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ELECTROCHEMICAL REDUCTION OF TANTALUM IN MOLTEN $NaCl$-KCl-K_2TaF_7 ①

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ABSTRACT

The cathode process of tantalum ion in molten $NaCl-KCl-K_2TaF_7$ at 720 ℃ was investigated by three transient electrochemical techniques. The results show that the electroreduction reaction of Ta^{5+} involves a single reversible five electron step. The diffusion coefficients of the complexion containing Ta^{5+} measured by above mentioned techniques are alike such as 1.15×10^{-5} by cyclic voltammetry, 1.10×10^{-5} by chronopotentiometry and 1.15×10^{-5} by chronoamperometry respectively. The effect of electroactive species containing oxygen on tantalum reduction process was also studied.

Key words: electrochemical reduction tantalum molten $NaCl-KCl-K_2TaF_7$

1 INTRODUCTION

The mechanism of electrochemical reduction of tantalum is not yet very clear. Drossbach *et al*[1] and Efros *et al*[2] considered two reduction steps had occurred in $NaCl-KCl-K_2TaF_7$ molten system: $Ta^{5+}+2e = Ta^{3+}$ and $Ta^{3+}+3e \rightleftharpoons Ta$. But, Konstantinov *et al*[3] investigated the reduction process of tantalum in $KCl-KF-K_2TaF_7$ system at 700 ℃ and a single five electron reduction step was found to be $[TaF_8]^{3-}+5e \rightleftharpoons Ta+8F^-$. Therefore, the results are quite different from each other.

The aim of the present work is to further explore the behaviour of tantalum reduction in $NaCl-KCl-K_2TaF_7$ molten system and examine the influence of oxide ions on the electrode process.

2 EXPERIMENTAL

The experimental apparatus consisted of a can made of Hastelloy C-22 and a glass header with tight Torion joints as tubing and electrode passage. The salt was introduced in a vitreous carbon crucible placed at the bottom inside the Hastelloy crucible. A molybdenum wire (dia. 1 mm) or tungsten wire (dia. 1.3 mm) fixed to a nickel leader was used as working electrode; a graphite rod (dia. 6 mm) of spectral purity served as counter electrode; and a Ni/Ni^{2+} electrode with a boron nitride diaphragm was employed as reference. The melt in the electrode was a solution of 1 mol% NiF_2 in $NaCl-KCl$.

All chemicals used were reagent grade. $NaCl$ (50 mol%) and KCl (50 mol%) were

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accurately weighed, mixed, carefully dehydrated in apparatus under reduced pressure and finally purified by pre-electrolysis. After that K_2TaF_7 was introduced in the NaCl-KCl molten salt in desired portion. During experimental run, argon gas was kept flowing throughout the can and the temperature error was controlled within ±2℃ by a thermocontroller.

The generation of different potenial or current programs was carried out with a Tacussel GSTP4 programmer. The transient responses were collected on a Sefram X–Y recorder, unless stored in a Nicolet 310 digital storage oscilloscope as an intermediate stage.

3 RESULTS AND DISCUSSION

3.1 *Mechanism of Electrochemical Reduction Reaction of* Ta^{5+}

A cyclic voltammogram is shown in Fig. 1 in a range of potential sweep window of 1.0 to −1.7 V. It is clear that there is a cathodic wave at a peak potential of about −0.5 V responded to an anodic wave at a peak potential of 0.1 V. Increasing cathodic polarization, the reduction process of alkali metal appears at the potential of about −1.7 V. On the right hand side of voltamogram, there are two waves at 1.0 V and 0.3 V related to the reduction and oxidation process of tungsten working electrode respectively. Fig. 2 is a cyclic voltamogram in the potential range of 0.4 to −0.6 V at different potential sweep rates. From the data shown in Fig. 2, it can be seen that E_p^c and $I_p^c / v^{1/2}$ are constant with the variation of potential sweep rate. The product electrodeposited at a potential close to the foot of the cathodic wave was examined to be pure metallic tantalum by X–ray diffraction analysis. This behavior may be interpreted in terms of the redox reaction $Ta^{5+}+5e \rightleftharpoons Ta$.

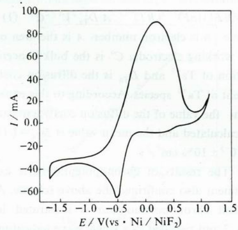

Fig. 1 Cyclic voltammetry of the molten $NaCl–KCl–K_2TaF_7$ at 720 ℃

$C^0_{K_2TaF_7} = 8.0 \times 10^{-2}$ mol / L;

potential sweep rate $V = 0.3$ V / s;

$A = 0.6$ cm^2; potential window 1, −1.7V

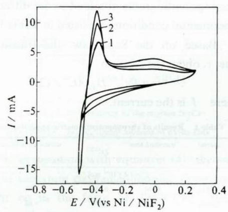

Fig. 2 Cyclic voltammetry of the molten $NaCl–KCl–K_2TaF_7$ at 720 ℃

$C^0_{K_2TaF_7} = 4.0 \times 10^{-2}$ mol / L; poteneial sweep rate

$V = 0.3$(curve 1); 0.2(curve 2); 0.5(curve 3) V / s;

$A = 0.5$ cm^2; potential window 0.4, − 0.6 V

The cathodic peak current, I_p^c, was proportional to the square root of potential sweep rate, V in agreement with following classical equation[5]

$$I_p^c = 0.611(nF)^{3/2}(RT)^{-1/2} A\, D_{\mathrm{Ta}}^{1/2} V^{1/2} C^{\circ} \quad (1)$$

where n is electron number; A is the area of the working electrode; C° is the bulk concentration of Ta^{+5} and D_{Ta} is the diffusion coefficient of Ta^{+5} species. According to this equation, the value of the diffusion coefficient can be calculated and the mean value is $D_{\mathrm{Ta}} = 1.15 \times 10^{-5} \pm 10\%\ \mathrm{cm}^2/\mathrm{s}$.

The results of chronopotentiometric experiment also confirmed the above scheme. A typical chronopoteniogram is illustrated in Fig. 3 and revealed as a single wave indicating a single step reaction. The reduction reaction was also studied by double-pulse chronopotentiometry. The ratio of forward and backward transition time, τ_f / τ_b, is approximately equal to 1, indicating the product of electrode reaction is insoluble. The data taken from chronopotentiograms obtained under different experimental conditions are listed in Table 1.

Based on the Sand law, the transition time, τ, obeys the relation

$$\tau^{1/2} = n F \pi^{1/2} D_{\mathrm{Ta}} A C^{\circ} / (2I) \qquad (2)$$

where I is the current.

Table 1 Results of chronopotentiometric experiments

current I / A · cm^{-2}	transition time τ / s	$I\tau^{1/2}$	diffusion coefficient D_{Ta} / x10^{-5}cm^2 · s^{-1}
	$C^0 = 4.4 \times 10^{-2}$ mol / L		
0.0637	0.900	0.060	1.03
0.0796	0.590	0.059	1.06
0.1115	0.279	0.059	0.98
0.1752	0.127	0.062	1.10
0.2550	0.067	0.060	1.23
	$C^0 = 8 \times 10^{-2}$ mol / L		
0.1100	1.000	0.110	1.03
0.1400	0.630	0.111	1.06
0.2000	0.300	0.110	1.03
0.2800	0.160	0.112	1.07
0.3900	0.082	0.112	1.07
	$C^0 = 2 \times 10^{-1}$ mol / L		
0.3300	0.829	0.300	1.29
0.8900	0.108	0.293	1.12

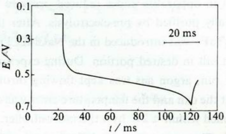

Fig. 3 Chronopotentiometry of the molten $\mathrm{NaCL{-}KCl{-}K_2TaF_7}$ at 720 ℃

$C^{0}_{\mathrm{K_2TaF_7}} = 4 \times 10^{-2}$ mol / L;

$I = 110$ mv; $A = 0.5$ cm^2

The data D_{Ta} obtained by the above equation are reported in Table 1. When the variation of concentration is not very large, the influence of concentration on the value of diffusion coefficient can be ignored. Hence the mean value of D_{Ta} calculated from various concentrations of Ta^{5+} is $D_{\mathrm{Ta}} = 1.1 \times 10^{-5} \pm 15\%\ \mathrm{cm}^2/\mathrm{s}$.

In the present investigation the chronoamperometry was also applied to determinate the diffusion coefficient of Ta^{5+}. The typical chronoamperogram at constant overpotential of 400 mV is shown in Fig. 4. When the potential step is sufficiently high, the limiting current should be reached on the working electrode, thus the Cottrell equation can be used to calculate the diffusion coefficient.

$$I = n F C^{\circ} D_{\mathrm{Ta}}^{1/2} / (\pi t)^{1/2} \qquad (3)$$

where I is the current density; t is the time. A plot of I vs $t^{-1/2}$ is a straight line shown in Fig. 5 with a slope of $n F C^{\circ} D_{\mathrm{Ta}}^{1/2} \pi^{-1/2}$, from which the diffusion coefficient can be determined as $1.15 \times 10^{-5}\ \mathrm{cm}^2/\mathrm{s}$ that is in good accordance with the results measured by cyclic voltammetry and chronopotentiometry.

According to dynamic equilibria between

various tantalum complex ions (see equation 4) proposed by Inman *et al*[9], the tantalum ion in the melt of present experiment should exist in the form of TaF_7Cl^{3-}.

$$TaF_6^- \xrightleftharpoons{F^-} TaF_7^{2-} \xrightleftharpoons{Cl^-} TaF_7Cl^{3-} \xrightleftharpoons{F^-} TaF_8^{3-} \quad (4)$$

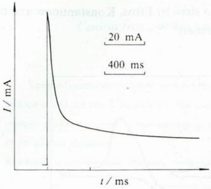

Fig. 4 Chronoamperometry of the molten $NaCL\text{–}KCl\text{–}K_2TaF_7$ at 720 ℃

$C^{\circ}_{K_2TaF_7} = 2.0 \times 10^{-1}$ mol / L;

$\eta = 400$ mV; $A = 0.5$ cm^2

3.2 *Influence of Oxide Ions on the Electrode Process*

Oxide ions are common impurities of molten salts, which can perturb the electrochemical reaction and affect the quality of the deposited metal. It was found that when the dehytration of the salt mixture was not really sufficient, a shoulder and an additional wave, as shown in Fig.6 apeared during the cathodic sweep at about the foot of cathodic wave and 0.77 V other than that of the second wave related to the reduction of tantalum ion at −0.5 V. We considered that both additional processes are all ascribed to electrochemcal reduction reactions of tantalum oxygen-containing complexes. The products deposited at constant potential of −0.75 V were detected by X-ray to be metallic tantalum and unknown compounds which need further exploration.

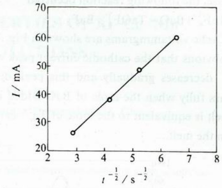

Fig. 5 $I\text{–}t^{-1/2}$ relationship

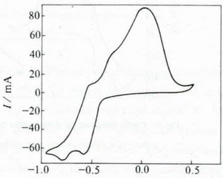

Fig. 6 Cylic voltammetry of the molten NaCl–KCl–K_2TaF_7 bearing small amount of oxide ions

In connection with equation (4), the species of tantalum oxygen-containing complexes might be in the form of $TaOCl_xF_y^{z-}$, (here $z = x + y - 3$). The nature of these complexes is not yet elucidated. In a similar medium e. g. KCl–KF, it has been shown from spectroscopic studies that addition of oxides favored the formation of the complex $TaOF_6^{3-}$ [10].

For the further study on the behavior of electrochemical reduction of such complexes, we introduced BaO (in three portions) into $NaCl\text{–}KCl\text{–}K_3TaF_8$ molten system up to the ratio $n_{BaO} / n_{Ta^{5+}} = 1$ ($n_{BaO} / n_{Ta^{5+}}$ is the mole fraction of oxide / mole fraction of Ta^{5+}). In this case, the following reaction occurred

$$TaF_8^{3-}+BaO=TaOF_6^{3-}+BaF_2$$

Cyclic voltammgrams are shown in Fig. 7. It is obvious that the cathodic current peak of TaF_8^{3-} decreases gradually and this peak disappears fully when the mole of BaO added in the melt is equivalent to the mole of Ta^{5+} existing in the melt.

The situations mentioned above indicate that a little amount of oxide ions in the melt can seriously perturb the electrochemical processes. This may be the reason why the electrochemical reduction of tantalum in molten $NaCl-KCl-K_2TaF_7$ was wrongly interpreted in two steps by Efros, Konstantinow and other researchers[2-3].

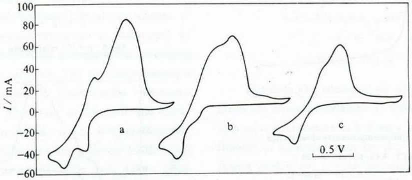

Fig. 7 Cyclic voltammetry of the molten $NaCl-KCl-K_3TaF_8$ containing increasing amount of BaO

a, b, c—the voltamograms after adding each portion of BaO, potential window 0, −1.2V

4 CONCLUSION

Transient techniques, such as cyclic voltammetry and chronopotentiometry indicate that the electroreduction of Ta^{5+} involved a single reversible five electron step $Ta^{5+}+5e \rightleftharpoons Ta$. It was found that the presence of oxideions in the melt perturbs the reduction process. The diffusion coefficient of Ta^{5+} was measured by cyclic voltammetry, chronopotentiometry and chronoamperometry as 1.15×10^{-5}, 1.10×10^{-5} and 1.15×10^{-5} cm^2/s, respectively, that reveals more believable results.

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