Study of Stress Reducers in Nickel-Tungsten Electroforming Baths

By C.-H. Huang, W.Y. She & H.M. Wu

Stress reducers used in nickel-tungsten electroforming can be categorized as either Type L that decrease the stress at a lower current density, or Type H that decrease the stress at a higher current density. An optimum combination of these two types reduces the stress over a wide range of current density. Because the hardness of the alloy deposits is associated with stress, the effect of stress reducers on the hardness was also studied. No criteria are available to evaluate stress or hardness in terms of the amount of sulfur or hydrogen incorporated in the alloy deposit.

Hardness of an electroform is an important indicator of its appropriateness for applications. Because the hardness of a nickel-tungsten alloy electroform is significantly enhanced with respect to that of nickel,¹ in this study, we developed an electroformed nickel-tungsten alloy with high hardness. Although hardness is increased when the electroformed nickel is codeposited with tungsten, the internal stress in the alloy deposit exceeds that of the corresponding nickel electroforms.² Because the addition of reducers is the primary means of controlling the stress and other properties of the alloy deposit, ten stress reducers were tested in the induced nickeltungsten alloy baths³ to decrease the stress. According to our results, no single reducer decreases the stress at both lower and higher current densities. These reducers were therefore divided into the two types mentioned above: Type L reduces the stress at a lower current density while Type H reducers

decrease the stress at a higher current density. In addition, combinations of these two types were evaluated to obtain a lower stress over a wide range of current density $(2.5 \sim 40 \text{ A/} \text{dm}^2)$. These results can lead to a more effective approach in selecting reducers in terms of minimal internal stress.

Electroformed nickel-tungsten alloy with low stress is always accompanied by a corresponding decrease in hardness. To have a sound alloy electroform with both low stress and high hardness, this study examined how these reducers influence the conflicting phenomena of stress and hardness.

Experimental Procedure

To avoid deterioration of the electroforming bath, acidic electrolyte formation containing 400 g/L of nickel sulfamate $[Ni(NH_{a}SO_{a})_{a} \cdot 4H_{a}O], 40 g/L sodium tungstate (Na_aWO₄)$ \cdot 2H₂O), and 36 g/L of citric acid (C₆H₈O₇ · H₂O) was adopted to prepare the electroformed nickel-tungsten alloy. Stress reducers investigated in this study were sodium benzene sulfonate (L1), benzene sulfonamide⁴ (L2), bis(benzenesulfonyl)imide (L3), ortho-benzosulfimide (L4), sodium vinyl sulfonate (H1), sodium allyl sulfonate (H2), disodium 1,5-naphthalene disulfonate (H3), trisodium 1,3,6-naphthalene trisulfonate (H4), phthalimide (H5), and succinimide (H6). The concentration of each added reducer was 0.4 g/L unless otherwise stated. The alloy baths containing these reducers were designated as Bath-L1, Bath-L2, Bath-L3, Bath-L4, Bath-H1, Bath-H2, Bath-H3, Bath-H4, Bath-H5 and Bath-H6, respectively. Nickel-tungsten alloy was elec-



Fig. 1—Variation of internal stress with current density when reducer H4 was added to baths containing reducer L3.



Fig. 2—Variation of internal stress with current density when reducer H4 was added to baths containing reducer L4.

Table 1

Variation of Internal Stress with Current Density When Concentration of Reducers is 0.4 g/L

	Internal Stress, MPa					
	2.5	5	10	20	30	40
Reducer	A/dm ²	A/dm ²	A/dm ²	A/dm ²	A/dm ²	A/dm ²
Ni*	2	0	0	3	0	0
Ni-W*	16	20	68	cracked		
L1	18	20	70	cracked		
L2	26	30	92	110	cracked	
L3	7	9	14	18	25	59
L4	0	0	10	20	112	cracked
H1	cracked	25	20	18	5	4
H2	45	40	25	24	8	7
H3	100	90	20	18	5	5
H4	cracked	51	19	17	0	0
H5	81	46	24	24	19	5
H6	101	51	17	15	10	8

* Ni electroforming bath; Ni-W is the alloy bath. No reducer in these baths.

troformed on bright, flat, 3 x 3 cm stainless steel specimens in a 1-L solution at 60 °C. Electrolyzed nickel anodes were used. When the deposit reached the required weight of around 0.8 g, the electroformed layer was separated mechanically. Electron dispersive spectroscopy (EDS) technique was employed for tungsten determination in the alloy electroforms. Hydrogen content in the alloy deposit was determined by a combustion analyzer. Internal stress was determined by spiral contractometer. Hardness of deposits was determined by a Vickers microhardness tester under 200 g load.

Results & Discussion

Stress Reducers

According to Table 1, the internal stress in a nickel-tungsten alloy deposit obtained from a reducer-free bath exceeds that of the corresponding nickel deposit. Accordingly, only cracked deposits are obtained when the current density is increased to



Fig. 3—Variation of internal stress with current density when reducer H5 or H6 was added to baths containing reducer L4.

Table 2 Variation of Current Efficiency with Bath Composition & Current Density

	Cathode Current Efficiency, %					
	2.5	5	10	20	30	40
Reducer	A/dm ²	A/dm ²	A/dm ²	A/dm ²	A/dm ²	A/dm ²
Ni-W	52.4	58.1	64.5	—	—	—
L1	49.5	57.1	59.5			
L2	28.8	56.3	59.1	65.2		—
L3	33.4	46.3	53.9	66.6	68.1	74.9
L4	44.6	48.2	60.0	62.7	66.7	
H1	—	45.2	63.4	65.5	65.7	66.2
H2	26.8	44.2	63.1	64.3	71.4	72.7
H3	9.6	16.4	47.1	59.8	65.4	67.2
H4		40.4	57.2	64.0	65.8	67.2
H5	27.2	51	63.5	66.4	66.7	71.5
H6	22.5	43.1	47.8	64.3	64.1	66.5

20 A/dm². As is generally known, Class I brighteners of the Watts-type nickel bath reduce the tensile stress in the nickel deposit.⁵ Accordingly, in this study, some Class I brighteners, together with other organic additives, were investigated to decrease the stress in Ni-W alloy deposits. The stress data concerning these reducers in the alloys vary widely and conflict with each other. Table 1 indicates that the stresses in the alloy deposits changed slightly when the Ni-W baths contained reducer L1 or L2, while reducers L3 and L4 were more effective and reduced the stresses to zero or even compressive at a lower current density. A bright alloy deposit with -10 MPa stress was obtained from Bath-L4, therefore, when the current density was decreased to 1.25 A/dm^2 . The stress in the alloy deposits decreased at a lower current density in the presence of reducers L1, L2, L3, and L4, which were designated Type L reducers.

In contrast, from the lower half of Table 1, stress decreased with increasing current density when the alloy baths contained reducers H1, H2, H3 or H4. Among these, reducer H4 more strongly influences the stress. Consequently, zero stress



Fig. 4—Variation of hardness with current density when reducer H4 was added to baths containing reducer L3.

was sustained even when the current density was increased to 80 A/dm^2 . In addition, two sulfur-free stress reducers, organic imides H5 and H6, were tested to study the effect of sulfur content on stress. As shown in Table 1, the sulfur-free H5 and H6 also decreased the stress at a higher current density. These six reducers were designated as Type H reducers. Alloy deposits obtained from reducer-containing baths were fine-grained.

Table 1 also reveals that reducers L3, L4, and H4 heavily influence the stress in the alloy deposit. Moreover, the effect of sulfur content on the stress can be studied in the presence of sulfur-free reducers, H5 and H6. More experimental data were accumulated therefore on these five reducers and their possible combinations.

Stress reducers play a prominent role in decreasing stress in the deposit, whether resulting from lattice mismatch with the substrate, or to hydrogen incorporation in the deposit, or sulfur incorporation.⁶ Our earlier work⁷ on nickel electroforming found no linear relation between the sulfur content and the stress. Although less sulfur is included in the alloy deposit in the presence of a sulfur-free reducer than with a sulfur-based reducer,⁸ either sulfur-based or sulfur-free reducers of Type H reduced the stress at a higher current density. For instance, the variations of stress with current density for Bath H5 and Bath H6 closely resembled those of Baths H2 and H3. Correspondingly, no general criteria are available to evaluate the stress in terms of the sulfur content in the alloy deposit.

These stress reducers appear to reduce the value of current efficiency (Table 2).⁹ Such a low current efficiency strongly suggests that a considerable amount of hydrogen evolves at the cathode.¹⁰ The hydrogen adsorption, as well as the residual hydrogen content, may alter the deposit stress.¹¹ Previous literature provides the following account of intrinsic stress caused by the incorporation of hydrogen.⁶ Tensile stress can develop as a result of diffusion of hydrogen out of the deposit surface layer or toward the substrate, causing a shrinkage of the surface or expansion of the layer beneath. Compressive stress is caused by hydrogen remaining in the

surface layer, filling voids and expanding them. Such behavior may change the stress from tensile to compressive, whereas analyzing the distribution of hydrogen content among the deposit is extremely difficult. In addition to analysis of the hydrogen situation, the total amount of hydrogen in the alloy deposit was determined. Table 3 reveals large amounts of hydrogen in the alloy deposits, at either a lower or higher current density. Correspondingly, no linear behavior was found between the stress and the total amount of hydrogen in the alloy deposit.

The variation of hydrogen content with current density coincides with the tungsten content in the alloy deposit. As shown in Table 4, a nonlinearity of the tungsten content and current density was found. According to thermodynamic principles, both hydronium ions and tungsten oxides are easily reduced to hydrogen and tungsten, respectively, at lower current density, because of a lower pH at the depletion layer of the cathode.^{12,13} Greater amounts of hydrogen and tungsten were produced, therefore, and incorporated in the deposits at a lower current density. Moreover, because some tungstate ions were reduced by hydrogen in the Helmholtz layer, then included in the deposits, large amounts of hydrogen produced at lower current density partially increase the tungsten content in the deposits. Correspondingly, the tungsten content increases with decreasing current density. On the other hand, a higher current density increases the pH at the depletion layer of the cathode and, accordingly, the reduced amounts of hydrogen and tungsten were decreased. Because of a higher pH of the solution at the depletion layer, increasing the hydroxide concentration at the cathode results in hydrogen and tungsten depositing in precipitates as hydroxides,^{9,14} causing tungsten in elemental form or as the hydroxide to be included in the deposit. Consequently, a higher content of tungsten was also found at a higher current density. Meanwhile, the hydrogen component in the hydroxide also increased the total hydrogen content in the alloy deposit. For instance, increasing the current density to 80 A/dm² increased the hydrogen content in the alloy deposits obtained from Baths H5 and H6 to 117 and 78 ppm, respectively.



Fig. 5—Variation of hardness with current density when reducer H4 was added to baths containing reducer L4.



Fig. 6—Variation of hardness with current density when reducer H5 or H6 was added to baths containing reducer L4.

Table 3

Variation of Hydrogen Content in Alloy Deposit With Bath Composition & Current Density

	Hydrogen Amount, ppm					
	2.5	5	10	20	30	40
Reducer	A/dm ²	A/dm ²	A/dm ²	A/dm ²	A/dm ²	A/dm ²
L3	44	23	39	45	63	73
L4	38	23	49	56	64	75
H4	65	35	32	44	57	62
H5	64	55	51	68	70	78
H6	45	21	21	49	70	78
0.3 g/L L3 0.1 g/L H4	38	30	45	52	62	103
0.3 g/L L3 0.3 g/L H4	65	23	31	32	44	45
0.3 g/L L3 0.6 g/L H4	84	24	26	30	37	42
0.3 g/L L4 0.1 g/L H4	83	35	23	34	32	34
0.3 g/L L4 0.3 g/L H4	58	36	43	43	42	47
0.3 g/L L4 0.6 g/L H4	35	29	31	31	30	32
0.3 g/L L4 0.3 g/L H5	40	35	25	29	37	53
0.3 g/L L4 0.3 g/L H6	52	43	42	39	41	44

Significantly, non-linear relations between current density and the hydrogen or tungsten contents were observed.

Because of the acidic characteristic (below 2.0) of the alloy bath, nickel deposits preferentially, that is, the percentage of tungsten in the deposit is smaller than its metal-percentage in the electrolyte.² Tungsten content in these alloy deposits was therefore below six percent.

The hydrogenation rate of the reducers at the cathode surface affected the amount of adsorption, incorporation and subsequent distribution of hydrogen. Accordingly, the crystalline structure, dislocations of the alloy deposit and then the stress were changed by the molecular structure of the reducers.¹³ For the sulfo reducers,⁴ the degree of hydrogenation of mono-nuclear aromatic species (Type L reducers) is lower than that of Type H reducers (alkene sulfonates or dinuclear aromatic sulfonates), causing different amounts of hydrogen to be adsorbed and absorbed.¹⁴ Perhaps this is the reason why Type L reducers have different effects on the stress, with variation of current density, from that of Type H reducers. The nature of the internal stress in the alloy deposits remains unclear. For a better understanding of the effect of the degree of hydrogenation of these reducers on the stress, further study will be conducted in greater detail on this point.

Combined Effects of Types H & L Reducers

Each of the reducers studied decreases the stress only at a higher or lower current density. To obtain low stress over a wide range of current density, the effect of combining Type L and Type H reducers would have on the stress was investigated. As shown in Table 5, the trend of the variation of stress with current density remained unchanged when the concentration of reducers was changed from 0.4 g/L to 0.2 or 0.6 g/L. In addition to 0.4 g/L, other concentrations were also

Table 4

Variation of Tungsten Content of Alloy Deposit With Bath Composition & Current Density

Tungsten, %					
2.5	5	10	20	30	40
A/dm ²	A/dm ²	A/dm ²	A/dm ²	A/dm ²	A/dm ²
3.2	1.4	0.5	1.2	1.6	2.4
3.7	2.6	1.2	1.5	2.7	2.5
0.5	0.7	0.8	0.5	0.5	0.6
1.2	1.4	0.7	0.9	1.4	1.7
1.1	1.1	1.0	0.6	1.6	1.4
	2.5 A/dm² 3.2 3.7 0.5 1.2 1.1	2.5 5 A/dm² A/dm² 3.2 1.4 3.7 2.6 0.5 0.7 1.2 1.4 1.1 1.1	Tungs 2.5 5 10 A/dm² A/dm² A/dm² 3.2 1.4 0.5 3.7 2.6 1.2 0.5 0.7 0.8 1.2 1.4 0.7 1.1 1.1 1.0	Tungsten, % 2.5 5 10 20 A/dm ² A/dm ² A/dm ² A/dm ² 3.2 1.4 0.5 1.2 3.7 2.6 1.2 1.5 0.5 0.7 0.8 0.5 1.2 1.4 0.7 0.9 1.1 1.0 0.6	Tungsten, % 2.5 5 10 20 30 A/dm² A/dm² A/dm² A/dm² A/dm² 3.2 1.4 0.5 1.2 1.6 3.7 2.6 1.2 1.5 2.7 0.5 0.7 0.8 0.5 0.5 1.2 1.4 0.7 0.9 1.4 1.1 1.0 0.6 1.6

Table 5

Variation of Internal Stress with Current Density When Concentration of Reducers is Other than 0.4 g/L

	Internal Stress, MPa					
	2.5	5	10	20	30	40
Reducer	A/dm ²	A/dm ²	A/dm ²	A/dm ²	A/dm ²	A/dm ²
0.2 g/L L3	12	22	35	42	51	52
0.6 g/L L3	5	12	20	24	31	47
0.2 g/L L4	0	7	18	20	29	80
0.6 g/L L4	9	17	26	30	110	cracked
0.2 g/L H4	80	29	20	18	7	0
0.6 g/L H4	cracked	110	30	26	17	9
0.1 g/L H5	51	29	20	11	12	0
0.2 g/L H5	89	47	41	20	18	0
0.2 g/L H6	64	30	21	12	12	0
0.6 g/L H6	cracked	82	28	23	18	19

Table 6 Variation of Hardness of Alloy Deposit With Bath Composition & Current Density

	Hardness, HVN						
	2.5	5	10	20	30	40	
Reducer	A/dm ²						
L3	420	400	402	408	386	377	
L4	566	562	501	518	602	—	
H4		350	126	132	166	204	
H5	370	372	359	321	352	233	
H6	411	362	322	277	246	182	
0.2 g/L L4	516	417	404	405	361	414	
0.6 g/L L4	641	572	558	544	522	—	

selected to examine the combined effects of Type H and Type L reducers. Because of the lower solubility of Reducer H5, the concentrations listed in Table 5 were 0.1 and 0.2 g/L. Figures 1 and 2 indicate that the higher stresses in the deposit obtained from the L3- and L4-containing baths at a higher current density were reduced by the presence of reducer H4, particularly the steep increase of the tensile stress of curve (a) of Fig. 2. As shown in Fig. 3, reducer H5 or H6 also decreased the stresses in the deposits obtained from an L4-containing bath at a higher current density. At a lower current density, reducer H4, H5, or H6 slightly influenced the stresses, perhaps a result of the stronger adsorption of reducers L3 and L4 at the cathode. This finding is significant in that alloy deposits with a stress below about 20 MPa over a wide range current density (2.5 to 40 A/dm²) were obtained when the alloy baths contained an optimum combination of reducers L3 or L4 with H4. H5 or H6.

Either sulfur-based reducer H4 or sulfur-free reducers H5 and H6 similarly influenced the stress in the deposit obtained from an L4-containing bath at a higher current density. The results of combined stress reducers support the fact that the amount of sulfur incorporated in the alloy deposit is not a critical point for stress.

Table 3 indicates that when the alloy baths contained a combination of Type L and Type H reducers, large amounts of hydrogen were still determined at lower or higher current densities. No linear relations between the total hydrogen content and stress were obtained experimentally, either for the alloy bath containing a simple reducer or a combination of two types of reducers.

Hardness

Stress reducers are adsorbed at active sites on the cathode. Consequently, they or a product of their cleavage are frequently incorporated into the deposits at grain boundaries, where the movement of dislocations is obstructed, thereby changing the hardness. Table 6 reveals that perhaps as a result of the difference of hydrogenation rate, as well as adsorption and decomposition of these reducers at the cathode, the deposits obtained from Baths L-3 and L-4 had a higher hardness than those of Baths H-4, H-5 and H-6. The action of reducer L-4 is particularly strong. Deposits with greater values (above HV 500) of hardness and low stress (below 20 MPa), therefore, can be obtained from Bath L4, where the current density is $2.5 \sim 20$ A/dm². Although higher hardness could be obtained when the concentration of L4 was increased to 0.6 g/L (Table 6), the stress was simultaneously increased (Table 5). On the other hand, both stress and hardness were decreased when the concentration of L4 was decreased to 0.2 g/L. To obtain a sound alloy electroform with high hardness and low stress, the conducted current density was narrowed when the concentration of reducer L4 was shifted to 0.2 or 0.6 g/L. Accordingly, the better concentration of reducer L4 is 0.4 g/L.

Because reducers H4, H5 and H6 reduced the stress in the deposit obtained from L3- and L4-containing baths, the effect of the combination of reducers on the hardness was investigated to increase the range of conducted current density. Figure 4 indicated that most of the hardness of the deposit obtained from L3-containing baths is decreased in the presence of reducer H4. The hardness generally decreases when increasing the concentration of reducer H4, resulting in the hardness of these deposits being below HV 400. Although the hardness of the deposit obtained from L4-containing baths still decreases in the presence of reducers H-4, H-5, and H-6, as shown in Figs. 5 and 6, some deposits still have hardness above HV 500 at a higher current density resulting from the effect of reducer L4. Based on the results of curve (c) of Fig. 2 and curve (b) of Fig. 5, therefore, electroformed Ni-W alloy with low stress (below 20 MPa) and high hardness (above 500 HV) was obtained from an alloy bath containing 0.3 g/L L4 and 0.3 g/L H4, where the current density was $30 \text{ to } 40 \text{ A/dm}^2$. Similarly, according to curve (b) of Fig. 3 and curve (a) of Fig. 6, the alloy electroform with low stress and high hardness was also obtained with an alloy bath containing 0.3 g/L L4 and 0.3 g/L H5 and current density is $20 \sim 40$ A/dm².

Similar to the results for internal stress, no linear relations between the hardness and hydrogen or sulfur content were found, either for the alloy bath containing a simple reducer or by combining Type L and Type H reducers.

Findings

Results of this study identify two types of stress reducers useful in Ni-W alloy electroforming. Type L reducers decrease the stress at a lower current density, while Type H reducers decrease the stress at a higher current density. The high stress in the alloy deposit obtained from Type Lcontaining bath at a higher current density can be reduced by adding Type H reducer. When the alloy bath contains both types of reducers, alloy deposits with a low stress over a wide range of current density can be obtained.

Electroformed Ni-W alloy with low stress and high hardness was obtained from Bath L4 at a lower current density. Moreover, the conducted current density increases when the alloy bath contains a combination of reducers L4 and H4 or H5.

No criteria are available to evaluate the hardness or stress in terms of the amount of hydrogen or sulfur content in the alloy deposits.

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Huang

About the Authors

Chein-Ho Huang* is a professor in the Chemistry Department of Soochow University, Shih-Lin, Taipei, Taiwan, Republic of China. He received an MS in chemistry from the National Tsing Hua University and has more than 26 years' teaching experience. His research interests include plating electrolytes, surfactants and wastewater treatment. He is the editor of the Chinese Supplement to P&SF.

Dr. Wen-Young She is an associate research engineer at the Material R&D Center of Chung Shan Institute of Science & Technology, Taiwan. He received his PhD in polymer science from the National Taiwan University. He specializes in surface treatment and electroforming technology.

Dr. Hsien-Ming Wu is employed in the Material R&D Center of Chung Shan Institute of Science and Technology, Taiwan. He received his PhD from the National Tsing Hua University. His research interests include development of conductive polymers for organic battery systems, as well as study of photopolymer systems in holographic recording.

* To whom correspondence should be addressed.