DEVELOPMENT OF ELECTRODEPOSITION OF COBALT - TUNGSTEN ALLOYS FROM ACIDIC BATH CONTAINING CATIONIC SURFACTANTS

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SUMMARY

The present work was devoted to replacement the chromium coating by another coating has good properties and non-polluted nature. Optimum conditions of electrodeposition of tungsten-cobalt alloy were studied. The surface properties of cationic surfactants were determined through surface tension measurements of the solution / air interface. Data of some surface and thermodynamic properties of the components were calculated. The alloys were subjected to heat treatment under nitrogen atmosphere at 400 °C. The surface morphologies of cobalt – tungsten alloy electrodeposits, have been studied before and after thermal treatment. The properties of the alloys such as, microhardness and corrosion resistance were also examined and compared with chromium deposit.

Keywords: Electrodeposition, Alloy plating, Tungsten alloy, Chromium plating, and Corrosion resistance

1 INTRODUCTION

Decorative chromium coatings are applied from hexavalent chromium processes based on chromic acid (CrO₃). The chromates have been recognized as both highly toxic and carcinogenic chemical [1]. Due to these reasons, replacement of chrome coatings by another coating has good properties. Tungsten metal and its alloys are used in ultra-high temperature applications. Many authors had investigated the process of electrodeposition of tungsten with iron - group metals from water solutions [2-6]. Tungsten forms hard alloys with cobalt, retaining some of its unusual properties, such as magnetic, highest tensile strength, electrochemical and high corrosion resistance. Accordingly, the electrodeposition of tungsten alloys has become subject of pronounced practical significance.

The goal of the current investigation is the deposition of cobalt - tungsten alloys from acidic bath. The influence of electroplating conditions is studied in details. The mechanism of the deposition in the present and absence of the surfactants is studied. The surface and thermodynamic properties of some organic additive are also calculated. Some significant properties of as plated such as microhardness and corrosion resistance is studied. The effect of heat-treatment is also investigated.

2 EXPERIMENTAL PROCEDURE

Electrodeposition of tungsten- cobalt films were plated from a bath containing cobalt sulphate 5 - 30 g/l, sodium tungstate 4 – 12 g/l, sodium sulphate 45 g/l, sodium chloride 10 g/l, boric acid 10 g/l, and organic additives such as 1,6 - diammonium hexane and 1,8 diammonium octane \((10^{-2} \text{ to } 10^{-4} \text{ mol/l})\). The bath was maintained at pH 3.5 – 6, temperature 30 – 60 °C, and c.d. 0.5 - 3 A/dm², and the plating time was 30 min during which the bath was agitated. The coatings were plated onto copper sheet as cathodes. Platinum sheets were used as anodes. 1,6-diammonium hexane \(H_2N(CH_2)_6NH_2\) (DAH) and 1,8 diammonium octane \(H_2N(CH_2)_8NH_2\) prepared by Omar [7]. Surface tension was measured using a Du-Novy Tensiometer (Kruss Type 8451, Germany).

The composition and surface characteristics of each coating were examined using an X-ray florescence. The surface morphology of the coating was carried out by using a scanning electron microscope (SEM). The microhardness was determined by an indentation technique at 100 gf load with diamond pyramid indentor technique TUKON SERIES B200 MICROHARDNESS TESTER. The coated alloy deposits were tested for corrosion resistance by a salt spray test as ASTM B117 by using 5 % NaCl at 35 °C and at pH 3 by adding acetic acid, and compared with chromium deposit. Potentiodynamic polarization studies were made using a potentiostat, Autolab PG STATE 30. The heat treatment of the alloys was subject under nitrogen atmosphere at 400 °C.

3 RESULTS AND DISCUSSIONS

3.1 Optimization the operating conditions

The electrodeposition of tungsten alloys is investigated in acid bath. The effects of all the plating variables upon the composition of the deposit are investigated. The effect of concentration of Na₂WO₄ at constant concentration of cobalt sulphate (30 g/l) and at 50 °C, pH 5 and current densities 0.75 and 2.5 A/dm² on the tungsten weight percent in the deposits is shown in Fig. 1. It is observed that, the tungsten weight percent \((\%W)\) in the deposit increases significantly as concentration of Na₂WO₄ increases and eventually reaches a maximum at about 8 g/l. With further increase in the Na₂WO₄ concentration, the weight percent of tungsten in the deposits decreases. The advantages of using a low concentrated solution of Na₂WO₄ are good cathode current efficiencies and highly conductivity. An increase in concentration under given conditions
decreases the cathode polarization and thereby, decreases the deposition rate and the tungsten weight percent in the deposit. The effect of the concentration of cobalt sulfate at 8 g/l Na₂WO₄, 50 °C, pH 5, and c.d. 2.5 A/dm² on the tungsten weight percent in the deposit is shown in Fig. 2. The results reveal that, the tungsten weight percent in the deposit increases significantly as the concentration of CoSO₄ increased and eventually reaches a maximum at about 30 g/l. The degree of hydrolysis of sulphate ion increases with increasing of the content of CoSO₄ in the electrolyte. In that case, it can be suggested that increasing concentration of CoSO₄ is the reason for increase the activity of tungsten ion and increase the cathodic current efficiency of the plating solution.

The effect of current density on the weight percent of the tungsten in the deposit at the optimum conditions with 8 g/l Na₂WO₄, 30 g/l CoSO₄ is shown in Fig. 3. It is clear that, the weight percent of the tungsten increases with increasing the current density up to 2.5 A/dm², due to the improvement in cathodic current efficiency, beyond it, the weight percent of tungsten decreases. As a result, the maximum c.d. is reached when the rate of movement of metallic ions Co²⁺ and WO²⁻ from the bulk solution to the cathode surface is equal to the rate of deposition. At high current density occurs sharp increase of hydrogen evolution so; it is probable that it retards inclusion of the tungsten in the deposits.

The effect of operating bath temperatures on the weight percent of tungsten in the deposit is demonstrated in Fig 4. The curve assumes that, the weight percent of the tungsten in the alloy increases with increasing the temperature up to 50 °C. The data reveal that, at optimum temperature the cathode current efficiency is high, the coat is smooth, and bright. It seems that the increase of temperature favors the tungsten transport to the cathodic surface due to increase the mobility of the ions and decreases the viscosity of the plating solution, so that the cathode film is more rapidly replenished, making its co-deposition easy. Above this temperature, the decrease in the amount of tungsten is found, due to more moderate hydrogen evolution at high temperature agreement with Holts et.al [8, 9].

3.2 Effect of organic additive

The physical properties of the additives 1,6-diammonium hexane (DAH) and 1, 8-diammonium octane (DAO) are calculated using methodology of Rosen et. al [10]. Values of the surface tension at 30, 40, and 50 °C obtained for various concentrations of aqueous solution of the cationic surfactants are shown in Table 1 and graphically in Fig.5.

From the intersection points in the surface tension γ vs. Log C curves, the critical micelle concentration (CMC) was determined at each temperature. The CMC values show an increasing trend with increasing temperature due to description of the water surrounding the hydrophilic group (---NH₂). This effect disfavors micellization. Also, the CMC decrease with increasing chain length of hydrocarbon. Table 1 indicates that the chain length of hydrocarbon and temperatures plays an important role in determining the surface excess concentration \( I_{\text{max}} \) and area occupied per molecule \( A_{\text{min}} \) at the aqueous solution/air interfaces. Increasing the chain length results in a significant reduction in the value of \( A_{\text{min}} \). This increase in \( A_{\text{min}} \) with raising the temperature may be related to the increased molecular motion at higher temperatures. Increasing \( I_{\text{max}} \) lead to improvement in the efficiency of the surfactants for deposition [11]. The values of \( \Delta G_{\text{mic}} \) indicate that all values are negative and at different temperatures as well this means that the micellization process is spontaneous (\( \Delta G_{\text{mic}} < 0 \)) and temperature favors micellization process. At optimum conditions of plating deposition, different concentration of DAH and DAO are added to the plating solution. The variation of alloy composition with different concentration of DAH and DAO are shown in Fig. 6. The data indicate that the tungsten weight percent in the deposit increased up to 32 % and 18 wt% with increasing the concentration of DAH and DAO up to 10⁻³ mol/l respectively then decreased slightly with further increase in the concentration of DAH or DAO. It is clear that DAH is preference than DAO and its efficiency depends on \( I_{\text{max}} \) which agreement with another work studied elsewhere [11]. The role of the additive can be discussed as following:

The reagent DAH and DAO ionize in aqueous solution by protonation.

\[
\text{NH}_2–\text{R}–\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{N}^+–\text{R}–\text{N}^+ \text{H}_3 + \text{OH}^{-} \\
(K = 4.5 \times 10^4)
\]  

Individual surfactant out ions adsorbs as counter ions at WO₄²⁻ liquid interface by electrostatic attraction, while NH₂–R–NH₂ form loose complex with Co⁵⁺. As a result increase rate of deposit of tungstate and retard deposition of cobalt with tungstate anions. As the concentration of DAH and DAO increase, the adsorption density of surfactant becomes sufficiently high, where interaction between hydrocarbon chains of DAH and DAO ions occurs through Wan der Waals forces. Further increase above CMC of each surfactant, the adsorption density of ion decreases.

The results indicate that, the efficiency of DAH and DAO depends on its CMC, which reflects on the freedom of motion of the surfactants at the solution/air interface, at higher concentration another layer formed in the area of the CMC, so the deposition decrease and tungsten weight percent decrease.

According to Pope and Vagra [12] the mechanism of alloy plating can explained according the following equations:

\[
\text{Co}^{2+} + 2e \rightarrow \text{Co} \quad (\text{Retard by NH}_2–\text{R}–\text{NH}_2) \\
\text{WO}_4^{2-} + 4\text{H}_2\text{O} + 6e \rightarrow \text{W} + 8\text{OH}^{-} \quad (\text{Enhance by H}_3\text{N}^+–\text{R}–\text{N}^+ \text{H}_3)
\]
Sarojamma et al. [13, 14].

The effect of heat treatment on the surface morphology of Co-W alloy deposit has been studied. SEM micrographs of Co-32 W% alloy coating before and after thermal treatment at 400 °C is shown in Fig. 7. It is quite evident that the structure of the deposit alloys before heat treatment is characterized by fiber morphology (Fig. 7a), while, thermal treatment led to refining the structure and the deposits become tight, dense with fine grain (submicron Fig. 7b). The effect of thermal treatment on the hardness of Co-W alloy is shown in Table 2. The data reveals that, the microhardness of the alloy without treatment is 600 VHN and its slightly increase with increasing temperature up to 400 °C it reaches about 880 VHN. Increasing in hardness after thermal treatment may be resulted from the formation of very thin layer of oxide and due to the formation of hardening phase formed at 400 °C against corrosion.

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### 3.4 Corrosion resistance

Potentiodynamic polarization studies for Co-W alloys and compared with chromium deposit were carried out to evaluate the actual corrosion rate. Table 3 lists the electrochemical corrosion parameters including corrosion potential, corrosion current density and corrosion rate. It can be seen that, the corrosion rate of chromium is $3 \times 10^{-6}$ mpy, this value decreases up to $7 \times 10^{-7}$ mpy for Co-32 %W alloy.

The result show that Co-W alloy can electrochemically protect the substrates from corrosion greater than chromium deposit. It can be seen that, this result indicates protective properties of the oxide layer and the hardening phase formed at 400 °C against corrosion. The result of salt spray testing is in a good agreement with the electrochemical corrosion tests. With chromium deposits and Co-W alloys no corrosion product was observed after 72 h (ASTM 117B) indicating that, Co-W film protects steel against corrosion as chromium layers.

### Table 1: Surface and thermodynamic properties of DAH and DAO at 50 °C

<table>
<thead>
<tr>
<th>Parameters</th>
<th>DAH</th>
<th>DAO</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC</td>
<td>8×10⁻³</td>
<td>2×10⁻³</td>
</tr>
<tr>
<td>$\Gamma_{\text{max}} \times 10^{6}$</td>
<td>1.4×10⁻³</td>
<td>2×10⁻³</td>
</tr>
<tr>
<td>$A_{\text{min}}$</td>
<td>1.1</td>
<td>0.83</td>
</tr>
<tr>
<td>$\Delta G_{\text{mic}}$</td>
<td>-23.8</td>
<td>-22.2</td>
</tr>
</tbody>
</table>

### Table 2: Effect of thermal treatment on the microhardness of Co-W alloy

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>VHN</th>
</tr>
</thead>
<tbody>
<tr>
<td>As plated</td>
<td>600</td>
</tr>
<tr>
<td>100</td>
<td>700</td>
</tr>
<tr>
<td>200</td>
<td>750</td>
</tr>
<tr>
<td>400</td>
<td>880</td>
</tr>
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</table>

### Table 3: Corrosion data from potentiodynamic polarization

<table>
<thead>
<tr>
<th></th>
<th>Chromium</th>
<th>Co-32W% alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{corr}}, \text{mV}$</td>
<td>-391</td>
<td>-556</td>
</tr>
<tr>
<td>$I_{\text{corr}}, \mu \text{A}/\text{cm}^2$</td>
<td>$1.02 \times 10^{-3}$</td>
<td>$1.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>Corrosion rate, mpy</td>
<td>$3 \times 10^{-6}$</td>
<td>$7 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

### 4 CONCLUSIONS

1. Cobalt-32 wt% tungsten was electrodeposited from bath containing 30 g/l CoSO₄ and 8 g/l Na₂WO₄ and 0.001 g/l DAH at 50 °C, pH 5 and 2.5 A/dm².
2. The efficiency of DAH and DAO on the composition of the alloy deposits depends on its critical micelle concentration.
3. Co-W alloy containing 32 wt% tungsten electroplated from an acidic bath containing DAH was morphologically smooth, uniform, luster and with fine-grained.
4. Comparison of corrosion characteristics of chromium and Co-W alloy showed that the Co-W exhibits superior corrosion resistance.

### 5 REFERENCE