MECHANISM OF ELECTRODEPOSITION OF

TUNGSTEN IN MOLTEN KF-B$_2$O$_3$-K$_2$WO$_4$ [①]

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ABSTRACT

The mechanism of electrodeposition of tungsten in molten KF-B$_2$O$_3$-K$_2$WO$_4$ has been investigated by cyclic voltammetry and chronopotentiometry. The results show that the electrochemical reduction of tungsten is a reversible and diffusion-controlled process which occurs in two steps: $W(VI)+4e=W(II)$; $W(II)+2e=W(0)$, and the product is insoluble. The values of the diffusion coefficients of the complexion containing $W(VI)$ measured by the techniques mentioned above are alike. Tungsten electrode is suitable for quasi-reference in this melt.

Key words: molten KF-B$_2$O$_3$-K$_2$WO$_4$ tungsten electrodeposition mechanism

1 INTRODUCTION

The electrodeposition of tungsten has been investigated by several researchers in various molten salt systems[1-6]. However, the mechanism of the electrochemical reduction of tungsten ion in molten salts has seldom been studied. Senderoff et al [7] observed by chronopotentiometry that the reduction of tungsten from its ion in FLINAK showed a single reduction step involving a four-electron transfer in an irreversible process. Ito et al[8] investigated the electrochemical behaviour of tungsten ion in molten LiCl-KCl-K$_2$WO$_4$ using the method of cyclic voltammetry and found that $W(VI)$ was reduced in several steps involving electrochemical and disproportionation reactions, and it depended on the different reduction atmosphere.

In present paper, we aim to study the mechanism of electrochemical reduction of tungsten in molten KF-B$_2$O$_3$- K$_2$WO$_4$ by cyclic voltammetry and chronopotentiometry.

2 EXPERIMENTAL

The experimental apparatus is shown in Fig. 1. The vessel is made of stainless steel and kept gas tight. All chemicals used are analytical grade. Anhydrous KF is prepared in polytetrafluoroethylene beaker by drying KF·2H$_2$O at 120 ℃ and then in platinum crucible at 350 ℃ for 4 h. K$_2$WO$_4$ is dehydrated at 400 ℃ for 4 h before used. The prepared KF and K$_2$WO$_4$ as well as
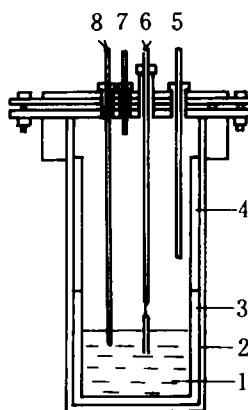
Fig. 1 Experimental apparatus

1—melt; 2—stainless steel vessel;
3—graphite crucible; 4—graphite tube;
5—gas inlet; 6—electrodes;
7—gas outlet; 8—thermocouple

B_2O_3 powders are introduced in a graphite crucible, placed in stainless steel vessel and dried in vacuum at 200 ℃ for 15 h, then at 500 ℃ for 4 h. After that, the melt is pre-electrolysised at $20\sim80\,A/m^2$ cathodic current density for $7\sim12\,h$ at 800 ℃. All experiments are performed under a flowing argon atmosphere and the temperature is controlled to 2 ℃ precision by a thermocontroller.

A three-electrode cell is used in all experiments. The working electrode (WE) is a $d = 0.5$ mm platinum wire. A tungsten wire is used as a quasi-reference electrode (WQRE). Before used, the WE and WQRE are scoured in concentrated HF acid and washed with distilled water and acetone. The graphite crucible used as a container for the melt serves simultaneously as the counter electrode (CE).

The measuring instrumentation consists of a DHZ-1 electrochemical comprehensive instrument, a LZ-3 X/Y functional recorder and a DSS-6521 digital-storage oscilloscope.

3　RESULTS AND DISCUSSION

3. 1　*Reference Electrode*

Because there is no suitable reference electrode in the melt containing oxide, the platinum and tungsten quasi-reference electrodes are tested in molten $KF\text{-}B_2O_3\text{-}K_2WO_4$ (62-37-1 mol. -%) at 805 ℃. Experimental conditions and results are concluded as follows:

(1) Stability

Two W electrodes are dipped into the melt, the potential difference between them reaches steady state in 2 min and the change of the potential difference is no more than 1 mV. Unlike W electrode, the potential difference between Pt electrodes is not stable; the change of the potential difference is more than 10 mV.

(2) Repeatability

Two W (or Pt) electrodes are dipped into the melt; one of them is polarized with $\pm1\,500\,A/m^2$ current density separately during 30 s. The potential dfference returns to former value in 10 min.

(3) Reversibility

A W (or Pt) electrode is used as reference; an-

other W (or Pt) electrode is given with a triangle wave from $+0.5\,V$ to $-0.5\,V$. The cyclic voltammogram results are shown in Fig. 2. The current of W electrode is linear with potential at the potential range of $+0.5\sim-0.5\,V$ and the current of cathodic process coincides with that of anodic process approximately. However, the currents of cathodic and anodic processes on Pt electrode do not coincide with each other.

The results show that it is suitable for W electrode to be used as quasi-reference in this melt. Because the Pt electrode is sensitive to O^{2-} activity, the Pt electrode is unsuitable. The same behaviour of Pt electrode in molten FLINAK containing oxyanions was observed by Stern[9].
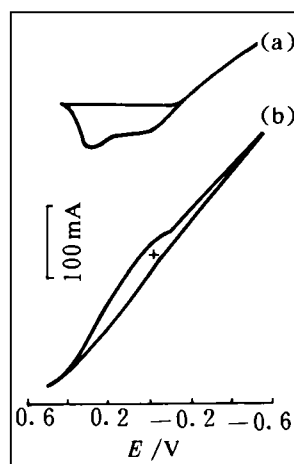
Fig. 2　Cyclic voltammograms in molten
$KF\text{-}B_2O_3\text{-}K_2WO_4$(62-37-1 mol. -%) at 805 ℃
(a)—WE: Pt, $A = 0.157\,cm^2$,
RE: Pt, $v = 0.062\,V/s$; (b)—WE: W, $A = 0.22\,cm^2$,
RE: WQRE, $v = 0.062\,V/s$

3. 2　*Molten Salt Background*

Purified $KF\text{-}B_2O_3$ (62.6-37.4 mol. -%) is investigated on Pt electrode by cyclic voltammetry (Fig. 3). Potassium ions are reduced to metallic potassium when the cathodic potential reaches about $-0.35\,V$ (vs WQRE). So the cathodic potential should not be below $-0.35\,V$ in this melt.

3. 3　*Cyclic Voltammetry*

The investigation is carried out under the dif-

ferent concentrations   of KF- B₂O₃- K₂WO₄ (62-37-1 mol. -%, $C_{K_2WO_4}$ = 0. 295 mol/ L; 62- 35- 3 mol. -%, $C_{K_2WO_4}$ = 0. 856 mol/L). Fig. 4 is a typical cyclic voltammogram obtained on Pt electrode. It shows that there is a cathodic peak at about — 0. 17 V corresponding to an anodic peak at about + 0. 16 V. Controlled potential electrolysis is carried out at — 0. 17 V and a black deposit is obtained which exhibits a distinct X-ray diffraction pattern of metallic tungsten. The data drawn from cyclic voltammograms are listed in Table 1. It can be seen that E_{pc} and $i_{pc}/v^{1/2}$ are constant with the variation of potential sweep rate. The cathodic peak
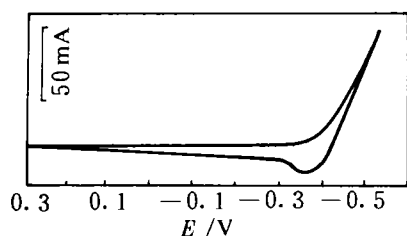
currents are plotted against the square root of sweep rates in Fig. 5 and straight lines are obtained passing through the origin. Therefore, it might be suggested that the peak at — 0. 17 V exhibits a diffusion-controlled and reversible process; the product is insoluble. However, according to the equation (1)[10]

$$E_{pc} - E_{pc/2} = -0.77(RT/nF) \qquad (1)$$

the electron number transferred in above mentioned process is only approximately 1.

For further analysis, a small amplitude cyclic voltammetry is employed. Fig. 6 shows the cyclic voltammograms under the condition of smaller cathodic polarization. It is clear that there are two

Fig. 3   Cyclic voltammogram in molten
KF-B₂O₃(62. 4-37. 6 mol. -%) at 800 °C
WE:Pt, A =0. 157 cm²; RE:WQRE, v =0. 062 V/s
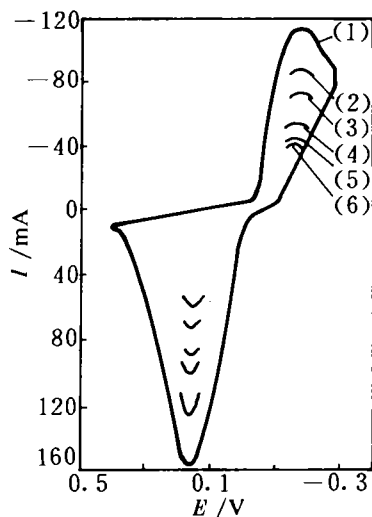
Fig. 4   Cyclic voltammograms in molten
KF-B₂O₃-K₂WO₄ at 814 °C
$C_{K_2WO_4}$ =0. 856 mol/L; WE: Pt, A =0. 173 cm²;
RE: WQRE, v =0. 184, 0. 120, 0. 082 5, 0. 042,
0. 030 and 0. 023 V/s for (1), (2), (3), (4), (5),
and (6) respectively.

Table 1   Cyclic voltammetric data
in molten KF-B₂O₃-K₂WO₄

$C_{K_2WO_4}$ /mol·L⁻¹	T /°C	v /V·s⁻¹	i_pc /A·cm⁻²	E_pc/2 /V	E_pc /V	i_pc /v^{1/2}
0. 295	795	0. 023	0. 078	−0. 080	−0. 168	0. 52
		0. 035	0. 097	−0. 080	−0. 168	0. 52
		0. 044	0. 107	−0. 075	−0. 168	0. 51
		0. 087	0. 150	−0. 075	−0. 168	0. 51
		0. 130	0. 183	−0. 075	−0. 169	0. 51
		0. 173	0. 206	−0. 075	−0. 168	0. 50
0. 856	814	0. 023	0. 225	−0. 067	−0. 165	1. 48
		0. 030	0. 254	−0. 080	−0. 170	1. 47
		0. 042	0. 301	−0. 077	−0. 170	1. 46
		0. 083	0. 416	−0. 067	−0. 165	1. 45
		0. 120	0. 502	−0. 065	−0. 160	1. 45
		0. 184	0. 624	−0. 071	−0. 175	1. 45
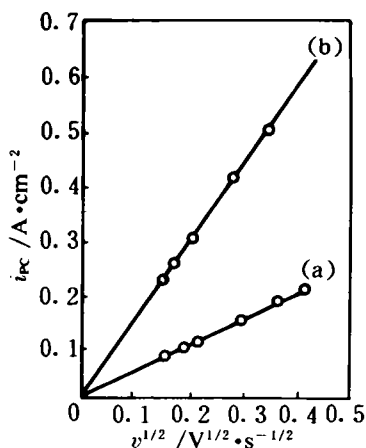
Fig. 5 i_{pc} versus $v^{1/2}$
(a)— $C_{K_2WO_4}$ =0. 295 mol/L;
(b)— $C_{K_2WO_4}$ =0. 856 mol/L

electroreduction processes which begin at the cathodic potential of about $-0.055\,V$ and $-0.085\,V$ separately. Since the reduction potentials of the two steps are close to each other, only one composite cathodic peak can be observed in Fig. 4.
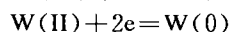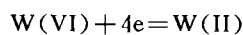
The reduction current values i at different time are measured from Fig. 4. A series of convolutive current $I_c(t)$ can be calculated with computer according to the equation(2)[11]; $I_c(t)$ and $\ln[(I_{cl} - I_c(t))/I_c(t)]$ vs E are shown in Fig. 7.

$$I_c(t) = \frac{1}{\pi^{1/2}} \sum_{j=1}^{j=k} \frac{i(j\Delta t - 1/2\Delta t)\Delta t^{1/2}}{(k - j + 1/2)^{1/2}} \qquad (2)$$

At $-0.055\sim0.080V$ and $-0.11\sim-0.24\,V$ potential ranges, $\ln[(I_{cl} - I_c(t))/I_c(t)]$ vs E are straight lines with different slopes. This confirms that the reduction of $W(VI)$ is a reversible process at above potential ranges. According to the equa-

Fig. 6 Cyclic voltammograms in molten KF-B₂O₃-K₂WO₄ at 795 ℃

$C_{K_2WO_4} = 0.295\,mol/L$;

WE: Pt, $A = 0.126\,cm^2$; RE: WQRE, $r = 0.05\,V/s$

Fig. 7 Convolutive cyclic voltammogram of (1) in Fig. 4

tion (3)[11]:

$$E = E_{1/2} + (RT/nF)\ln[(I_{cl} - I_c(t))/I_c(t)] \qquad (3)$$

where $E_{1/2}$ is half wave potential; I_{cl} is the convolutive limit current, the value of n_1 is 4 calculated by the slope of straight line at the potential range of $-0.055\sim-0.080$ V. Since the total electron number is 6, the electron number transferred in the second step is 2. Therefore, the electrodeposition of tungsten in molten KF-B₂O₃-K₂WO₄ is a reversible and diffusion-controlled process; the product is insoluble. It occurs in two steps:

$$W(VI) + 4e = W(II)$$
$$W(II) + 2e = W(0)$$

$I_c(t)$ vs E is a S-shape steady state polarization curve; $I_c(t)$ reaches the limit value I_{cl} when E is enough negative. According to the equation (4)[11]

$$I_{cl} = nFAC^* D^{1/2} \qquad (4)$$

where C^* and D are the bulk concentration and diffusion coefficient of electroactive species separately; A is the area of electrode. The values of diffusion coefficient of $W(VI)$ (D_w) are calculated as follows:

$C_{K_2WO_4} = 0.295\,mol/L$ ($T = 795$ ℃),

$D_w = 1.69\times10^{-10}\,m^2/s$;

$C_{K_2WO_4} = 0.856\,mol/L$ ($T = 814$ ℃),

$D_w = 1.65\times10^{-10}\,m^2/s$.

3.4   Chronopotentiometry

A typical chronopotentiogram is shown in Fig. 8 (a). The data taken from chronopotentiograms under different experimental conditions are listed in Table 2. The values of $i\tau^{1/2}/C_{K_2WO_4}$ are constant under different currents and concentrations. This indicates that electroreduction of W (VI) in the melt is a simple electrode process. It can be seen from Fig. 8(b) that a linear relationship with a slope of $k = 0.037$ is obtained. According to the equation (5)[11]:

$$E = E_{\tau/4} + 2.303RT/nF\lg(\tau^{1/2} - t^{1/2}) \qquad (5)$$

the calculated value of n is about 6. This suggests that electroreduction of W (VI) in molten KF-B₂O₃-K₂WO₄ is a reversible process and the product is insoluble. The total electron number transferred is 6. The results are coincident with that obtained
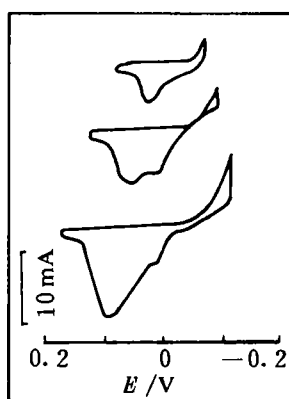
by cyclic voltammetry. In Fig. 8 (a) only one wave is observed, it is because reduction potentials of the two steps are very near each other, at this time, $\tau = \tau_1 + \tau_2$. D_w can be calculated according to Sand equation:

$$i\tau^{1/2} = \pi^{1/2}(n_1 + n_2)FAD^{1/2}C^* /2 \qquad (6)$$

The results are shown as follows:
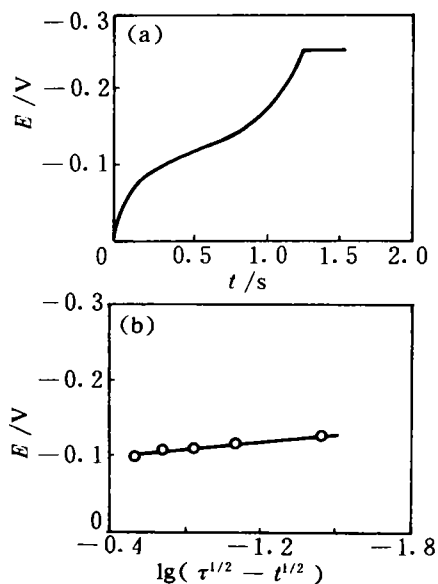
$$C_{K_2WO_4} = 0.295 \, mol/L \quad (T = 795 \, ℃),$$

Fig. 8   Chronopotentiogram (a) in molten KF-B$_2$O$_3$-K$_2$WO$_4$ at 814 ℃ and semilogarithmic plot (b) obtained from (a)

$$C_{K_2WO_4} = 0.856 \, mol/L;$$

WE: Pt, $A = 0.173 \, cm^2$;

RE: WQRE, $i = 0.665 \, A/cm^2$

Table 2   Results of chronopotentiometric experiment

$C_{K_2WO_4}$ /mol·L^{-1}	$T/℃$	t /A·cm^{-2}	τ/s	$i\tau^{1/2}$	$i\tau^{1/2}$ / $C_{K_2WO_4}$
		0.516	0.18	0.22	
		0.634	0.11	0.21	
0.295	795	0.711	0.09	0.21	712
		0.791	0.07	0.21	
		0.953	0.045	0.21	
		0.549	1.25	0.61	
		0.665	0.85	0.61	
0.856	814	0.867	0.47	0.60	706
		0.954	0.42	0.62	
		1.129	0.26	0.58	

$$D_w = 1.93 \times 10^{-10} \, m^2/s;$$
$$C_{K_2WO_4} = 0.856 \, mol/L \quad (T = 814 \, ℃),$$
$$D_w = 1.89 \times 10^{-10} \, m^2/s.$$

4   CONCLUSION

The electrodeposition of tungsten in molten KF-B$_2$O$_3$-K$_2$WO$_4$ is a reversible and diffusion-controlled process; the product is insoluble. It occurs in two steps as follows:

$$W(VI) + 4e = W(II)$$
$$W(II) + 2e = W(0)$$
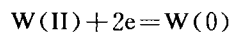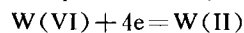
Under different concentrations and temperatures, the diffusion coefficient values of W(VI) are calculated:

$$C_{K_2WO_4} = 0.295 \, mol/L \quad (T = 795 \, ℃),$$
$$D_w = (1.69 \sim 1.93) \times 10^{-10} \, m^2/s;$$
$$C_{K_2WO_4} = 0.856 \, mol/L \quad (T = 814 \, ℃),$$
$$D_w = (1.65 \sim 1.89) \times 10^{-10} \, m^2/s.$$

W quasi-reference electrode is suitable for the investigation of the electrodeposition of tungsten in molten KF-B$_2$O$_3$-K$_2$WO$_4$.

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