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Kinetic mechanism of anodic oxidation of tantalum in nitrate melts①

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[Abstract] The data of anodic oxidation of tantalum in high temperature nitrate melts were regressed according to 41 kinds of probable kinetic mechanism. The results show that the process follows the parabolic law $\alpha^2 = kt$, which means that the process of anodic oxidation of tantalum is limited by the movement of positive vacancies of tantalum ions. The voltage has an effect on the rate constant in prior period, which implies that the electromigration exists at the beginning of film growth. The breakdown of films exists in whole process. The films obtained are composed of orthorhombic β-Ta_2O_5 and TaO_y.

[Key words] kinetics; anodic oxidation; tantalum
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1 INTRODUCTION

Tantalum can be oxidized at low temperature into inactive Ta_2O_5 with compact texture and specific resistance of 10^{18} Ω·cm[1], which entitles tantalum good corrosion resistance and electric resistance, and also makes it impossible to get thick Ta_2O_5 films at low temperature. The oxidation of tantalum in different circumstances had been investigated[2~10]. But the temperatures at which their experiments were carried out was lower than 400 ℃. The spinnerets are key parts in textile machinery for chemical fibers on which scattered more than 1300 horn-shaped microholes with diameter of 0.05 ~ 0.1 mm per square centimeter. Spinnerets of thickness of 0.25 ~ 0.45 mm, through which fibers inject with the speed of 75 ~ 130 m/min, have to undergo the pressure of 0.8 MPa. So spinnerets must have enough hardness, resistance to deformation and corrosion resistance, etc. The kinetics of anodic oxidation of tantalum in elevated temperature is researched in this paper so as to modify hardness, surface roughness, resistance to deformation and corrosion resistance of tantalum spinnerets for chemical fibers.

2 EXPERIMENTAL

2.1 Material and method of experiments

Industrial pure tantalum slab was made by PM with purity of 99.96 %(mass fraction). Solutions of salt baths were nitrates of analytical purity. The crucible was made of nickel. Temperature, which was controlled with the meters of PID circuits, can be limited ±1 ℃ above that specified. In order to avoid the effects of large current on electric resource and the occurrence of micro-arc in films, the electric resource of anodic oxidation was controlled in constant current density way with current density of 0.5 A/m^2, until the voltage rose to given level with the films thickening, then changed automatically to constant voltage way. In fact, the time for electric resource working in constant current way was less than 1 min. The plots of current density to time and voltage to time were recorded. The structure and morphology of films obtained were investigated with D/max-ⅡB X-ray diffractometer and X-650 scanning electronic microscope.

2.2 Method of kinetics

The probable control steps of process of anodic oxidation of tantalum at elevated temperature were as follows:

1) Anodic reactions[3]

$$NO_3^- = [O] + NO_2 + e \qquad (1)$$

$$\frac{2}{5}Ta + [O] = \frac{1}{5}Ta_2O_5 \qquad (2)$$

2) Process involved in solid phase such as diffusion, nuclei growth and nucleation, etc.

3) The reactions and migration process of material and electricity in liquid phase, which is less likely to be control step because it progresses more quickly than that involved in solid.

In the equation of kinetics for surface reaction

$$d\alpha/dt = kf(\alpha) \qquad (3)$$

where α is the fraction reacted at time t, k is rate constant, $f(\alpha)$ is a function determining the mechanism of reaction and $g(\alpha)$ is the integral form of $f(\alpha)$, i.e.

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$$g(\alpha) = \int \frac{d\alpha}{f(\alpha)} = kt \quad (4)$$

where $g(\alpha)$, $f(\alpha)$ are 41 mechanism functions representing chemical reactions, diffusion, nuclei growth and nucleation respectively[11] (as shown in Table 1). Assuming

$$d\delta / dt = C \times J \quad (5)$$

where δ is the thickness of films, J is the oxidation current density, C is a constant.

Table 1 41 probable mechanisms of dynamics for surface reactions

Mechanism	$g(\alpha)$	r
Nuclei and growth	$-\lg(1-\alpha)^r$	1/4, 1/3, 2/5, 1/2, 2/3, 3/4, 3/2, 1, 2, 3, 4
	α^r	1/4, 1/3, 1/2, 1, 3/2, 2
	$\lg(\alpha^r)$	1, 2
	$\lg[\alpha(1-\alpha)]$	
Chemical reaction	$1-(1-\alpha)^{1-r}$	1/2, 2/3
	$1-(1-\alpha)^r$	1/4, 1/3, 1/2, 2, 3, 4
	$(1-\alpha)^{-r}$	2, 1, 1/2
	$(1-\alpha)^{-1}-1$	
1-dim. diffusion	α^2	
2-dim. diffusion	$\alpha+(1-\alpha)\lg(1-\alpha)$	
	$[1-(1-\alpha)^{1/2}]^r$	2, 1/2
3-dim. diffusion	$[1-(1-\alpha)^{1/3}]^r$	2, 1/2
	$1-2\alpha-(1-\alpha)^{2/3}$	
	$[(1+\alpha)^{1/3}-1]^2$	
	$[(1-\alpha)^{-1/3}-1]^2$	

According to the assumption above, one can obtain

$$\delta_t = C\int_0^t J(t)\,dt \quad (6)$$

Then α is defined as follows:

$$\alpha(t) = \frac{\delta_t}{\delta_\infty} = \frac{C\int_0^t J(t)\,dt}{C\int_0^\infty J(t)\,dt} = \frac{J_{t_0} \cdot t_0 + \int_{t_0}^t J(t)\,dt}{J_{t_0} \cdot t_0 + \int_{t_0}^\infty J(t)\,dt} \quad (7)$$

where J_{t_0}, t_0 are the constant current density and the time span in constant current density way respectively. Then $J(t)$ can be translated into $\alpha(t)$ by numerical integration with a computer. k, T obtained in the first regression were regressed again based on Arrhenius equation:

$$k = A\exp(-E/(RT)) \quad (8)$$

where T is temperature, E is activation energy, A, R are constants.

It must be pointed out that the $\int_{t_0}^\infty J(t)\,dt$ is unavailable, so the $\max(\int_{t_0}^{t_{\max}} J(t)\,dt)$ is used to substitute for it, in which $t_{\max}$ is the time span that the data covered, which enables α larger, then k larger in shorter $t_{\max}$, but which does not affect the average regression result, Re_{av}, so does not affect the analysis of kinetic mechanism.

3 RESULTS AND DISCUSSION

3.1 Typical $J(t)$ and calculated $\alpha(t)$ plots

Two typical J-t plots and their correspondent α-t plots are shown in Fig 1. It is found that the voltage imposed has an influence on $J(t)$ at the beginning.

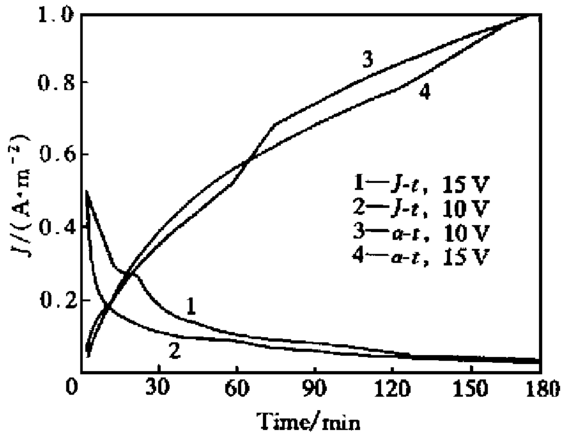

Fig.1 Typical J-t and α-t plots at 500 ℃

3.2 Regression results under different voltages

The two mechanisms of 10 V/15 V, 60 min with the highest Re_{av}, which represent diffusion of materials in solid phase in 1-dimension and 3-dimension, are shown in Table 2. As a matter of fact, the Re_{av} of all mechanisms representing diffusions in different conditions are pretty high.

Table 2 Regression results of 10 V/15 V, 60 min

10 V, 60 min			15 V, 60 min		
$g(\alpha)$	$\frac{Re_{av}}{\text{Rank}}$	n_{Re}	$g(\alpha)$	$\frac{Re_{av}}{\text{Rank}}$	n_{Re}
α^2	$\frac{0.9925}{1}$	0.32	α^2	$\frac{0.9935}{1}$	0.33
$[(1+\alpha)^{1/3}-1]^2$	$\frac{0.9910}{2}$	0.37	$[(1+\alpha)^{1/3}-1]^2$	$\frac{0.9929}{2}$	0.41

Note: Re_{av} is average correlation coefficient of the first regression, n_{Re} is correlation coefficient of the second regression, rank is the rank of Re_{av} and n_{Re} in 41 mechanisims from high to low

3.3 Regression results in different periods

Different E, R, n_{Re}, Re_{av} obtained in regressions of data in different time spans are shown in Table 3. It is obvious that effects of electric voltage and temperature on k diminished as time going, which implies that there are more than one kinetic mechanisms.

The regression results between 60 ~ 180 min show that the oxide films grow linearly and neither temperature nor voltage has any effect on the kinetic process.

Table 3 Relations of E, k, Re_{av}, n_{Re} vs time based on model $\alpha^2 = kt$

Time / min	E / (kJ·mol^{-1})	$k_{15\text{ V}}$ / min^{-1}	Re_{av}	n_{Re}	$k_{10\text{ V}}$ / min^{-1}
1 ~ 30	14.013	0.0337	0.9928	0.41	0.0319
1 ~ 45	15.158	0.0235	0.9926	0.72	0.0203
1 ~ 60	3.980	0.0168	0.9935	0.32	0.0173
1 ~ 180	2.534	0.0074	0.9932	0.06	0.0074

3.4 Structure and morphology of oxide films

XRD spectrum of the sample oxidized in conditions of 15 V, 500 ℃ for 3 h shows that the oxide films are composed of orthorhombic β Ta_2O_5 and TaO_y (shown in Fig.2). The strong background implies that there exists amorphous phase in films. The morphology of the same sample with the help of SEM shows that the films are porous (shown in Fig.3), their thickness is about 15 μm, and there are micro-fissures and arc craters on their surfaces (shown in Fig.4).

3.5 Regression results according to electromigration mechanism

If Einstein equation is employed:

$$k_b = k_d/(RT) \tag{9}$$

where k_b is the rate constant of electromigration, k_d is the rate constant of thermal diffusion, R is gas constant, then we obtain

$$k_b = \frac{k_d}{RT} = \frac{A\exp(-E/(RT))}{RT} \tag{10}$$

$$\ln(k_b RT) = \ln A - E/(RT) \tag{11}$$

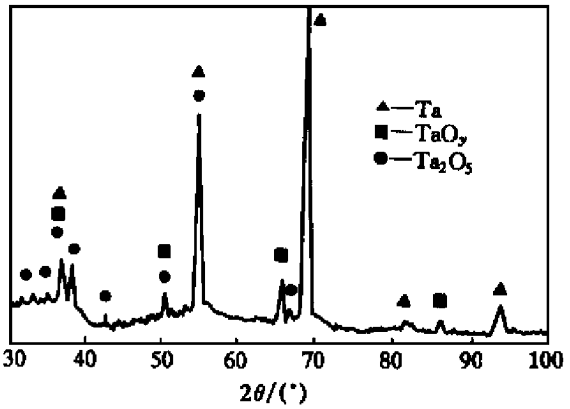

Fig.2 XRD spectrum of tantalum oxide

Fig.3 Morphology of cross section

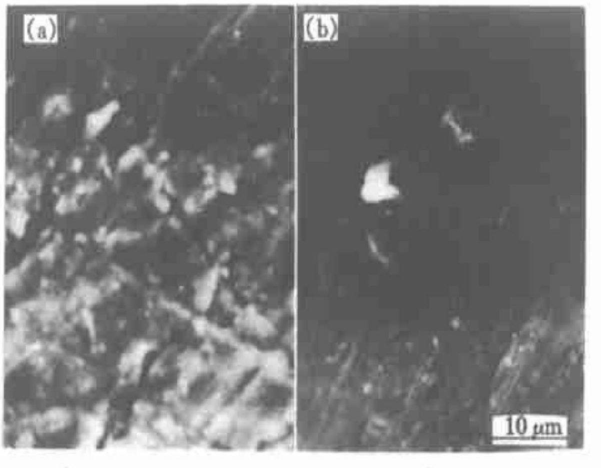

Fig.4 Micro-fissures and arc craters on surfaces of tantalum oxides

(a) — Micro fissure; (b) — Arc craters

k, T of 15 V obtained in the first regression are regressed according to Eqn.(11), shown in Table 4. It is obvious that the n_{Re} is higher than those obtained according to Arrhenius formula, which confirms the primary function of electromigration; and also confirms that there is no possibility of the control of kinetic process of anodic oxidation of tantalum by any step other than the step of movement of materials in oxide films. As a whole, the n_{Re} is not as high as expected. Because there are more than one mechanisms involved, so the relation between k and T does not follow Eqn.(8) or (11) simply.

Table 4 Second regression results according to Eqn.(11)

t_{max}/ min	E/ (kJ·mol^{-1})	n_{Re}
30	20.2	0.55
45	21.4	0.84
60	10.2	0.66
180	8.8	0.20

4 DISCUSSION

The first regression gives the best fit to the parabolic law in all cases. Because the oxides of tantalum are metal-lack type[12], the control step of anodic oxidation of tantalum should be the movement of tantalum ion vacancies in oxide films. Since the concentration gradient and electric field existed from beginning to end, both mechanisms of the thermal diffusion and electromigration certainly have effects on the kinetic process and follow parabolic law. The following is to make sure which one is primary control step by their differences.

For electromigration, according to Wagner theorem[12], there is

$$k_b = \frac{2qkn_e(n_c + n_a)V}{\rho F} = f_1(V) \qquad (12)$$

where q is equivalent number of oxide, k is specific conductivity, F is Faraday constant, ρ is density of oxide; n_e, n_a, n_c is migration fraction of electron, cation and anion respectively; V is voltage cross the film. While as to thermal diffusion, there is

$$k_d = C \cdot D = f_2(T) \qquad (13)$$

where D is diffusion coefficient, C is constant. That is to say voltage has effect on the process of electromigration, while temperature has effect on process of thermal diffusion.

It is necessary to discuss the process after voltage is imposed. At first, voltage drops lay in electrolyte solution to build the gradient of ion concentration and double electric layers in solution. But this process is shorter than 1 min. Then voltage drops transfer to the film produced in which a strong electric field is built. According to Fig.1 and Table 2, at the beginning k is affected strongly by voltage. The higher V is, the larger k is. The relation between k and T does not follow the Arrhenius formula. Consequently, the low n_{Re} of regression according to Eqn.(10) is gained. A higher n_{Re} can be gained if the data are regressed according to Eqn.(13), which shows that electromigration is the main control step. Of cause the effects of thermal diffusion and electric arc exist throughout the whole process. So the n_{Re} obtained can not be as high as expected. In the last period, k is nothing to do with both T and V. $\alpha(t)$ increases linearly, which implies that there is other mechanism working rather than diffusion and electromigration.

The specific resistance of Ta_2O_5 is 10^{18} Ω·cm, The thickness of film of this experiment is about 15 μm, so the resistance of film should be 1.5×10^{15} Ω, but the measured resistance is $V/J_\infty = 2.9 \times 10^4$ Ω, much less than expected. A conclusion can be reached that the film is porous which is confirmed by the results of SEM. It is thought that the porous texture is given rise to by the breakdown of the film[5]. The existence of breakdown has been confirmed by the existence of arc craters on the surfaces of films. It is easy to image that the breakdowns exist in whole process and their frequency decreases with the electric field density decreasing when the film thickens. So, in the prior period, the breakdown is not the control step, but it becomes to be after long period. According to the discussion above, it can be referred that breakdowns and micro-fissures control the process of film thickening in later period, which makes the linear growth of films independent of the T and V.

Dependence of E calculated on time is due to the dependence of functions of thermal diffusion, electromigration, arc and micro-fissures on time and is also due to the effects of electric field on the diffusion coefficient and diffusion activation energy. Generally speaking[11]:

$$E = E_r - E_a = E_r - ea\Xi N_a = E_r - eaVN_a/\delta \qquad (14)$$

where E_r is real diffusion activation energy, E_a is the effect of electric field on the diffusion activation energy, e is electric charge of diffusion particle, a is the minimal distance of migration at one time, N_a is Afogadro constant, Ξ is density of electric field.

If we let $e = 5 \times 1.6 \times 10^{-19}$ C, $a = 2.5 \times 10^{-10}$ m (the radius of a tantalum atom), $V = 10$ V, then $\delta = 1$ μm, $E_a = 12$ kJ/mol.

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