A Study of the Effects of Diammonium Citrate On Electroformed Nickel-Tungsten Alloy

By Chein-Ho Huang

The effect of diammonium citrate on electroformed nickel-tungsten alloy from a sulfamate bath was studied, using citric acid as a buffer. Addition of diammonium citrate in the alloy bath increased the percentage of tungsten in the alloy electroforms, but the internal stress was concurrently increased. To overcome the increased internal stress, two stress reducers, namely sodium benzene sulfonate and benzene sulfonamide were tested. Moreover, the effect of diammonium citrate on the hardness after thermal treatment of the alloy electroforms was also considered.

Diammonium citrate has been used as a complexant by many workers[1-3] to raise the bath pH and the tungsten content of the deposits of nickel-tungsten alloy. In this study, low-stress nickel-tungsten electroforms were prepared, then the effect of added diammonium citrate on the current efficiency, surface morphology, tungsten content, internal stress and hardness of the alloy electroforms was investigated.

The nature of internal stress is one of the most important physico-mechanical features of nickel-alloy electroforming. Although a sulfamate electrolyte was selected to decrease the internal stress of the electroforms, the stresses were greater than that of the corresponding nickel electroforms, especially in the case of diammonium citrate-containing solutions. Therefore, two stress reducers, sodium benzene sulfonate (SBS) and benzene sulfonamide (BSA), were tested in alloy baths to avoid stress distortion of the electroforms.

The hardness of a heated electroform is an important indication of its utility for certain high-temperature applications. Perhaps the hardness of tungsten alloys is their most interesting property; not only are they relatively hard, as obtained from the bath, but they also have considerable hardness after being thermally treated.[4] Accordingly, the hardness of an electroformed nickel-tungsten alloy, after thermal treatment, is a worthwhile feature for study. Our results indicated that the hardness change after thermal treatment was affected by the presence of diammonium citrate and stress reducer in the alloy bath.

Experimental Procedure

After preliminary experiments in a 267-mL Hull Cell, along with the result of our earlier works,[5] the nickel-tungsten electroforming solutions in Table 1 were developed. The concentration of each added stress reducer was 0.4 g/L. Nickel-tungsten alloy and its corresponding nickel layers were electroformed 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 about 0.8 g, the electroformed layer was separated mechanically. An X-ray energy dispersive spectroscopy (EDS) technique[6] was used for tungsten and oxygen determination in the alloy electroforms. The morphology of the electroforms was examined, using a scanning electron microscope (SEM). Internal stress was determined by spiral contractometer. Thermal treatment was conducted, using a thermoanalyzer[a] in a dry helium atmosphere at 300, 500, and 700 °C for one hr. Heating rate was 20 °C/min. The thermally treated electroforms were tested for hardness at room temperature by a Vickers microhardness tester under 200 g load.

Current efficiency, internal stress, and hardness of corresponding nickel electroforms, obtained from Baths a, b, and c, and listed in Table 1, were measured for comparison with those of electroformed nickel-tungsten alloy, under identical conditions.

Results and Discussion

Bath Composition

Sodium tungstate was used as the electrolyte in the induced nickel-tungsten alloy electroforming.[7] In addition to the advantage of lower internal stress, the nickel sulfamate system had higher tungsten content, hardness, and current efficiency than those of the nickel sulfate system;[8] therefore, nickel sulfamate was selected as the source of induced metal. Because the acidity of boric acid or sulfamic acid was not sufficient for the bath containing nickel sulfamate and sodium tungstate, citric acid was used as a buffer in the experimental solutions. With the increased acidity and complexing ability of the citric acid, the solubility of the electrolytes with high metal content was complete and
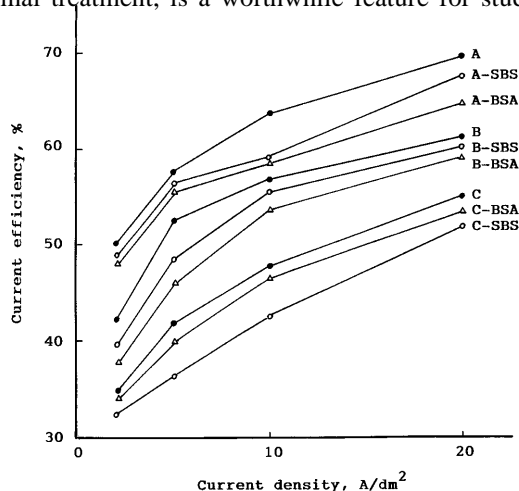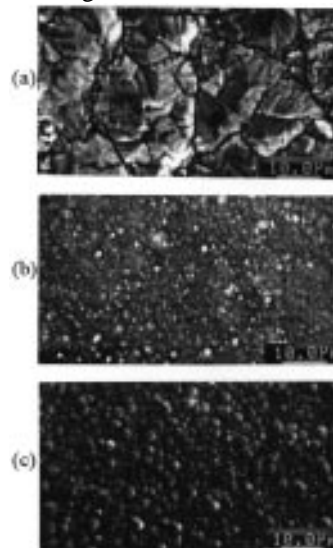
Fig. 1—Current efficiency of nickel-tungsten alloy electroforming as a function of current density. Letters adjacent to curves represent nickel-tungsten solutions, where SBS and BSA indicate that 0.4 g/L of SBS and BSA were added.

Fig. 2—SEM photograph of electroformed Ni-W alloy obtained from: (a) Bath A; (b) Bath B; (c) Bath C; current density 2 A/dm².

Table 1
Nickel & Nickel-Tungsten Bath Compositions*

Bath	$Na_2WO_4 \cdot 2H_2O$ g/L	$(NH_4)_2C_6H_6O_7$ g/L	Initial bath pH
A	40	0	1.59
B	40	9	1.88
C	40	36	1.95
a	0	0	1.43
b	0	9	1.53
c	0	36	1.56

* Each bath containing 400 g/L of $Ni(NH_2SO_3)_2 \cdot 4H_2O$ and 36 g/L of citric acid ($C_6H_8O_7 \cdot H_2O$).

white precipitation of tungsten oxides was prevented.[2] Further, the change in bath pH was not appreciable with respect to the duration of electroforming, the resulting pH change after each preparation of electroforms was less than 0.1.

Instead of sodium citrate, diammonium citrate was used to increase the bath pH and the tungsten content of the alloy deposit. Consequently, many kinds of complexes were formed when the solution contained both citric acid and diammonium citrate. This was obvious visually in the preparation of the solution. To study the effect of diammonium citrate on the properties of alloy electroforms, the amounts of nickel, tungsten, and citric acid were held constant (Table 1), while the amount of diammonium citrate was varied.

The complexing activity of diammonium citrate decreased the current efficiency of electroforming. Accordingly, as shown in Fig. 1, the current efficiency of nickel-tungsten alloy electroforming decreases with an increase of the added amount of diammonium citrate. Similarly (Fig. 1), the current efficiency of the corresponding nickel electroforming was also decreased by the presence of diammonium citrate. Low current efficiency enhances the problem of solution imbalance during the alloy electroforming; therefore, current density equal to, or greater than, 2 A/dm^2 is required for practical applications.

Because of its apparent greater complexing and buffering ability, diammonium citrate changed the surface morphology of the alloy electroforms. Typical results are shown in Fig. 2. The alloy electroforms with finer grain morphology were obtained when the electroforming solutions contained diammonium citrate.
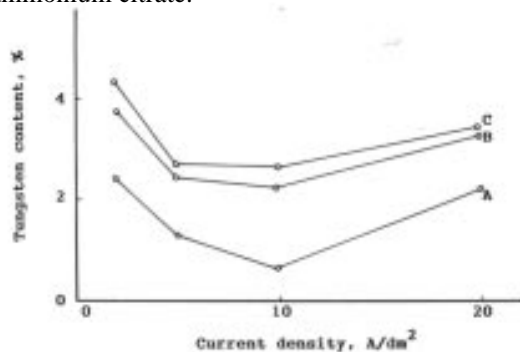

Fig. 3—Tungsten content of Ni-W alloy as a function of current density. Letters adjacent to curves refer to particular Ni-W solutions.

Tungsten Content & Internal Stress

The non-linear relation between the current density and the tungsten content of the alloy electroforms obtained from Bath A is shown in Fig. 3. Similar to irregular codeposition,[2] a greater amount of hydrogen was obtained at lower current density in reduction of tungstate at the cathode, resulting in higher tungsten content in the alloy electroforms at lower current density.[9] This fact is supported by the results of Fig. 1—that a greater amount of hydrogen evolved at low current density resulted in low current efficiency. On the other hand, the higher tungsten content obtained at high current density was partially a result of the higher pH of the solution in the depletion layer. This higher pH is obtained at higher current density,[10] causing significant alkalization of the solution layer adjacent to the cathode. The hydroxo-compounds of tungsten produced are codeposited to increase the tungsten content of the alloy electroforms.[11] The increased occluded oxygen in the alloy deposit obtained at higher current density was evidenced by EDS determination. Perhaps because of the complexed interaction of diammonium citrate at the depletion layer and the increased bath pH (Table 1), as shown in Fig. 3, it is thought that the tungsten content of the alloy electroforms is increased by the presence of diammonium citrate in the electroforming solution.

As the internal stresses of all nickel electroforms obtained from Baths a, b, and c were close to zero, no significant effect of diammonium citrate on the internal stress of the nickel electroforms was found. As shown in Table 1, the effect of diammonium citrate on the bath pH is greater in the alloy solutions than in corresponding nickel solutions. Therefore, as shown in Table 2, the internal stress of the alloy electroforms increases with an increase of diammonium citrate in Bath A. At high current density, more codeposited inclusions were contained in the electroformed alloys, resulting in a higher internal stress. Consequently, only irregular, cracked alloy electroforms are obtained when the current density is increased to 20 A/dm^2. Also, perhaps because of the complexed interaction of diammonium citrate at the depletion layer and the increased bath pH, the internal stress of the alloy electroforms increases with an increase of the added amount of diammonium citrate. Accordingly, when the added amount of diammonium citrate in Bath A was greater than 36 g/L, the alloy electroforms were cracked and exfoliated even when
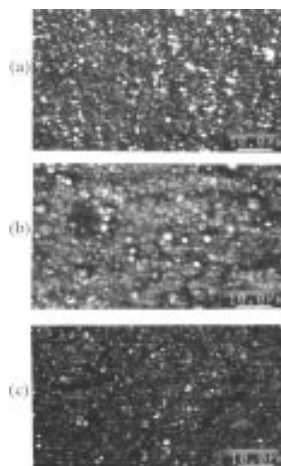

Fig. 4—SEM photograph of electroformed Ni-W alloy obtained from: (a) Bath A-BSA; (b) Bath B-BSA; (c) Bath C-BSA; current density 2 A/dm^2.

the current density was decreased to 2 A/dm^2. On a practical basis, therefore, 36 g/L of diammonium citrate is the addition limit in this system. Because stress control is important in electroforming to prevent deformation, current density and the added amount of diammonium citrate are limited, resulting in limited tungsten content that can be deposited.

Stress Reducers

To decrease the serious drawback of diammonium citrate on the internal stress, two stress reducers, SBS and BSA,[12,13] were tested. As shown in Table 2, the internal stress of most

Table 2
Variation of Internal Stress
with Bath Composition & Current Density

Internal Stress, MPa

Bath	(2 A/dm²)	(5 A/dm²)	(10 A/dm²)	(20 A/dm²)
A	16	20	68	cracked*
B	72	94	cracked	cracked
C	98	cracked	cracked	cracked
A-SBS	18	20	70	cracked
B-SBS	65	90	108	cracked
C-SBS	92	100	cracked	cracked
A-BSA	26	30	92	110
B-BSA	25	72	103	cracked
C-BSA	51	51	97	cracked

*Alloy electroforms were considered failed when the internal stress
climbed to about 120 MPa and the electroforms cracked.

Table 3
Variation of Tungsten Content with Current Density
in the Stress Reducer-containing Baths

Tungsten content, %

Bath	(2 A/dm²)	(5 A/dm²)	(10 A/dm²)	(20 A/dm²)
A-SBS	4.0	3.1	1.7	2.5
A-BSA	4.4	2.2	2.8	4.2
B-SBS	3.8	3.0	2.3	4.8
B-BSA	4.3	3.5	3.2	4.1
C-SBS	2.3	2.0	1.2	3.1
C-BSA	3.2	2.3	2.5	2.8

alloy electroforms is decreased by the presence of these two stress reducers. BSA has an even greater effect than SBS in the diammonium citrate-containing solutions.

The presence of these two stress reducers also affected other properties. As a result of the polarization effect,[14] as shown in Fig. 1, the current efficiencies of Baths A, B and C are decreased. Although bath pH was not increased, as shown in Table 3, SBS and BSA slightly increase the tungsten content in the alloy electroforms obtained from Baths A and B, but when the concentration of diammonium citrate was increased to 36 g/L in Bath C, the tungsten content of the alloy electroforms was not increased by these two stress reducers. They also enhance the surface morphology of the electroforms; typical SEM results (Fig. 4) indicate that large grains on the electroforms are reduced to fine grains only, when BSA is added to Baths A, B and C.

Hardness

Because tungsten retains a considerable hardness at higher temperatures, the hardness of thermally treated alloy electroforms is an interesting property. As shown in Fig. 5, the hardness of nickel electroforms obtained from Bath A was increased by the addition of diammonium citrate. Although cracked and exfoliated alloy electroforms were obtained

from most of the Baths B and C, the hardness of the crack-free electroforms also indicated that the hardness of alloy electroforms was increased by the presence of diammonium citrate. The hardness of these alloy and nickel electroforms was decreased after thermal treatment, however, especially the electroforms obtained from the diammonium citrate-containing solutions and treated at 700 °C. Hardness of the alloy electroforms obtained from Bath A is increased with increased current density, but the hardness decreased with increased current density when Bath A contained diammonium citrate. The results of Fig. 5 also indicate that most alloy electroforms have higher hardness than that of corresponding nickel electroforms.

Although the bath pH was not increased by addition of these stress reducers, as shown in Fig. 6, the hardness of the alloy electroforms was significantly changed by them. In contrast to Bath A, the hardness of alloy electroforms obtained from Baths A-SBS and A-BSA decreased with increasing current density, while the hardness increased with increasing current density when Baths A-SBS and A-BSA contained diammonium citrate, especially in the case of BSA-containing solutions, except for the two curves for treatment at 700 °C. As a result, the alloy electroforms obtained from Bath A-BSA had higher hardness (> 500 HVN) at low current density. On the other hand, the alloy
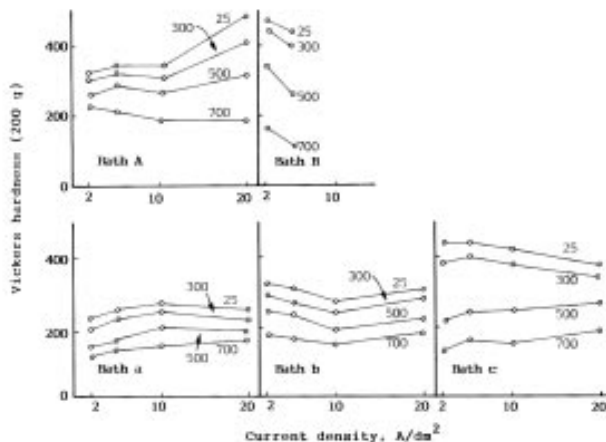

Fig. 5—Hardness of electroforms obtained from stress-reducer-free solutions as a function of current density. Numbers adjacent to curves represent treatment temp in °C. Number 25 means no heat treatment.
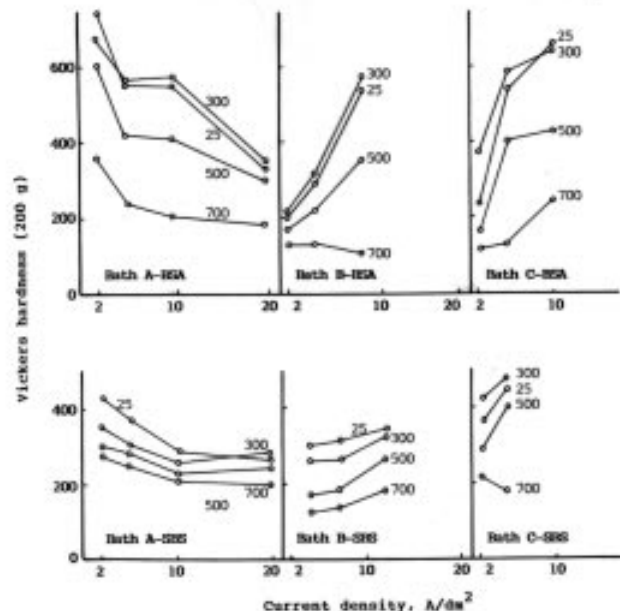

Fig. 6—Hardness of electroforms obtained from stress-reducer-containing solutions as a function of current density. Numbers adjacent to curves represent treatment temp in °C. Number 25 means no heat treatment.

electroforms obtained from Baths B-BSA and C-BSA had higher hardness at high current density. Although the hardness of alloy electroforms obtained from BSA-containing solutions was noticeably decreased after 700 °C thermal treatment, the results shown in Fig. 6 indicated that the alloy electroforms obtained from BSA-containing solutions retain or increase in hardness after 300 °C treatment.

Findings

Crack-free electroformed nickel-tungsten alloys were obtained from nickel-tungsten solutions at low current density. Although diammonium citrate increased the tungsten content and hardness of the alloy electroforms, internal stress was concurrently increased. The adverse effect of diammonium citrate on the internal stress was decreased by the addition of stress reducers, sodium benzene sulfonate and benzene sulfonamide.

Nickel-tungsten alloy electroforms with outstanding hardness and low stress were obtained when the benzene sulfonamide-containing alloy solution (Bath A-BSA) operated at low current density. When diammonium citrate was added to Bath A-BSA, alloy electroforms with greater hardness were obtained at higher current density. The hardness of these electroforms obtained from BSA-containing solutions was sustained when subjected to 300 °C thermal treatment.

[a] Model TG-50, Mettler-Toledo AG, Greifensee, Switzerland.

Editor's note: Manuscript received, August, 1996; revision received, December 1996.

References

1. F. Campbell and J.A.V. Fraunhofer, *Surface Technology*, **5**, 345 (1977).
2. V.B. Singh, *Surface Technology*, **7**, 443 (1978).
3. R.M. Krishnan *et al., Metal Fin.*, **93**(7), 33 (1995).
4. A. Brenner, *Electrodeposition of Alloys, Vol. II*, Academic Press, New York, NY, 1963; p. 391.
5. C.H. Huang, *Metal Fin.*, **91**(6), 107 (1993).
6. A.H. Graham *et al., Plat. & Surf. Fin.*, **83**, 67 (Feb. 1996).
7. V.B. Singh and P.K. Tikoo, *Surface Technol.*, **7**, 229 (1978).
8. K. Wikiel and J. Osteryoung, *J. Appl. Electrochem.*, **22**, 506 (1992).
9. J. Crousier, M. Eyraud and J.P. Crousier, *J. Appl. Electrochem.*, **22**, 749 (1992).
10. C.H. Huang and T.H. Shang, *Proc. 15th AESF/EPA Pollution Prevention and Control Conf.*, 1994; p. 187.
11. J. Przyluski, J. Bielinske and M. Kucharski, *Surface Technol.*, **9**, 179 (1979).
12. C.H. Huang, *Plat. & Surf. Fin.*, **71**, 104 (May 1984).
13. A. Bodneras and J. Zahavi, *Plat. & Surf. Fin.*, **81**, 75 (Dec. 1994).
14. H.M. Wu *et al., Plat. & Surf. Fin.*, **79**, 66 (Sep. 1992).

About the Author

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 National Tsing Hua University and has more than 23 years' teaching experience. His research interests include plating electrolytes, surfactants and wastewater treatment. He is the editor of the Chinese Supplement to P&SF.