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Thermionic properties of Mo-La_2O_3 cathode wires ①

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[Abstract] The recent advances in Mo-La_2O_3 thermionic cathode materials were presented. It is shown that Mo-La_2O_3 cathode has better ductility, radioactive pollution-free, excellent thermionic electron-emission properties and lower operating temperature compared with W-ThO_2 cathode. At operating temperature 1 350~1 400 ℃, the average saturation current of the Mo-La_2O_3 cathode is 118 mA, the corresponding average current density is 367 mA/cm^2, and the average emission efficiency is 11.8 mA/W. The lifetime of diode is more than 2 000 h when the stable emission current is 80 mA. Moreover, the lifetime of practical 6T51-type triode is more than 1 000 h. These advances show that the Mo-La_2O_3 cathode electron tube is closer to industry application.

[Key words] molybdenum; rare earth oxide; cathode; thermionic emission
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1 INTRODUCTION

Thoriated tungsten (W-ThO_2) has been the traditional thermionic cathode materials for powerful electron tubes, which widely used in industry such as broadcast, communication, military devices owing to its high creep-resistant property at elevated temperature, as well as good and stable electron emission capacity since 1930s. However, the serious problems such as radioactive pollution, much higher operating temperature (~1 800 ℃) and its drastic brittleness after carbonization have not been solved for several decades. In the past ten years, molybdenum, another important refractory metal, was considered as heated cathodes to replace the radioactive W-ThO_2 cathode by doping with rare earth oxides such as La_2O_3, Y_2O_3, and Sc_2O_3. The previous research work has shown that the Mo-La_2O_3 cathode not only has high-temperature strength and good ambient ductility, but also possesses very good electron-emission capacity at lower operating temperature, high emissive efficiency, and a pulse ratio superior to that of the W-ThO_2 cathode[1]. However, it was found that the stable emission only last several hours, and emission current of the Mo-La_2O_3 electron tube attenuated with time rapidly. In order to obtain stable emission of Mo-La_2O_3 tubes, much effort have been done on the material composition, the tube design, and its suitable technical parameters and operating mechanisms in recent years[2~4]. Thus the great progress has been made in the emission stability of Mo-La_2O_3 tubes.

2 EXPERIMENTAL

An aqueous solutions of $La(NO_3)_3$ containing 4.0% La_2O_3 (mass fraction) was added to MoO_2 powder. The doped MoO_2 powder was reduced to molybdenum metallic powder in dry hydrogen, respectively, from 550 ℃ to 950 ℃. The Mo powder was then pressed in steel dies and sintered by electric resistance heating in dry hydrogen at 90% of its fuse current for 20 min. The density of sintered ingot is $(9.8\sim 9.9)\times 10^3$ kg/m^3. The sintered ingots were then swaged and drawn into wires of 0.26 mm and 1.04 mm, respectively in diameter from 1 300 ℃ to 500 ℃.

The experimental diodes were specially designed with straight wire or screw cathodes of Mo-La_2O_3 wires of 0.26 mm in diameter and a cylinder Mo anode, and a practical 6T51-type triode was also designed with screw cathode of Mo-La_2O_3 wires of 1.04 mm in diameter. The basic emitting properties and lifetime have been systematically examined. The phases and their distribution were analyzed by means of XRD and XPS.

3 RESULTS AND DISCUSSION

3.1 Changes of dopants in Mo powder and sintered ingot

Different dopants are found in Mo powder and sintered ingot. XRD results show that rare earth dopants exist in the form of both single rare earth oxide (La_2O_3) and compounds (La_2MoO_6, $La_2Mo_3O_{12}$)

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in Mo powders, but only single rare earth oxide (La_2O_3) exists in sintered ingot, as shown in Fig. 1.

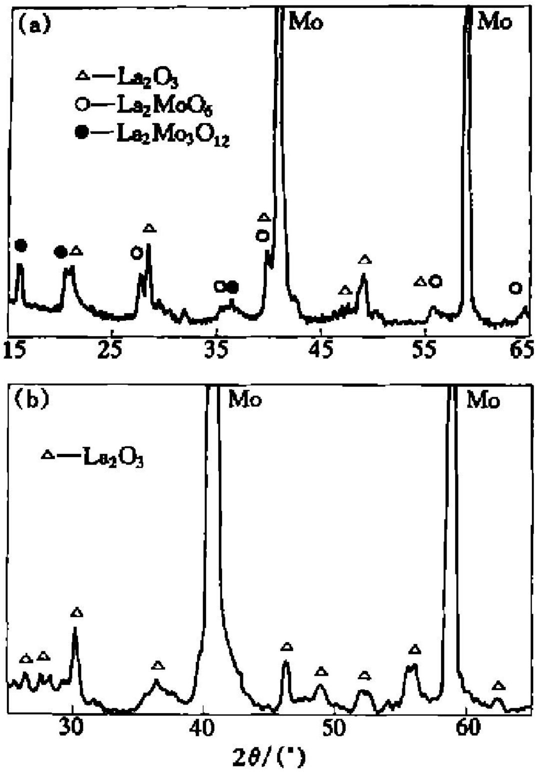

Fig. 1 XRD patterns of doped Mo powder and ingot
(a) —Mo powder; (b) —Sintered Mo ingot

3.2 Design of standard diode and emission properties of Mo-La_2O_3 cathode

A "standard" diode with a straight wire cathode of 0.26 mm in diameter has been designed and tested. The anode is 75 mm in inner diameter and 10 mm in height. The relationship between the standard diode current and voltage is given as

$$I_a = 35.89 \times 10^{-3}\ V_a^{3/2} \tag{1}$$

where I_a is the anode current, V_a the anode voltage.

The theoretical calculation and experimental results are compared in Table 1, showing good agreement. At the operating temperature of 1 210 ℃, the average saturation current of Mo-La_2O_3 standard diode is 29.8 mA, as shown in Fig. 2. The corresponding current density reaches 367 mA/cm^2, and the emission efficiency is 13.6 mA/W. Up to now, the lifetime of these diodes is 1 340 h, as shown in Fig. 3, indicating that thermionic emission is stable.

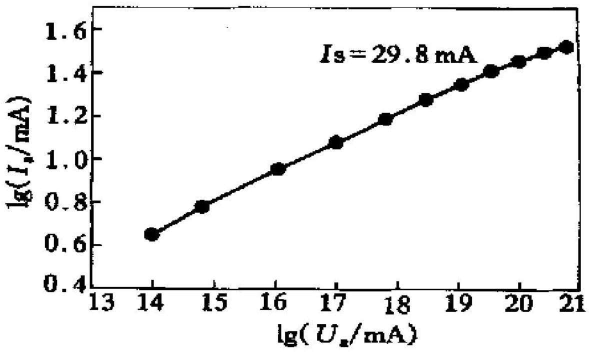

Fig. 2 Dependence of anode current on voltage of Mo-La_2O_3 diode

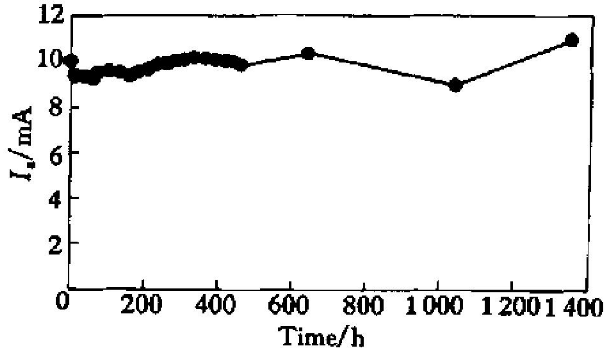

Fig. 3 Relationship between lifetime and emission current in Mo-La_2O_3 diode (1 240 ℃)

3.3 Emission properties of practical diode of Mo-La_2O_3 cathode

On the basis of a "standard" diode, the practical diode was made with a screw cathode and tested. At operating temperature of 1 350~1 400 ℃, the average saturation current of ten tubes is 118 mA, the corresponding average current density is 367 mA/cm^2, and the average emission efficiency is 11.8 mA/W. In particular, the lifetime tested in the standard procedure is more than 3 000 h when the stable emission current is 80 mA.

3.4 Lifetime of practical triode of Mo-La_2O_3 cathode

The practical triode equipped with the Mo-La_2O_3 cathode was designed according to the size and shape of W-ThO_2 cathode in 6T51-type electron tube. The Mo-La_2O_3 cathode was carbonized at 1 460 ℃, whose temperature is about 250~300 ℃ lower than that of W-ThO_2 cathode. The Mo_2C with thickness of 20~30 μm has been formed on the surface of Mo-La_2O_3

Table 1 Relationship of current with voltage in Mo-La_2O_3 standard diode (mA)

Tubes	20 V	25 V	30 V	40 V	50 V	60 V	80 V	100 V
Theoretical	3.2	4.5	5.9	9.1	12.7	16.7	25.7	35.9
1#	–	4.5	5.8	8.8	12.2	15.5	23.5	31.5
2#	–	4.5	6.0	9.2	12.8	16.2	24.8	32.5
3#	–	4.5	5.8	9.0	12.5	15.8	24.0	32.5

wires. When the operating temperature is 300 ℃ lower than that of W-ThO_2 tube, the pulse emitting-property reaches the technical standard of W-ThO_2 tube. More importantly, the service lifetime of the 6T51-type tube with Mo-La_2O_3 cathode has been 1200 h under on-off working conditions, and emission is still very stable (Fig. 4), indicating that the 6T51-type electron tube with Mo-La_2O_3 cathode has reached the criterion of industrial application.

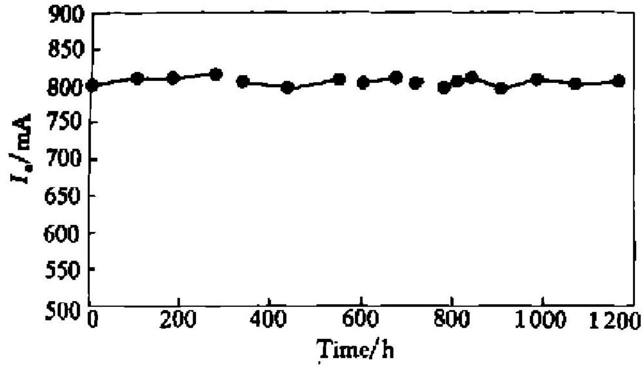

Fig. 4 Stable emission current in practical 6T51-type electron tubes up to 1200 h

3.5 Emission mechanisms of Mo-La_2O_3 cathode

The emission stability of Mo-La_2O_3 cathode is largely dependent on the behavior of La or La_2O_3. The high temperature XPS results indicate that the concentration of La_2O_3 on the cathode surface obviously increased with increasing temperature. With semiquantitative calculations at 1350~1450 ℃, it is about 4 times as much as that at room temperature[5,6]. However, the valence of La in electron tube is difficult to be determined though more effort have been done because of the experimental skill restriction and rare earth element reactivity. In order to exactly know the existing form of La on the surface of Mo-La_2O_3 cathode wire at high temperature, a dynamic experiment in XPS spectrometer chamber was designed. An area of 4.0 mm × 4.0 mm Mo-La_2O_3 sheet with thickness of 0.5 mm was carbonized at 1400 ℃ to form Mo_2C on the surface. Then the sample was heated at 1350 ℃ for 10 min, and La 3d spectra were obtained and analyzed. A new important results was found to show confirmly that the reaction between Mo_2C and La_2O_3 can take place at a temperature lower than 1250 ℃ to produce the elemental La (as shown in Fig. 5). According to this experimental fact, the emission mechanism of the Mo-La_2O_3 cathode is similar to the mono-atomic layer mechanism of the W-ThO_2 cathode, and the emission stability can be reasonably explained according to the mechanism. The emission stability for Mo-La_2O_3 cathode depends on the equilibrium between the diffusion and evaporation of La. As the diffusion and evaporation are both controlled by temperature, an optimum activation and operating temperature is the key to produce highly stable emission current. The systematic experiments indicated that the stability is much sensitive to the temperature. As the melting point of La is 920 ℃, much lower than that of Th (1650 ℃), the stable emission of Mo-La_2O_3 cathode should be restricted to lower than 1400 ℃.

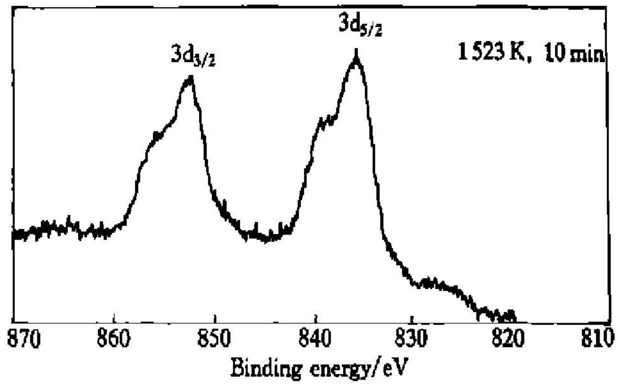

Fig. 5 X-ray photoelectron spectra of La 3d in carbonized Mo-La_2O_3 material

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