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A study of diffusion behavior of elements lanthanum and oxygen in Mo–La_2O_3 cathode

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Abstract

The diffusion behavior of elements lanthanum and oxygen in Mo–La_2O_3 cathode has been carried out by using Auger Electron Spectroscopy. Lanthanum and oxygen ions (La^{3+} and O^{2+}) diffuse from the grain boundaries to the surface. The experimental results were analyzed by kinetics of grain boundary diffusion. In the temperature range 1123 K–1423 K, the diffusion coefficients of La^{3+} and O^{2+} ions were found to fit with the following expression:

$$D_{La} = 3.6703 \times 10^{-16} \exp(-1.01639 \times 10^5/RT)\ m^2\ s^{-1}$$

$$D_O = 1.5122 \times 10^{-16} \exp(-8.13066 \times 10^4/RT)\ m^2\ s^{-1}$$

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Keywords: Diffusion; Lanthanum; Oxygen; Cathode; Kinetics; Mo–La_2O_3

1. Introduction

Mo–4 wt% La_2O_3 cathode is a new kind of cathode that appeared in recent three decade, which can substitute Th–W cathode with radioactive pollution [1–3]. In this material, lanthanum and oxygen exist in the form of lanthanum oxide (La_2O_3). When temperature raising, the amount of lanthanum oxide on the surface of cathode is increased. But how lanthanum oxide segregates onto the surface, in the form of molecule La_2O_3 or in the form of La^{3+} and O^{2+} ions (which combine into molecules La_2O_3 again on the surface), haven't been decided yet. This paper reports the investigation of diffusion of lanthanum and oxygen in Mo–La_2O_3 cathode by using Auger election microscopy

2. Experimental methods and materials

The experimental samples were three Mo–4 wt%La_2O_3 thin sheets (4 mm×4 mm×0.3 mm). Then the sheets were welded respectively onto Mo tubes which were 3.3 mm in diameter, 0.05 mm thick, 15 mm long and mounted on a standard chamber manipulator. Argon ion bombardment at 400 ev, 1 uA cm^{-2}, 10^{-10} Torr decreased the C and N below detectability and the oxygen to its initial value in the material. The sample was heated by accelerated electrons which bombarded the Mo tube and La–Mo plate. The temperature was measured with a bioptix pyrometer, temperature fluctuation within 0.5 k and relative temperature are accurate to 15 k. In the chamber pressures of $1–2\times10^{-10}$ Torr were routinely obtained with maximum pressures during heating at ~1400 k of less than 10^{-8} Torr. In this experiment, these samples were held at the temperature 1123 K, 1273 K, 1423 K for some time separately.

3. Experimental results and analysis

3.1. Results

Typical Auger electron spectra characteristic of the La–Mo surface annealed at different temperature for some time are shown in Fig. 1. It is easy to see that at room temperature the amounts of lanthanum and oxygen were low. With temperature increasing, the heights of 625 ev lanthanum Auger peak and 503 ev oxygen Auger peak

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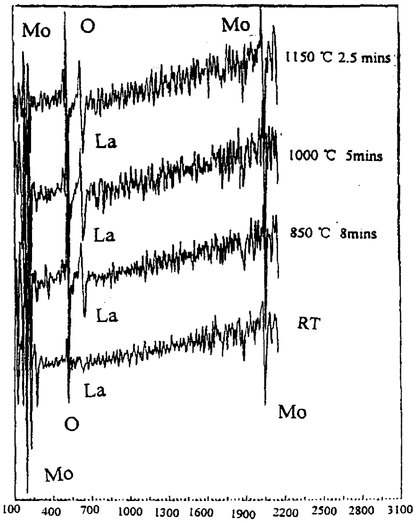

Fig. 1. Auger electron spectra of La–Mo surface.

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

t(min)	0	2	4	8	12
C_{La}/C_O 1123 K	0.2835	0.3992	0.4304	0.4582	0.4681
t(min)	0	1	3	5	7
C_{La}/C_O 1273 K	0.2835	0.4582	0.5307	0.5280	0.5409
t(min)	0	0.5	1.5	2.5	5
C_{La}/C_O 1423 K	0.2835	0.4980	0.5258	0.5334	0.5375

becomes bigger, whereas the height of 186 ev Molybdenum peak becomes smaller.

The concentration of lanthanum and oxygen on the surface can be calculated according to the peak strength for different elements measured in each spectrum. Fig. 2 shows the ratio of surface concentration of different elements to their equilibrium concentration. It can be seen in Fig. 2, 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.

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 temperature and time. 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^{3+} and 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).

We can calculate the diffusion coefficient of ions La and O 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 diffusion along the grain boundary.

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 link 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 Cb respectively. According to Fick's second Law, therefore the relevant diffusion equation is

$$\frac{\partial C}{\partial t} = \rho \frac{\partial^2 C}{\partial X^2} \tag{1}$$

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

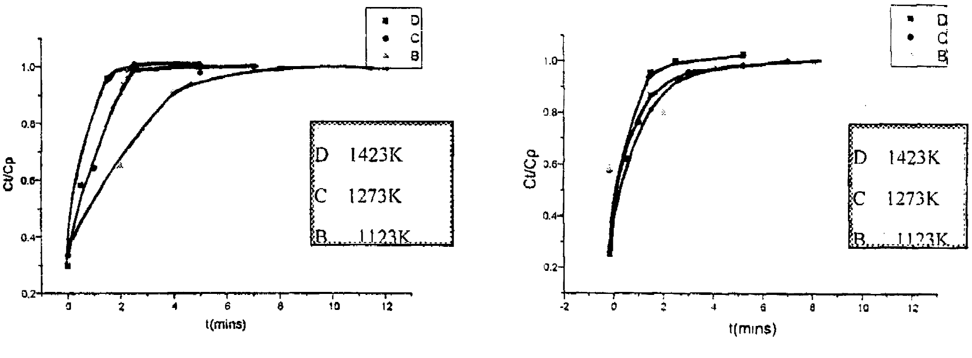

Fig. 2. The time dependence of the ratio of surface concentration of different elements to their equilibrium concentration.

$$\rho\left(\frac{\partial C_x^t}{\partial X}\right)_{x=0} = d\left(\frac{\partial C_s^t}{\partial t}\right) = \beta d\left(\frac{\partial C_x^t}{\partial t}\right)_{x=0} \qquad (2)$$

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

$$\begin{cases} D\left(\dfrac{\partial^2 C_x^t}{\partial X^2}\right) = \dfrac{\partial C_x^t}{\partial t} \\ D\left(\dfrac{\partial C_x^t}{\partial X}\right)_{x=0} = \beta d\left(\dfrac{\partial C_x^t}{\partial t}\right)_{x=0} \\ C_x^t = C_b \quad (x \to \infty) \end{cases} \qquad (3)$$

the solution is

$$C_x^t = C_b - C_b\left(1 - \frac{1}{\beta}\right)\exp\left(\frac{x}{\beta d} + \frac{\rho t}{\beta^2 d^2}\right) erfc\left(\frac{x}{2\sqrt{Dt}} + \frac{\sqrt{Dt}}{\beta d}\right) \qquad (4)$$

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 Eq. (4) in the form

$$\frac{C_s^t}{C_s^\infty} = 1 - \left(1 - \frac{1}{\beta}\right)\exp\left(\frac{Dt}{\beta^2 d^2}\right)\left(1 - erf\,\frac{\sqrt{Dt}}{\beta d}\right) \qquad (5)$$

where β can be calculated according to the experimental results. In 4 wt% La_2O_3–Mo materials, the bulk concentration of elements lanthanum and oxygen is 0.024 and 0.0363 (atomic weight), respectively. The value of surface segregation factor β at different temperature is shown in Table 2. Suppose

$$\frac{\sqrt{Dt}}{\beta d} = w \qquad (6)$$

$$F = erfw$$

Then formula (5) can be simplified as

$$\frac{C_s^t}{C_s^\infty} = 1 - \left(1 - \frac{1}{\beta}\right)\exp(w^2)(1 - F) \qquad (7)$$

Table 3
Diffusion coefficient of elements lanthanum and oxygen at different temperature

T (K) $D(\times 10^{-20}\ m^2\ s^{-1})$	1123	1273	1423
La	0.7572	1.9860	7.7217
O	2.8582	5.1356	18.5940

The ratio C_s^t/C_s^∞ as a function of w is shown in Fig. 3. In Fig. 2 (Experimental curve for the ratio C_s^t/C_s^∞ vs. time) and Fig. 3 (Theoretical curve for the ratio C_s^t/C_s^∞ vs. w), when the straight line (that is, C_s^t/C_s^∞ = constant) parallel to t axis (in Fig. 2) and w (in Fig. 3) is drawn, three corresponding time points and w points can be obtained respectively. According to the time and the value of w at different temperature, by formula (6), the diffusion coefficients of ions La^{3+} and O^{2-} at different temperature can be obtained, shown in Table 3.

The diffusion coefficient expression is

$$D = D_0 \exp\left(-\frac{E}{RT}\right) \qquad (8)$$

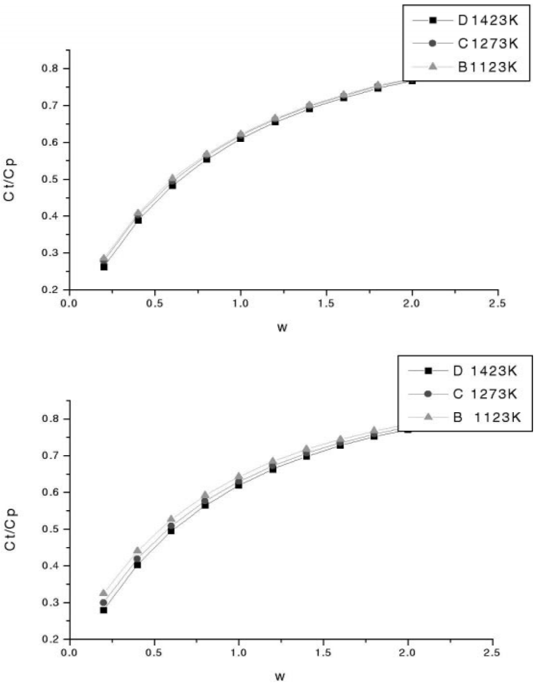

Fig. 3. Theoretical curves for w dependence of ratio of concentration of lanthanum and oxygen to their equilibrium concentration a. La b. O.

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

T	1123 K	1273 K	1423 K		1123 K	1273 K	1423 K
C_{LaP}	0.1466	0.1812	0.2216	C_{oP}	0.3132	0.3350	0.4123
β_{La}	6.5078	7.4876	9.1570	β_0	8.6281	9.2287	11.3581

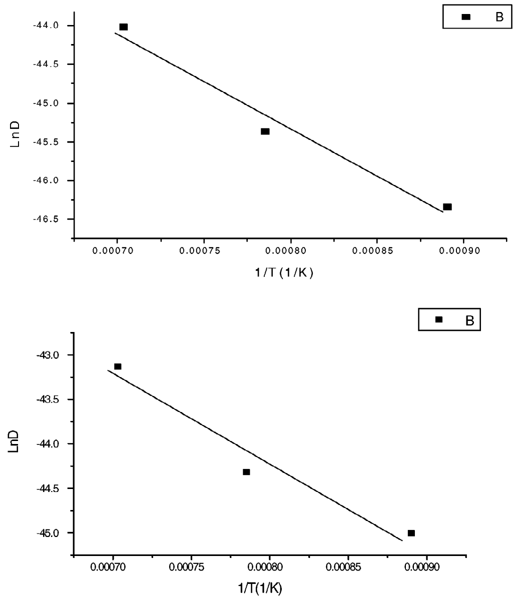

Fig. 4. Ln $D - 1/T$ curve for elements Lanthanum and Oxygen.

Then

$$\mathrm{Ln}\, D = \mathrm{Ln}\, D_0 - E/RT \tag{9}$$

Fig. 4 shows the LnD–$1/T$ linear relationship for ions La^{3+} and O^{2-} in the cathode materials. By the slopes of lines a and b in Fig. 4, the diffusion activation energy of ions La^{3+} and O^{2-} can be obtained respectively. The intersection on longitudinal axis is the value of logarithmic diffusion coefficient prefactor. Then the following general expression for grain boundary diffusion of ions La^{3+} and O^{2-} can be got:

$$D_{\mathrm{La}} = 3.6703 \times 10^{-16} \exp(-1.01639 \times 10^5/RT)\ \mathrm{m^2\ s^{-1}}$$

$$D_{\mathrm{O}} = 1.5122 \times 10^{-16} \exp(-8.13066 \times 10^4/RT)\ \mathrm{m^2\ s^{-1}}$$

4. Conclusions

(1) Lanthanum oxide in Mo–La_2O_3 cathode materials segregate onto the surface in the form of ions La^{3+} and O^{2+} and recombine into La_2O_3 molecules on the surface.

(2) The temperature dependence of grain diffusion coefficients of ions La^{3+} and O^{2+} in 1123 K–1423 K temperature range could be expressed by the following equations:

$$D_{\mathrm{La}} = 3.6703 \times 10^{-16} \exp(-1.01639 \times 10^5/RT)\ \mathrm{m^2\ s^{-1}}$$

$$D_{\mathrm{O}} = 1.5122 \times 10^{-16} \exp(-8.13066 \times 10^4/RT)\ \mathrm{m^2\ s^{-1}}$$

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