Electroplating of Co-W and Co-Mo Alloys from Na$_2$WO$_4$ Ionic Melts

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The cathodic reduction processes of cobalt (III), tungsten (VI) and molybdenum (VI) in Na$_2$WO$_4$ melts are discussed. Electrochemical behavior of cobalt in a tungstate melt, as well as the effect of electrolysis conditions on the composition and structure of Co-W and Co-Mo alloys deposits from tungstate-molybdate melts is also studied. With a decrease in the concentration of cobalt ions and an increase in the concentration of molybdenum (tungsten) ions in the melt, the phase composition of cathodic deposits is shown to change from individual cobalt to individual molybdenum (tungsten) via a series of cobalt-molybdenum (tungsten) compounds of various compositions.

Keywords: Co-W and Co-Mo alloys, ionic melts, tungstate-molybdate melts, electroplating

Electrolysis of aqueous solutions and melts is often used for obtaining the Ni-W and Ni-Mo alloys. However, most if not all of literature data show that some undesirable side processes occur in aqueous solutions. They result in the diminution of current efficiency and, in some cases, are responsible of incomplete cathodic reduction of molybdates or tungstates. Most melts considerably also suffer from this disadvantage. The literature has many studies on electrodeposition of metallic Mo, W, Co and Co-Mo alloys from ionic media.[1-9] Electrochemical behavior of nickel as well as electroplating of nickel-molybdenum (tungsten) alloys from oxide tungstate-molybdate nickel-containing melts was studied in our previous work [10]. In the earlier works [11-13], common regularities of codeposition of iron family metals with titanium from halide melts were described in [10]. The reference electrode was a platinum-oxygen electrode, namely, a Pt wire immersed in a 80 mol% NaCl-KCl melt and blown round with air in a cell provided with an alundum diaphragm.

The deposits obtained were studied by X-ray diffraction analysis, X-ray energy dispersive microanalysis and metallographic method with the use of DRON-4.0, Cameca, and Neophot-21 equipments. The microhardness was measured with a PMT-3 equipment.

Experimental part

The used melts were: Na WO$_4$-CoO-MoO$_3$ and Na WO$_4$-MoO$_3$ prepared from pure substance (Sigma-Aldrich, 99%). Working temperature was in the range 1123-1173 K.

As the main technique of investigation, we used cyclic voltammetry with the scan rates of 5 · 10$^{-2}$ to 10 V/s corresponding to either quasi-steady-state or transient polarization conditions.

Experiments were carried out in air atmosphere in a quartz reactor. The design of electrochemical cell, preparation of reagents, methods of monitoring and estimating the kinetic parameters of the electrode process were described in [10]. The reference electrode was a platinum-oxygen electrode, namely, a Pt wire immersed in a 80 mol% Na WO$_4$-20 mol% WO$_3$ melt and blown round with air in a cell provided with an alundum diaphragm.

The deposits obtained were studied by X-ray diffraction analysis, X-ray energy dispersive microanalysis and metallographic method with the use of DRON-4.0, Cameca, and Neophot-21 equipments. The microhardness was measured with a PMT-3 equipment.

Results and discussions

An analysis of equilibrium potentials was made in aqueous solutions for the most popular system containing citric complexes of Co(II) and molybdate anions.[17,18] The well-known material balance equations made possible to calculate the distribution of the ionic species components and to use this information for the estimation of equilibrium potentials of the corresponding cathodic processes. The conclusion was that the reduction of cobalt (II) is possible, but the complete tungsten or molybdate reduction is possible only at sufficiently negative potentials where the reduction of H$^+$ ions should prevail. Thus the thermodynamic regularities are indicative of the certain bath. These alloys are of practical importance in the production of cobalt-containing structural materials by means of the high-temperature electrochemical synthesis of molybdenum and tungsten carbides. Cobalt additives substantially increase the ductility of molybdenum and tungsten as pure metals.

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complications regarding the electrolysis of aqueous solutions. In this connection, the main attention was focused in this work on the melts.

**Electrochemical behavior of Cobalt (II) ion in a tungstate melt**

A reduction wave was observed at -0.8 to -0.9V in voltammetric curves (fig. 1) recorded from a Na₂WO₄ melt containing cobalt (II) oxide. An increase in the Co(II) concentration led to the increase in the wave height and to its shift of potential in the positive direction.

The reduction process of Co(II) proceeded in a single stage. An increase in the polarization rate to 5.0 V/s made it impossible to determine the mechanism of the process. Potentiostatic electrolysis at potentials of the wave observed resulted in cobalt metallic coating. The dependence of peak current density (i_p) on the concentration of cobalt oxide at various polarization rates (v), (fig. 2) was linear.

![Fig. 2. The dependence of peak current density on the CoO concentration in Na₂WO₄ melt at various scans; Pt cathode, T=1173K.](image)

Also we found that the i_p/v^1/2 ratio was nearly constant in a polarization rate range of 0.05 to 2.0 V/s (fig. 3). The mass transfer constant i/nFC corresponding to the steady-state voltammetric dependences and characterizes the supply of reagent Co(II) to the electrode surface, was equal to (2.1-2.7) 10^-4 cm/s that confirms the diffusion control of the process of Co(II) reduction. Hence, under these polarization conditions, the formation rate of Co metal grains did not limit the process in question.

Linear dependence of the cathodic peak current with the cobalt (II) oxide concentration, the constancy of i_p/v^1/2 ratio in a wide range of the polarization rates, and the i_p/nFC value indicate that the diffusion of Co(II) ions to the electrode surface is the limiting stage of the electrode process.

The electrodeposition mechanism may be explained based on a supposition about the existence of acid-base equilibria in tungsten melts, in which tungstate and bitungstate ions are involved [10]. Upon the addition of cobalt (II) oxide, the activity of oxygen ions increased, due to the equilibrium (1):

$$\text{CoO} \rightleftharpoons \text{Co}^{2+} + \text{O}^2- \quad (1)$$

Therefore the electrode process under these conditions may be written as a two-electron transfer:

$$\text{Co}^{2+} + 2e^- \rightleftharpoons \text{Co} \quad (2)$$

According to the experimental dependence of the equilibrium potential of the cobalt electrode on the cobalt (II) oxide concentration in a sodium tungstate melt, the number of electrons per an electrochemically active Co(II) ion equals 1.9–2.2. Similar values were obtained by recording the steady-state voltammetric curves which were analyzed in a semilogarithmic E-log i/(i_d-i) coordinates; the current density and i_d, the limiting current density. The slopes of these linear dependences at various CoO concentrations were 103 to 122 mV, while n was 1.7 to 2.1. A theoretical slope of the reversible two-electron reaction is 112 mV.

The agreement of the experimentally estimated slope with the theoretical value indicates the reversibility of the charge transfer stage for Co electrodeposition from Na₂WO₄ melt. This was also confirmed by other following experimental observations. The deposition potential and the half-wave potential are independent of the polarization rate up to 0.2 V/s, and the dependence of the equilibrium potential on CoO concentration was well described by the Nernst equation.

The number of electrons involved in the electrode process was also determined from the difference between the peak and half-peak potentials of the cyclic voltammetry curves: E_p/E_p/2 = 2.2 RT/F. At various CoO concentrations and scan rates of 0.05 - 0.2 V/s, the number of transferred electrons fell in a range of 1.7 to 2.0.

At a scan rate higher than 0.5 V/s, the reversible electrode process became quasi-reversible. This was manifested also in the deviation from the i_p/v^1/2 linear dependence and in the dependence of the peak and half-peak potentials on the scan rate. Thus, analysis of the experimental data
Electrochemical co-reduction of Co(II) and W(VI) ions [as well as co-reduction of Co(II) and Mo(VI) ions] with from a Na₂WO₄ bath and electroplating of Co-W (or Co-Mo) alloys

Upon addition of tungsten (VI) oxide to Na₂WO₄ melt, WO₄²⁻ ions are formed in the bath [16] and these bitungstate ions are cathodically reduced:

\[ \text{WO}_4^{2-} + 6e^- \rightleftharpoons W + 4\text{O}^{2-} + 30^2, \] (3)

that was thoroughly studied in [15]. The difference between the deposition potentials of cobalt and tungsten is 0.070 to 0.105 V at 1173K, and, by contrast to halide and halide–oxide melts, the reduction potential for cobalt is more noble than for tungsten in an oxide melt. As the blank bath for electroplating Co-W alloys of diverse compositions, we took a Na₂WO₄ -1.5 mol% WO₃ melt. From this bath, upon its purification by preliminary electrolysis, tungsten coatings were electroplated with the use of a tungsten soluble anode in a temperature range of 1123 to 1173K at cathodic current densities of 0.04-0.14 A/cm² in order to determine the structure of tungsten metal deposits. It was found that using a current density of 0.04-0.10 A/cm², W coatings have a columnar structure with a layer thickness of 150-200 µm and a microhardness of 340-420 kgf/mm². The maximum thickness of the coatings was 500 µm. When co-depositing two metals, the tungsten anode was replaced with a more noble cobalt anode, and the electrolysis was carried out at a cathodic current density, lead to an increase in the cobalt content in the deposit. From the melts containing 0.08-1.0 mol% CoO at temperature of 1123 to 1173K, continuous dense layers of Co-W and Co W intermetallic compounds are deposited sequentially. The formation possibility of the latter is confirmed by binary phase Co-W diagram [19]. Both compounds have fine-crystalline or lamellar structure (fig. 4b). From the Na₂WO₄-CoO melts containing WO₃, at a current density of up to 0.05 A/cm², continuous cobalt metal layers with a block or columnar-block structure, thickness of lower than 50 µm and microhardness of 150-180 kgf/mm² are deposited. Upon further thickening of cobalt coatings or with an increase in the current density above 0.05 A/cm², they transform into dendrites. The analysis of cobalt and tungsten concentration distribution among the coating and nickel substrate indicate the mutual diffusion of the coating and substrate elements, which provides a good coherence between them.

Adding molybdenum (VI) oxide to the cobalt oxide containing Na₂WO₄ melt results in the appearance of the bimolybdate ion reduction wave:

\[ \text{MoO}_4^{2-} + 6e^- \rightleftharpoons \text{Mo} + 4\text{MoO}_4^{2-} + 30^2, \] (4)

that was studied in detail in [19]. The difference between the deposition potentials of cobalt and molybdenum is 0.060 to 0.090 V at 1173K, the cobalt’s one being more positive. The technique of plating the alloys is similar to that described above from the original bath of the following composition: Na₂WO₄ -5.0 mol% MoO₃. The results of experiments using a steel substrate are listed in table 2.

The regularities of Co-Mo alloys electroplating are similar to those observed in the case of Co-W alloys. The MoO₃ content in this bath was maintained in a range of 1.0 to 5.0 mol%, while the CoO concentration was varied from 0.01 to 2.0 mol%, so that the molar molybdenum-to-cobalt ion ratio fell in a range from 500 to 0.05. From the baths containing 0.1-0.8 mol% CoO at temperature of 1123 to

Table 1

| CoO, mol% | WO₃, mol% | T, K | Iₛ, A/cm² | Phase composition of deposit | Hardness, H, kgf/mm² | Structure |
|-----------|-----------|------|-----------|-----------------------------|---------------------|-----------|
| 0.01      | 1.5       | 1123 | 0.12      | W                           | 372                 | Columnar  |
| 0.1       | 1.0       | 1123 | 0.10      | W, CoW                      | 411                 | Columnar  |
| 0.1       | 0.3       | 1173 | 0.12      | CoW                         | 823                 | Lamellar  |
| 0.5       | 0.3       | 1173 | 0.08      | CoW, Co₃W                   | 656                 | Lamellar  |
| 0.7       | 0.2       | 1173 | 0.07      | Co₃W                        | 590                 | Lamellar  |
| 1.0       | 0.1       | 1173 | 0.05      | Co                          | 156                 | Columnar  |

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1173K, continuous CoMo and Co Mo layers were deposited sequentially on the cathode. The possibility of the formation of these intermetallic compounds is confirmed by the Mo-Co phase diagram [20]. Both alloys have fine-crystalline or lamellar structure (fig. 5a), with microhardness decrease from 650 to 300 kgf/mm² when the molybdenum-to-cobalt ratio is decreased (fig. 5b). From the baths free of MoO₃ at a current density lower than 0.05 A/cm², continuous cobalt metal layers with block or columnar-block structure were deposited. The analyses of the cobalt and molybdenum concentration distribution in the coating and steel substrate indicate that there is a mutual diffusion of the coating and substrate elements, which also provides a good coherence between them.

### Table 2

| CoO mol% | MoO₃ mol% | T K | lA/cm² | Phase composition of deposit | Hardness, H kgf/mm² | Structure |
|----------|-----------|-----|--------|-------------------------------|---------------------|-----------|
| 0.01     | 5.0       | 1173| 0.07   | Mo                            | 185                 | Columnar  |
| 0.01     | 2.5       | 1123| 0.10   | Mo                            | 179                 | Columnar  |
| 0.1      | 0.5       | 1123| 0.07   | Mo, CoMo                      | 293                 | Columnar  |
| 0.1      | 0.2       | 1173| 0.08   | CoMo                          | 650                 | Lamellar  |
| 0.5      | 0.2       | 1173| 0.08   | CoMo, CoMo                    | 524                 | Lamellar  |
| 0.8      | 0.2       | 1173| 0.07   | CoMo                          | 387                 | Lamellar  |
| 1.5      | 0.1       | 1173| 0.05   | Co                             | 150                 | Columnar  |
| 2.0      | –         | 1123| 0.04   | Co                             | 164                 | Columnar  |

**Fig. 5.** (a) SEM surface image of the cobalt metal coating (x800) and (b) a micro cross-section photo of a steel specimen covered with cobalt (x400) at 1.0 mol% CoO content, T=1173K, i=0.05 A/cm², and t=1.0 h

### Conclusions

The results demonstrate that molybdenum (tungsten)-cobalt alloys may be plated on cathode as continuous layers from oxide melt baths. Changing the content of the corresponding components in the melt, the temperature, and the current density may control the composition and structure of the deposit. The general regularities of the electroplating are similar to these typical of the molybdenum (tungsten)-nickel alloys.

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