



Carbonization Kinetics of La_2O_3 -Mo Cathode Materials

Wang Jinshu, Zhou Meiling, Zuo Tiejong, Zhang Jiuxing, Nie Zuoren

School of Materials Science and Engineering, Beijing Polytechnic University, Beijing 100022,

P R China

Correspondent: Wang Jinshu, Tel:86-10-67392755, Fax:86-10-67391536,

E-mail: wangjsh@bjpu.edu.cn

Summary

The carbonization kinetics of La_2O_3 -Mo cathode materials has been studied by thermal analysis method. Three-stage model of the carbonization has been presented in this paper. The carbonization rate is initially controlled by chemical reaction, then controlled by chemical reaction mixed with diffusion, finally controlled by diffusion. After the initial experimental data are processed according to this model, the correlation coefficients of the kinetic curves are satisfactory. The apparent activation energy of carbonization of La_2O_3 -Mo cathode materials has been obtained. At the same time, we have deduced the empirical expressions of the amount of weight increased per unit area after carbonization, temperature and time in the temperature range 1393K-1493K.

Key words:

Carbonization, La_2O_3 -Mo, Cathode, TG, Kinetics

1. Introduction

Carbonization of cathode is a key process in ThO_2 -W cathode's manufacturing. Carbonized ThO_2 -W filaments are produced from plain ThO_2 -W filaments by subjecting the formed and mounted filaments to a heat

treatment in a hydrogen atmosphere consisting of benzene, acetylene, naphthalene, or xylene vapors which are usually carried to the treating chambers by a stream of hydrogen under controlled flow conditions. When heating a filament in this atmosphere to a temperature, the hydrocarbon is decomposed at the hot filament surface to form tungsten carbide, W_2C , which diffuses into the tungsten. Compared with original cathode, the carbonized cathode can show better performance at lower temperature. The structure and decomposition of carbide layer have been studied a lot in the past[1-3]. Although ThO_2 -W cathode has good emission properties, the radioactivity of ThO_2 leads problems to its manufacturing and application. As an alternative of ThO_2 -W cathode, La_2O_3 -Mo cathode appeared in the mid. of 1970s. However, because of its poor emission stability, La_2O_3 -Mo cathode has not been used commercially. As mentioned above, carbonization is very important in cathode's manufacturing, so many studies on the function of carbide layer in the emission of the cathode have been carried out. The porous carbide layer can store active substance and carry them to the surface[4]. The bulk diffusion coefficient of lanthanum atoms increase after carbonization, besides, carbon reduces the bonding between La atoms with Mo surface [5-6]. The minimum work function can be obtained in a wider temperature range after carbonization[7-8]. Mo_2C formed in the carbonization process can reduce La_2O_3 to metallic La, which is favorable for the emission[9]. Our previous

studies show that good emission property and long lifetime can be got at the proper carbonization degree. Therefore, how to get the optimum carbonization degree is quite important. In this paper, the relationship among the amount of weight increased per unit area after carbonization, temperature and time have been obtained by the study of carbonization kinetics of La_2O_3 -Mo cathode, which can serve a guide for the carbonization degree control.

2. Experimental Method

La_2O_3 -Mo cathode materials was cut into $8 \times 6 \times 1 \text{ mm}^3$ in size. After grinding, polishing and cleaning, geometric parameters of the specimens were measured. The carbonization experiments in the temperature range of 1393-1493K were carried out in a benzene atmosphere which is carried to the treating chamber by a stream of mixed atmosphere of argon and hydrogen (5% in volume) of natural flow 40ml/min. The heating rate is 20K/min.

3. Experimental results and discussion

3.1 Theoretical analysis

We have considered the process of carbonization reaction of La_2O_3 -Mo cathode can be divided into three steps:

- a. Carbon decomposed by benzene is absorbed on the surface of carbide layer.
- b. Carbon diffuses to the Mo-Mo₂C interface across the carbide layer.
- c. Carbon has a chemical reaction with Mo on the interface to form Mo₂C.

So the rate of carbonization reaction should be controlled by three stages, that is, in the initial stage the reaction rate should be 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. Carbon atom diffuses ceaselessly to the Mo-Mo₂C interface through carbide layer, then react with molybdenum, that causes the concentration of molybdenum atoms at the reaction interface to decrease. Thus the molybdenum atom in the matrix diffuses into Mo-Mo₂C interface region to leave vacancy in it. Therefore the density of molybdenum matrix decrease with the increase of the time of carbonization.

Let L represents the thickness of a La₂O₃-Mo plate; ρ_{Mo_2C} for the density of carbide layer; ρ_{Si} and ρ'_{Si} for the density of molybdenum before and after carbonization respectively; A stands for the total surface area; y is the thickness of carbide layer (Compare y with L, y is so small that can be negligible, so the thickness of the La₂O₃-Mo plate is considered not changed during carbonization process). Thus the rate of carbonization is

$$V = A \frac{dx}{dt} d_c \quad (1)$$

here, d_c is the content of carbon per unit volume. After carbonization the weight increased per unit area is

$$\frac{\Delta W}{A} = \frac{W - W_0}{A} \quad (2)$$

here, W_0 and W are La₂O₃-Mo plate weights before and after carbonization

respectively.

The carbonization reaction can be written as follows



According to the conservation of amount of substance before and after carbonization, that is

$$\frac{\rho_{\text{Mo}_2\text{C}} \cdot xA}{M_{\text{Mo}_2\text{C}}} + \frac{2A\rho'_{\text{Mo}}L}{M_{\text{Mo}}} = \frac{2A\rho_{\text{Mo}}L}{M_{\text{Mo}}} \quad (4)$$

$M_{\text{Mo}_2\text{C}}$ and M_{Mo} are the mass of Mo_2C and Mo in mol respectively.

Then

$$\frac{\Delta W}{A} = \frac{\rho_{\text{Mo}_2\text{C}} \cdot xA}{A} + \frac{\rho'_{\text{Mo}}LA}{A} - \frac{\rho_{\text{Mo}}AL}{A} = x\rho_{\text{Mo}_2\text{C}} + L(\rho'_{\text{Mo}} - \rho_{\text{Mo}}) \quad (5)$$

Combining (4) and (5), we get:

$$x = \frac{\frac{\Delta W}{A}}{\rho_{\text{Mo}_2\text{C}} \left(1 - \frac{M_{\text{Mo}}}{2M_{\text{Mo}_2\text{C}}} \right)} \quad (6)$$

Adding (6) them into (1), we obtain

$$V = \frac{Ad_c}{\rho_{\text{Mo}_2\text{C}} \left(1 - \frac{M_{\text{Mo}}}{2M_{\text{Mo}_2\text{C}}} \right)} \cdot \frac{d\left(\frac{\Delta W}{A}\right)}{dt} \quad (7)$$

3.1.1 In the first stage of carbonization

In this stage, the carbonization rate is controlled by chemical reaction at interface

$$V = V_c = Kc'AC \quad (8)$$

Here, Kc' is a constant of the chemical reaction rate; C is carbon concentration at molybdenum surface. Combining (7) and (8), we can get:

$$\frac{Ad_c}{\rho_{Mo_2C} \left(1 - \frac{M_{Mo}}{2M_{Mo_2C}}\right)} \cdot \frac{d\left(\frac{\Delta W}{A}\right)}{dt} = K_C' AC \tag{9}$$

Integrating formula (9), we get:

$$\frac{\Delta W}{A} = \frac{K_C' C \rho_{Mo_2C} \left(1 - \frac{M_{Mo}}{2M_{Mo_2C}}\right)}{dc} t = K_C \cdot t \tag{10}$$

$$K_C = \frac{K_C' C \rho_{Mo_2C} \left(1 - \frac{M_{Mo}}{2M_{Mo_2C}}\right)}{dc}$$

K_C is a constant of reaction rate in the first stage.

3.1.2 In the middle stage

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

$$v = \frac{AC}{\frac{x}{D} + \frac{1}{K_C'}} \tag{11}$$

D is the carbon diffusion coefficient in the carbide layer.

Combining (7) and (11), we obtain

$$\frac{Ad_c}{\rho_{Mo_2C} \left(1 - \frac{M_{Mo}}{2M_{Mo_2C}}\right)} \cdot \frac{d\left(\frac{\Delta W}{A}\right)}{dt} = \frac{AC}{\frac{x}{D} + \frac{1}{K_C'}} \tag{12}$$

Integrating (12) and adding (6) into it, we get

$$\left(\frac{\Delta W}{A}\right)^2 + \frac{2D\rho_{Mo_2C} \left(1 - \frac{M_{Mo}}{2M_{Mo_2C}}\right)}{K_C'} \left(\frac{\Delta W}{A}\right) = \frac{2DC \left[\rho_{Mo_2C} \left(1 - \frac{M_{Mo}}{2M_{Mo_2C}}\right)\right]^2}{d_c} t \tag{13}$$

$$\text{Let } K_M = \frac{2D\rho_{M_{O_2}C} \left(1 - \frac{M_{M_{O_2}C}}{2M_{M_{O_2}C}}\right)}{K'_C}$$

K_M is a constant of reaction rate in the middle stage.

3.1.3 In the last stage of carbonization

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

$$V = V_D = AC \frac{D}{x} \quad (14)$$

Combing (7) and (14), we obtain

$$\frac{Ad_c}{\rho_{M_{O_2}C} \left(1 - \frac{M_{M_{O_2}C}}{2M_{M_{O_2}C}}\right)} \cdot \frac{d\left(\frac{\Delta W}{A}\right)}{dt} = AC \frac{D}{x} \quad (15)$$

Integrating (15), we obtain

$$\left(\frac{\Delta W}{A}\right)^2 = \frac{2CD}{dc} \left[\rho_{M_{O_2}C} \left(1 - \frac{M_{M_{O_2}C}}{2M_{M_{O_2}C}}\right) \right]^2 t = K_D t \quad (16)$$

$$K_D = \frac{2CD}{dc} \left[\rho_{M_{O_2}C} \left(1 - \frac{M_{M_{O_2}C}}{2M_{M_{O_2}C}}\right) \right]^2$$

K_D is a constant of reaction rate in the last stage.

According to the expression of K_C and K_D , we can get:

$$\frac{K_D}{K'_C} = \frac{\frac{2CD}{dc} \rho_{M_{O_2}C}^2 \left(1 - \frac{M_{M_{O_2}C}}{2M_{M_{O_2}C}}\right)^2}{K'_C C \rho_{M_{O_2}C} \left(1 - \frac{M_{M_{O_2}C}}{2M_{M_{O_2}C}}\right)} = \frac{2D\rho_{M_{O_2}C} \left(1 - \frac{M_{M_{O_2}C}}{2M_{M_{O_2}C}}\right)}{K'_C} = K_M \quad (17)$$

Then equation (13) can be written as:

$$\left(\frac{\Delta W}{A}\right)^2 + K_M \left(\frac{\Delta W}{A}\right) = K_D t \quad (18)$$

3.2 Data Processing

After the initial experimental data are processed according to this model, the dots which represent the data will appear on straight lines and their correlation coefficients are satisfactory, as shown in table 1 and Fig 1.

Table1 Carbonization rate constant and correlation coefficient in various carbonization stages at different temperature for sample La₂O₃-Mo

Temperature (K)	Reaction stage	Rate constant	Relevant coefficient
1393	first	365.9998×10^{-6}	0.9997
	middle	9.3366×10^{-3}	0.9956
	last	3.4172×10^{-6}	0.9953
1443	first	620.0001×10^{-6}	0.9998
	middle	23.2231×10^{-3}	0.9969
	Last	14.4000×10^{-6}	0.9961
1493	first	1480.6663×10^{-6}	0.9978
	middle	28.5394×10^{-3}	0.9978
	last	42.2571×10^{-6}	0.9959

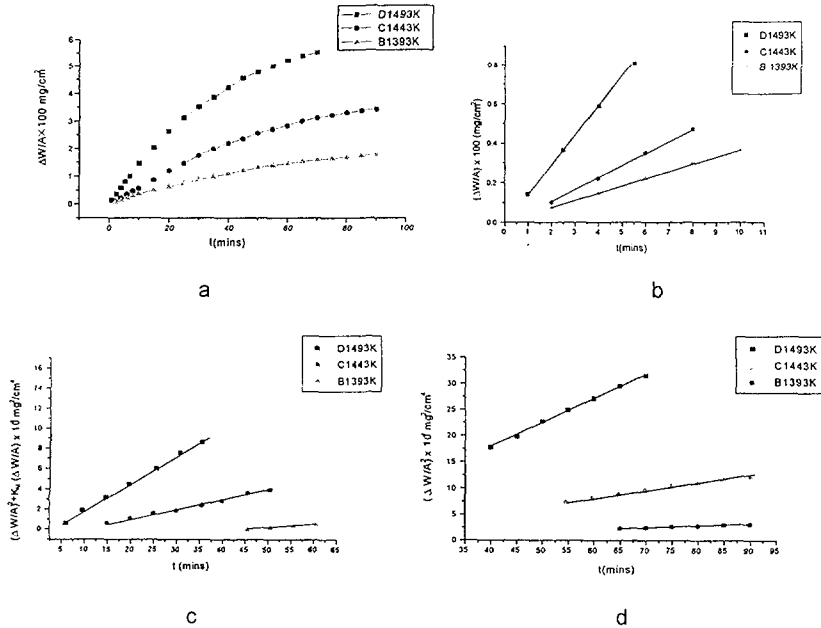


Fig 1 Carbonization kinetic curve for sample La₂O₃-Mo

a. in the whole process b. in the first stage c. in the middle stage d. in the last stage

The data in table 1 can be further processed by mathematical method, then we can obtain the reaction rate constants of the first, middle and last stages. The apparent activation energy of different stages and the empirical expressions of the rate constant and temperature can all be got by using Arrhenius formula ($K = K_0 \exp(-\frac{E}{RT})$), as shown in table 2.

Table2 Carbonization rate constant ,apparent activation energy, frequency factor and correlation coefficient in various carbonization stages for sample La₂O₃-Mo

		First stage	Middle stage	Last stage
Rate constant	1393K	365.9998×10^{-6}	9.3366×10^{-3}	3.4172×10^{-6}
	1443K	620.0001×10^{-6}	23.2231×10^{-3}	14.4000×10^{-6}
	1493K	1480.6662×10^{-6}	28.5394×10^{-3}	42.2571×10^{-6}
Apparent activation energy (J)		2.4075×10^5	1.9455×10^5	4.3114×10^5
Frequency factor K ₀		3.6668×10^5	2.0517×10^5	5.2782×10^{10}
Relevant coefficient		-0.9871	-0.9863	-0.9980

So expressions of the carbonization rate constants in three stages for sample La₂O₃-Mo are as follows:

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

$$K_M = 2.0517 \times 10^5 \exp\left(-\frac{1.9455 \times 10^5}{RT}\right)$$

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

4. Conclusions

The mechanism of carbonization of La₂O₃-Mo cathode materials was investigated. The carbonization process obeys a three-stage rule. The relationship among the amount of weight increased per area after carbonization, temperature and time in the temperature range 1393K-1493K in three stages can be shown as follows.

In the first stage:
$$\frac{\Delta W}{A} = 3.6668 \times 10^5 \exp\left(-\frac{2.4075 \times 10^5}{RT}\right) t$$

In the middle stage:

$$\left(\frac{\Delta W}{A}\right)^2 + 2.0517 \times 10^5 \exp\left(-\frac{1.9455 \times 10^5}{RT}\right) \left(\frac{\Delta W}{A}\right) = 5.2782 \times 10^{10} \exp\left(-\frac{4.3114 \times 10^5}{RT}\right) t$$

In the last stage:
$$\left(\frac{\Delta W}{A}\right)^2 = 5.2782 \times 10^{10} \exp\left(-\frac{4.3114 \times 10^5}{RT}\right) t$$

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