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Properties and microstructure of nickel electrodeposited from a sulfamate bath containing ammonium ions

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Abstract

A 70 μm thick Ni layer was electrodeposited from a sulfamate bath containing various amounts of ammonium ions onto a copper plate. The detailed microstructure of the Ni deposits was characterized using a plane-view and cross-sectional transmission electron microscopy (TEM). The textures of the Ni deposits were also determined using conventional X-ray diffraction. Experimental results indicated that ammonium ions suppressed the lateral growth of Ni deposits and favoured out growth, thus leading to the growth of [1 1 0] and [3 1 0] oriented deposits. A structural refinement effect was observed after ammonium ions were added to the sulfamate bath. Ammonium ions also increased the internal stress and hardness of the deposits. A general Hall–Petch relationship was observed for the dependence of deposit hardness on the average grain size of the Ni deposits. The adsorption of atomic hydrogen and the polar NH_3 molecule explains the effect of ammonium ions on the electrocrystallization of Ni.

1. Introduction

Nickel sulfamate baths are widespread in high-speed electrodeposition, electroforming, and electrojoining processes because the resulting nickel deposits exhibit low internal stress and good ductility [1–4]. However, in certain commercial implementations requiring prolonged and repeated use of the same electrolyte, the increasing level of ammonium ions resulting from the hydrolysis of sulfamate ions can lead to undesirable Ni deposits. That is, sulfamate ions tend to suffer hydrolysis upon acidifying and are gradually converted into sulfate and ammonium ions [4]. Meanwhile, sulfate and ammonium ions in a sulfamate bath increase the internal stress and hardness of the Ni deposits [4]. Therefore, the critical level of ammonium ions accumulated in the plating bath in an industrial production line needs to be specified, particularly for high-speed, high current density operations [5].

The properties and structures of Ni electrodeposits are closely related to electrolyte composition and electroplating parameters, such as current density, electrolyte temperature, pH and agitation operations [6–24]. Texture, the most vital of the various structural features of the Ni deposit, is generally defined as the non-random orientation distribution of the crystallities of the deposits [16]. Previous studies indicate that plating conditions markedly affect the growth mode and resulting texture of Ni deposits, particularly pH and current density [9, 14–17]. For example, Amblard et al. investigated how electrochemical parameters affect the texture of Ni deposits plated from a Watts bath [15, 16]. Various textures generally develop with the different inhibitors adsorbed on the cathode surface. Specially, the [1 1 0] and [2 1 0] textures are associated, respectively, with the atomic and molecular forms of adsorbed hydrogen prevailing in a more acidic solution. At high pH $Ni(OH)_2$ precipitates and inhibits every growth mode except [2 1 1]. In more severely inhibited conditions, such as when an organic additive consumes much more cathodic hydrogen, [2 1 1] is replaced by [1 1 1]. Ye and Lee demonstrated that the preferred orientation of Watts Ni deposits shifts from the [1 1 0] or [2 1 0] texture to the [1 0 0] texture as the current density increases [17].

Although the effect of electrolytic conditions on the texture of Ni deposits plated from sulfate baths has been thoroughly studied, the texture of the Ni layer electrodeposited using sulfamate baths has seldom been addressed. Furthermore, the effect of ammonium ions in the sulfamate bath on the texture and microstructure of Ni deposits has received only limited attention. This work studies how ammonium ions influence the texture and structure of the Ni deposits plated from a sulfamate bath. The detailed microstructure of the Ni deposits is characterized using plane-view and cross-sectional transmission electron microscopy (TEM). Results indicate that ammonium ions markedly affect the texture and defect density of the Ni deposits, thus determining their internal stress and hardness.

2. Experimental details

After being mechanically ground and polished and then activated in a 5% sulfuric acid solution, the 0.3 mm thick copper plate was electrodeposited with 70 μm thick layer of Ni from a sulfamate bath at a current density of 200 A m^{-2}. Table 1 shows the electrolyte composition and operating conditions. Besides the basic electrolyte, various amounts of ammonium ions were added, ranging from 100 to 800 ppm (parts per million). The operating temperature of a sulfamate bath ranges from room temperature up to 65 °C, with 50 °C, as the most commonly used temperature [1]. Our previous study demonstrated the differences between the textures of Ni deposits plated at 40 and 50 °C [24]. The bath temperatures were thus set at 40 and 50 °C, respectively.

Cross-sectional metallography specimens were prepared by sandwiching two electrodeposited Ni copper plates together with Ni deposits facing each other. After mechanical-grinding and polishing with a Al_2O_3 slurry down to 0.05 μm the cross sections were chemically-etched in a solution comprising 20 ml nitric acid, 30 ml acetic acid and four drops each of hydrochloric and phosphoric acid. A conventional twin-jet polishing method was employed to prepare the plane-view TEM specimens, while a combined mechanical grinding and ion-beam thinning technique was employed to prepare the cross-sectional TEM specimens. The TEM specimens were observed via a JEM 200CXII microscope or a JEM 3010 microscope. After mechanical polishing and then chemical polishing in 10% hydrofluoric acid to remove the damaged surface layer, the preferred crystallographic orientation of the Ni deposits was measured via X-ray diffraction using the Schulz back reflection method. The (200) pole figure of the Ni deposits was determined using a Seimens D-500 (X-ray) diffractometer with Mo radiation. The average (200) intensity at each Khi angle was calculated from pole figure data and employed to represent the texture of the Ni deposits. Measuring the deflections of the Ni deposited on the copper stripes allowed calculation of the internal stress of the Ni deposits using the Stoney formula [25]. The hardness of the Ni deposit was measured on the cross-sectional surface by a Vickers hardness tester (Mitutoyo MVK-E3 hardness tester) with an applied load of 50 g, with the hardness of each individual deposit being reported as the average of five measurements.

Table 1. Electrolyte composition and operating conditions

	Concentration/g l^{-1}
Ni ion	95
Boric acid	40
$NiCl_2.6\ H_2O$	3
Wetting agent	2 ml l^{-1}
pH	4.0
Anode	Depolarized Ni disc
Temperature	40, 50 °C
Ammonium ions	nil, 100~800 ppm

3. Results and discussion

3.1. *Texture of the Ni deposits*

Figures 1 and 2 illustrate the effect of ammonium ions on the (200) intensity-Khi distribution of the Ni deposits plated at 40 and 50 °C, respectively. The Ni deposits plated from basic sulfamate baths at 40 °C exhibited a strong [1 0 0] texture, which became weak [1 0 0] and then weak [1 1 0] as the levels of ammonium

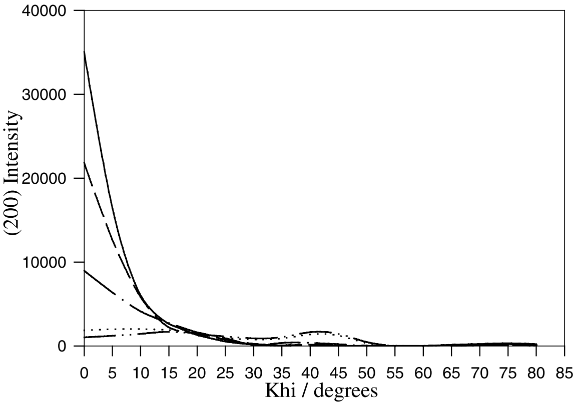

Fig. 1. Effect of ammonium ion content on the texture of Ni deposits plated at 40 °C. Key: (——) 0, (– –) 100, (— · —) 300, (— ·· —) 500 and (·· · ··) 800 ppm.

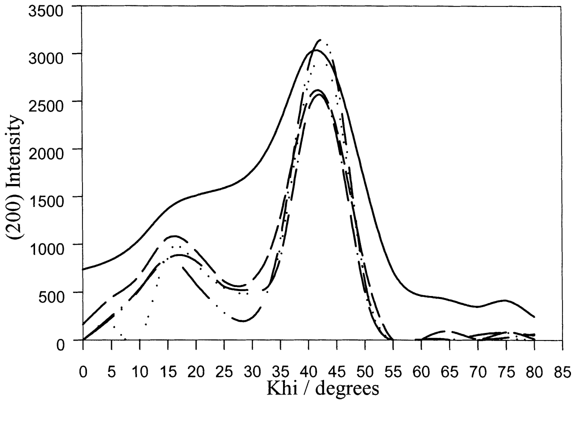

Fig. 2. Effect of ammonium ion content on the texture of Ni deposits plated at 50 °C. Key: (——) 0, (– –) 100, (— · —) 300, (— ·· —) 500 and (·· · ··) 800 ppm.

ions increased. With the addition of over 500 ppm ammonium ions, the Ni deposits displayed a weak [1 1 0] texture. In contrast to the Ni deposits plated at 40 °C, those plated from basic sulfamate baths at 50 °C exhibited a weak [1 1 0] texture. With the addition of 100 ppm ammonium ions, the Ni deposits had a mixture of [1 1 0] and [3 1 0] textures. No additional texture change was observed for deposits plated from baths in which the additions of ammonium ions exceeded 100 ppm.

The crystal orientation of electrodeposited metals is related to the mode of crystal growth [9, 26]. For example, out growth deposits have the most densely packed lattice rows of deposit crystals perpendicular to the substrate surface, while lateral growth deposits have a densely packed lattice plane that contains the most densely packed lattice rows parallel to the substrate surface. In f.c.c. metals, out growth deposits exhibit a [1 1 0] texture, whereas lateral growth deposits have a [1 0 0] or [1 1 1] texture. The growth of the Ni deposits plated from a Watts bath was characterized by Amblard et al. [16] as a free mode of growth, characterized as [1 0 0] oriented deposits, and inhibited mode of growth such as [1 1 0], [2 1 0], [2 1 1] and [1 1 1] textures. Herein, the Ni deposits plated from 40 °C sulfamate baths exhibit a strong [1 0 0] texture, which belongs to the lateral growth mode, also known as the free growth mode. Ammonium ions in the 40 °C bath effectively suppress free growth and instead favour inhibited growth (i.e., [1 1 0] texture). Several interfacial inhibitors are adsorbed on the cathode/electrolyte interface and inhibit the lateral growth of the Ni deposits [16, 27, 28]. For example, Amblard et al. [16] demonstrated that for Ni deposits plated from a Watts bath, the inhibited modes such as [1 1 0] and [2 1 0] textures are associated, respectively, with the atomic and molecular forms of adsorbed hydrogen which prevail in more acidic solution. Since the acidity of ammonium ions ($K_a = 6 \times 10^{-7}$) is higher than that of water, additional ammonium ions increase the amount of discharged hydrogen. Atomic hydrogen adsorption then suppresses the lateral growth of the Ni deposits, subsequently causing [1 1 0] oriented deposits to form. Additionally, the hydrolysis of ammonia creates polar molecules of NH_3. As such polar molecules approach the cathode, the lone paired electron of the NH_3 molecule causes the induced charge separation between the polar molecule and Ni deposit. The attraction between the lone paired electron and the positive charge induced on the cathode surface favours the adsorption of NH_3 molecules on the preferred nucleation and growth sites of the Ni deposits, further suppressing the lateral growth of the Ni deposits.

3.2. *Structure of the Ni deposits*

Figures 3 and 4 show the optical micrographs of the Ni deposits plated at 40 and 50 °C, respectively. The Ni deposits plated from the basic sulfamate baths at 40 °C exhibited a well-defined columnar structure, ((Figure 3(a)). Meanwhile, adding ammonium ions to the 40 °C baths markedly refined the grain structure of the Ni deposits, as shown in Figures 3(b) and (c). Ni deposits plated from the baths containing over 100 ppm ammonium ions exhibited a fibrous structure which is a refinement of the columnar structure [29]. Furthermore, the fibre width of the Ni deposits decreased with increasing addition of ammonium ions, as illustrated in Figure 3(b) and (c). When using the same bath, the structure of the Ni deposits plated at 50 °C was finer than that of the Ni deposits at 40 °C, as shown in a comparison of Figures 4 and 3. That is, the Ni deposits plated at 50 °C displayed a fine fibrous structure. Furthermore, the effect of ammonium ions in 50 °C baths on the deposit structure could not be resolved by a conventional chemical etching technique owing to the fine grain structure of the Ni deposits, as illustrated in Figures 4(b) and (c).

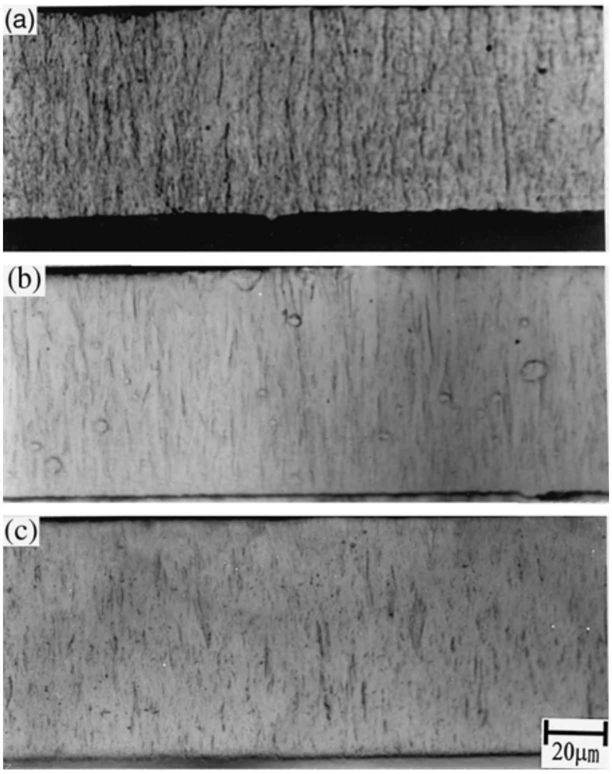

Fig. 3. Cross-sectional optical micrographs of Ni deposits plated from 40 °C baths containing various amounts of ammonium ions: (a) nil, (b) 100 and (c) 800 ppm, showing the increasing fine fibrous structure of the Ni deposits.

As mentioned earlier, all Ni deposits plated at various electrolyte compositions and bath temperatures exhibit a fibre-like structure belonging to the FT class (field-oriented texture type) when cross-sectionally examined under an optical microscope [27, 28]. The long-axes of the fibrous grains are always perpendicular to the Cu substrate and travel in the field direction. Furthermore, the deposits with strong [1 0 0] texture tend to grow along the field direction much more than those with

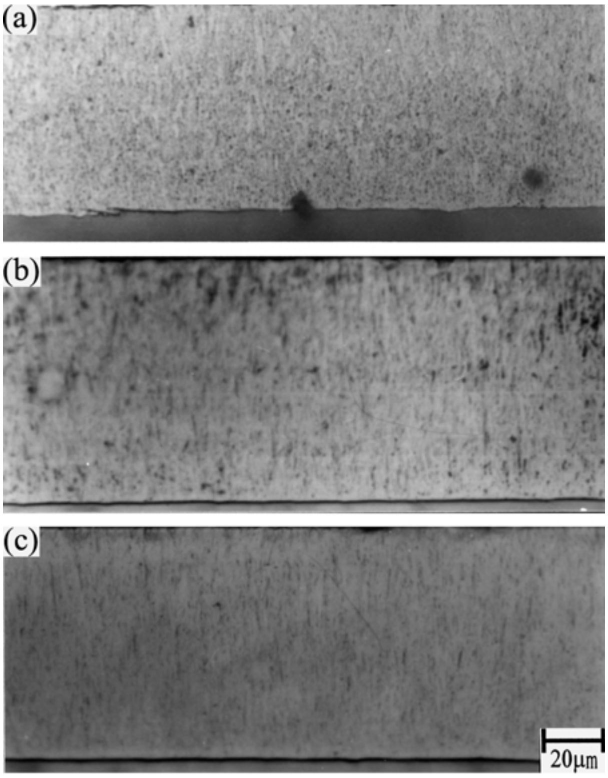

Fig. 4. Cross-sectional optical micrographs of Ni deposits plated from 50 °C baths containing various amounts of ammonium ions: (a) nil, (b) 100 and (c) 800 ppm, showing the increasing fine fibrous structure of the Ni deposits.

weak [1 1 0] or [3 1 0] texture, as illustrated in Figures 3 and 4. This relationship between the fibre length and texture of the sulfamate Ni deposits correlates with the results of Amblard et al. [16] who demonstrated that Ni deposits produced from a Watts bath exhibit a fibre structure in which the lengths of the fibres depend on the fibre axis: [1 1 0] and [2 1 0] exhibit the shortest fibres while fibres of [1 0 0] and [2 1 1] orientations are more developed.

The plane-view TEM revealed that the Ni deposits plated at 50 °C exhibited a bimodal grain structure (Figure 5(a)), in which the relatively large grains were surrounded by a cluster of fine grains. A similar bimodal grain structure has been observed on Ni deposits plated from the sulfamate bath [18, 21, 22, 24] and the Watts bath [12, 13]. Furthermore, the Ni grains contained high-density dislocations and numerous twins, as illustrated in Figure 5(a). Previous investigations indicate that twins are observed on Ni deposits plated from sulfamate [18, 21, 22, 24] and Watts baths [11–14, 16]. Twins were further identified as being associated with the crystal symmetry of the Ni deposits plated from a Watts bath [14, 16]. For example, deposits of [1 1 0] texture obtained at a high cathodic potential have a fivefold symmetry, and the Ni grains are made up of five identical areas separated by twins. Meanwhile, the Ni deposits of [2 1 1] texture exhibit a twofold symmetry, and the Ni grains are divided into two parts by group of twins of uneven number [14, 16]. Twins in the Ni deposits plated from the sulfamate bath have also been shown to significantly influence the feasibility of recrystallization of the Ni deposits during high-temperature annealing [30].

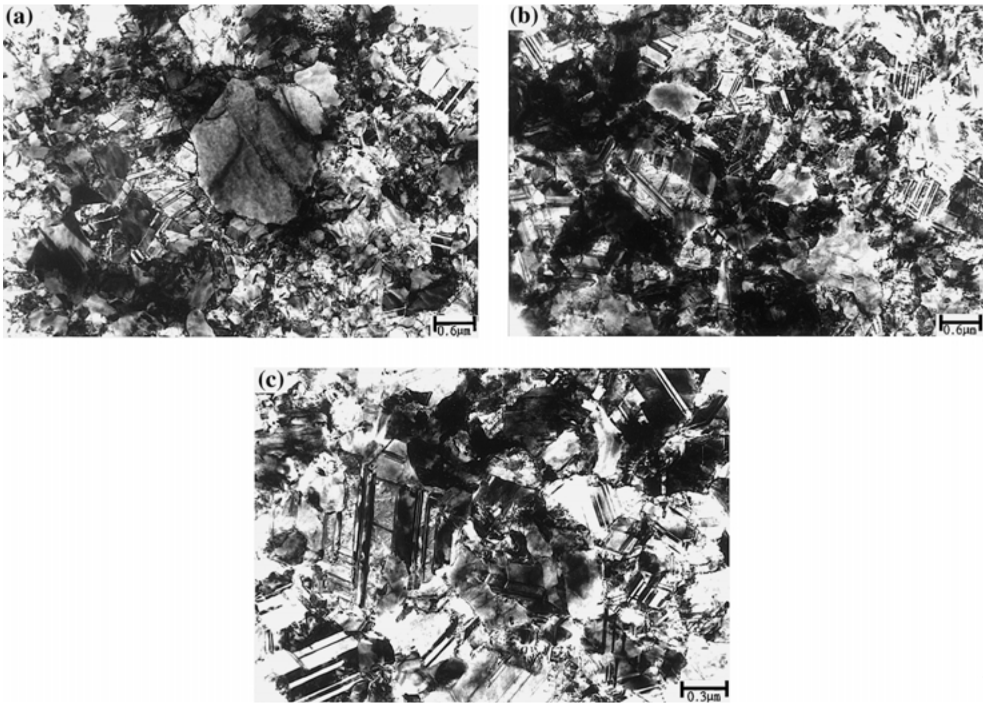

Fig. 5. Plane-view TEM micrographs illustrating the microstructure of Ni deposits plated from 50 °C baths containing various amounts of ammonium ions: (a) nil, (b) 100 and (c) 500 ppm. Note the grain size of the Ni deposits decreased with increasing additions of ammonium ions.

Table 2. Effect of ammonium ions on the grain size of the Ni deposits plated at 50 °C

NH_4^+/ppm	Relatively large grain size d_l/μm	Clustered small grain size d_s/μm	Volume fraction of relatively large grains, f_l/%	Volume fraction of clustered small grains, f_s/%	Average grain size $d_lf_l + d_sf_s/\mu$m
nil	1.80	0.40	50	50	1.10
100	1.28	0.30	45	55	0.74
300	1.14	0.28	40	60	0.62
500	1.07	0.25	40	60	0.58
700	0.91	0.24	40	60	0.51

The Ni deposits plated from the baths with the addition of ammonium ions also exhibited a bimodal grain structure, as illustrated in Figure 5(b) and (c). Figure 5 further reveals that the average size of both large and small grains decreased slightly as more ammonium ions were added. Meanwhile, the defect density was higher for the Ni deposits plated from the bath containing more ammonium ions. Table 2 summarizes the effect of ammonium ions on the average size and volume fraction of both large and small Ni grains, respectively.

Similar to the Ni deposits plated at 50 °C, the Ni deposits plated at 40 °C also exhibited a bimodal grain structure (Figure 6(a)). However, on average the Ni deposits plated at 40 °C had significantly larger grains than those plated at 50 °C. This observation correlates with the fact that the Ni deposits exhibiting the lateral growth mode contain larger grains than those from the out growth mode. The Ni deposits plated from 40 °C baths in which ammonium ions were added still exhibited a bimodal grain structure, as illustrated in Figure 6(b) and (c). However, the average grain size, as illustrated in Table 3, markedly decreased with addition of ammonium ions, especially for the relatively large grains. In contrast to the Ni deposits plated at 50 °C, the large grains of deposits plated from the basic sulfamate bath at 40 °C were comparatively free of twins. However, the density of twins increased with the amount of ammonium ions in the sulfamate bath, as illustrated in Figure 6(a)–(c).

Deposits plated at 50 °C displayed columnar grain structures when observed using a cross-sectional TEM (Figure 7(a)). Two types of crystalline defects were also observed: high-density dislocations and twins. Notably, the twin plane remained parallel to the columnar axis of the columnar grains. In additional to the columnar grains, a cluster of fine equiaxed grains was frequently observed. The columnar grains narrowed slightly with increasing levels of ammonium ions, as illustrated in Figure 7(b) and (c). Furthermore, the lattice of the columnar grains was highly distorted and contained a high density of twins.

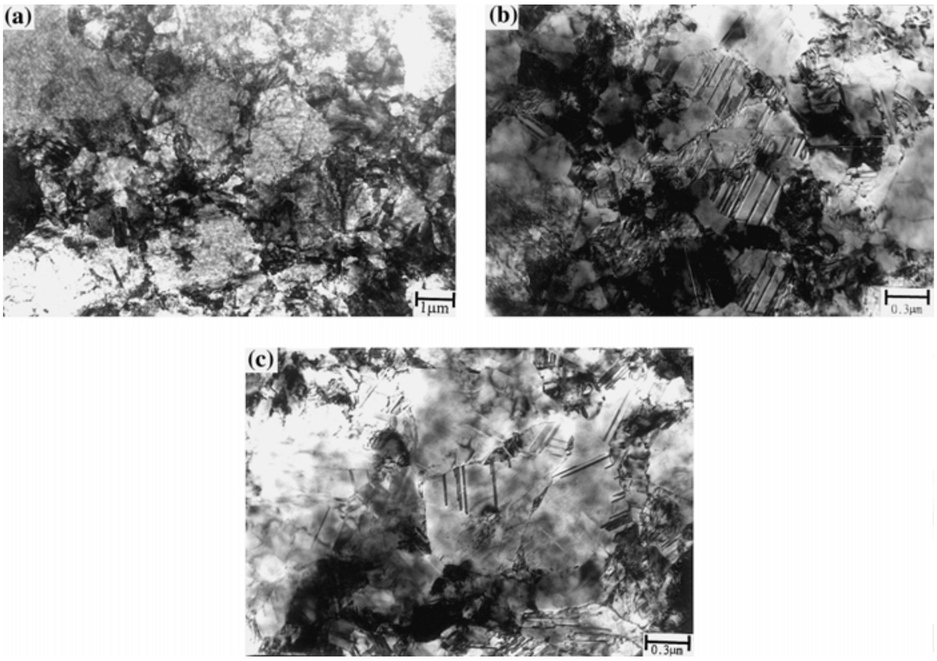

Fig. 6. Plane-view TEM micrographs illustrating the microstructure of Ni deposits plated from 40 °C baths containing various amounts of ammonium ions: (a) nil, (b) 100 and (c) 500 ppm. Notably, the grain size of the Ni deposits decreased with increasing additions of ammonium ions.

Table 3. Effect of ammonium ions on the grain size of the Ni deposits plated at 40 °C

NH_4^+/ppm	Relatively large grain size $d_l/\mu m$	Clustered small grain size $d_s/\mu m$	Volume fraction of relatively large grains, f_l/%	Volume fraction of clustered small grains, f_s/%	Average grain size $d_lf_l + d_sf_s/\mu m$
nil	3.17	0.42	60	40	2.07
100	0.88	0.38	50	50	0.63
300	0.83	0.32	40	60	0.52
500	0.81	0.15	40	60	0.41
700	0.70	0.10	40	60	0.34

Figure 8(a) reveals that the Ni deposit plated in a 40 °C basic sulfamate bath exhibited a well-defined columnar structure. The lattice was less distorted for deposits plated at 40 °C than for those plated at 50 °C. Consequently, the columnar boundaries of the deposits at 40 °C were distinct and the large columnar grains were free of twins. Conversely, twins were still frequently observed on the fine grains. The width of the columnar grains decreased significantly once 100 ppm ammonium ions were added to the bath, as illustrated in Figure 8(b). Further increases in ammonium ions caused a slight decrease in the width of the columnar grains, and ammonium ions in the bath increased the lattice distortion of the Ni grains.

Ammonium ions in the bath generally favour the inhibited mode of growth and refine the grain structure of the Ni deposits. Furthermore, the density of lattice defects is higher for deposits exhibiting an inhibited mode of growth than those exhibiting a free mode of growth.

3.3. *Properties of the Ni deposits*

Figure 9 shows how adding ammonium ions to the bath affects the internal stress of the Ni deposits. All the deposits examined exhibited tensile internal stress. For the 40 °C bath, the internal stress increased with the amounts of ammonium ions and reached saturation at around 48 MPa when more than 300 ppm ammonium ions were added. For the 50 °C bath, maximum internal stress occurred after the addition of 300 ppm

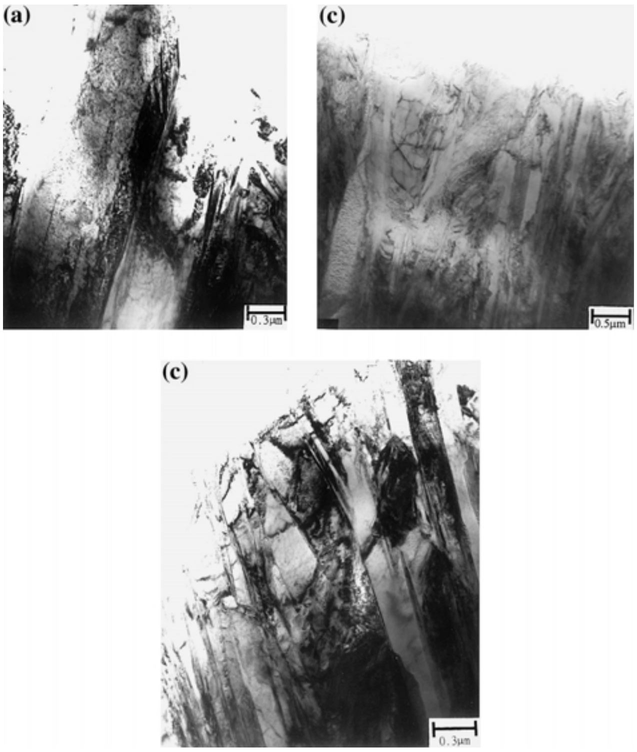

Fig. 7. Cross-sectional TEM micrographs showing the microstructure of Ni deposits plated from 50 °C baths containing various amounts of ammonium ions: (a) nil, (b) 100 and (c) 800 ppm, showing that the columnar width of the Ni deposits decreased with increasing additions of ammonium ions.

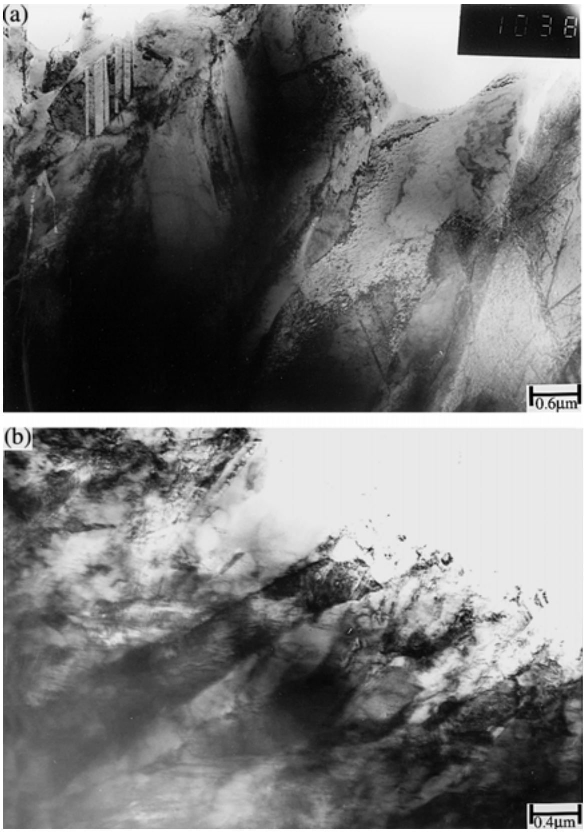

Fig. 8. Cross-sectional TEM micrographs showing the microstructure of Ni deposits plated from 40 °C baths containing various amounts of ammonium ions: (a) nil and (b) 100 ppm, showing that the columnar width of the Ni deposits decreased significantly once 100 ppm ammonium ions were added.

ammonium ions. Further increases in levels of ammonium ions caused a slight decrease in the internal stress of the deposits. Generally, the internal stress of the Ni deposits increased markedly when 100 ppm ammonium ions were added to the bath, regardless of bath temperatures. Consequently, for electroforming with low internal stress and good ductility, ammonium ions are undesirable since they increase the internal stress. Although commercial sulfamate baths can be operated at near zero, or even, with compressive stress, if a special organic compound is generated electrolytically, the organic compound can reduce the ductility of the Ni deposits, particularly at elevated temperatures [1, 32]. Thus, the amount of ammonium ions accumulated in the sulfamate bath for prolonged and repeated use must be controlled to achieve the desired plating quality.

Figure 10 illustrates the dependence of deposit hardness on the amount of ammonium ion. The Ni deposits plated at 40 and 50 °C were observed to harden with increasing bath ammonium ion content. For the 50 °C bath, hardness increased abruptly once 100 ppm ammonium ions were added. The hardness of the deposits then remained constant up to the addition of 800 ppm ammonium ions. In contrast to the deposits plated at 50 °C, the hardness of the deposits increased more gradually with bath ammonium ion content for the 40 °C bath. Relating hardness to the texture, the Ni deposits with strong [1 0 0] texture are clearly softer than those with other orientations, since [1 0 0] oriented deposits mostly grow laterally and contain less lattice defects. Evans confirmed that [1 1 0] oriented deposits are associated with higher values of internal stress and hardness, whereas deposits with a [1 0 0] texture are associated with decreased values [8]. Consequently, when employing the same electrolyte, Ni deposits plated at 50 °C are harder than those plated at 40 °C. However, the deposits plated at 40 and 50 °C were equally hard when more than 500 ppm ammonium ions were added to the bath, implying that the effect of ammonium ions exceeded that of bath temperature once a critical amount was added to the bath.

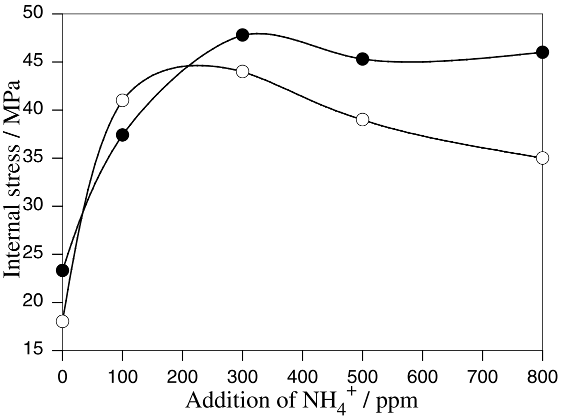

Fig. 9. Internal stress of the Ni deposits as a function of the amount of ammonium ions added. Key: (●) 40 °C and (○) 50 °C.

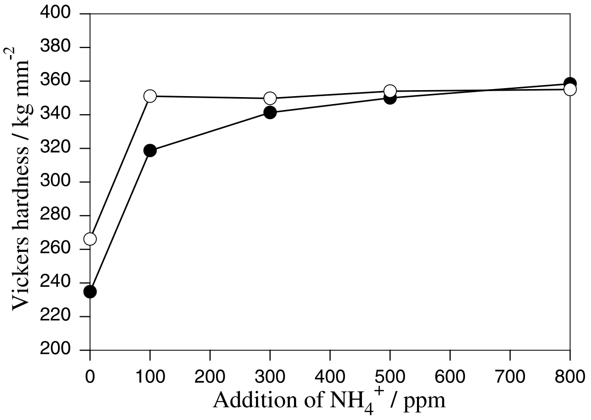

Fig. 10. Hardness of the Ni deposits as a function of the amount of ammonium ions added. Key: (●) 40 °C and (○) 50 °C.

Evidently, ammonium ions in the bath refine the grain structure and increase the hardness of the Ni deposits. Figure 11 plots the relationship between the hardness and average grain size, revealing a general Hall–Petch type relationship. However, the slope of the linear regression line became smaller for data associated with small-sized grains, namely those smaller than 0.6 μm. Banovic et al. noted a Hall–Petch relationship for the dependence of Knoop microhardness on the columnar grain width of Ni deposits plated from a sulfamate bath at current densities above 1 A dm^{-2} [23]. For the deposits plated from sulfamate baths, Jacobson and Sliwa observed a Hall–Petch relationship for the effect of grain size on the yield strength [21]. However, the yield strength of Ni grains of below 1 μm deviated slightly to a smaller value than that extrapolated from the Hall–Petch line related data for Ni grains above 1 μm. On the other hand, Thompson and Saxton reported that grain size slightly influenced the yield strength of deposits of grain diameters below 1 μm [31]. The Hall–Petch type relationship observed herein agrees with that reported by Jacobson and Sliwa. The slope change of the Hall–Petch relationship line as the Ni grain size is smaller than a critical value suggests that, besides the grain boundary strengthening mechanism, lattice defects of the deposits also significantly influence the hardness.

4. Conclusions

For basic sulfamate baths, Ni deposits plated at 40 °C exhibited a strong [1 0 0] texture, whereas those plated at 50 °C displayed a weak [1 1 0] texture. Ammonium ions in the sulfamate bath modified the electrocrystallization of the deposits plated at 40 or 50 °C. That is, as levels of ammonium ions in the 40 °C bath increased, the texture of the Ni deposits changed to weak [1 0 0]

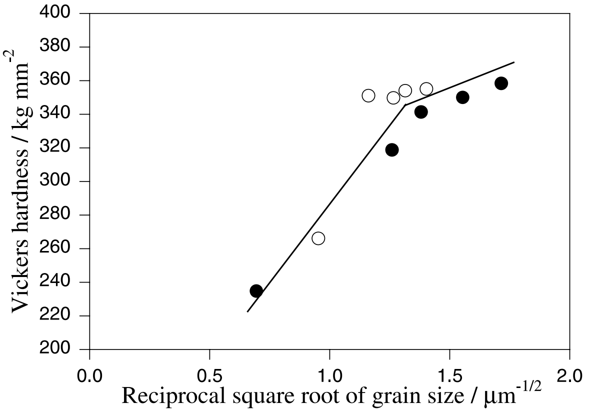

Fig. 11. Dependence of the deposit hardness on the average grain size of the Ni deposits. Key: (●) 40 °C and (○) 50 °C.

and then weak [1 1 0]. The deposits exhibited a mixture of [1 1 0] and [3 1 0] textures as 100 ppm ammonium ions were added to the 50 °C bath. Textures remained largely unchanged as over 100 ppm ammonium ions were added to the 50 °C bath. Regardless of bath temperatures, ammonium ions in the sulfamate bath generally favoured the inhibited growth mode, such as the [1 1 0] and [3 1 0] textures. Observed cross-sectionally, all Ni deposits exhibited a field-oriented structure. Strong [1 0 0] oriented deposits comprised well-defined columnar grains whose columnar width was significantly larger than that of the Ni deposits with [1 1 0] or [3 1 0] texture. Meanwhile, plane-view TEM revealed that all Ni deposits exhibited a bimodal grain structure. The average grain size was larger for the [1 0 0] oriented deposits, and they also contained fewer lattice defects. Conversely, the [1 1 0] and [3 1 0] oriented deposits contained numerous dislocations and twins. Ammonium ions in the bath significantly refined the grain structure and increased the density of the lattice defects.

The internal stress of the Ni deposits increased markedly once 100 ppm ammonium ions were added. Additionally, ammonium ions in the bath created harder Ni deposits. Therefore, ammonium ions are undesirable in the sulfamate bath for electroforming Ni deposits with low internal stress and good ductility. A general Hall–Petch relationship was observed for the dependence of hardness on average grain size. Ammonium ions in the bath reduced the grain size and increased the number of lattice defects. Consequently, the deposit hardness increased with the amount of ammonium ions in the bath.

The mechanical properties and microstructures of the Ni deposits are closely related to texture. For example, the columnar grains of the [1 0 0] oriented Ni deposits were better developed along the field direction than those associated with the [1 1 0] and [3 1 0] orientations. Furthermore, the [1 0 0] oriented deposits were softer than those with the [1 1 0] and [3 1 0] textures because the [1 0 0] oriented deposits had larger columnar grains and contained fewer lattice defects.

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