RESERCHES CONCERNING THE ELABORATION AND CHARACTERIZATION OF Ni BASED COATINGS

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Abstract: *Several studies have been made on the Ni-P alloys, particularly on the amorphous phases, because of their good corrosion resistance in environments containing. Ni-P alloy coatings were prepared by electroplating in a nickel sulfate bath containing phosphorous acid (H_3PO_4). Hardening mechanism of Ni-P alloys were further discussed based on the microstructure evolution during the heat treatment. These composition ranges corresponding to the microstructure with high hardness proposed are believed to be useful for the industrial applications and further study.*

Keywords: Ni-P, electrodeposition, micrographie.

INTRODUCTION

Due to their excellent properties, such as corrosion and wear resistance, low friction and environmental friendliness, both amorphous and nanocrystalline Ni–P alloys have been extensively employed by the industries [1]. Therefore, the corrosion mechanism of Ni–P alloy in acidic and neutral electrolytes has been the active research field for several decades. The development of electrolytic methods (e.g. CECD – Conventional Electrodeposition [1,2]; SCD – Sediment Codeposition [3]) for incorporation of inert particles into a metal matrix has gained in importance over the past years, since uniform particle distribution and satisfied deposition rates can be obtained at relatively low costs. The most extensive studies were performed on nickel matrix composites reinforced with SiC particles [1,2]. Incorporation of hard ceramic phase results in a significant improvement of mechanical properties of the metal such as wear resistance, yield strength and hardness For electrodeposited Ni-P alloys the transition from the crystalline to amorphous structures takes place progressively over a range of several atomic percent of phosphorus and NiP coatings are amorphous when the phosphorus content exceeds 15 at.% [1].Crystallization of the amorphous alloys can be achieved by heat treatment with subsequently decomposition to Ni3P and f.c.c. nickel crystals at temperature above 350 C [2].The corrosion properties of NiP alloys, concerning the nature of its anodic dissolution, ability to passivate and susceptibility to pitting are not yet clearly established. The NiP passivation can be attributed to the non-complete phosphorus oxidation in high potentials and to the fact that, after polarization, the surface of the alloy becomes phosphorus-rich as result of selective dissolution of nickel during polarization.Ni3(PO4)2 is then formed, acting as a barrier against dissolution [3]. Diegle et al. suggest that NiP alloy does not developed a classical passive film and proposed that the passivation process is controlled by the formation and adsorption of hypophosphite anion, which forms a barrier layer between the alloy and the electrolyte. Schenzel et al. concluded that the transformation of the amorphous NiP alloy into a continuous layer of Ni_3P containing isolated areas of nickel crystals renders electroless nickel extremely resistant to corrosion pitting[2]. The required time and temperature depend on the phosphorus content of the coating. However, the local corrosion resistance is limited by a high chloride concentration [2], and the phosphorus quantity fluctuation on the coating may lead to the formation of microgalvanic pairs that can be the cause of the local corrosion of these alloys, when there are no macroscopic defects. Krolikowski and Butkiewicz showed that the anodic behaviour of NiP depends very strongly on the structural state of this alloy, and Parente et al. confirm the role of the structural condition of the alloy [3]. NiP coatings containing dispersed particles have received considerable attention lately, specially because of their resistance to wear and improved tribological properties. Due to their high wear resistance and the low cost of ceramic powder, metal matrix composite coatings with SiC have been investigated for the protection

of friction parts [1-3]. Many studies [1-3] concerning the incorporation of silicon-carbide particles in electrodeposited nickel matrix and about the characterization of the tribological properties have been made. Several authors expressed interest in the influence of operational parameters such as particle concentration in suspension, stirring speed, current density, effect of the addition of surfactants and others on the particle incorporation rate, based on the characteristic of volumetric fraction.

EXPERIMENTAL PROCEDURES

The metal matrix composite coatings can be prepared either by electrodeposition or autocatalytic (electroless) deposition on cooper substrate (s = 7 cm^2). The process consists of incorporating particles to the metallic matrix from an electrolyte containing particles in suspension with an agitation support. Convection forces move the particles straight to the surface that is to be coated, where they are adsorbed before being definitely incorporated to the growing coating. The solutions used in this investigation on Ni–P alloy electrodeposition consisted of $NiSO_4$ * 6 H_2O, $NiCl_2$ *6 H_2O, H_3PO_4, Na_2PO_4 and Na_2SO_4. at pH values of 1.5 and 2.0 and at the temperature of 90°C. The solutions were prepared from analytic grade chemicals and double distilled water, without addition of any other substances such as additives, complex agents or supporting electrolyte. Interfacial pH measurements were carried out by means of a nonintrusive in situ setup that consists of a platinum grid (3.5 cm2), used as working electrode and held at the end of flat-bottomed pH electrode.

Figure 1. Deposition bath

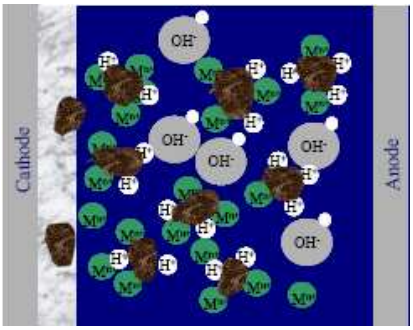


Figure 2. Electrodepostion process

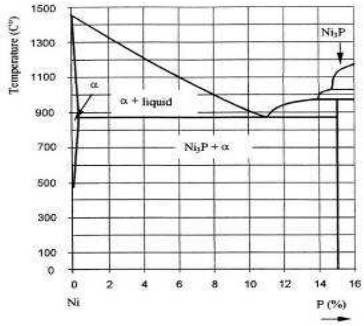


Figure 3. Ni-P diagram

Two different mechanisms have been proposed to describe the electrodeposition process (see figure 2) after Ni-OP diagram.(see fig.3). From the direct mechanism, first proposed by Brenner [3], the following three reactions occur simultaneously and independent one from each other: reduction of the ource of P, normally hypophosphite, Ni^{2+} and H^+ reduction. Since pure phosphorous cannot be generated electrolytically from aqueous solutions, the author [3] then stated that it could only occur during Ni–P electrodeposition due to the assistance brought about by the polarization of Ni deposition.

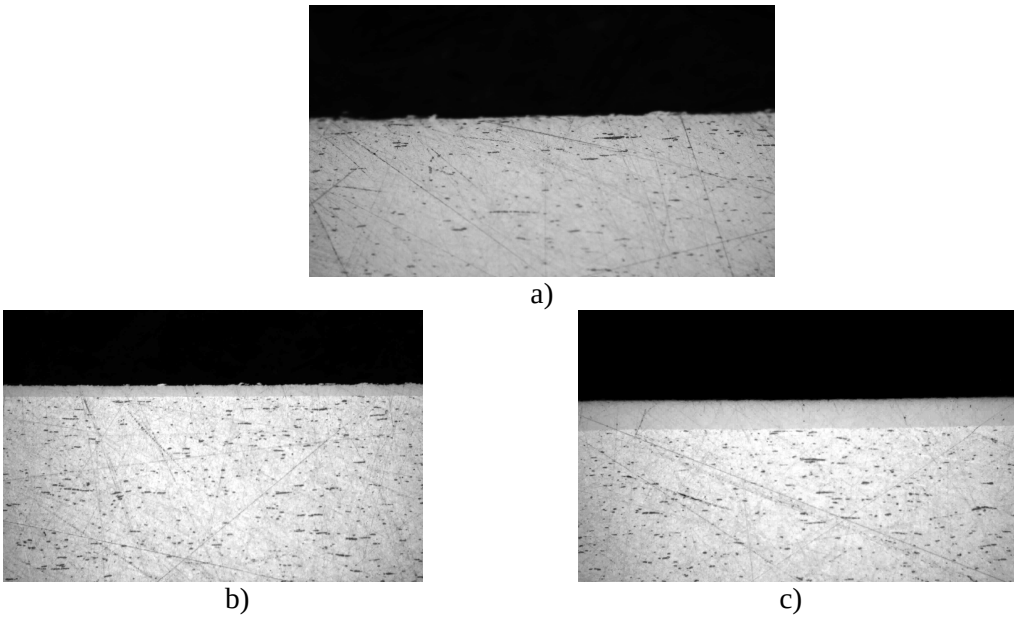
$$H_2PO_2^- + 2H^+ + e^- \rightarrow P + 2H_2O \quad (1)$$
$$Ni^{2+} + 2e^- \rightarrow Ni \quad (2)$$
$$2H^+ + 2e^- \rightarrow H_2 \quad (3)$$

The indirect mechanism suggests that the phosphorous oxyacid reduction depends on H+ reduction with the formation of a gaseous intermediate phosphine (PH_3). Ni^{2+} reduction and PH_3 oxidation would then occur simultaneously:

$$6H^+ + 6e^- \rightarrow 6H \quad (4)$$
$$H_3PO_3 + 6H \rightarrow PH_3 + 3H_2O \quad (5)$$
$$2PH3 + 3Ni^{2+} \rightarrow 3Ni + 2P + 6H^+ \quad (6)$$

RESULTS AND DISCUSSION

Using the Optical microscopy and Scanning electron microscopy it can be determined the adherence and the morphology of Ni-P coatings obtained by electrodeposition. In order to study the adherence of coatings on the cooper substrate the optical the micrographs are represented in figure 2.



a) b) c)

Figure 2. Optical micrographs of cross-section: a) cooper substrate, b) Ni-P coating, duration 45 min and c) Ni-P coating, duration 90min (500X)

The micrographs present the formation of an adherent and uniform coating on substrate. In order to study the morphology of coating the Scanning Electron Microscopy was chosen (figure 3). Usually, Ni-P coatings may have different structures from polycrystal, microcrystal, nanocrystal to amorphous state due to their different phosphorous contents, and acidic condition may promote the final amorphous state and high P content [2–4]. In our experiment, the bath is the same for two coatings alloys and the micrographs indicate to apparition of Ni_3P intermetallic compound.

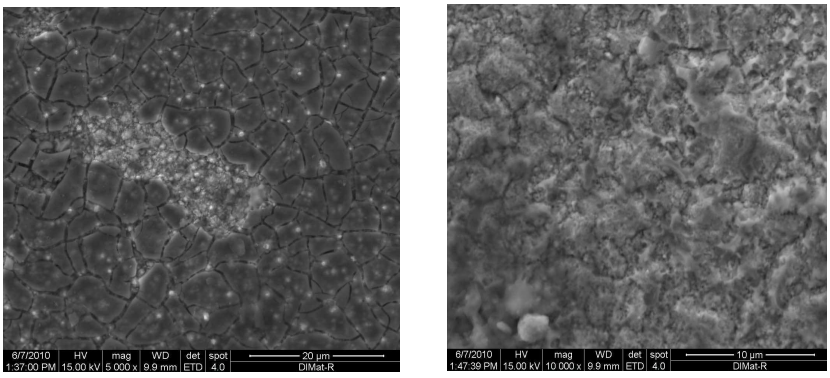


Figure 3. SEM micrographs of the coatings at 45 min and 90 min

Energy dispersive spectrum (EDS) analysis shows that the P presence in the coating like in figure 4.

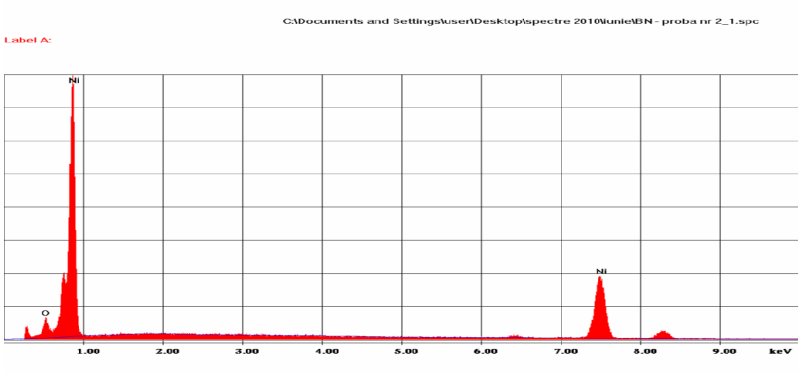


Figure 4. EDS spectrum of deposited layers

The EDS spectrum completes the SEM in formations witch show the phosphorous incorporation during the Ni deposition on cooper substrate. The experimental data obtained by the Vickers microhardness for forces F applied on the indenter ranging below 10 g for all investigated samples are presented in table 1.

Table 1. The hardness values

Duration of the electrodeposition (min)	$HV_{0.01}$ on surface	$HV_{0.01}$ in coating
45	**200.4**	**346.6**
90	**234**	**336.33**

The test of hardness on surface shows that with the increasing of duration of the electrodeposition increase the hardness and decrease across the coating. The increasing of process duration increases the hardness of obtained coating which reserve future application in wear resistance and surfaces with good tribological properties.

CONCLUSION

The electrodeposition process represents a useful electrolytic method to obtain Ni-P coating with great adherence and uniformity on cooper substrate, with good reproducibility on industrial scale. The increasing of process duration increases the hardness of obtained coating which reserve future application in wear resistance and surfaces with good tribological properties. The present study offers the possibility of development of preparation new composite layers Ni-P with CeO_2 or SiC for good combination mechanical and anticorrosive properties.

REFERENCES

[1] **C.F. Malfatti , J. Zoppas Ferreira , C.B. Santos ,B.V. Souza a, E.P. Fallavena , S. Vaillant , J.-P. Bonino**, *NiP/SiC composite coatings: the effects of particles on the electrochemical behaviour*, Corrosion Science 47, pag. 567–580, 2005.
[2**]. N. Sulimanu, F. Brînzã,** *Structure-properties relationships in electrodeposited Ni-W thin films with columnar nanocrystallites*, Journal of Optoelectronics and Advanced Materials Vol. 5, No. 2, p. 421- 427, June 2003.
[3]. **A.P. Ordine, S.L. Dıaz,1, I.C.P. Margarit, O.E. Barcia, O.R. Mattos,** *Electrochemical study on Ni–P electrodeposition*, Electrochimica Acta 51, pag. 1480–1486, 2006.

[4]. M.I. Petrescu, "Theoretical and experimental researches on the correlation between hardness and crystal chemistry
of sulfides and sulfosalts", Ph Thesis, University of Bucharest, **2000**.