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Electrochemical way of molybdenum extraction from the Bimetallic systems of Mo-W

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Abstract. Electrochemical dissolution of molybdenum and tungsten was investigated in water-dimethylsulfoxide (DMSO) media at different concentrations of lithium chloride and magnesium perchlorate. The terms of efficient extraction of molybdenum from bimetallic systems of Mo-W have been determined. The polarization curves of the electrooxidation of molybdenum in the solution of 0.25 M LiCl in the DMSO at the different rates of rotations and the scan rate equal to 50 mV/s were obtained. In the presence of the addition of water at the potential of 0.1-0.75 V the small area of polarizability occurs, then with increasing potentials above 1.5 V there is a sharp increase of the oxidation current. Comparison of the current values of anodic dissolution of molybdenum and tungsten showed that the rate of anodic dissolution of molybdenum significantly exceeds the rate of anodic dissolution of tungsten. In the case of molybdenum, the dissolution process is limited by diffusion, in the case of tungsten - by the passive film formation on the electrode surface.

1. Introduction

The chemical etching process is widely used in contemporary lamp production for molybdenum extraction from bodies of incandescent, wherein the dissolution of molybdenum from the Mo-W bimetallic systems takes place [1]. At the etching process the highest rate of dissolution of molybdenum can be achieved at the lowest weight loss of spirals, and the lowest consumption of pickling liquids. The solution consisting of a mixture of the nitric acid (56%) and the sulfuric acid (78%) in the volume ratio 1: 3 was used for the etching process [2].

The nitric acid well oxidizes the surface of the metal molybdenum till MoO_3. But the molybdenum oxide obstructs the access of acid to the metal surface and thereby it slows the dissolution of the metal. The sulfuric acid dissolving MoO_3 and accelerates the dissolution of metallic molybdenum. It is important to keep the ratio of acids because the decrease of the amount of nitric acid leads in loss weight of tungsten and the reduction of sulfuric acid slows the rate of etching. The end of the evolution of nitrogen oxide brown fumes accompanying the process of etching indicates the completion of the reaction. After washing with running water, the spirals were immersed in the boiling solution of 5% sodium hydroxide to neutralize the acids and for purification from oxides formed on the spiral surface by acids. Then the spirals was washed in hot running water and dipped 2-3 times into a bath with acetone or alcohol and dried in the oven at a temperature not higher than 100°C.

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When etching molybdenum core, the tungsten is covered with an oxide film which well soluble in alkali. The loss in weight is determined by comparing the mass of spirals etched and mechanically removing the core. The weight loss of spirals should not exceed 3-5%.

The spirals dried after etching must have a metallic gray surface without traces of oxides and stains. The dark colour of the spirals indicates the incomplete removing of the molybdenum.

The process of chemical dissolution is environmentally dangerous, as it leads to the formation of the strongly acidic molybdenum containing solutions of the approximate composition (wt. %): H_2SO_4 - 18, HNO_3 - 8, Mo (VI) - 1,6-3, and also these solutions can contain SO_2 and nitrogen oxides [1]. The concentration of Mo (VI) in the washing water reaches 8 mg/l. The maximum allowable concentration of Mo(VI) is equaled to 0.0012 mg/l. It is impossible to achieve the maximum allowable concentration of [Mo(VI)] at the waste water treatment [1].

Thus, the disadvantages of this method of etching molybdenum cores are:

- formation and evolution of nitrogen oxides,
- the high aggressiveness of etching solutions,
- the etching process is virtually ungovernable,
- the low efficiency of molybdenum capture from spent solution (50%). In this connection, the problems of environmental, technological and resource-saving character take place.

Currently, there are a significant number of ways to remove the core samples from the tungsten [3-14]. However, they have some disadvantages: they are expensive, difficult to operate (number of them requires adjustment of the technological process of spiral production), decrease the rate of dissolution of the molybdenum.

The purpose of the work is to study the possibility of the selective dissolution of molybdenum from the bimetallic system of Mo-W in the water - dimethylsulfoxide (DMSO) solution of lithium chloride and magnesium perchlorate. In this work the anodic dissolution of molybdenum and tungsten was carried out in the solution of 0.5 M $Mg(ClO_4)_2$ and 0.25 M LiCl in the solutions of water - DMSO. The electrolyte is devoid of the most of the drawbacks pointed above at the process of chemical etching [15].

2. Experimental

The study of the electrooxidation of molybdenum and tungsten was carried out by means of the potentiostat-galvanostat *AUTOLAB PG101/101 M* (Switzerland) in the thermostatic three-electrode cell.

The rotating and stationary molybdenum and tungsten rods pressed in Teflon were used as a working electrode (anode). Before each experiment, the electrodes were polished with help of the micron sandpaper to a mirror finish and washed with working solution.

When using a stationary electrode, the measurements were performed in another three-electrode glass cell. The cell before the experiments was washed with hot soda solution, the large amount of water, and then with bi-distilled water. Then the cell was steamed and dried under vacuum. Immediately before the test the cell was rinsed with the working solution. The platinum plate was used as an auxiliary electrode and the silver chloride electrode was used as a reference electrode placed in a capillary with the saturated electrolyte solution of LiCl in the DMSO.

Before each experiment the setup was prepared by accordance with the requirements. The polarization of the electrode was carried out in the range of potentials from 0.00 till +2.0 V in depending on the working electrode and the conditions of the electrochemical process (all potentials were given with respect to the silver chloride electrode).

3. Results and discussion

Figure 1 demonstrates the polarization curves of the electrooxidation of molybdenum in 0.25 M LiCl in DMSO solution at the different speeds of rotations and the scan rate of 50 mV/s. In the presence of the water addition at the potential of 0.1 - 0.75 V the small area of polarizability occurs. Then the increasing of the potentials above 1.5 V results in the extreme increase of the oxidation current because the lowest oxides of molybdenum (δ and γ-phase) are formed [15] which have a high electronic conductivity. With increasing of scanning speed, the speed of the electrochemical dissolution of Mo increases.

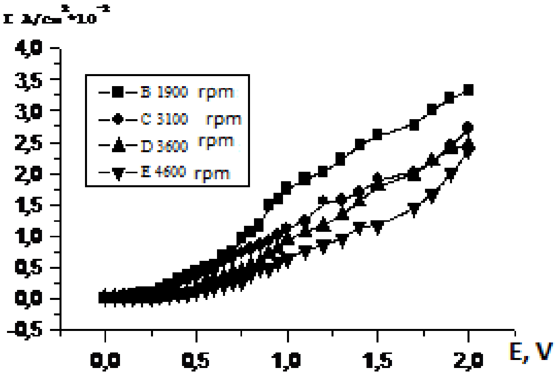

Figure 1. The polarization curves of the anodic dissolution of molybdenum in 0.25 M LiCl in DMSO.

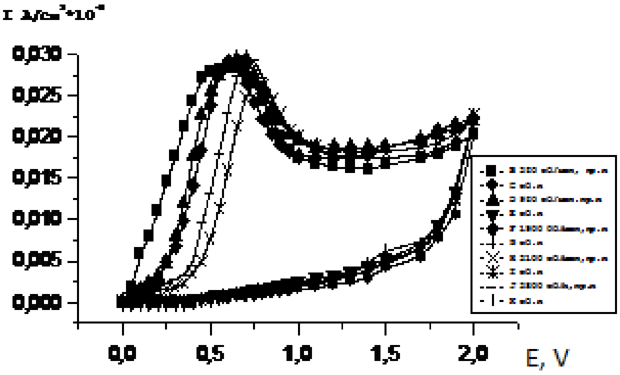

Figure 2. The polarization curves of the anodic dissolution of tungsten in 0.25 M LiCl in DMSO.

Figure 2 shows the polarization curves of tungsten electrooxidation in 0.25M LiCl at the different rates of rotation. It is shown from the figure 2 that the growth of potential leads to the sharp increase of the current which reaches a maximum at 0.5 - 0.7 V. Then in a relatively small potential range from 1.1 V to 1.5 V the rate of oxidation of the metal reduces. The oxidation current of tungsten decreases and then from 1.45 V to 2 V, the oxidation rate slightly increases. The area of the passive state potential is limited by super passivation accompanied by the formation of oxygen compounds of WO_3 (α-phase). Hence the maximum at potential is approximately equaled to + 0.7 V and the subsequent decrease of the speed of the anodic dissolution of tungsten indicates the full coating of the surface by oxides of poorly conducting film from the α-phase [12].

Comparison of the current values of anodic dissolution of molybdenum and tungsten showed that the rate of anodic dissolution of molybdenum significantly exceeds the rate of anodic dissolution of tungsten. In the case of molybdenum, the dissolution process is limited by diffusion, in the case of tungsten - by the passive film formation on the electrode surface [11].

Using data obtained the values of the coefficient of efficiency of anodic dissolution of molybdenum in the presence of tungsten at the different potentials and different concentrations of LiCl were calculated according to the formula:

$$K_{эфф} = i_{Mo}/i_{W,}$$

where i_{Mo} и i_W - the density of current of the anodic dissolution of Mo and W, respectively, at the same values of potentials.

Figures 3 and 4 show that the increase of the potential the concentration of LiCl differently influents on the process (Figure 3), but in comparison with the perchlorate solutions, the coefficient of effectiveness of the anodic dissolution of molybdenum is higher in a solution of LiCl. The influence of water additions in [LiCl] solutions (Figure 4) was investigated. As can be seen from the Figure 4 the increase of water concentration causes the growth of the effectiveness coefficient of the anodic dissolution of Mo at the both concentrations of LiCl. The most efficient extraction of molybdenum from the bimetallic systems of Mo-W proceeds at 0.5 M LiCl in 5.2 M DMSO solution, the concentration of water 32.2 mol/l in the potential range of 1 - 2.2 V.

The most effective electrolyte composition is equaled to 0.25 M or 0.5 M LiCl in 5.2 M DMSO and 32.2 M H_2O. Therefore, we conducted the electrolysis in the selected area of concentrations of the components. The electrolysis was carried out in the glass electrochemical cell with separated spaces.

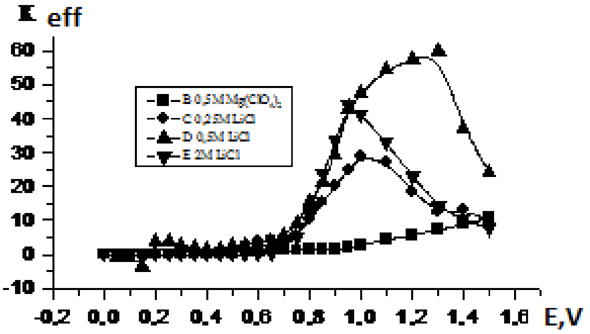

Figure 3. The dependence of the effectiveness coefficient of anodic dissolution of molybdenum on potential at the different concentrations of LiCl and 0.5 M $Mg(ClO_4)_2$.

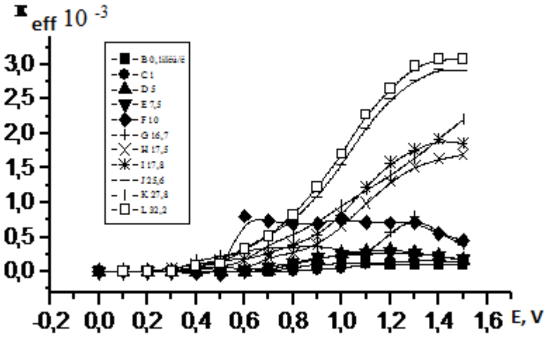

Figure 4. The dependence of the effectiveness coefficient of anodic dissolution of the molybdenum on potential of 2M LiCl at the different concentrations of water.

The indifferent metal (Pt) was cathode, and the tungsten - molybdenum spiral wound around the molybdenum rod was used as a anode. The process was carried out at the room temperature and a current density of 220 mA / cm^2. The amount of metal has passed into solution was adjusted by the difference between the initial and final masses of the anode.

Also for the determination of element contents after the anodic dissolution of the bimetallic system the solution was analyzed by atomic absorption method and mass spectrometric methods.

Agilent 7500 (Agilent Technologies) is the mass spectrometer with inductively coupled plasma. This apparatus is characterized by the ability to detect trace amounts of micro impurities (up to the level of ng/g) and by rapid investigation of the quantitative content of elements (over than 70) for information on the composition of the samples studied.

The Chemstation Software of Agilent 7500 automates the analyses and promotes the accurate decoding of the data. The atomic absorption analysis of Mo and W on the AAS1N device in nitrous oxide-acetylene flame was carried out at the wavelength of 285.2 nm. The content of metals was identified by means of the calibration curve. The calibration was obtained using the accurate weight of molybdenum with metal purity of 99.99%.

The table 1 shows the results for various electrolyte solutions.

Table 1. The results of analysis of the electrolyte solution after the electrolysis.

Electrolyte composition	Concentration in solution, mg/l	
	Mo	W
0.25 MLiCl, 32.2 M H_2O, 5.2 M DMSO	24,400	0,0214
0.5MLiCl, 32.2 M H_2O, 5.2M DMSO	98,247	0,0218

Based on the data presented in the table 1, it can be concluded that in the selected electrolyte is a significant dissolution compared with molybdenum and tungsten concentration of this region is the most suitable for the selective dissolution. Thus, in an electrolyte containing 0.25 M LiCl the concentration of molybdenum passed into the solution on ~ 4000 times higher than the concentration of tungsten, and in 0.5 M LiCl solution is higher by 1000 times.

4. Conclusions

The most effective extraction of molybdenum from the Mo-W bimetallic systems was observed at the next electrolyte composition: 0.25 M or 0.5 M LiCl; 5.2 M DMSO; 32.2 M H_2O in the range of potentials from 1 to 2.2 V.

The dependence of the coefficient of efficiency of the anodic dissolution of molybdenum on the potential value was determined with the presence of the different electrolytes. The ratio of rates of the anodic dissolution of Mo and W is 4000: 1 (in the terms f the experiment). The results obtained give the possibility to use the proposed solutions as an electrolyte mixture for the selective dissolution of molybdenum in the presence of tungsten.

The proposed method is different from the known ones and it significantly increases the selectivity of dissolution and simplifies the process.

References

[1] Yapryntseva O A, Kolosnitsyn V S, Yatsyk N A and Krasnogorskaya N N 2002 Anodic dissolution of molybdenum and tungsten in solutions of sodium sulfate *Russian Journal of Applied Chemistry* **75(4)** 678-9

[2] Ulmishek L G 1958 *The Production of Electrical Incandescent Lamp* (Leningrad)

[3] Binder L, Rathwallner G, Mollay B and Nauer G 2004 The electrochemical dissolution of molybdenum *Proc. 55th of the International Society of Electrochemistry Meeting* (Greece: Thessaloniki) S7FP3

[4] Binder L 1988 The electrochemical dissolution of molybdenum *Proceedings 39th of the International Society of Electrochemistry Meeting* (UK: Glasgow) 547

[5] Armstrong R, Bell M and Metcalfe A 1977 The anodic dissolution of molybdenum in alkaline solutions electrochemical measurements *Journal of Electroanal. Chem.* **84** 61-72

[6] Abbas Q and Binder L 2011 The electrochemical dissolution of molybdenum in non-aqueous media*Int. Journal of Refractory Metals and Hard Materials* **29** 542-6

[7] Hull M 1972 On the anodic dissolution of molybdenum in acidic and alkaline electrolytes *Journal of Electroanal. Chem.* **38** 143-57

[8] Anikeev K M, Ginzburg A A and GandelsmanI L 1966 *A Method for Removing of Molybdenum from Tungsten Spiral of Electron Tubes* (USSR: AC 185064, MPK C 22B 34/30, Bulletin 16)

[9] Jurkiewicz J N and Kolenkov K Y 1969 *The Electrolytic Separation of Tungsten and Molybdenum in the Processing of the Tungsten-molybdenum Alloys* (USSR: AC 223347, MPK C 22B 34/00, Bulletin 10)

[10] Gurevich E A, Polyakov B I, Tsyganov G A, Zakarchevny DI and Kalkov A A 1971 *The Electrolytic Separation of Molybdenum with Refractory Metals* (USSR: AC 290948, MPK C 22B 49/00, Bulletin 3)

[11] Muta Myusudzaki and Fidzikay Kutato Intedzetto 1989 *Method of Selective Dissolution of Molybdenum* (Japan: AC 145734, MPK C 22B 34/36)

[12] Zworykin A Y, Perelman F M and Rode E YA 1950 *Method for Recovering of Tungsten and Molybdenum from Ores and Concentrates* (USSR: AC 116335 MPK C 22B 34/00)

[13] Alkatsev M I and Guriev V R 2002 *Method of Recycling Carbide* (USSR: AC 2189402 MPK B 25B 1/00)

[14] Kozlov N B, Noskov A V, Lilin S A and Zuev A V 1999 About the selectivity of electrochemical dissolution of molybdenum and tungsten *Russian Journal of Applied Chemistry* **72(1)** 101-4

[15] Kudreeva L K 2006 Electrooxidation of molybdenum and tungsten in water - dimethyl sulfoxide solution of electrolytes (Kazakhstan:Al-Farabi Kazakh National University, Ph.D thesis)