Properties of Nickel-Tungsten Alloys Electrodeposited from Sulfamate Electrolyte

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Tungsten and its alloys are of interest in both theoretical and applied aspects because of their specific tribological, magnetic, electrical and electro-erosion properties. Electrodeposited Ni-W alloys successfully vie even with ceramics and graphite by virtue of high thermo-resistance.[1] Another perspective is their application in magnetic heads, bearings, magnetic relays, catalysis of the processes of oxygen- and carbon-containing components of tungsten, electrodes for hydrogen energetics, etc.[2,3] Interest in these alloys has expanded unusually rapidly in recent years because of scientific and industrial applications in electrodeposition of compositionally modulated multilayers (CMM).

Compositionally modulated multilayers are emerging as new materials with artificial microstructure and basically consist of a stack of very thin layers of two different materials arranged alternately. These materials have ultrafine structure and possibilities for unusual properties—optical, x-ray, supermodular effects, electroconductivity, superconductivity and special tribological effects.[4-7]

The properties mentioned do not exhaust the fields of potential application of electrochemically obtained tungstate alloys with iron group metals, but do explain the specific attention called to these systems.

Notwithstanding the earnest efforts of scientists to solve the problems of mutual co-deposition of tungsten with iron-group metals (particularly Ni), many questions concerning the mechanism of their electrolytic growth as factors on which their properties depend have not yet been clarified.

The process of mutual electrodeposition of tungsten with iron-group metals from water solutions has been investigated by many authors.[1-3, 8-31] Brenner[8] showed some peculiarities of induced co-deposition of tungsten—it has not been deposited alone from aqueous solution, but only in conjunction with deposition of another metal. There is an upper limit to the content of W in the alloy. Under certain conditions, W deposits preferentially, that is, the percentage of W in the deposit is larger than its metal-percentage in the electrolyte. Electrodeposition of tungsten alloys usually occurs at potentials more positive than those at which the iron-group metals deposit. The metals in the alloys are intimately mixed, forming either a solid solution or an amorphous mixture that yields no X-ray diffraction pattern. Only a limited number of elements seems capable of bringing about induced codeposition of W; the iron-group metals accomplish this far more readily than any other metals.

The data in the existing literature concerning W co-deposition in alloy mechanisms are rather different and contradictory. The multi-steps of the processes and the anomalous codeposition of W with metals of the iron group are the main reasons for the lack of theoretical elucidation. There are some hypotheses:[1,8,13] Catholytic influence of the cathodic surface on W co-deposition; formation in the electrolyte of an internal orbital complex; ennobling of the deposition potential of W as a result of the alloy formation; formation of an active complex on the cathode; increase of the "equilibrium" solubility of W; tendency to passivation of W; and the radical-oxide model.

Wasko[1] supposed the formation of high molecular nickel tungstates as the first step of the electrochemical alloy formation process. The model metal-semiconductor-electrolyte has been realized in this case. The semiconductive layer consists of nickel heteropolytungstates with low electronic conductivity.

There is no complete explanation of the mechanism and kinetics of W codeposition. Pope and Vagra[19] expressed the opinion that electroreduction of $[H_2W_{12}O_{40}]^{+6}$ ion can be realized by formation of a tungstate polymer. The first investigation for clarification of the mechanism of Ni and W electrodeposition from sulfamate electrolytes was implemented by Crupin and Rotinyan.[20] They showed WO_4^{-2} de-

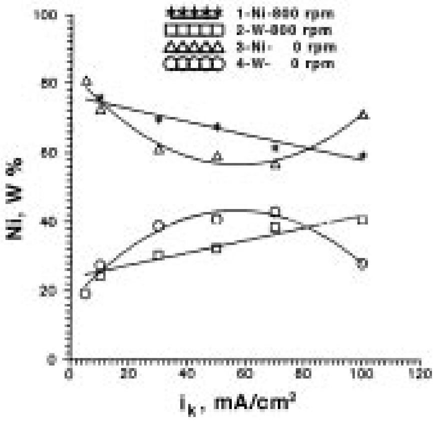

Fig. 1—Influence of cathodic current density on alloy composition.

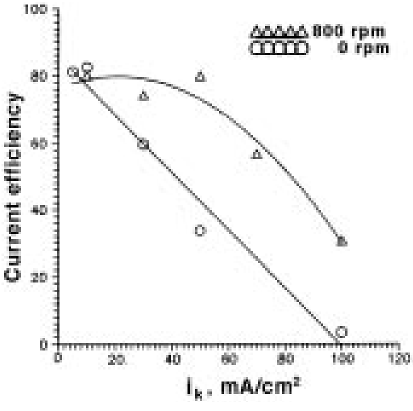

Fig. 2—Influence of cathodic current density on current efficiency.

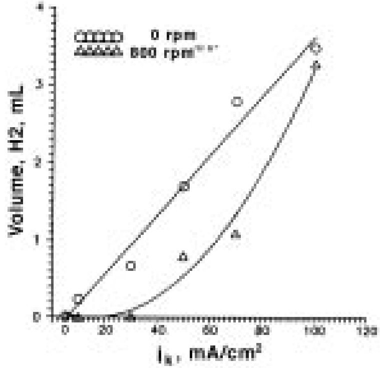

Fig. 3—Hydrogen evolution amount dependent on cathodic current density.

posits by diffusion control in the absence of complexing agents in acid media at low concentrations of WO_4^{-2}. At high concentrations of WO_4^{-2}, the determining factor is kinetic control, conditioned by retarded chemical reaction, in which incorporation of the first electron constitutes the slowest stage of the reaction.

Francevich and Zabludovskayia[21] contend that from ammonium chloride electrolytes, the rate of electrochemical reduction of WO_4^{-2} to the metal is determined by the transport to the point of discharge, in comparison with electrodeposition of Ni, Fe and Co, where the decelerating stage is the discharge of their ions.

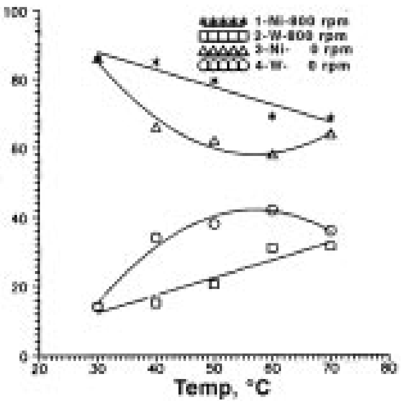

Fig. 4—Influence of temp on alloy composition.

The opinion of Socha[22] concerns W co-deposition with iron-group metals dependent on a number of factors, not explained heretofore. Moreover, none of the existing hypotheses can explain the full process, nor can anyone say why tungsten has not been deposited alone from aqueous solution. It is not clear whether tungsten has been included in deposits in elemental form or as WO_4^{-2}. Alekhina[14] considers that in electrodeposition from sulfamate electrolytes, the Ni-W alloy formation is effected by inclusion of W in the already-formed Ni matrix.

An additional reason for the lack of united opinion is the great number of electrolytes (predominantly alkaline), the number of additives and concentrations of different components in the electrolytes. All of this proves Brenner's opinion that the formation of an "induced" type of Ni-W alloy system is more complex compared with alloys of anomalous behavior.[8]

As is well known, in addition to the parameters of the electrolytic process, optimal selection of the type of electrolyte is of great importance. In this way, it is possible to include a definite amount of W to obtain reproducibility of the structure and the properties of the alloys.

The aim of this study is investigation of the process of electrochemical deposition of Ni-W alloys and their properties with a maximum W amount from sulfamate electrolytes consisting only of source components at pH close to neutral.

Experimental Procedure

Pretreatment included degreasing in ethyl alcohol, in alkaline solution and etching in acid solution. The Ni-W electrodeposition was performed using baths containing:

Nickel sulfamate	16.5 g/L
Sodium citrate	90 g/L
$Na_2WO_4 \cdot 2H_2O$	30 g/L

The baths operated at 30 to 70 °C, with cathodic current density 5 to 100 mA/cm^2, pH 4 to 8, nonstirred and magnet-stirred at 800 rpm. The anodes were soluble S, depolarized. Copper samples (20 x 10 x 0.5 mm) were used as substrates. Layer thickness was more than 20 µm. The corrosion polarization measurements were conducted in a 150-mL three-electrode cell. A potentiostat was utilized for potentiodynamic polarization curves at a scan rate of 200 mV/min. As a reference electrode, Ag/AgCl was used. The potential values are presented toward the normal hydrogen electrode. The layers were analyzed by SEM, ERMA-EDS method. Microhardness was measured by microhardness meter (100-g load).

Results and Discussion

The nature of the change in the amount of tungsten dependent on cathodic current density at different hydrodynamics—without stirring and with intensive stirring—is rather different, as shown in Fig. 1. In the unstirred electrodeposition (curve 4), the amount of included W passed through a maximum at i_k 50 to 70 mA/cm^2. With vigorous stirring, the dependence (curve 2) is linear and the amount of W increases with increase of i_k. It is surprising that with an unstirred regime and middle i_k, the W amount is about 6 to 7 percent larger than with agitation. The similar dependence of W increasing with the cathodic current density up to 600 mA/cm^2 has been observed by M. De Bonte[25] from sulfamate electrolyte at 600 rpm, by Przywoski[12] from sulfate electrolytes up to i_k 60 mA/cm^2 at room temperature, and by Domnikov[26] from peroxide electrolyte. Figure 2 shows results of the role of hydrodynamics on the current efficiency (CE) of a stirred bath; at i_k greater than 20 mA/cm^2, CE is 15-40 percent higher compared with an unstirred bath. Note the sharp increase of hydrogen evolution with cathodic current density (Fig. 3), especially with the lack of agitation. It is probable that the difficulties of inclusion of W at i_k greater than 70 mA/cm^2 (Fig. 1, curve 4) depend on this factor. It can be supposed that the movement of W to the cathodic surface was accelerated because of screening of discharged hydrogen or its evolution—a rival reaction of hydrogen on the same parts of the electrode surface.

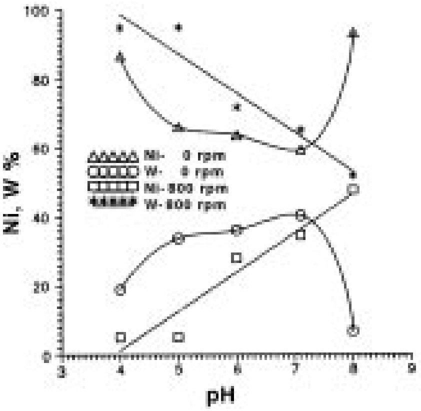

Fig. 5—Influence of electrolyte pH on alloy composition.

As can be seen from Fig. 4, the character of the W change as a function of temperature in unstirred conditions is analogous to the dependence on the cathodic current density (Fig. 1). The W amount increases with increasing temperature. In the stirred bath, the dependence of W inclusion is linear. The values in an unstirred bath (curve 4) are about 10 percent higher, passing through a maximum at 60 °C. Above this temperature, the decrease in the amount of W is less, probably

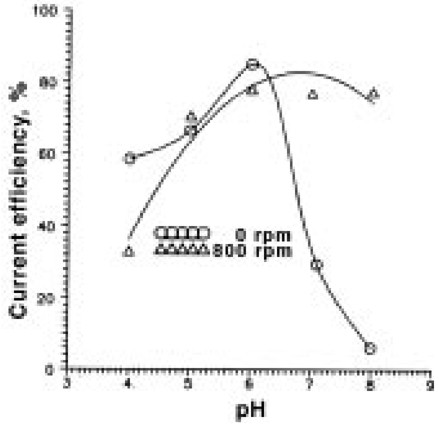

Fig. 6—Current efficiency dependence on pH.

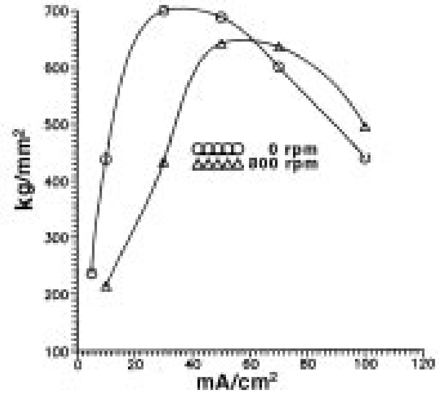

Fig. 7—Influence of cathodic current density on microhardness.

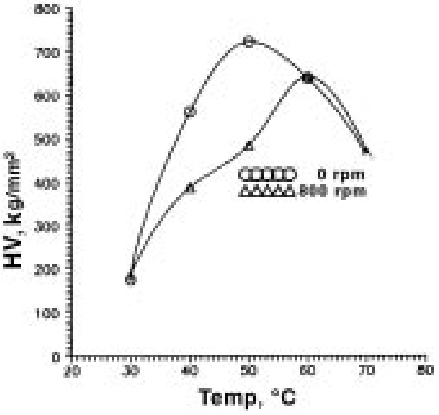

Fig. 8—Influence of temp on microhardness.

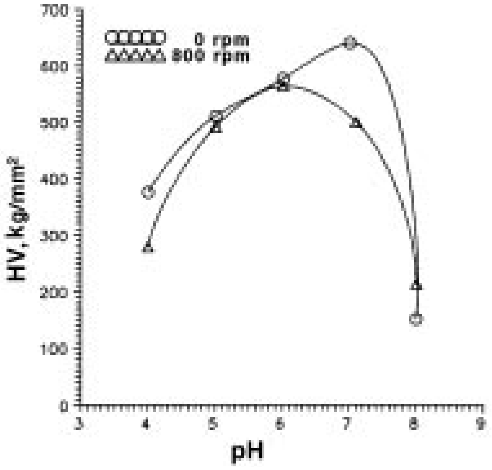

Fig. 9—Influence of pH on microhardness.

because of more moderate hydrogen evolution at high temperatures. It seems that the increase of temperature favors the W transport to the cathodic surface, making its co-deposition easy. It is possible that the degree of the hydrolysis of sulfamate ion above 50 °C is the main reason for the diminished activity of tungstate ion. Its inclusion in the coating decreases at high temperatures, as mentioned above. The amount of W included depends strongly on pH in the absence of stirring, as can be seen from Fig. 5. Its values decrease sharply outside the pH 5-7 region. An interesting aspect of this effect is the current efficiency dependence of W on pH (Fig. 6). At the pH 5-7 interval, the quantity of electricity for W deposition has practically not been dependent on the hydrodynamics of the process. By stirring the bath, the shifting of pH out of this region leads to the sharp decrease of CE. Clarification of the data for these figures can be found in the supposition of C-H. Huang.[27] At low pH, the degree of hydrolysis of sulfamate ion increases. In that case, it may be supposed that decreasing concentration of sulfamate ion is the reason for decreased activity of tungstate ion in joint complex, as well as its smaller amount in the coating. Other authors[25] established the alkalization of the electrolyte for obtaining Ni-W precipitated sediment, consisting of the necessary amount of tungsten. Obviously, it leads to decrease of active concentration of W near the cathode and can clarify the behavior of curve 2 of Fig. 5 at pH > 7. Pope and Vagra[19] consider that at high pH, the possibility of inclusion of W decreases as a result of decomposition of the active complex facilitating the discharge of W. The sharp decrease of included W in alkaline media, according to Alekhina,[24] can be referenced to known probability of formation of tungstate complexes-hydroxypolymers, whose active concentration at pH 5-7 has been increased.

Taking into consideration the suppositions[8,19,20] discussed above, it can be accepted that it is possible that the observed small effect of W or CE on pH in a stirred bath (Fig. 6, curve 2) results from elimination of non-metallic deposits, enabling inclusion of W up to 48 percent. In other words, in an unstirred bath, a barrier of non-metallic contaminations prevents tungsten from reaching the cathodic surface.

From the results obtained, it can be accepted that the absence of a maximum in W dependence on i_k, T and pH are a consequence of removal of diffusion limitations in the discharging of tungstate ions. The change of the alloy composition with stirring of the bath proves the presence of diffusion control in codeposition of Ni and W, as was proposed in a previous paper.[29]

The influence of the electrolytic parameters on microhardness (HV) of Ni-W layers is shown in Figs. 7-9. The common factor in all dependences is the presence of a clearly observed maximum. Similar to the above-mentioned dependences for W inclusion, HV is higher when the bath is not stirred. A maximum value (about 700 kg/mm^2) of HV in the absence of stirring can be observed in the region where i_k is 30-50 mA/cm^2 (50-70 if stirred), temperature 50 °C (60 °C if stirred), pH 7 (pH 6 if stirred).

Considering the character of the change in the amount of W dependent on electrolyte parameters (Figs. 1, 4, 5), probably the decrease of HV at high values of included W result from structural changes of the deposited layers; for example, change from a solid solution to an intermetallic compound, as has been supposed by some authors.[14,15,18]

In an unstirred bath, the dependence of HV on cathodic current density has followed the composition dependence. In

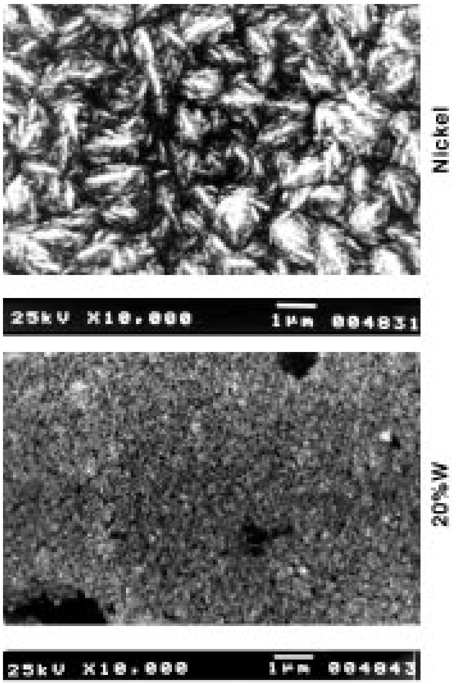

Fig. 10—SEM micrographs of Ni and Ni-W layers.

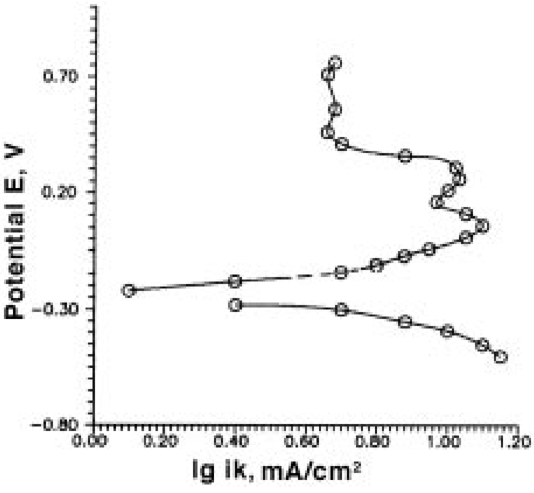

Fig. 11—Corrosion curves in 1 N H_2SO_4.

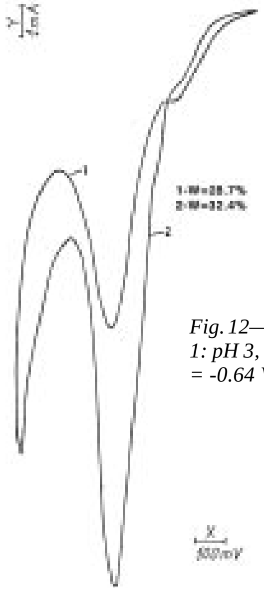

Fig. 12—Corrosion curves in 3-percent NaCl; 1: pH 3, E = -0.55 V to +0.73 V; 2: pH 5.4, E = -0.64 V to +0.65 V.

a stirred bath, the lineal dependence of the composition changes with the presence of a maximum at i_k = 50 mA/cm^2. The probable reason is the size of the crystallites. With some of the observed dependences, there is a correlation with the amount of tungsten.

The results obtained concerning morphology of the investigated layers are not sufficient to establish HV dependence on crystallite size. To be more precise, there is a HV influence on the amount of included W. As tungsten increases, the size of the crystallites decreases. Fine crystallites can be observed in the SEM photographs (Fig. 10) with inclusion of W in the coatings.

Some of the initial investigations of the behavior of layers studied in model corrosion media are shown in Figs. 11 and 12. The corrosion resistance of Ni-W alloys, obtained from sulfamate electrolytes, has been investigated by Offermans[30] and Rogoll,[31] but the regimes and electrolyte compositions are rather different and make the conclusions difficult.

The cathodic and anodic polarization curves show the different behavior of Ni-W alloys. For the anodic curve in 1 N H_2SO_4, even the region of active dissolution up to i_k = 1.1 mA/cm^2 (Fig. 11) shows the presence of two semipassive regions. In 3-percent NaCl (Fig. 12), they are absent. Figure 12 shows the corrosion curves of the alloys with different compositions at various values of pH. In 1 N H_2SO_4, E_{corr} = -0.25 V, i_{corr} = 3.3 mA/cm^2; in 3-percent NaCl, E_{corr} = 0.04 V, i_{corr} = 0.5 mA/cm^2 for W = 28.7 percent. For W = 32.4 percent, E_{corr} = -0.04 V, i_{corr} = 0.8 mA/cm^2. It is clear that with increasing W content, the corrosion resistance of the alloy decreases. The pH influence of 3-percent NaCl on corrosion parameters shows increasing corrosion stability with alkalization of the media (more noble corrosion potential and decrease of corrosion current). Figure 13 shows a SEM photograph of Ni-W coating after cathodic and anodic corrosion curves. The sample investigated in 1 N H_2SO_4 was essentially enriched with W. At the beginning, the W amount is 31.2 percent and at the end of the anodic polarization curve W = 42.5 percent; in 3-percent NaCl, W = 35.6 percent.

From these investigations, it can be concluded that the corrosion behavior of Ni-W alloy is rather complicated and that the behavior is determined by the amount of W in the alloy and the structure of the layers studied, the different phase compositions and grain size.

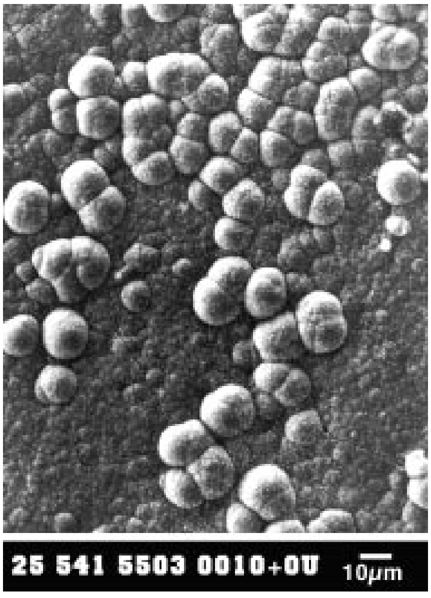

Fig. 13—SEM micrograph of Ni-W alloy after corrosion tests.

Summary

1. The influence of electrolytic parameters on the composition of Ni-W alloys was investigated; deposits were from sulfamate electrolytes consisting only of reagent grade components.
2. The character of the dependence of the included W on cathodic current density, temperature and pH is qualitatively different with different process hydrodynamics.
3. It has been shown possible, with the electrolytes used, to deposit layers with microhardness of 970 kg/mm^2. The microhardness change with the electrolytic parameters has a maximum; the different hydrodynamics did not change the character of the dependence.
4. The results obtained constitute reasons to suppose an influence of the phase composition and grain size on HV.
5. The corrosion behavior of Ni-W alloy is rather complicated and different in different corrosion media, and is determined by different forms of W included in the layers.

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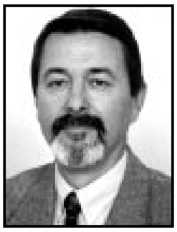

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