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Stress measurements in nanocrystalline Ni electrodeposits

A.M. El-Sherik[a], J. Shirokoff[b,*], U. Erb[c]

[a] *Dofasco Inc., P.O. Box 2460, Hamilton, Ontario, Canada L8N 3J5*
[b] *Faculty of Engineering and Applied Science, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X5*
[c] *Department of Metallurgy and Materials Science, University of Toronto, Toronto, Ontario, Canada M5S 3E4*

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Abstract

X-ray diffraction method was used to assess the internal stresses in nanocrystalline nickel coatings electrodeposited onto various substrates. In addition, internal stresses in nanocrystalline nickel deposits without substrates were also investigated using the same technique. The preferred orientation of nanocrystalline nickel deposits was found unaffected by substrate type and bath addition. All deposits showed that compressive internal stresses are present. The substrate type was found to affect the magnitude of internal stresses in these deposits. Furthermore, compared with microcrystalline coatings, the nanoprocessed deposits contained higher compressive stresses. The addition of small amounts of sodium lauryl sulphonate to a saccharin-containing Watts' bath was found to decrease the internal stresses in deposits. It is concluded that nanoprocessed Ni-coatings are strong contenders for applications requiring high fatique strength of the underlying substrate metal.

Keywords: Nanocrystalline coatings; Electrodeposition; X-ray diffraction

1. Introduction

The study of internal stress in electrodeposits is of great technological and fundamental importance. Internal stresses in coatings can cause adverse affects on some of the most important protective, mechanical and physical properties of electrodeposits (e.g., corrosion resistance, a wear, hardness, adhesion, fatigue strength, and toughness etc.) [1]. It is well established that tensile stresses in electrodeposits are deleterious, and the higher the stress the lower the fatigue strength of the substrate [2]. However, stress may serve a useful purpose. For example, in the deposition of magnetic films for use in high speed computers, stress in iron, nickel and cobalt electrodeposits will bring about preferred directions of easy magnetization [2]. Three kinds of stresses exist in plated coatings: (1) lattice misfit stresses resulting from distortion due to differences in lattice parameters at the interface between the coating and substrate (2) thermal stresses arising due to differences in thermal coefficient of expansion at the interface between the substrate and coating, and (3) residual or intrinsic stress that results from particular plating conditions and bath composition. It is far more difficult to account for intrinsic stress, and no single universally accepted theory has been put forward. Many theories have been proposed such as the co-deposited hydrogen theory, crystallite-joining theories, dislocation theory, excess energy theory, Kushner theory, and Gabe and West theory [3].

Residual stress has been measured in polycrystalline nickel [4], nanocrystalline nickel [5], nanocrystalline metals [6,7], nanocrystalline metal alloys [8,9] and nanocomposites [10] using various methods. For electrodeposited polycrystalline nickel the residual stress has been measured to be −130 MPa (compression) by X-ray diffraction ($\sin^2\Psi$ method) [4]. Nanocrystalline nickel (9–25 nm) produced by DC magnetron sputtering under varied conditions (up to −100 V bias) was measured at 500–1000 MPa residual stress (tension) determined by a method involving the curvature change due to deposition in a Si-wafer cantilever beam [5]. DC magnetron sputtered nanocrystalline iron (7.7–16 nm)

* Corresponding author. Tel.: +1-709-737-2601; fax: +1-709-737-4042.
E-mail address: shirokof@engr.mun.ca (J. Shirokoff).

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had a residual stress (tension) reported as 600 MPa which became increasing compressive for increasing alloy additions (Ta, Si, Al, and N) up to −900 MPa for composition Fe-10%TaN using a Flexus 2320 thin-film stress measurement by way of cantilever beam wafer curvature change [6]. In another study, nanocrystalline Pd (6–17 nm) and Cu (6–34 nm) deposited by inert gas condensation was found to have a residual stress (compression) of −20 to −105 MPa for increasing depth below the surface using the $\sin^2\Psi$ method [7]. The residual stress in electrodeposited (at high over potential conditions) nanocrystalline (5.5–7 nm) alloys of Fe (12–15%Ni) was 1400 MPa (tension) measured by a flexible beam curvature method similar to the others [8]. Electrodeposited nanocrystalline (3 nm) alloy Ni20%W produced a stress of up to 2300 MPa using an Instron-type tensile testing machine on 35 μm thick samples [9]. In a study using neutron diffraction to measure residual stress in nanocomposites of Al_2O_3/SiC (12–115 nm mean particle size) a mean matrix stress of 150–200 MPa (tension) and reinforcement stresses of −1600 to −1750 MPa (compression) was found [10].

Generally speaking, any method capable of producing materials with ultra fine grains can be employed in the synthesis of nanocrystalline solids. However, a number of processes have proven to be more feasible than others in terms of overcoming engineering barriers to mass production; these methods include inert gas condensation, ball milling and electroplating [2]. Both direct current and pulsed current plating have been successful in producing a variety of nanocrystalline materials [11–15]. For example, a number of nanocrystalline metals (Ni, Co), binary alloys (Ni–Fe, Co–W and Zn–Ni) ternary alloys as well as metal matrix composites have been produced. For applications as coatings and electrode position has many advantages over other nanoprocessing techniques including (1) the potentially very large number of pure metals, alloys and composite systems which can be deposited with grain size less than 100 nm (2) the comparatively low initial capital investment required to synthesize these materials (3) high production rates (4) fewer size and shape limitations and (5) the relatively minor 'technological barriers' to be overcome in transferring this technology from the research laboratory to existing electroplating and electroforming industries.

Over the past years, we have particularly studied the synthesis, structure and properties of nanocrystalline nickel [16]. We have already shown [17–20], that grain refinement of electroplated nickel into the nanometer range (<100 nm) results in unique and, in many cases, improved properties as compared to conventional polycrystalline nickel. For example, the hardness of electrodeposited nickel initially increases linearly far into the nanocrystalline range from the hardness of about 150kg/mm^2 for deposits with 100 μm grain size to about 650kg/mm^2 at 10 nm [17]. However, starting at grain sizes less than 30 nm, a clear deviation from the regular Hall–Petch relationship [21,22] is observed leading to a plateau in the hardness curve at about 650kg/mm^2 for grain size of 10 nm. Further decrease in grain size down to 6 nm resulted in a decrease in hardness (inverse Hall–Petch) down to 560kg/mm^2 [22]. Microhardness testing of nanoprocessed nickel coatings having a grain size of 10 nm deposited onto various substrates showed that substrate type had no effect on the hardness values on these coatings [23]. Similarly, coating/substrate adhesion of nanocrystalline nickel coatings was found unaffected by substrate type, surface finish and coating thickness [23]. The wear resistance of nanocrystalline nickel electrodeposits with an average grain size of 10 nm was greatly enhanced as compared with conventional polycrystalline nickel [24]. Potentiodynamic testing of nanocrystalline nickel electrodeposits in 2N H_2SO_4 showed the regular active–passive-transpassive behaviour that is common for normal crystalline nickel [25]. Although the overall dissolution rates in the passive range were somewhat enhanced in nanoprocessed material, it was found that nanocrystalline nickel exhibits superior resistance to localized corrosion [25]. The corrosion resistance of nanocrystalline nickel coatings in 3.5% NaCl neutral salt spray environment was similar to conventional polycrystalline nickel coatings with grain size of 10 μm [23].

Given its excellent wear, adhesion and corrosion properties, nanocrystalline nickel can be a more suitable coating candidate than conventional nickel. However, for this new class of coatings to gain industry acceptance, knowledge of the type and magnitude of residual stresses in these coatings is of great importance.

The purpose of the present paper is to assess internal stresses in these novel coatings using X-ray diffraction methods. The effects of substrate type, coating thickness, grain size and bath additions on the internal stress of nanocrystalline nickel deposits will be discussed. The effects of substrate type, grain size and bath additions on preferred orientation of nickel will be presented.

2. Experimental

Nanocrystalline nickel coatings of 99.95% purity were pulse-plated from a modified Watts' bath A and B containing organic additives [23]. The electroplating parameters were adjusted to produce Ni electrodeposits with a grain size of 10 nm as determined by transmission electron microscopy (TEM) and X-ray line broadening techniques. In addition, microcrystalline nickel deposits with a grain size of about 3–5 μm were plated from an additive-free Watt's bath C using similar pulse plating parameters. Table 1 shows the composition and plating conditions for baths A, B and C used for the deposition of nanocrystalline and microcrystalline nickel, respectively. Nanocrystalline coatings with thickness of 25 μm were electrodeposited onto copper, brass and mild steel substrates. A microcrystalline coating with a thickness of 75 μm was initially deposited onto Ti substrates prior to mechanically peeling them off. Table 2 shows the parameters involved for each coating/substrate system. In all cases, surface preparation of the substrates involved the following steps: (1) grind-

Table 1
Chemical composition of the plating baths and plating conditions for production of nanocrystalline (baths A and B) and microcrystalline (bath C) Ni electrodeposits

Chemical composition	Bath A	Bath B	Bath C
$Ni_2SO_4.7H_2O$ (g/L)	300	300	300
$NiCl_2.6H_2O$ (g/L)	45	45	45
Boric acid (g/L)	45	45	45
Saccharin (g/L)	5.0	5.0	5.0
Sodium lauryl sulphonate (g/L)	0.25	0.25	0.25
pH	≈2.0	≈2.0	≈2.0
Temperature (°C)	65	65	65

ing of substrates down to 800 grit using SiC emery paper (2) mechanical polishing down to 0.05 μm Al_2O_3 (3) washing with soap and cleaning with a jet of distilled water and (4) degreasing ultrasonically in acetone prior to plating.

Brightfield and darkfield transmission electron micrographs were taken for the examination of the structure and grain size of nanocrystalline deposits. The grain size of the nanocrystalline electrodeposits was determined directly from darkfield transmission electron micrographs by measuring approximately 250 grains. X-ray diffraction patterns for the investigation of residual stress of the nickel deposits were obtained using CuK_α radiation (λ=1.54184 Å) on a diffractometer with Ψ–tilt and θ–2θ scanning.

The $\sin^2\Psi$ analysis method was used to measure internal stress in the nickel electrodeposits [26,27]. The diffraction data and patterns were generated using a Cu X-ray tube operating at 45 KV and 30 mA and a monochromator. This analysis was computer assisted so that the inter-planar spacing values can be corrected for the instrument error function by analyzing a silicon standard and subsequent analysis method. The internal stress in the deposit coatings is related to the slope of the plot of strain $\varepsilon = \Delta d/d_0$ versus $\sin^2\Psi$ using the following Eq. (1):

$$\varepsilon = \frac{(1-\upsilon)\sigma\sin^2\psi}{E} \quad (1)$$

Where E is Young's modulus, ν is the Poisson's ratio and σ is the stress coefficient.

The d-spacing measurements were conducted on the Ni (3 1 1) plane at Ψ = 0°, 10°, 20°, and 30° (higher angles) known to improve the accuracy of the stress measurement. The Δd-spacing plotted against $\sin^2\Psi$ for each of the six samples Ni-1–Ni-6. Calculation of the residual stress was done using the slopes m, from these graphs and Eq. (2).

$$\sigma = \frac{mE}{d_0(1+\upsilon)} \quad (2)$$

Values for Young's modulus E = 28,900 psi were used for both microcrystalline and nanocrystalline nickel and Poisson's ratio ν = 0.31.

3. Results and discussion

3.1. Structural analysis

XRD patterns of microcrystalline nickel deposited onto mild steel used in this study previously reported elsewhere were found to have a strong (2 0 0) fibre texture [15]. This result is commonly consistent with the texture previously reported for nickel produced from organic-free Watts' baths operated under similar conditions [28,29]. XRD patterns of nanocrystalline nickel coatings of 25 μm thicknesses on mechanically polished mild steel, copper and brass substrates all indicated line intensities similar to those found in samples with random grain orientation distribution with the exception of the (2 2 0) line which is somewhat reduced in intensity. Also, XRD patterns of nanocrystalline nickel coatings of 75 μm thickness prepared from baths A and B and initially deposited onto Ti substrates all showed line intensities similar to those found in samples with random grain orientation distribution with the exception of the (2 2 0) line which is somewhat reduced in intensity. In all samples, the crystal orientation of nickel was observed to be unaffected by substrate type.

TEM brightfield, darkfield and selected area (electron) diffraction patterns of the nickel deposits indicated a uniform structure with an average grain size of about 10 nm electrodeposited to a coating thickness of 25 μm on mechanically polished copper substrates [15]. It is also known from density measurements that these materials have negligible porosity [31]. Grain size measurements of the same deposit using the X-ray line broadening technique showed similar results as those obtained from the TEM analysis.

3.2. Internal stress analysis

Table 3 presents results of internal stresses in nickel electrodeposits. It is clear that all these nickel deposits have

Table 2
Sample substrates, thickness, lattice mismatch, bath additives and grain size parameters

Sample	Substrate	Coating thickness (μm)	Lattice mismatch (%)	Bath additives	Grain size (nm)
Ni-1	Copper	25	2.51	SA + SLS	10
Ni-2	Brass	25	17.20	SA + SLS	10
Ni-3	Steel	25	18.66	SA + SLS	10
Ni-4	Steel	10	18.66	N/A	≈5000
Ni-5	N/A	75	N/A	SA + SLS	10
Ni-6	N/A	75	N/A	SA	10

(SA: Saccharin, SLS: Sodium lauryl sulphonate).

Table 3
Calculated internal stresses for nanocrystalline and microcrystalline nickel electrodeposits with and without various substrates as measured by XRD using Cu K-diffraction from (3 1 1) planes

Sample	Lattice mismatch (%)	Internal stress (kg/mm^2)	Internal stress (MPa)
Ni-1	2.51	−46.12	−452.3
Ni-2	17.20	−80.05	−785.1
Ni-3	18.66	−85.85	−841.9
Ni-4	18.66	−14.60	−143.2
Ni-5	N/A	−68.48	−671.6
Ni-6	N/A	−76.17	−747.0

Table 4
Room temperature coefficient of thermal expansion of the materials studied in the present work

Material	Thermal expansion coefficient
Copper	17.1
Brass (70Cu–30Zn)	19.9
Steel (0.23C, 0.6Mn)	12.2
Nickel	13.2

compressive stresses. The presence of compressive internal stresses has been previously reported in microcrystalline (polycrystalline) nickel electrodeposits [4] as well as in nanoprocessed deposits which is in agreement with published literature for nickel deposits prepared from Watts' baths containing sulfur-containing organic compounds [29,30] such as saccharin. However, compressive stresses in microcrystalline nickel deposit (Ni-4) prepared from additive-free Watts' bath is in contradiction with published literature for nickel deposits produced from similar baths using conventional DC plating. This may be explained in terms of the effect of pulse plating on decreasing the hydrogenation of the coatings. It can also be seen from this table that the internal compressive stresses in nanoprocessed nickel coatings increase with increasing coating/substrate lattice misfit. This is expected as the stresses from distortion due to differences in lattice parameters at the interface between the coating and substrate (Tables 3 and 4). Comparison of samples Ni-5 and Ni-6 deposited from baths A and B, respectively, shows that Ni-5 has lower internal stresses. This may be attributed to the presence of the surfactant SLS in bath A leading to low hydrogenation of deposit Ni-5.

4. Conclusions

For the conditions studied in this work, all nickel deposits contained compressive internal stresses. The internal stresses in nanoprocessed (10 nm) nickel coatings are affected by substrate type. Furthermore, the nanoprocessed coatings showed about six times (−841.9 MPa) the internal stress of microcrystalline (5000 nm) nickel (−143.2 MPa) with a similar substrate type. Given the excellent wear resistance, undiminished adhesion and corrosion resistance to salt spray environment coupled with its enhancement of fatigue strength of the underlying substrate, manufacturers and end-users of protective coatings may benefit from nanoprocessed nickel electrodeposits.

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