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The effect of current density on the grain size of electrodeposited nanocrystalline nickel coatings

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Abstract

The aim of this work was to investigate the effect of current density on the grain size of electrodeposited nickel coatings. For this purpose, nanocrystalline nickel coatings were deposited from a Watts bath containing 5 g/l sodium saccharin as an additive, by direct current electroplating at different current densities. X-ray diffraction analysis and modified Williamson–Hall relation were used to determine the average grains size of the coatings. The experimental results showed that the coating grains size decreased sharply by increasing the current density from 10 mA/cm^2 to 75 mA/cm^2. Nanocrystalline nickel coating with average grain size smaller than 30 nm can be achieved at the current densities higher than 50 mA/cm^2. Furthermore, a general and simple theoretical model based on atomistic theory of electrocrystallization has been made in order to find out the relationship between the grain size and current density. According to this model the variation of log (d) versus log (i) was linear which is in accordance with experimental results for the current densities lower than 75 mA/cm^2.

Keywords: Current density; Grain size; Nanocrystalline; Nickel coating; Theoretical model

1. Introduction

Recently, the production and characterization of nanocrystalline coatings, with the grain size typically smaller than 100 nm, have been the subject of intensive researches [1,2]. Various techniques, such as electrodeposition, physical vapor deposition (PVD), chemical vapor deposition (CVD), laser beam deposition, ion implantation, plasma and high-velocity oxygen fuel (HVOF) spraying have been developed for synthesis of these coatings [2,3]. Among these methods, electrodeposition has been recognized as the most technologically feasible and economically superior technique for production of nanocrystalline coatings with low residual porosity. Compared to other methods, the advantages of electrodeposition are: (a) low cost and industrial applicability, as it involves little modification of existing electroplating technologies, (b) easy of control, as the electrodeposition parameters can be easily tailored to meet the required crystal size, microstructure and chemistry of products, (c) versatility, as the process can produce a wide variety of pore free coatings and (d) high production rates [4,5].

It has long been known that the properties of electrodeposits are dependent on their microstructure, which can be substantially influenced by the deposition parameters [6–11]. The tailoring of the properties of nanocrystalline coatings through synthesis process control requires a profound understanding of the process–microstructure relations of the involved materials. It is of great interest to understand the relation between the grain size of nanocrystalline coatings and their synthesis technique parameters both from the fundamental and performance standpoints because the properties of these coatings is intrinsically size dependent. For example, a decrease in the grain size from 100 μm to 10 nm, increases the hardness of electrodeposited nickel coating from ~1.5 GPa to ~6.5 GPa [12]. Further grain refinement appears to decrease the hardness

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of the coating [13]. This behavior has also been observed in other nanocrystalline coatings [14,15].

The current density plays an important role on the grain size of electrodeposited coatings. In general, high current densities promote the grain refinement [6–10]. An increase in the current density results in a higher overpotential that increases the nucleation rate [16]. Moreover, when the current density increases, the cluster density can be increased [17]. However, between the numerous studies which have investigated this effect for nanocrystalline nickel coatings [11,18–23], some has reported a contrary behavior [11,18,19,23]. Hence, the effect of current density on the average grain size of electrodeposited nanocrystalline nickel coating still needs more experimental and theoretical studies.

The purpose of this investigation was to study the influence of current density on the average grain size of electrodeposited nanocrystalline nickel coating. Based on the atomistic theory of nucleation, a general quantitative relationship was obtained between the average grain size and current density. Theoretical findings were then discussed in connection with experimental results.

2. Experimental procedure

Nanocrystalline nickel coatings were deposited on copper substrates by direct current (DC) electroplating using a circulated electrolyte system described by Tóth-Kádár et al. [23]. A nickel sheet of 99.99% purity with dimensions of $100\times50\times5$ mm^3 was used as anode and pure annealed copper plate with dimensions of $20\times15\times2$ mm^3 as cathode materials.

Prior to deposition, the copper substrates were mechanically polished with silicon carbide papers of 400, 600, 800, 1200 grits and alumina suspensions of 8, 1 and 0.25 μm, then rinsed with distilled water and activated in 10% H_2SO_4 solution at room temperature for 30 s. Nickel coatings were deposited from a Watts bath containing 300 g/l nickel sulfate ($NiSO_4{\cdot}6H_2O$), 30 g/l nickel chloride ($NiCl_2{\cdot}6H_2O$), 30 g/l boric acid (H_3BO_3) and 5 g/l sodium saccharin ($C_7H_4NO_3S.Na$) as a grain refiner and stress reliever agent. The current density varied in the range of 10–300 mA/cm^2. The plating temperature was kept at 55 °C and pH of the bath was adjusted to 4.0 ± 0.2 by addition of drops of HCl (1 N) or NaOH (1 N). The coatings thickness was fixed to about 100 μm by controlling the plating time.

X-ray diffraction (XRD) studies were carried out using a Philips X'Pert-Pro instrument operated at 40 kV and 30 mA with CoKα radiation ($\lambda=1.789$ A°) at a scan rate of 0.05° s^{-1} in the range of 40–130° and 0.02° step size. The average grain size of the nickel coatings was calculated from XRD patterns via modified Williamson–Hall relation given by [24,25]:

$$\Delta K_{\mathrm{FWHM}} = \frac{0.9}{d} + \left(K\overline{C}^{1/2}\right)^2 + O\left(K\overline{C}^{1/2}\right)^4 \quad (1)$$

where $\Delta K_{\mathrm{FWHM}} = \frac{2\beta\cos(\theta_0)}{\lambda}, K = \frac{2\sin(\theta_0)}{\lambda}$, λ and θ_0 are the wavelength of radiation and the Bragg diffraction angle, respectively, α is a numerical constant depending on the dislocation density, O stands for higher order terms in $K^2\overline{C}$,$\overline{C}$ is the average dislocation contrast factor calculated according to Ref. [26] and β is the intrinsic (true) profile full width at half maximum intensity (FWHM). The β parameter was calculated using the Cauchy–Cauchy relation [2]:

$$\beta = \beta_{\mathrm{exp}} - \beta_{\mathrm{ins}} \quad (2)$$

where β_{exp} and β_{ins} are the FWHM of experimental and instrumental profiles, respectively. β_{exp} and β_{ins} were determined by Lorentzian (Cauchy) curve fitting using a custom-built Matlab software. The annealed nickel with average grain size of 30 μm was used as reference sample. The average grain size of the coatings was calculated by a plot of ΔK_{FWHM} versus $\left(K\overline{C}^{1/2}\right)^2$, using the (111), (200), (220), (311) and (222) diffraction peaks and curve fitted by applying a second-order polynomial.

3. Results and discussion

3.1. Experimental results

Fig. 1 shows the XRD patterns of the nickel coatings produced at various current densities. For comparison, the XRD pattern of reference sample (annealed nickel) has also been shown in this figure. It can be observed that the crystal structure of the coatings is pure fcc nickel and no characteristic peaks of other phases have been recorded.

In Fig. 1, the peak broadening of the samples is not completely clear, because the FWHM is small. In order to have a better distinction between the samples, it is necessary that the intensity of (hkl) reflection, (I_{hkl}), be normalized in the form of $I_{N,\mathrm{hkl}}=I_{\mathrm{hkl}}/I_{p,\mathrm{hkl}}$ and $I_{N,\mathrm{hkl}}$ be plotted versus diffraction angle, (2θ) for the same reflection. For this purpose, the intensity of (111) reflection for nickel coatings deposited at various current densities and also reference sample (annealed nickel) were normalized and presented in Fig. 2.

As it can be seen, the XRD peaks of nickel coatings are wider than the annealed nickel and the peak width increases by increasing the current density. The variation of the average grain size, calculated from modified Williamson–Hall relation, versus current density has been presented in Fig. 3. For comparison, the data reported by some other researchers for nickel deposits from Watts bath [21,27–31] and nickel sulfate electrolyte [1] were also presented in this figure. As seen, the results are in

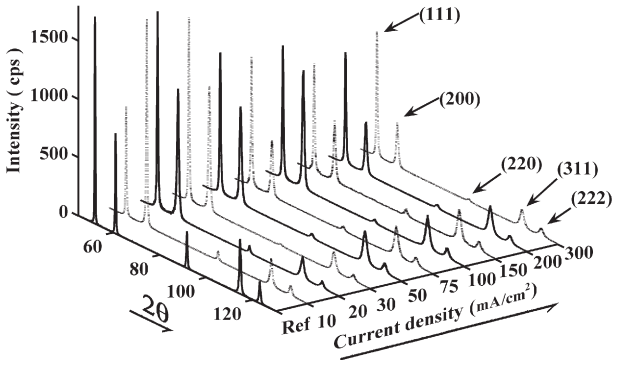

Fig. 1. XRD patterns of Ni coatings produced at various current densities.