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SCIENCE DIRECT

Surface & Coatings Technology 200 (2006) 3675–3681

SURFACE & COATINGS TECHNOLOGY

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Influence of codeposition of copper on the structure and morphology of electroless Ni–W–P alloys from sulphate- and chloride-based baths

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Received 24 August 2004; accepted in revised form 10 September 2004
Available online 27 October 2004

Abstract

Quaternary Ni–W–Cu–P coatings were deposited by using alkaline-citrate-based nickel sulphate and nickel chloride baths. The structure and morphology of these deposits are reported for the first time and compared with ternary Ni–W–P deposits from the same baths without copper addition. Incorporation of copper has marginal influence on the nickel, phosphorus and tungsten contents of the coatings. Increase in grain size with the incorporation of copper was found in B1-based coatings, but in the case of B2 coatings, no change is observed. In case of ternary deposits, morphology of B1-based coatings was coarse, and nodular, whereas that of B2-based coatings were smoother. Addition of copper in both B1 and B2 coatings had resulted in very smooth nodular-free deposits. XPS studies showed that addition of copper increases the elemental form of W in the chloride-based deposits towards that of sulphate-based deposits. Copper has no detrimental effect on the hardness but improves the surface quality.

Keywords: Electroless Ni–W–P; Ni–W–Cu–P; XRD; SEM; AFM; XPS; Hardness

1. Introduction

Electroless plating is carried out via the redox reaction of an oxidizer and a reductant in an electrolyte solution. It is an autocatalytic process, which is widely used for the production of uniform, less porous, adherent deposit for many industrial applications. Among electroless plating of metals, electroless nickel has gained more popularity due to its excellent properties such as high hardness, wear and corrosion resistance and has been applied to various kinds of automobile, aircraft and electronic applications. These properties can be further improved through codeposition of one or two metallic elements in electroless nickel deposits.

Among the metals, tungsten has a significant importance due to its high hardness and high melting point. Electroless ternary alloys with elements other than the iron family, namely, Ni–W–P, have been first reported by Pearlstein et al. [1]. Inclusion of tungsten in binary Ni–P deposit affects the deposition rate, composition and deposit properties such as hardness, thermal stability, wear, corrosion and electrical resistance, etc. [2–6]. Ni–W–P coatings find application as heat resistors in low-energy consumption thermal heads, which are used in printing operations [7]. Surface morphology of ternary Ni–W–P deposit depends on the factors such as bath pH and included tungsten in the deposit. It was reported that when the bath's pH was 9 and incorporated tungsten in the deposit was more than 8 wt.%, the deposit was homogenous, very fine and more compact [8]. XPS studies have been carried out on Ni–P and Ni–W–P alloys [9–11]. These studies have shown that tungsten addition influences the incorporation of Ni and P in the coating, and tungsten is present in elemental as well as oxide form [10–12]. However, Bangwei et al. reported that phosphorus and tin are favorable elements, and copper is a nonfavorable element for formation of an amorphous quaternary Ni–Sn–Cu–P [13]. To our knowledge, there are no reports on the electroless plating of quaternary Ni–W–Cu–P deposits using nickel sulphate and nickel chloride. Hence, systematic

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doi:10.1016/j.surfcoat.2004.09.010

studies were carried out on the preparation of ternary Ni–W–P and quaternary Ni–W–Cu–P deposits by electroless plating and characterized for their structure, morphology and microhardness. In this paper, we report our findings on the role of copper additive on the state of W in the ternary Ni–W–P alloys and the resulting changes in the microstructure and properties.

2. Experimental procedures

The composition of the basic baths used for depositing sulphate (B1)- and chloride (B2)-based coatings and their operating conditions are given in Table 1. B1-based coatings were obtained by adding 20 g/l nickel sulphate and B2-based coatings by adding 18 g/l nickel chloride while keeping the other ingredients constant. Mild steel specimens (2.5×2.5×0.08 cm) were degreased, electrolytically cleaned, washed with deionized water, deoxidized in 50 vol.% sulphuric acid solution, rinsed in deionized water and suspended in the plating bath.

XRD measurements were made for the deposits in a plated condition with a Rigaku D/max 2200 powder diffractometer using Cu Kα radiation. Surface morphology and elemental composition of the deposits were determined by means of scanning electron microscopy (Model Leo 440I) with EDX (Oxford) attachment. Morphology of the deposits in the initial stages of growth was studied by depositing for 60 s on mild steel samples, which were metallographically polished to a roughness level of 11 nm. Deposit structure was examined by atomic force microscopy (AFM; Model SSI, CSEM). The maximum scan range for AFM in *X*, *Y*-directions was 20×20 μm^2 and 2–3 μm in the vertical direction.

The X-ray Photoelectron spectra were acquired in a VG Scientific ESCA-3 Mark II spectrometer using Al Kα radiation at 1486.6 eV. Survey spectra and high-resolution core level spectra of elements were acquired at 100 and 50 eV pass energy, respectively. The samples were cleaned with methanol before loading in to UHV system and sputter-cleaned at 5 kV Argon ions for 3 min prior to acquisition of spectra. In estimating the atomic percentages, the entire area under the core level spectra with the spin orbit doublets was used. The atomic sensitivity factors as given in [14] were used for Ni2p, P2p, Cu2p and W4f core levels. All the binding energies are referenced with respect to C1s core level at a binding energy of 284.6 eV and are given with an accuracy of ±0.2 eV. After subtraction of a linear background, the W4f core level spectra were curve-fitted with Gaussian peaks to identify different charge states. In the fitting procedure, a higher full width at half maximum was used for W in different charge states as compared to that in its elemental state.

Some samples were heat-treated for 1 h at a temperature of 400 °C to measure the change in hardness. Microhardness measurements were made on both as-plated and heat-treated deposits using a Vickers microhardness tester (Buehler) employing a load of 100 g. Five readings were taken on each deposit, and the values were then averaged.

Table 1
Composition and operating conditions of the plating bath

Constituents of plating bath	Concentration (g/l)	
	Ni–W–P	Ni–W–Cu–P
$NiSO_4 \cdot 6H_2O/NiCl_2 \cdot 6\ H_2O$	18–20	18–20
$Na_2H_2PO_2 \cdot H_2O$	20	20
$Na_3C_6H_5O_7 \cdot 2H_2O$	35	35
$CH_3 \cdot CHOH \cdot COOH$	5	5
$(NH_4)_2SO_4$	30	30
$Na_2WO_4 \cdot 2H_2O$	30	30
$CuSO_4 \cdot 5H_2O$ (mM)	–	3
Operating conditions		
pH	8.0	
Temperature (°C)	90±2	
Deposition rate (μm/h)	12–14	

Table 2
Composition of as-plated electroless Ni–W–P and Ni–W–Cu–P coatings determined through EDX analysis

Type of coating	Ni (at.%)		P (at.%)		W (at.%)		Cu (at.%)	
	B1	B2	B1	B2	B1	B2	B1	B2
Ni–W–P	89.0	85.9	9.9	11.8	1.1	2.3	–	–
Ni–W–Cu–P	86.0	82.5	9.0	10.8	1.4	1.9	3.6	4.8

3. Results and discussion

The compositions of the as-plated electroless nickel coatings analyzed by SEM-EDX are listed in Table 2. B1-

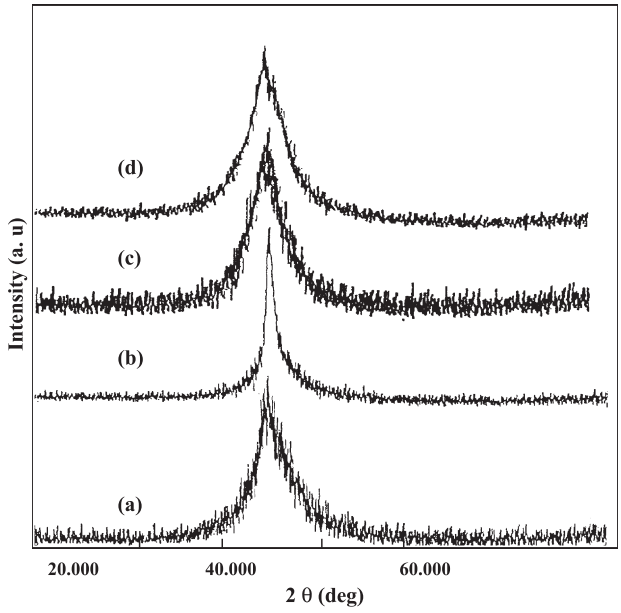

Fig. 1. XRD patterns of electroless ternary and quaternary coatings. (a) Ni–W–P and (b) Ni–W–Cu–P from B1 baths; (c) Ni–W–P and (d) Ni–W–Cu–P from B2 baths.