of the metal. The displacement reaction will generate the deposition of metals on the substrate surface. The deposition of poor catalytic metals will block part of the catalytic surface. Consequently, bigger elements will allow blocking a bigger part of the surface and will influence the rate of deposition and stabilization.

Also, these properties of a stabilizer are influenced by several parameters such as concentration, pH, temperature, solution fluid dynamics, the concentration of reducing agent, presence of foreign bodies,

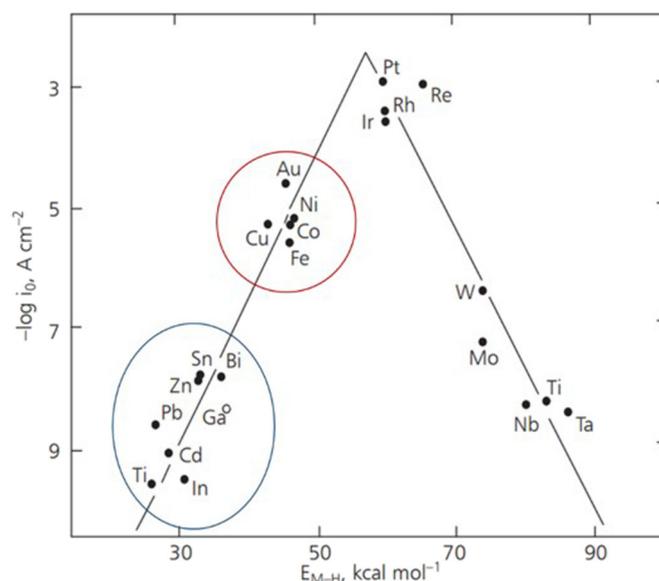


Fig. 3. Volcano-type relationship obtained by plotting the logarithm of exchange current densities for cathodic hydrogen evolution vs the bonding adsorption strength of the intermediate metal-hydrogen bond. (Adapted from [44]).

etc. As demonstrated before, the concentration of the additives is considered the most critical parameter since these additives can act as accelerators or inhibitors of the deposition depending on their concentration in the plating bath.

3.4. Coatings observations

The previous part proved the stabilizing properties of indium, germanium, copper, bismuth and tin. However, these results did not mean that baths stabilized by these elements could form uniform, adherent and wear-resistant coatings. First microscopic observation of the generated coatings is presented in this section. Fig. 4 shows the cross-section for In, Cu, Bi and Sn stabilizers. The first one is indium. Indium presents an irregular cross-section with approximately 2.5 μm thickness. The presence of a columnar growth can be observed in the first 0.5 μm . The observed thickness is much lower than expected based in the weigh increase presented on Fig. 2 (7.72 μm), this can be understood after observation of Fig. 5, where the surface morphology of the sample is shown.

The polished sample used for cross-section didn't reveal that particles are distributed in the surface. As can be seen on the surface morphology image, the coatings formed in a bath stabilized by indium are uniform at the beginning of the deposition. After a few minutes of plating, semi-spherical islands start to develop on the surface. This is probably due to an atypical growth mode. At first view, this morphology suggests colloidal nickel particles that are formed in the bath and subsequently adsorbed on the coating surface. However, this hypothesis is not a good explanation because no particles were found at the bottom of the plating bath. The reason for this kind of growth mode can be related to the redox potential of In. As explained before, heavy metal ions such as Pb^{2+} stabilize the plating bath by depositing on the active metal surface through displacement reaction between the stabilizer and the substrate (iron) and thus inhibiting the reduction of nickel. Besides, adsorbed stabilizers can limit the lateral growth of electroless Ni, resulting in a columnar deposit in the case of lead. When compared with Pb^{2+} , In^{3+} has a lower reduction potential (-0.126 V and -0.338 V respectively) [45]. The displacement reaction is thus less intense which leads to a less severe limitation of the lateral growth [46]. However, this theory does not entirely explain the morphology

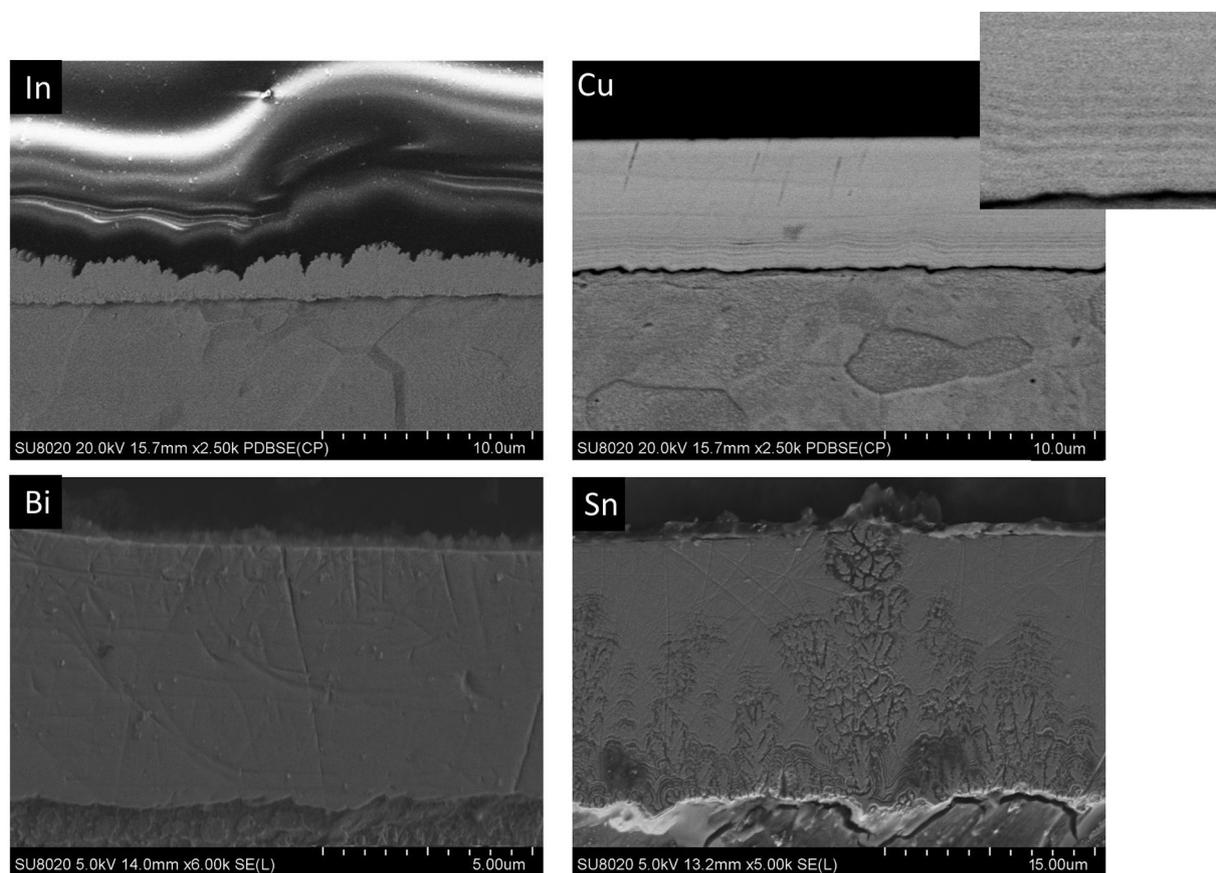


Fig. 4. New stabilizers, In, Cu, Bi and Sn, coatings cross-section morphology observation.

because thallium Tl has a redox potential similar to Indium In (-0.336 V) and allows the generation of entirely columnar morphologies [12] (with thicker columns than for coatings from lead-stabilized baths). However, an essential difference between Tl and In is the size of the atoms. As Tl is a larger element, the surface blocked by a Tl atom is bigger than the surface blocked by an In atom.

The second element to be analyzed is Cu; coating cross-section is presented in Fig. 4. Due to the known possible codeposition phenomena [37], the image was obtained by backscattered electrons (BSE) (heavy elements, high atomic number, produce more backscattered electrons than light elements, low atomic number, and thus appear brighter in the image). Nickel and copper are neighbours and have a close atomic number, so it is not easy to differentiate them in BSE images. However, EDX (Energy-dispersive X-ray spectroscopy) analysis showed that samples presented distinct layers: the first two layers are composed of about 20 wt% Cu and 80 wt% Ni, respectively, (concentrations are only indicative as boron is not detected by EDX). Due to the high redox potential of cupric ions (0.337 V) [45], the initiation process, in this case, should start with an intense displacement reaction between Cu and iron generating a dense copper layer with the presence of some reduced Ni atoms. Afterwards, due to the small size of Cu (when compared with the other heavy metal stabilizers), the deposited Ni can grow laterally and form a layer. After this first step, what happens is a co-deposition of Cu and Ni, as shown in Fig. 4, Cu can be reduced by borohydride. Due to the small amount of Cu in the bath, the element is present only in the first 1.5 μm . After that, only nickel is present, due to the scarcity of Cu in the bath. Cu can thus not be considered a stabilizer, but it is an element that can be co-deposited while, due to its high redox potential, stabilizing the plating initiation. The surface of Cu stabilized samples is presented in Fig. 5; some pits are present in the coating, probably due to the low stability of the bath after 1 h of plating.

The third image is from a coating synthesized with a bismuth-

stabilized bath. In this case, we observe a homogeneous and dense coating, without features or columns (Fig. 4). The surface morphology (Fig. 5) shows a uniform, and smooth coating, however, the usual cauliflower feature is not observed. Bismuth appears to be an efficient stabilizer that can generate coatings of good quality. Also, porosity is not detected, nor delamination.

Lastly, the coating generated with tin as a stabilizer is presented. Similarly to Bi as a stabilizer, a conventional coating is formed. This time, a tree-like structure is observed. In addition, the coating looks free from porosity and does not present delamination. The surface morphology (Fig. 5) shows the top of the structure with a uniform rough texture. As presented in Fig. 2, the Sn stabilization curve shows a sharp peak, and a further study in this range of concentration must be necessary. A more detailed discussion about the influence of stabilizers on the morphology is presented below.

3.4.1. Stabilizers distribution in the coatings

In order to determine how stabilizers were distributed in the coating, baths with three different time of deposition were realized, 5, 30 and 60 min. After that samples were dissolved in aqua-regia and analyzed by ICP. Obtained results were used to calculate the stabilizer concentration in the first 5 min, from 5 to 30 and from 30 to 60. Results are presented in Fig. 6. As expected, the level of stabilizers decreases with deposition time, due to the small amounts added at the beginning of the bath. This also explains why Bi samples have no cauliflower morphology after 1 h plating, and why Cu samples have a non-uniform surface after the same time. Sn and In samples have a more uniform distribution of stabilizer in the coating. The uniform distribution generates a uniform surface for Sn samples after 1 h, however in the case of In the Morphology feature still not explained.

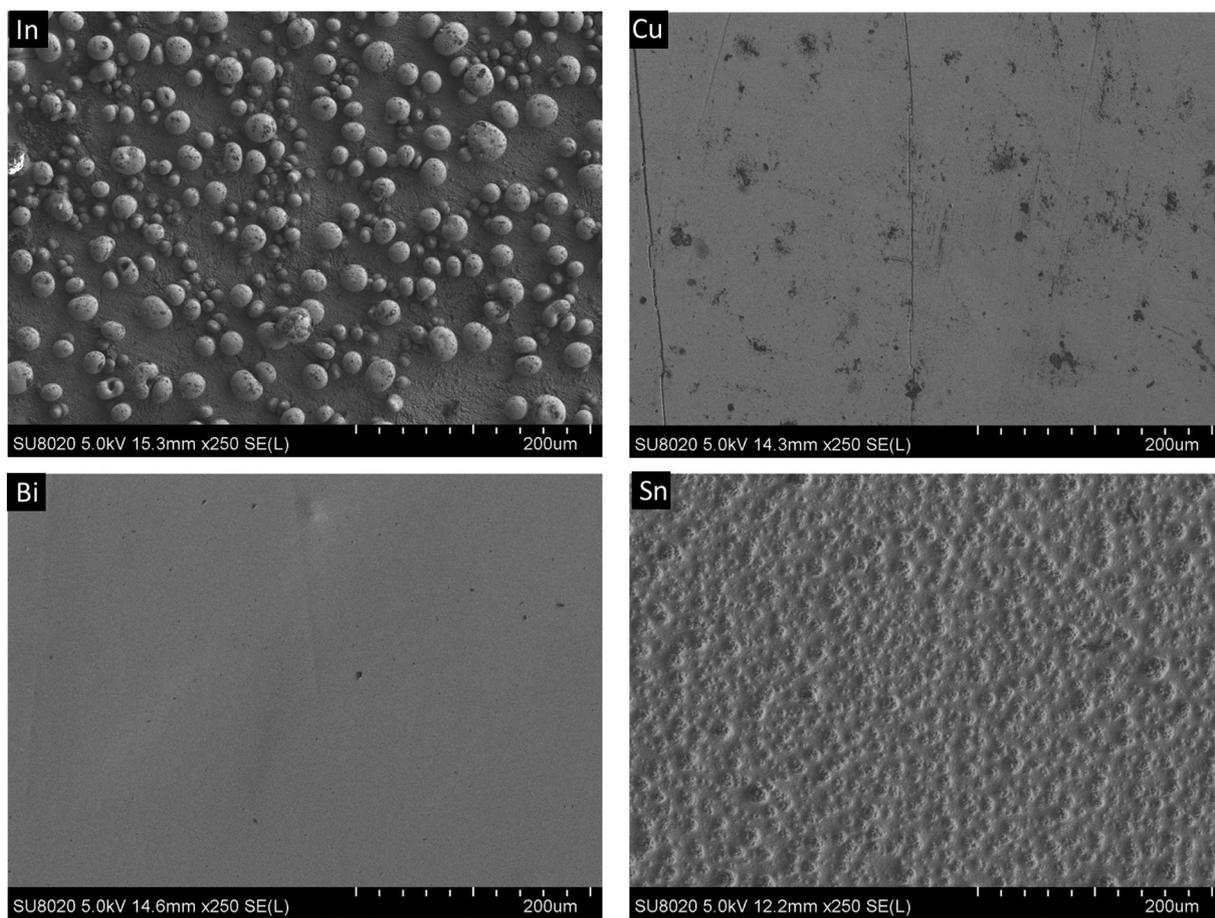


Fig. 5. New stabilizers, In, Cu, Bi and Sn, coatings surface morphology observation.

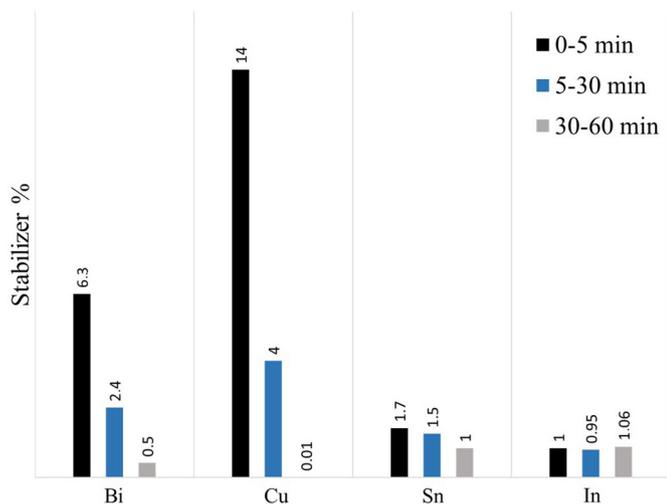


Fig. 6. New stabilizers, In, Cu, Bi and Sn, perceptual in the different phases of deposition.

3.5. Influence of heavy metal on the coating morphology

The choice of a heavy metal stabilizing agent and its concentration has a significant influence on the morphology of the coating synthesized with the plating bath. The simplest form of chemical plating is the so-called metal displacement reaction or galvanic displacement. This type of reaction is the first step towards the autocatalytic deposition process.

As illustrated in the first part of Fig. 7, just after the stabilizer

addition in the plating bath, a galvanic displacement takes place between the substrate (S) and the stabilizer (M). Depending on its position in the electrochemical series, a substrate higher up in the series may be covered (plated) with a stabilizer lower down in the series. The rate of this reaction will depend on two factors: the first one is the stabilizer concentration in relation to the total substrate surface, and the second is the redox potential difference ΔE between substrate and stabilizer. The displacement reaction between iron and tin will have a lower rate when compared with the one between iron and bismuth (an element with a higher redox potential).

As soon as the displacement reaction begins, the surface of the substrate, iron in our case, becomes a mosaic of catalytic active (iron) and non-catalytic (stabilizer-covered) areas. Before the surface is entirely covered by the stabilizer, the autocatalytic reduction of nickel takes place. The displacement reaction between Lead and Iron was analyzed previously for NiB baths [47]. As shown in the second part of Fig. 7, the presence of stabilizer on the catalytic substrate surface will block certain areas and preclude a planar deposition. The presence of a high concentration of stabilizer leads to the formation of columns due to the blocking of the lateral growth of nickel. The columnar growth is thus completely correlated with the stabilizer concentration at the surface of the substrate, as an increase in concentration is responsible for thinner columns in comparison to samples where the stabilizer concentration at the surface is lower (Fig. 7).

As shown in the last part of Fig. 5, when compared with Tl^{1+} and Pb^{2+} , Bi^{3+} has a much higher redox potential (-0.126 , -0.336 and 0.293 V, respectively). Consequently, a more intense displacement reaction observed in the presence of Bi^{3+} . As a consequence, the size of the regular column generated by these stabilizers also respects the reduction potential progression: NiB-Tl ($0.5-3.5 \mu m$), NiB-Pb

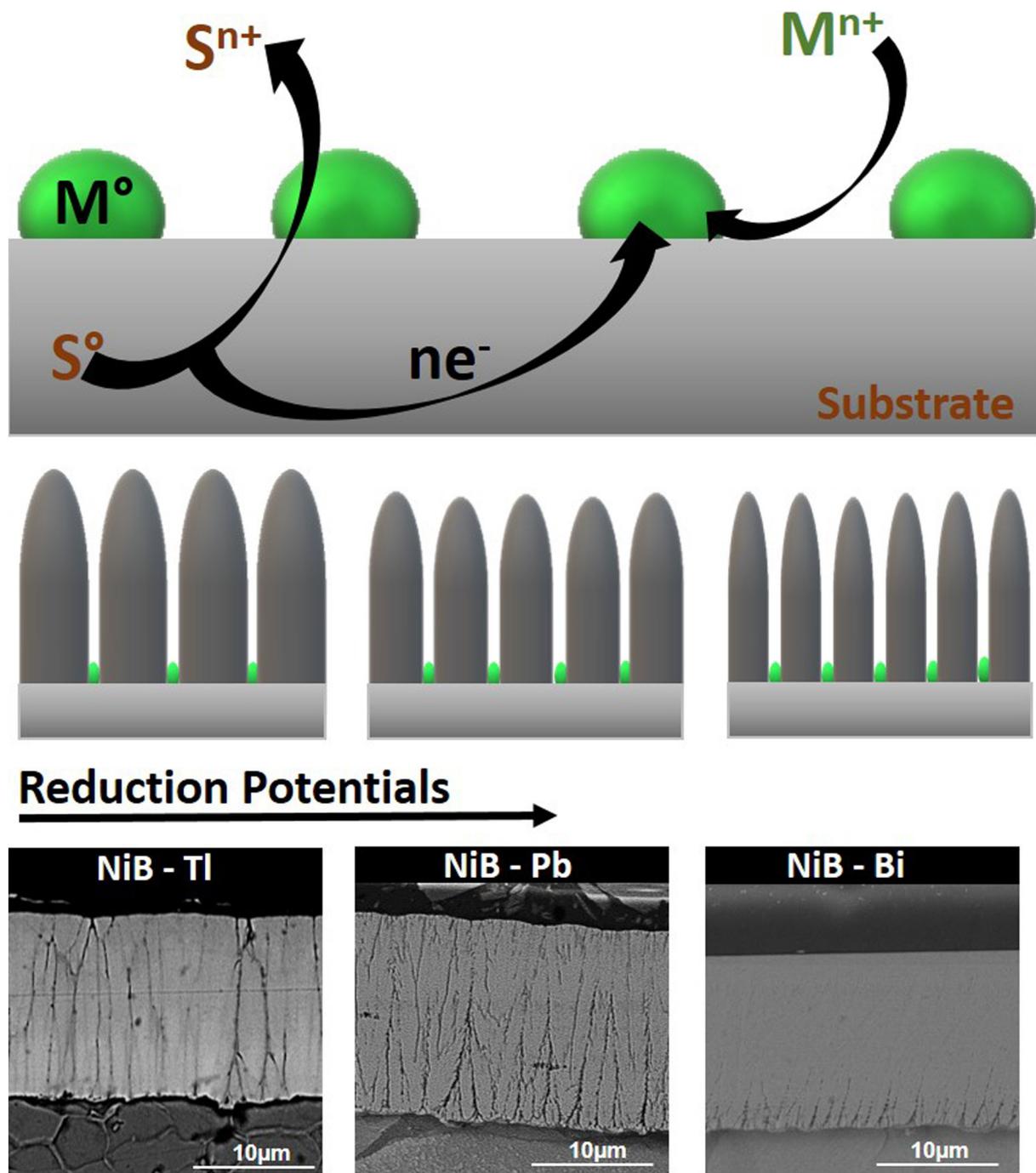


Fig. 7. Displacement reactions influence on the columnar structure. S represents the substrate and M the stabilizer.

(0.1–2.0 µm) and NiB-Bi (0.1–1.5 µm). The observation of this relation is quite essential because it allows to control and adapt the size and density of columns for different applications. However, this is not the only factor that influences the morphology.

The size of the stabilizer atoms can also influence the morphology. As shown in Fig. 8, just after the galvanic displacement, the first layer of nickel is autocatalytically deposited between the stabilizer atoms. In sequence, the second layer of nickel is instantly plated. In the case where stabilizer atoms are much larger than the metal to be deposited, the lateral growth of the second layer is also blocked due to the presence of the stabilizer, giving rise to the formation of a columnar structure. However, if the stabilizer size is close to the size of the metal to be deposited, the second layer is just partially blocked, and a partial lateral growth is possible. Therefore, by controlling the ratio between

the atomic sizes of the deposited metal and the stabilizer, different structures can be obtained.

In the case of two elements with the same redox potential but different sizes, the resulting morphology can be completely different. For instance, Pb and Sn have close redox potential (−0.126 V and −0.140). However, Pb is larger and generates an entirely columnar structure deposition. On the other hand, the smaller size of Sn creates a tree-like structure, as can be seen in Fig. 4.

4. Conclusion

Recently there has been a significant shift in electroless nickel technology, due primarily to European environmental legislation. Also, every year, new restrictions on hazardous substances are created. In

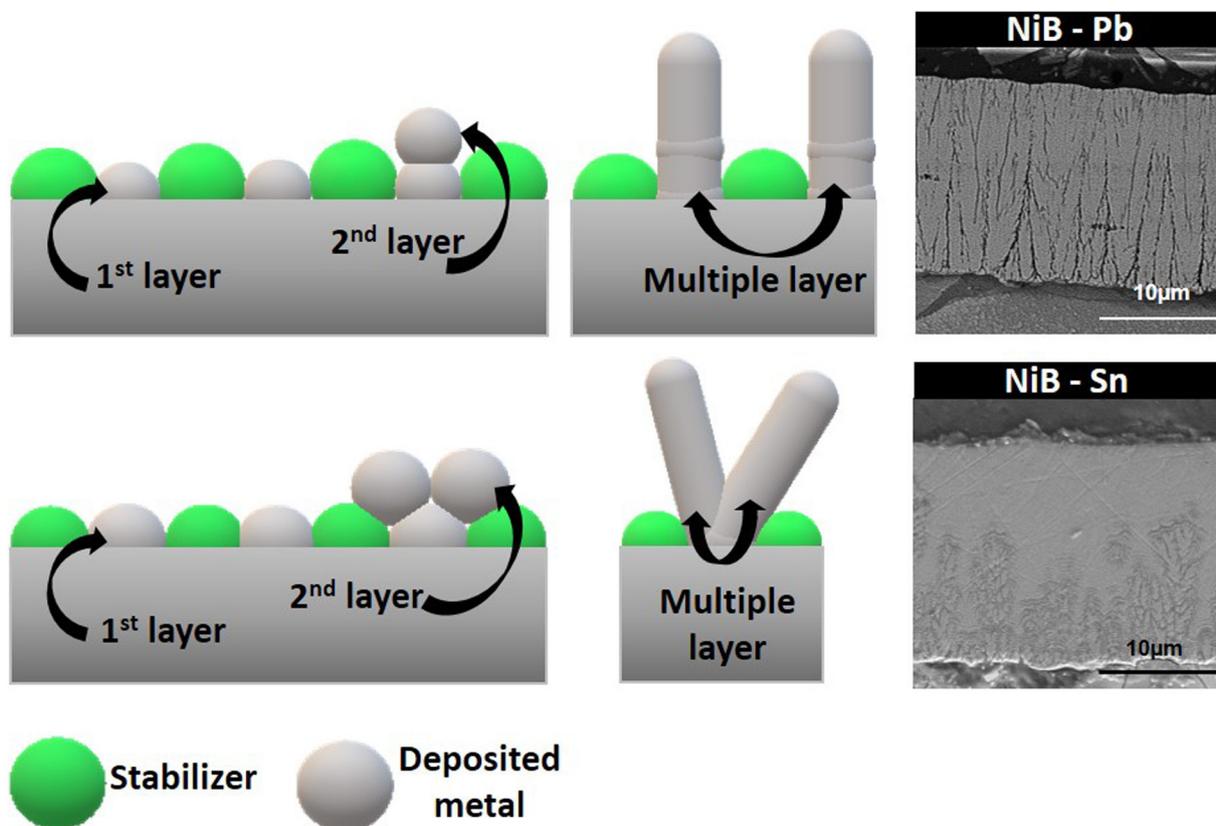


Fig. 8. Influence of stabilizer atomic size on the columnar structure.

consequence, exploration of electroless nickel boron inorganic stabilizers that are environmental-friendly and also as effective as the traditionally used lead(II) salt was needed. The paper has also focused on the understanding of effective stabilizer properties and stabilizing mechanisms.

The investigation was based on the fact that stabilizers can stop the deposition in high concentration, once stabilizers also act as inhibitors depending on the concentrations—four distinct groups were observed:

- Cu^{2+} , Zn^{2+} , Ge^{4+} , Ce^{3+} , Zr^{4+} , In^{3+} , Sn^{2+} and Bi^{3+} , can keep the solution stable for at least 1 h.
- Ti^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Nb^{5+} and W^{6+} causes bath decomposition in less than 5 min.
- Mo^{5+} , Ag^{1+} and V^{3+} activate the bath, and the solution decomposes in less than 1 min.
- Pb^{2+} and Tl^{1+} , are toxic stabilizers already studied in the literature.

Three significant characteristics were defined as a factor that enables a chemical to stabilize an electroless bath.

- The redox potential of the metal cation/metal pair,
- The catalytic activity of the metal,
- The atomic size of the metal.

The effort aiming at exploring green electroless nickel boron stabilizer has resulted in the finding of two new promising types of stabilized baths, which are Bi^{3+} stabilized baths and Sn^{2+} stabilized baths. These two cations proved to be able to regulate the oxidation rate of sodium borohydride ion. The different stabilizers did not significantly influence the operation of the electroless process. However, the characteristics of NiB deposits were modified.

Furthermore, the study of different stabilizers and stabilization methods made it possible to correlate the stabilizer concentration and

size with the growth modes of the coatings. A theory about the elements that can stabilize a bath and the elements that cause destabilization was created based on three factors: the redox potential, the catalytic activity and the size of the element. This work opens new opportunities of specific properties design for electroless coatings, based in the stabilizer elements.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

CRediT authorship contribution statement

L.B. and V.V. conceived of the presented idea. F.D. encouraged started this work in the group. All authors discussed the results and contributed to the final manuscript. L.B. carried out the experiment and wrote the manuscript with support from V.V and F.D. All authors provided critical feedback and helped shape the research, analysis and manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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