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Surface segregation of La_2O_3 molecules in Mo-La_2O_3 cathode materials①

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[Abstract] The surface segregation of La_2O_3 in Mo-La_2O_3 cathode was carried out by Auger electron spectroscopy. Lanthanum and oxygen ions (La^{3+} and O^{2-}) diffuse from the grain boundaries to the surface respectively, and these ions recombine into La_2O_3 molecules on the surface. The results were analyzed by kinetics of grain boundary diffusion. In the temperature range of 1 123 ~ 1 423 K, the diffusion coefficients of La^{3+} and O^{2-} ions were found to fit with the following equations:

$$D_{La} = 3.6703 \times 10^{-16} \exp(-1.01639 \times 10^5 / RT)$$

$$D_O = 1.5122 \times 10^{-16} \exp(-8.13066 \times 10^4 / RT).$$

[Key words] segregation; lanthanum; oxygen; cathode; kinetics; Mo-La_2O_3

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1 INTRODUCTION

Large-power electron tube plays an important role in space and the military area. Th-W cathode is now widely used in the large-power electron tube. After a series of activation treatment, Th atoms situated in Th-W cathode, segregate onto the cathode surface, thus its work function decreases and the emission current density increases. La-Mo cathode is a new kind of cathode developed in recent three decades, and its emission current density is superior to Th-W cathode[1~3]. In this material lanthanum exists in form of lanthanum oxide (La_2O_3) molecule[4] which distributes along grain boundaries. When temperature increases, the amount of lanthanum oxide on the surface of cathode is increased. The active lanthanum on the surface can lower the escaping work of molybdenum, so the emission property of Mo-La_2O_3 cathode can be improved[5~10]. Because the emission density depends on the amount of lanthanum oxide on the surface, it is necessary to investigate the surface segregation of La_2O_3. How lanthanum oxide segregate onto the surface, in the form of La_2O_3 molecules or in the form of La^{3t} and O^{2t} ions (which combine into La_2O_3 again on the surface), can't be decided yet. This paper reports the investigation of La_2O_3 segregating onto the surface by Auger electron spectroscopy (AES).

2 EXPERIMENTAL

2.1 Sample preparation

The experimental materials were Mo-4% La_2O_3 thin sheets (4.0 mm × 4.0 mm × 0.3 mm). Then the sheet was welded respectively onto Mo tube which was 3.3 mm in diameter, 0.05 mm in thickness, 15 mm in length. A tungsten filament was mounted in the molybdenum tube, and the molybdenum tube was mounted on a standard chamber manipulator.

2.2 AES experiment

The AES experiment was performed in a VG-ESCALAB5 malfunction spectrometer. There are two chambers in the spectrometer-chamber for analysis and chamber for sample treatment. Mo-La_2O_3 sample was heated in the treatment chamber, then transferred to the analysis chamber by mechanic hand. The sample was heated by accelerated electrons which bombarded the Mo tube. The temperature was measured with a bioptix pyrometer. The analysis chamber was vacuumed to $(1 \sim 2) \times 10^{-8}$ Pa. The maximum pressure during heating at ~1 400 K in specimen treatment chamber was 10^{-6} Pa. In order to minimize the alteration of peak strengths caused by other factors, close peaks in the spectra were chosen for analysis. Thus, the 625 eV lanthanum peak and 503 eV oxygen peak were measured along with 186 eV molybdenum peak. In this experiment, three samples were respectively held at 1 123 K, 1 273 K and 1 423 K.

3 RESULTS AND ANALYSIS

3.1 Results

Typical Auger electron spectra characteristic of the La-Mo surface at different temperatures are shown in Fig.1. It is easy to find out that at room

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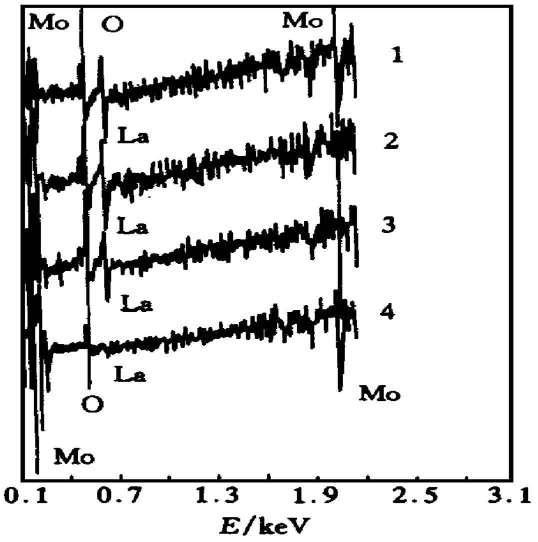

Fig.1 Auger electron spectra of La-Mo surface at different temperatures for different times
1 —1 150 ℃, 25 min; 2 —1 000 ℃, 5 min;
3 —850 ℃, 8 min; 4 —RT

temperature the amount of lanthanum and oxygen is low. With increasing temperature, the heights of 625 eV lanthanum Auger peak and 503 eV oxygen Auger peak becomes bigger, whereas the height of 186 eV molybdenum peak becomes smaller.

For quantitative analysis, the peak strength for different elements was measured in each spectrum. According to Eqn.(1), the content of lanthanum and oxygen on the surface can be calculated. Suppose when the sample was just heated to a temperature, the elements did not segregate onto the surface. In this case, the surface concentration of La and O is equal to that in Mo-La materials. Then we can get the surface concentration of different elements at different temperatures and different times. The time dependence of the ratios of surface concentration (W_t) of different elements to their equilibrium concentration (W_p) is shown in Fig.2.

$$C_{X_i} = \frac{I_i}{S_i} / \sum_{j=1}^{n} \frac{I_j}{S_j} \qquad (1)$$

where C_{X_i} —peak to peak height, S_X ($X = i, j$) —sensitivity factor.

Fig.2 shows that when the specimen was heated at a temperature it would take some time for La and O ions to segregate onto the surface and get equilibrium with bulk finally. The higher the temperature, the shorter the time needed for equilibrium segregation.

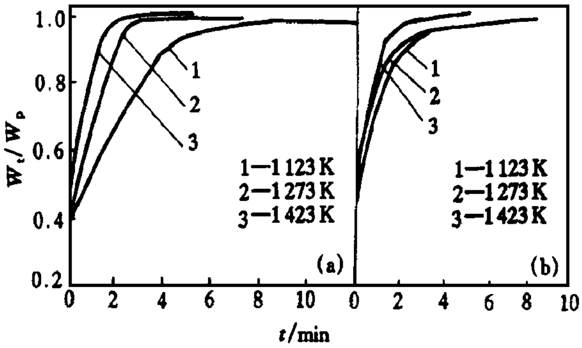

Fig.2 Time dependence of ratios of surface concentration of different elements on their equilibrium concentration
(a) —La; (b) —O

3.2 Discussion

Table 1 is the ratio between concentration of lanthanum to that of oxygen on the surface of La-Mo materials at different temperatures and different times. It is evident from Table 1 that C_{La}/C_O is not a constant at a certain temperature, so we can think that lanthanum and oxygen segregate onto the surface in the form of ions La and O (La^{3+}, O^{2-}), and these ions recombine into La_2O_3 on the surface. (If La_2O_3 diffuses to the surface in the form of molecules, the ratio will not change with time at a certain temperature).

The diffusion coefficient of ions La^{3+} and O^{2-} can be calculated, respectively. In Mo-La_2O_3 cathode, La_2O_3 molecules distribute along the molybdenum grain boundaries[4], so the surface segregation of ions La^{3+} and O^{2-} can be attributed to diffusing along the grain boundary, the process of surface segregation is shown in Fig.3 schematically. There are two steps in segregation process: La^{3+} and O^{2-} ions diffuse to the surface from grain boundaries when heated, then these ions diffuse over the surface. Because the surface diffusion activation energy is lower than bulk diffusion activation energy, the diffusion coefficients of La^{3+} and O^{2-} ions along grain boundaries are much smaller than that on the surface. Thus the surface segregation of these ions is determined by the diffusion along the grain boundaries.

Table 1 Ratio between concentration of lanthanum to that of oxygen on surface of La-Mo material

No.	T/K	t/min	C_{La}/C_O	No.	T/K	t/min	C_{La}/C_O	No.	T/K	t/min	C_{La}/C_O
1	1 123	0	0.283 5	6	1 273	0	0.283 5	11	1 423	0	0.283 5
2	1 123	2	0.399 2	7	1 273	1	0.458 2	12	1 423	0.5	0.498 0
3	1 123	4	0.430 4	8	1 273	3	0.530 7	13	1 423	1.5	0.525 8
4	1 123	8	0.458 2	9	1 273	5	0.528 0	14	1 423	2.5	0.533 4
5	1 123	12	0.468 1	10	1 273	7	0.540 9	15	1 423	5	0.537 5

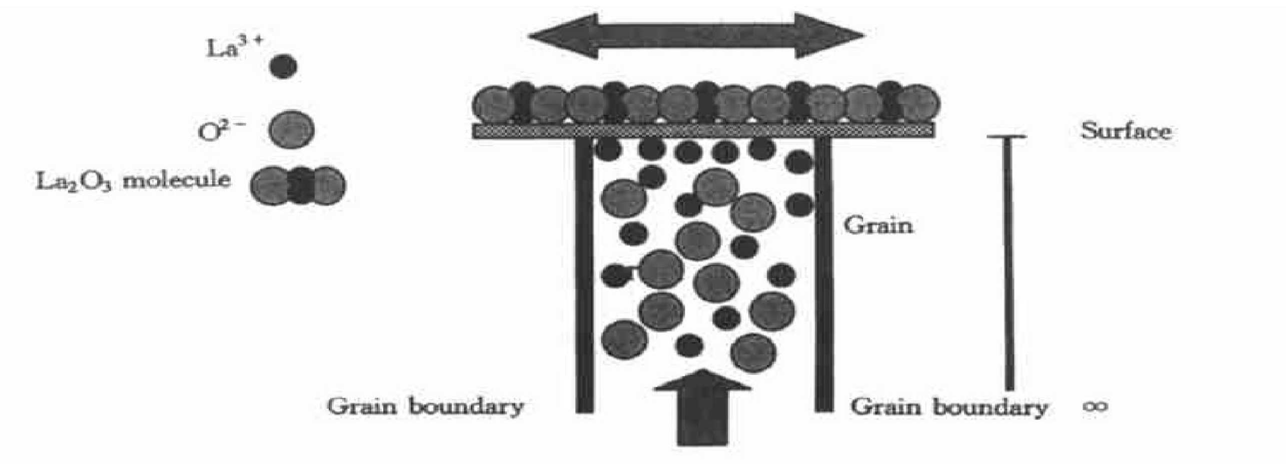

Fig.3 Sketch for diffusion

Suppose the diffusion is one-dimensional diffusion of ions La^{3+} and O^{2-} from the grain boundary to a semi-infinite plane. The grain boundary links with one another, so they can be considered as a well without end. The concentration of La and O far away from the surface at grain boundary is assumed as their bulk concentration C_b respectively. According to Fick's second Law, therefore the relevant diffusion equation is

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial X^2} \tag{2}$$

Suppose when ions La^{3+} and O^{2-} in the bulk get to surface, they spread quickly, then the surface concentration C_s^t is the same everywhere. Imagining for convenience there is one activator atom layer on the surface, and an interface between surface and bulk located precisely at $X = 0$. Then, at any time at some temperature, the concentration in the bulk at $X = 0$ is $C^t = C_0^t/\beta$ (β is enrichment ratio factor). Hence the interface condition is

$$\begin{aligned} D\left(\partial C_X^t/\partial X\right)_{X=0} &= d\left(\partial C_s^t/\partial t\right) \\ &= \beta d\left(\partial C_X^t/\partial t\right)_{X=0} \end{aligned} \tag{3}$$

where d is the ion La^{3+} or O^{2-} layer thickness, that is the diameter of ion La^{3+} or O^{2-}.

In summary, the equations which describe the diffusion of ions La^{3+} and O^{2-} along grain boundary under certain boundary conditions are as follows:

$$\left.\begin{aligned} &D\left(\partial^2 C_X^t/\partial X^2\right) = \frac{\partial C_X^t}{\partial t} \\ &D\left(\partial^2 C_X^t/\partial X\right)_{X=0} = \beta d\left(\frac{\partial C_X^t}{\partial t}\right)_{X=0} \\ &C_X^t = C_b \qquad (X \to \infty) \end{aligned}\right\} \tag{4}$$

The solution is

$$\begin{aligned} C_X^t = C_b - C_b\left(1 - \frac{1}{\beta}\right)\exp\left(\frac{X}{\beta d} + \frac{Dt}{\beta^2 d^2}\right) \cdot \\ \operatorname{erfc}\left(\frac{X}{2\sqrt{Dt}} + \frac{\sqrt{Dt}}{\beta d}\right) \end{aligned} \tag{5}$$

where D is the diffusion coefficient of ions La^{3+} or O^{2-} along the grain boundary at a temperature; β is the ratio of equilibrium surface concentration C_s^∞ at a temperature to bulk concentration; C_b is the concentration of La, assumed constant; t is the time; X is the distance between one point in the bulk and the surface.

On the surface, $X = 0$, $C_X^t = C_0^t = C_s^t/\beta$. At equilibrium $C_b = C_s^\infty/\beta$ putting Eqn.(4) in the form

$$\begin{aligned} \frac{C_s^t}{C_s^\infty} = 1 - \left(1 - \frac{1}{\beta}\right) \cdot \\ \exp\left(\frac{Dt}{\beta^2 d^2}\right)\left(1 - \operatorname{erf}\frac{\sqrt{Dt}}{\beta d}\right) \end{aligned} \tag{6}$$

where β can be calculated according to the experimental results. In Mo-La_2O_3 materials, the bulk concentration of elements lanthanum and oxygen is 0.024 and 0.0363 (mole fraction) respectively. The value of surface segregation factor β at different temperatures is listed in Table 2.

Table 2 Surface segregation factor of lanthanum and oxygen at different temperatures

T/K	C_{LaP}	C_{OP}	β_{La}	β_O
1123	0.1466	6.5078	0.3132	8.6281
1273	0.1812	7.4876	0.3350	9.2287
1423	0.2216	0.4123	9.1570	11.3581

Suppose

$$\frac{\sqrt{Dt}}{\beta d} = w \tag{7}$$

$F = \operatorname{erf} w$

Then Eqn.(5) can be simplified as

$$\frac{C_s^t}{C_s^\infty} = 1 - \left(1 - \frac{1}{\beta}\right)\exp[w^2(1 - F)] \tag{8}$$

The ratio C_s^t/C_s^∞ as a function of w is shown in Fig.4. In Fig.2 (Experimental curve for the ratio C_s^t/C_s^∞ vs time) and Fig.4 (Theoretical curve for the ratio C_s^t/C_s^∞ vs w), when the straight line (C_s^t/C_s^∞ = constant) parallel to t axis and w axis is drawn, three corresponding t points and w points can be obtained respectively. According to the time and value of w at different temperatures, by Eqn.(7), the diffusion coefficients of ions La^{3+} and O^{2-} at different temperatures can be obtained, as listed in Table 3.

Table 3 Diffusion coefficients of elements lanthanum and oxygen at different temperatures

T/ K	D_{La}($\times 10^{-20}$)/($m^2 \cdot s^{-1}$)	D_O($\times 10^{-20}$)/($m^2 \cdot s^{-1}$)
1 123	0.757 2	2.858 2
1 273	1.986 0	5.135 6
1 423	7.721 7	18.594 0

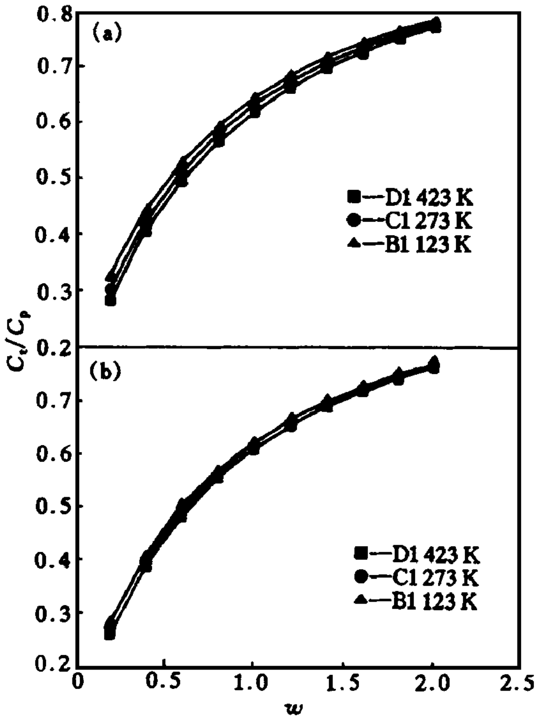

Fig.4 Theoretical curves for w dependence of ratio of concentration of lanthanum and oxygen to their equilibrium concentration

(a) —La; (b) —O

The diffusion coefficient expression is

$$D = D_0 \exp\left[-\frac{E}{RT}\right] \tag{9}$$

Then

$$\ln D = \ln D_0 - E/RT \tag{10}$$

Fig.5 shows the $\ln D$—$1/T$ linear relationship for ions La^{3+} and O^{2-} in the cathode materials. The slopes of lines 1 and 2 in Fig.4 are equal to the ratio of the diffusion activation energy of ions La^{3+} and O^{2-} to (- R) respectively. The intersection on longitudinal axis is the value of logarithmic diffusion coefficient prefactor.

Then the following general expression for grain boundary diffusion of La^{3+} and O^{2-} can be got:

$$D_{La} = 3.670\ 3 \times 10^{-16} \exp(-1.016\ 39 \times 10^5/RT)$$

$$D_O = 1.512\ 2 \times 10^{-16} \exp(-8.130\ 66 \times 10^4/RT)'$$

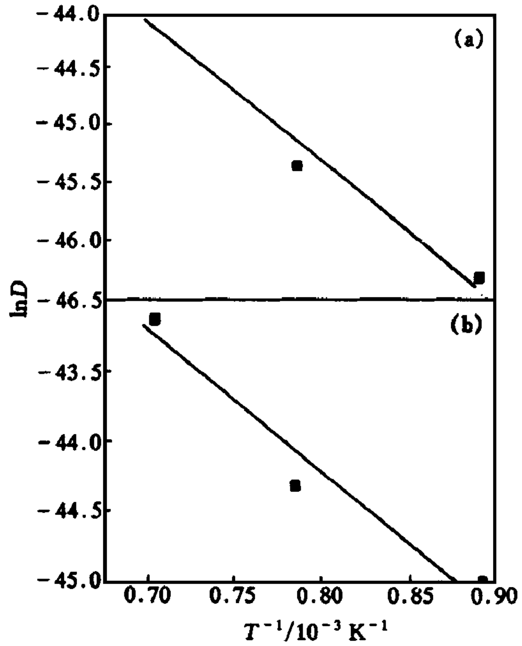

Fig.5 ln D—1/ T curves for elements lanthanum and oxygen

(a) —La; (b) —O

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