# Electrodeposition & Characterization Of Co-W Alloys

By B.N. Maruthi, L. Ramesh, S.M. Mayanna & D. Landolt

**Cobalt-tungsten alloys have been electroplated from alkaline bath solutions under different plating and bath conditions. Diammonium hydrogen citrate and dimethyl sulfoxide in the bath solution have produced good quality deposits. The hardness and magnetic properties of the alloys are found to depend on composition and heat treatment. Cyclic voltammetric and spectral studies revealed the complexation of cobalt ions with diammnonium hydrogen citrate in the plating bath solution. Dimethyl sulfoxide has activated the codeposition of tungsten. The alloys are amorphous under plating conditions and become partially crystalline upon heat treatment. AES analysis revealed the absence of oxygen, chlorine and carbon on the surface of the coated alloys. Working conditions were optimized to get good quality deposits with appreciable coercivity and hardness values.**

Tungsten forms hard alloys with cobalt, retaining some of its unusual properties, such as magnetic, electrochemical and mechanical (even at elevated temperature) and high corrosion resistance to acidic and alkaline media.[1-4] Accordingly, the electrodeposition of W alloys has become a subject of pronounced practical significance.

Earlier reviews reported on the subject are noteworthy.[5,6] The alloy plating is a complex process and the functional properties depend on mechanical and structural aspects of the alloy coating, which in turn depend on the bath composition and plating conditions.[7,8] Attempts have been made to electroplate Co-W alloys from acidic and alkaline baths.[9-11] Even though Co-W alloys display a variety of highly useful properties, a comprehensive work on the system is rather limited.[12] As a result, it is felt to develop good quality Co-W alloys by electrochemical method through comprehensive studies.

## Experimental Procedure

Solutions were prepared using analytical grade chemicals and double-distilled water. Plating of Co-W alloys was carried out on cylindrical copper rod (99.9%). It was fixed in Tygon tubing to get a surface area of 0.5 cm$^2$. The copper surface was mechanically polished using different grades of emery paper with alcohol as lubricant, then electropolished in 60-percent $H_3PO_4$ at an anodic cell potential of 1.2 V for 30 min with a copper foil as the cathode.[13] A scanning potentiostat/galvanostat was used as a source of current. Saturated calomel and a carbon rod were used as reference and auxiliary electrodes, respectively. Deposition potentials were recorded at regular intervals, using a digital voltmeter (±2 mV). The microstructural and surface characteristics of each coating were examined using an X-ray diffractometer and Auger Electron Spectrometer, respectively. Cyclic voltammetric studies were made by using standard experimental procedure.[7] The composition of the alloy was determined using atomic absorption spectroscopy. Experiments were repeated to ensure reproducibility.

Table 1
Bath Composition & Operating Conditions

| **Composition** | | **Conditions** | |
|---|---|---|---|
| $CoSO_4 \cdot 7H_2O$ | 0.10 M | pH | 7.5–9.0 |
| $Na_2WO_4 \cdot 2H_2O$ | 0.02 M | Temperature | 50 °C |
| DAHC | 0.10 M | cd | 2.5 A/dm$^2$ |
| $Na_2SO_4 \cdot 10H_2O$ | 0.30 M | Time | 30 min |
| NaCl | 0.20 M | Cathode | Copper |
| $H_3BO_3$ | 0.05 M | Anode | Carbon rod |

## Results & Discussion

### Plating Variables

Plating experiments were conducted using a tentatively fixed bath solution and operating conditions (Table 1). Several organic compounds (each 0.05 M) were used individually and, in some cases, in combinations to determine their ability for complexation with Co and W or both, and the resultant effect on the quality and composition of the alloy. In each case, the quality of the deposit was observed under a metallurgical microscope and the composition of the alloy was obtained. After analyzing some of these preliminary results, it was decided to use an alkaline bath solution containing diammonium hydrogen citrate (DAHC) and dimethylsulfoxide (DMSO). This bath solution was able to yield good-quality Co-W alloys (fine-grained, bright, with good adhesion).

Experiments were carried out to study the effect of plating variables, namely, metals ratio (Co/W) in the bath solution, pH, temperature and the concentrations of the complexing agents on the composition of the alloy. In all these experiments, the pH of the bath solution was maintained constant by using boric acid. Co-W alloys were electroplated at 0.5 A/dm$^2$ to a constant thickness (20 µm) at 50 °C and pH 7.5 with various metal ratios in the presence of 0.05 M each of DAHC and DMSO. Under these plating conditions, preferential deposition of W over Co was noticed at lower percentage W in the bath. This tendency decreased considerably with increase in percentage W in the bath. Some of these results at various current densities (cd) are shown in Fig. 1. The increase in cd, however, increased the preferential deposition of W.

Experiments were also carried out at different current densities (0.5-10 A/dm$^2$), using solutions containing various

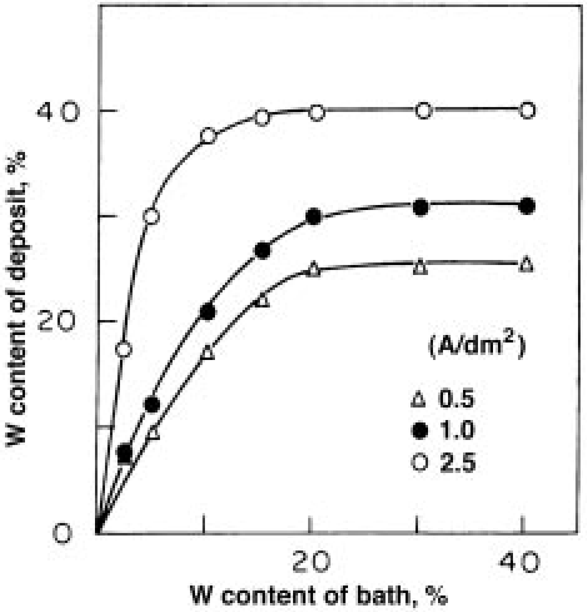

*Fig. 1—Dependence of W content of the deposit on the time in the bath at different current densities.*

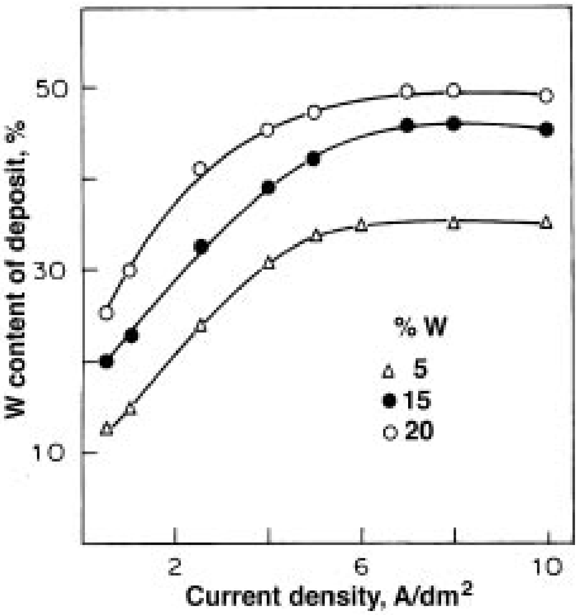

*Fig. 2—Dependence of W content of the deposit with current density at fixed bath concentration.*

metal ratios and 0.05 M each DAHC and DMSO at 50 °C and pH 7.5. The percent W in the deposit electroplated from the bath containing a definite ratio of metals increased, then attained a constant value with increase in cd (Fig. 2). Under a given set of plating conditions: bath composition (Co/W = 80/20), cd O.5 A/dm$^2$, pH 7.5 and temperature 50 °C, alloys were electroplated in the presence of various concentrations of DAHC and DMSO. Figure 3 illustrates the dependence of the percentage of W in the deposit on the concentrations of complexing agents. The percent W in the deposit increased slightly with an increase in DMSO concentration. In the presence of DAHC, however, a reverse trend in the dependence of the percent W on the concentration of DAHC was noticed.

Usually, the functional properties of the alloy depend on the distribution of the composition of the alloy across the thickness. To know the dependency of the composition of the alloy on thickness, therefore, alloys were electroplated to various thicknesses (5-25 µm) at different current densities (O.5-2.O A/dm$^2$) from the bath containing fixed metals ratio (Co/W = 80/20), and O.05 M each DAHC and DMSO with pH 7.5 at a working temperature of 50 °C. Figure 4 shows the variation of W content in the deposit with thickness. The composition of the alloy varied slightly with thickness.

### Cathodic Current Efficiency & Deposition Potential

Cathodic current efficiency was calculated for each set of plating conditions. The efficiency varied slightly with the plating conditions (Table 2). The calculated current efficiency values are in the expected range for an industrial plating system.

Plating potentials were recorded at different times during plating of Co-W alloys. At each cd, the plating potential increased slightly with time, then attained a steady value. The steady potential varied, however, with the composition and plating conditions. Some of these results are shown in Fig. 5. The overpotential ($\eta$) increased rapidly, then gradually, with increasing cd. At a given cd, increase in pH or decrease in temperature enhanced the value of overpotential.

### Metallurgical Properties

Co-W alloys electroplated under various plating conditions were subjected to heat treatment under nitrogen atmosphere at 400 °C. These samples were subjected to XRD analysis. The crystalline nature of the alloy varied with the W content. The alloy with W > 25 percent was brittle. The alloy with W < 20 percent was amorphous; however, upon heat treatment, the deposit became partially crystalline. Some of the XRD results are shown in Table 3. The microhardness of Co-W alloy (as plated) containing 30 percent W, with sufficient thickness (30 µm), was found to be 724 HV (50g). Upon heat treatment for four hr at 400 and 600 °C, the hardness was reduced to 223 HV and 211 HV, respectively. The hardness of the alloy containing less than 20 percent W increased with heat treatment, however. Figure 6 shows the variation of hardness with temperature.

### Surface Analysis

The surface of the electrodeposited Co-W alloy was examined under a metallurgical microscope. At a given cd and with the optimum bath composition, the deposit appeared bright and uniform. The grain size of the deposit increased gradually with increase in temperature or thickness of the deposit. The increase in cd, however, decreased the grain size of the deposit. Co-W thin films (~2 µm) with 40% W electroplated under optimum plating conditions, were subjected to surface analysis in a combined AES/XPS system using a single pass cylindrical mirror analyzer and a differentially pumped rasterable ion generator. The detailed results were presented in an earlier communication.[14] A typical measurement sequence included initial AES survey (0-1000 eV) levels to characterize initial surface conditions (bsp) followed by final AES depth profile analysis. Stable steady-state signals for Co and W were noticed with at least 6O min sputtering time. The surface was free from Cl, O and C and the surface composition (% W) was in accordance with the

Table 2
Cathodic Current Efficiency at 50 °C & pH 7.5
With Optimum Bath Composition

| Current density A/dm$^2$ | Current efficiency percent |
|---|---|
| 1.0 | 91.0 |
| 10[a] | 89.0 |
| 10[b] | 95.0 |
| 10[c] | 82.0 |
| 10[d] | 86.0 |
| 10[e] | 95.0 |

[a][DMSO] 0.1 M; [b][DAHC] 0.075 M; [c]pH 8.5; [d] Temp 40 °C; [e] Agitation

Table 3
XRD Data Obtained for Co-W Codeposits*

| As Plated | | | Heat treated | | |
|---|---|---|---|---|---|
| 2θ | d nm | Phase | 2θ | d nm | Phase |
| 47.780 | 2.2120 | $Co_3W$(200) | 47.770 | 2.2117 | $Co_3W$(220) |
| 58.960 | 1.8797 | $Co_3W$(102) | 51.366 | 2.0663 | $Co_3W$(002) |
| 89.078 | 1.2798 | $Co_3W$(220) | 54.520 | 1.9567 | $Co_3W$(201) |
| | | | 70.262 | 1.5562 | $Co_7W_6$(216) |
| | | | 88.760 | 1.2806 | $Co_3W$(220) |

* Cu K radiation

composition of the alloy obtained by atomic absorption spectroscopy.

### Magnetic Properties

Thin films (500-1000 nm) were electroplated on copper for microscopic studies. The magnetic measurements were carried out by using a finer type vibrating sample magnetometer. Parallel and perpendicular hysteresis loops were obtained with fields ranging from 0-10 kOe. The coercivity value obtained ranges from 60 to 350 Oe in partially crystalline form and decreased slightly in the amorphous form.

### Cyclic Voltammetric Studies

To understand the behavior of each component in the plating solution, cyclic voltammetric (CV) studies were made by using an optimum solution. The effect of scan rate (10-200 mV/sec) on CV patterns was examined in the potential range 1.0 to -1.2 V. The increase in scan rate increased both cathodic and anodic peak currents. For detailed study, 50 mV/sec scan rate was used. Deposition of Co and Co-W alloy takes place, with simultaneous hydrogen evolution, in the potential range -0.7 V and -1.2 V. The hump present on the cathodic rising part of the voltammogram suggests the metal reduction process,[15] namely,

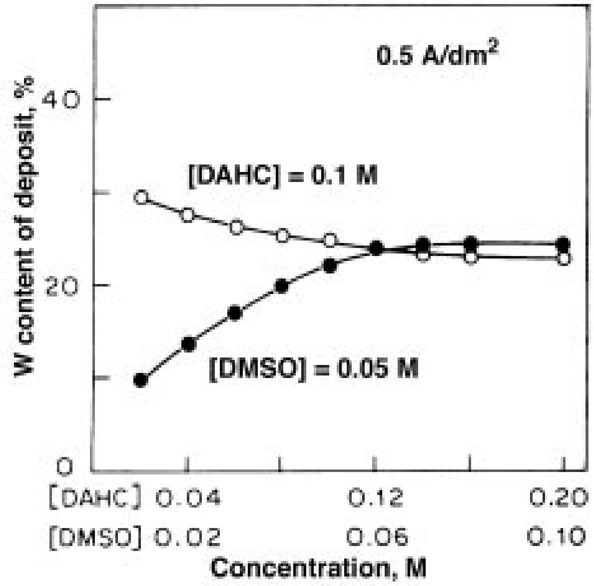

*Fig. 3—Dependence of W content of the deposit on the concentration of DAHC and DMSO.*

$$Co^{+2} + 2e^- \longrightarrow Co \qquad (1)$$
$$WO_4^{-2} + 4H_2O + 6e^- \longrightarrow W + 8OH^- \qquad (2)$$

takes place together with

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \qquad (3)$$

The potential of the hump at -0.70 V in Fig. 7a suggests the deposition of $Co^{+2}$. The change in potential to -0.80 V (Fig. 8b) indicates the deposition of both $Co^{+2}$ and $WO_4^{-2}$. Appearance of a new anodic peak signifies formation of a new phase that may be either $Co_3W$ or $Co_5W_7$ or both. This is in confirmity with the XRD result which reveals the presence of multiphases in the deposit. The rise in anodic peak current by the addition of DMSO implies that small amounts of DMSO facilitates the codeposition of W along with Co. Similar results are observed during the deposition process (Fig. 3).

### Spectral Analysis of Bath

The UV and IR spectral studies of the compounds extracted from the solution indicated the complexation of Co with DAHC. The visible absorption spectrum of the complex showed a sharp peak at 532 nm and a very weak peak at 718 nm, assigned to the transitions $^4T_{1g}$—$^4T_{1g}(P)(r_3)$ and $^4T_{1g}$—$^2A_{2g}(r_2)$, respectively, for cobalt in an octahedral arrangement. It led to the composition of the complex as $[Co(H_2O)_3]SO_4$.

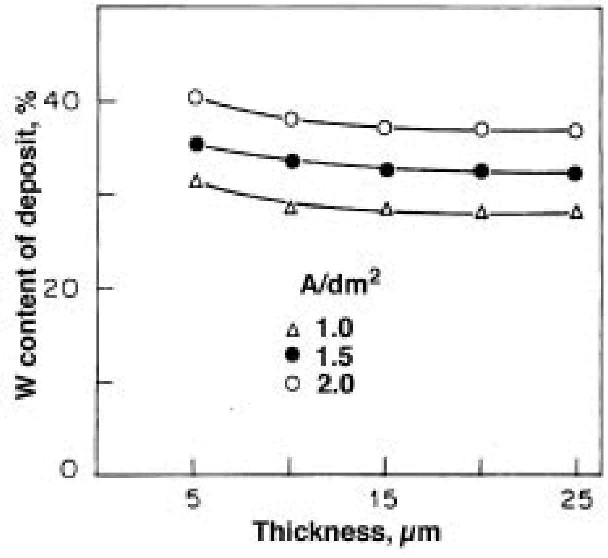

*Fig. 4—Variation of W content of the deposit with thickness.*

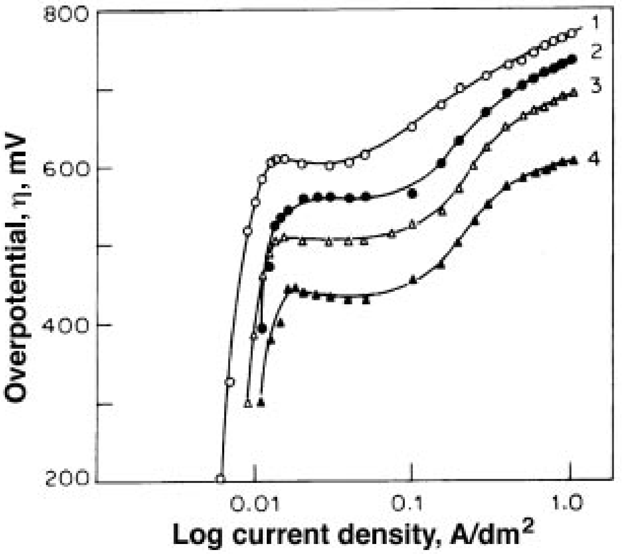

*Fig. 5—Polarization behavior during Co-W deposition: (1) pH 8, 300 °C; (2) pH 7.5, 500 °C; (3) pH 8, 500 °C; (4) pH 9, 500 °C.*

In the present system, DMSO does not participate in the complex formation. It may be considered that DMSO is specifically adsorbed on the cathode surface and stimulates an electrochemical discharge reaction. This favors the codeposition of W.[16] Several hypotheses have been proposed to explain the mechanism of the induced codeposition of W. None of these hypotheses was found to be satisfactory in accounting for the experimental results obtained during the plating of Co-W alloys.

Co-W films containing a variety of metastable phases can be obtained by altering the deposition parameters appropriately. Films having the hcp, the high-temperature fcc of the amorphous phase structure, as well as a mixture of phases, are readily deposited because of the sluggishness of the hcp allotropic modification of cobalt.[10] It has been suggested[17] that at high pH, hydroxide rather than hydrogen, codeposits within the film, which hinders the transformation of hcp to fcc.

It has been observed that the deposited Co-W alloy consists of basic tetrahedral units, each composed of one W and three Co atoms, which provide a tetrahedral site for the W atom. The tetrahedral clusters in dense aggregate do not exhibit crystal symmetry. This accounts for the induced codeposition of Co-W alloy, formation of the amorphous phase, and a saturation concentration of W in Co, corresponding to the $Co_3W$ stoichiometry.

## Findings

Tungsten deposits in preference to Co and this tendency is predominant at lower percentages of W in the plating solution, high cd, as well as in the presence of DMSO. DAHC acts as a complexing agent for $Co^{+2}$ in the plating bath. Under optimum conditions, the current efficiency is in the expected range for an industrial plating process. The plated alloys were amorphous and become partially crystalline upon heat treatment. The hardness of the alloy (<25% W) is increased significantly by heat treatment. AES studies indicate lateral as well as depth homogeneity and freedom from O, Cl and C. The alloys in the form of thin films are magnetic and will be potential candidates for a wide range of applications in the electronics industries. Cyclic voltammetric study indicates the influence of each bath component and its effect on alloy deposition.

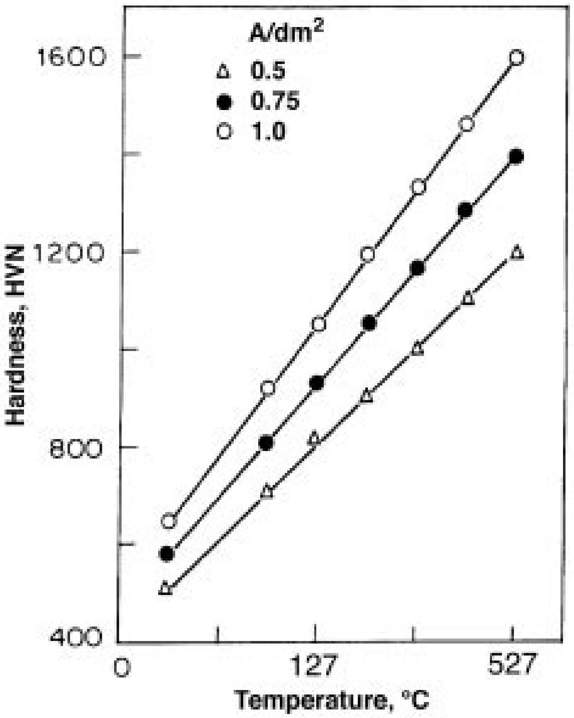

*Fig. 6—Variation of hardness (VHN) of Co-W alloy with heat treatment at different temperatures.*

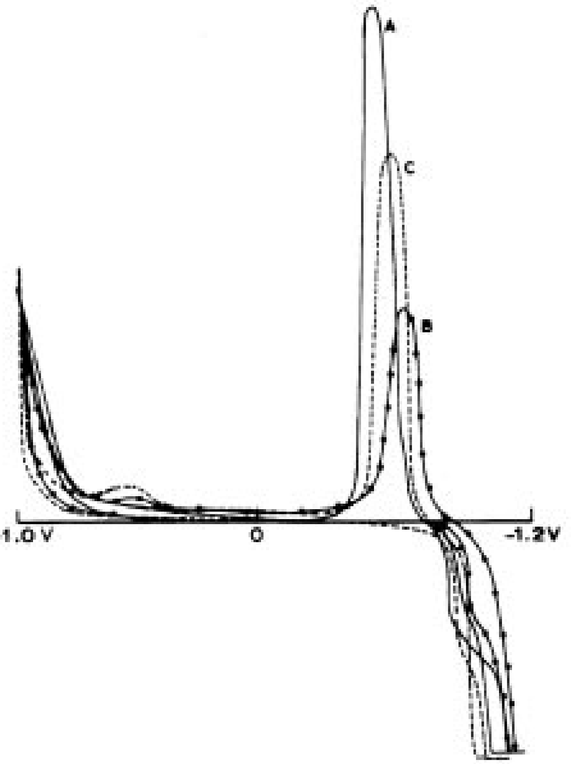

*Fig. 7—Voltammogram of Co-W bath.*
*A: CS + DAHC, B: CS + DAHC + ST, C: CS + DAHC + ST + DMSO.*

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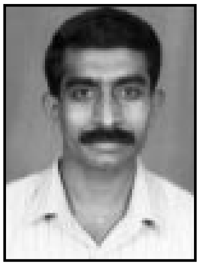

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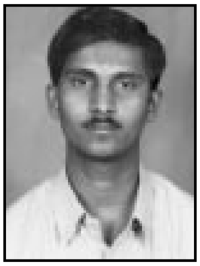

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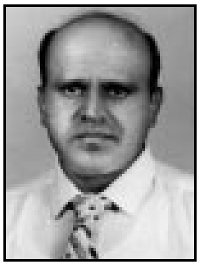

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