

**CHARACTERIZATION OF Ni-P AND Ni-P-PTFE
ELECTROLESS THIN FILMS BY ELLIPSOMETRY
AND BY SEVERAL SURFACE MICROSCOPIES**

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SUMMARY

In this work, Ni-P and Ni-P-Teflon electroless thin films were optically characterized by ellipsometry. The measured ellipsometric angles Δ and Ψ are used to calculate the dielectric constant spectra of these materials. Effective medium theories (Bruggeman and Maxwell-Garnett) have been employed to determine the quantity of Teflon particles in Ni-P-Teflon systems. To complement ellipsometric data, SEM/EDS and SIMS analysis have been used as well as AFM imaging.

INTRODUCTION

The diversity of applications in metal finishing industry of electroless films is widely known. Due to its nature, the electroless nickel process produces deposits of uniform thickness with excellent corrosion resistance [1, 2], due to the inherent passivity of the nickel-phosphorus alloys, and to their almost pore-free morphologies [3]. The scope of electroless nickel has been further increased by the incorporation of special materials such as silicon carbides and fluoropolymers, among others. The codeposition of SiC improves the hardness and wearability of the deposited layer, whereas the inclusion of PTFE particles diminishes the friction coefficient and increases the lubricity of the film [4].

The purpose of this work is to compare some properties of Ni-P deposited layers with those of a composite material, Ni-P-Teflon, and to determine the quantity and the distribution of Teflon particles in the latter ones.

In fig. 1 are schematised two series of Ni-P layers (A) and Ni-P-Teflon layers (B) at several stages of film growth. The questions which may have to be answered are:

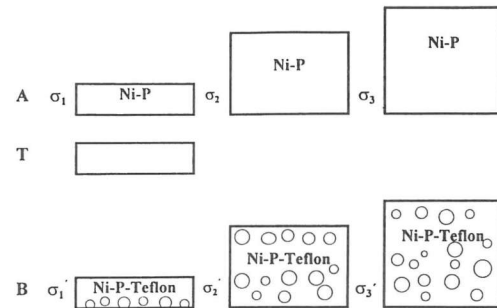


Figure 1 - Representation of layers thickness.

Are the properties and composition of Ni-P in the composite Ni-P-Teflon the same as in Ni-P itself? The answer will be searched for, in ellipsometric measurements. The configurations of Ni-P and Ni-P-Teflon are they the same? AFM pictures will allow the comparison.

EXPERIMENTAL

The characteristics of different samples are summarised in Table 1.

ENTHONE-OMI ENPLATE™ Ni 380	Ni-P (A)	Ni-P-PTFE (B)
ENPLATE 380 A (ml/l sol.)	50	50
ENPLATE 380 B (ml/l sol.)	200	200
ENLUBE PTFE dispersion (ml/l sol.)	-	10
T (°C)	88 - 89	88 - 89
t _{dep} (min)	5 10 15 30 60 120	5 10 15 30 60 120
σ (7.8 ≤ d ≤ 8.2) (μm)	2.0 4.0 6.0 10 22 43	
σ (d = 6.1) (μm)		0.8 1.6 2.4 4.0 8.2 18

Table 1 - Experimental conditions and layers thickness obtained of Ni-P (A) and Ni-P-PTFE (B) electroless films.

Optical experiments were carried out using an ellipsometer with phase and azimuth modulation, described elsewhere [5]. The characteristic parameters Δ and Ψ, were

- Is the composition of A and B samples a function of layer thickness? In other words, does the composition vary along the film growth? The answer will be given by SEM and SIMS experiments.

- What is the partial volume occupied by Teflon particles?

SEM/EDS analysis were performed with a Scanning Electron Microscope from PHILIPS, model 501B (15 KV) with an X-Rays detector of Si(Li) equipped with analytical system LINK. SIMS apparatus comprises an electronic microprobe from CAMECA, IMS 4F (Cs⁺ source at 200 nA and 14.5 KV with a scanning beam of 250×250 μm²).

determined in the wavelength range of 425 nm < λ < 675 nm (energy range of 1.83 eV to 2.92 eV). If φ₀ was the incidence angle, the complex dielectric function (ε₁ - jε₂) of the samples was calculated from the following equations [6]:

$$\epsilon_1 = \sin^2 \phi_0 \left(1 + \frac{\text{tg}^2 \phi_0 (\cos^2 \Psi - \sin^2 2\Psi \sin^2 \Delta)}{(1 + \sin 2\Psi \cos \Delta)^2} \right)$$

$$\epsilon_2 = \frac{\sin^2 \phi_0 \text{tg}^2 \phi_0 \sin 4\Psi \sin \Delta}{(1 + \sin 2\Psi \cos \Delta)^2}$$
(1)

(ε₁ is related with polarizability of materials, whereas ε₂ is proportional to the optical absorption coefficient).

AFM images were obtained with Nanoscope III from Digital Instruments.

RESULTS AND DISCUSSION

1. Composition of Ni-P electroless systems

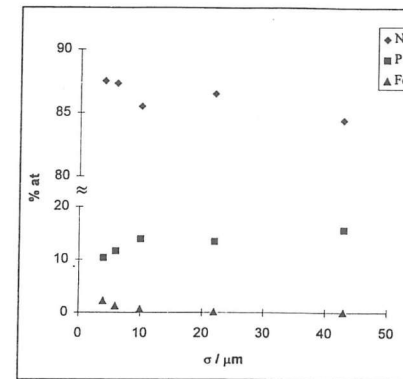


Figure 2 - Concentration profiles of Ni and P in Ni-P electroless samples.

In fig. 2 it is represented the concentration profiles of Ni and P during film growth, determined by SEM/EDS. The volume this analysis is concerned to a layer of about 1 μm thick. The curves show that during the first deposition stages (σ < a few μm) the concentration of P in Ni-P films increases from about 10 %(at), before reaching a plateau at about 15 %(at).

SIMS analysis were performed onto two Ni-P-Teflon samples (4 μm and 18 μm, thick) and confirms that the distribution profile of P and Ni is similar as in pure Ni-P layers.

Ellipsometric determination of ε spectra was carried out with several Ni-P samples. These measurements concern the surface region of absorbing materials (σ ≤ λ/10 nm) [6]. It is then justifiable to represent in fig. 3 the variation of ε₂ determined for several samples and with different wavelengths, against the corresponding surface concentration of P. It can be observed quasi linearity for this

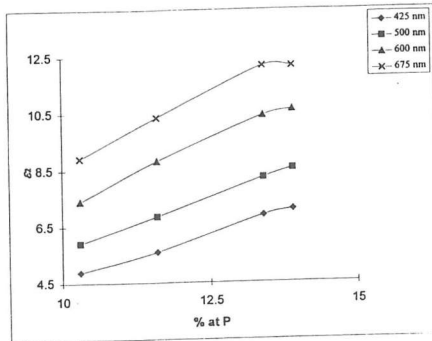


Figure 3 - Variation of ϵ_2 with P composition on Ni-P electroless films.

could be expected for a mixture with a conducting (absorbing) material and an isolating (non-absorbing) one: values of $|\epsilon_1|$ and ϵ_2 are smaller.

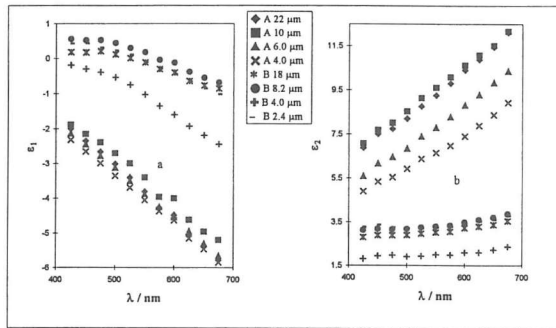


Figure 4 - Dielectric constant spectra in its real (a) and imaginary (b) parts, as a function of the wavelength used.

the results of fig. 3. It would then be well established to compare samples of Ni-P and Ni-P-Teflon having similar thickness.

3. Analysis of the dielectric function of Ni-P-Teflon

3.1 Effective medium theories

In the simple model where spherical particles of one material are dispersed in a second material and provide the particles are not too large in comparison with wavelength ($\phi \leq \lambda / 2\pi$), two main theories can be considered [7] which relate the effective dielectric function of Ni-P-Teflon (ϵ_B) to the dielectric functions of both components Ni-P (ϵ_A) and Teflon (ϵ_T), and to the effective volume v_T of Teflon particles into the composite:

variation, what proves that optical absorption is a sensitive detector for Ni-P composition.

2. Comparison of optical spectra of Ni-P and Ni-P-Teflon

In figs. 4a and 4b are represented the optical spectra for several films, of both materials. They show that:

2.1 The spectra of Ni-P-Teflon are more different from those of Ni-P, than it

To account for this difference classical theories of effective media, developed in section 3, were used.

2.2 It was verified a dispersion of the spectra with the thickness of the layers, for both materials, specially for Ni-P films, confirming

• Maxwell-Garnett equation assumes that there is no interaction between particles, which is generally true for dilute mixtures ($v_T \ll 1$)

$$\frac{\epsilon_B - \epsilon_A}{\epsilon_B + 2\epsilon_A} = v_T \frac{\epsilon_T - \epsilon_A}{\epsilon_T + 2\epsilon_A} \quad (2)$$

• Bruggeman equation assumes that each particle interacts with the overall composite, which is true for mixtures where $v_T \approx 0.5$.

$$(1 - v_T) \frac{\epsilon_A - \epsilon_B}{\epsilon_A + 2\epsilon_B} + v_T \frac{\epsilon_T - \epsilon_B}{\epsilon_T + 2\epsilon_B} = 0 \quad (3)$$

ϵ_A and ϵ_B being complex parameters, both equations (2) and (3) must be splitted into real and imaginary parts.

3.2 Ni-P-Teflon spectra

Whatever the equation, it is necessary to select the unknown parameters in the system:

• Assuming that v_T and ϵ_T are unknown whereas ϵ_A is the same in Ni-P-Teflon as well as in Ni-P layers of similar thickness, it was found that $v_T \approx 0.46$ and ϵ_T values were slightly smaller than experimental ones.

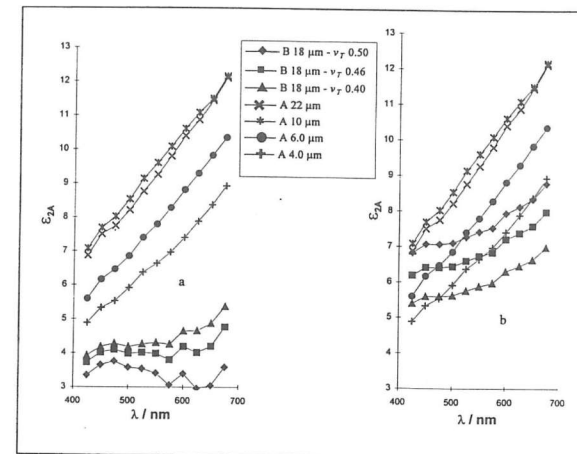


Figure 5 - Calculated ϵ_2 spectra of Ni-P (A) matrix, by Bruggeman (a) and by Maxwell-Garnett (b) theories.

both theories are compared with experimental ϵ_{2A} for pure Ni-P. It is obvious that results by Bruggeman theory do not fit the experimental spectra. Then, even with $v_T \approx 0.5$, interactions between those particles would be negligible.

Assuming now that ϵ_A is different in both Ni-P and Ni-P-Teflon films, using experimental values of ϵ_T and giving several values to v_T ($0.4 < v_T < 0.5$), it was obtained the calculated spectra for ϵ_A into the mixtures. In figs. 5a and 5b,

With Maxwell-Garnett theory, the obtained ϵ_{2A} spectra have the same order of magnitude as experimental spectra. Nevertheless the general shapes of experimental and calculated spectra are rather different, indicating that Ni-P structure would be different in pure sample than in Ni-P-Teflon.

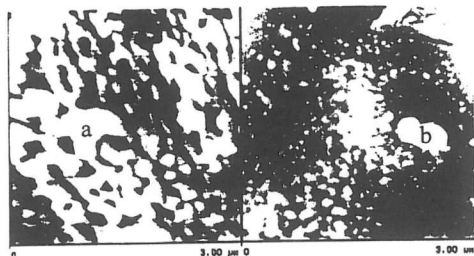


Figure 6 - AFM images of Ni-P-Teflon (a) and Ni-P (b) with the same film thickness, 10 µm.

4. AFM images of Ni-P and Ni-P-Teflon

Images in fig. 6, among several others, illustrate that the configuration of Ni-P is appreciably different in Ni-P-Teflon than in pure Ni-P.

CONCLUSIONS

The composition of Ni-P electroless deposits varies during the first stages of the film growth.

Ellipsometry reveals an efficient technique to characterize composite materials (e.g. Ni-P and Ni-P-Teflon) and the main conclusions that can be taken are:

- The effective volume of Teflon in Ni-P-Teflon is about 50 %.
- The microstructure of Ni-P is different in both pure Ni-P and Ni-P-Teflon, being this confirmed by AFM images.

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CHEMICAL AND ELECTROCHEMICAL REACTIONS OF LIGANDS ON MOLYBDENUM AND TUNGSTEN COMPLEXES

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1. Introduction

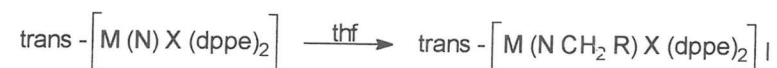
Molybdenum dinitrogen complexes have been proposed as structural models for the nitrogenase active site. Chat [1,2] reported the production of ammonia by protolysis of cis - $[\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$ and postulated the nitride complexes trans - $[\text{Mo}(\text{N})\text{X}(\text{dppe})_2]$ as intermediates in the reduction of molecular nitrogen to ammonia catalyzed by the enzyme nitrogenase. Subsequent work by Pickett et al [3-5] showed that ammonia can be produced from dinitrogen complexes in a cyclic process, including protonation and electronation steps, that parallels the Lowe and Thorneley [6] mechanism for the biological fixation of nitrogen.

Research undertaken on the chemical models of nitrogenase, besides allowing the establishment of chemical precedents for the transformation of enzymic substrates, resulted in the development of new chemistry and electrochemistry.

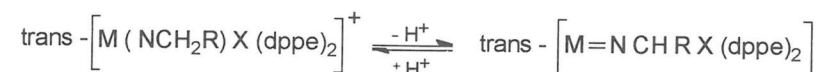
The aim of this lecture is to outline electrochemical processes leading to the electrosynthesis of dinitrogen complexes and organo-nitrogen compounds. The electron transfer chemistry of molybdenum and tungsten carboxylate-hydrides presented shows that carboxylate can be a leaving group at a reduced metal center exposing a site where dinitrogen or other substrates of nitrogenase can coordinate.

2. Chemical and electrochemical reactions of trans - $[\text{M}(\text{N})\text{X}(\text{dppe})_2]$ complexes

The nitride ligand in the complexes trans - $[\text{M}(\text{N})\text{X}(\text{dppe})_2]$ (M = Mo or W; X = halide; dppe = diphenylphosphinoethane) is a strong nucleophile and reacts with organic iodides, ICH_2R (R = alkyl, benzyl, carboxylate) to form imide complexes, according to the reaction [7-10]:



The α - carbon protons are acidic and, in the presence of a base, an amide complex is formed that can be reprotated [11]:



The amide complexes have an incipient carbanionic character and can be methylated at the α - carbon atom. As expected a racemic mixture of trans - $[\text{MoX}\{\text{NCH}(\text{CH}_3)\text{R}\}(\text{dppe})_2]^+$ is obtained.

Cyclic voltammetry of trans - $[\text{M}(\text{NCH}_2\text{R})\text{X}(\text{dppe})_2]$ (R = alkyl, benzyl) in thf/TBAB