Adhesion & Corrosion Performance Of Nanocrystalline Ni Coatings

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Standard ASTM tests for the evaluation of coating/ substrate adhesion and corrosion resistance to salt spray environment were conducted on recently developed nanocrystalline nickel coatings electrodeposited on various substrates. The surface morphology, preferred orientation, grain size and coating/substrate adhesion were found unaffected by substrate type and surface finish, as well as coating thickness. Moreover, compared with microcrystalline coatings, the nanoprocessed deposits showed similar substrate/ coating adhesion and resistance to neutral salt spray environment. It is concluded that nanoprocessed Ni-coatings are strong contenders for applications requiring good corrosion protection and high wear resistance.

Nanocrystalline solids with grain size of less than 100 nm are a new and novel class of advanced materials currently receiving considerable attention in the scientific and business communities. Since their introduction in the early 1980s,¹ rigorous scientific activity in the areas of synthesis, microstructural characterization and property determination of these materials has resulted in the development of a number of manufacturing techniques capable of producing various materials with much improved properties over conventional materials.² Consequently, several industrial applications and new market opportunities have emerged from this field and are continuing to increase in number.

Most current efforts toward large-scale production of nanostructured solids are concerned with consolidating nanocrystalline precursor powders produced by techniques such as gas condensation, ball milling, or spray conversion.² Film deposition techniques, such as physical and chemical vapor deposition, sol-gel techniques, etc., are also under intensive investigation.²Electroplating has been identified as a technologically feasible and economically superior technique for production of nanocrystalline pure metals and alloys, as well as nanocomposites.^{3,4}

Generally, any method capable of producing materials with ultrafine grains can be employed in the synthesis of nanocrystalline solids. Over the past few years, a number of processes have proven to be more feasible than others, however, in terms of overcoming engineering barriers to mass production; these methods include inert gas condensation, ball milling and electroplating. While the former two produce particulates that subsequently require consolidation, electroplating is capable of producing materials in bulk form or as coatings with no post-processing requirements. It is interesting to note that the scientific community initially ignored electrodeposition as a means of producing nanostructured materials, despite the fact that this approach is probably one of the oldest to synthesize such structures. There are numerous reports in the literature on electrodeposits with ultrafine structures,^{5,6} but no systematic studies of the synthesis of nanocrystalline materials by electrodeposition methods were published prior to 1989.^{7,8} Such studies were directed toward optimization of certain properties by deliberately controlling the volume fractions of grain boundaries and triple junctions in the material by grain size reduction.

Both direct-current and pulsed-current plating have been successful in producing a variety of nanocrystalline materials. Over the past few years, we have identified electrochemical processing windows for a number of pure metals (Ni³, Co⁹), binary alloys (Ni-Fe,¹⁰ Co-W,¹¹ Zn-Ni³), ternary alloys (Ni-Fe-Cr),¹² as well as metal matrix composites (Ni-SiC).³ The operating windows are selected such that nucleation of new grains is favored over the growth of existing grains during deposition. Such circumstances are brought about by careful selection of electroplating variables, such as bath composition, pH, temperature, current density, duty cycle, etc.

For application as a coating, electrodeposition has many advantages over other nanoprocessing techniques, including (1) the potentially very large number of pure metals, alloys and composite systems that can be deposited with grain sizes 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 facilities.

Over the past five years, the structure and properties of pulse-plated nanocrystalline nickel has been the particular subject of study.¹³ We have already shown that grain refinement of electroplated nickel into the nanometer range (< 100 nm) results in unique and, in many cases, improved properties, compared to conventional polycrystalline nickel.14-17 For example, the hardness of electrodeposited nickel initially increases linearly far into the nanocrystalline range from a hardness of about 150 kg/mm² for deposits with 100 µm grain size, to about 580 kg/mm² at 30 nm.¹⁴ Starting at grain sizes less than 30 nm, however, a clear deviation from the regular Hall-Petch relationship^{18,19} is observed, leading to a plateau in the hardness curve at about 650 kg/mm² for the smallest grain size of 10 nm. The wear resistance of nanocrystalline nickel electrodeposits with an average grain size of 10 nm was greatly enhanced, compared with conventional polycrystalline nickel.¹⁵ Potentiodynamic and potentiostatic testing of nanocrystalline nickel electrodeposits in 2N H₂SO₄ showed the regular active-passive-transpassive behavior common to normal crystalline nickel.^{16,17} 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.^{16,17}

Given its excellent wear properties and enhanced resistance to localized corrosion, nanocrystalline nickel can be a more suitable coating candidate than conventional nickel. For this new class of coatings to gain industry acceptance, however, industry-recognized evaluation tests to assess coat-





Fig. 2—XRD patterns showing that coating thickness has no effect on preferred orientation of nanocrystalline nickel deposited on mechanically polished (a) mild steel; (b) copper; (c) brass substrates.

Fig. 1—XRD pattern of a microcrystalline nickel coating, $10 \,\mu$ m thick, deposited on mechanically polished mild steel substrate.

ing/substrate adhesion characteristics and corrosion resistance in a salt spray environment must be applied.

The purpose of this paper is to assess the adhesion and corrosion performance of these novel coatings, using standard ASTM tests. The effects of substrate type, surface preparation and coating thickness on surface morphology, grain size, and preferred orientation of nanocrystalline nickel deposits will also be discussed.

Experimental Procedure

Nanocrystalline nickel coatings of 99.95 percent purity were pulse-plated from a modified Watts bath A, containing organic additives.^{13,20} 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 to 5 µm were plated from an additive-free Watts bath B, using similar pulse plating parameters. Table 1 shows the composition and plating conditions for baths A and B used for the deposition of nanocrystalline and microcrystalline nickel, respectively. Coatings with thicknesses of 10, 25 and 50 µm were electrodeposited onto copper, brass and mild steel substrates. The substrates had two different surface finishes—one set being ground down to 600 grit, using SiC emery paper; the second set was mechanically polished down to 0.05 μ m Al₂O₂.

Vickers microhardness measurements of nanocrystalline and microcrystalline nickel coatings were carried out at loads of 50 g and 25 g, respectively, applied for 20 sec at room temperature. These hardness measurements were conducted on mirror-finish specimens with coating thicknesses of about $25 \,\mu$ m. At least 8 hardness measurements were conducted on each nickel coating.

The ASTM B 571-91 standard bend test method for metallic coatings²¹ was used to assess the adhesion of nanocrystalline and microcrystalline nickel coatings to the substrates. Three substrates of each surface finish were coated and subsequently bent to ensure reproducible results.

The ASTM B 117 (DIN 50021) 5-percent neutral salt spray test for evaluating the corrosion performance of metal-

lic coatings²² was used for coatings deposited on mild steel substrates. A standard salt spray corrosion cabinet and a solution of 5 wt percent NaCl at 35 °C and a pH of 7 were used. Sample preparation for salt spray testing involved the following steps: (1) grinding of substrates down to 800 grit using SiC emery paper, (2) washing with soap and cleaning with a jet of distilled water, and (3) degreasing ultrasonically in acetone prior to plating. Following this, the steel panels were plated with microcrystalline or nanocrystalline nickel to a coating thickness of about 12 µm. The plated samples were cleaned with acetone and distilled water prior to placing them on a plastic rack inside the salt spray cabinet. The edges and the back side of the plated steel panels were covered with Microstop lacquer to expose an area of about $2 \times 2 \text{ cm}^2$. The coatings were visually inspected; initially, every two hr for the first 8 hr and every 24 hr thereafter for a total exposure time of 11 days. The initiation and progress of the red rust-covered area was recorded.

Scanning electron microscopy (SEM) was used for observation of the surface morphology of the as-plated surface of the electrodeposits. Bright-field and dark-field transmission electron micrographs were taken for examination of the structure and grain size of nanocrystalline deposits. The grain size of some nanocrystalline electrodeposits was determined directly from dark-field transmission electron micrographs by measuring approximately 250 grains. X-ray diffraction patterns (XRD) were obtained using CuK_{α} radiation ($\lambda = 1.54184$ Å) on a standard θ -2 θ diffractometer.

Results and Discussion

Structural Analysis

Figure 1 shows an XRD pattern of microcrystalline nickel deposited on mild steel. A strong (200) fiber texture may be inferred from the relative intensities of the peaks in this graph. This is consistent with the texture previously reported for nickel produced from organic-free Watts baths operated under similar conditions.^{23,24} Figures 2a, b and c illustrate XRD patterns of nanocrystalline nickel coatings of varying thicknesses on mechanically polished mild steel, copper and brass substrates, respectively. All diffraction patterns show line intensities similar to those found in samples with random grain orientation distribution, with the exception of the (220) line, which is somewhat reduced in intensity. It can also be seen from this figure that the crystal orientation is unaffected by substrate type and coating thickness. In addition, X-ray peaks, marked S, originating from the substrate, can also be seen in some spectra. The substrate peaks, as expected,



Fig. 3—XRD patterns showing that substrate surface finish has no effect on preferred orientation of nanocrystalline nickel coatings on (a) ground and (b) mechanically polished mild steel substrates.

Fig. 4—Transmission electron micrographs of nanocrystalline nickel coating deposited on mechanically polished copper substrate: (a) bright-field; (b) dark-field; (c) electron diffraction pattern.

diminish in intensity with increasing coating thickness. It is worth noting that at any given coating thickness, the substrate peaks in the diffraction patterns of deposits on copper substrates (Fig. 2b) are much stronger than for deposits on steel and brass substrates. This is a consequence of the very strong texture of the copper substrate. Figure 3 shows the influence of substrate surface finish on the X-ray diffraction patterns of nanocrystalline nickel coatings. It can be seen that the surface finish has no effect on the preferred orientation of the deposits. These results show that no epitaxial growth of nickel deposits occurs under these plating conditions and bath composition.

100 nm

Figures 4a, b and c show bright-field and dark-field micrographs, as well as the electron diffraction pattern for a nickel deposit with an average grain size of about 10 nm, electrodeposited to a coating thickness of 10 μ m on mechanically polished copper substrate. It is clear from the bright-field and dark-field micrographs, that these nanocrystalline nickel electrodeposits have uniform structure. In addition, it was found by density measurements that they have negligible

Table 1 Plating Bath Compositions & Conditions					
Composition	Bath A nanocrystalline	Bath B microcrystalline			
	97L	97L			
$NISO_4 \cdot 7H_2O$	300	300			
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	45	45			
Boric acid	45	45			
Saccharin	5	0			
Sodium lauryl sulfonate	e 0.25	0			
рН	≈2.0	≈4.5			
Temp	65 °C	60 °C			



Fig. 5—Surface morphologies of microcrystalline nickel coating on (a) mild steel and (b) nanocrystalline nickel coatings on mild steel; (c) copper and (d) brass substrates.

porosity.²⁵ Grain size measurements of the same deposit using the X-ray line-broadening technique showed results similar to those obtained from the TEM analysis.

Figure 5 shows the surface morphologies of nanocrystalline nickel coatings deposited on mechanically polished copper, brass and mild steel substrates. For comparison, the surface morphology of a microcrystalline nickel coating deposited on a mechanically polished mild steel substrate is also shown. The microcrystalline nickel deposit (Fig. 5a) is dull in appearance, with significant surface roughness. In contrast, the nanocrystalline nickel coatings (Figs. 5b, c and d) exhibit very smooth surfaces with bright appearance. This is expected for nickel electrodeposited from Watts baths with sulfur-containing organic additives,²⁶⁻²⁹ such as saccharin and sodium lauryl sulfonate. Also, it can be seen from these micrographs that the type of substrate has no effect on the surface morphology. Similar observations were also reported by Dennis and Fuggle²⁷ for 5-µm-thick Watts nickel deposits on various substrates. The grain size of these deposits was not reported, however.

Microhardness and Adhesion

Table 2 summarizes the Vickers microhardness measurements conducted on the nanocrystalline and microcrystalline nickel coatings deposited on mechanically polished substrates. The hardness of the nanocrystalline coatings is approximately 2 to 3 times higher than the hardness of microcrystalline deposits. This is consistent with earlier work,^{14,30} where it was shown that the hardness of nanocrystalline nickel deposits with a grain size of 10 nm reaches values of about 650 kg/mm².¹⁴ This increase in hardness has mainly been attributed to grain size refinement. The hardness values listed in Table 2 reveal that the type of substrate has little influence on the measured hardness values. This may be expected in light of the similar crystal orientation (Figs.

Table 2 Vickers Microhardness						
Structure Substrate	Na Copper	nocrysta Brass	alline Mild Steel	Microcrystalline Mild Steel		
Hardness Range kg/mm²	666-752	655-739	9 605–726	214-301		
Average VHN	705	698	672	252		



Fig. 6—Through-coating cracks developed in nanocrystalline nickel coatings upon bending: (a) mild steel; (b) brass and (c) copper substrates.



Fig. 7—Fracture morphology of cracks developed in microcrys talline nickel coatings upon bending. Mild steel substrate.

2a-c), grain sizes (Figs. 4a-c) and surface morphologies (Figs. 5b-d) of these deposits.

The results of bend tests indicate that none of the coated specimens showed poor adhesion, defined in ASTMB 571-91 as the tendency to peeling or flaking as a result of bending. All coatings, however, developed cracks in the bend area. The development of cracks is not necessarily an indication of poor adhesion unless the coating can be peeled back with a sharp instrument. Prying with a sharp blade did not cause lift-off of the coating, indicating good adhesion. Figures 6a, b and c are low-magnification SEM micrographs showing cracking behavior of nanocrystalline nickel coatings deposited on mild steel, brass and copper substrates, respectively. The wider cracks observed in the case of brass and copper substrates (Figs. 6b and c) are a result of thicker substrates and, consequently, larger area of curvature upon bending. Figures 7a-d and 8a-d show the bend area of microcrystalline and nanocrystalline nickel coatings, respectively, deposited on mild steel substrates of the same thickness. Comparison of Figs. 7a and 8a shows that the microcrystalline nickel coatings developed shorter cracks, indicative of crack-blunting processes resulting from ductile fracture mechanisms. This may be expected in view of the lower hardness values of the microcrystalline coatings. The higher magnification micrographs (Figs. 7c and d, and Figs. 8c and d) clearly show that microcrystalline coatings undergo considerable plastic deformation prior to fracturing, as indicated by the fine dimples characteristic of ductile materials. In contrast, nanocrystalline coatings (Figs. 8c and d) show limited ductility prior to fracture, indicative of more brittle fracture. The higher hardness of nanocrystalline nickel coatings may, in part, be responsible for this fracture behavior.

Salt Spray Performance

Figure 9 shows the variation in red rust-covered area vs. exposure time of microcrystalline and nanocrystalline nickel coatings to salt spray environment. For comparison, the red rust-covered area for uncoated mild steel substrates is also included. The data plotted in this figure are the average of







Fig. 8—Fracture morphology of cracks developed in nanocrystalline nickel coatings upon bending. Mild steel substrate.



Fig. 9—Variation of red rust-covered area with exposure time to salt spray environment.

three test panels. It is evident from this figure that both microcrystalline and nanocrystalline nickel coatings provide corrosion protection to the steel substrates. With increasing exposure time, the red rust-covered area increases rapidly before reaching a plateau at longer exposure times. Moreover, the corrosion performance of the nanoprocessed coating is similar to its coarse-grained counterpart.

Conclusions

For the conditions studied, the preferred orientation, grain size, surface morphology and coating/substrate adhesion of nanocrystalline nickel coatings are unaffected by substrate type, surface finish and coating thickness. In addition, these coatings showed two to three times the hardness of microcrystalline nickel with the substrate type having no effect on the hardness values. Upon bending, nanocrystalline nickel coatings show very limited ductility, whereas ductile behavior is observed for microcrystalline deposits. Nanoprocessed and conventional nickel coatings show similar corrosion performance in neutral salt spray environment. Given the excellent wear resistance, coupled with the undiminished adhesion and corrosion resistance to salt spray environment of nanocrystalline nickel, manufacturers and end-users of protective coatings may benefit from nanoprocessed nickel electrodeposits.

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