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Elaboration by electroless and characterization of Ni-Sn-P alloy

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ABSTRACT

The aim of this study is to develop a Ni-Sn-P coating by electroless. The plating bath was formulated with tin chloride and nickel sulfate as a source of metal ions, sodium hypophosphite as a reducing agent and tri-sodium citrate as complexing. This electrolyte is stable over time and the resulting coating is adherent and uniform. The tin content is about 14.5%. The deposition rate calculated by gravimetry is 2µm/h substantially lower than that obtained in the chemical nickel plating baths. This result was confirmed by cyclic voltammetry and electrochemical impedance measurements. The addition of the stannous ions in the bath results in some change in the shape of voltammograms compared to those obtained in the electroless nickel bath. The peak corresponding to the oxidation of the coating crystalline phase has disappeared suggesting that the deposit Ni-Sn-P would be substantially amorphous in contrast to deposit Ni-P which is biphasic.

Keywords: Coating; electroless; alloy Ni-Sn-P; voltametry; electrochemical impedance.

INTRODUCTION

The Ni-P coatings alloys are widely used in industry due to their excellent corrosion resistance and electrical and magnetic properties [1-2]. The addition of tin in the Ni-P deposit could improve the properties of these alloys. Indeed, many researchers have shown that the addition of Cu, Sn, Zn, Fe, W, Re and Mo to the nickel alloys brought improvements in their properties [3-10].

In this study, we were interested in the development of Ni-Sn-P coating by electroless. We chose this technique for its ease of implementation and its application in industry. By overcoming the current, it is possible to coat uniformly a substrate regardless of its geometry.

Chemical tinning baths often use formaldehyde or its derivatives as a reducing agent due to the high deposition rate generated and excellent mechanical properties of the deposits obtained [11-13]. However, the use of formaldehyde is only effective from alkaline pH greater than 11. This high pH is not compatible with some dielectric or photosensitive materials. Also, the formaldehyde is a carcinogenic volatile liquid. Currently, many researchers do not choose formaldehyde as reducing agent but sodium hypophosphite for its relative safety and low cost [14-18].

MATERIALS AND METHODS

Electrolysis cell

The electrolysis cell is a borrosilcate glass (Pyrex®) cylinder closed by cap with five apertures (Figure II.1). Three of them were used for the electrodes. The other two allow deaeration of the solution by bubbling nitrogen and temperature control. We used glassy carbon with surface area of 0.07cm^2 as working electrode, Pt plate as the counter while a saturated calomel electrode (SCE) as the reference electrode to which potentials will be referred in the following. For the realization of thick deposits, iron substrates with area of 0.2 cm^2 were used.

Electrochemical measurements

The electrochemical measurements were carried out using Potentiostat/Galvanostat/Voltalab PGZ 100 monitored by a personal computer. The voltammetric measurements were performed in the potential range between -1,2V to + 0.3V with a scan rate of 10 mV/s and impedance studies in a frequency range of 100 KHz to 10 mHz with the amplitude of ± 10 mV.

Characterization

The morphology of the deposits was examined by scanning electron microscopy (SEM) type Quanta 200, the composition was estimated by EDX analysis.

RESULTS AND DISCUSSION

Formulation baths

The aim of our study is to develop an alloy coating Ni-Sn-P by electroless. Our approach was to add stannous ions in a chemical nickel bath. To develop the alloy coating Ni-P, we used a plating electrolyte Ni-P already exploited in our laboratory [19] (Table 1, electrolyte 1). It will be considered as reference electrolyte.

Table 1: Electrolytes composition

	$NiSO_4$, $6H_2O$ Mole/L	NaH_2PO_2, H_2O Mole/L	$Na_3C_6H_5O_7$, $2H_2O$ Mole/L	$SnCl_2$ Mole/L
Electrolyte 1	0.1	0,28	0,2	-
Electrolyte 2	0.1	0,28	0,2	10^{-4}
Electrolyte 3	0.1	0,28	0,2	5.10^{-4}

The pH is adjusted around 5 by acetic acid and the temperature is set at 85 ± 2 ° C. The deposition rate on iron substrate, from this reference bath, is the order 5 µm/h. The coating composition by weight is 13% phosphorous and 87% nickel [20].

We added $SnCl_2$ in low concentration (Table 1, Electrolyte 2) to elaborate Ni-Sn-P coating. The pH is always adjusted to 5 by acetic acid and the temperature is set at 85 ± 2 ° C.

We observe a slight decrease in the deposition rate after adding stannous ions in the bath. It reaches 4 µm/h. Moreover, we note the absence of tin in the elaborated coating (Fig 1), the composition by weight of the coating is given in Table 2.

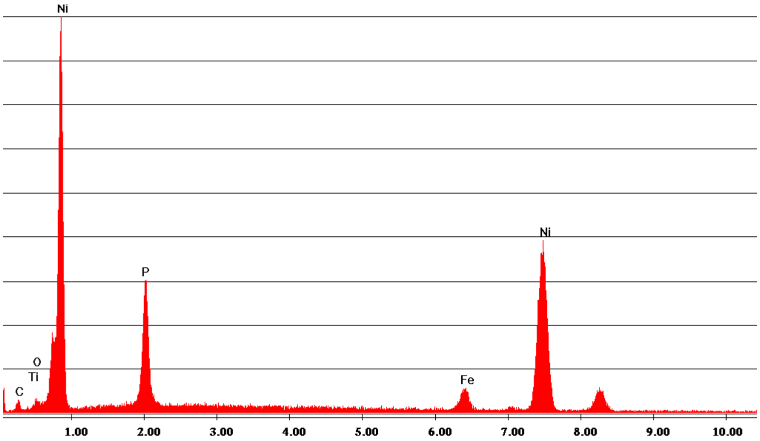

Figure 1: EDX analysis of the coating carried with the electrolyte 1

Table 2: Weight Composition of the coating elaborated from the electrolyte 2

Elements	Content (%)
C	7,43
O	1,86
P	12 ,67
Fe	4,91
Ni	73 ,13

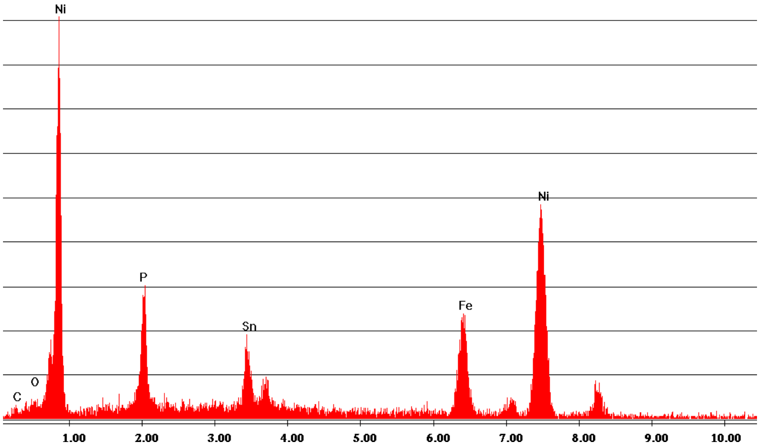

Figure 2: EDX analysis of the coating carried with the electrolyte 3

Thus, we gradually changed the stannous ion concentration to incorporate tin in the alloy. The pH is adjusted to 5 by adding acetic acid and the operating temperature is set at 85 ± 2 ° C. Indeed, the analysis by EDX shows the existence of a tin peak at concentration 5.10^{-4} mole/L (Fig 2), the tin content by weight in the coating is 14.25% (Table 3). Moreover, we find that the deposition rate decreased further, it reaches 2.0 µm/h. It appears that the presence of stannous ions inhibits the kinetics of electroless plating. To confirm this hypothesis, we varied the stannous ion concentration from 1.10^{-4} mole/L to 1.10^{-2} mole/L. In fact, for a concentration 1.10^{-2} mole/L, we get a rate practically zero (Table 4).

Table 3: Weight composition of the coating elaborated from the electrolyte 3

Elements	Content (%)
P	10,05
Sn	14,25
Ni	75,70

Table 4: Deposition rate as a function of tin chloride concentration

Tin Concentration (mole/L)	0	1.10^{-4}	5.10^{-4}	1.10^{-3}	5.10^{-3}	1.10^{-2}
Deposition rate (µm/h)	5	4	2	1,5	0,5	0.05

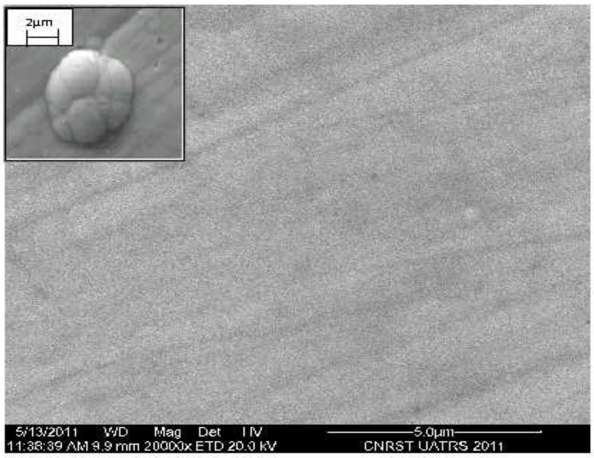

Figure 3: SEM photograph of tin deposit obtained by electrolyte 3

Coatings characterization

SEM examination of the deposit obtained by electrolyte 3 shows uniform and smooth surface without any cracks, nodular form of coatings containing nickel is confirmed (Fig.3). These coatings remain amorphous structure [21].

Cyclic voltammetry study

Figure 4 shows the voltammogram recorded from the reference electrolyte. Scan starts at an anodic potential to avoid any initial deposit. We can distinguish four peaks [22-23]:

- A cathodic peak K representing the reduction reaction of Ni^{2+}, Sn^{2+}, $H_2PO_2^-$ and H_3O^+ ions.

- An anodic peak “A” located at -0.8 mV relating to the oxidation of $H_2PO_2^-$ ions and hydrogen atoms adsorbed to the surface of the electrode
- Two peaks B and C of dissolution of the deposit Ni-P. The first located at -0.43V representing the dissolution of the crystalline phase of alloy and the second at 0.40 V representing the dissolution of the amorphous phase.
- During the second scan, the shape of voltammogram does not evolve by against wave heights decreases slightly due to the change of the surface condition.

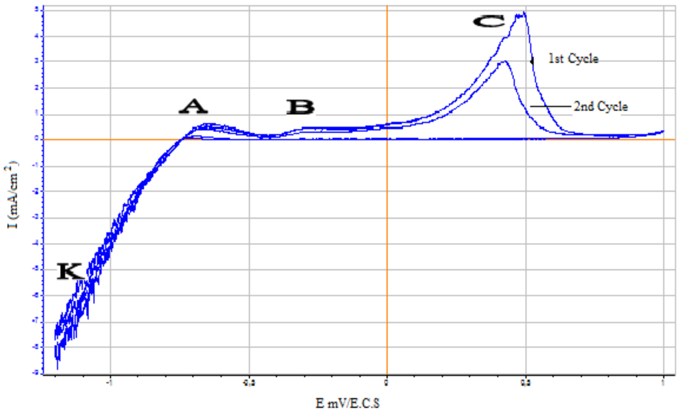

Figure 4: Voltammogram recorded from the reference electrolyte, v = 10 mV.s^{-1}

As shown in figure 5, the voltammogram obtained from the electrolyte 3 containing Sn^{2+} presents some variations relative to that obtained from reference electrolyte (Fig.4). We note a slight shift in the potential and a decrease of the intensity of the peak A. These observations confirm the inhibition of hypophosphite oxidation and therefore the electroless process as previously noted by the decrease of the deposition rate.

The peak B at E = -0.43V corresponding to the dissolution of crystalline phase has almost disappeared but we find the peak at 0.35 V. This would mean that the coating structure is amorphous as previously claimed.

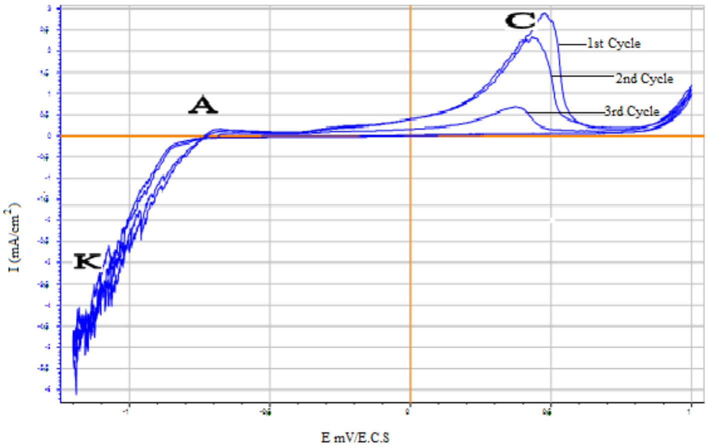

Figure 5: Voltammogram recorded from the electrolyte 3, v = 10 mV.s^{-1}

Impedance behaviour

we carried out electrochemical impedance measurements to better appreciate the kinetics taking place at the metal-solution interface. The impedance diagram performed at plating potential from the reference electrolyte presents two loops (Fig.6) :

- The high frequency loop is related to the relaxation of the double layer capacitance in parallel with the charge transfer resistance, Rt, which is inversely proportional to the plating rate [24]. The charge transfer resistance is around 20 $\Omega.cm^2$ and the capacitance of the double layer 80 $\mu F.cm^{-2}$.
- At low frequencies: a capacitive loop characteristic of electrocrystallization nickel process is observed [19].

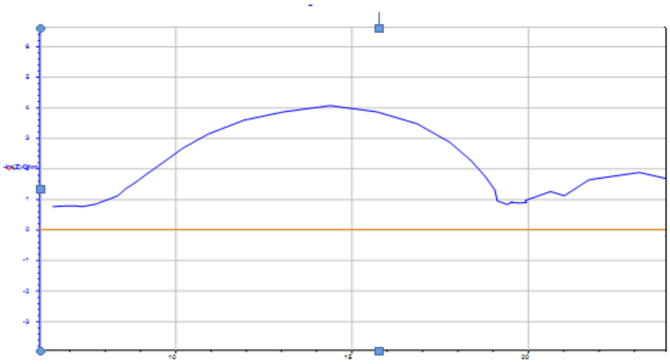

Figure 6: Impedance diagram realized at deposition potential in reference electrolyte

In the impedance diagram achieved at deposition potential from the electrolyte (3) (Fig.7), we note that the size of the first capacitive loop increases and thus the charge transfer resistance increase indicating inhibition process. This effect confirms the action of Sn^{2+} ions on the deposition kinetics.

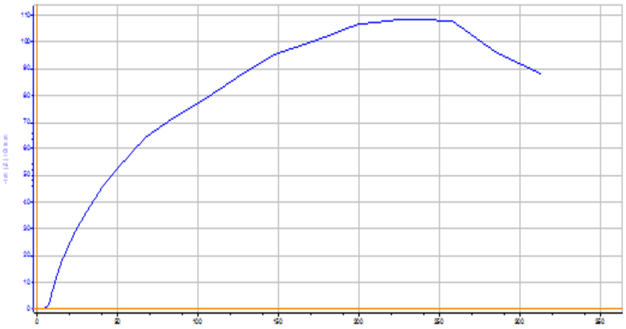

Figure 7: Impedance diagram realized at deposition potential in electrolyte (3)

CONCLUSION

We were able to realize Ni-Sn-P alloy deposit by electroless. The coating is uniform and adherent with a content of 75.70% nickel, 14.25% tin and 10.05% phosphorus. The deposition rate is the order 2 µm/h lower than to elaborate the Ni-P coating.

The studies by cyclic voltammetry and electrochemical impedance confirmed this result. Indeed, the decrease of the hypophosphite oxidation peak and the metal ions reduction peak and the increase of the charge transfer resistance when the bath contains stannous ions prove inhibiting deposition process.

Acknowledgments

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