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Influence of pulse parameters on the microstructure and microhardness of nickel electrodeposits

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Abstract

Square-wave cathodic current modulation was used to electrodeposit fine-grained nickel from an additive-free and saccharin-containing Watts bath. The influence of pulse on-time, off-time, peak current density and saccharin on the grain size, surface morphology, crystal orientation, and microhardness was determined. The study showed that at constant off-time and peak current density, the crystal size of the deposits was found initially to decrease with pulse on-time before it started to increase with further increase in on-time. The crystal orientation progressively changed from a (111) texture at the on-time of 0.1 ms to a strong (200) texture at an on-time of 8 ms. An increase in the pulse off-time at constant on-time and peak current density resulted in a progressive increase in crystal size. However, the crystal orientation remained unaffected with increasing off-time. An increase in peak current density resulted in considerable refinement in crystal size of the deposits. The crystal orientation progressively changed from an almost random distribution at the lowest peak current density of 0.2 A/m^2 to a strong (200) texture at a peak current density of 2.0 A/m^2. The nanocrystalline nickel with grain size in the order of 30 nm can be produced from saccharin-containing Watts' baths. In contrast, when using an organic-free Watts' bath and similar pulse-plating conditions, the grain size can only be refined down to about 80–100 nm. The microhardness of deposits is related with grain size: when the grain size is large, the microhardness is consistent with Hall–Petch law (HPL); when the grain size is ultrafine, "nano-effect" would be generated, the microhardness is against HPL.

Keywords: Pulse plating; Microstructure; Nano-effects

1. Introduction

Nanocrystalline material has characteristics of small grain size, large number of interface, and large volume fraction of interface, so compared with traditional materials, it has many unique physical and chemical properties and receives extensive attention in the field of material. Usually, methods used to prepare nanocrystalline materials are sol–gel, sputtering sparks, high-energy ball milling, crystallizing from amorphous and electroplating. In comparison to traditional preparation methods of nanocrystalline material, under relatively simple conditions, electroplating can get various nanocrystalline materials, such as metal, alloy, semiconductor, wire, multilayer and composite system. Electroplating methods include direct current electrodeposition [1], pulse electrodeposition [2,3], jet electrodeposition, composite electrodeposition and so on. Nanocrystalline materials, prepared by electroplating, have high tightness and small porosity, even completely compact. Electroplating will not be restricted by the size and shape of substrate material, it usually can be completed once for all without further complicated subsequent treatment, the acquired nanocrystalline materials have some unique properties.

Over the past decade, more research about the electroplating of nanocrystalline material was carried out, with its preparation process developing from direct current electrodeposition to pulse electrodeposition. Compared with direct current electrodeposition, pulse electrodeposition can adopt higher current density and therefore can get nanocrystalline deposits with finer grains and compacter structure [4–7].

The performance of nickel electrodeposits is related with their microstructure (such as grain size, surface morphology and crystal orientation), which depended on electroplating conditions and composition of plating bath [8]. So importance has

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been gradually attached to study in this field in recent years. Nanocrystalline nickel electrodeposits with different grain size, prepared by pulse electrodeposition, were researched in this paper. The influence of pulse electrodeposition parameters and saccharin on the texture and microhardness of nickel electrodeposits was inspected particularly.

In general, experimental results of pulse electrodeposition of different researchers are difficult to compare, even contradictory in many cases. This is because of (1) many experimental factors involved in pulse electrodeposition, (2) the complexity of electrodeposition process and (3) the lack of standards about influence of pulse parameters on deposition. As to the third point, most researchers [9,10] usually study influence of duty cycle (γ) or pulse frequency (f) on structure and properties of electrodeposits, where $\gamma = T_{on}/(T_{on}+T_{off})$, $f = 1/(T_{on}+T_{off})$, T_{on} and T_{off} represent pulse on-time and pulse off-time respectively. However, f and γ do not reflect the effects of T_{on} or T_{off} separately on microstructure and performance of deposits. To study effects of the peak current density (J_p) on deposits, two methods were used commonly [11]. In the first method, T_{on} and average current density (J_m) were kept constant, J_p was increased. However, T_{off} could not be kept constant, it was unable to determine whether changes on surface morphology and microstucture of electrodeposits were caused by changes of T_{off} and/or J_p. In the second method, pulse charge (the number of coulombs per pulse, $J_p \cdot T_{on}$) and J_m were kept constant, J_p was increased. T_{off} changed slightly, but T_{on} changed obviously, therefore it was also difficult to evaluate the impact of J_p on the deposit. In this paper, modified Watts Ni baths was used, influence of saccharin and plating parameters on the microstructure and microhardness of deposits were researched under the premise of strict definition of pulse parameters.

2. Experimentation

2.1. Preparation method

A modified Watts Ni baths and electroplating process conditions are shown in Table 1. The solutions were prepared from analytic grade chemicals and double distilled water. The pH value of bath was measured by HM-20E pH-meter and was adjusted to appropriate values with $NH_3 \cdot H_2O$ (25 wt.%) and H_2SO_4 (25 wt.%) solution.

AISI 431 stainless steel sheet (15 mm × 15 mm × 0.1 mm) was used as a substrate, and a high purity (99.99%) electrolytic nickel plate was used as the soluble anode. Its surface area was approximately 10 times greater than that of the cathode to ensure that there were no problems arising from anode polarization, particularly at high current densities. The substrate was first chemically degreased, rinsed with distilled water, and then scrubbed with alcohol, acetone. The substrate was then acid-cleaned and activated, and finally rinsed with distilled water [12]. After that, it was placed vertically in the electroplating cell of 0.5 dm^3 with magnetic stirring, parallel to the anode, with anode–cathode distance of 5 cm.

Table 1
Bath composition and plating condition for nickel electrodeposition

$NiSO_4 \cdot 6H_2O$	250 g/L
$NiCl_2 \cdot 6H_2O$	40 g/L
H_3BO_3	35 g/L
Lauryl sodium sulfate	0.05 g/L
Saccharine	0–5 g/L
Temperature	45 °C
pH	4
Peak current density (J_p)	0.1–2.0 A/cm^2

In all experiments, the electroplating terminated when the total charge passed was 288 C/cm^2. Pulse parameter T_{on} was less than the calculated value of migration time τ (the time needed for interfacial concentration to reach zero) in formula(1), but more than calculated value of double-layer charge time t_c in formula(2)[13,14].

$$\tau = \left\{\pi D (C_0)^2 (zF)^2\right\} / 4 (J_p)^2 \quad (1)$$

$$t_c = 17/J_p \quad (2)$$

where the unit of τ and t_c is microsecond (μs). J_p is peak current density (A/cm^2), z is the number of electrons (2, for the case of nickel), F is Faraday constant (96500 C), C_0 is the initial concentration of Ni^{2+} (mol/L), D is the diffusion coefficient of Ni^{2+} (cm^2/s). In addition, the shortest pulse off-time was several orders of magnitude longer than the discharge time of the double layer as calculated from formula(3)[14].

$$t_d = 120/J_p \quad (3)$$

Units of t_d and J_p are μs and A/m^2, respectively. In the calculation of τ, the initial concentration of Ni^{2+} is 0.95 mol/L (calculated on the base of the concentration of $NiSO_4 \cdot 6H_2O$ in Table 1). In addition, diffusion coefficient of Ni^{2+} is $D = 0.76 \times 10^{-5}$ cm^2/s [15]. Limits on pulse parameters have close relations with migration time, and these limits would inhibit depleted phenomenon of Ni^{2+} in pulsating diffusion layer [11].

In the experiment, the largest average current density was less than the limiting current density for the electroplating bath used in present work. The limitation on average current density helped to restrain the depletion in the stationary diffusion layer, therefore, furthest eliminated the influence of mass transfer on the microstructural changes of deposits.

2.2. Examination on electrodeposits

The surface morphology of the nickel deposits was investigated with a scanning electron microscope (SEM, Cambridge S360).

Microhardness of nickel deposits was measured by HVS-1000-microhardometer, the load was 0.49 N, loading time was 10 s, operation time was 20 s, and unloading time was 10 s.

Structural studies by X-ray diffraction (XRD, D/max-RB) using monochromatic Cu Kα ($\lambda = 1.5406$ Å) radiation were carried out on specimens in the "as-plated" condition. X-ray diffraction was used to study textural development.