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La₂O₃-Gd₂O₃-Mo secondary emission material^①

WANG Jir-shu(王金淑), LIU Juan(刘娟), ZHOU Mei-ling(周美玲),
LI Hong-yi(李洪义), ZHANG Jiu-xing(张久兴), ZUO Tie-yong(左铁镛)

(Key Laboratory of Advanced Functional Materials, Ministry of Education,
School of Materials Science and Engineering, Beijing Polytechnic University, Beijing 100022, China)

Abstract: A new kind of materials La₂O₃-Gd₂O₃-Mo has been produced by powder metallurgy method. The composition and microstructure of the material were studied by XRD and SEM. It shows that no chemical reaction takes place among La₂O₃, Gd₂O₃, Mo and the rare earth oxides exist along molybdenum grain boundaries and in the pores. The emission property measurement results of this material show that adding rare earth oxide into molybdenum can improve the secondary emission coefficient of the emitter, and the emission property depends on the activating temperature. After La₂O₃-Gd₂O₃-Mo was activated at 1 360 °C, the maximum secondary emission coefficient can be high to 2.62, which has exceeded that for practical uses(2.0).

Key words: La₂O₃-Gd₂O₃-Mo; secondary emission; cathode

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1 INTRODUCTION

The magnetron tube has been used widely in many fields with the development of the electronic technology. The secondary emission plays important roles in the magnetron tube working process. The 90% of the anode current in the magnetron tube is acquired by the secondary emission. Nowadays, the cathodes of high power magnetron tube used in the above fields are mainly Ba-W cathodes^[1] and some Th-W cathodes^[2]. However, Ba-W cathode is hard to make and its anti-bombing property is not good enough because a thin film of active substance on the cathode surface is relatively easy to be bombed away. High working temperature and large power consumption and the radioactivity of Th-W cathode lead to problems in its application and manufacturing. The manufacturing size of the Th-W material becomes smaller and the yields of this material cannot meet the needs. Therefore a new kind of material should be developed. La₂O₃-Mo(La-Mo for short bellow) thermionic cathode material in electron tube has been developed and its thermionic emission properties and emission mechanism have been investigated systematically since the late of 1970s. Up to now, a great achievements on this material have been made^[3-8]. The former studies show that rare earth oxide doped molybdenum has better performance than La-Mo^[9-11]. Based on our former research experience of the rare earth doped molybdenum thermionic cathode material, we produced La₂O₃-Gd₂O₃-

Mo secondary emission material used in magnetron tubes. The secondary emission properties and the microstructure of this material have been studied in this paper.

2 EXPERIMENTAL

The rare earth oxide La₂O₃(7.5%) and Gd₂O₃(22.5%) were added to Mo oxide. The doped oxide powders were reduced into metallic molybdenum powder by dry hydrogen at 1 000 °C for 6 h. The La₂O₃, Gd₂O₃ doped Mo powders were isostatically pressed with pressure of 200 MPa and sintered at 1 800 °C for 2 h by electric resistance heating. The sintered La₂O₃-Gd₂O₃-Mo bar was manufactured to thin flakes(*d* 10 mm × 1 mm). The secondary emission property of the material were measured in a special instrument designed for testing the secondary emission coefficient. The microstructure observation of this cathode material was performed in Scanning Electron Microscope(XL SERES PHILIPS XL30 and S-450) and element analysis on the cathode surface was carried out in a (PH-610) multifunction spectrometer.

3 RESULTS AND ANALYSES

3.1 Preparation of La₂O₃-Gd₂O₃-Mo material

Fig. 1 shows the X-ray diffraction pattern of powder mixture of La₂O₃, Gd₂O₃, Mo after being doped molyb-

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Correspondence: Dr. WANG Jir-shu, + 86-10-67391101

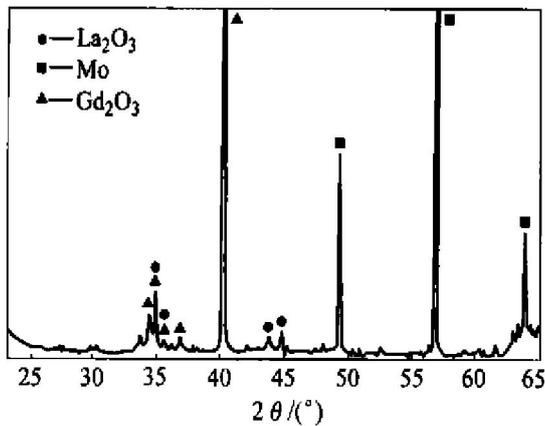


Fig. 1 X-ray diffraction pattern of powder mixture of La₂O₃-Gd₂O₃-Mo after reduced at 1000 °C by hydrogen

denum oxide powder reduced at 1000 °C by hydrogen.

The result shows that La₂O₃, Gd₂O₃ and Mo exist in the mixture. La₂O₃ and Gd₂O₃ are produced by the decomposition of La(NO₃)₃ and Y(NO₃)₃ during the reduction process. After La₂O₃, Gd₂O₃ doped Mo powder is pressed in isostatics press into a certain shape and sintered at high temperature, the composition of this material remains the same. Fig. 2 shows the SEM images of La₂O₃-Gd₂O₃-Mo sample. It can be seen that the porosity in the substrate is high and fracture model of this material is brittle break along grain boundaries (Fig. 2(a)). The EDS analysis results show that the components of white spots in Fig. 2(a) are the rare earth La and Gd. The distribution of the rare earth on the fracture surface is shown in Fig. 2(b). The experimental result shows that the rare earth mainly locates in the holes or at molybdenum grain boundaries, and the distribution of these elements is not homogenous. Fig. 2(c) shows the SEM observation of the sample surface. In Fig. 2(c), it can be seen that there are many open pores in the material. The components of white strips in Fig. 2(c) are La and Gd. The segregation of these rare earth elements results from powder mixing unevenly in the initial step for preparation of rare earth doped molybdenum.

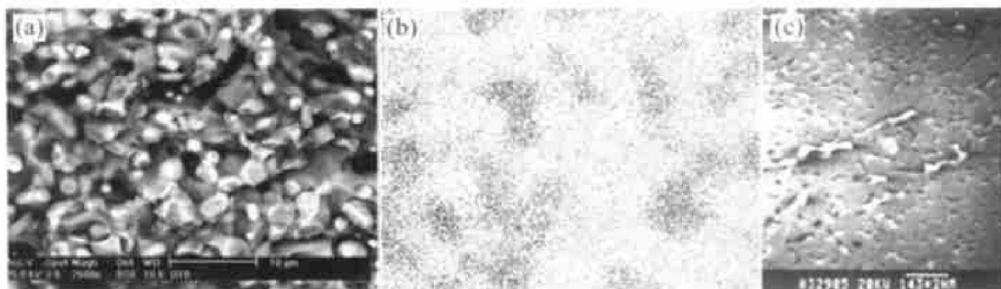


Fig. 2 SEM images of La₂O₃-Gd₂O₃-Mo sample

(a) —Fracture section; (b) —Distribution of rare earth on fracture surface; (c) —At surface

3.2 Secondary emission properties of materials

Fig. 3 shows the secondary emission property of La₂O₃-Gd₂O₃-Mo materials activated at different temperatures, tested at 600 °C. The result shows that the secondary emission coefficients (δ) of this material change with the primary electron energy in the form of parabola. When the primary electron energy is lower than 400 eV, the secondary emission coefficient increases with primary electron energy. When the primary electron energy is in the range of 400 - 600 eV, the secondary emission coefficients remain nearly the same. When the primary electron energy is higher than 600 eV, the secondary emission coefficient decreases with primary electron energy. This phenomenon may be explained as follows. When the bombing voltage is low, the energy of primary electron is low. These primary electrons go into the materials in so short distance that the number of inner secondary electrons activated by primary electrons is little. With the primary electron energy increasing, the number of secondary electrons activated by the primary electrons increases, so the secondary emission coefficient increases. However, when the primary electron energy is higher than 600 eV, the primary electrons go into the material so deeply that some secondary electrons activated cannot escape from the material because their energy loss increases with the distance to the surface of the material. When the primary electron energy is in a certain range, the maximum secondary coefficient can be gotten, as shown in Fig. 3.

Fig. 3 also shows that activating temperature affects secondary emission coefficient of the material greatly. When the temperature is lower than 1360 °C, δ increases with the temperature and comes up to the maximum ($\delta = 2.62$) at the temperature of 1360 °C. When the temperature is higher than 1360 °C, δ decreases with the temperature. But all the maximum secondary emission coefficients of this material at different temperatures are higher than that of pure molybdenum (1.25). This result shows that adding rare earth oxide into molybdenum can improve the secondary emission coefficient of the emitter.

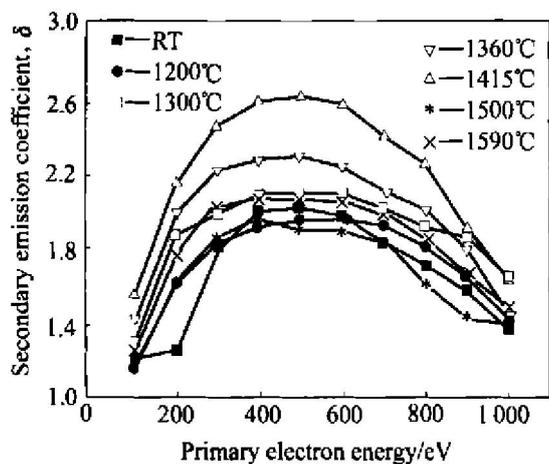


Fig. 3 Secondary emission coefficients of $\text{La}_2\text{O}_3\text{-Gd}_2\text{O}_3\text{-Mo}$ materials after being activated at different temperatures, tested at 600 °C

Because the emission property of the cathode correlates with the components on the surface of the cathode, the components on the surface of the material before and after emission have been studied by Auger Electronic Spectra method. The result of AES analysis for the material after emission is shown in Fig. 4. As shown in Fig. 4, elements lanthanum, gadolinium, oxygen and molybdenum exist on the surface of the cathode. The peak position and peak shape of La3d and Gd3d show that the chemical states of lanthanum, gadolinium and oxygen remain the same. It means that lanthanum and gadolinium still exist as La^{3+} and Gd^{3+} . The mechanism that the rare earth improves the secondary emission property of the emitter is as follows. In any material, the secondary emission process includes the secondary electrons producing, moving to the surface, overcoming the surface barrier potential and escaping from the surface. The rare earth distributed on the surface lowers down the work function of the emitter^[12], so the secondary electrons escape from the surface easily. As a result, the secondary emission coefficient increases. On the other hand, La and Gd exist in the form of La_2O_3 and Gd_2O_3 which have poor conductivity and fewer conduction electrons. The energy loss of the secondary electrons in these rare earth oxides is decreased because the collision between secondary electrons with the conduction electrons is decreased during secondary electrons moving to the surface. As a result, many secondary electrons can overcome the surface barrier potential and escape from the surface. Then the secondary emission coefficient is improved. However, there are many free electrons in molybdenum. The secondary electrons will collide with these free electrons and lose a lot of energy during their moving to the surface. So the secondary emission coefficient of the material is low because only a small amount of secondary electrons can

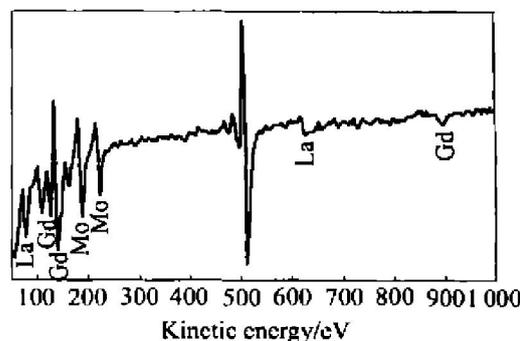


Fig. 4 AES analysis of $\text{La}_2\text{O}_3\text{-Gd}_2\text{O}_3\text{-Mo}$ cathode surface

escape from the surface.

The secondary emission coefficient of the material activated at temperature of 1 360 °C is the highest among all the secondary emission coefficients of the material activated at different temperatures (1 200, 1 300, 1 360, 1 415, 1 500, 1 590 °C). This result can be explained by the theory of the rare earth segregation and evaporation from the surface. The content of rare earth on the surface of cathode before and after emission test has been calculated by XPS method. These results are listed in Table 1 and Table 2. Before the emission, the mole ratio of La to Gd ($x_{\text{La}}/x_{\text{Gd}}$) is 3. 12, and the total mole fraction of La and Gd is 4. 46. After cathode was activated at temperature 1 590 °C, tested at 600 °C, the mole ratio of La to Gd ($x_{\text{La}}/x_{\text{Gd}}$) is 1. 05, and the total mole fraction of La and Gd is 3. 1. These results show that the content of the rare earth on the surface of the $\text{La}_2\text{O}_3\text{-Gd}_2\text{O}_3\text{-Mo}$ material changes in cathode emitting. We have studied the diffusion behavior of La_2O_3 in $\text{La}_2\text{O}_3\text{-Mo}$ thermionic cathode material^[12], and the result shows that the La_2O_3 diffuses to the surface of the cathode in form of ions La^{3+} and O^{2-} and then recombines into the La_2O_3 molecule at high temperature. During the cathode operating and

Table 1 Mole fraction of elements at surface of $\text{La}_2\text{O}_3\text{-Gd}_2\text{O}_3\text{-Mo}$ after secondary emission

Element	Peak area	Mole fraction/ %
La	2 696. 32	3. 38
Gd	3 770. 17	1. 08
O	6 993. 43	81. 69
Mo	5 763. 95	13. 85

Table 2 Mole fraction of elements at surface of $\text{La}_2\text{O}_3\text{-Gd}_2\text{O}_3\text{-Mo}$

Element	Peak area	Mole fraction/ %
La	1 300. 38	1. 59
Gd	5 144. 34	1. 51
O	9 208. 10	79. 74
Mo	1 970. 96	17. 16

activating, the rare earth oxides diffuse from the interior to the surface and then evaporates from the cathode surface. At 1 200 °C and 1 300 °C, the diffusion rates of the rare earth are low and the amount of rare earth elements segregated on the surface are little. So the emission of the cathode is poor. However, when the temperature is too high, the amount of rare earth segregated on the surface becomes small and the emission of the cathode is also poor because the evaporation rate of rare earth is higher than the diffusion rates. Just at about 1 360 °C, the evaporation rate is approximately equal to the diffusion rate with the result of the secondary emission coefficient comes to the maximum.

4 CONCLUSIONS

1) Rare earth oxide doped molybdenum cathode has better secondary emission property than clean molybdenum has. After activated at proper temperature, the secondary emission coefficient of the La₂O₃-Gd₂O₃-Mo cathode is up to 2. 62.

2) During the operating of the cathode, there exists a diffusion and evaporation process of the rare earth. When the evaporation rate is approximately equal to the diffusion rate, the secondary emission coefficient comes to the maximum.

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