Technical Article

Influence of 1,3,6 Naphthalene Trisulfonic Acid on Microstructure & Hardness in Electrodeposited Ni-layers
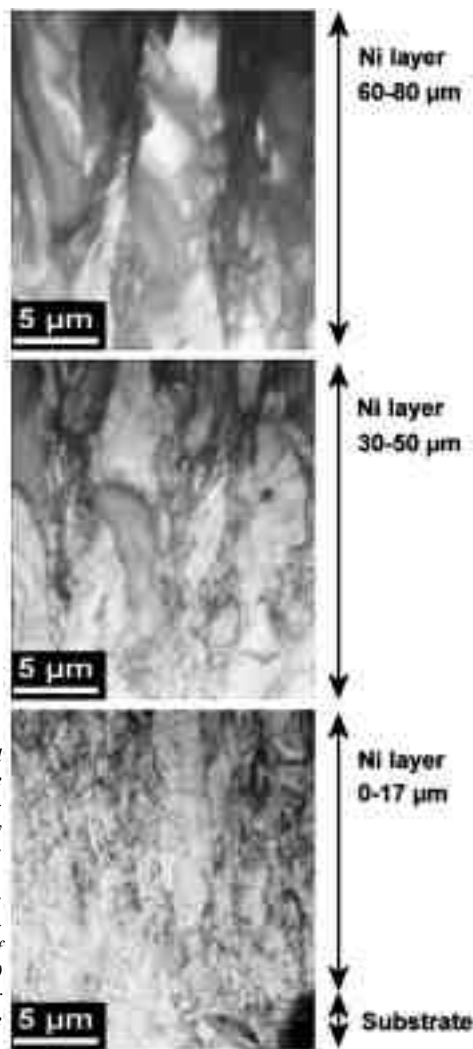
by A.A. Rasmussen,[*] P. Møller & M.A.J. Somers

Fig. 1—TEM images of a nickel layer deposited from the sulfamate bath without 1,3,6 naphthalene trisulfonic acid at a current density of 3 A/dm² (28 A/ft²). Lower image: The first 17 µm of the nickel layer, deposited on a nickel substrate; approximately 3 µm of the substrate can be seen at the bottom of the image. Middle image: from 30 to 50 µm of the nickel layer. Upper image: from 60 to 80 µm of the nickel layer.

The influence of the additive 1,3,6 naphthalene trisulfonic acid on the microstructure and hardness of electrodeposited nickel layers was investigated. The microstructure was characterized using transmission electron microscopy; the Vickers hardness was measured in cross sections. The additive was found to refine the grain size and enhance hardness. The efficiency of the additive in enhancing the hardness was found to depend on the current density during deposition.

Electrodeposited nickel layers find wide application in the manufacturing of micromechanical components and tools for replication processes. The progressive miniaturization of micro-components demands increased control of the deposit properties. Tailoring the properties through process control requires a profound understanding of the process, microstructure and property relations. This work considers the influence of the additive 1,3,6 naphthalene trisulfonic acid (hereafter referred to as NTS) on nickel layers deposited from a nickel sulfamate bath. This additive is known to increase the hardness and to decrease residual stress in the electrodeposited nickel layer.[1,2] Moreover, it has a brightening effect on the deposit[3,4] and is neither consumed nor codeposited during deposition. It has been reported that NTS slightly increases the cathode potential during deposition,[5] *i.e.*, additional energy in the form of a higher voltage must be supplied to the nickel cations in order to form a deposit at a given current density. Hence, nickel is more difficult to deposit when NTS is present.

An improved understanding of the effect of NTS on the microstructure developing in a nickel layer is required in order to be able to further optimize the deposit properties. For example, a high concentration of NTS can cause brittleness. A thorough understanding of the influence of the additive will contribute to finding alternative, possibly even more effective additives. In this paper, the effect of NTS, at various controlled current densities, on the microstructure and microhardness of the nickel layer, is described.

Experimental Procedure

Electrodeposition of Nickel Layers

Nickel layers, 100 µm (3.94 mils) thick, were deposited on cold-rolled and temper-annealed nickel substrates, from a 17 L (4.5 gal) sulfamate bath, consisting of:

Nuts & Bolts:
What This Paper Means to You

This work was funded by the Small Grants Program of AESF Research. Electroformed nickel use is growing in the manufacture of ever-smaller micromechanical components and tools for replication processes. The best example is the finer features in DVD masters when compared to those for CDs. With the smaller pits in DVDs, reducing grain size and increasing hardness is even more critical. Here, the authors checked out the effect of adding 1,3,6 naphthalene trisulfonic acid (NTS) on the microstructure and hardness. NTS shows promise.

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Fig. 2—TEM images of the nickel layer deposited at a current density of 3 A/dm^2 (28 A/ft^2) from the sulfamate bath without 1,3,6 naphthalene trisulfonic acid on the nickel substrate. The image indicates that epitaxial growth of the electrodeposited nickel can occur on certain grains of the substrate. This phenomenon was occasionally observed at the interface.
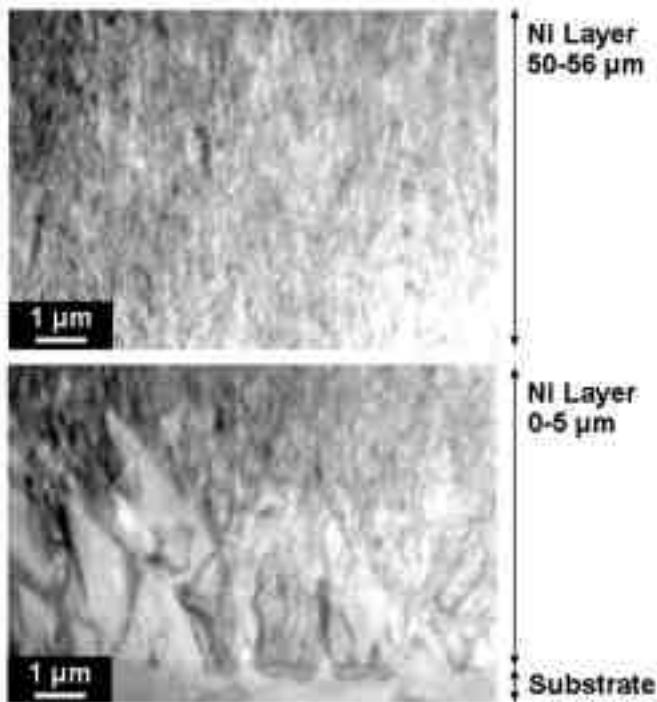
Fig. 3—TEM images of the nickel layer deposited from the sulfamate bath with 4 g/L (30 oz/gal) of 1,3,6 naphthalene trisulfonic acid at a current density of 3 A/dm^2 (28 A/ft^2). Lower image: The first 5 µm of the nickel layer, deposited on the nickel substrate; approximately 1 micron of the substrate can be recognized at the bottom of the image. Upper image: from 50 to 56 µm of the nickel layer.

310 g/L (42 oz/gal) Ni(NH$_2$SO$_3$)$_2$· 4H$_2$O
30 g/L (4 oz/gal) NiCl$_2$·6H$_2$O and
35 g/L (5 oz/gal) H$_3$BO$_3$,

varying the concentration of 1,3,6 naphthalene trisulfonic acid. In order to avoid possible organic impurities, the bath was placed in a glass container with a quartz-heating filament and a glass specimen holder. Sulfur-containing nickel anodes were used. Air agitation and continuous carbon filtration were applied to ensure refreshment of the electrolyte and to prevent organic contamination. The temperature was held at 50°C (122°F) and the current density was varied between 0.5 and 20 A/dm^2 (5 and 186 A/ft^2). Prior to plating, the nickel substrates were pretreated to remove grease and native oxide. Cathodic degreasing was first carried out in a cyanide-containing bath for 2 min followed by rinsing in water. Next, the substrates were activated in 50% nitric acid for 30 sec, followed by water rinsing.

Transmission Electron Microscopy (TEM)

Examination of the microstructure of the nickel deposits was carried out using a transmission electron microscope (TEM), equipped with a LaB$_6$ filament operated at 300 kV. For specimen preparation, a nickel overlayer from another nickel bath yielding a different microstructure, was carried out, until a total thickness of 3 mm (0.12 in.) was obtained. Slices 1.0 mm (0.04 in.) in thickness were cut parallel to the growth direction of the electrodeposit. These slices were ground down to a thickness of 200 µm (about 8 mils) maximum. Subsequently, small discs with a diameter of 3 mm (0.12 in.) were punched out of the slab. The thin nickel deposits were made electron transparent by electropolishing in a solution of 10% perchloric acid in ethanol, using a jet polish apparatus at a temperature in the range of -25 to -30°C (-13 to -22°F) and at a total current of about 1 A . Electropolishing was continued until a hole appeared in the nickel deposit.

Microhardness Measurements

A Vickers microhardness tester, using a 50 g load, was used to determine the microhardness of the nickel layers. Each value presented is the average of five independent indentations on cross sections at a depth corresponding to half the thickness of the deposited nickel layer. Any effect of the surface and/or the interface with the substrate on the microhardness measurements was considered to be negligible since the size of the indentations is smaller than five times the layer thickness. The microhardness tester was calibrated by using standard calibration blocks before measurement.

Results & Discussion
Effect of NTS Addition on Microstructure In Nickel Layers

The TEM images in Fig. 1 show the microstructure of a nickel layer, deposited without NTS. The nickel substrate is observed in the first few microns at the bottom of the image. Generally the electrodeposited layers were observed to have a fiber morphology. The fiber width increased with the layer thickness. The fiber width close to the substrate was about 1µm (39.4 µ-in.). Apparently the growth of some fibers is preferred over the growth of others, resulting in fiber widths ranging from 0.5 to about 5 µm (20 to about 200 µ-in.) at about 30 to 50µm (1.2 to 2.0 mils) from the substrate. In the outer layers of the specimens the morphology showed several relatively wide fibers, up to 5µm (20 µ-in.) wide, and relatively small areas with small grains and narrow fibers. The small grains were often situated at the interface between two wide fibers. The length of the fibers varied considerably, some extending from the substrate throughout the thickness of the nickel layer, *i.e.*, 100 µm (about 4 mils). Generally, the grain size was small close to the substrate. However, a few regions with relatively large grains were observed close to the substrate (Fig. 2). Apparently epitaxial growth on favorably oriented grains in the substrate had occurred at these locations.

Addition of NTS was observed to have a significant influence on the grain size in the nickel layer (Fig. 3). A tendency for a fiber morphology can still be observed. The microstructure appeared to be relatively homogeneous throughout the layer. Occasionally, the first few microns were observed to be influenced by the substrate (Fig. 3). At higher resolution grain sizes down to a few nanometers were observed at some locations (Fig. 4). The fiber morphology could still be recognized at these higher magnifications. Tilting the specimen in
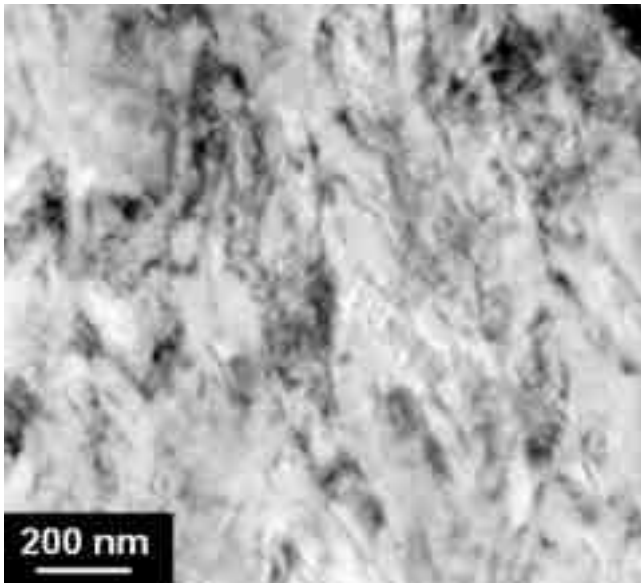
Fig. 4—TEM images of the nickel layer deposited from the sulfamate bath with 4 g/L (30 oz/gal) of 1,3,6 naphthalene trisulfonic acid at a current density of 3 A/dm² (28 A/ft²).
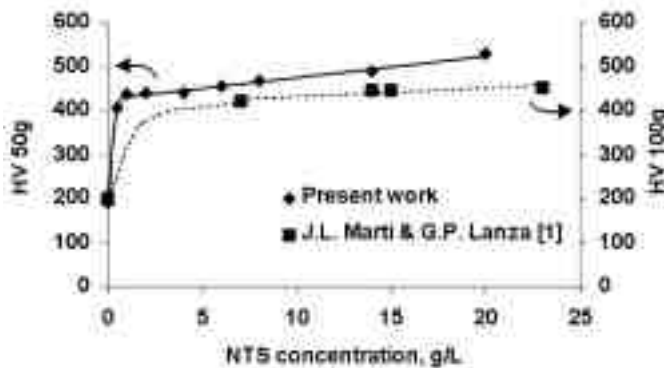

Fig. 5—Hardness vs. concentration of 1,3,6 naphthalene trisulfonic acid for the experimental results of the present work, and for the results presented by J. L. Marti and G. P Lanza.[1]

the electron microscope indicated that the fibers consisted of small grains separated by low angle grain boundaries. The grain sizes were mainly in the range of 10 to 200 nm (0.4 to 7.9 µ-in.).

Effect of Additive Concentration on Hardness In Nickel Layer

The hardness of the nickel layer increased rapidly with relatively small additions of NTS, *i.e.*, less than 1.0 g/L (7.5 oz/gal) (Fig. 5). For concentrations exceeding 1 g/L, the hardness still increased with concentration, but at a lower rate. The hardness values measured here are in good agreement with results presented in the literature.[1] The divergence of values at higher hardnesses can be partially explained by the fact that different loads were used in the two studies. Furthermore the effectiveness of NTS may have been influenced by other deposition parameters such as current density, temperature and the bath content. The effect of current density on the effectiveness of NTS is discussed below.

Effect of Current Density On Microstructure & Hardness

Previous work has indicated that changes in the current density have only a limited effect on the grain size in nickel layers deposited from a sulfamate bath without additives.[6] After adding NTS to the sulfamate bath the grain size was more sensitive to current density during deposition. TEM images of nickel layers deposited from a bath with 4.0 g/L (30 oz/gal) NTS are shown in Fig. 6. The left-hand image shows nickel deposited at a current density of 0.5 A/dm² (4.6 A/ft²), while the right-hand image shows nickel deposited at a current density of 20 A/dm² (186 A/ft²). Clearly, the grain size was considerably reduced by increasing the current density. The dependence of the hardness of the nickel layer on the current density in a sulfamate bath with and without NTS follows from comparison of the curves in Fig. 7. If no additive is present the hardness is virtually independent of current density. With 4.0 g/L (30 oz/gal) NTS present, the hardness increases significantly with current density.

This difference in sensitivity can be explained as follows. The observed effect of the additive is likely caused by its adsorption at the cathode during deposition. The amount of adsorbed NTS can be expected to increase with cathode potential. Increasing the current density will increase the cathode potential.
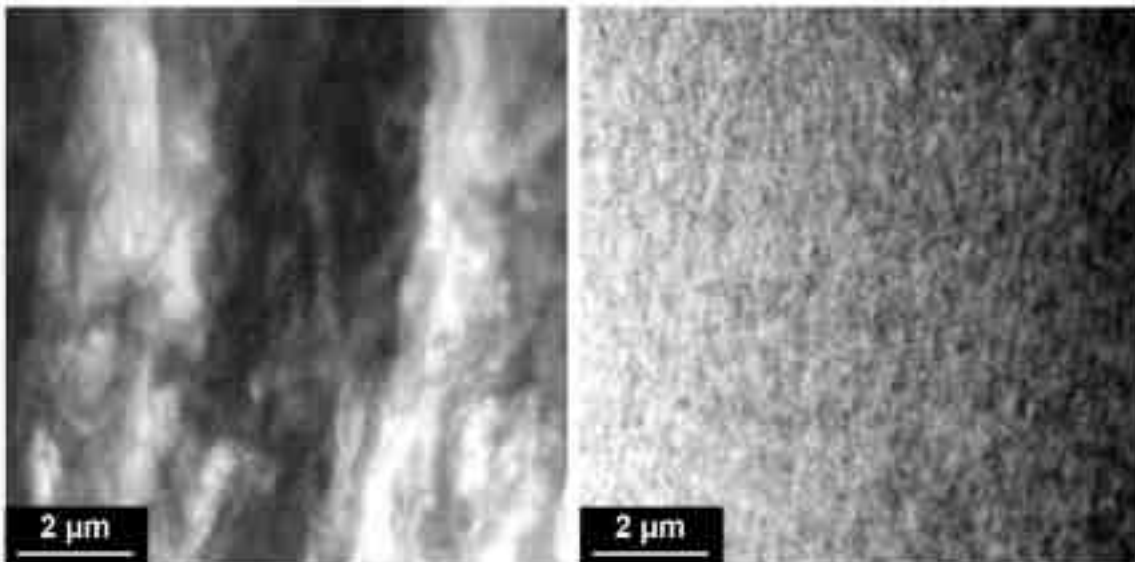

Figure 6 - TEM images of nickel layers deposited from the sulfamate bath with 4g/L (30 oz/gal) of 1,3,6 naphthalene trisulfonic acid at two current densities. Right image: i = 0.5 A/dm² (4.6 A/ft²). Left image: i = 20 A/dm² (186 A/ft²).

Comparison of Microstructure & Hardness

The effect of NTS can be attributed to adsorption of this substance at the surface of newly developed cathode material. Apparently, this adsorption hindered freshly formed nuclei from growing by making the nucleation of new nuclei more energetically favorable. Consequently, an effective reduction of the size of nickel crystallites in the layer was achieved, leading to an increase in hardness by grain boundary strengthening. On the basis of the Hall-Petch relation[7,8], an empirical description for the relation between hardness (or, equivalently, yield strength) and grain size, the hardness would be expected to increase proportionally with the reciprocal of the square root of grain size.

Conclusions

The use of the additive 1,3,6 naphthalene trisulfonic acid in a sulfamate nickel bath resulted in reduced grain size and higher hardness in the deposited nickel layer. The effectiveness of the additive depended on the current density. Increasing the current density increased the hardness for a given concentration of NTS. The mechanism responsible for the observed effects was most likely adsorption of this substance at the cathode during deposition.

Acknowledgments

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Anette Alsted Rasmusssen received her MSc in materials science from the Technical University of Denmark in 1999, and is now working on the PhD project, "Strengthening Mechanisms in Electrodeposited Layers."

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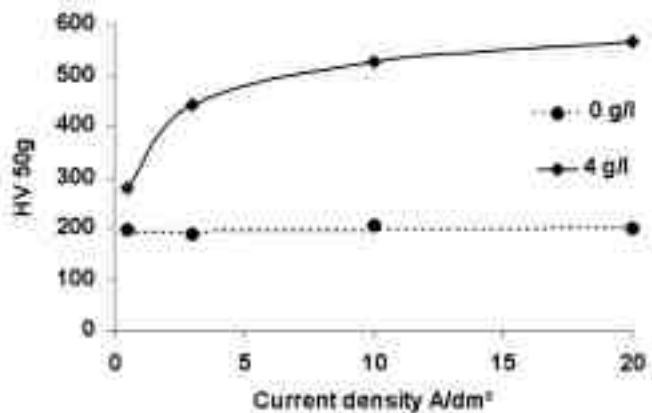
Fig. 7—Hardness vs. current density for nickel deposited from a sulfamate bath with 0.0 g/L and 4.0 g/L (30 oz/gal) 1,3,6 naphthalene trisulfonic acid.

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