

Carbonization kinetics of $\text{La}_2\text{O}_3\text{-Mo}$ cathode materials^①

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[Abstract] The carbonization kinetics of $\text{La}_2\text{O}_3\text{-Mo}$ cathode materials was studied by thermal analysis method. Three-stage model of the carbonization was presented. The carbonization rate is initially controlled by chemical reaction, then by chemical reaction mixed with diffusion, finally by diffusion. The experimental data are processed according to this model and the correlation coefficients of the kinetic curves are satisfactory. The apparent activation energy of carbonization of $\text{La}_2\text{O}_3\text{-Mo}$ cathode materials was obtained. At the same time, the empirical expressions of the rate constant against temperature in the temperature range of 1393~1493 K were deduced.

[Key words] carbonization; cathode; kinetics

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1 INTRODUCTION

Carbonization of cathode is a key process in $\text{ThO}_2\text{-W}$ cathode manufacture. When $\text{ThO}_2\text{-W}$ filaments are heated in a hydrogen atmosphere consisting of benzene, acetylene, naphthalene or xylene vapors, the hydrocarbon is decomposed at the hot filament surface to form tungsten carbide. Compared with original cathode, the carbonized cathode shows better performance at low temperature. The structure and decomposition of carbide layer were studied a lot in the past^[1~3]. Although $\text{ThO}_2\text{-W}$ cathode has good emission properties, the radioactivity of ThO_2 leads to problems in its manufacture and application. As an alternative of $\text{ThO}_2\text{-W}$ cathode, $\text{La}_2\text{O}_3\text{-Mo}$ cathode appeared in the middle of 1970s. However, because of its poor emission stability, $\text{La}_2\text{O}_3\text{-Mo}$ cathode has not been used commercially. At present, many studies on the function of carbide layer in the emission of the cathode are carried out. The porous carbide layer can store active substance and carry them to the surface^[4]. After carbonization the bulk diffusion coefficient of La atoms increases; the bonding energy between La atoms and Mo surface reduces^[5,6] and the minimum work can be obtained in a wider temperature range^[7,8]. Otherwise, Mo_2C formed in the carbonization process can reduce La_2O_3 to metallic La. All of these are favorable for the emission^[9]. Our previous studies show that good emission property and long lifetime can be got at the proper carbonization degree. In this paper, the relationship among mass gain after carbonization, temperature and time is studied by carbonization kinetics of $\text{La}_2\text{O}_3\text{-Mo}$ cathode, which can serve as a guide for the carbonization

degree controlling.

2 EXPERIMENTAL

$\text{La}_2\text{O}_3\text{-Mo}$ cathode materials were cut into 8 mm × 6 mm × 1 mm. After grinded, polished and cleaned, the specimens were carbonized at 1393~1493 K in a benzene atmosphere which consisted of argon and 5% hydrogen (volume fraction). The flow rate was 40 mL/min. The heating rate was 20 K/min.

3 RESULTS AND DISCUSSION

3.1 Theoretical analysis

The carbonization reaction of $\text{La}_2\text{O}_3\text{-Mo}$ cathode can be divided into three steps:

- 1) carbon decomposed by benzene is absorbed on the surface of carbide layer;
- 2) carbon diffuses to the $\text{Mo-Mo}_2\text{C}$ interface across the carbide layer;
- 3) carbon has a chemical reaction with Mo on the interface to form Mo_2C .

The rate of carbonization reaction is controlled by three stages. In the initial stage, the reaction rate is controlled by chemical reaction; in the last stage the rate is controlled by diffusion; in the middle stage it is controlled by chemical reaction mixed with diffusion. The carbonization reaction causes the concentration of Mo atoms at the interface decrease, meanwhile Mo atoms in the matrix diffuse into $\text{Mo/Mo}_2\text{C}$ interface to leave vacancy in the matrix, therefore the density of the matrix decreases with the carbonization going on.

The thickness of the $\text{La}_2\text{O}_3\text{-Mo}$ plate can be con-

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sidered no change during carbonization process. Thus the rate of carbonization

$$v = A \frac{dx}{dt} c_c \quad (1)$$

where c_c is the carbon content per unit volume, A is the surface area, x is the carbonized thickness.

After carbonization the mass gain per unit area is

$$\frac{\Delta m}{A} = \frac{m - m_0}{A} \quad (2)$$

where m_0 and m are the mass of La₂O₃-Mo plate before and after carbonization respectively.

The carbonization reaction can be written as



According to the conservation law of substance before and after carbonization, then

$$\frac{\rho(\text{Mo}_2\text{C}) x A}{M(\text{Mo}_2\text{C})} + \frac{2A \rho'(\text{Mo}) L}{M(\text{Mo})} = \frac{2A \rho(\text{Mo}) L}{M(\text{Mo})} \quad (4)$$

where $\rho(\text{Mo}_2\text{C})$ is the density of carbide layer, $\rho(\text{Mo})$ and $\rho'(\text{Mo})$ are the densities of molybdenum before and after carbonization respectively. $M(\text{Mo}_2\text{C})$ and $M(\text{Mo})$ are the molar mass of Mo₂C and Mo respectively. Then

$$\begin{aligned} \frac{\Delta m}{A} &= \frac{\rho(\text{Mo}_2\text{C}) x A}{A} + \frac{\rho'(\text{Mo}) L A}{A} - \frac{\rho(\text{Mo}) A L}{A} \\ &= x \rho(\text{Mo}_2\text{C}) + L [\rho'(\text{Mo}) - \rho(\text{Mo})] \end{aligned} \quad (5)$$

Combining Eqns. (4) and (5), then

$$x = \frac{\Delta m}{A \rho(\text{Mo}_2\text{C}) \left[1 - \frac{M(\text{Mo})}{2M(\text{Mo}_2\text{C})} \right]} \quad (6)$$

Adding Eqn. (6) into Eqn. (1), then

$$\begin{aligned} v &= \frac{A c_c}{\rho(\text{Mo}_2\text{C}) \left[1 - \frac{M(\text{Mo})}{2M(\text{Mo}_2\text{C})} \right]} \cdot \\ &\quad \frac{d(\Delta m/A)}{dt} \end{aligned} \quad (7)$$

In the first stage of carbonization, the carbonization rate is controlled by chemical reaction, then

$$v = v_c = K'_c \cdot A \cdot c_s \quad (8)$$

where K'_c is the chemical reaction rate constant; c_s is carbon concentration at Mo surface. Combining Eqns. (7) and (8) and integrating yields

$$\begin{aligned} \frac{\Delta m}{A} &= \frac{K'_c c_s \rho(\text{Mo}_2\text{C}) \left[1 - \frac{M(\text{Mo})}{2M(\text{Mo}_2\text{C})} \right]}{c_c} t \\ &= K_c \cdot t, \\ K_c &= \frac{K'_c c_s \rho(\text{Mo}_2\text{C}) \left[1 - \frac{M(\text{Mo})}{2M(\text{Mo}_2\text{C})} \right]}{c_c} \end{aligned} \quad (9)$$

In the middle stage of carbonization, the carbide layer of some thickness has formed at Mo surface. The rate of interface chemical reaction is equal to that of diffusion^[10], so the carbonization rate is controlled by both of them,

$$v = \frac{A \cdot c_s}{x/D + 1/K'_c} \quad (10)$$

where D is the carbon diffusion coefficient in the carbide layer. Combining Eqns. (7) and (10) and in-

tegrating yields

$$\begin{aligned} \left[\frac{\Delta m}{A} \right]^2 + \frac{2D \rho(\text{Mo}_2\text{C})}{K'_c} \cdot \\ \left[1 - \frac{M(\text{Mo})}{2M(\text{Mo}_2\text{C})} \right] \left[\frac{\Delta m}{A} \right] = \\ \frac{2D c_s \left[\rho(\text{Mo}_2\text{C}) \left[1 - \frac{M(\text{Mo})}{2M(\text{Mo}_2\text{C})} \right] \right]^2}{c_c}, \\ K_M = \frac{2D \rho(\text{Mo}_2\text{C}) \left[1 - \frac{M(\text{Mo})}{2M(\text{Mo}_2\text{C})} \right]}{K'_c} \end{aligned} \quad (11)$$

In the last stage of carbonization, carbide layer is very thick and diffusion path of carbon atoms is quite long. So the carbonization rate is controlled by diffusion,

$$v = v_D = A c_s D / x \quad (12)$$

Combining Eqns. (7) and (12) and integrating yields

$$\begin{aligned} \left[\frac{\Delta m}{A} \right]^2 &= \frac{2c_s D}{c_c} \left[\rho(\text{Mo}_2\text{C}) \cdot \right. \\ &\quad \left. \left[1 - \frac{M(\text{Mo})}{2M(\text{Mo}_2\text{C})} \right] \right]^2 t \\ &= K_D t, \\ K_D &= \frac{2c_s D}{c_c} \left[\rho(\text{Mo}_2\text{C}) \left[1 - \frac{M(\text{Mo})}{2M(\text{Mo}_2\text{C})} \right] \right]^2 \end{aligned} \quad (13)$$

K_c , K_M and K_D are the reaction rates in the first, middle and last stages of carbonization respectively. According to the expression of K_c and K_D , then

$$\frac{K_D}{K_c} = K_M \quad (14)$$

Then Eqn. (11) can be written as

$$\left[\frac{\Delta m}{A} \right]^2 + K_M \left[\frac{\Delta m}{A} \right] = K_D t \quad (15)$$

3.2 Results and discussion

The carbonization kinetic curves for La₂O₃-Mo cathode at different carbonization stage are shown in Fig. 1. After the experimental data in Fig. 1 are processed according to the above model, the reaction rate constants of the first, middle and last stages are obtained, as shown in Table 1.

Table 1 Carbonization rate constant and relevant coefficients in various carbonization stages at different temperatures for La₂O₃-Mo sample

Temperature / K	Reaction stage	Rate constant	Relevant coefficient
1 393	First	365.9998×10^{-6}	0.9997
	Middle	9.3366×10^{-3}	0.9956
	Last	3.4172×10^{-6}	0.9953
1 443	First	620.0001×10^{-6}	0.9998
	Middle	23.2231×10^{-3}	0.9969
	Last	14.4000×10^{-6}	0.9961
1 493	First	1480.6663×10^{-6}	0.9978
	Middle	28.5394×10^{-3}	0.9978
	Last	42.2571×10^{-6}	0.9959

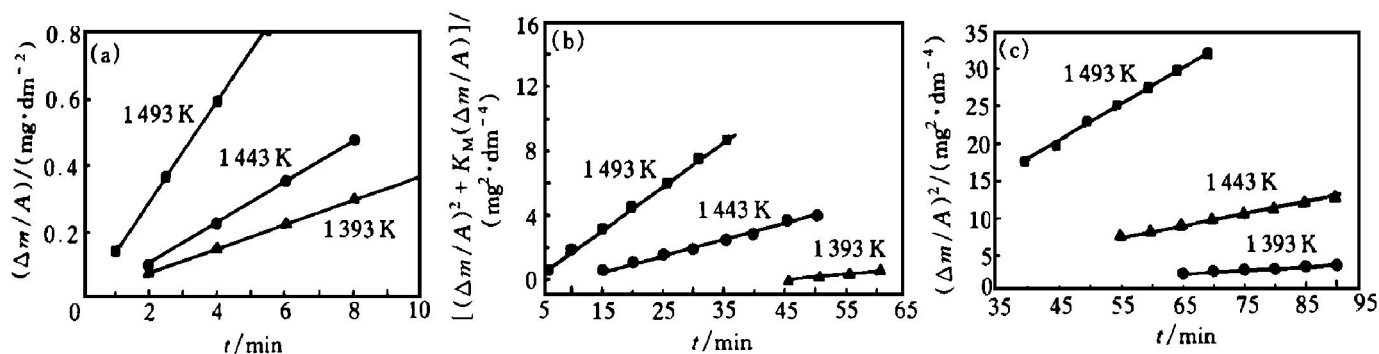


Fig. 1 Carbonization kinetic curves for $\text{La}_2\text{O}_3\text{-Mo}$ sample

(a) —In first stage; (b) —In middle stage; (c) —In last stage

The data in Table 1 can be further processed by mathematical method, then the apparent activation energies of different stages and the empirical expressions of the rate constant and temperature can be got by using Arrhenius formula, as shown in Table 2.

Table 2 Apparent activation energy, frequency factor and correlation coefficient in various carbonization stages for $\text{La}_2\text{O}_3\text{-Mo}$ sample

Stage	Apparent activation energy/($\text{J}\cdot\text{mol}^{-1}$)	Frequency factor	Relevant coefficient
First	2.4075×10^5	3.6668×10^5	-0.9871
Middle	1.9455×10^5	2.0517×10^5	-0.9863
Last	4.3114×10^5	5.2782×10^{10}	-0.9980

So the expressions of the carbonization rate constants in three stages for $\text{La}_2\text{O}_3\text{-Mo}$ sample are

$$K_C = 3.6668 \times 10^5 \exp\left[-\frac{2.4075 \times 10^5}{RT}\right]$$

$$K_M = 2.0517 \times 10^5 \exp\left[-\frac{1.9445 \times 10^5}{RT}\right]$$

$$K_D = 5.2782 \times 10^{10} \exp\left[-\frac{4.3114 \times 10^5}{RT}\right]$$

4 CONCLUSIONS

The carbonization process obeys a three-stage rule. The relationship among the mass gain, temperature and time in the temperature range of 1393~1493 K in three stages are as follows.

In the first stage:

$$\frac{\Delta m}{A} = 366680 t \cdot \exp\left[-\frac{240750}{RT}\right]$$

In the middle stage:

$$\left[\frac{\Delta m}{A}\right]^2 + 205170 \exp\left[-\frac{194550}{RT}\right] \left[\frac{\Delta m}{A}\right] =$$

$$5.2782 \times 10^{10} t \cdot \exp\left[-\frac{431140}{RT}\right]$$

In the last stage:

$$\left[\frac{\Delta m}{A}\right]^2 = 5.2782 \times 10^{10} \exp\left[-\frac{4.3114 \times 10^5}{RT}\right] t$$

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