Electrochemical reduction of tungsten(VI) oxide from a eutectic melt CaCl₂–NaCl under potentiostatic conditions

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Abstract: The paper presents results of the study of the electrochemical reduction of tungsten(VI) oxide in a melt of the eutectic composition 52 mol% CaCl₂ and 48 mol% NaCl at a liquid gallium electrode. Scanning electron microscopy and X-ray diffraction methods were used to study the microstructures of the obtained powders. The Rietveld method which is based on diffraction patterns were used to calculate the quantitative content of phases in WO₃ reduction products. The thermodynamic properties of the electrolysis process were investigated by voltammetry. It is shown that a necessary condition for the electrochemical reduction of WO₃ is electrolysis at potentials higher than the standard electrode potential of decomposition of calcium tungstate, which is formed by the interaction of tungsten oxide with calcium chloride. The reduction can take place by both electrochemical and metallothermic mechanisms depending on the conditions of electrolysis. The reduction product is fine tungsten with a particle crystallite size of up to 1 μm.

Keywords: reduction of WO₃; potentiostatic electrolysis; tungsten oxide; melts; calcium and sodium chlorides.

INTRODUCTION

Tungsten has a unique physical and chemical properties, that is why alloys and composites based on it are widely used in various fields of modern science and technology such as metallurgy, mechanical and instrument engineering, electrical engineering, structural materials, *etc*.[1–5] Analysis of the scientific and technical literature shows that the demand for tungsten and products made from it is growing, and that the prices for tungsten products are rising accordingly.[6,7] The known methods of producing tungsten by reducing its oxide compounds with

hydrogen are characterized by high specific energy consumption and require a complex technological equipment.[8,9] Recent studies have shown that a promising method for producing refractory metals can be direct electrochemical reduction of their oxides in melts based on calcium compounds (FFC – Cambridge Process).[10,11]

The articles showed the possibility of electrochemical production of tungsten powder from molten mixtures $NaCl–KCl–Na_2WO_4$, $KCl–NaCl–NaF–Na_2WO_4$ and $NaCl–KCl–NaF–WO_3$.[12–14] The possibility in principle of electrochemical reduction of $CaWO_4$ to tungsten in melts based on calcium chloride in the temperature range of 873–1173 K is shown in.[15,16]

Despite the currently accumulated experimental material, the information on the conditions for the reduction of tungsten oxide in molten electrolytes is extremely limited. For example, according to the research,[16] tungsten trioxide cannot be electrochemically reduced to tungsten metal in the eutectic melt of sodium and calcium chlorides without large losses, while the works-proof that this process can be implemented in molten mixtures of LiCl–KCl and KF–KCl, CsF–CsCl.[17,18] There is no information on large losses of tungsten due to the formation and sublimation of volatile tungsten compounds. Given the above, the study of the processes that occur during the electrochemical reduction of tungsten oxide is an important not only applied but also scientific task.

The aim of this work is to identify the influence of electrolysis conditions on the composition of reduction products, current yield and the degree of extraction of tungsten from dispersed WO_3.

EXPERIMENTAL

The electrochemical reduction of tungsten trioxide was carried out in an argon atmosphere in a quartz reactor (n) with a Teflon lid (e), in which were installed the tubes for argon inlet (a) and outlet (b) by using rubber seals, and also current collectors (c) of tungsten wire with a diameter of $1.0–2.6×10^{-3}$ m to the graphite anode (f) and liquid gallium cathode (g). The tungsten wires were covered with quartz or corundum tubes (d) to avoid contact with the molten electrolyte. The schematic drawing of the cell assembly is shown in Fig. 1. The reactor was installed in a shaft furnace to ensure the required temperature of electrolysis. Tungsten(VI) oxide (h) was loaded into a corundum crucible (k, outer diameter 37 mm, height 60 mm) on the surface of molten gallium.

About 70.0±0.5 g of a thoroughly dehydrated electrolyte mixture (j) of the composition 52 mol% $CaCl_2$ and 48 mol% NaCl was used in every experiment. This composition has a melting point of 780 K,[19] and it was prepared from analytically pure compounds with a main reagent content of > 99.9 wt.%. Gallium mark GL-1 with a purity of 99.9% was used as the cathode (g). In each experiment, 1.40±0.10 g of gallium was charged into the crucible (m). For the reduction, tungsten (VI) oxide containing at least 99.9999 wt.% WO_3 with a particle size of 30–80 μm was used. The amount of tungsten oxide loaded on the cathode was 0.5 g in each experiment. The anodes were made of low-porosity graphite MPG-7 (f). The working temperature was controlled at 1013±1 K. The electrolysis temperature was monitored using a platinum: platinum–rhodium thermocouple (R-type) thermocouple placed just outside the

quartz vessel near the bottom of the reactor (n). Electrochemical reduction was carried out with a stabilized DC source MPS-3010L-1 (Matrix Technology Inc., China, 30 V, 10 A). In each experiment, 0.30±0.05 A·h of electricity was passed through the cell.
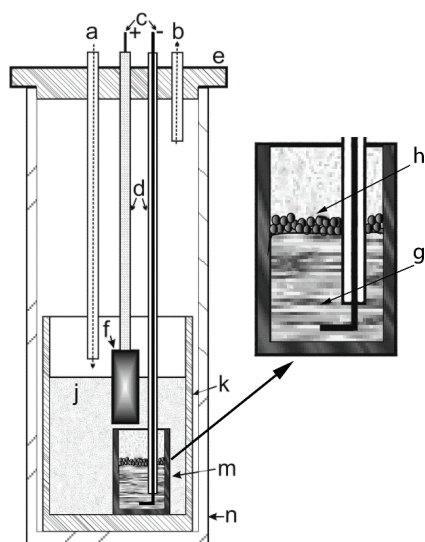

Fig. 1. Schematic diagram of the reactor for the electrochemical reduction of oxygenated tungsten(VI) compounds in molten electrolytes on a liquid gallium cathode.

The lid (e) with the electrodes was removed from the reactor after electrolysis, and the contents of the crucible (m) were poured into a thoroughly dried stainless steel vessel. The salt and metal phases were easily separated from each other due to the large difference in the crystallization temperature of the molten electrolyte (780 K) and gallium (~303 K). The salt phases and the fine powder that remained on the surface of the vessel after the separation of gallium were weighed, transferred to a glass beaker and poured over with an aqueous solution of 0.1 M HCl. The solution and the fine phase were separated by decantation after the complete dissolution of the salt phase. The formed fine phase was washed several times with distilled water until there was no qualitative reaction (with a silver nitrate solution) to the presence of chlorine anions in the decantate.[20] The precipitate was washed free from the electrolyte residues and dried at 393 K to constant weight, and its morphology and phase composition were investigated. The gallium what was unloaded from the crucible (m) and the melt in the crucible (k) were used after weight adjustment to reduce next portions of tungsten oxide.

The X-ray phase analysis (X-ray diffraction) of electrolysis products was performed on a diffractometer DRON-3M with CuKα radiation. The phase composition was identified using the computer software Match! Crystal Impact ver. 3.3 with databases ICDD PDF-2.[19] The Rietveld method using the software Jana 2006 and the database COD (Crystallography Open Database) was used to determine the quantitative content of the phases. Crystallographic data for tungsten (spatial group Im-3m, crystallographic parameters: a = 3.1648 Å) and CaWO₄ (spatial group I 41/a:2, crystallographic parameters: a = 5.2429 Å, c = 11.3737) were used in the calculations.[22,23]

The morphology of the reduction products was studied using a scanning electron microscope JEOL JSM-35.

The voltammetric research was performed using a potentiostat PI-50-1 with a programmer PR-8 in a three-electrode cell. The working electrode was a platinum plate with an area of 2.3 cm^2, the auxiliary electrode was a glassy carbon plate with an area of $S \approx 5.3$ cm^2. The potential of the working electrode was recorded and reported relative to the unpolarized platinum reference electrode. The voltammograms were recorded with a two-coordinate self-recording potentiometer LKD-4 and digitized using the software GetData Graph Digitizer 2.26. All electrodes were pre-ground to get a mirror surface before each measurement, then washed with distilled water and dried. The study was performed at a temperature of 1013 K.

RESULTS AND DISCUSSION

To determine the possibility of the direct electrochemical reduction of tungsten trioxide, the values of standard electrode potentials ($E^\ominus$) of reactions that can take place at the cathode were calculated:

$$MCl_n + ne^- \rightarrow M + nCl^-, \text{ where M: Na, Ca} \tag{1}$$

$$WO_3 + 6e^- \rightarrow W + 3O^{2-} \tag{2}$$
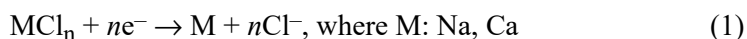
In addition, it is known that tungsten trioxide interacts with calcium chloride in the molten state to form slightly soluble calcium tungstate and volatile tungsten oxochloride:[9,16]

$$2WO_3 + CaCl_2 \rightarrow CaWO_4 + WO_2Cl_2, \tag{3}$$

therefore, calcium tungstate may also be involved in the reduction:

$$CaWO_4 + 6e^- \rightarrow W + 4O^{2-} + Ca^{2+} \tag{4}$$
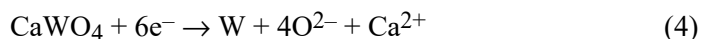
According to research,[15] the solubility of calcium tungstate at 1025 K is ~0.2 wt.%. This shows in favor of that the predominant amount of calcium tungstate should be reduced in the solid-state. The participation of tungsten oxychloride in electrode processes was not taken into account, because at temperatures above 484 K it turns into a gaseous state and is comes out of the melt.[16,22] The calculations were performed using a well-known relation:

$$E^\ominus = \Delta G^\ominus / nF \tag{5}$$

where $\Delta G^\ominus$ is the Gibbs energy change of formation of the corresponding component of the reaction mixture, n is the number of electrons participating in the electrode reaction, F is the Faraday constant and thermodynamic data given in the reference book.[24] The results of the calculations are given in Table I.

From the above data it is seen that tungsten trioxide has the lowest standard electrode potential and that in cathodic polarization, it must primarily participate in electrochemical transformations in the molten electrolyte mixture. If the interaction of tungsten oxide with the melt takes place (3), as a result of which calcium tungstate is formed, its reduction should take place in the potential range between the reduction potentials of tungsten trioxide and calcium and sodium chlorides. The reduction of NaCl and CaCl$_2$ should occur at larger values of the electrode potentials in almost the same interval.

Analysis of the results of voltammetric studies confirms this prediction. The nature of the platinum electrode voltammograms in an electrolyte mixture, without tungsten trioxide, indicates that no processes occur in the cathodic region of potentials except for the joint discharge (1) of calcium and sodium cations (Fig. 2, curve 1).

TABLE I. Thermodynamic characteristics of the components of the reaction mixture, ΔG / kJ mol^{-1}; $E^{\ominus}$ / V

| Component		Temperature, K			
		700	800	900	1000
WO₃	$\Delta G^{\ominus}$ / kJ mol^{-1}	−660.184	−635.098	−610.269	−585.679
	$-E^{\ominus}$ / V	1.14	1.10	1.05	1.01
NaCl	$\Delta G^{\ominus}$ / kJ mol^{-1}	−346.096	−336.836	−327.722	−318.768
	$-E^{\ominus}$ / V	3.59	3.49	3.40	3.30
CaCl₂	$\Delta G^{\ominus}$ / kJ mol^{-1}	−686.518	−671.630	−656.856	−642.183
	$-E^{\ominus}$ / V	3.56	3.48	3.40	3.33
CaWO₄	$\Delta G^{\ominus}$ / kJ mol^{-1}	−1397.999	−1363.770	−1329.773	−1295.992
	$-E^{\ominus}$ / V	2.41	2.36	2.30	2.24
CaO	$\Delta G^{\ominus}$ / kJ mol^{-1}	−561.854	−551.594	−541.345	-531.087
	$-E^{\ominus}$ / V	2.91	2.86	2.80	2.75
Na₂O	$\Delta G^{\ominus}$ / kJ mol^{-1}	−322.190	−308.121	−294.253	-280.590
	$-E^{\ominus}$ / V	3.34	3.19	3.05	2.91
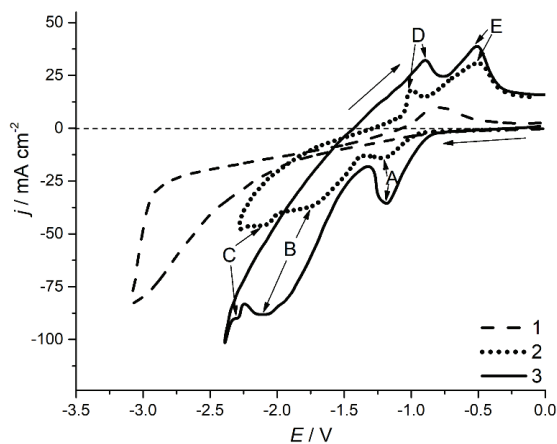
Fig. 2. j–E characteristics of a platinum electrode in the eutectic melt CaCl₂– NaCl without tungsten oxide (1) and in its presence: 4.7×10^{-4} (2) and 9.3×10^{-4} mol cm^{-3} (3). The potential scan rate is 0.05 V s^{-1}, the temperature is 1013 K.

On the reverse scan of the voltammogram in the region of potentials close to –1.0 V, the voltammogram exhibits in the anodic region currents that characterize the joint ionization of sodium and calcium. In the presence of tungsten oxide, the voltammograms exhibit in the cathodic region three waves, the height of which increases with increasing its content in the melt. On the reverse scan of the voltammogram, it exhibits in the anodic region only two waves, the height of

which also increases with increasing the WO_3 content of the melt. Because tungsten oxide is poorly soluble in a eutectic mixture of sodium and calcium chlorides, argon was bubbled through it to suspend the oxide in the bulk electrolyte before recording the voltammograms. The coordinates of the maximum values of the waves recorded on the voltammograms are given in Table II.

TABLE II. Coordinates of the extreme point of the waves that characterize the electrochemical reduction of WO_3

Wave	Potential, V		Current density, mA cm^{-2}	
	Curve 2	Curve 3	Curve 2	Curve 3
A	–1.2	–1.2	–13.9	–35.2
B	–1.8	–2.1	–37.8	–87.8
C	–2.1	–2.3	–46.1	–90.0
D	–1.0	–0.9	17.8	32.2
E	–0.5	–0.5	30.9	38.7

Considering the values of the standard electrode potentials given in Table I, we can assume that wave A corresponds to process (2), and wave B to process (4).

Wave C characterizes the discharge of calcium cations bound to oxygen anions, which must accumulate in the cathode layer of the molten electrolyte due to the course of processes (2) and (4). This will inevitably lead to the formation of oxides of calcium and sodium, thermodynamic decomposition potentials, which are less than the decomposition potentials of chlorides of these metals (Table I). The increase in current density recorded on voltammograms after peak C is already associated with the discharge of sodium and calcium cations, which are bound to chlorine anions and are part of the basic electrolyte – a molten mixture of calcium and sodium chlorides. It should be noted that in this section of the voltammetry (after peak C) the platinum electrode will be partially covered by calcium. It is known that the discharge of metal cations, on the cathode made of the same metal or partially covered with it, occurs at a much lower overvoltage.[25] Wave D, which is observed on the reverse scan of the voltammograms most likely characterizes the anodic dissolution of sodium and calcium alloy, which is formed during the forward potential scan on the surface of the platinum cathode, and wave E characterizes tungsten dissolution.

In order to identify the products formed during the electrochemical reduction of WO_3, electrolysis was performed under potentiostatic conditions at different potentials, in particular those that are lower than the standard potential of the process (4) and exceed it.

In contrast to the known process (FFC Cambridge process),[26] the electrochemical reduction of tungsten oxide was carried out using a liquid gallium cathode, omitting the stage of preliminary preparation, which includes granulation and sintering. Gallium has a very high boiling point (2477 K) and at the reduct-

ion temperature (1013 K) does not evaporate and does not react with the molten electrolyte mixture, tungsten oxide or tungsten. Due to the large difference in the specific mass of gallium and tungsten, W settled to the bottom of the crucible (m, Fig. 1), which protected it from interaction with the components of the molten electrolyte mixture. The liquid gallium cathode not only provides reliable contact with tungsten oxide, but also creates more favorable conditions for its reduction because the area of contact of fine powder with the liquid phase is much larger than that of granulated and sintered WO_3 samples with the solid leads. In addit-ion, it should be noted that the electrolytic reduction of the initial compounds (tungsten oxide, calcium tungstate) in the solid-state is accompanied by a signi-ficant decrease in molar volume (almost 5 times in the case when calcium tung-state is reduced to tungsten). The reduction mode proposed by the authors pro-vides uniform polarization of each particle of oxygen-containing tungsten com-pounds, unimpeded removal of electrolysis products from the reduction zone and avoids blocking the cathode surface by both initial compounds and reduction products. Such electrolysis conditions provide uniform polarization of each tung-sten oxide particle, avoid blocking both their surface and the cathode surface by reduction products.

The analysis of the obtained results (Table III, Fig. 3) showed that the reduction products at potentials exceeding the values of the standard potentials of the process (2) at the cathode form a mixture of tungsten and calcium tungstate, the amount of which significantly exceeds the amount of tungsten.

TABLE III. The composition of the products of electrochemical reduction of WO_3 depending on the conditions of electrolysis

Reduction potential, V	Phase content of the formed product, wt. %		Definition error
	W	CaWO₄	
–1.3	1.35	98.65	Less than 1.83 %
–2.0	21.20	78.80	Less than 2.60 %
Higher than or equal to –2.4	100.00	–	–

Pure tungsten is formed at the cathode only at potentials exceeding the stan-dard electrode potential of the process (4), Fig. 3d. Tungsten, which does not contain impurity phases, is also formed when electrolysis is carried out at poten-tials exceeding the standard electrode potential of reaction (1). In this case, metallothermic reduction reactions of tungsten oxide is possible at the cathode:

$$WO_3 + 3nM \rightarrow W + 3M_nO \qquad (6)$$
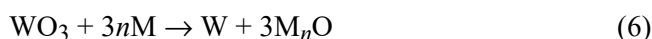
where $n = 2$ when sodium participates in the reduction and $n = 1$ when the reducing agent is calcium. The probability of the process (6) is very high, if we take into account the fact that due to alloy formation, on liquid cathodes, metal cations are discharged at more positive potentials than on solid ones.[25] If we add

together Eqs. (1) and (6), we obtain an equation that generally corresponds to the process (2). Thus, the obtained results give grounds to believe that the reduction of tungsten trioxide, depending on the implementation conditions, can occur both by the electrochemical mechanism (processes (2), (4)) and by the metallothermic one (6).
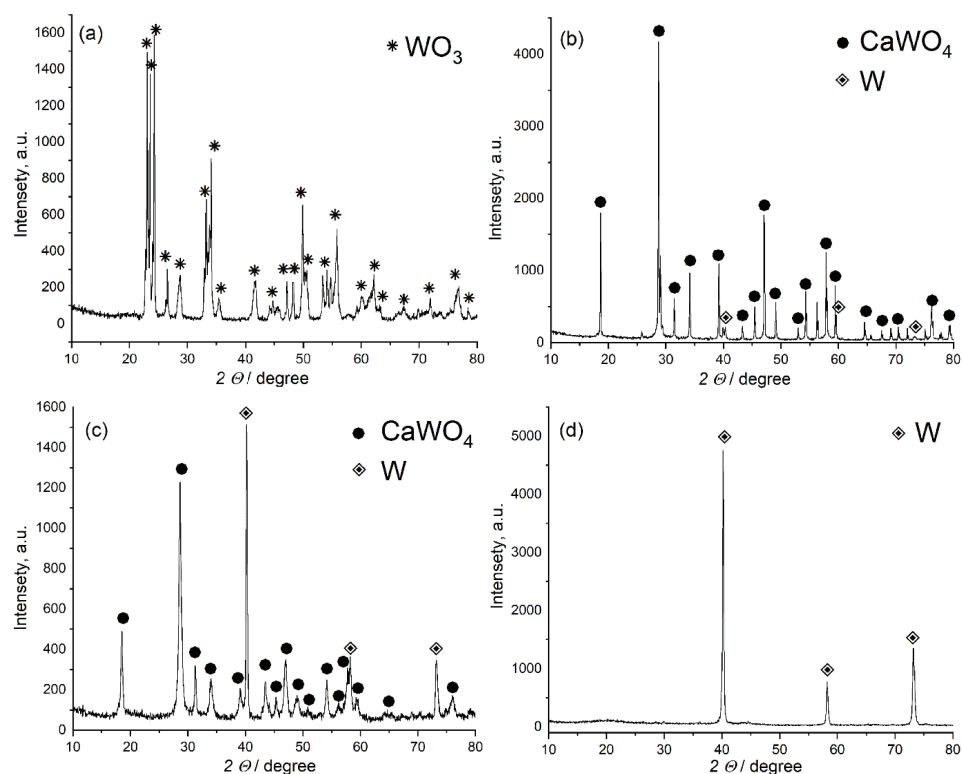

Fig. 3. Typical diffraction patterns of WO_3 before electrolysis (a) and of products obtained after electrolysis at E from –1.0 to –1.3 V (b); from –1.4 to –2.3 V (c); negative to –2.4 V (d).

The maximum degree of extraction of tungsten (W) from tungsten oxide was not lower than 58.00±0.01 %. It was calculated from the formula (7):

$$W = 100\frac{m_{pract}}{m_{theor}} \qquad (7)$$

where m_{pract} is the mass of tungsten obtained by reduction; m_{theor} is the mass of tungsten contained in the weighed amount of WO_3 loaded on the cathode. The current yield did not exceed 57.27±0.01 %.

The course of the processes (3) and (6) may be the cause of low values of the degree of extraction of tungsten from the oxide and current yields. To avoid these

undesirable processes, it is advisable to use $CaWO_4$ instead of WO_3 as the initial compound for reduction and to carry out electrolysis under conditions that minimize the contribution of electrochemical decomposition of electrolyte mixture components (1) to the general process of tungsten production. In the case of the use of calcium tungstate it can be represented by the scheme (4).

Fig. 4 shows a SEM image of the original tungsten(VI) oxide (a) and metallic tungsten (b) obtained by electrolysis at a potential of –2.4 V. These results indicate that the electrochemical reduction of tungsten oxide compounds is accompanied by the formation of crystallites of much smaller volume. The size of the formed dendritic groups is several tens of micrometers. The crystallized particles were observed as an individual (less than 1 μm), and as dendrites (average length up to 10 μm).
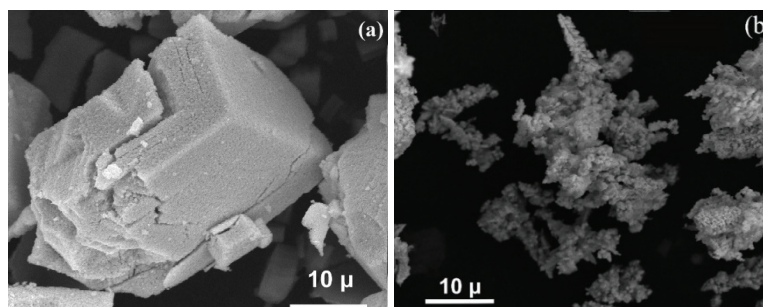

Fig. 4. Typical SEM images: a) WO_3; b) electrolysis product (W).

CONCLUSION

A necessary condition for the electrochemical reduction of tungsten(VI) oxide in a molten eutectic mixture of sodium and calcium chlorides on a liquid gallium electrode is electrolysis at potentials exceeding the standard electrode potential of decomposition of calcium tungstate, which is formed by the interaction of oxide with calcium chloride. The reduction can take place by both electrochemical and metallothermic mechanisms depending on the conditions of potentiostatic electrolysis. The reduction product is fine tungsten with a crystallite size of not larger than 1.00×0.88 μm. The current yield, under conditions that provide pure tungsten is 57.27 %, and the degree of extraction 57.99 %. The reason of the low values of current yield and the degree of extraction may be side processes of interaction of WO_3 with the components of the molten electrolyte mixture, and also the reduction of sodium and calcium at the liquid cathode. It is more expedient for the electrochemical production of tungsten, from a molten eutectic mixture of calcium and sodium chlorides, to use $CaWO_4$ as an initial compound instead of WO_3.

И З В О Д

ЕЛЕКТРОХЕМИЈСКА РЕДУКЦИЈА ВОЛФРАМ(VI)-ОКСИДА ИЗ ЕУТЕКТИЧКОГ
РАСТОПА CaCl₂–NACl У ПОТЕНЦИОСТАТСКИМ УСЛОВИМА

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У раду су приказани резултати испитивања електрохемијске редукције вол-
фрам(VI)-оксида из растопа еутектичког састава CaCl₂–NaCl (52–48 mol%) на електроди
од течног галијума. Микроструктура добијених прахова је испитивана методама скени-
рајуће електронске микроскопије и дифракције X-зрака. Rietveld анализом дифракто-
грама је одређен квантитиван фазни састав производа редукције WO₃. Термодина-
мичке карактеристике процеса електролизе су испитиване волтаметријом. Показано је
да је неопходан услов за редукцију WO₃ да током електролизе потенцијал катоде буде
виши од стандардног електродног потенцијала разлагања калцијум-волфрамата, који је
формиран интеракцијом волфрам(VI)-оксида и калцијум-хлорида. Редукција се може
одиграти и електрохемијским и металотермијским механизмом у зависности од услова
електролизе. Производ редукције је фини прах волфрама величине кристалита до 1 μm.

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