THERMODYNAMIC ANALYSIS OF Mo-La_2O_3 THERMIONIC CATHODE WIRE①

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ABSTRACT Both thermodynamic calculation and experimental observation show that no elemental lanthanum can be obtained by reduction or thermal decomposition at high temperature. The emission mechanism of Mo-La_2O_3(Mo-La) cathode is much different from the mono-atomic layer mechanism of Th-W cathode. A new emission mechanism of Mo-La cathode has been put forward, which can reasonably explain the emission behavior of Mo-La_2O_3 cathode.

Key words molybdenum La_2O_3 cathode thermodynamics

1 INTRODUCTION

With the rapid development of broadcast and television, and the increasing need of large or middle-power high frequency heater in industry, the large-power electron tubes have been becoming one of the most important and irreplaceable electron vacuum instruments. The cathode of large-power tubes is made of tungsten-thorium oxide (Th-W) wire or sheet, which has disadvantage of drastic brittleness, radioactive pollution and higher operating temperature (more than 1 800 ℃). In the late 1970s, a kind of coated Mo-La cathode had been developed by Charley Brown[1-3]. Also the indirect Mo-La sintered cathode has been developed by researchers of California University of U. S. A, which can produce large current plasma, and used for plasma sources in vacuum instruments[4]. Since the middle 1980s, we have been making a systematic study on the properties and microstructures of Mo wires or sheets doped with lanthanum oxide (Mo-La_2O_3), and found that the mechanical properties of Mo are greatly improved and the work function of Mo is lowered by addition of lanthanum oxide to molybdenum. The electron tubes equipped with the Mo-La cathode were designed according to the size and shape of Th-W cathode in a FU 805-type electron tube, and it is shown that Mo-La tubes have as much emission current as Th-W tube, but higher emission efficiency and 150~ 200 ℃ lower operating temperature than Th-W tube[5]. However, the current of Mo-La tube was attenuated with time, whereas the current of Th-W tube was stable. Buxbaum *et al* thought that the emission mechanism of Mo-La cathode is similar to that of Th-W cathode, that is, so called mono-atomic layer mechanism, which can be described as: A carbide layer was formed on surface of cathode after carbonization. Using carbide as a reductant, the La or Th atom was reduced from La_2O_3 or ThO_2 at certain temperature, then La or Th atoms formed mono-atomic layer on cathode surface, which lowered the work function of Mo or W. The stable emission depends on the balance between evaporation of surface atoms and the diffusion of La or Th atom from the bulk to surface. We think that the emission mechanism of Mo-La cathode is greatly different from that of Th-W cathode, and a new emission mechanism is proposed on the basis of thermody-

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namic analysis and XPS observation.

2 THERMODYNAMIC CALCULATION

As reported in Ref. [6], La_2O_3 may be reduced by Mo_2C into La element at high temperature. The chemical reaction involved can be written as:

$$3Mo_2C + La_2O_3 = 2La + 3CO\uparrow + 6Mo \quad (1)$$

According to the Gibbs free energy expression, we have

$$\Delta G = \Delta G_{298} + \int_{298}^{T} \Delta C_p \, dT - T\int_{298}^{T} \Delta C_p / T \, dT \quad (2a)$$

$$\Delta C_p = 2C_p(La) + 3C_p(CO) + 6C_p(Mo) - 3C_p(Mo_2C) - C_p(La_2O_3) \quad (2b)$$

Allowing for the allotropic transformation (1 141 K) and phase transition (1 193 K) of lanthanum, the calculated values(J) of Gibbs free energy of reaction (1) is as follows:

$$\Delta G_1 = 1\,629\,804.89 + 60.65T\ln T - 12.79\times10^{-3}T^2 - 23.38\times10^{5}T^{-1} - 892.78T \quad (T < 1\,141\ K) \quad (3)$$

$$\Delta G_2 = 1\,126\,568.20 + 44.52T\ln T - 6.10\times10^{-3}T^2 - 23.35\times10^{5}T^{-1} - 345.77T \quad (1\,141\ K < T < 1\,193\ K) \quad (4)$$

$$\Delta G_3 = 1\,126\,035.48 + 42.85T\ln T - 6.10\times10^{-3}T^2 - 23.35\times10^{5}T^{-1} - 333.44T \quad (1\,193\ K < T < 3\,693\ K) \quad (5)$$

At operating temperature T = 2 000 K, the value of Gibbs free energy by substituting T = 2 000 K into reaction (5), may be written as:

$$\Delta G = 1\,087\,404.08 > 0$$

which means reaction (1) can not happen, that is, La_2O_3 is not able to be reduced into elemental lanthanum. The following experimental results will confirm this caculation.

3 EXPERIMENTAL PROCUDURE AND RESULTS

XPS analysis of the tested Mo-La cathode wires from Mo-La tested shows that no elemental La is found on cathode surface. Either the wire is too thinner (d 0.27 mm) or La reacts easily with oxygen affects the correctness of XPS results. In order to eliminate the factors of sample size, we prepared the samples large enough for XPS and treated them in atmosphere of purified N_2.

The carbide Mo_2C was synthesized with a mixture of 2 mol Mo powder and 1 mol C powder at high temperature in a furnace. Then Mo_2C powder was mixed with La_2O_3 powder and pressed into rectangular slabs and sintered at 1 600 ℃, 8 h in an atmosphere of flowing argon. The samples have a cross section of 5 mm × 5 mm, and were broken in a high pure N_2. The XPS and XRD analyses were carried out on PHL-5300 X-ray phonon spectrometer and PW1700 X-ray diffractometer, respectively. The thermal weight analysis of La_2O_3 powder was also conducted on a thermal pan.

The XPS analysis shows that elements of Mo, C, O and La exist in the sintered samples, as shown in Fig. 1. From the values of binding energy, it is known that these elements exist in the form of La_2O_3 and Mo_2C, and the valence of La is plus three. XRD result is in agreement with XPS analysis, showing La exists in the form of La_2O_3 (Fig. 2). From both XPS and XRD analyses, it is conclucled that La in the samples does exist in the form of La_2O_3, exhibiting plus three valence, and no elemental La was observed.

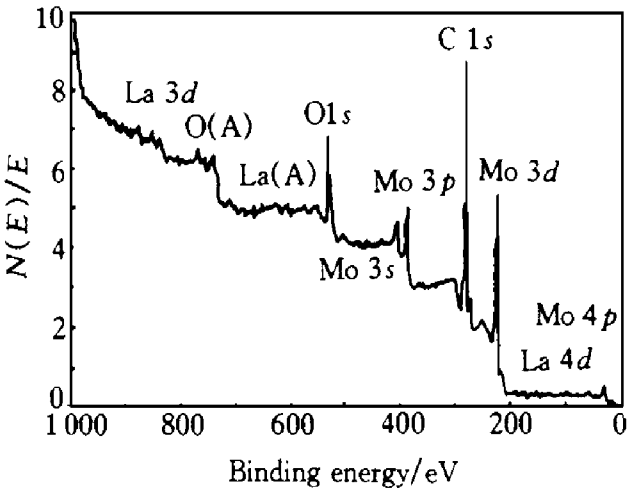

Fig. 1 XPS spectrum of La_2O_3+ Mo_2C samples

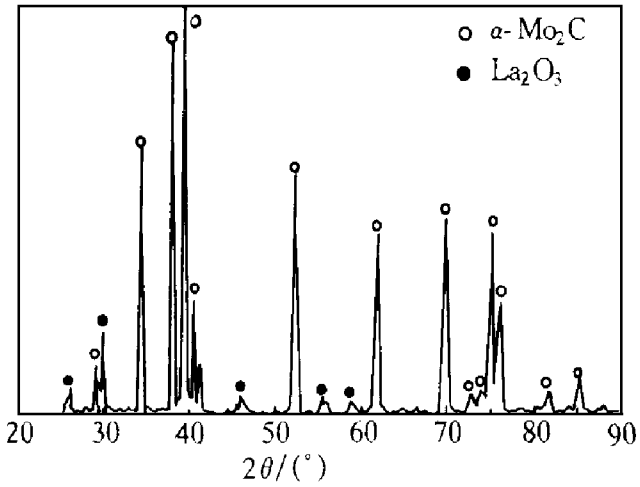

Fig. 2 XRD pattern of La_2O_3(20%) + Mo_2C sintered at 1 600 ℃ for 8 h

Although the elemental La can not be produced by reduction, is there any possibility that elemental La is liberated from the compound at high temperture? Fig. 3 shows the result of thermal weight analysis of La_2O_3. As well known, La_2O_3 is easy to absorb water vapour and carbon dioxide. When it is heated to certain temperature, La_2O_3 will lose its bonded water and give out the absorbed gas, resulting in weight loss of La_2O_3. The theoretical calculation based on relation between the reaction free energy and balance constants indicates that the thermal decomposition pressure of La_2O_3 is lower than 10^{-14} Pa at 2000 K. Thus La_2O_3 can not be decomposed in the usual vacuum tube with a pressure in the range of 10^{-1} to 10^{-5} Pa. The thermal weight curve also demonstrates that La_2O_3 is very stable and no decomposition occurs above 1 000 ℃.

As mentioned above, both theoretical calculation and experimental observation shows no elemental decomposition of La_2O_3. Therefore, the electron emission behavior of Mo-La cathode can not be explained reasonably by mono-atomic layer mechanism of Th-W cathode. A new emission mechanism of Mo-La cathode is proposed.

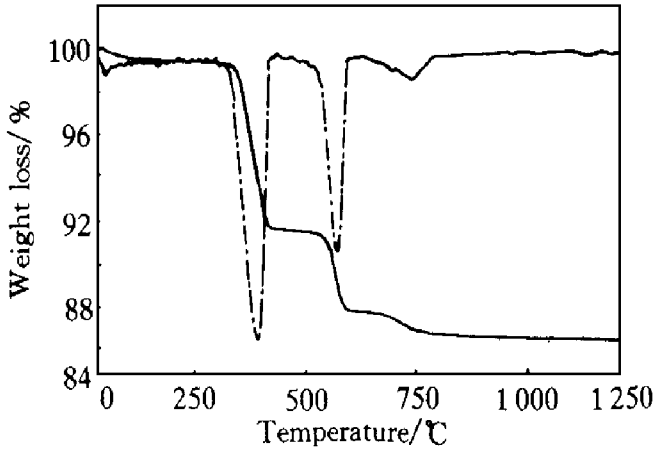

Fig. 3 Thermal weight curve of La_2O_3

4 ELECTRON EMISSION MECHANISM OF Mo-La CATHODE

In Mo-La cathode, a large amount of La_2O_3 particles with an average size of 1 μm is distributed dispersely in matrix and on surface of molybdenum.

Lanthanum is an active metal element and is easy to lose electrons, becoming plus three ion, when it combines with nonmetallic elements such as oxygen. As an electrical field is applied between cathode and anode, the molecule La_2O_3 is inclined to be arranged along a preferred orientation on cathode surface. Thus the plus ion La^{3+} is toward the surface of cathode, and the minus ion O^{2-} is far from the surface of cathode(Fig. 4). The electrons in La^{3+} and that on the surface layer of Mo may react with each other, resulting in formation of dipoles on the surface of Mo. Thus a high emission current density is obtained. Because a lot of emission centre is formed on the surface of Mo (5.04×10^{10} La_2O_3 molecules per cubic micrometer). Finally, the high total emission current can be obtained in

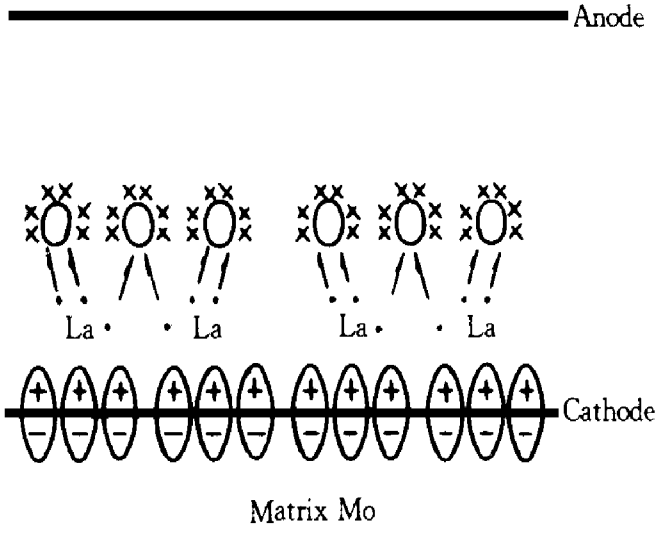

Fig. 4 Interactions of La_2O_3 arranged on cathode surface with matrix Mo

Mo-La cathode.

In our previous research, it was found that the carbonization is very helpful to increase the emission current of Mo-La cathode[5]. The structure of carbonized Mo-La wire is shown in Fig. 5. The lump carbide Mo_2C is formed on the surface of cathode wire, which is favorable for the transport of La_2O_3 from Mo matrix towards the surface, and maintains the balance between evaporation and transportation of La_2O_3. Thus, a stable and high emission is entirely obtained in Mo-La cathode tubes. The detailed transporting mechanism of La_2O_3 is under investigation.

Fig. 5 Microstructures of carbonized Mo-La cathode wire

5 SUMMARY

The theoretical calculation and experimental observations show that the elemental La can not be produced by reduction and thermal decomposition at high temperature. The La_2O_3 is a stable compound at high temperature. The emission mechanism of Mo-La cathode is much different from the mono-atomic layer mechanism of Th-W cathode because no elemental La is found. The La_2O_3 particles distributed dispersely on the surface of cathode may be arranged in some preferred orientation in the function of electrical field and form a lot of emission centre, thus a higher and stable emission current is obtained in Mo-La cathode tubes.

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