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Electrolytes for Tungsten Refining

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Abstract—Chloride–fluoride and phosphate–fluoride salts of alkali metals with additions of sodium tungstate and tungstic anhydride are studied as electrolyte systems for tungsten refining. The results demonstrate that the melts of these systems are suitable for electrolytic processes. Coarse crystalline tungsten powder with reduced concentrations of some impurities is prepared.

INTRODUCTION

Purity is among the most important characteristics of tungsten and its alloys for technological applications. At present, tungsten is commonly prepared via hydrogen reduction. After remelting or the fabrication of articles by the ceramic route, the material has insufficient plasticity. Its brittleness is due to interstitial impurities, particularly carbon, which precipitates during cooling in the form of grain-boundary carbide inclusions [1].

Among many studies that dealt with the preparation of tungsten metal via fused-salt electrolysis of its compounds, a number of works by Russian [1–5] and foreign [6, 7] researchers focused on the electrochemical reduction of tungstic anhydride, alkali tungstates, scheelite, and other tungsten compounds in oxide and halide melts. There has been less work on the electrorefining of tungsten and its alloys [1, 2, 8]. Attempts to use chloride, phosphate, and borate melts with tungsten hexachloride or tungstate additions were unsuccessful: either the cathode deposit consisted of tungsten bronzes, or the deposited metal was difficult to separate from the electrolyte, or the current efficiency was extremely low.

This work focuses on the electrochemical behavior of tungsten in oxide–chloride–fluoride melts and the possibility of using such melts as electrolytes in tungsten refining processes. Our main purpose was to find conditions for reproducible preparation of tungsten metal and optimize the process in terms of the current efficiency, shape and size of deposited crystals, control over the quality of the cathode deposit, consumption of the anodic material, etc. In our experiments, we varied the electrolyte composition, concentration of dissolved tungsten, process temperature, cathode and anode current densities, and other parameters.

EXPERIMENTAL

Electrolytes for tungsten refining were studied in a one-cathode electrolyzer—an easy-to-disassemble apparatus consisting of a retort with an inner diameter of 100 mm and a water-cooled, insulated lid with a cathode port in its center. Mounted in the retort were a graphite crucible, large enough to contain 1000 g of the electrolyte, and a perforated diaphragm. Into the annular space between the crucible and diaphragm, we loaded a precrushed anodic material. The material to be refined was tungsten waste containing Mo 800, Fe 300, Si 60, V 3, Mg 2, Ti 250, and Al 90 ppm. As cathodes, we used tungsten and molybdenum rods 5 mm in diameter.

Since tungsten is one of the most electropositive metals, the electrolyzer was made of graphite to avoid contamination of the cathodic tungsten with other metals. The system was filled with argon. The temperature of the molten electrolyte was maintained with a stability of ±5°C and was monitored using a recording potentiometer.

The power to the electrolyzer cell was supplied by an SIP-30 regulated dc source. The quantity of electricity passed through the cell was measured by a Kh15 electrochemical detector. To follow the process, we measured the reverse emf between the electrodes during short-term switching-off. The completion of the process was inferred from the quantity of electricity passed through the cell.

After each experiment, the electrolyzer was cooled and disassembled, and the electrolyte, anodic residue, and cathode (covered with the tungsten deposit) were withdrawn.

The residual electrolyte was removed from the cathodic tungsten by washing in three steps. After preliminary purification in a 3–5% alkaline solution, a finer purification step was performed. Next, the deposit was stripped from the cathode, and a fresh solution was used.

RESULTS AND DISCUSSION

Halide–tungstate electrolytes. The melting point of Na_2WO_4 is 698°C. In mixtures with alkali halides, it

Table 1. Effects of electrolyte composition and temperature on the electrolysis results

Run no.	Electrolyte composition, wt %					t, °C	Current efficiency, %		Electrolyte content of the deposit, wt %
	$Na_4P_2O_7$	$NaPO_3$	NaF	NaCl	WO_3		cathode	anode	
1	5	–	20	56	19	830	100	96	64.2
						880	100	91	50.5
						930	92.5	80	33.2
2	10	–	20	51	19	830	100	97	62.0
						880	98.5	90	46.5
						930	94.5	78	40.1
3	20	20	–	10	25	850	74	39	84.2
4	20	20	10	35	25	1050	98	18	32.0

melts at lower temperatures [9] and readily dissolves in NaCl and NaF solutions.

We tested NaCl + Na_2WO_4 and NaCl + NaF + Na_2WO_4 (80 wt % NaCl + 20 wt % NaF) mixtures at a cathode current density of 0.2 A/cm^2, anode current density of 0.04 A/cm^2, temperatures in the range 850–950°C, and electrode separation of 35 mm. The electrolytes were prepared from predried analytical-grade NaCl, NaF, and Na_2WO_4. The Na_2WO_4 content of the melts was 10 or 20 wt % (in terms of W).

In the chloride–tungstate electrolytes, tungsten was deposited on the cathode in the form of fine powder, most of which spalled off the surface and fell to the bottom of the electrolyzer. The cathode current efficiency was 40–50% in terms of W(VI), and the anode current efficiency was 60–70%. Electrolysis proceeded at a high reverse emf of 1.2–1.8 V. Breaks of the sealing led to flashes in the cathodic zone, attributable to the liberation and oxidation of Na. In the inert atmosphere of the bath, a significant amount of cathodic sodium reacted with tungstate anions, reducing tungsten(VI) to W metal; the rest of the Na sublimed. This increased the acidity of the electrolyte and favored the cathodic deposition of tungsten bronze crystals of composition $Na_2O \cdot WO_2 \cdot nWO_3$ with n from 1 to 4 [10]. The cathode deposits obtained at 850°C in chloride electrolytes containing 10 and 20 wt % W consisted of W and a tungsten bronze phase.

The W powder prepared in Na_2WO_4-containing chloride–fluoride melts was free of bronzes. The electrochemical processes were similar to those in the electrolysis in chloride–tungstate melts. The cathodic tungsten, deposited in the form of dark powder, contained Mo 400–600, Si 80, Cr 30–70, Ni 10–20, Ca 1000, Mg 10, Fe 300, Ti 10, and Al 10 ppm. Complete dissolution of the anodic tungsten caused no significant changes in impurity concentrations.

Chloride–fluoride melts, more complex systems compared to chloride melts, contain simple and complex fluorine-containing ions. In the initial stages of electrolysis, the cathodic process was the deposition of Na metal, which then reduced tungsten in oxofluorotungstate complexes. The fluoride ions resulting from the decomposition of the complex again combined with the tungsten oxide anions forming on the anode to form new oxofluorotungstate groups, which stabilized the process without significant changes in the composition of the cathode deposit.

Phosphate electrolytes. The low melting points of meta- and pyrophosphates, their ability to dissolve tungstic anhydride, and encouraging electrolysis [11, 12] and W refining [8] results led us to continue the study of such systems, with NaF additions and higher WO_3 concentrations.

Electrolytes were prepared from remelted analytical-grade $Na_4P_2O_7 \cdot 10H_2O$, pure-grade $NaPO_3$, and analytical-grade NaCl and NaF. The WO_3 content of the melts was 15 and 20 wt % in terms of W.

The cathode and anode current densities were 0.18–0.25 and 0.025 A/cm^2, respectively. The process temperature was 830–1050°C.

It can be seen from Table 1 that the introduction of NaF increases both the cathode and anode current efficiencies. The $Na_4P_2O_7$ concentration has no effect on the process. The low anode current efficiencies in runs 3 and 4 indicate that the corresponding electrolytes are unsuitable for tungsten electrorefining.

In all the runs, the current efficiency of the cathodic process was lower than that of the anodic process. The difference in weight between the W deposited on the cathode and the W dissolved on the anode corresponds to the metal deposited on the cathode as a result of secondary electrolysis on the walls of the graphite bath, accompanied by the decomposition of the oxide anion

Table 2. Effects of electrolyte composition and temperature on the electrolysis results

Run no.	Electrolyte composition, wt %				*t*, °C	Current efficiency, %		Electrolyte content of the deposit, wt %
	NaF	NaCl	KCl	WO_3		cathode	anode	
1	60	27.5	–	12.5	930	98.7	79	51.4
2	60	13.75	13.75	12.5	930	85.7	69	21
3	20	–	12.5	12.5	980	96.7	50	18
					930	97.5	80	19.4
					880	100	94	25.4
4	1	–	12.5	12.5	930		83	19.6
	0				880	100	90	22.1
					830	100	97	26.5
5	20	27.5	25	25	980	70	45	9
6	20	55	25	25	930	100.2	79	6.3
					880	100	91	16.6
					830	97	96	21.2

complex and release of oxygen. Some of the oxygen reacts with carbon according to the scheme

$$2C + O_2 \longrightarrow 2CO,$$

$$C + O_2 \longrightarrow CO_2.$$

The secondary processes occur concurrently with the anodic process. Their rate depends on the anode current density, temperature, W content of the electrolyte, and the design of the anodic cell and electrolyzer facing. As a rule, increasing the anode current density and temperature or reducing the tungsten content of the melt increases the amount of oxygen released on carbon. The pores produced at the crucible–electrolyte interface by the resulting carbon-containing gases can be observed visually in the solidified electrolyte.

The cathode deposits obtained at high temperatures typically have a coarse microstructure composed of intergrowths, each consisting of a central crystal from which smaller, needlelike crystals protrude. As the temperature is lowered or the tungsten concentration in the melt decreases, the crystals become smaller, and the yield of fine powder rises.

The electrolyte can easily be removed from the cathode deposit in solutions of hydrochloric acid and sodium oxide hydrate. Only the deposits obtained at 830°C or under the conditions of run 3 presented some problems. Those deposits consisted of fine-particle tungsten, a large amount of salts originating from the electrolyte, and lower tungsten oxides. Embedded in the electrolyte, the oxides formed a dense layer on the cathode surface, which was difficult to leach out.

The refined tungsten contained Mo 500–700, Si 30, Cr 20–70, Ni 30, Mg 50, Fe 600, Ti 20, and Al 50 ppm.

Chloride–fluoride electrolytes with WO_3 additions. The high effectiveness of electrolysis processes, the possibility of depositing large tungsten crystals on the cathode, and high WO_3 solubility in NaF-containing phosphate melts, prompted us to test electrolytes consisting of WO_3 and alkali chlorides and fluorides.

The MCl–NaF–WO_3 (M = Na, K) electrolyte systems offer the advantages of low melting points, availability of the components, and good solubility in water.

Electrolysis was carried out at cathode and anode current densities of 0.2–0.3 and 0.03–0.05 A/cm^2, respectively, and temperatures in the range 830–980°C. The tungsten content of the melt was 10 and 20 wt %. The conditions and results of several runs are summarized in Table 2 (each value is the average of three or four replicates).

It follows from these data that, for achieving a high anode current efficiency and depositing large crystalline particles with a low electrolyte content, the optimal electrolyte compositions are 10–40 wt % NaF + 35–65 wt % NaCl + 10–25 wt % WO_3. At other electrolyte compositions, as well as in the presence of KCl, the current efficiency is lower, and the percentage of the cathodic tungsten deposited via secondary electrolysis is larger.

The microstructure of the cathode deposit depends significantly on the electrolyte composition and process temperature. At high contents of alkali fluorides (40–60 wt %) and a WO_3 content of 12.5 wt %, the deposit has the form of a fine-particle sponge. At a WO_3 content of 20 wt %, the deposit consists of flakes and separate aggregates with a large surface area.

With decreasing fluoride content, the particle size of the deposited tungsten rises markedly. The metal deposited from an electrolyte containing 10–20 wt % NaF and 10–20 wt % W consisted of lustrous needle-like dendrites up to 10 mm in length. Increasing the temperature, W content of the melt, or electrolysis duration also increases the particle size of the deposit.

The electrolytic tungsten contained Mo 600, Fe 100–200, Si 40, V 1–3, Mg 2, Ti 10–20, Al 1, and Cr 3 ppm.

The extent of secondary reactions was found to depend on the grade of the graphite for the facing of the bath and the arrangement of the anodes in the cell. Vertical anodes ensure better electrolysis conditions than do horizontal anodes. With vertical anodes, most of the slime settles on the bottom of the electrolyzer; in contrast, with a horizontal electrode, the slime remains on the surface, contributing to the discharge of tungsten oxofluoro anions on carbon.

As for the carbon-containing material, note that dense graphites are less reactive with anodic oxygen. Particularly high chemical stability is offered by glassy carbon and dense graphites coated with pyrolytic carbon.

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