Surface & Coatings Technology 291 (2016) 130–140

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Influence of mode of electrodeposition, current density and saccharin on the microstructure and hardness of electrodeposited nanocrystalline nickel coatings

Nitin P. Wasekar [a,]*, Prathap Haridoss [b], S.K. Seshadri [b], G. Sundararajan [a,b]

[a] International Advanced Research Centre for Powder Metallurgy and New Materials, Hyderabad 500 005, India
[b] Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras (IITM), Chennai 600 036, India

ARTICLE INFO

Article history:
Received 3 December 2015
Revised 9 February 2016
Accepted in revised form 10 February 2016
Available online 11 February 2016

Keywords:
Electrodeposition
Nickel
Sulfur
Grain size
Hardness
Texture

ABSTRACT

The main purpose of the present work is to study the influence of current density, deposition mode and the presence of saccharin as an additive on the microstructure, sulfur content, grain size and microhardness of nanocrystalline Ni coatings. Towards this purpose, nanocrystalline nickel (Ni) coatings were deposited at various current densities in Watt's bath using direct, pulse and pulse reverse current (PRC) electrodeposition and subsequently characterized for sulfur content, grain size and hardness. It was observed that, the current density has no influence on the grain size/hardness of nanocrystalline Ni coatings in direct and pulsed current electrodeposition mode. However, the grain size increased from ~ 20 to ~ 200 nm with decrease in current density in PRC mode of deposition. In addition a substantial change in microstructure and texture of PRC Ni coatings was also evident. The experimental results have been rationalized based on the adsorption–desorption type of mechanism during electrodeposition.

1. Introduction

Nanostructured coatings are of great industrial importance because of their improved strength and tribological properties over their microcrystalline counterparts. Given their advantages, over the last two decades, considerable research has been focused on the synthesis of these materials using a variety of technologies available at laboratory scale [1]. While the synthesis of nanocrystalline materials in small quantities is relatively easy, it is more difficult to produce bulk structural parts or coatings, especially with controlled properties. One of the simple, economical methods of depositing porosity free, bulk nanocrystalline materials is pulsed electrodeposition. Electrodeposited nanocrystalline Ni is an extensively studied metal in respect of its structural, physical and tribological properties. The physical properties of electrodeposited coatings such as texture, hardness, roughness and grain size depend upon the chemistry of bath, pH and temperature [2]. In literature, both direct current and pulsed current electrodeposition has been reported in order to control the properties of electrodeposited Ni in addition to variation of bath, pH and temperature. In the case of direct current deposition (DC), only current density, pH and temperature can alter the properties for a given bath chemistry. For example, Ebrahimi [3] and Cziraki et al. [4] reported that the increase in current density increases the grain size of the electrodeposits due to hydrogen evolution in an additive free Ni sulfamate and sulfate bath respectively. However, the increase in hydrogen evolution leads to a localized increase in pH thereby causing formation of metal hydroxide near the cathode surface. As a consequence the depletion of metal ions near a cathode–electrolyte interface limits the current density employed in direct current deposition [5]. The adsorption of the hydrogen bubble formed leads to increased roughness in the final deposit. Excessive hydrogen evolution can be alleviated by using pulse current (PC) and pulse reverse current (PRC) electrodeposition [6–7]. The effect is more pronounced in PRC deposition. In addition, the current distribution problems are less in PRC deposition. In the case of pulsed electrodeposition, there are three additional parameters (on time, off time and peak current density), that can be varied independently. In the pulsed electrodeposition, the deposition is carried out using current pulses of large current densities, the duration of which is of the order of a one to a few hundred milliseconds interspersed with pauses of the same or a higher duration. The major advantage of pulse plating over DC plating is that, while high current density can momentarily polarize the cathode for a given duration, during the pause time the concentration polarization reduces and this results in a smooth and fine grained deposit.

There are several reports for controlling properties such as the grain size of Ni deposits [3,4,8–10] using the electrodeposition technique, however they are contradictory. In contrast to the work of Ebrahimi [3] and Cziraki et al. [4], Natter et al. [10] observed a decrease in the grain size of nanocrystalline gold from 40 to 12 nm when the current density was increased from 50 to 500 mA/cm^2 without additives. Using DC current deposition, it has been reported that the grain size

---

* Corresponding author.
E-mail address: nitin.arci@gmail.com (N.P. Wasekar).

http://dx.doi.org/10.1016/j.surfcoat.2016.02.024
0257-8972/

can be brought down from 300 nm to 30 nm by decreasing the current density from 50 to 5 A/dm^2 in sulfamate bath [8]. El-Sherik [9] obtained a considerable refinement of grain size down to 110 nm by varying various pulse parameters especially by increasing the current density using PC electrodeposition in an additive free Watt's bath. Thus, there is a limitation to the minimum possible grain size obtained in DC as well as PC deposition even though several parameters are available for controlling it. Therefore, it can be concluded that both in the case of DC as well as PC deposition, grain refining agents (organic additives) have to be added for obtaining nanocrystalline deposits. In this direction, El-Sherik [11] demonstrated that the grain size of electrodeposited Ni can be controlled within a 40–10 nm range by the addition of saccharine from 0.5 g/l to 10 g/l in Watt's bath using pulsed electrodeposition. The addition of saccharine also resulted in an improvement in the brightness of electrodeposits. Rashidi et al. [12] observed a refinement of Ni grain size down to 24 nm from 182 nm when current density was increased from 10 to 75 mA/cm^2 under direct current deposition mode from Watt's bath in the presence of saccharin (5 g/l). The organic additives (e.g. saccharin) act as growth inhibitors, resulting in smooth and fine grained deposits. However, these organic additives increase the sulfur and carbon content in the final deposits and leads to another important issue to be considered i.e. the impurity content which significantly affects the physical properties of electrodeposits. Dini [13,14] reported higher sulfur (S) content in coatings deposited at lower current density during direct current deposition. It was also noted that the carbon (C) and hydrogen (H) content reduced significantly when the deposition was carried out without the wetting agent. El-Sherik [11] reported 600–1600 ppm sulfur and 200–500 ppm carbon in the electrodeposited Ni after deposition. The role of saccharin is twofold viz., hydrogenation without detachment of sulfur and complete desulfurization [15] leading to an uptake of sulfur in the Ni coating.

The S content of electrodeposits can be reduced significantly by avoiding the stress relieving and wetting agent in the bath itself. However, this approach leads to a pitting effect and to avoid pitting, intense stirring is required. Therefore, there is always a tradeoff between the options available. In order to avoid the impurities in the coating, it is necessary to find an alternative which can control the properties of deposits and at the same time reduce the impurity content.

Pulse reverse current (PRC) electrodeposition was extensively used for controlling the hydrogen and roughness in the coatings [10,16]. PRC is known to perturb the electrocrystallization process thereby changing the morphology, texture and properties of coatings [17]. It also changes the composition at the cathode–electrolyte interface by adsorption–desorption phenomena [17]. It was observed that, the mechanism during PRC is analogous to the addition of organic additives. Hence, it is possible that, the control of species during the deposition can be adjusted using pulse reversal of the current. Given the advantage and the mechanism during PRC, recently Detor et al. [18] controlled the properties of Ni by variation of tungsten (W) during deposition thereby changing the hardness of the Ni–W alloy coatings. Although, the alloying can considerably influence the properties of electrodeposits, it would be a significant cost saving if the properties can be controlled without the change in composition of the coating.

In light of above, and the literature available, there is however, not much work carried out on the influence of PRC on the structure and properties of nanocrystalline nickel coatings. In addition, there is no systematic study available in open literature regarding the influence of current density on the properties of electrodeposits using DC, PC and PRC at a time. The perusal of recent literature depicts the overall influence of DC, PC and PRC on the microstructure and properties of Co [19], Ni–Co alloy [20] and Ni–Co/CNT composite [21] coatings although only Ni is the widely used coating metal in the electroplating industry.

Therefore, the main purpose of the present work is to study the influence of current density, deposition mode and the presence of saccharin as an additive on microstructure, impurity content, grain size and the microhardness of the coatings. Since, it is not possible to control on and off time in direct current deposition, in the present study we varied only current density (a parameter common to all modes of deposition) in the presence and the absence of saccharin.

2. Experimental details

2.1. Pulsed electrodeposition of nickel coatings

Nickel coatings were electrodeposited on AISI 1045 mild steel (C—0.45%, Si—0.25%, Mn—0.75%, P, S—0.05% and the rest Fe, all in wt.%) substrates (60 × 60 × 5 mm) and on titanium substrate (to obtain free standing coatings for S, C analysis) using a Dynatronix DPR 20-50-200 pulse power rectifier. Pulse waveform (schematic and actual) applied during deposition is depicted in Fig. 1. Under direct current deposition, average current density (i_{avg}) is the same as peak current density (i_p) since the duty cycle (γ) is 100%. However, in PC deposition, the average current is given by,

$$i_{avg} = i_p \times \gamma \quad (1)$$

where, duty cycle $(\gamma) = t_{on} / (t_{on} + t_{off})$.

In the case of PRC deposition, the average current is calculated as,

$$i_{avg} = (i_c \times t_{on} - i_a \times t_{rev})/(t_{on} + t_{rev}) \quad (2)$$

where i_c and i_a are the cathodic and anodic peak current densities respectively. t_{on}, t_{off} and t_{rev} are cathodic (forward) on time, off time and anodic (reverse) off time respectively.

Bath composition and pulse parameters employed in the present study are presented in Table 1. All experiments were carried out in the presence and absence of saccharin. The deposition was carried out for 2 h in each case. Prior to electrodeposition, the samples were polished to mirror finish and etched using dilute hydrochloric acid to enhance the adhesion between the coating and the substrate. The samples for structure, surface morphology, and phase analysis were generated from a coated mild steel substrate using electrodischarge machining and precise slow speed cutting.

2.2. Phase composition, surface morphology and grain size determination

The phase compositions of PED coatings were analyzed using an X-ray diffractometer (D8-Advance, Brooker, Germany, Cu-Kα radiation, Bragg–Brenton geometry, 40 kV, 40 mA, 0.02°/s scan rate). A scanning electron microscope (Hitachi Model S-4300SE/N, Japan) in conjunction with EDAX was employed for analyzing the coating morphology, worn surface and elemental analysis. The grain size (crystallite size) of the coatings was determined using a Scherrer equation [22] utilizing the peak broadening of the (111) diffraction peak using,

$$\beta = 0.94\lambda/(d \times \cos\theta) \quad (3)$$

where, β is the peak broadening in radians, λ is wavelength in A°, d is crystal size in A° and θ is peak position. The grain size (d-especially above 100 nm) was determined using an FEI TECNAI 20G2-transmission electron microscope (TEM) and subsequent image analysis. The samples were prepared using twin jet electropolishing to obtain an electron transparent Ni foil. Linear intercept method was employed to measure the grain size. The TEM images depicting grain size variation can be referred from our earlier work [23].

2.3. Carbon and sulfur analysis

The carbon and sulfur contents in the coatings were analyzed using a Leco CS 600, USA analyzer. The machine was calibrated before testing using a standard having a predetermined quantity of C and S.