Research Article

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Electrochemical reduction mechanism of several oxides of refractory metals in FClNaKmelts

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Abstract: The dissolution characteristics and electrochemical reduction mechanism of oxides of refractory metals ZrO$_2$, HfO$_2$ and MoO$_3$ in NaCl-KCl-NaF melts are studied. The results shows that there are no chemical reaction of ZrO$_2$ and HfO$_2$ in NaCl-KCl-NaF melts, the dissolution of MoO$_3$ is chemically dissolved, and MoO$_3$ react with melts to form Na$_2$Mo$_2$O$_7$. The reduction process of zirconium in the NaCl-KCl-NaF-ZrO$_2$ melts is a reversible process of one-step electron transfer controlled by diffusion. The electrochemical reduction process of ruthenium is a one-step reversible process and the product is insoluble; Electrochemical reduction of metallic molybdenum in melts is controlled by the diffusion and electron transfer process of active ion Mo$_2$O$_7^{2-}$. The electrochemical reduction process of the metal molybdenum in the melts is carried out in two steps.

Keywords: Oxides of refractory metals; melts; solubility characteristics; electrochemical

1 Introduction

Oxides of refractory metals have good high temperature strength, good corrosion resistance to molten alkali metals and vapors, and have wide applications in some special fields. The main research methods for refractory metal production are melts electrolysis, FFC (Fray-Farthing-Chen) [1], SOM (Solid oxygen-ion membrane) [2], OS (One-Suzuki) [3], etc.

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Melts electrolysis is mainly used to produce metal elements whose electrode potential is much more negative than hydrogen. These metals cannot be produced by aqueous solution electrolysis, including light metals, refractory metals, rare earth metals and certain non-metals. The traditional melts electrolysis method is to dissolve the mixture in melts for electrolysis, and the basic idea is derived from electrolytic aluminum [4]. Finding the electrolyte based on cryolite is the key to the ultimate industrialization of electrolytic aluminum. However, some metal oxides have low solubility in melts. For example, the solubility of Ta$_2$O$_5$ in K$_2$TaF$_7$-Ta$_2$O$_5$/KCl-KF melts is only 0.2%–0.3% (mass fraction) [5]. Fray, Farthing, and Chen proposed the FFC method for the direct electrowinning of titanium by titanium oxide [6].

Based on the above studies, Chen et al. [6], Elena et al. [7], Chen et al. [8], and Schwandt and Fray [9] prepared metal chromium, titanium and titanium alloys; Yan et al. [10–12] prepared metal ruthenium; Hironori, Toshiyuki and Rika obtain a coating of metallic molybdenum from ZnCl$_2$-NaCl-KCl-MoCl$_3$ of melts by electroplating, but the coating is thin, easy to fall off and there are a large number of cracks; under the same conditions, KF is added to the melts to obtain a thick and dense Metallic molybdenum plating [13]. Preparation of some metals by NaCl-KCl-NaF melts as a base salt have also been reported [14–17]. In this paper, the electrochemical behavior of ZrO$_2$, HfO$_2$ and MoO$_3$ in the melts was analyzed by using NaCl-KCl-NaF melts as the base salt.

2 Experimental

Analytically pure NaCl, KCl, NaF, ZrO$_2$, HfO$_2$, and MoO$_3$ were selected for the experiment. The chemical reagents were first ground into powder in a mortar, and then dried in an electric oven at 200°C for 8 h to remove adsorbed water and crystal water, and then cooled for use.

Solubility experiments were carried out using a tubular resistance furnace. NaCl, KCl and NaF were well mixed and the molar ratio was 1:0.86. ZrO$_2$, HfO$_2$, MoO$_3$ was added at 10% of the total mass, and placed at the bottom
of NaCl-KCl-NaF melts. Moved the salt-containing mash to the furnace and the temperature was heated to 700°C, and the furnace was protected by high purity argon gas (99.999%). At different times, the upper salt of the melts was sampled using a quartz tube. The extracted melts was quenched and ground to a powder, and subjected to X-ray fluorescence spectroscopy (XRF, AXIOS, PANalytical B.V.) analysis [18, 19]. The amount of oxide dissolved in the melt was calculated according to the formula [20]:

\[ w_{MeO_2} = \frac{w_{Me}}{M_{Me}} \times M_{MeO_2} \]

Where \( w_{MeO_2} \) is the amount of oxide dissolved; \( w_{Me} \) is the amount of metal dissolved; \( M_{Me} \) is the relative molecular mass of metal; \( M_{MeO_2} \) is the relative molecular mass of oxide.

NaCl, KCl and NaF were well mixed and the molar ratio was 1:1:0.86. Then, 0.044% ZrO\(_2\), 0.111% HfO\(_2\), and 10% MoO\(_3\) were added in a mass ratio on the bottom of the file. The salt was placed in a high-purity graphite crucible and placed in a tubular resistance furnace at 200°C for 10 h. Then, the temperature was raised to 700°C for 4 h, protected by high purity argon gas, and temperature was measured by a S-type thermocouple. All electrochemical experiments were performed using a Zahner IM6ex electrochemical workstation using a three-electrode system with platinum wire (99.99%) for the working (Φ0.5 mm, immersion depth is 1 cm), auxiliary (Φ1 mm, immersion depth is 2.5 cm) and reference (Φ0.5 mm, immersion depth is 1 cm) electrodes.

3 Results and discussion

3.1 Dissolution characteristics

Figure 1 showed the dissolution characteristics of ZrO\(_2\) and HfO\(_2\) in a NaCl-KCl-NaF melts. It could be seen from Figure 1 that ZrO\(_2\) and HfO\(_2\) were substantially unchanged in the NaCl-KCl-NaF melts at 700°C for 3 h. The XRD results of the upper melts at 700°C were NaCl, KCl, NaF and HfO\(_2\). No new material formation indicated that ZrO\(_2\) and HfO\(_2\) did not react chemically in the NaCl-KCl-NaF melts.

At 700°C, Figure 2 was an XRD and laser Raman spectroscopy analysis of MoO\(_3\) in a NaCl-KCl-NaF melts. It could be seen from Figure 2(b) that molybdenum oxo groups were present at 340 cm\(^{-1}\), 375 cm\(^{-1}\), 472 cm\(^{-1}\), 665 cm\(^{-1}\), 810 cm\(^{-1}\), 844 cm\(^{-1}\), 978 cm\(^{-1}\), 992 cm\(^{-1}\), and 1022 cm\(^{-1}\). The stretching vibration peak was made of MoO\(_3\) or Na\(_2\)Mo\(_2\)O\(_7\), which was consistent with the results of references [21–24]. It could be seen from Figure 2(a) that there were four substances of NaCl, KCl, NaF and Na\(_2\)Mo\(_2\)O\(_7\) in the melts of NaCl-KCl-NaF-MoO\(_3\), but no MoO\(_3\) existed. Combined with the thermodynamic analysis of the melts, the standard Gibbs free energy \( \Delta G^\theta < 0 \) about the reaction of NaCl, NaF and MoO\(_3\) at 700°C. The reaction could be spontaneously carried out, and Na\(_2\)Mo\(_2\)O\(_7\) was formed. Therefore, the stretching vibration peak of the molybdenum oxo group was Na\(_2\)Mo\(_2\)O\(_7\). The dissolution of MoO\(_3\) in the NaCl-KCl-NaF melts was mainly chemical dissolution.
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3.2 Electrochemical experiment and electrodeposition producted analysis

Figure 3 was a cyclic voltammetry curve of ZrO$_2$, HfO$_2$ and MoO$_3$ in NaCl-KCl-NaF melts at 700°C. Figure 3 (1) was a cyclic voltammetry curve of NaCl-KCl-NaF melts. When the scanning range was −2 V~0.3 V, an oxidation peak appears at −1.65 V during forward scanning, which corresponded to the oxidation process of sodium. As the potential changed, an increased in current occurs at 0.6 V, which corresponded to the precipitation of gas. In the reverse scan, the reduction peak that occurred at −2.0 V was the sodium reduction process. Sodium reduction peak at −2.0 V during reverse scan. Figure 3(2) showed the cyclic voltammetry curve of ZrO$_2$ in NaCl-KCl-NaF melts. A pair of redox peaks a’/a (−0.82 V/−0.96 V) appeared which corresponding to the redox process of zirconium. Figure 3(3) showed the cyclic voltammetry curve of HfO$_2$ in NaCl-KCl-NaF melt. A pair of redox peaks b’/b (−0.76 V/−1.14 V) appeared which corresponding to the redox process of hydrazine. Figure 3(4) showed the cyclic voltammetry curve of MoO$_3$ in NaCl-KCl-NaF melts. Three pairs of redox peaks c’/c (−0.17 V/−0.55 V), d’/d (−0.40 V/−0.91 V) and e’/e (−0.99 V/−1.27 V) appeared in the −2 V~0.7 V scan range, corresponded to a multi-step redox process of molybdenum.

Table 1 showed the relationship between theoretical electrolytic potentials $E^\theta$ and $T$ of ZrO$_2$ and HfO$_2$ at 700°C calculated by HSC 6.0 thermodynamics software. The more positive theoretical electrolysis potential occurred, the more reduction reaction happened. The ionic state of Hf was Hf$^{4+}$ and Hf$^{2+}$. The Hf stepwise reactions were Hf$^{4+}$/Hf$^{2+}$ (−4.80 V) and Hf$^{2+}$/Hf (−0.05 V), respectively. The potential of Hf$^{3+}$ reduced to Hf (−2.43 V) was more positive than the potential of Hf$^{4+}$ reduced to Hf$^{2+}$ (−4.80 V), indicating that Hf$^{4+}$ was reduced by a one-step reduction process, that consistent with the cyclic voltammetry results of Hf showed in Figure 3(1). The ionic state of Zr was Zr$^{4+}$, and the reduction of Zr$^{4+}$ to zirconium metal was a one-step reaction process, which was consistent with the cyclic voltammetry curve of Zr shown in Fig...
With the scanning speed increases, which was because the theoretical electrolysis potential of reaction (1) was higher than the cathodic reaction on the CV curve was a reversible reaction and the product was insoluble, that was, the reduction process of the cathode was completed under diffusion control. The relationship between the reversible reaction \( E_{pc} \) and \( n \) satisfies the equation:

\[
E_{pc} - E_{pc/2} = -0.77(\frac{RT}{nF})
\]

Where \( E_{pc} \) (V) is the peak potential and \( E_{pc/2} \) (V) is the half-peak potential; \( n \) is the electron transfer number and \( F \) (96485 C·mol\(^{-1}\)) is a Faraday’s constant; \( R \) (8.314 J·mol\(^{-1}\)·K\(^{-1}\)) is the molar gas constant, \( T(K) \) is the temperature.

The average value of the number \( n \) of reaction electrons corresponding to the reduction peak in Figure 5(a) was calculated to be about 4. Therefore, it could be concluded that the \( Zr^{4+} \) ion in the melt was reduced to elemental zirconium in one step, so the cathode reaction on the CV curve was: \( Zr^{4+} + 4e = Zr \).

4h constant potential electrolysis was carried out at \(-1.15V\) to obtain a material having a metallic luster on the surface, and the energy spectrum analysis product was mainly zirconium. It was indicated that the reduction peak appearing at a potential of \(-0.935V\) corresponded to the precipitation process of \( Zr \).

Figure 7(a) showed the cyclic voltammetry curves of \( \text{NaCl-KCl-NaF-HfO}_2 \) at different sweep speeds, and Figure 7(b) showed the \( i_{pc} \) and \( v^{1/2} \) curves obtained from the
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**Figure 5:** Cyclic voltammetry curve of NaCl-KCl-Na$_2$ZrO$_2$ at different scanning speeds (a) Cyclic voltammetry curve (b) $i_{pc} \sim v^{1/2}$ & $E_{pc} \sim v^{1/2}$ (rate scan: 300-500mV/s, vs. Pt)

**Figure 6:** EDS of Zr electrodeposited layer

**Figure 7:** Cyclic voltammetry curve of NaCl-KCl-NaF-HfO$_2$ at different scanning speeds (a) Cyclic voltammetry curve (b) $i_{pc} \sim v^{1/2}$ & $E_{pc} \sim v^{1/2}$ curve (rate scan: 300~600 mV/s, vs. Pt)
Figure 8: EDS and XRD of Hf electrodeposited layer

Data in Figure 7(a). It could be seen from Figure 7(b) that $i_{pc}$ had a linear relationship with $v^{1/2}$, and the reduction peak potential $E_{pc}$ did not change with the change of the scanning speed. $i_{pa}/i_{pc} > 1$ was showed in Figure 7(a), therefore, the electrode reaction corresponding to the reduction peak of the cyclic voltammetry curve was reversible and the product was insoluble, that was, the reduction process of the cathode was completed under diffusion control. The calculated value of the number n of reaction electrons corresponding to the reduction peak in Figure 7(a) was about 4. Therefore, the reduction process of HfO$_2$ in NaCl-KCl-NaF melt was a one-step electronic reaction, Hf$^{4+} + 4e = $ Hf.

The potentiostatic electrolysis was carried out under the conditions of $-1.3$ V and 4 h, and the surface energy spectrum of the electrolysis product was analyzed. The results were shown in Figure 8. From the energy spectrum, the main substance of the deposited layer was Hf.

Figure 9 showed the cyclic voltammetry curve of NaCl-KCl-Na-MoO$_3$ as the scanning speed changes. As could be seen from Figure 9(a), as the scanning speed increased, the peak current density gradually increased because the electrochemical reaction rate was affected by the scanning speed. Using the data in Figure 9(a), the relationship between $i_{pc} \sim v^{1/2}$ and $E_{pc} \sim v^{1/2}$ was obtained, as shown in Figure 9(b). The $i_{pc}$ of peak c was linear with the change of $v^{1/2}$, and the potential of peak c’/c moved to the positive and negative directions of the potential with the increase of scanning speed. The scanning speed increased, and the peak c’ gradually disappeared and changed towards irreversible. Therefore, the number of electrons lost could be calculated from the irreversible reaction. As the scanning speed $v$ increased, the $E_{pa}$ and $E_{pc}$ of the peak d’/d moved...
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Figure 9: Cyclic voltammetry curves of different scanning speeds of NaCl-KCl-Na-MoO$_3$ (a) Cyclic voltammetry curve (b) $i_{pc} \sim \nu^{1/2}$ & $E_{pc} \sim \nu^{1/2}$ curve (rate scan: 200-500mV/s, vs Pt)

Figure 10: $\ln \nu$ vs. $E_{pc}$

to the positive and negative directions respectively, and $i_{pc}$ and $\nu^{1/2}$ did not have a linear relationship. Therefore, the peak d was a quasi-reversible reaction process. The potential $E_{pc}$ of the peak e moved in the negative direction of the potential with the increase of the scanning speed $\nu$, $i_{pc}$ was linear with $\nu^{1/2}$, and there was no corresponding obvious oxidation peak, so the peak e was an irreversible reaction process.

According to the values of current density $i_p$ and potential $E_{pc}$ corresponding to each scanning rate peak c in Figure 9(a), a log $i_p$ vs. $E_{pc}$ was obtained in Figure 10.

As the scanning speed increased, the cathode peak potential $E_{pc}$ gradually shifts to the negative direction and had a linear relationship with the sweep speed $\ln \nu$, as shown in Figure 10. For the irreversible process $E_{pc} \sim \ln \nu$ satisfied the following formula [25, 26]:

$$E_{pa} = E^0 + \frac{RT}{anF} \ln \left( \frac{R\ell_0}{anF} \right) + \left( \frac{RT}{anF} \right) \ln \nu$$

$$E_{pc} = E^0 - \frac{RT}{(1 - \alpha) nF} \ln \left( \frac{R\ell_0}{(1 - \alpha) nF} \right) - \left( \frac{RT}{(1 - \alpha) nF} \right) \ln \nu$$

Where $\alpha$ is transfer coefficient, $\ell_0$ is standard rate constant of the reaction, $n$ is electron transfer number involved in the rate-determining step, $\nu$ is scan rate, $E^0$ is formal potential, $E_{pc}$ is the reduction peak potential, $E_{pa}$ is the oxidation peak potential ($T=973K$, $R=8.314J \cdot mol^{-1} \cdot K^{-1}$, $F=96485 C \cdot mol^{-1}$)

According to the above equation and the slope of the linear relationship of $E_{pc} \sim \ln \nu$ in Figure 10, the symmetry factor $\alpha$ was calculated as 0.2685. $n$ was calculated as 2.23 $\approx$ 2. Therefore, the peak c corresponds to the 2 electron reduction process. It was proved that the reaction (1) corresponds to a 2-electron process in which Mo$_2$O$_7^{2-}$ was reduced to MoO$_2$. From the nonlinear relationship of the peak d in Figure 9(b), the number of electrons to be lost could not be calculated by the formula. However, molybdenum in MoO$_2$ was tetravalent, and therefore, the reaction corresponding to peak d was a 4 electron reduction process of Mo$^{4+} \rightarrow$ Mo.

Using graphite as anode and low carbon steel as cathode, the temperature was set to 700°C, the molar ratio of melts system was NaCl: KCl: NaF = 1:1: 0.86, MoO$_3$ (mass fraction is 20%), and the mixture was evenly mixed. In pure corundum, the current density was 100mA·cm$^{-2}$ and the electrodeposition time was 60 min. After deposition, the surface of the substrate was loose and porous. From
the XRD results, it was found that metal molybdenum was formed after electrolysis.

4 Conclusions

The dissolution about oxides of refractory metals ZrO$_2$, HfO$_2$ and MoO$_3$ in NaCl-KCl-NaF melts was studied at 700°C. The electrochemical reduction mechanism of oxides of refractory metals in NaCl-KCl-NaF melts obtained by cyclic voltammetry analysis, the following conclusions were obtained:

1. When the molar ratio of NaCl, KCl and NaF was 1:1:0.86, ZrO$_2$ and HfO$_2$ did not undergo chemical reaction; MoO$_3$ was chemically dissolved, and MoO$_3$ mainly formed Na$_2$Mo$_2$O$_7$.

2. The reduction process of zirconium in melts was a reversible process of one step and four electron transfer controlled by diffusion, and the reduction reaction was: $\text{Zr}^{4+} + 4e^- \rightarrow \text{Zr}$. The electrochemical reduction process of hafnium in melts was a one-step reversible process, and the product was insoluble. The reduction mechanism was: $\text{Hf}^{4+} + 4e^- \rightarrow \text{Hf}$. In melts, the electrochemical reduction of metallic molybdenum was controlled by the diffusion and electron transfer process of the active ion $\text{Mo}_2\text{O}_7^{2-}$. The electrochemical reduction process of metallic molybdenum in the melts was divided into two steps. The process was as follows:

\[
\begin{align*}
\text{Mo}_2\text{O}_7^{2-} + 4e^- & = 2\text{MoO}_2 + 3\text{O}^{2-} \\
\text{MoO}_2 + 4e^- & = \text{Mo} + 2\text{O}^{2-}
\end{align*}
\]

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