Electroless Plating of Amorphous Nickel Alloys and Their Application in Thin Film Hard Disks

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The basic principles involved in the electroless plating of Ni-alloys and their application in computer magnetic thin film hard disks were reviewed. Electroless Ni-plating is an autocatalytic metal coating process which is a proven technology applicable to mechanical, petrochemical, and electronics industries. Electroless Ni-deposit provides a finished part with an uniform, hard, wear-resistant, pore-free, and highly corrosion resistant surface. In addition, NiP undercoat satisfies an critical requirement that it be capable of being polished to a very high finish. In thin film disk application, the high-phosphorus Ni-deposit showed nonmagnetic, exceptionally pore-free, and superior corrosion resistance. It is highly expected that electroless plating of nickel alloys is a cost-effective alternative to surface modification method, providing various benefits, mainly due to the combination of their physical properties. The background of effective use of NiP-deposit in thin film hard disk is discussed in the present article.

Keywords: Electroless plating, NiP deposits, disk substrate, magnetic thin film hard disks, texturing

I. Background and Purposes

Electroless Ni-plating is a term describing the deposition of alloys composed mainly of nickel and phosphorus. The process provides a continuous build-up of a metal or alloy coating on a suitable substrate by simple immersion into a plating solution. The process is unique in terms of producing metal coating by the controlled chemical reduction of metallic cations from aqueous solution, without the use of an externally applied electrical potential.[1] Electroless Ni-deposit provides a finished part with an uniform, hard, wear-resistant, pore-free, and highly corrosion resistant surface. The uniformity, structure, chemical composition and low porosity of an electroless Ni-alloy all contribute to its excellent corrosion resistance to most organic liquids, weak acids, and alkalis.[2] Even though these attractive properties have accounted for diversified uses of the deposit in variety of industrial applications, it has not been recognized yet as a cost-effective alternative to surface modification method in domestic industries, possibly due to the limited information.[3] The amorphous Ni-alloys containing over 10 atomic percent (at.%) of phosphorus were electroless plated to study surface features of textured NiP-underlayer under the atomic force microscope (AFM). The main purpose of this article is to review principles of electroless plating of nickel and to introduce some important properties of amorphous Ni-deposits as well as their applications with basic idea involved in this process.

II. About The Process

The deposited metal is reduced from its ionic state in solution by means of a chemical reducing agent supplying the electrons for the reduction of the metallic salts to their elemental form [4]:

$$M^{n+} + ne \rightarrow M^{o} \quad (1)$$

The reduction takes place only on a catalytic surface. This requires that the metal being deposited is itself catalytic. Figure 1 shows a schematic diagram of setup for the electroless plating. In the hypophosphite-based baths, the reaction mechanism proposed is that the actual reducing agent is a hydride ion formed by catalytic decomposition of the hypophosphite ion.[5] The hydride ion H^- then reacts with Ni^{++}. Hydride ion may also be consumed by reaction with hydrogen ion. In general, most electroless Ni-coatings are deposited by the catalytic reduction of nickel ions with sodium hydrophosphite. A series of reactions can be summarized as follow.[6]

$$H_2PO_2^- + 2H^+ \rightarrow HPO_3^{--} + 2H^+ + H^- \quad (2)$$
(hypophosphite ion) (phosphite ion)

$$2H^- + Ni^{++} \rightarrow Ni^o + H_2 \quad (3)$$
$$H^- + H^+ \rightarrow H_2 \quad (4)$$

The electroless plated Ni-deposit creates a positive chemical bond to the base metal, indicating that a true metallurgical bond exists. Electroless plating (ELP) is preferentially chosen because it provides one or more of the following advantages over electroplating. For example, ELP can provide good coverage of the substrate surface when all parts of the surface have been catalytically activated.[7] In contrast to the electroplated hard chrome (Cr), no excessive build-up happens on projections or edges because current distribution is of no concern in the process. This leads to the extremely uniform and accurate coating thickness, regardless of part geometry and size. Electroless deposits are usually less porous than their electrodeposits. In addition, deposits may be produced on any substrates irrespective of electrical conductivity with a surface activation prestep. However, ELP of a metal on a dielectric substrate usually requires the prior deposition of a catalyst for the activation of surface to be plated.

III. Electroless plating of amorphous NiP-deposits

The alloy deposit is dependent on the formulation of plating solution used and the kinetics of each individual reaction in the reduction process. Each of these reactions may be effected by various factors including bath pH, plating temperature, concentration of each species, and degree of agitation. The phosphorus content of deposit is affected by bath pH. In general, decrease in pH results in higher P content. Most acid baths produce deposits containing about 7 to 10% P, whereas most alkaline baths about 5 to 7% P. The high density magnetic thin film disks used for study of NiP-sublayer in this work were prepared by using sputter deposition of CoPtCr/Cr on the ELP nickel (11 at.% P). To begin with, the Al-Mg alloy substarte was electroless plated, at pH 5 and 90℃ in solutions, with a NiP layer about 15 μm in thickness. The plating solution contained nickel, complexing agents, buffers and stabilizers as main ingredients. Detailed information on chemical composition of the plating solution is given in Table 1. A mild non-etching alkaline cleaner was required in the initial stage of the preplate cycle. This is followed by an extremely acidic treatment was then used to remove oxide films from the Al-discs so it can properly receive the zincate treatment. The process cycle for ELP of nickel on both 5086 Al-alloy and plain carbon steel is summarized below. 1) Alkaline clean in a mild, non-etch cleaner, 2) Rinse, 3) Acid clean and deoxidize in a mild non-etch cleaner, 4) Rinse, 5) Zincate 20~25 seconds at room temperature, 6) Thorough rinse, 7) Strip the zincate deposit in 60%

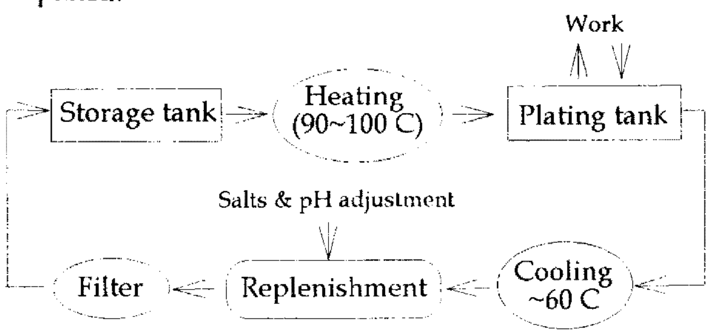

Figure 1. A schematic diagram of setup for the electroless plating

by volume nitric acid, 8) Rinse, 9) Zincate 15 seconds at room temperature, 10) Thorough rinse (double rinse, counter-flow), 11) Neutralize in a sodium bicarbonate solution, 12) Rinse with deionized (DI) water, and 13) Electroless N-plate. The plated NiP-substrate was initially polished to a submicron surface finish and then textured in the circumferential direction using extremely fine (4000 mesh) SiC abrasives.

Table 1. The composition of the electroless plating Ni-bath.*

Bath Composition	Plating Solution
Nickel chloride, $NiCl_2$-$6H_2O$	30
Sodium hypophosphite, NaH_2PO_2-H_2O	10
Sodium hydroxyacetate, $CH_2OHCOONa$	10
Thiourea, NH_2CSNH_2	0.001

* Given in g/liter

IV. Results and Discussion

IV.1 Structure and properties of ELP amorphous Ni-deposits

The physical properties of electroless plated NiP-deposits are summarized in Table 2. It is clear from the table that as-deposited NiPs show over VHN 500 and adhesion of over 30,000 psi to Al- and steel substrates. The microstructure of as-deposited alloys was amorphous, possessing no grain structure, and was very dense. The typical example of X-ray diffraction profile of the electroless plated NiP-deposit is shown in Figure 2. As can be seen from the figure, it reveals amorphous structure, leading to the unique combination of high hardness and good corrosion resistance. Microstructure point-of-view, the deposit formed during the reduction of nickel by hypophosphite consisted of supersaturated solid solutions of phosphorus in nickel, which means that they have no crystal or phase structure. As-plated hardness of ELP nickel was about 620 VHN_{100}, suggesting excellent protection against wear and abrasion. Figure 3 shows a cross-sectional microstructure of a NiP plated plain carbon steel immersed in 10% nital etchant for 10 seconds, revealing an excellent corrosion resistance of NiP over a substrate (plain carbon steel in this case). This coincides with previous studies showing excellent resistance to corrosion and abrasion. [2,4]

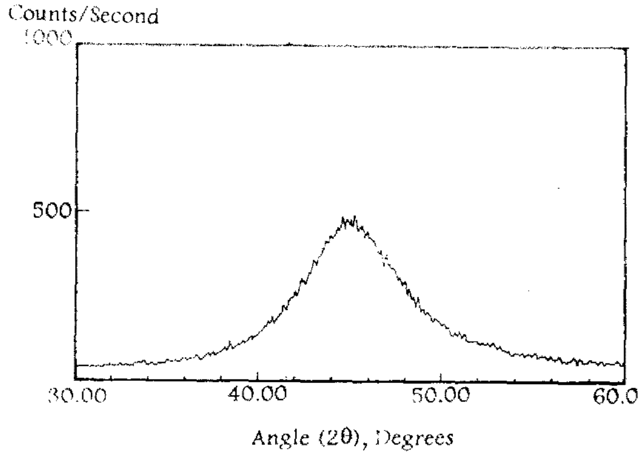

Figure 2. X-ray diffraction profile of as-plated nickel deposit (11 at.% P)

In order to meet the critical requirements of some engineering applications, the electroless Ni-plating solution must be selected based on the properties of its deposit. Depending on bath composition and plating conditions, ELP processes can produce phosphorus contents of up to 12 wt.%. In addition, depending on the phosphorus content, the microstructure and properties of the coatings can be varied within a wide range. In general, low phosphorus coatings are preferred for applications requiring solderbility, high as-deposited hardness, electrical conductivity and hot-alkali resistance. On the

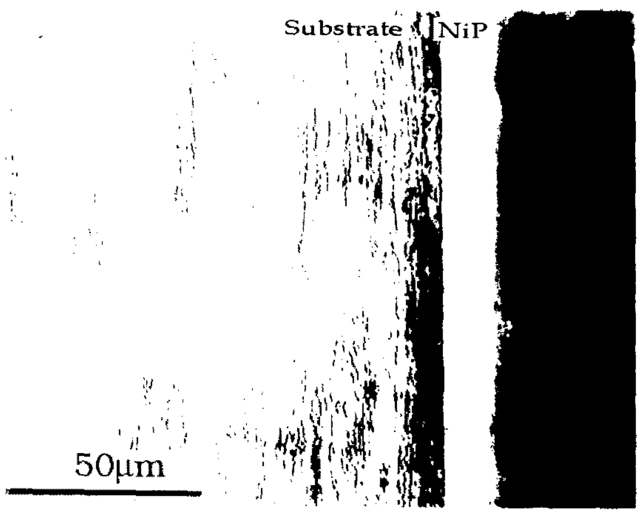

Figure 3. Cross-sectional microstructure of the electroless NiP plated plain carbon steel

Table 2. The physical properties of electroless plated NiP deposits

Composition	88~97 at.% Ni, 3~12 at.% P
Melting point	880~890℃
Adhesion	30,000~60,000 psi (to steel substrate)
	40,000~60,000 psi (to Al-substrate)
Hardness (as-deposited)	500~650 Vickers (VHN_{100})
Hardness (as-heat treated)	1000~1100 Vickers (VHN_{100})
Elongation	2~6 % permanent strain
Thermal conductivity	0.01 cal/cm·sec.℃
Thermal expansion coefficient	~1.20×10^{-5} cm/cm/℃
Internal stress	-15,000 ~ +40,000 psi (-10.8 ~ +28 Kg/mm^2)
Reflectivity	45~50 %

other hand, high phosphorus deposits have low internal stress, low magnetic susceptibility and porosity, better ductility, acid resistance and thermal stability. Coatings with low phosphorus content are microcrystalline, while coatings with high phosphorus content (P> 8.5 wt.%) are amorphous and show high corrosion resistance. The variation of physical properties of as-plated NiP deposits is summarized in the Table 3.[8] ELP Ni-deposits containing more than 9 at.% phosphorus are considered nonmagnetic as plated. However, deposits containing more than 9% phosphorus show slightly magnetic upon heat treatment. A deposit with 11 at.% phosphorus has no measurable coercivity and are nonmagnetic. These properties shown in the earlier tables (2 and 3) are an important factor in the choice of ELP for magnetic thin film computer disks and other electronic applications to be discussed later.

IV.2 Application of ELP nickel in thin film hard disks

The ELP NiP-deposit serving as an undercoat for computer hard disks must be exceptionally pore-free and have superior corrosion resistance for enhanced durability and performance in the Co-alloy thin film media. Figure 4 shows a cross-sectional view of a computer hard disk. Al-alloy substrates are plated with approximately 15μm thick electroless NiP coating, and polished back to 13μm. Then, disks were circumferentially roughened by a process described in the section III. The disk's recording media require hard magnetics so that permanent magnetic domain can be produced. All materials in close proximity to or in contact with these magnetic materials must be nonmagnetic. This essentially true of the electroless plated NiP undercoat, which must be nonmagnetic as-plated and remain nonmagnetic even when exposed to preheating temperatures (usually $T_{sub} < 200^{o}C$) of substrate during the sputter deposition. Because

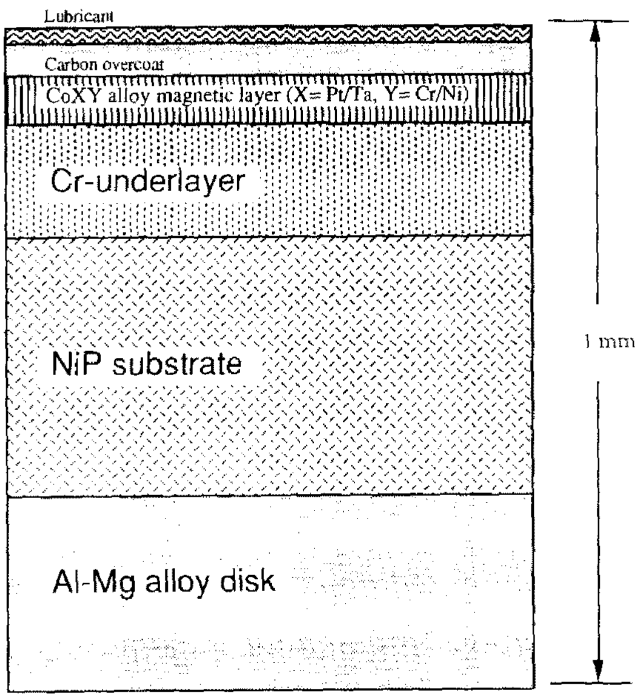

Figure 4. Schematic drawing of the magnetic thin film hard disks (cross-sectional view)

Table 3. Physical properties of ELP NiP-deposits as a function of P-contents

Properties	*P<3 at.%*	*3<P<8 at.%*	*P>9 at.%*
Density (g/cm^3)	8.5	8.1	7.9
Electrical resistivity (μΩ-cm)	20~30	50~70	110
Thermal conductivity (cal/cm-K)	-	-	0.02
Thermal expansion coeff. (μm/m/℃)	13	12	11
Coercivity (oersteds, Oe)	10	1~2	0
	FM *	WM	NM

* FM: ferromagnetic, WM: weakly magnetic, NM: nonmagnetic

the electroless NiP-undercoat is exposed to the magnetic field used to record data on the Co-alloy media. If the undercoat retains any magnetism, a change in recording and erasing energy would be required. Retained magnetism in the ELP NiP-undercoat could cause the recording signal to be weaker or could erase the recording signal, depending on the strength of the retained magnetism. According to the previous studies, even a small amount of retained magnetism results in a loss of signal and noise. It was shown from the process that NiP-undercoat satisfies an critical requirement since it was completely free of all defects, including surface roughness and pits. Therefore, it was turned out to be capable of being polished to a very high finish, even after texturing (Figure 5). The circumferential texturing was originally incorporated to reduce the real contact

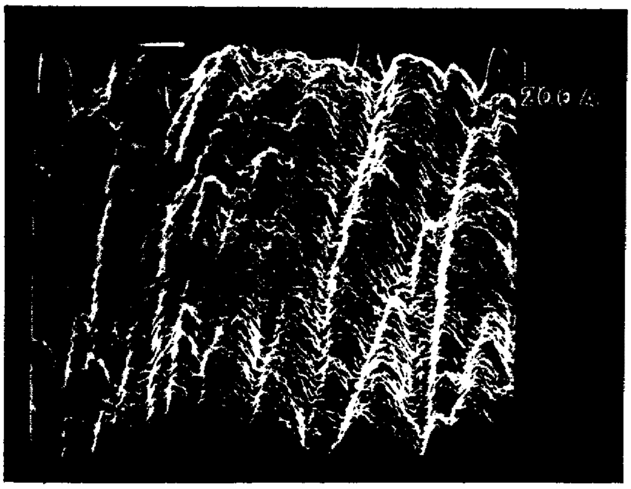

Figure 5. AFM micrograph of as-textured NiP-surface to be used for the disk substrate

area between the head and disk, and thus reduce the stiction forces. It also plays a important role that the texture grooves induce an anisotropy in magnetic layer.[8,9] In a case of sputtered media, texturing clearly improves the characteristics of signal modulation most probably due to anisotropies produce in in-line deposition systems. Sputter deposited longitudinal thin film media with magnetization easy axis along the circumferential direction show higher squareness and better performance in read/write characteristics compared to the isotropic media. [10,11] Based on the previous study [11], the controlled texturing of the polished NiP surface prepared for this study was very effective for controlled magnetic properties and improved stiction performance.

VI. Summary

Electroless nickel plating is an autocatalytic metal coating process which is a proven coating technology applicable to mechanical parts and electronic devices. It was shown from the results of electroless plating that amorphous nickel containing 11 at.% of phosphorus concluded satisfactorily for NiP-sublayer as a underlayer of thin film hard disk. As shown in the features of as-plated and textured surfaces, electroless nickel demonstrated a finished part with an uniform, hard, wear-resistant, pore-free, and highly corrosion resistant surface. Electroless plating of Ni-alloys provides various benefits, mainly due to the combination of physical properties as a cost-effective alternative to surface modification method in variety of industrial applications. It is highly expected that electroless Ni-deposits continue to expand in variety of applications.

VII. References

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