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Electroless nickel deposition on mild steel by using a new bath formulation and its characterization

Rahul A Babhale, R S Sonawane, S S Bodhale, S K Apte & B B Kale*

Centre for Materials for Electronics Technology (C- MET), Scientific Society, Ministry of Information Technology, Government of India, Pune 411 008, India

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A new bath formulation has been developed to prepare the Ni-P deposits on mild steel substrates. The alkaline bath formulation contains $NiCl_2$ as a Ni source and sodium hypophosphite as reducing agent. The Ni-P alloy with higher phosphorus content was obtained by using this new bath formulation. The uniform deposits of Ni-P (1.98-12.5) were obtained. The change in rate of deposition with time, temperature and pH was studied. The effect of concentration of nickel and reducing agent on the deposition was investigated. The samples obtained were characterized by using SEM, XRD, DSC and ICP-OES techniques. The Ni-P deposits were amorphous in nature and upon heat treatment in between 300 to 450°C, it changes to crystalline Ni_3-P phase. The phosphorus content of the deposits increases with the deposition time and highest P content is obtained on the samples prepared at 3 h time.

Recently extensive studies have been made on the deposition of Ni-P alloy on metal substrates. The Ni-P alloy has wide industrial applications because of its excellent corrosion resistance, wear resistance and non-magnetic properties. The electroless nickel deposits using sodium hypophosphite as a reducing agents result in deposits of binary alloys of nickel and phosphorus on the surface[1]. The phosphorus content of the deposits varies with the pH of the solution [2]. The deposits plated from alkaline solution had a lower phosphorus content and are crystalline[3,4] whereas the deposits from acidic solution had a higher phosphors content. Generally more than 7 wt.% phosphorous were known as amorphous or microcrystalline.

Goldenstein *et al.*[5] in their study of deposits containing 7 to 10% phosphorous concluded on the basis of X-ray diffraction results that, as plated deposits were amorphous. Makhshoos *et al.*[6-8] studied the microstructure and phase transformation behaviour using Scanning Electron Microscope (SEM) and *in situ* electron beam heating of electrode deposited Ni-P alloys. They found that as plated deposits containing 12 to 26% phosphorous were amorphous and dendrite transformation spread out from the beam center, which might be caused by the nucleation and growth of crystallites from amorphous solid. Some other investigators examined the TEM and interference function for electroless Ni-P deposits and concluded that the deposits had an amorphous like structure[9-12]. In contrast to these, Grahm *et al.*[13] concluded on the basis of electron and X-ray diffraction and some other considerations that as plated electroless nickel deposits containing 4.6 to 9.4 wt.% phosphorous were supersaturated solid solutions of phosphorus dissolved in crystalline nickel with numerous staking faults. Parker[14] also found that crystalline nickel had a (111) fibrous texture in as plated state. Cargill[15] and Dixmier and Duwez[16] studied the X-ray interference function for electro-deposited or electroless plated Ni-P alloys and found a higher degree of short-range order than in a liquid.

These conflicting results are thought to be due to the unstable structure of the deposited alloys and the detailed structures of electroless Ni-P deposits are not well-understood. Therefore, more basic studies are required to determine whether electroless nickel deposits are microcrystalline supersaturated solid solution or amorphous. The transformation process from amorphous structure to crystalline structure has two stages. First, short-range atomic movement causes decomposition to the equilibrium phases. On the other hand, the phase transformation behaviour of microcrystalline supersaturated binary solid solution alloy has only one transformation process, which is very similar to the second stage mentioned above. All

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*For correspondence (E-mail: bbk@cmetp.ernet.in/ kbbb1@yahoo.com)

Table 1—Raw materials for the bath

Chemicals	Formula	Make	Purity %
Nickel chloride	$NiCl_2.6H_2O$	Loba	98
Sodium citrate	$Na_3C_6H_5O_7.2H_2O$	Qualigens Fine Chemicals	98-100
Sodium hypophosphite	$Na_2H_2PO_2.H_2O$	CDH	98
Ammonium chloride	NH_4Cl	Qualigenes Fine	99.5
Ammonia	NH_3	S. D. Fine	25 (NH_3)

Table 2—Bath Formulation

Constituent	Solutions g/L
Nickel chloride ($NiCl_2$)	30
Sodium citrate ($Na_3C_6H_5O_7.2H_2O$	84
Sodium hypophosphite ($Na_2H_2PO_2.H_2O$)	10
Ammonium chloride (NH_4Cl)	50

the previous work[17] has been done by using reported bath formulations. Very few workers have tried to develop new bath. The purpose of this work is to study the performance of the new bath, the microstructures and the crystallization behaviour of electroless Ni-P deposits. In the present investigation, a new bath formulation for the deposition of Ni-P alloy on mild steel tubes by using an alkaline bath and sodium hypophosphite as a reducing agent is developed. The formulated bath is quite stable and can be used repeatedly. Uniform homogenous deposits were obtained by using this new bath formulation. The phosphorous content obtained by using this new bath formulation was higher than that of the usually reported alkaline baths. The effects of temperature and pH on the quality of deposits, deposition rate and microstructure were studied.

Experimental Procedure

All the chemicals and reagents used in this process were of analytical grade and used without further purification. The raw materials used for experimental work are shown in Table 1.

In this study, the nickel chloride was used as a Nickel source, sodium hypophosphite as a reducing agent and sodium citrate as complexing agent. Ammonium chloride was used as an accelerator and ammonia (1:1) solution was used to adjust the desired pH. The substrate used for plating were mild steel tubes with diameter of 4 mm and 20 mm in length. Before deposition the substrate was first polished with emery paper followed by cleaning and degreasing. The chemical composition of bath used to obtain uniform nickel deposits is shown in Table 2.

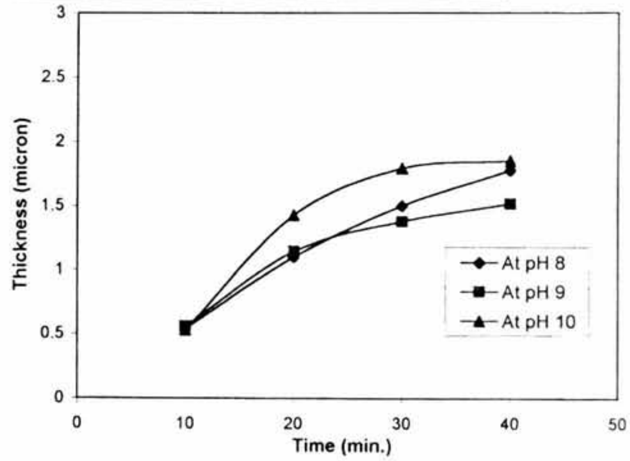

Fig. 1—Effect of pH on electroless Ni-P deposition at 70°C

Results and Discussion

The deposition of nickel on mild steel substrates by electroless method is very well-known and many researchers[17] have proposed the mechanism for this process. The bath formulation (Table 2) gave a very stable bath and was found to be economical for the industrial application. In view of this, the further detailed study with optimization has been made. The sodium citrate used as a complexing agent is having long chain of carbon so it does not allow any Ni-precipitation in bath resulting in better bath stability. Figs 1-3 show the rate of deposition in terms of thickness of deposit in microns of specified surface area of mild steel substrates at different temperatures, time and pH. From the figures it was observed that, the rate of deposition increases with increase in pH of the bath at constant temperature i.e. increase in OH^- ion concentration favours the higher deposition rate. This formulation can be used over the pH range of 8 to 11 and the bath was quite stable within this pH range. It was also observed that the temperature of the bath plays an important role in the deposition process. The temperature of the bath was varied between 70-90°C and among the three temperatures studied, the rate was higher at 90°C.

Generally the actual nickel reduction is due to atomic hydrogen, which acts by heterogeneous

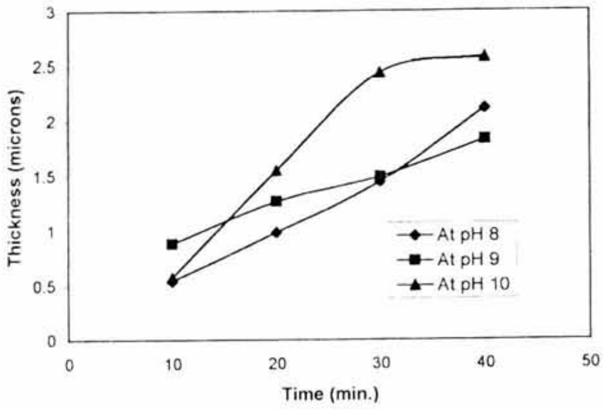

Fig. 2—Effect of pH on electroless Ni-P deposition at 80°C

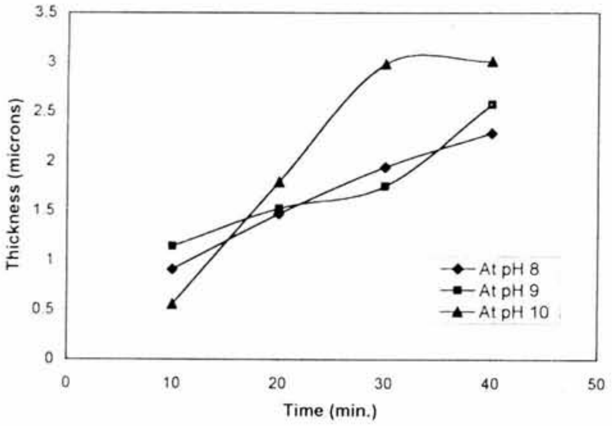

Fig. 3—Effect of pH on electroless Ni-P deposition at 90°C

catalysis at the catalytic nickel surface. The atomic hydrogen generated by the reaction of water with hypophosphite is absorbed at the catalytic surface. The absorbed atomic hydrogen reduces nickel ions at the catalytic surface. The secondary reaction between hypophosphite and atomic hydrogen results in the formation of elemental phosphorous. The metallic nickel catalytic surface has a direct reaction with elemental phosphorous to deposit nickel phosphorous alloy coating. The brightness of the coating depends on the content of the phosphorous in the Ni-P. High phosphorous content in alloy results in good and bright surface of the substrate.

Structure analysis

The X-ray diffraction analysis was performed on Rigaku X-ray Diffractometer with Cu, K$_\alpha$ radiation and Ni filter. The X-ray diffraction results (Fig. 4) show first broad and shallow peak, representing the face centered cubic nickel crystallites precipitated in amorphous matrix. The crystallization behaviour was studied by heating the sample deposited at pH 9 for 2 h and heated in between the temperatures 200-500°C. Upon heating at 250°C, slight sharp peak has been observed along with broad peak, which means there is initiation of nucleation before crystal growth. The sample heated at 400°C shows the complete transformation of amorphous to crystalline phase because further heating at higher temperature does not show much change in intensity of the peaks. The crystallization temperature was also confirmed by Differential Scanning Calorimetry (DSC) method.

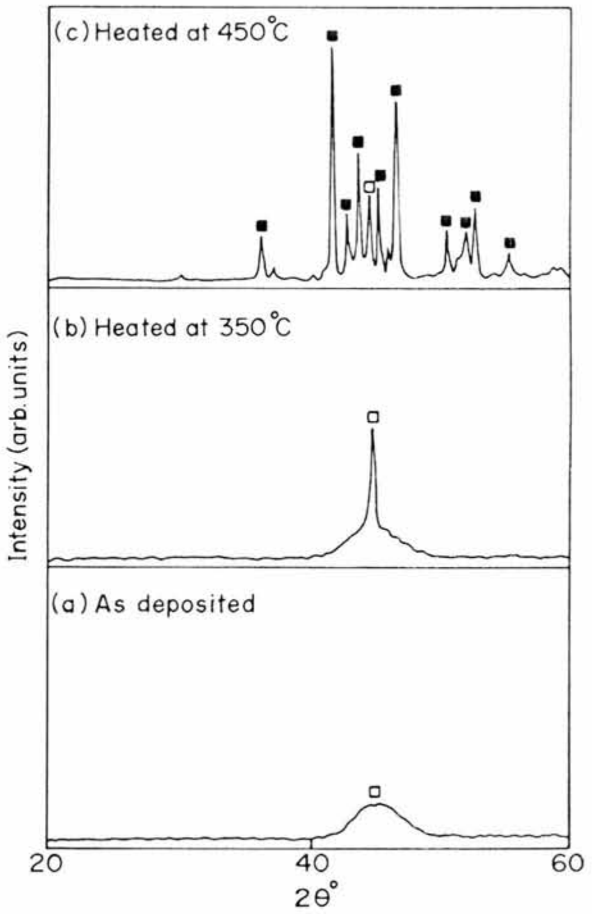

Fig. 4—X-ray diffraction pattern of the electroless Ni-P deposits obtained at pH-9, temperature 90°C for 2 h; {□-Pure Ni, ■-Ni$_3$-P}

Thermal analysis by differential scanning calorimetry

The DSC was performed on the Metler-Toledo DSC instrument at a heating rate of 10°C per minute. The sample obtained from the electroless Ni deposition at 90°C and at pH 9 for 2 h was used for the DSC analysis. The sample was heated between 25-

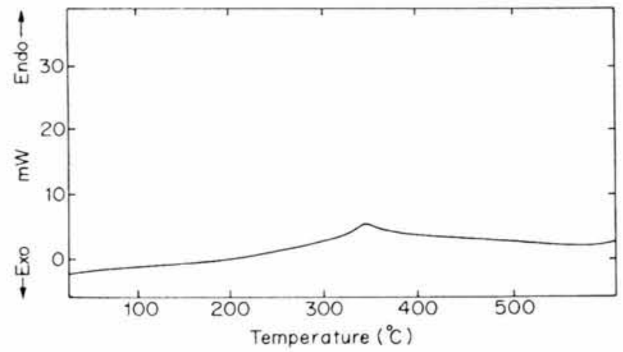

Fig. 5—Differential scanning calorimetry curve of the crystallization process for the electroless nickel deposit obtained pH-9, tempeature 90°C for 2 h.

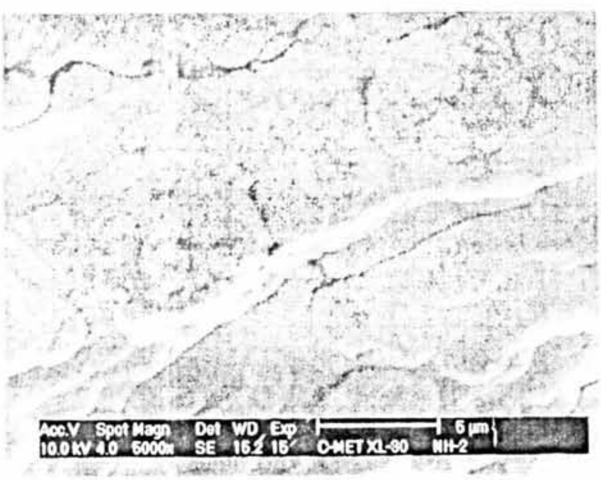

Fig. 6—SEM of the electroless Ni-P deposition at pH-9, temperature 90°C and time –2h

600°C in the nitrogen atmosphere (N_2 flow -100 mL/min) at the heating rate 10°C per minute. DSC data shows a small peak at about 350°C (Fig. 5). This peak is caused by the crystallization of the Ni_3-P, which is also confirmed from the XRD results.

Fig. 6 represents the Scanning Electron Microgram (PHILIPS XL30) of the Nickel plated sample at 90°C and pH 9 for 2 h. From the Fig. it is observed that there is a layer of Ni-P at amorphous state and the same has been confirmed by XRD.

Elemental analysis by ICP-OES

The sample of Ni-P deposited was analyzed for its nickel and phosphorous content by using Inductively-Coupled Plasma Optical Emission Spectrometer (ICP -OES, Perkin-Elmer-P-1000). For this analysis, a known quantity of sample was dissolved in acid and analyzed for phosphorous content at wavelength 213.5 nm and nickel at 231.6 nm. The results are as follows:

Time	Nickel %	Phosphorous %
½ h	2.76	N.D
1 h	3.32	1.98
2 h	6.34	6.53
3 h	11.9	12.5

From the above results it was found that the nickel and phosphorous content increases with time. Only Ni is detected in the sample prepared at 30 min time and there is no phosphorous content which shows that only Ni is deposited in the first half an hour and after half an hour the Ni-P deposition starts. This indicates that the reduction of nickel complex takes place at the beginning followed by the formation of Ni-P alloy. Generally in acidic bath, phosphorous deposition is more but in the above alkaline bath first time more phosphorous deposition is observed. This will be quite clear after studying the kinetics of the deposition. This is the interesting phenomenon, which needs further studies.

Conclusions

From the study, it can be concluded that, the new bath formulation is very suitable for the deposition of Ni-P deposits containing higher concentration of phosphorous in alkaline medium. The electroless nickel deposition increases with pH and time. It was observed that the deposition rate increases with bath temperature. As deposited sample shows Ni-P deposits which are amorphous in nature or consisting of extremely small grains. The Ni-deposited substrate heated at 250°C shows the beginning of crystallization and at 450°C shows the complete transformation of amorphous to crystalline phase. The sample heated below 450°C shows most of the diffraction peaks of Ni_3P crystallites and very weak peak of Ni which concludes that, in the early stage pre-existing FCC nickel grains coarsened and on further heating, the Ni_3P crystallites nucleated in the P rich matrix and grew rapidly by encircling nickel grains. On further heating to 450°C nickel grains grew up fully to the diffraction pattern. The crystallization behaviour has been confirmed by DSC where crystallization peak was observed at 350°C. In the half an hour there is pure nickel plating and after half an hour there is the initiation of Ni-P deposition.

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