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Electroless Nickel Coatings on Glass Substrate: Physical and Electrochemical Properties

A process for electroless deposition of NiP films on a transparent non-conductive soda lime glass is investigated. The process requires at least two repetitive cycles of etching and activation. The annealing process of the NiP films at 400 and 600˚C has been studied and the optimal heat treatment condition has been established. Different Ni bath with different pH has been employed to assess the NiP deposition. Characterization of the deposits by optical and scanning electron microscopy has provided information on the nature of crystallites and on the surface topography.

I. Introduction

The interest in nickel oxide thin films is rapidly growing due to its importance in many applications in science and technology. Besides acting an electrochromic (EC) material, it can also be used as a functional layer material for gas sensors. Electroless nickel coatings have gained popularity due to their inherent properties like excellent corrosion, wear and abrasion resistance [1-3]. In contrast to conventional electrolytic plating processes, electroless nickel plating does not use an electric current to produce a deposit, but operates chemically. It is an autoatalytic process that produces a nickel deposit on certain catalytically active substrates using a controlled chemical reaction [4-5]. The following chemical reactions are responsible for the electroless co-deposition of nickel and phosphorus [6] on the surface of the substrate:

$$Ni^{+2} + 2\,H_2PO_2^- + 2\,H_2O \leftrightarrow Ni + 2\,H_2PO_3^- + H_2 + 2\,H^+ \quad (1)$$

$$2\,H_2PO_2^- + H^+ \leftrightarrow 2\,H_2PO_3^- + P + H + H_2O \quad (2)$$

The ability of hypophosphite to reduce metal ions from their salt solution is in principle utilized in electroless nickel plating. The necessary electrons are delivered by the hypophosphite, which is oxidized to its ions [7]. The phosphorus element can co-deposit with nickel, resulting in the formation of a Ni–P alloy, during electroless plating process [8-10]. Ni–P alloys have attracted the attention of researchers in the last few decades due to its characteristics concerning the effect of phosphorous content on its crystalline structure. Crystalline Ni–P structures can be obtained by heat treatment above 350˚C, where crystallization of nickel and precipitation of nickel phosphide Ni3P took place [11]. Factors such as type and concentrations of the reducing agent, pH bath and deposition temperature influenced both the properties and the structural behavior of deposits [12-13]. Deposition of electroless Ni–P coatings on various substrates e.g. magnesium and its alloys [14-15], copper[16], titanium [17], carbon fibers [18], glass fiber [19], W-Cu alloy[20] and carbon nanotubes[21] can be obtained through controlling the bath chemistry and deposition conditions. Limited work has been published concerning the influence of chemical composition of deposits on physical and corrosion resistant property of electroless Ni–P black coatings. In the present work the chemical composition and physical characteristics of the post-etched Ni–P alloy were investigated. Moreover, thermal treatment of the coating was evaluated by X-ray diffraction analysis (XRD) and cyclic voltammetry.

II. Experimental

Medium glass pieces (20×20 mm2 and 0.5 mm thick) were used as substrates for electroless nickel deposition. The substrates were firstly degreased with acetone. Subsequently, they were etched for 3 minutes in a concentrated HF +H2SO4 solution maintained at room temperature, followed by immersing for 10 minutes in 30% NaOH. After rinsing with deionized water, the substrates were activated by dipping in an aqueous acidic solution of palladium chloride followed by immersing the substrates in an electroless nickel plating solution which normally comprises (a) a source of nickel ions usually nickel sulphate or nickel chloride, (b) a reducing agent such as hypophosphite, and (c) an alkali which is a metal hydroxide such as sodium hydroxide. Following the deposition of the nickel, the plated substrate is rinsed and baked to drive out any moisture in the final product. The composition of the plating baths was listed in Table 1. The as-deposited electroless nickel surfaces were characterized by X-ray diffraction (XRD, Model D8 Advance, BRUKER/AXS, Germany). The surface morphology of the coatings was observed using scanning electron microscopy (SEM-JEOL, Japan). The elemental composition was analyzed by means of energy dispersive X-ray Spectroscopy (EDS). The reaction properties of heat treated NiP at 600˚C was studied under cyclic voltammetry in alkaline KOH solution.

Chemical	Concentration (g/L)		
	Solution 1	Solution 2	Solution 3
Lactic acid	40g		
Propionic acid	6g		
Nickel sulphate	20	30	35
Sodium hypophosphite	15	25	20
Sodium hydroxide	150g		
Sodium pyrophosphate		50	
Triethanolamine		100	
Ammonia		+	
Sodium citrate			50
Sodium acetate			5
pH	5	9-10	6

Table 1: Employed chemicals and their concentrations in the plating bath for the Ni–P depositions via electroless plating process.

III. Results and Discussion

The effect of heat treatment on the crystalline structure of electroless Ni–P deposits was examined by XRD analysis. The X-ray patterns obtained after annealing at 400˚C & 600˚C for 1 h are shown in Figs1&2. It should be pointed out that the untreated Ni–P deposit is amorphous. The XRD patterns of the annealed films have exhibited better degree of crystallinity. The crystalline phase present in these films is mainly identified as the Ni3P for the annealed film at 400°C, Fig.1. Annealing at higher temperature 600°C for 1 hr results in the appearance of peaks corresponding to NiO besides the Ni3P already identified at 400°C.

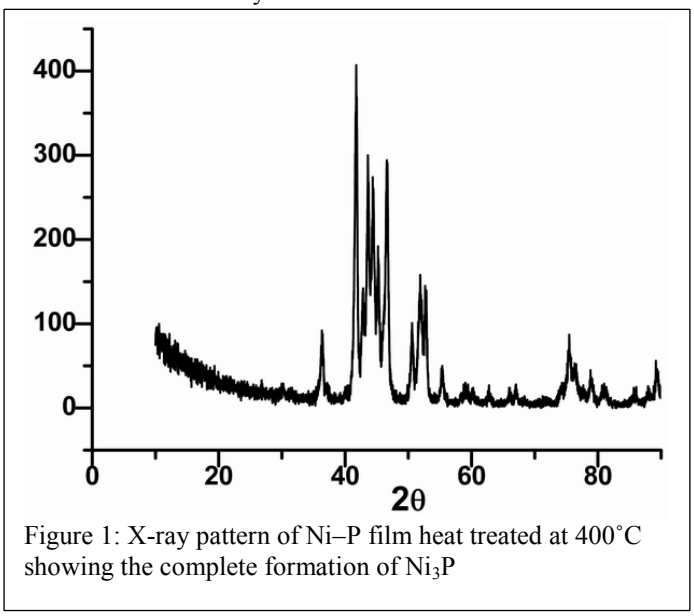

Figure 1: X-ray pattern of Ni–P film heat treated at 400˚C showing the complete formation of Ni_3P

Different kinds of NiP coating on glass have been produced by modifying the composition of the bath used. Depending on the chemical composition and the pH, different morphologies and characteristics of the deposits have been observed Fig.3. Homogenized deposit covering the whole area has been produced using a bath containing solution number 1. However, the deposits obtained from the three solutions have a clear-cut spherical shape. SEM micrographs of the films annealed at 400 &600˚C were illustrated in Figs 4&5. The films were constituted of fine-grains; highly agglomerate to form uniformly distributed interconnected spherical clusters. The study has also revealed that the films under investigation are highly dense and compact in nature i.e. these samples in general exhibited lower degree of porosity.

Figure 6 displays the curves recorded with glass electrode of area 2 cm2 in the solution of 0.25 M KOH. Cyclic voltammogram of curve (1) is obtained without agitating. It is observed that the current density increase gradually with increasing scan direction from 0 to -1.5V. At the cathodic potential of -1.5 V a high increase of current takes place up to 3 mA cm-2 corresponding to hydrogen ion reduction. During the positive going scan, the recorded anodic current is likely due to hydroxyl decomposition. The absence of anodic peaks indicates the absence of metallic corrosion on substrates. With the increase of the speed of agitation to 200 rpm (curve 2) the cathodic current density becomes higher than that recorded in the non-agitated one (curve 1). By increasing the agitation rate, the thickness of the adjacent cathodic layer was reduced, which in turn shortened the diffusion path of the bath content and consequently led to increasing the cathodic current density. The field of the industrial applications of the nickel coatings has been furthermore increasing. So far the majority of research on electroless nickel (EN) deposition have been restricted to metal alloys, our motivation for the present study was to explore the possibility of developing EN on non-conducting glass substrate.

IV. Conclusion

Ni–P electroless films have been prepared by varying the sodium hypophosphite concentration and the pH of the deposition solution. The deposition of NiP from the solution having a lower pH and containing lower concentration of sodium hypophosphite is characterized by a uniform distribution of spherical grains .Both the structure and morphology of the acidic solution can be modified by heating the films at 400 &600˚C. A more detailed investigation regarding the optical and mechanical characterization of EN deposition is the focus of an on-going study for assessing the potential of these coatings for a variety of industrial applications.

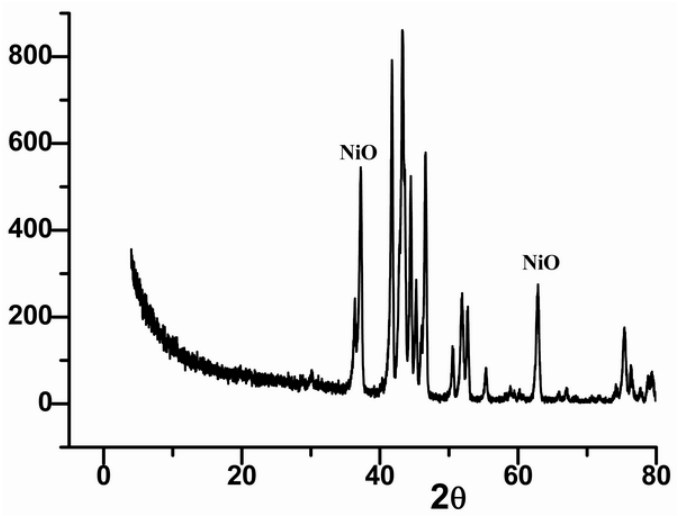

Figure 2: X-ray diffractogram of Ni–P film, deposited from a solution having a pH = 5, after subjected to heat treatments at 600˚C for 1 h showing the formation of Ni_3P and NiO. The non-labelled peaks belong to Ni_3P

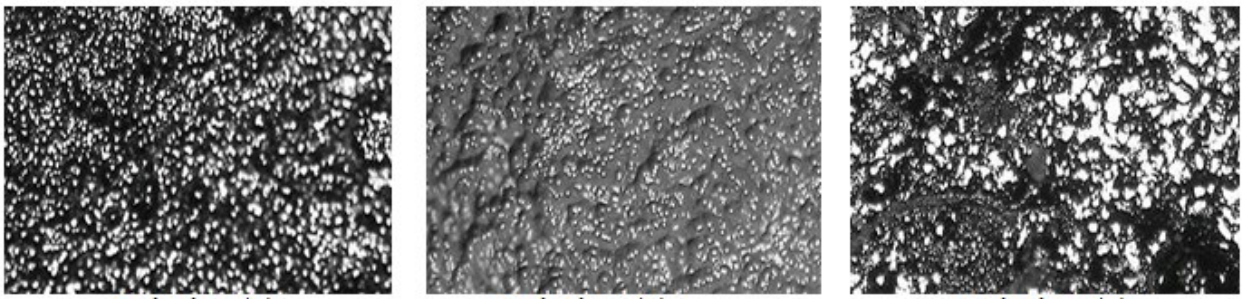

Figure 3 Optical micrographs of NiP coating obtained from different Nickel bath having various pH

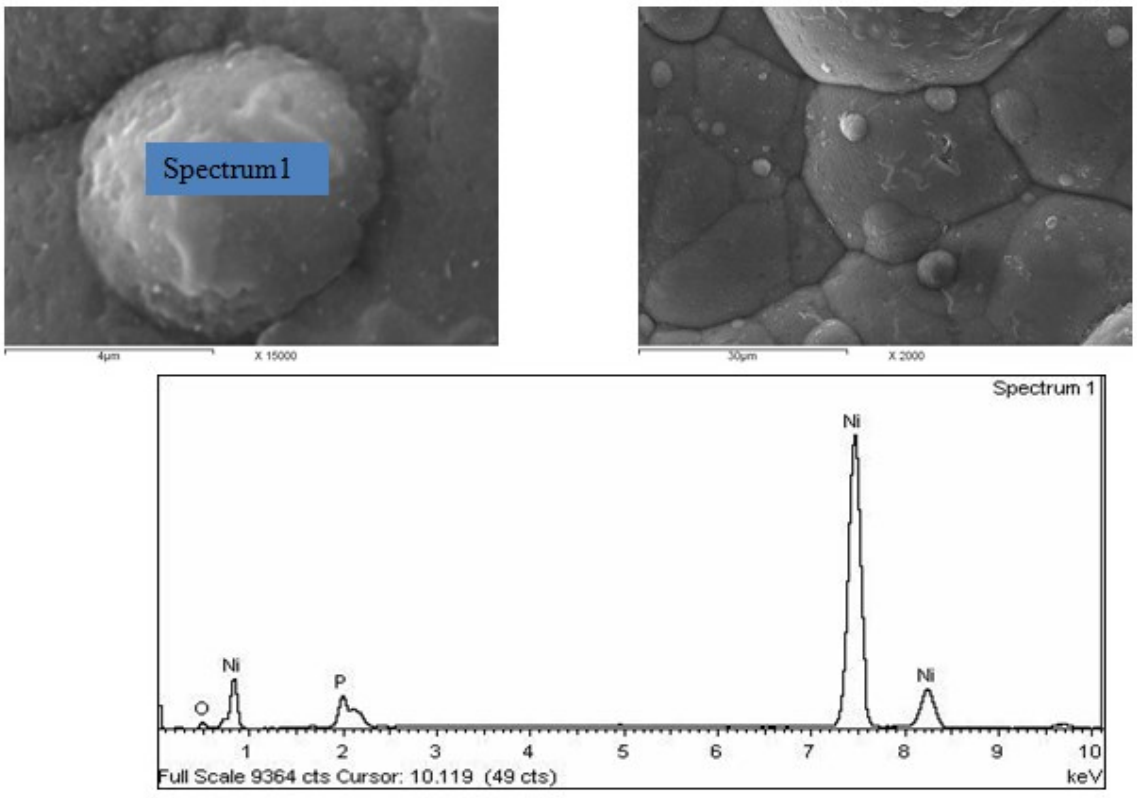

Figure 4 SEM micrographs of the NiP film annealed at 400 °C (solution 1)

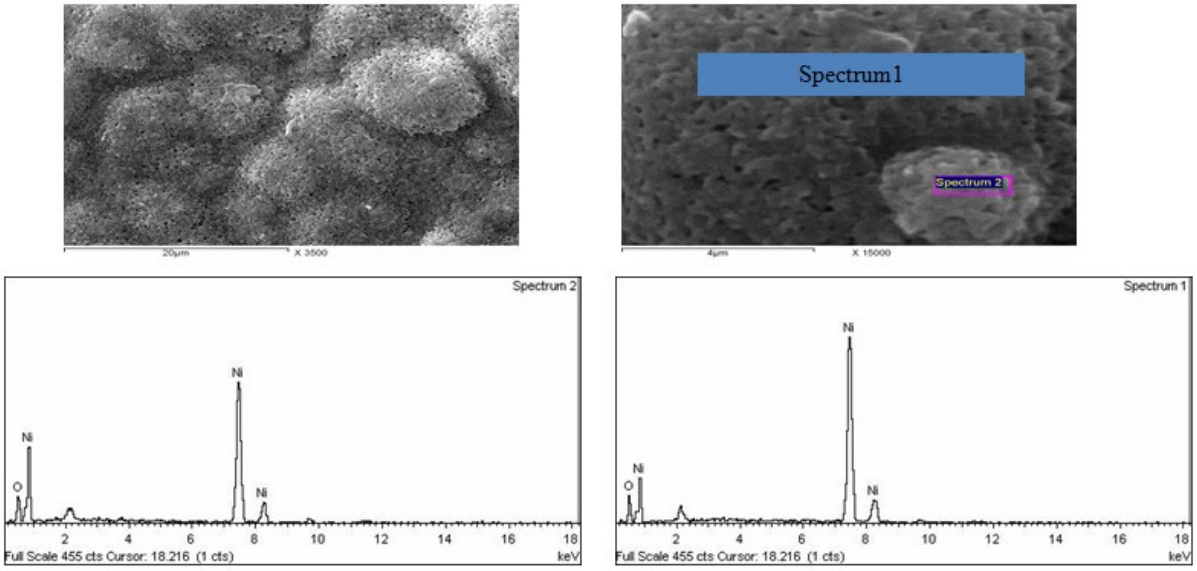

Figure 5. SEM micrographs of the annealed electroless nickel coating at 600° C (solution1)

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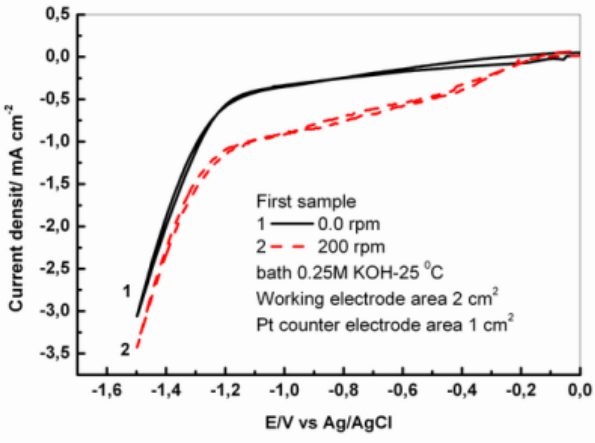

Figure 6: Cyclic voltammograms measured on a glass cathode using a solution of 0.25 M KOH (1) without stirring and (2) with stirring rate 200 rpm at 25 ^{0}C. Potential sweep rate= 10 mV S^{-1}