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## FORMATION OF AMORPHOUS NICKEL-PHOSPHORUS ALLOY FILM

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### ABSTRACT

The behavior of electrodeposition of amorphous nickel-phosphorus has been studied from the point of deposition mechanism, kinetic parameters, morphology and formation of alloy films. The electrode reaction and electrode kinetics of deposition of nickel were significantly influenced by the content of phosphorus. The cathodic deposition of nickel-phosphorus alloy might be governed by the diffusion process of phosphorous acid. The direction of growth layer of the nickel-phosphorus alloy was different with substrate material. The formation of nickel-phosphorus alloy films was affected considerably by the solution compositions, electrolytic conditions and properties of the material as an underlayer.

### INTRODUCTION

The amorphous nickel-phosphorus alloy thin films are used as the industrial materials<sup>1)</sup>. This amorphous alloy has become special interest recently for functional films. Therefore, physical properties such as morphology and structure of the deposited nickel-phosphorus alloy films has been studied by many authors<sup>2)</sup>.

The formation of nickel-phosphorus alloy thin films has been considered to be the induction of the nickel<sup>3)</sup> or deposition rate was decreased by the adsorption of phosphorus on the reaction interface<sup>4)</sup>. However, the electrode reaction of the nickel-phosphorus deposition has not intensively studied. In this paper, codeposition behavior of the phosphorus in the nickel have described. The reaction mechanism, kinetic parameters, morphology

and formation of nickel-phosphorus alloys are investigated from the measurement of polarization or analysis of deposited films.

### EXPERIMENTAL PROCEDURE

The measurement was carried out in watts bath ( $240\text{g} \cdot \text{dm}^{-3} \text{NiSO}_4 + 45\text{g} \cdot \text{dm}^{-3} \text{NiCl}_2 + 30\text{g} \cdot \text{dm}^{-3} \text{H}_3\text{BO}_3$ , pH 1.0~3.0) containing a small amount of phosphorous acid. The temperature of solution was kept at 50°C. A rolled nickel or copper (purity : 99.99%) were used for working electrodes. The electrodes were polished with emery paper and chemically etched with 30wt% nitric acid. The potential was measured against a silver-silver chloride electrode at 50°C and it was measured with a high impedance voltmeter. The cathodic potentiostat. The codeposition process or electrode reaction of nickel-phos

phorus deposition has been studied using rotating disk electrode techniques. The morphology of the deposited nickel-phosphorus surface was analyzed by means of an electron microscope and the composition of alloy films was determined by the X-ray diffraction or electron probe microanalysis.

## RESULTS AND DISCUSSION

### Electrodeposition process of nickel phosphorus alloy

The influence of concentration of phosphorous acid on the cathodic polarization curve of nickel was investigated by the rotating disk electrode techniques. In the range of cathodic potential less than  $-300\text{mV}$  (against  $\text{Ag}/\text{AgCl}$  sat.  $\text{KCl}$ ), nickel begins deposit.

The codeposition of phosphorus in the electrodeposited nickel under galvanostatic or potentiostatic electrolysis takes place at about  $100\text{mV}$  nobler cathodic potential than the potential without phosphorous acid. Limiting current density of nickel deposition is indicated at cathodic potential about  $-550\text{mV}$ . The influence of concentration of phosphorous acid and rotation speed of electrode on the cathodic limiting current density is shown in Fig. 1. The values are increased with an increasing phosphorous acid or rotation speed. Deposition of nickel-phosphorus was accelerated by raising the phosphorous acid content of the bath. From the Nernst equation, the potential of hydrogen evolution and nickel deposition corresponds to less than  $-530\text{mV}$  and  $-690 \sim -790\text{mV}$ , respectively<sup>5)</sup>.

Therefore, it is considered that the codeposition of phosphorus is produced at potential in the vicinity of limiting current density.

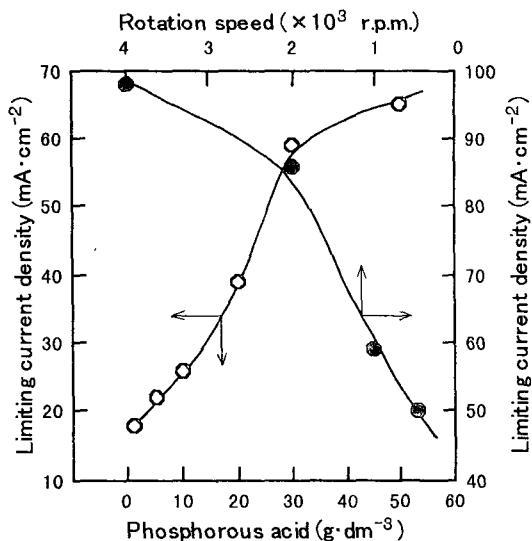


Fig. 1 Influence of phosphorous acid and rotation speed on the limiting current density of nickel electrodeposition.

The relation between logarithm of current density and cathodic potential was linearly at the cathodic potential region of  $-320 \sim -430\text{mV}$ . The Tafel equation is applicable at this potential region and the charge-transfer reaction was rate-determining step. The kinetic parameters such as exchange current density or coefficient of Tafel b can be obtained from the Tafel plots. The stoichiometric number ( $\nu$ ) can be calculated from the Tafel equation. Table 1 shows the influence of con-

Table. 1 Influence of phosphorous acid on the kinetic parameter of electrodeposition.

$\text{H}_3\text{PO}_3$ concentration ( $\text{g}\cdot\text{dm}^{-3}$ )	$i_0$ ( $\text{mA}\cdot\text{cm}^{-2}$ )	b ( $\text{mV}\cdot\text{decade}^{-1}$ )	$\nu$
0	$1.6 \times 10^{-4}$	116.4	1.91
1	$7.5 \times 10^{-6}$	59.7	
10	$2.6 \times 10^{-6}$	61.7	0.95
30	$1.9 \times 10^{-6}$	60.3	
50	$1.2 \times 10^{-6}$	63.4	

centration of phosphorous acid on the kinetic parameters of nickel electrodeposition.

The exchange current density of nickel deposition decreased rapidly and the coefficient of Tabel b or stoichiometric number reduced by approximately one-half when the phosphorus codeposited with the nickel. The electrode reaction of nickel was remarkably influenced by the codeposition of phosphorus. From the value of stoichiometric number( $\nu$ ), it was considered that the electrode reaction of nickel and nickel-phosphorus deposition were controlled by the charge-transfer reaction with one-electron-two-step<sup>6)</sup> and two-electron-one-step process, respectively.

### Analysis of deposited nickel-phosphorus alloy

The surface structure of nickel-phosphorus alloy obtained with galvanostatic or potentiostatic electrolysis was analyzed by the X-ray diffraction patterns or EPMA.

The influence of phosphorous acid and rotation on the peak intensity and half peak width of the X-ray diffraction patterns of electrodeposited nickel(111)plane is shown in Fig. 2. The peak intensity decreased and half peak width of electrodeposited nickel(111) and (200)planes increased with and increase in the phosphorous acid content of the bath or rotation speed. Table 2 shows the influence of current density, solution pH, and rotation on the phosphorus content in the electrodeposited nickel alloys. Parenthesis is indicated the phosphorus content without agitation. The phosphorus content increased with lower bath pH, Lower current density and higher rotation speed.

The amorphous nickel-phosphorus films

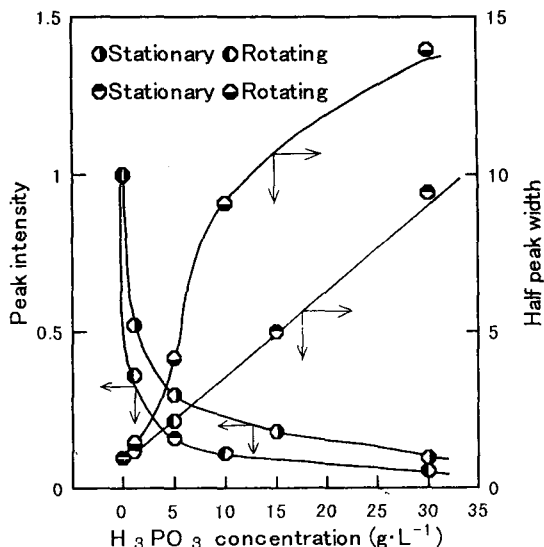


Fig. 2 Influence of phosphorous acid and rotation on the peak intensity and half peak width of X-ray diffraction pattern of electrodeposited Ni(111) plane.

Table. 2 Influence of current density, solution pH and agitation on the phosphorus content (wt%) in the electrodeposited nickel film.

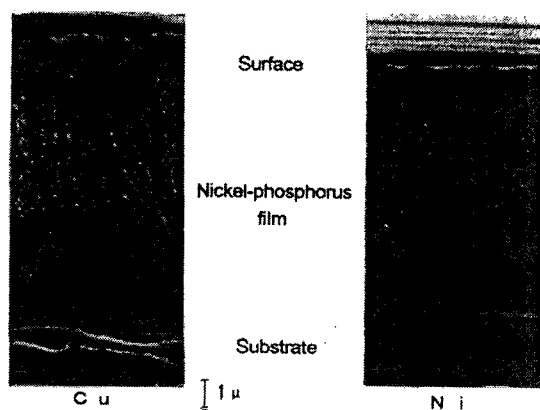
pH	Current density ( $\text{mA} \cdot \text{cm}^{-2}$ )						
	5	10	30	50	60	70	80
1.5	18.91 (19.52)		18.30 (14.90)	(9.01)		13.61	3.84
2.0	16.86 (17.80)		(8.49)	(8.45)		11.26	4.10
2.5	14.88 (13.61)			12.05	10.60		

was formed in the current density region of 5 to  $70 \text{ mA} \cdot \text{cm}^{-2}$  or cathodic potential region of  $-560$  to  $-700 \text{ mV}$ . The deposit with laminar structure was observed. The phosphorus in the nickel alloy deposits was included about 10~80 wt% of hat of nickel and it was relatively high in the initial stage of low overpotential (noble cathodic potential) or low current density electrolysis. The influ-

Table 3 Influence of plated underlayer on the cathodic potential, current efficiency, phosphorus content and structure of deposited nickel alloy.

Substrate	Cathodic potential (mV)	Current efficiency (%)	P content (wt%)	Cross-section
Copper	-682	69.7	16.1	Vertical growth
Nickel	-722	72.6	15.9	Horizontal growth

Photo. 1 Influence of substrate material on the cross-section of deposited nickel phosphorus film.



ence of substrate material on the cathodic potential, current efficiency, phosphorus content and structure of deposited nickel alloy is shown in Table 3. The deposition behavior of nickel-phosphorus alloys was affected significantly by the cathodic overpotential of the substrate. The cross-section of the deposited nickel-phosphorus film on nickel substrate was layered structure, while the vertical growth was observed with copper substrate (Photo 1). This is probably due to the overpotential of the substrate material. The formation of nickel-phosphorus alloys was affected considerably by the bath compositions, electrolytic conditions and properties of the material as an underlayer. The amorphous nickel-phosphorus alloys was formed

easily under rotating conditions. The dodeposition of phosphorus is related to thickness of diffusion layer. It was considered that the cathodic deposition process of nickel-phosphorus alloy might be dominated by the diffusion process of phosphorous acid.

## CONCLUSION

The electrodeposition of nickel-phosphorus alloy has been studied using galvanostatic or potentiostatic techniques, and the nickel-phosphorus deposits were analyzed by means of an electron microscope or X-ray diffraction.

The kinetic parameters and electrode reaction of nickel were changed by the codeposition of phosphorus. The formation of amorphous nickel-phosphorus alloys was controlled by the diffusion of phosphorous acid and was affected by the bath compositions or electrolytic conditions. The direction of growth layer of the nickel-phosphorus alloy was different by the material as an underlayer.

## REFERENCES

1. Y. Tanaka, *Kinzoku Zairyo*, 16, 58 (1976)
2. M. Ogata, *J. of Surface Finishing Society of Japan*, 41, 1274 (1990)
3. T. Omi, *J. of Surface Finishing Society of Japan*, 40, 368 (1989)
4. T. Watanabe, *J. of Surface Finishing Society of Japan*, 40, 275 (1989)
5. S. Tajima, *Denki Kagaku Tsuuron*, Kyoritu Syuppan, 1969, p.186.
6. T. Masuda, T. Yamashita, 26th Denchi Symposium, 1985, p.325.