[Article ID] 1003 - 6326(2000)05 - 0576 - 04

Emission mechanism of Mo-Y_2O_3 cathode①

WANG Jin-shu(王金淑), ZHOU Mei-ling(周美玲), NIE Zuo-ren(聂祚仁), ZHANG Jiu-xing(张久兴), LUO Feng-hua(罗丰华), ZUO Tie-yong(左铁镛)
(School of Materials Science and Engineering, Beijing Polytechnic University, Beijing 100022, P.R.China)

[Abstract] The valence of element yttrium of Y_2O_3-Mo cathode material was studied by thermal analysis, X-ray diffraction analysis, scanning electron microscopy and X-ray photoelectron spectra, and the emission mechanism of Mo-Y_2O_3 cathode was discussed. It was proved that reaction between powder Y_2O_3 and Mo_2C can happen at 1173 K, and Y_2O_3 be reduced to metallic yttrium. After the powder mixture of Y_2O_3 and Mo_2C is heat treated at 1873 K, yttrium exists in two kinds of state—yttrium of zero valence and yttrium of three valences. The formation of monoatomic layer of metallic yttrium at the surface of filament is the cause of emissivity of the cathode. Yttrium at the surface doesn't provide emission current, but the momoatomic active surface layer has a lower work function than clean molybdenum.

[Key words] emission mechanism; Mo-Y_2O_3 cathode; valence; yttrium
[CLC number] TG146.4; O462.1; O614.33 [Document code] A

1 INTRODUCTION

Mo-Y_2O_3 is a new kind of rare earth-molybdenum thermionic cathode materials[1]. It is expected to substitute radioactive W-ThO_2 cathode materials in the future. Since the middle of 1970s, people have mainly done research on one kind of rare earth-molybdenum cathode—Mo-La_2O_3 cathode[2~6]. At the same time, the emission mechanism of Mo-La_2O_3 cathode has been discussed. The emission of Mo-La_2O_3 cathode can be explained by three mechanisms. Imitating the traditional monoatomic mechanism of Th-W cathode, people think that the monoatomic layer of metallic lanthanum at the surface of cathode can be created after reduction of La_2O_3(ThO_2 in W-ThO_2 cathode) to metallic lanthanum (Th in W-ThO_2 cathode) by Mo_2C (W_2C in W-ThO_2 cathode) during the activating and operation period of the cathode. Lanthanum at the surface doesn't provide emission current, but the monoatomic active surface layer has a lower work function than clean molybdenum. The other two emission mechanisms, molecule polarization mechanism[7] and nanoparticle(film) mechanism[8], appeared in recent years. In these two mechanisms, La_2O_3 molecules or LaO_x ($x < 1.5$) nanoparticles play an important role in the emission. The key to the correct emission mechanism is the valence of element lanthanum (zero for metallic lanthanum, positive three for La_2O_3, or less than three for LaO_x). The manufacturing process of Mo-Y_2O_3 cathode materials is similar to that of Mo-La_2O_3 cathode materials. Mo-Y_2O_3 cathode has lower emissivity than Mo-La_2O_3 cathode, but has better emission stability than Mo-La_2O_3 cathode. In the emission of Mo-Y_2O_3 cathode, the valence of yttrium in the cathode during the operation period of Mo-Y_2O_3 cathode is the key to discussing the emission mechanism of this cathode. Yttrium and lanthanum are both rare earth elements. They have the similar physical and chemical properties. Therefore, the analysis of valence of yttrium is very useful for the analysis of valence of rare earth element in other kinds of rare earth-molybdenum cathodes, and the study of emission mechanism of Mo-Y_2O_3 cathode can serve as a guide for that of other rare earth-molybdenum cathodes.

2 EXPERIMENTAL

According to monoatomic layer emission mechanism, Mo_2C may reduce Y_2O_3 to metallic yttrium at high temperature. The chemical reaction involved can be written as

$$Y_2O_3 + 3\,Mo_2C = 2\,Y + 6\,Mo + 3\,CO \quad (1)$$

Allowing for the allotropic transformation and phase transformation of yttrium, the calculated value (J) of Gibbs free energy of Reaction (1) is as follows:

$$\Delta G^{\ominus} = 149.336\times10^{-3}T^2 - 1313.168T - 211.812\times10^{5}T^{-1} + 1777195.708 + 105.733T\ln T \quad (1500 < T < 1752)$$

$$\Delta G^{\ominus} = -20.816\times10^{-3}T^2 - 1158.204T - 16.506\times10^{4}T^{-1} + 83.617T\ln T + 1771767.164 \quad (1752 < T < 1799)$$

$$\Delta G^{\ominus} = -20.815\times10^{-3}T^2 - 1089.827T +$$

① [Foundation item] Project (G1998061316) supported by "973" Program
[Received date] 1999-09-20; [Accepted date] 2000-01-30

$$49.518\times10^5\,T^{-1}+74.077\,T\ln T+1\,806\,801.67 \quad (1\,799<T<2\,000)$$

The working temperature of Mo-Y_2O_3 cathodes in electron tubes is more than 1 573 K. The vacuum in the tubes is 10^{-4} Pa. Taking the evaporation of yttrium into consideration, we can get the Gibbs free energy expression:

$$\left.\begin{aligned}\Delta G=\Delta G^{\ominus}+19.147\,T\lg\frac{p_Y^2\cdot p_{CO}^3}{(p^{\theta})^5}\\ p^{\theta}=1.013\times10^5\ \text{Pa}\end{aligned}\right\} \quad (2)$$

Under the working condition, the value of Gibbs free energy of Reaction (1) is negative, so the reaction above can take place. A book by Minanov[9], however, showed that except Eu_2O_3, Sm_2O_3 and Yb_2O_3, the other kinds of rare earth oxides have very good chemical stability because of their high heat of formation. The three kinds of rare earth oxide above will transform into oxides containing less oxygen in ultra high vacuum and at high temperature. According to Minanov, yttrium oxide can not be reduced by molybdenum carbide. The above two conclusions contradict each other. It needs experiments to testify whether the Reaction (1) could take place, so the following experiments have been carried out.

2.1 Thermal analysis

The powder mixture of carbon and molybdenum was held at 1 673 K for 2 h to form Mo_2C. Then Y_2O_3 40 % by mass was mixed with Mo_2C 60 % by mass. The powder mixture was heated to 1 723 K at a heat rate of 20 K/min in a STA Scientific-1500 Thermal Analysis Instrument under the protection of argon.

2.2 XRD and XPS analysis

The powder mixture Y_2O_3 (40 %) and Mo_2C (60 %) was heated to 973 K, 1 673 K separately and held for 2 h. After cooling to room temperature under the protection of argon, XRD analysis on the composition of mixture was carried out. The powder mixture (Y_2O_3 40 %, Mo_2C 60 %) was held at 1 873 K for 2 h under the same condition. After cooling to room temperature, the mixture was sealed in a bottle full of high purity argon. The bottle was opened in a chamber full of high purity nitrogen. After the powder mixture was milled, it was sent to the ultra vacuum chamber supplied with PHL-5300 Spectromer.

3 RESULTS AND DISCUSSION

3.1 Thermal analysis

Fig.1 shows the result of thermal analysis of powder mixture of Y_2O_3 and Mo_2C. The sample loses the absorbed water at 533 K. Nothing happens at 573 ~1 173 K. When it is heated to 1 173 K, the sample becomes lighter because of gas evolution, and then endothermic reaction happens at about 1 271 K. With increasing the temperature, some substances change its structure at about 1 523 K because there is no thermal mass loss when an endothermic peak appears. Molybdenum changes its structure at 1 475 K[10]. Because the temperature is increased rapidly during the thermal analysis experiment (20 K/min), the structure change takes place at higher temperature. So the endothermic peak at 1 523 K in the thermogravimetric curve may result from the change of molybdenum structure. Molybdenum is the reaction product of Y_2O_3 and Mo_2C.

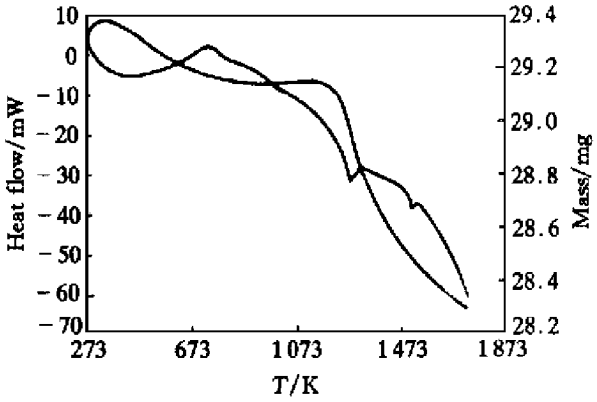

Fig.1 Thermogravimetric curve for powder mixture of Y_2O_3 and Mo_2C

From the analysis above, it can be concluded that the chemical reaction between Y_2O_3 and Mo_2C takes place at 1 173 K. The following experiments have been carried out in order to make the reaction process clear.

3.2 Study of reaction process

After the powder mixture of Y_2O_3 and Mo_2C was held at 973 K for 2 h, the XRD analysis result shows no phase transformation takes place in the sample. After the sample was held at 1 673 K for 2 h, molybdenum peaks were found apart from Y_2O_3 and Mo_2C peaks (Fig.2). This result agrees with the thermal analysis result. After the powder mixture of Y_2O_3 and Mo_2C was held at 1 873 K for 2 h, Mo_2C peaks disappeared in the XRD spectrum, and only molybdenum and Y_2O_3 peaks were found (see Fig.2 (b)). The shape of powder mixture shows a little sintered state (see Fig.3(a)), compared with that after heat treated at 1 673 K for 2 h (in the shape of powder) (see Fig.3(b)). The shape change of powder mixture shows that a liquid substance appears during heat treatment. This substance must be yttrium because only yttrium in the mixture can melt at 1 873 K. The melting points of all substance in the mixture are: 2893 K for Mo, 2708 K for Y_2O_3, 2678 K for Mo_2C, 1 799 K for Y. No substance melts at 1 673 K, so the mixture exists in the shape of powder. No yttrium being found in the XRD spectra can be explained by the rapid oxidation of active metallic

yttrium when exposed to oxygen.

The conclusion above shows that Mo_2C may reduce Y_2O_3. XPS analysis result (Fig.4) confirms this conclusion. The $Y3d_{5/2}$ spectrum of powder mixture after held at 1 873 K for 2 h is composed of two overlapping peaks at 155.85 eV and 156.85 eV. The position of peak indicates a binding energy of 156.85 eV for Y_2O_3, 155.85 eV for metallic yttrium. The $Y3d_{3/2}$ spectrum also indicates that yttrium in powder mixture exists in two chemical state, i.e. Y^0 and Y^{3+}. The atomic percentage of yttrium in different chemical states shows that there are 19 % metallic yttrium and 81 % yttrium of three valences.

4 DISCUSSION

Because yttrium oxide can be reduced to metallic yttrium by molybdenum carbide, the emission of Mo-Y_2O_3 cathode can be explained by the monoatomic layer mechanism. The yttrium atoms on the surface of molybdenum do not provide emission current, but the monoatomic active surface layer has a lower work function than clean molybdenum and help the electrons to escape from the molybdenum substrate.

When metallic yttrium atoms are absorbed on the surface of molybdenum, yttrium atoms become polarized. Compared with molybdenum, yttrium has positive charges, so the positive parts of yttrium dipoles arrange toward the outside, as shown in Fig.5. These dipoles are induction dipoles. The polarization of these dipoles results from the displacement of the center of electron cloud from atomic nucleus in the electronic field. If yttrium atoms form a uniform atomic layer on the surface of molybdenum, the barrier potential decreases by enp/ε_0 (n—the number of atoms absorbed on the surface of the substrate; p—dipole moment; ε_0—capacity factor). The work function decrease by

$$\Delta \Phi = enp/\varepsilon_0 \quad (3)$$

In Eqn.(3), p is not constant, and it will change with the field strength. When the surface of molybdenum is covered with a small amount of yttrium atoms, the interactions among dipoles are weak, so p can be taken as a constant. When the surface is

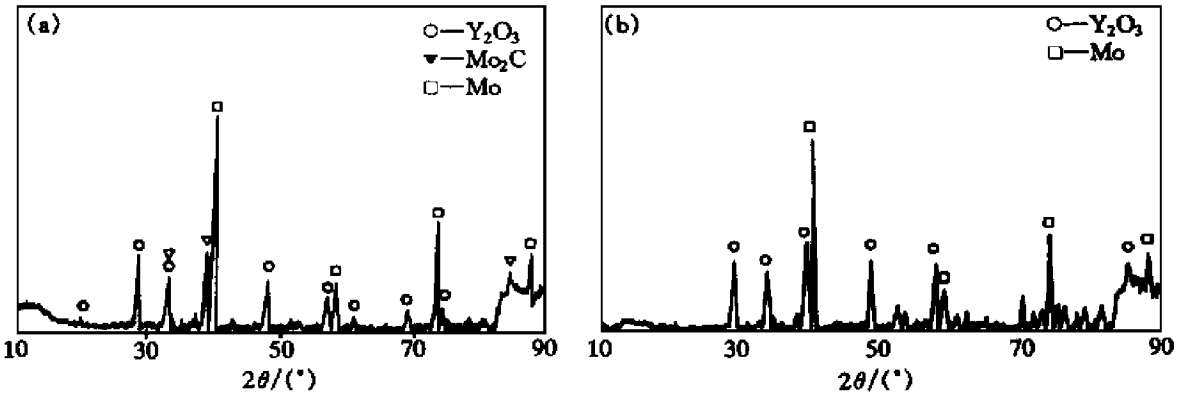

Fig.2 XRD patterns of powder mixture of Y_2O_3 and Mo_2C after held for 2 h at different temperatures
(a) —1 673 K; (b) —1 873 K

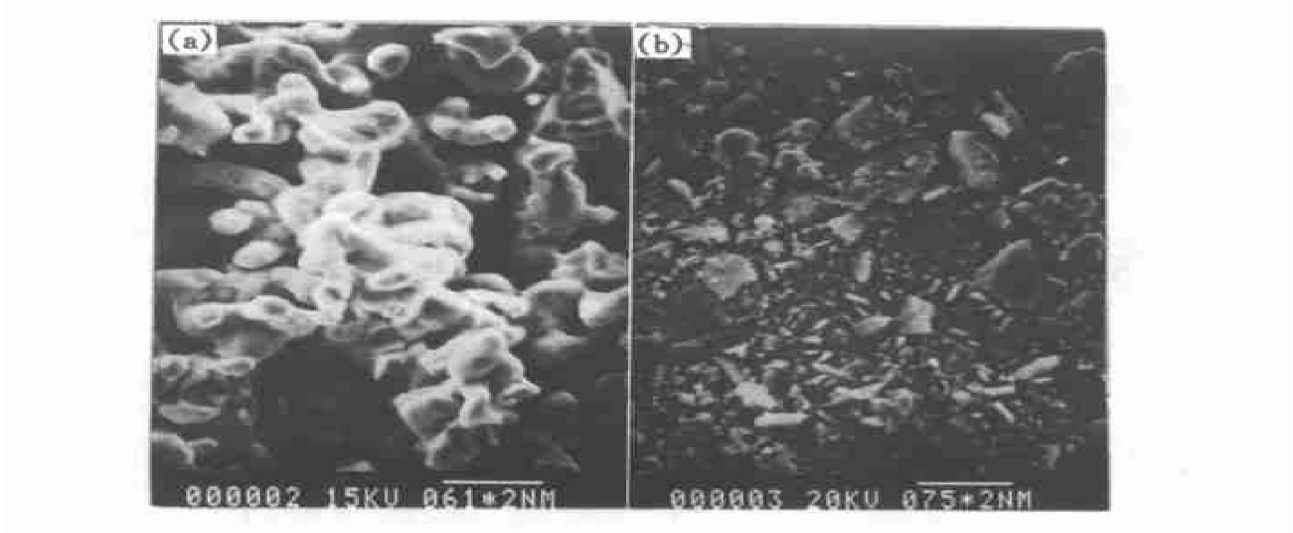

Fig.3 Micrographs of powder mixture of Y_2O_3 and Mo_2C after held 2 h at different temperatures
(a) —1 873 K; (b) —1 673 K

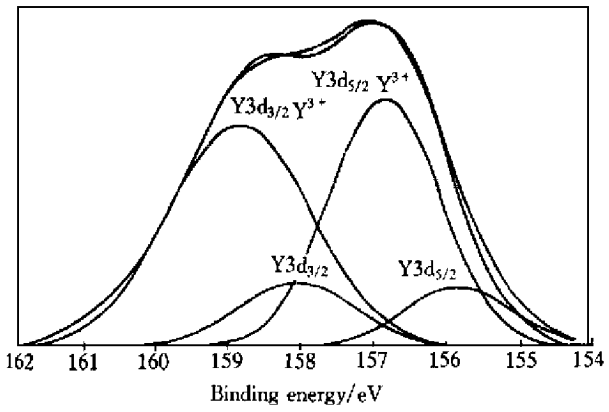

Fig.4 XPS spectra of yttrium for valence analysis

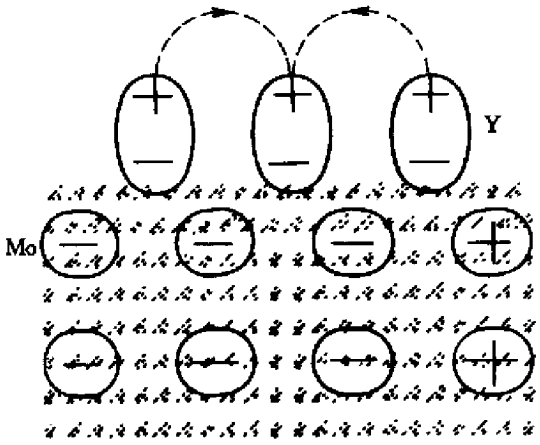

Fig.5 Sketch for polarization of yttrium atoms

covered with a large amount of yttrium atoms, the interactions become strong, and depolarization among these dipoles arises. In this case, the dipole moments become smaller. The decrease in work function is determined by two factors — n and p. The work function decreases with increasing n. But with n increasing, p decreases because of the depolarization. Thus, the work function increases. When n gets to an appropriate value, the decrease in work function with n increasing is equal to the increase in work function with p decreasing, and then the decrease in work function gets to the maximum. Therefore, the highest emission current of the cathode can be obtained.

5 CONCLUSIONS

1) The reaction between molybdenum carbide and yttrium oxide to produce metallic yttrium can take place at 1 173 K. When reaction product is exposed to atmosphere, metallic yttrium oxidizes into Y_2O_3 quickly.

2) After the powder mixture of Y_2O_3 and Mo_2C is heat-treated at 1 873 K, yttrium exists in two kinds of chemical state — yttrium of zero valence (Y^0) and yttrium of three valence (Y^{3+}).

3) The emission of Mo-Y_2O_3 cathode can be explained by the monoatomic layer mechanism. Yttrium oxide can be reduced to metallic yttrium by molybdenum carbide during activating period and operation of the cathode. The yttrium atoms cover the surface of molybdenum with a monoatomic layer which has a lower work function than clean molybdenum.

[REFERENCES]

[1] NIE Zuo-ren, ZHOU Mei-ling, ZHANG Jiu-xing, et al. Thermionic emission of Mo-Y_2O_3 filament cathode [J]. Journal of Rare Earth, (in Chinese), 1998, 16(1): 80 - 83.

[2] Buxbaum C and Gessinger G. Reaction Cathode [P]. US4019081, 1977.

[3] Buxbaum B C and Goebel D M. La-Mo emitter in hollow cathode [J]. Review of Science Instrument, 1980, 51 (11): 1468 - 1470.

[4] Gessinger G and Buxbaum C. Der einflub von platinmetallen auf das emissions verhalten von lanthankathoden [J]. High Temperature-High Pressures, 1978, 10: 325 - 328.

[5] ZHOU Mei-ling, CHEN Zhong-chun and ZHANG Jiu-xing. A study of the properties of Mo-La_2O_3 thermionic electron-emission material [J]. High Temperature-High Pressures, 1994, 26: 145 - 149.

[6] Buxbaum C. "LM Kathode" — Einneue drahtkathode mithoker thermischer elecktronenemission stromdichte [J]. NTG-Fachberichk, 1983, 85: 223 - 227.

[7] ZHOU Mei-ling, WANG Jin-shu, ZHANG Jiu-xing, et al. Thermodynamic analysis of Mo-La_2O_3 thermionic cathode wire [J]. Trans Nonferrous Met Soc China, 1996, 6(4): 56 - 60.

[8] NIE Zuo-ren. Study on Thermionic Emission of Rare-earth Molybdenum/Tungsten Cathode Materials [D], (in Chinese). Changsha: Central South University of Technology, 1997.

[9] Minanov X M. Application of Rare Earth on Catalyst [M], (in Chinese). LIU Heng-yi transl. Beijing: Science Press, 1987, 13.

[10] CHE Yin-chang. Thermodynamic Data Manual for Inorganic Substance [M], (in Chinese). Shenyang: Northeast University Press, 1990, 100.

(Edited by YUAN Sai-qian)