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INFLUENCE OF ANNEALING ON CRYSTALLINITY OF ELECTROLESS Ni-P DEPOSITS

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ABSTRACT

Electroless nickel is one of the widespread commercial and industrial coatings owing to its unique properties, such as good wear and corrosion resistance, thickness uniformity etc. The crystallinity of the deposits is one of the important factors which are influencing the properties. In this investigation, electroless Ni-P is deposited on mild steel substrate. The deposits were annealed at various temperatures for 2 hours. The crystallization process of these deposits was studied using single line profile analysis, employing pseudo-Voigt profile function. To de-convolute the overlapped reflections from different phases PRO-FIT software package was used. The data which are taken from the X-ray diffraction profile was used to find the crystallite size and microstrain using the in-house software 'PROFAN'. The XRD reveals the formation Ni_3P at and above 300^0C. The amorphous phase becomes unstable and more or less disappears around 360^0C which confirms the completion of recrystallization. The crystallite size increased sharply above 360°C, accompanied by a steep reduction in the microstrain, indicating the onset of precipitation.

Keywords: Electroless nickel, Annealing, Crystallization, XRD, Profile Analysis

1. Introduction

Electroless nickel is one of the most widespread commercial and industrial coatings owing to its unique properties, such as good wear and corrosion resistance, thickness uniformity etc [1]. The crystallinity of the deposits is one of the important factors which are influencing the properties. The crystallization processes in Eletroless Ni-P deposits that accompany their heat treatment have been studied by several researchers employing a variety of equipments and techniques involving Transmission Electron Microscope (TEM), Differential Scanning Calorimeter (DSC), Vibrating Sample Magnetometer (VSM), X-ray Diffraction (XRD), etc. Graham et al [2], based on XRD and TEM studies, report that the deposits containing 5 wt.% P were microcrystalline in nature. But Kazuyuki Sugita and Nobuo Ueno [3] show the structure of low phosphorous (<7 wt.%P) deposits to be crystalline. They prepared the deposits produced from the hypophosphite bath with an alkaline-citrate as stabilizer. Ramesh Agarwala et al [4] reported the presence of one or several of the Ni-P compounds such as NiP_2, Ni_5P_4, $Ni_{12}P_5$, Ni_5P_2 etc., in the as deposited condition based on electron diffraction study of nickel phosphorous alloys. The precipitation of microcrystalline nickel and Ni_3P occurs around 250^0C on annealing for about 4 hrs [5]. Based on Vibrating Sample Magnetometry (VSM), Ray et al [6] reported the transformation of $Ni_{12}P_5$ to Ni_3P and crystallization of residual amorphous phase to Ni_3P for deposits having 6 to 13.8-wt %P. This inference was the confirmation of previous studies through differential thermal analysis [7].

Suhoon Park et.al [8] studied the effect of heating rate on phase transformation and found that the phase transformation temperature increased linearly with heating rate. The presence of Ni_3P is established after annealing at 330^0C through observations based on TEM diffraction patterns. Sampath kumar and P.K.Nair [9] studied the crystallization behaviour of electroless Ni-P deposits by XRD and X-ray line profile analysis. Complete crystallization with the precipitation of Ni_3P phase on heat treatment at 330^0C is reported. Tyagi et al [10] studied the crystallization behaviour of electroless Ni-P through the response to annealing in terms of resistivity and the magnetic moment of non-crystalline phases in the temperature range of 300K to 800K. Shih et al [11] reported on heating to 500 °C for 4 h, the precipitation of Ni and Ni_3P is completed. Hence there are various opinions about the ranges for the completion of precipitation process are available in the literature.

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Even though many researchers concentrated their effort on the crystallization analysis, very few researchers have employed XRD analysis for quantitative comparison of degree of crystallinity [12,13]. Also, completion of precipitation process and changes in the amorphous phase on heat treatment which are expected to affect the properties need to be studied. Hence the objective of this work is to study the effect of heat treatment on crystallization of electroless Ni-P deposits.

2. Experimental Procedure

2.1 Initial Preparations

In this work, mild steels discs of about 22 mm diameter and 7 mm thickness were prepared from rod stock to be used as substrates. All discs were then solutionised at 800^0C for 2 hrs and air cooled to ensure uniform initial conditions.

The step-by-step cleaning procedure employed prior to plating consists of

1. Cleaning the substrate with soap
2. Rinsing with distilled water
3. Ultrasonic cleaning in methanol
4. Acid pickling for 1 min. [8% H_2 SO_4 by volume]
5. Rinsing in distilled water followed by a methanol wash.

2.2 Production of Electroless Ni-P deposits

The composition of the plating bath is given in table 1. The pH of the bath was maintained in between 9 and 10 by addition of sufficient quantity of ammonia solution as and when required. The pH was monitored by using commercially available pH indicating 'Indikrom papers'. The experimental set up is shown in figure 1. The electrolyte was heated indirectly by an electrically heated oil bath whose temperature was regulated by a Proportional Integral Derivative (PID) controller. The temperature of the oil medium was controlled and the corresponding temperature of the electrolyte was monitored using a thermometer. This procedure was adopted because conventional thermocouples, if immersed directly in the plating bath, will get immediately coated with nickel, making the temperature reading inaccurate.

Table 1: Plating bath constituents for electroless Ni-P deposits

Constituents	Role	Quantity (g / l)
Nickel chloride	Source of nickel	30
Sodium hypophoshite	Reducing agent	40
Sodium citrate	Stabilizer	25
Ammonium chloride	Complexing agent	50

2.3 X-ray diffraction analysis

X-ray diffraction data were collected using a computer controlled Phillips vertical diffractometer. Iron radiation with a graphite mono-chromator was used. The X-ray tube was operated at 30KV, 20mA. Step scanning technique was employed with a step width of 0.02° (2θ) and counting time of 5 Sec/step in all cases.

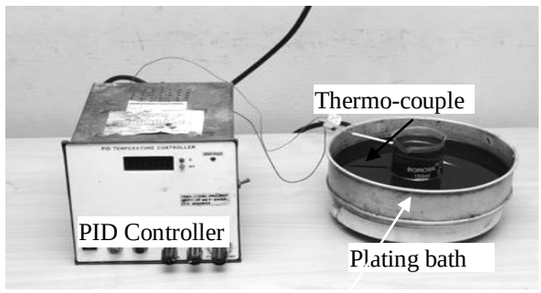

Fig. 1 Experimental set-up for production of electroless nickel deposits

2.4 Estimation of the Degree of Crystallinity

Studies on crystallinity of the deposits were based on X-ray diffraction data. A typical X-ray diffractogram obtained from electroless Ni-P deposit in the as coated condition is shown in figure 2. The following terms could be defined with reference to this diffractogram.

a) Integrated Intensity: Integrated intensity is defined as the area under the relevant intensity profile. In this investigation, the ratio (I_A/I_C), where I_A and I_C are the integrated intensities of the diffraction profile from the amorphous phase and the crystalline phase respectively and they could be considered as a measure of the relative proportion of the amorphous and crystalline phases present. The reflections from crystalline and amorphous phases were separated by the software PROFIT. The deconvoluted profiles corresponding to figure 2 are shown in figure 3.

b) Full width at half maximum (FWHM): is defined as the width of the relevant diffraction profile at half of the total peak intensity (height).

c) Integral breadth: is defined as the breadth of the rectangle having equal height and area as that of the diffractionprofile.

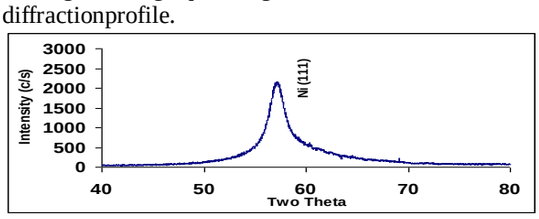

Fig .2 Diffractogram obtained from electroless Ni-P deposit in the as coated condition.

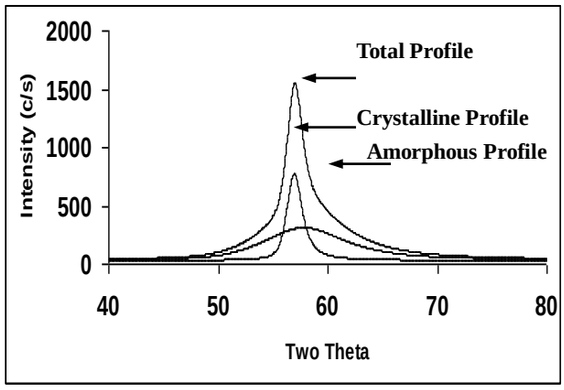

Fig .3 Deconvoluted profile for the diffractogram shown in figure 2

The data which are taken from the X-ray diffraction profile was used to find the crystallite size and microstrain using the in-house software 'PROFAN'. For all the deposits single line profile analysis, employing pseudo-voigt profile function was carried out. To deconvolute the overlapped reflections from different phases, PRO-FIT software package [14] was used.

3. Results and Discussions

The response to heat treatment of electroless nickel had indicated the existence of three prominent regimes with distinctive features. These approximately fall in the range of: a) room temperature to about 300^0C, b) 300 to 360^0C and c) 360 to 600^0C.

3.1 Effect of heat treatment on Phases

In order to study the effect of heat treatment at annealing temperatures, on phase content and crystallization behaviour of electroless Ni-P deposits, the coated substrates were annealed for 2 hours at 100^0C, 200^0C, 300^0C, 330^0C, 340^0C, 350^0C, 360^0C, 400^0C, 500^0C and 600^0C and then air cooled. The typical diffractograms obtained from these samples in the as coated condition and after the above mentioned treatment schedule are presented in figures 4 to 6.

Till about 300^0C, only one sharp reflection, extensively overlapped by the broad amorphous profile, at about 57^0 (2θ) is clearly visible. However, in case of the diffractogram obtained from the sample annealed at 300^0C (Figure 5), one can clearly observe other relatively sharp reflections from crystalline phases.

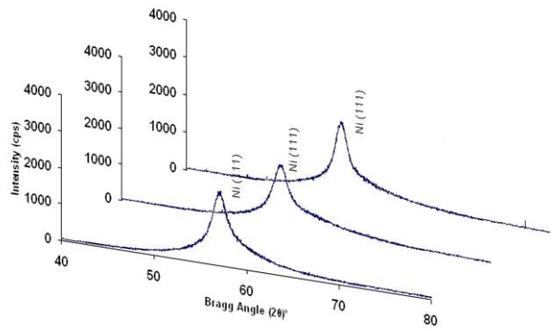

Fig. 4 Typical X-ray diffraction profiles of electroless Ni-P deposit in the as deposited as well as annealed at 100 and 200^0C.

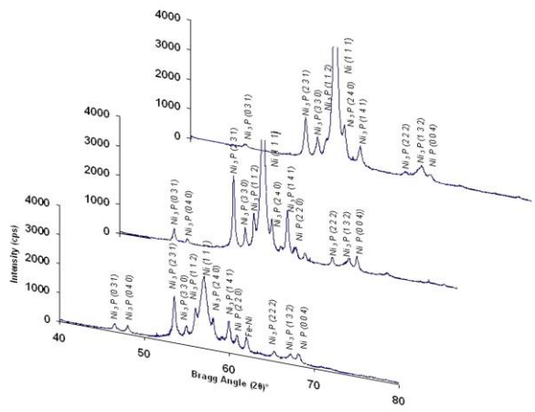

Fig .5 Typical X-ray diffraction profiles of electroless Ni-P deposits annealed at 300, 330, 340^0C) condition

Additional Bragg reflections corresponding to body centered tetragonal nickel phosphides (Ni_3P) could be identified. Further, the (111) reflection of nickel becomes progressively sharper as the annealing temperature goes up. Between 300^0C to 360^0C, the precipitation process of Ni_3P is continuing and at around 360^0C the precipitation process is completed. At 360^0C, the mechanical properties like hardness, wear resistance, etc are expected to be increased because of its precipitation hardening effect. In precipitation hardening, the atoms of the solute diffuse to a specific crystallographic plane with an atomic arrangement that resembles the array of atoms on a plane in the structure of the precipitate.

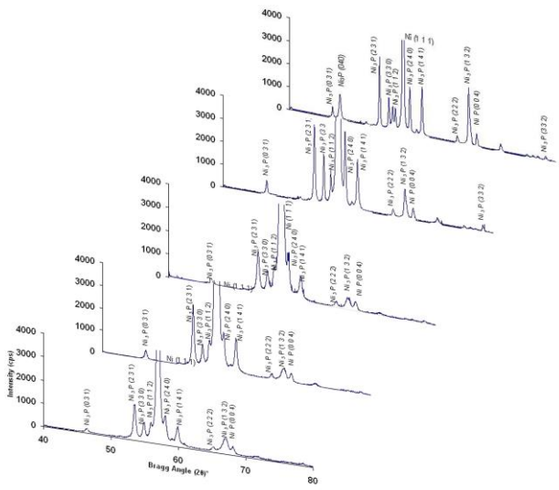

Fig . 6 Typical X-ray diffraction profiles of electroless Ni-P deposit after annealing at 350, 360, 400, 500 and 600^{0}C

As the atoms attempting to precipitate are collected together, they are forced to conform to the structure of the solvent. This forced coherency between matrix of the solvent and atoms attempting to form the precipitate structure causes severe localized stresses in the matrix which would be responsible for the increase in hardness. When increasing the annealing temperature above, 360^{0}C, additional Ni_3P peaks are identified and the peaks observed in the previous diffractograms are sharpened further (figure 6).

3.2 Effect of heat treatment on Crystallinity

From the diffractograms obtained, using single line profile analysis, employing pseudo-Voigt profile function, various parameters such as integrated intensity of amorphous / crystalline, integral breadth, crystallite size and micro-strain are calculated.

3.2.1 Variation in the Integrated Intensity Ratio

The effect of annealing temperatures on the variation in the integrated intensity ratio (I_A/I_C) is shown in figure 7. The ratio of integrated intensity of amorphous to the integrated intensity of crystalline phase is denoted as I_A/I_C. It can be seen that there is a gradual sharpening and a relative increase in the intensity of the Bragg reflection from the crystalline fraction. This corresponds to a gradual reduction in the amorphous fraction of the deposit, as can be seen from the variation of the ratio of integrated intensities (I_A/I_C) with annealing temperature. In the 300 to 360^{0}C range, the amorphous phase becomes unstable and more or less disappears around 360^{0}C. It appears that annealing at 360^{0}C is sufficient for this class of electroless Ni-P deposits to get completely converted to crystalline material. The amorphous phase has disappeared and the Bragg reflections from the crystalline phase get progressively sharper with increasing temperature of annealing.

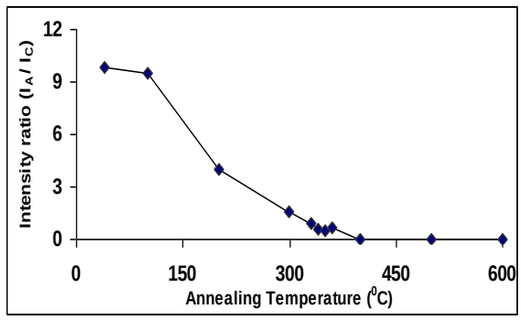

Fig .7 Variation in the integrated intensity ratio (I_A/I_C) as a function of annealing temperatures

3.2.2 Variation in the Integral Breadth

The variations in the integral breadth of diffraction profiles from crystalline and amorphous phases present in the deposits, on heat treatment are shown in figures 8 and 9 respectively. From figure 8, it is observed a slight but systematic reduction in the integral breadth of the diffraction profiles of crystalline material up to 330^{0}C. However, there is no corresponding appearance of other reflections from the crystalline phase except in the case of samples annealed at 300^{0}C and above. The reduction in integral breadth up to this temperature could be due to rearrangement of atomic positions to lower energy configurations which is somewhat similar to the recovery process. However the annealing temperature region from 330^{0}C to 340^{0}C, there is a sharp reduction in the integral breadth of the crystalline reflection signaling extensive crystallization of the matrix, accompanied by a similar reduction in the amorphous fraction of the deposit (figure 8).

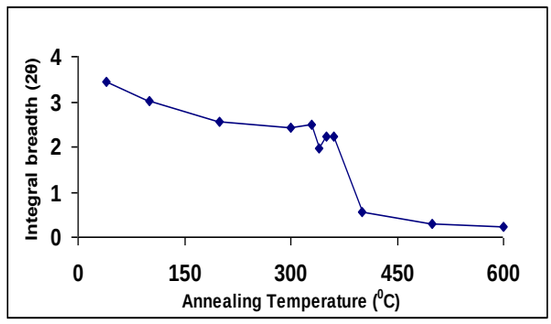

Fig .8 Variation in integral breadth of crystalline phase as a function of annealing temperatures

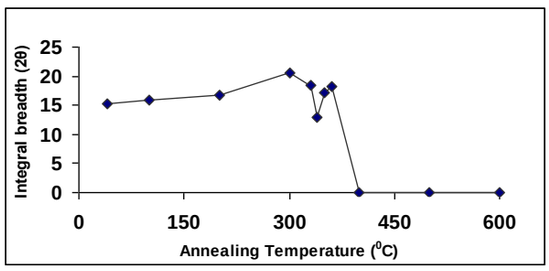

Fig .9 Variation in integral breadth of amorphous phase as a function of annealing temperatures

In contrast, the breadth of the diffraction profile increases in this range before dropping sharply to a lower value just before extensive recrystallisation of the amorphous phase (figure 9). A steep reduction in the Integral breadth of diffraction profiles from crystalline phase is observed for the specimens annealed above 350^0C. This reduction in the magnitude of integral breadth is indicative of annihilation of atomic scale defects and reduction in the phosphorous content in the crystalline portion of the matrix material. The integral breadth of the amorphous material also gets affected in a similar manner and at around 400^0C it becomes close to zero.

3.2.2 Variation in the Crystallite size and Micro-strain

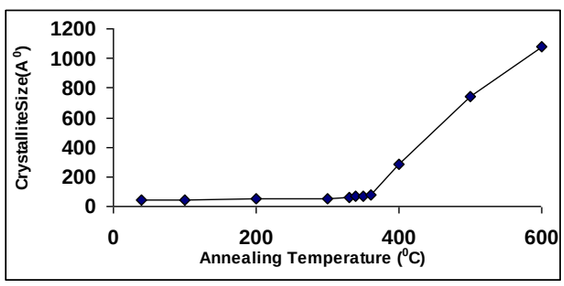

Fig. 10 Variation in crystallite size as a function of annealing temperatures.

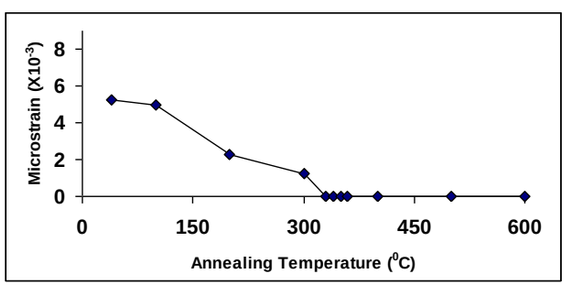

Fig. 11 Variation in micro-strain as a function of annealing temperatures.

The variation of crystallite size with annealing temperature is presented in figure 10. The crystallite size is gradually increasing with annealing temperature. And a gradual reduction of microstrain upto 300^0C can be observed from figure 11. The reason could be the rearrangement of defects into low energy configurations in the microcrystalline nickel lattice. From the annealing temperature from 300^0C to 360^0C one can easily observe the reduction in microstrain. The relaxation of crystalline nickel matrix and consequent decrease in the coherency strains between the nickel matrix and Ni_3P precipitates could be the reason for this reduction in the microstrain. A sharp increase in crystallite size appears to be the main feature of annealing above 360^0C, indicating grain growth.

4. Conclusions

Based on the experimentation and analysis, following conclusion was drawn:

1. A complete conversion to crystalline phase is occurred at 360^0C, accompanied by the completion of precipitation of Ni_3P phases.
2. Up to 330^0C, the integral breadth is reducing due to rearrangement of atomic positions.
3. Above 350^0C, Integral breadth of diffraction profiles from crystalline phase is reduced drastically which would be an indicative of annihilation of atomic scale defects
4. The crystallite size is increasing with annealing temperature, but reduction in microstrain is observed for the annealing temperature from 300^0C to 360^0C.

5. References

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