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ARTICLE

Synthesis and Thermal Stability of Nanocrystalline Nickel Coatings by Direct Current Electrodeposition

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Abstract: The influences of current density and saccharin concentration on nanocrystalline nickel coatings synthesized by direct current electrodeposition were analyzed. Results show that in the current density range from 0.5 A/dm^2 to 1.5 A/dm^2, nanocrystalline nickel coatings with broad microhardness HV distribution from 4150 MPa to 6030 MPa can be synthesized by adjusting saccharin concentration. The preferred orientation in the deposits exists at 0.5 A/dm^2, (111), (200) double orientation texture changes to a (200) orientation texture as saccharin concentration and (200) intensity increase. The internal stresses of the samples prepared at 0.5 A/dm^2 decrease to nearly 0 MPa as saccharin concentration increases to 1.2 g/L. The results of DSC curves show that the grains start to grow until 600 °C and keep the thermal stability near to bulk nickel when grain sizes are in the range from 28 nm to 98 nm. However, when the grain size is 10 nm, the grains grow abnormally at 317 °C, and their thermal stability decrease sharply.

Key words: nanocrystalline nickel; electrodeposition; microhardness; thermal stability

Advanced nanostructured materials such as nanocrystalline metals have gained considerable interest because they exhibit exceptionally high strength [1,2]. There are several routes to obtain nanocrystalline coatings such as pulsed laser deposition, electrodeposition, chemical vapour deposition and thermal spray. Among them, direct current electrodeposition is a convenient and economical method to produce dense nanocrystalline, pure metal and composite materials [3-6].

The mechanical properties of electrodeposits depend on their microstructures, which can be substantially influenced by the electroplating conditions and the composition of plating bath [7-12]. It is of great interest to understand the relationship between the grain sizes of nanocrystalline coatings and their synthesis technique parameters both from the fundamental and performance standpoints because the properties of these coatings are intrinsically size-dependent. A recent study [9, 13] has shown that a broad grain size distribution was the key factor to increase the ductility of nanocrystalline materials without losing their intrinsic high strength. Current density has a significant function on the grain sizes of electrodeposited coatings. High current density causes high overpotential and nucleation rates, which further promote grain refinement [14,15]. The grain refining via saccharin concentration increase in nickel plating bath was analyzed by Erb [16] and Yuan[17]. However, the exact circumstances of production and grain refinement methods are not known by the tester because the production and mechanical analyses were not executed by the same groups. Existing studies always focus on preparing nanocrystalline nickel with a narrow grain size distribution, whereas those that prepare nanocrystalline nickel with a broad distribution remain scarce. In the present study, we determined the influence of the low current density and saccharin concentration on nanocrystalline nickel, and found the best conditions to produce this material with a

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broad microhardness distribution. Moreover, the thermal stability of the nanocrystalline nickel coatings was researched.

1 Experiment

All nickel coatings were synthesized via direct current electrodeposition on copper substrates by a Watts bath at 50 °C. The details of the conditions and coatings preparation procedures were described in Ref. [13]. The coatings were obtained with current densities and saccharin concentrations ranging from 0.5 A/dm^2 to 4.1 A/dm^2 and from 0.4 g/L to 5 g/L, respectively. The coatings with a thickness of approximately 120 μm are deposited under above conditions.

Microstructures of representative samples were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Grain sizes were calculated from diffraction line broadening using the Scherrer equation [18]. Internal stresses were measured qualitatively via the $\sin^2\psi$ method[19] by X-ray stress evaluations. Microhardness tests were performed on an HMV-2T microhardness tester with a Vickers indenter at a load of 50 g for duration of 15 s. During the hardness tests, the separation between indents was initially kept at more than three times as large as the diameter of each indent. Five measurements were averaged in order to determine the hardness of each specimen. Differential scanning calorimetry (DSC) experiments were performed in an HCT-2 differential thermal analyzer using argon as the purge gas. Measurements were performed between 50 and 700 °C at a heating rate of 10 °C/min.

2 Results and Discussion

2.1 Microstructure of the nanocrystalline Ni coatings

The macrograph and the surface morphology of the samples obtained by SEM are presented in Fig.1. These samples, which have bright and smooth surface morphologies, satisfy the surface quality requirement.

Fig.2a shows the XRD patterns of representative deposits produced at various current densities with a saccharin concentration of 0.4 g/L. The crystal structure of the samples is pure faced-centered cubic nickel and no characteristic peaks of other phases have been recorded. The strong intensity of peak at 2θ=44.6° is from Ni (111) plane together with other peak Ni (200) at approximately 2θ=52°. The peak broadening of the coating indicates grain refinement to nanoscale size. Increasing of the current density from 0.5 A/dm^2 to 4.1 A/dm^2 retains the preferred orientation, and $I_{(200)}/I_{(111)}$ [defined as the quotient of the intensity of (200) and (111) planes] decreases from 0.947 to 0.691. However, Fig.2b shows that the diffraction intensity of (111) texture of the deposit prepared at 0.5 A/dm^2 sharply decreases with increasing of saccharin concentration. $I_{(111)}/I_{(200)}$ changes from 1.055 to 0.047, thus indicating that

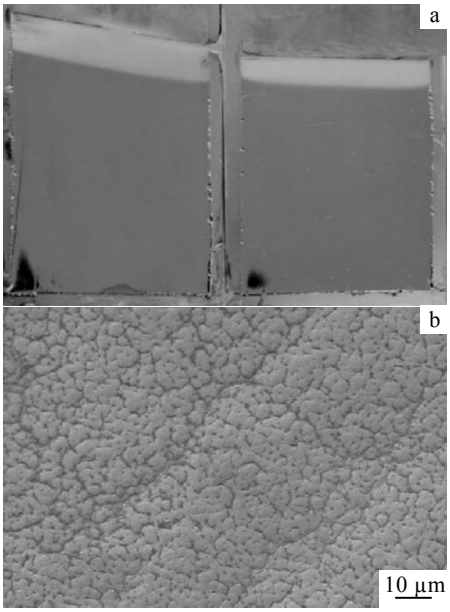

Fig.1 Macrograph of samples prepared at 0.5 A/dm^2 with saccharin concentrations of 0.4 g/L and 2.0 g/L (a); surface morphology of sample prepared at 0.5 A/dm^2 and saccharin concentration of 2.0 g/L (b)

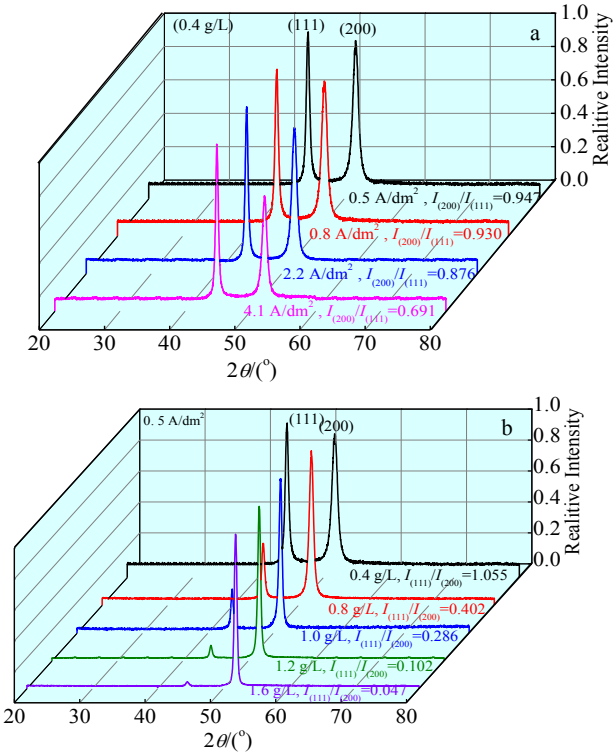

Fig.2 XRD patterns of nickel coatings prepared at a saccharin concentration of 0.4 g/L and different current densities (a); and different saccharin concentrations at 0.5 A/dm^2 (b)

the preferred orientation and the texture of the deposit are markedly influenced by saccharin concentration. This finding agrees with the study of Kerstin and Qin [9,13].