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Microstructural characterization and hardness of electrodeposited nickel coatings from a sulphamate bath

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Pure nickel plates were produced from a sulphamate bath by electrodeposition. A systematic variation of the current density, in the range 0.005 to 0.25 $\mathrm{A\,cm^{-2}}$, resulted in a variation of the coating microstructure and properties. Deposits plated below a current density of 0.01 $\mathrm{A\,cm^{-2}}$ had a surface morphology consisting of large, deep crevices surrounding smaller substructures. A banded or laminar type microstructure was observed in cross-section. Above this current density, truncated pyramidal structures, with ridged terraces oriented perpendicular to the growth direction, were found on the surface. The planar dimensions of the pyramidal surface features were found to increase with current density, as well as the columnar grain widths observed in the cross-sectional view. To evaluate the mechanical properties of the coatings, microindentation hardness tests were performed using a Knoop indenter. A Hall–Petch type relationship for the samples deposited at and above 0.01 $\mathrm{A\,cm^{-2}}$ was seen. © *1998 Chapman & Hall*

1. Introduction

It is well known that the structure of electrodeposited materials is related to the plating variables such as current density, electrolyte bath composition, pH, and temperature [1–12]. It is also well known that the properties of the coating are related to the deposited structure [13–17]. For nickel deposits from a sulphamate bath, extensive characterization of surface topographies and crystal structures has been performed without relating these studies to property measurements [1–4]. For example, Saleem *et al.* [1] plated nickel from a sulphamate bath which resulted in an increasing grain size with current density. They attributed the grain refinement at lower current densities to the incorporation of foreign ions, products from the breakdown of sulphamate ions, into the coatings. However, mechanical testing was not conducted to determine the influence of these foreign ions on the plated properties. Also, the effect of deposition parameters on hardness, ductility, and brightness have been investigated [13, 14]. Kendrick [13] studied these properties for deposits from a sulphamate bath as a function of the current density and found that the hardness decreased as the current density was increased. The hardening effect at lower current densities was again attributed to the incorporation of foreign ions produced by hydrolysis of the sulphamate ion. Unfortunately, microstructural evaluation was not conducted and the contributing strengthening mechanisms were not discussed. It is the objective of this paper to systematically vary the process parameter of current density in order to characterize the microstructure and mechanical properties of nickel electrodeposits produced from a sulphamate bath.

2. Experimental procedure

The sulphamate bath composition and parameters used for deposition can be found in Table I. Samples were electrodeposited on commercially pure nickel substrates ground to a 600 grit finish with silicon carbide papers and subsequently polished to a 0.05 μm colloidal silica finish. Prior to deposition, the cathode was pretreated with 10% sulphuric acid for 30 s in order to etch the surface (ASTM B343-92). The anode to cathode distance was constant at 30 mm. Current density was varied from 0.005 $\mathrm{A\,cm^{-2}}$ to 0.25 $\mathrm{A\,cm^{-2}}$.

After deposition, samples for microstructural characterization and cross-sectional micro-indentation tests were sectioned with a low speed diamond saw and mounted in cold-setting epoxy. The samples were ground to 1200 grit finish and again polished to a 0.05 μm colloidal silica finish. To observe the coating microstructure, a solution of 25 ml water, 25 ml acetic acid, and 50 ml nitric acid was used as an etchant.

Coating microstructures were characterized by light optical microscopy (LOM) and scanning electron microscopy (SEM) with an accelerating voltage of 5 kV and working distance of 11 mm. Using the mean linear intercept method, planar measurements of the surface features and cross-sectional columnar grain widths were determined from optical and scanning electron micrographs. Measurements were taken in each of 10 random fields and then averaged.

TABLE I Electrlyte bath composition and process parameters

Sulphamate bath composition
  400 $g\,l^{-1}$ Nickel sulphamate tetrahydrate [$Ni(NH_2SO_3)_2 \cdot 4H_2O$]
  30 $g\,l^{-1}$ Boric acid powder [H_3BO_3]
  5 $g\,l^{-1}$ Nickel (II) chloride hexahydrate [$NiCl_2 \cdot 6H_2O$]
  0.5 $g\,l^{-1}$ Sodium laurel sulphate [($CH_3(CH_2)_{10}CH_2OSO_3Na$]
  0.1 $g\,l^{-1}$ Coumarin [$C_6H_4OCOCHCH$]
Temperature: 50 °C ± 2 °C
pH: 4.0 ± 0.3
Mechanically agitated at 400 r.p.m.

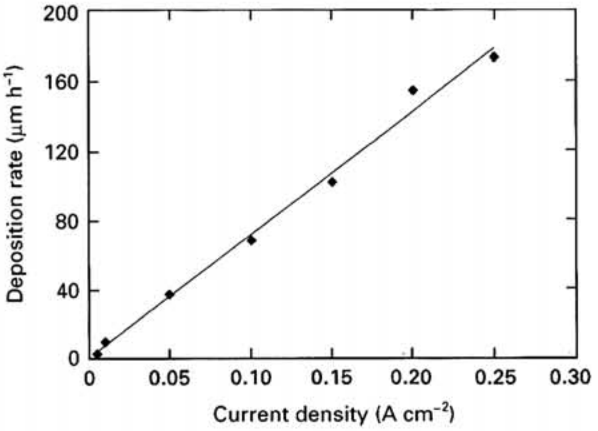

Figure 1 Coating deposition rate as a function of the plating current density.

Relative reflectivity of the sample surfaces were measured using a light optical microscope interfaced with an Olympus exposure control unit, normally used in photography. First a polished substrate was focused and the light intensity set so that the exposure time indicated 1.0 s. Without readjusting the intensity, the sample surfaces were then brought into focus and the exposure time recorded. An increase in exposure time indicated that less light was received by the detector, and hence, the surface of the sample was rougher than that of the polished nickel substrate.

Cross-sectional coating thickness was measured using a digitizing pad interfaced with a light microscope. In each of 10 random fields, three measurements were taken and averaged. Wet chemical analysis was performed on the deposited nickel plates in order to determine the sulphur content.

Microhardness tests were conducted on polished cross-sections of the coatings in accordance with ASTM standard E-384. A Knoop indenter was used with a load of 100 g held for 15 s. Averages were calculated from 15 to 20 measurements per sample. Samples were subsequently etched to assure that the indents were placed at distances far enough (at least five diagonal lengths), from both the edge of the coating and the substrate interface in order to avoid interference in the readings from these two areas.

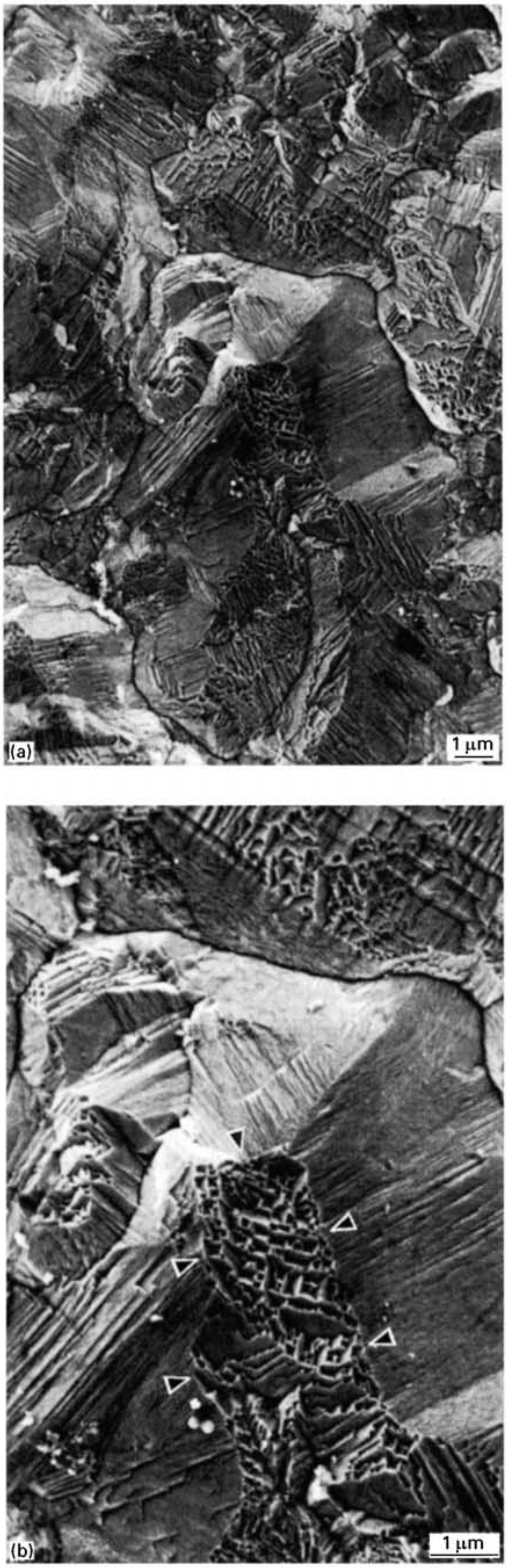

Figure 2 As-plated surface morphology of samples deposited at or above 0.01 A cm^{-2}, "truncated-pyramidal" structures. The ridged terraces, perpendicular to the growth direction, are outlined by arrows in (b).

3. Results and discussion

3.1. Processing

As can be seen from Fig. 1, for a given plating time, the deposition rate varied proportionally with current density, as expected from Faraday's Law. Using Fig. 1, plating times were then adjusted in order to produce coating thicknesses of approximately 100 μm for further evaluation of the deposits.

3.2. Surface morphology

Two different surface morphologies of the as-plated nickel deposits were observed. Samples deposited above a current density of 0.01 A cm^{-2} had "truncated pyramidal-type" structures (Fig. 2). The ridged terraces, perpendicular to the growth direction (centre of Fig. 2b), had substructures growing in what appears to be preferred crystallographic directions. Previous researchers have found that this type of growth occurs in order to expose high index faces to a greater supply of metal ions in the bulk solution [2, 3, 11]. With a faster plating rate, i.e. higher current density, the supply of metal ions to the cathode surface by diffusion through the bulk solution is not enough to maintain the current density over the entire cathode surface. Therefore, preferential deposition occurs only on those crystals favourably oriented, usually ⟨1 1 0⟩ for nickel, to give the fastest growth rate towards the less cation-depleted solution. This allows for an increase in rate of discharged metal ions at the cathode without a corresponding increase in the rate of supply of metal ions from the bulk. These types of structures were also observed for deposits from the Watts-type solution [5, 6].

The size of these surface structures was seen to increase with current density (Fig. 3). Large error bars, due to difficulty in defining some of the boundaries for the pyramidal structures, are found. Other authors [1, 3] have observed a similar trend in size with current density from various sulphamate baths. In addition, Weil and Cook [5] found this effect by decreasing the amount of an addition agent, coumarin, in the plating bath. The reflectivity measurements (Fig. 4) also suggest that the pyramidal structures are increasing in size and height with current density. As the current density increases, the exposure time increases, indicating that the reflectivity of the coating has decreased, or that the surface has become rougher. Kendrick [13] also observed brighter coatings at lower current densities for the same nickel concentration in the sulphamate bath.

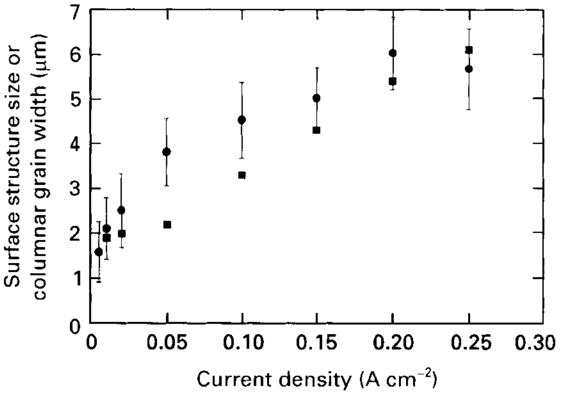

Figure 3 Surface structure size (●) and cross-sectional columnar grain width (■) as a function of the plating current density.

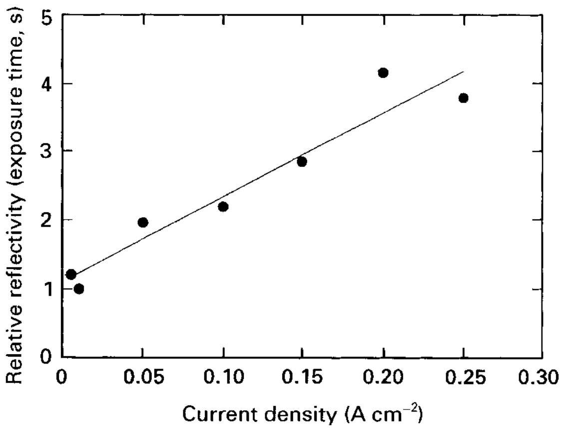

Figure 4 Relative reflectivity of the as-plated nickel electrodeposits showing that the surface becomes increasingly rougher with plating current density.

The second type of surface morphology can be seen in samples deposited below current densities of 0.01 A cm^{-2}. These coatings had large, deep crevices outlining groups of smaller substructures (Fig. 5). The size of the structures, outlined by the crevices marked by arrows on Fig. 5b, are on the order of 1–3 μm. The substructure within the boundaries could not be resolved through SEM.

These structures may be analogous to the "colonies" that Weil and Cook [5] observed using transmission electron microscopy (TEM) in nickel deposited from a Watts bath. These colonies were defined as a series of very fine grains that tend to form groups with relatively deep crevices surrounding them. Though the mechanism for formation of the crevices has not yet been fully determined, it has been suggested that the local absorption of foreign material, such as sulphur and/or carbon ions from the typical plating addition agents [18, 19] hinders the deposition. Crossley *et al.* [11] investigated the absorption of addition agents into growing nickel deposits and observed that the incorporated foreign ions were able to block the emerging screw dislocations, associated with pyramidal growth, and produce "truncated" structures on the surface. With the growth of the tops of the pyramids effectively stopped, the active sides can continue to grow laterally and result in a flatter surface. Therefore, the decrease in size of the pyramids, and their eventual disappearance at the lower current densities seen here may be a result of the incorporation of foreign ions into the deposits.

The techniques used in this research could not determine whether the observed structures were colonies or grain boundaries. While a colony boundary may be a grain boundary, a grain boundary is not necessarily defined by a colony boundary, which may contain finer grains. The only way to accurately distinguish between the two is through the technique of selected area diffraction [5, 9]. When viewed by SEM, grain boundaries tend to have the appearance of valleys, much like the crevices. Therefore, these surface features are often mistaken for one another when methods other than TEM are used.

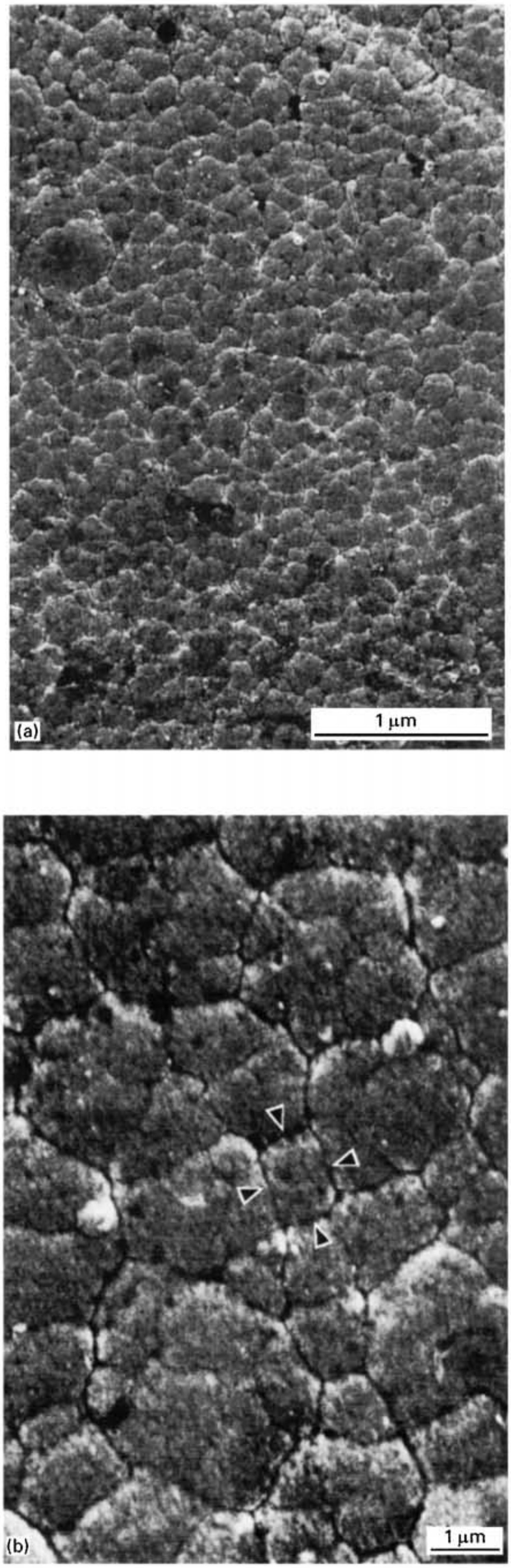

Figure 5 As-plated surface morphology of samples deposited at 0.005 A cm^{-2}, "colony" structure. A colony boundary is outlined by arrows in (b).

3.3. Cross-sectional microstructure

Light optical micrographs of the etched nickel electrodeposits at different current densities can be seen in Figs 6 and 7. Above 0.005 A cm^{-2}, the deposits have a columnar structure (Fig. 6). Towards the higher current densities, an increase in the cross-sectional columnar grain width is observed (Fig. 3), as well as grains spanning the entire thickness of the coating. The increase in cross-sectional columnar width corresponds well with the effect of current density on the surface measurements. A near 1:1 correlation between the two can be seen in Fig. 8, with variation due to the difficulty encountered in measuring the planar surface morphology.

The lack of epitaxial growth of the coating due to the structure of the substrate is also obvious. According to Weil and Sheppard [6], a deposited material will try to grow epitaxially when definite crystal planes and directions are parallel in the deposit and the substrate, respectively. However, this effect is lessened if the substrate surface is mechanically polished or will diminish as the coating thickness increases [4, 19], as is the case here.

Samples deposited at 0.005 A cm^{-2} had a banded or stratified structure (Fig. 7). These bands have been attributed to the incorporation of such foreign ions as sulphur or carbon, from the organic addition agents [18, 19]. If the co-deposited ions are non-uniformly distributed, they can lead to the banded structure, as well as crevices on the surface [6], as seen in Fig. 5. In iron–zinc coatings, these banded structures have also been observed and indicate a possible change of composition or temperature in the electrolyte bath or possible current fluctuations during the processing [20].

3.4. Knoop microindentation hardness testing

The effect of current density on microindentation hardness can be observed in Fig. 9. A decrease in hardness with an increase in current density was observed. Kendrick also reported the same effect of current density on the hardness of nickel deposits from a similar sulphamate bath [13]. From this data, a Hall–Petch type relationship [21, 22] was plotted in Fig. 10, demonstrating that the hardness of the coating is related to the square root of the columnar grain width, in the range of 2 to 6 μm. A slope of 14.8 kg mm$^{-5/2}$ was obtained by using a linear regression analysis of the data. Hughes *et al.* [17] showed a similar Hall–Petch relationship for electrodeposited nickel, from various baths, with a grain size range of 12 nm to 12 μm. A comparison of the data between the two investigations could not be made because of differences in the testing techniques: i.e. indenter and load.

The samples deposited at 0.005 A cm^{-2} were not plotted on Fig. 10 due to the inability to obtain a cross-sectional columnar grain width. In order for these samples to reside on the curve, the columnar grain width would have to be submicrometre, which would be inconsistent with the size of the surface

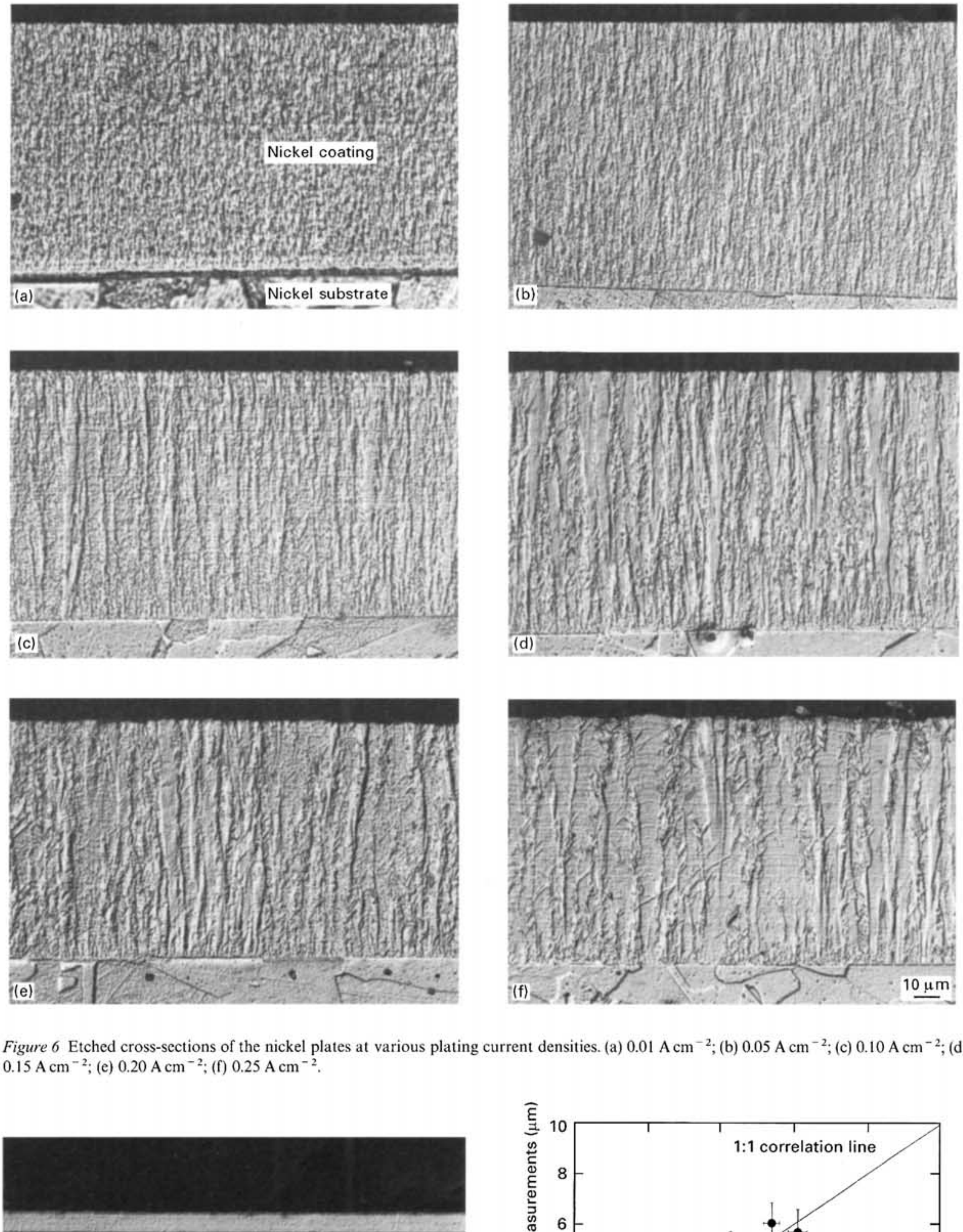

Figure 6 Etched cross-sections of the nickel plates at various plating current densities. (a) 0.01 A cm $^{-2}$; (b) 0.05 A cm $^{-2}$; (c) 0.10 A cm $^{-2}$; (d) 0.15 A cm $^{-2}$; (e) 0.20 A cm $^{-2}$; (f) 0.25 A cm $^{-2}$.

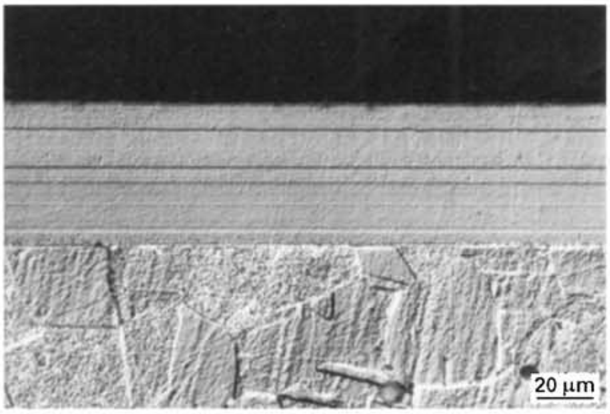

Figure 7 Etched cross-section of a sample deposited at 0.005 A cm $^{-2}$. The banded or stratified structure is indicative of incorporated foreign material during deposition.

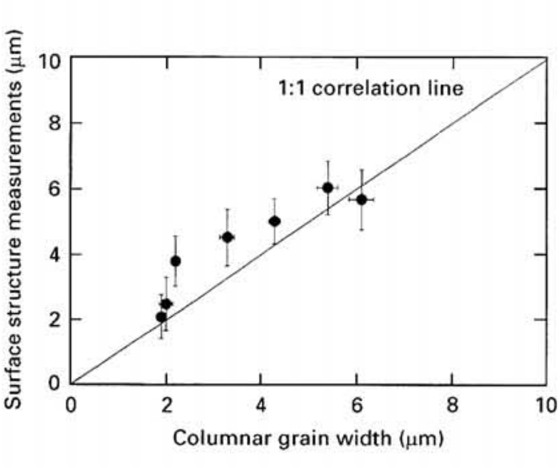

Figure 8 Correlation between the surface structure size and the cross-sectional columnar grain width. The sample deposited at 0.005 A cm $^{-2}$ is not plotted here due to the lack of a columnar grain width measurement.

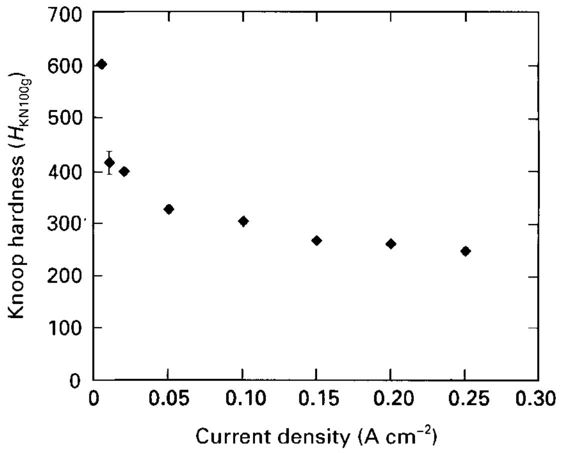

Figure 9 Knoop hardness (100 g load) as a function of the plating current density.

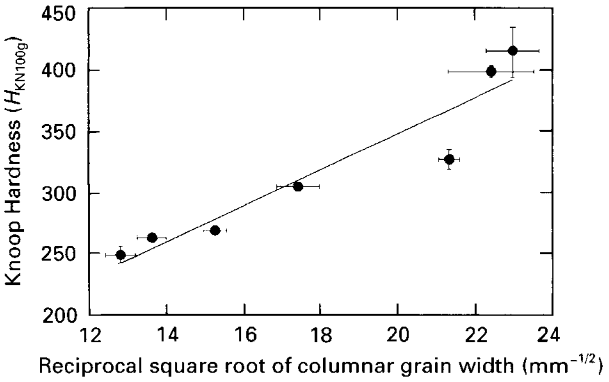

Figure 10 Plot demonstrating that the hardness of the coating is related to the square root of the cross-sectional columnar grain in the range of 2 to 6 μm.

TABLE II Wet chemical analysis for sulphur in electrodeposited samples

Deposition current density ($A cm^{-2}$)	Wt % of sulphur in deposit
0.005	0.003
0.05	0.042
0.15	0.003
0.25	0.009

colonies. Another possible hardening mechanism in this current regime may be due to increased incorporation of organic materials into the coating, as found by Huang [14]. He observed that the increased presence of ammonium and sulphate ions produced harder and higher stressed nickel coatings from sulphamate baths. Wet chemical analysis was performed on the selected coatings to determine if these samples had higher sulphur contents than those plated in the upper regime of the current density. However, no correlation could be made from these results (Table II).

4. Conclusions

The goal of this research was to determine the relationships between the processing, structure, and properties of electrodeposited pure nickel coatings from a sulphamate type bath. The plates were produced by varying the current density. Under these processing conditions, the following conclusions can be drawn:

1. Above a plating current density of 0.005 A cm^{-2}, a correlation between the current density and the size of the nickel structure was found. In addition, a near 1:1 correlation between the cross-sectional columnar grain width and truncated-pyramidal surface structures was found; as the grain width increased the surface morphology became coarser. A Hall–Petch type relationship was seen to relate the property of microhardness to the cross-sectional columnar grain width.
2. Samples deposited at 0.005 A cm^{-2} had a banded cross-sectional microstructure with a "colony-type" surface morphology, both indicative of a high degree of incorporated foreign material. The strengthening mechanism for these samples was unresolved, but was believed to be due to a combination of finer grain size, as well as the incorporation of foreign ions into the coating.

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