# **Technical Article**

# Ni-W Alloy Electrodeposition From a Bath Containing an Organic Amine Substitute for Inorganic Ammonia

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In this work, a simple organic amine, glycine, was used as a substitute for inorganic ammonia salts or free ammonia, which are generally used in nickeltungsten (Ni-W) alloy electrodeposition. The results indicated that glycine was more effective in increasing deposition efficiency. However, it also reduced the tungsten content, when compared with results from inorganic ammonia systems, all other plating parameters being the same. Therefore—glycine functioned similarly. Glycine however, forms a stronger complex with nickel ions than does  $NH_3$  and it has a completely different hydrolysis mode. Thus the deposition behavior from a solution containing glycine was somewhat different. Accordingly, we studied the effects of bath



Fig. 1—Tungsten content and deposition efficiency as a function of sodium tungstate concentration in the solution. **a** anW and **•**, amC.E. indicate the tungsten content of the deposit and the current efficiency in the bath with glycine, respectively; **a**, basW and **•**, basC.E. indicate the tungsten content of the deposit and the current efficiency in the bath with: 16g/L NiSO<sub>4</sub>  $6H_2O$ , 40g/L  $H_3$ [Cit] $H_2O$ , 50 g/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and 0.0, 1.6, 10, 20 and 32g/L Na<sub>2</sub>WO<sub>4</sub>  $:2H_2O$ . Plating parameters were pH 6.5, cathodic current density 6.0 A/dm<sup>2</sup> (55.7 A/f<sup>2</sup>) and temperature 65°C (149°F).

# Nuts & Bolts: What This Paper Means to You

Nickel-tungsten alloy deposits have great potential in wear applications. Unfortunately, the ammonia-based baths commonly used are unstable and present obvious problems with fumes. This work deals with a safe and improved substitute, replacing the ammonia with an organic—glycine. This just might be the key to more widespread use of this alloy coating in engineering applications. pH and glycine concentration. A significantly different structure was found in the Ni-W alloy deposited from the glycine-containing bath.



Fig. 2—Tungsten content and deposition efficiency as a function of glycine concentration.

Nickel-tungsten alloy electrodeposits have been of interest to many researchers because of their excellent physical and chemical properties. There are many published papers related to plating procedures, deposition mechanisms and structures/properties of the deposits. Up to the present, almost all successful processes have some basic requirements for the bath composition, as enumerated by Brenner.<sup>1</sup> He wrote that, besides the presence of metallic sources such as tungstate and the iron-group salt, it is essential to include: a) ammonium salts such as ammonium sulfate, b) excess ammonium hydroxide and c) at least one complexing agent such as citric or tartaric acid. Ammonium salts and free ammonia play a multiple role in Ni-W plating baths to increase a) cathodic efficiency, b) surface quality of the deposit and c) the solubility of the nickel compounds and thus stabilize the bath against precipitation. Ammonium salts and free ammonia are thus critically important in Ni-W plating.

On the other hand, ammonium salts and free ammonia can also cause problems. They are difficult to maintain at elevated temperatures because of their volatility. Thus the pH and solution chemistry are not as stable. Further, strict

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Fig. 3—Tungsten content and deposition efficiency as a function of current density.

industrial limits on air quality are incompatible with the irritant ammonia gases. As a result, in earlier days some researchers tried to use amines that were less volatile than ammonia in Ni-W alloy plating. Triethanolamine,<sup>2,3</sup> guanidine, hydrazine, ethanolamine,<sup>4,5</sup> tetraethanolamine and ethylenediamine<sup>6</sup> were studied and found to have no effect or even a negative effect (decrease in cathode efficiency, precipitation of metallic ions, etc.) during plating. In our previous work, using triethanolamine<sup>7</sup> and hydrazine<sup>8</sup> in an ordinary ammonia bath, we reached similar conclusions. Triethanolamine clearly decreased the current efficiency and slightly increased the tungsten content and surface quality of the deposits. Hydrazine strongly decreased the cathode efficiency and caused serious pitting on the deposit surface. The main focus of this study was to investigate another simple amine, glycine, as a substitute for inorganic ammonia or its salts.

## Experimental

Nickel-tungsten alloys were deposited from a low-concentration sodium tungstate solution containing no free ammonia or ammonium salts. Instead, specific quantities of glycine were added to the bath according to our experimental design. The plating solution contained 20 g/L nickel sulfate (NiSO<sub>4</sub>·6H<sub>2</sub>O), 50 g/L dihydrate sodium tungstate, 35 g/L monohydrate citric acid, 25 g/L boric acid and 15 g/L glycine.

The operating parameters were as follows except for those parameters under specific study:

pH	7.0 (adjusted with 10% NaOH or
	$10\% H_2 SO_4$ )
Cathode current density	$6.5 \text{ A/dm}^2$ (60.4 A/ft <sup>2</sup> )
Temperature	65°C (149°F)

Insoluble mixed metal oxide( $IrO_2/Ta_2O_5$ )(MMO)-coated titanium was used as anode material.<sup>9</sup> The deposit thickness for measurement was about 10µm (0.4 mil). Pure iron sheet with an area of 4 x 2.5 mm (0.16 x 0.10 in.) was used as a cathode. Before plating, the specimens were degreased chemically in a solution containing 25 g/L NaOH, 30 g/L Na\_2CO<sub>3</sub> and 25 g/L Na\_3PO<sub>4</sub> at 90°C (194°F) for about 20 min. Pickling and etching were performed in a solution containing 350 mL/L HCl (37%) at room temperature for about two to three minutes. All of the reagents used were of the chemically-pure grade.

Surface morphologies and compositions were studied using scanning electron microscopy (SEM) with added energy dispersed spectra (EDS) measurement equipment. X-ray diffraction (XRD) was used to identify the phases, using Cu K radiation, an acceleration voltage of 36 kV and a beam current of 26 mA.



Fig. 4—Tungsten content and deposition efficiency as a function of pH value of the bath.

# Results & Discussion Deposition Mechanism Studies

Figures 1 thru 5 show the influence of the plating parameters on tungsten content in the deposit and the cathode current efficiency. Figure 1 shows that the deposition efficiency decreased while the tungsten content in the deposit gradually increased with increasing sodium tungstate in the bath. The gradual, rather than sharp, change in the behavior of composition and Faraday s efficiency is consistent with that in the classical process from the bath containing inorganic ammonium salts or free ammonia.<sup>10,11</sup> This implies that, as a substitute for inorganic ammonia, glycine did not intrinsically change the deposition characteristics of the Ni-W alloy.

As a source of amine, glycine significantly raised the current efficiency when compared to the behavior with inorganic ammonia (Fig. 2). However, when the glycine concentration was more than 5 g/L, the current efficiency gradually decreased with further additions of glycine (the maximum is greater than 55%). The tungsten content of the deposit decreased with increasing glycine concentration in the range under study.

Cathodic current density (CD) is an important factor in the plating process. As shown in Fig. 3, the current efficiency first increased slightly and then decreased, while the tungsten content in deposit showed a reverse trend, but it was not as obvious.

Figure 4 shows the influence of pH on tungsten content and current efficiency. In the range from pH 4.5 to 8.0, the current efficiency gradually decreased with increasing pH, but the tungsten content sharply increased from about 15 wt% at pH 5.0 to about 38 wt% at pH 6.0. It then slowly decreased above pH 6.0. It should be pointed out that this characteristic is completely different from that observed in the solution containing inorganic ammonia, where current efficiency increased<sup>1,12</sup> and the tungsten content of the deposit exhibited the reverse behavior with pH. The difference in behaviors can be explained on the basis of different hydrolytic equilibria between NH<sub>4</sub>OH and glycine in the solution. This will be discussed further on.

Another factor that should be considered is temperature, which has an important influence on the plating process (Fig. 5). It is easy to understand that current efficiency increased with temperature because the higher temperature led to faster mass transport and higher reactivity of the reacting ions. As to deposit composition, the tungsten content increased from about 31 to 36 wt% when the temperature increased from 40°C to 50°C (104°F to 122°F), beyond which it remained nearly constant regardless of temperature.

In order to analyze glycine behavior, effects of inorganic ammonia should first be pointed out. From the results reported by Younes and Gileadi,<sup>11</sup> free ammonia may compete with citrate as a ligand, forming bonds to nickel ions to decrease the concentration of [(Ni)(Cit)]. The ternary complex  $[(Ni)(HWO_4)(Cit)]^2$  will then result in decreasing tungsten codeposition with nickel. In the normal solution with ammonia water or ammonium salts, the concentration of free ammonia, NH<sub>3</sub>, is changed with its precursor concentration and solution pH. From the hydrolytic reactions (1a), (1b), and the



*Fig.* 5—*Tungsten content and deposition efficiency as a function of plating temperature.* 



Fig. 6—SEM morphologies of deposits from the solution containing 20 g/L NiSO<sub>4</sub>·6H<sub>2</sub>O, 35 g/L monohydrate citric acid, 25 g/L boric acid, 15 g/L glycine, with concentrations of dihydrate sodium tungstate at (a) 1.6, (b) 10, (c) 20, (d) 50, (e) 65 and (f) 99 g/L.

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Ni(W) codeposition reaction (1c) below,<sup>11</sup> increasing the pH value or the concentration of ammonium hydroxide should decrease the tungsten content in the deposit. Accordingly the Faradaic efficiency increased because nickel could be directly reduced from the binary complex Ni(NH<sub>3</sub>)<sub>x</sub> (where x is a complex number). The effects of other plating parameters on the process may also be related to some extent to the hydrolytic equilibrium of ammonia during plating.

$$NH_4OH = NH_4^+ + OH^-$$
 (1a)

$$NH_4OH = NH_3 + H_2O$$
 (1b)

$$[(Ni)(HWO_4)(Cit)]^{-2} + 8e^{-} + 3H_2O$$
 NiW + 7(OH)<sup>-</sup> + Cit<sup>-3</sup> (1c)

In our experiment, as a substitute for inorganic ammonia, glycine  $(H_2NCH_2COOH)$  can be present in different forms in aqueous solution depending on the pH value:

$$H_{3}^{+}NCH_{2}COOH \qquad H_{2}NCH_{2}COOH + H^{+} \quad pKa = 2.47 \quad (2a)$$

$$H_2NCH_2COOH \qquad H_2NCH_2COO^- + H^+ \qquad pKa = 9.66 \quad (2b)$$

The amino group is protonated at pH values below 2.5, whereas glycine exists in its anionic form at pH values above 9.7.13 Its isoelectric point (IP) in aqueous solution is 5.97. Hence, in the intermediate pH range, glycine takes on a neutral form in equilibrium with its zwitterions, H<sub>2</sub>N<sup>+</sup>-CH<sub>2</sub>-COO<sup>-</sup>. However, the concentration ratio of the amino group H<sub>2</sub>N<sup>+</sup>-R cation to the carboxyl group R-COO<sup>-</sup> anion changes with pH. Under our experimental conditions, the protonated amino group of glycine had a function similar to ammonia as a ligand forming coordinate bonds to the Ni<sup>+2</sup> ions. Therefore increasing the glycine concentration (1) increased the concentrations of the amino group cation and the binary complex between Ni<sup>+2</sup> and H<sub>2</sub><sup>+</sup>NCH<sub>2</sub>COOH in solution, (2) increased the current efficiency and (3) decreased the tungsten content (Fig. 2). This is similar to the behavior observed with free ammonia from inorganic ammonium salt in the plating bath.11 However, glycine was more effective because it was much more effective as a ligand for the nickel ions when compared to free ammonia or inorganic ammonium salt (K<sub>unstable</sub> =  $1.86 \times 10^{.9}$  for  $[Ni(NH_3)_6]^{+2}$ ,  $K_{unstable} = 2.3 \times 10^{.11}$  for  $[Ni(Gly)_2]^{+2}$ ). Thus the current efficiency increased sharply to its maximum value with increasing, but very low, glycine concentration up to the range of 3.75 to 5.0 g/L, and then slowly decreased (Fig. 2). Accordingly, the current efficiency was higher and the tungsten content was lower when using glycine than when using inorganic ammonia, with the Na<sub>2</sub>WO<sub>4</sub> concentration in the range from 0.0 to 65.0 g/L (Fig. 1).

According to reactions (2a) and (2b), decreasing pH favored an increase in the amount of  $H_3^+NCH_2COOH$  cations, which may have formed a binary complex with nickel ions to be deposited directly on the cathode. Accordingly, less available Ni<sup>+2</sup> ions were available to assist in the deposition of tungsten. Thus, increasing pH had the reverse effect from increasing glycine concentration. Moreover, the lower the pH , the sharper the change of current efficiency and tungsten content. In the case of a pH value below the isoelectric point of glycine (IP<sub>glycine</sub> = 5.97), the predominant form was H<sub>3</sub><sup>+</sup>NCH<sub>2</sub>COOH cation. Further, the H<sub>2</sub>NCH<sub>2</sub>COO<sup>-</sup> anion was predominant as the pH rose above IP<sub>glycine</sub>. Drastic changes in current efficiency and tungsten content occurred as the pH was changed from 5.0 (under the isoelectric point) to 6.0 (over the isoelectric point) (Fig. 4). Thus, as shown in Fig. 4, only a small change was observed above pH 6.0.

The influence of current density can be also explained with the observations noted above. Because of the limitation of mass diffusion, hydrogen evolution reactions could be accelerated by increasing the current density. However, there was an accompanying decrease in current efficiency. On the other hand, the local pH



Fig. 7—X-ray diffraction patterns of Ni-W deposits with different tungsten contents (wt%): " $_{i}$ " = Ni; "?" = unknown diffraction peaks.

adjacent to the cathode may also increase and glycine would then tend to revert to the  $H_2NCH_2COO^-$  anion. Therefore, near the cathode, the concentration of  $H_3^+NCH_2COOH$  cations may decrease and less nickel bi-complex with the amino group of glycine will form to react directly when current density is increased, ultimately resulting in decreased current efficiency.

#### Surface Morphology & X-ray Diffraction Studies

The SEM morphologies of the deposits, versus tungsten content in the deposit (or  $Na_2WO_4$  concentration in the bath), are shown in Fig. 6. The deposits exhibited nodular morphologies and the nodule size decreased with increasing tungsten content. The result is similar to that for baths containing inorganic ammonia.<sup>10</sup>

Figure 7 shows the x-ray diffraction patterns of the deposits with varying tungsten content. The Ni-W alloy deposits here had a completely different structure from those deposited from a bath containing inorganic ammonia. Since the tungsten content was low, the Ni-W deposit was a solid solution of Ni(W) with a face-centered cubic nickel structure. When the tungsten content was increased from about 15 to 40 wt% however, another diffraction peak appeared at a 2 value of about  $41^{\circ}$ , in addition to the broadening of the nickel diffraction peaks.

Furthermore, with increasing tungsten content in the deposit, the intensity of the new peak first increased and then gradually decreased while the intensities of the nickel diffraction peaks decreased and broadened (or even disappeared, such as with the Ni (200)) at the same time. On the other hand, at tungsten contents above 30 wt%, there appeared to be broadening peaks at angles about 2° below those of Ni (220) and Ni (311). The peak profiles also seemed to change from appearing as single peaks. The peaks may have shifted from purely Ni (220) and Ni (311) or they may be evidence of an unknown phase.

When the tungsten content in the deposit was high enough (over about 42 wt%, near the eutectic composition), all the peaks disappeared except for a weak broadening of one near the Ni (111) diffraction position, implying the formation of an amorphous Ni-W alloy. These will be studied in our next paper.

# Conclusions

- 1. As a substitute for inorganic ammonia in a nickel-tungsten alloy plating solution, glycine drastically increased the Faradaic efficiency at lower concentrations. Higher glycine decreased the efficiency to some degree. Maximum efficiency was obtained between 3.0 and 5.0 g/L of glycine in solution.
- 2. Under equivalent operating conditions, nickel-tungsten alloys deposited from the glycine solution had a relatively lower tung-

sten content than those from a conventional inorganic ammonia bath. This was because of the stronger tendency of glycine to form ligands.

- 3. Because of the unique hydrolytic behavior of glycine, the deposition efficiency decreased but the tungsten content increased with increasing solution pH. Furthermore, this change was more drastic when the solution pH was close to the isopotential of glycine.
- 4. The nickel-tungsten deposits exhibited nodular morphologies. The nodule size decreased with increasing tungsten content in the deposit. With the tungsten content between about 15 and 40 wt%, new x-ray diffraction peaks appeared in addition to those for face-centered cubic nickel, suggesting that an unknown phase might have formed in the Ni-W alloy deposited from the glycine-containing solution.

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