Effects of Codeposited Tungsten on the Properties Of Low-Phosphorus Electroless Nickel Coatings

By Jun Li, Xinguo Hu and Dianlong Wang

Codeposition of tungsten in electroless Ni-W-P ternary plating can reduce the phosphorus content in deposits. The structure, solderability, wear resistance and electrical resistivity of Ni-W-P and Ni-P films with low phosphorus were investigated. The results of X-ray diffraction showed that addition of tungsten did not affect the crystalline structure of low-phosphorus Ni-P deposits. Both Ni-W-P and Ni-P alloy coatings with the same low phosphorus exhibited excellent solderability and could be completely wetted within 1-2 seconds by wetting time measurement method. It was confirmed that codeposition of tungsten improved the wear resistance and increased the electrical resistivity of low-phosphorus Ni-P deposits by Taber abrasion test and four-probe method, respectively.

Electroless Ni-P deposits containing less than five wt percent phosphorus are classified as low-phosphorus electroless Ni-P (LPEN) alloy deposits.[1] Because of low phosphorus content, they appear to have well-defined crystalline structure and excellent wear resistance, solderability, electrical resistivity, high as-plated hardness and strong hot-alkali resistance. Accordingly, LPEN deposits can meet many critical requirements of engineering applications.

Since the investigations of Pearlstein and Weightman in 1963,[2] many workers have reported the electroless Ni-W-P ternary alloy.[3-6] Although alloying with tungsten greatly improves the thermal stability and corrosion resistance of Ni-P deposits, it is also found that codeposition of tungsten can reduce the phosphorus content in alloy deposits. Therefore, in this paper, we discuss the properties of low-phosphorus electroless Ni-W-P ternary alloy by comparison with LPEN and try to find an effective process of obtaining low-phosphorus deposits.

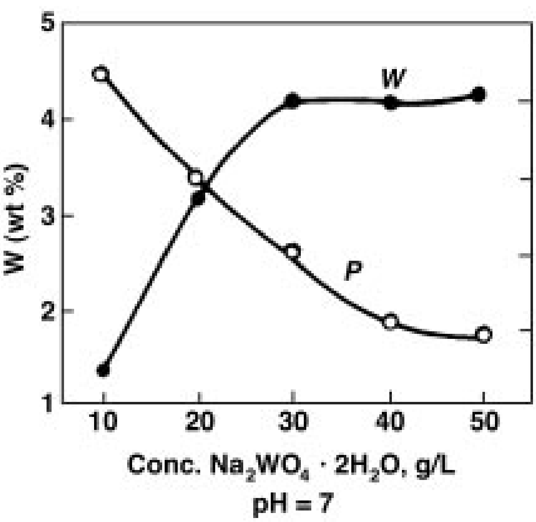

Fig. 1—Effect of Na_2WO_4 concentration on tungsten and phosphorus content of deposits.

Table 1
Composition and Plating Conditions
For Electroless Ni-W-P and Ni-P Alloy

Composition	Conc. of Ni-W-P g/L	Conc. of Ni-P g/L
$NiSO_4 \cdot 6H_2O$	20	20
$NaH_2PO_4 \cdot H_2O$	20	20
$Na_3C_6H_5O_7 \cdot 2H_2O$	35	30
$C_3H_6O_3$	5	—
$(NH_4)_2SO_4$	30	—
$Na_2WO_46 \cdot 2H_2O$	10~50	—
pH	5~9	5~9
pH adjustment	$NH_3 \cdot H_2O$	$NH_3 \cdot H_2O$

Experimental Procedure

The basic composition and plating conditions of electroless Ni-W-P and Ni-P plating baths are listed in Table 1. The carbon steel substrate surface was degreased in a hot alkaline solution at 60 °C, then activated with 20-vol-percent HCl prior to plating. The alumina substrate surface needed a two-step sensitization and activation immersion procedure after degreasing. The sensitizer was $SnCl_2 \cdot 2H_2O$, 1.0 g/L; 37-percent HCl, 1.0 mL/L; and the activator was $PdCl_2$, 0.1 g/L in 37-percent HCl, 0.1 mL/L.

The composition of the deposits was determined by electron probe microanalyzer; the structural characteristics were determined by X-ray diffraction analyzer. The Taber abrasion test was employed to examine the wear resistance. The diameter of the abrasive disc was 42 mm, wear time 15 min, load 300 N, and rotation speed 200 rpm. The electrical resistivity of deposits was measured by the four-probe method.

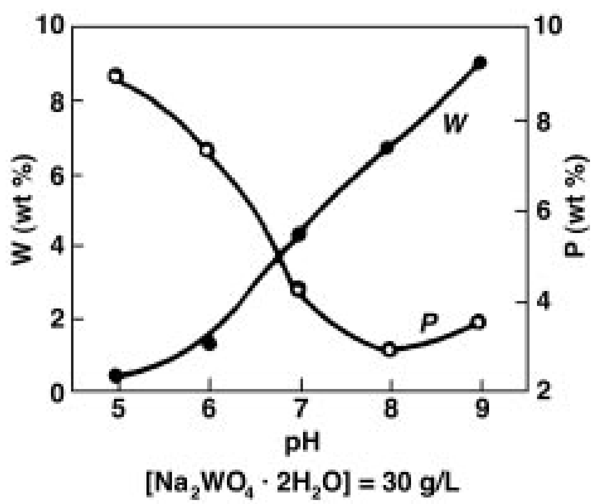

Fig. 2—Effect of pH on tungsten and phosphorus content of deposits.

Table 2
Electrical Resistivity of Alloy Deposits

Tungsten (wt %)	Phosphorus (wt %)	Resistivity μΩ-cm
0	2.8	28
0	3.2	30
0	4.6	39
4.3	2.2	55
9.6	3.6	62
3.5	4.1	73
1.5	7.4	126
0.4	9.1	133

To determine the solderability of Ni-W-P and Ni-P deposits, 10 specimens were immersed in Sn60-Pb40 solder at 250 °C after dipping in rosin flux. The immersion time was controlled from 1 to 10 sec. The solderability could be evaluated by wetting time. The deposits that could be completely wetted within two sec had the best solderability.

Results and Discussion

Deposit Composition and Structure

Different compositions of Ni-W-P deposits can be obtained by varying the concentration of Na_2WO_4 and the pH. As seen in Fig. 1, a marked increase in the tungsten content of the deposits and reduction in phosphorus resulted from addition of Na_2WO_4 to the electroless nickel bath. The tungsten content attains a constant value of 4.3 wt percent after the Na_2WO_4 concentration reaches 30 g/L. The phosphorus content can be easily lowered to about two wt percent when the pH is maintained at 7. This is very difficult in electroless binary Ni-P plating. Therefore, the codeposition of tungsten is an effective method of obtaining low-phosphorus alloy deposits.

Figure 2 shows that the effect of pH on the phosphorus content in Ni-W-P deposits is similar to that for electroless Ni-P plating. When the pH increases from 5 to 8, the phosphorus content is abruptly reduced from 8.5 to 2.8 wt percent, but the tungsten content continuously increases.

The X-ray diffraction patterns of the as-plated deposits are shown in Fig. 3. Both Ni-W-P and Ni-P deposits change from amorphous to crystalline structure with reduction in phosphorus content. When the phosphorus content is below three wt percent, Ni-W-P and Ni-P alloys have well-defined crystalline structure. This indicates that the crystalline state of the Ni-W-P deposits depends mainly on the phosphorus content, as it does for electroless nickel deposits, but when the phosphorus content approaches equality for both types of deposit, the crystallinity of Ni-W-P deposits is less than that of Ni-P deposits.

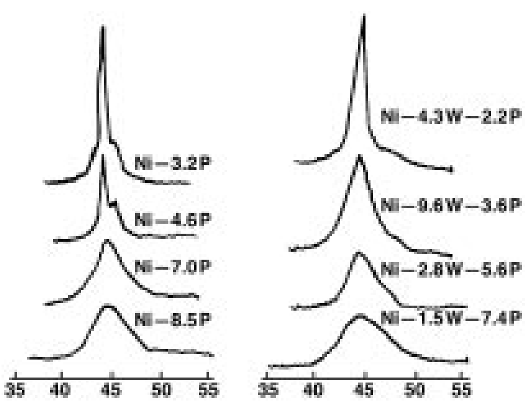

Fig. 3—X-ray diffraction patterns of as-plated N-W-P and Ni-P alloy deposits.

Table 3
Wear Resistance of Alloy Deposits

Deposits	Hardness HV	Wear Width (mm) 1	2	3	4	avg.
Ni-3.5wt%W-4.1wt%P	584	1.62	1.54	1.44	1.68	1.57
Ni-4.6wt%P	578	1.98	1.75	2.02	1.94	1.97

Table 4
Solderability of Alloy Deposits

Deposits	Wetted Area, percent 1 sec	2 sec	3 sec	4 sec	Grade
Ni-4.3wt%W-2.2wt%P	100				B
Ni-3.3wt%W-3.9wt%P	98	100			B
Ni-2.8wt%W-5.6wt%P	77	95	100		N
Ni-3.6wt%P	96	100			B
Ni-6.4wt%P	82	98	100		N

B - best, 1~2 sec; N - normal, 3~6 sec

Electrical Resistivity

Electrical resistivity values for as-plated Ni-P and Ni-W-P alloys are given in Table 2. The data show that the resistivity of Ni-W-P alloys containing low phosphorus is higher than that of LPEN deposits. Although the tungsten content decreases rapidly, the Ni-W-P alloy deposits similarly exhibit an increase in resistivity values when the phosphorus content increases. It is of interest that the results from this comparison agree well with the crystalline structure of deposits discussed earlier.

Wear Resistance

The wear resistance characteristic of the Ni-3.5wt%W-4.1wt%P and Ni-4.6wt%P alloy deposits, expressed in terms of the wear width, is listed in Table 3, which shows that the wear width of the Ni-W-P deposit is smaller than that of Ni-P. Accordingly, the Ni-W-P deposit is superior to LPEN deposits in wear resistance when the phosphorus content is kept nearly constant.

In sliding abrasion, the wear volume is often expressed quantitatively by

$$dv/dl = KP/3H$$

where dv is wear volume, P is perpendicular load, H is hardness of deposits, dl is sliding distance, and K is the wear coefficient.

It can be seen that the wear rate, dv/dl, is associated with load, hardness and wear coefficient. K is not constant and is considered the function of the following factors:

K, (sublayer deformation, crack initiation and crack propagation)
K2 (microstructure)
K3 (chemical composition, processing, temperature)

The data of Table 3 show that, in the as-plated condition, the codeposition of tungsten has no significant effect on hardness. As a result, it may be concluded that the codeposited tungsten improved the wear resistance of a Ni-P deposit mainly by influencing the wear coefficient, K. This possibility needs further investigation.

Solderability

It should be pointed out that the solderability of deposits given by the wetting time method is not absolute, but only a relative measure. It is well known that the LPEN deposits have excellent solderability. According to the data of Table 4, both Ni-W-P and Ni-P deposits with low phosphorus content are wetted within 1-2 sec, and consequently have extremely good solderability. When the phosphorus content increases, the Ni-W-P deposits show a tendency to degrade solderability, just as Ni-P deposits do.

Summary

Codeposition of tungsten can reduce the phosphorus content in deposits. The structure of Ni-W-P deposits is mainly determined by the phosphorus content. Both Ni-W-P and Ni-P with low phosphorus content exhibit a well-defined crystalline state and have excellent solderability. When the phosphorus content is kept constant, codeposition of tungsten improves the wear resistance, but increases the electrical resistivity of low-phosphorus electroless nickel deposits.

Editor's note: *Manuscript received, October 1995; revision received, May 1996.*

Acknowledgment

This study was financed by the State Key Laboratory for Corrosion and Protection, The Chinese Academy of Sciences, Shenyang.

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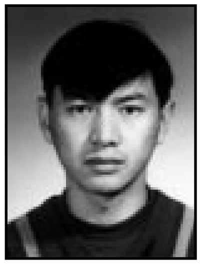

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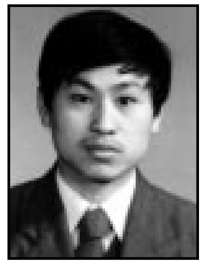

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