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Studies on the pressed yttrium oxide-tungsten matrix as a possible dispenser cathode material

Fan Yang, Jinshu Wang*, Wei Liu, Xiang Liu, Meiling Zhou

School of Materials Science and Engineering, Beijing University of Technology, Chaoyang District, Beijing, 100124, China

HIGHLIGHTS

- Yttrium oxide was chosen as the secondary emission substance based on first principle calculation result.
- A new kind of cathode has been successfully obtained.
- Pressed yttrium oxide-tungsten matrix dispenser cathode exhibits good emission properties.
- The improvement of the cathode emission can be well explained by the surface analysis results presented in this work.

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ABSTRACT

Yttrium oxide was chosen as the secondary emission substance based on calculation results through first principle theory method. A new kind of pressed yttrium oxide-tungsten matrix dispenser cathodes are prepared by a sol–gel method combined with high temperature sintering in dry hydrogen atmosphere. The results show that the growth of the grains is hampered by the pinning effect of Y_2O_3 distributing uniformly between the tungsten particles, resulting in the formation of small grain size. It is found that Y_2O_3 improves the secondary electron emission property, i.e., the secondary emission yield increases with the increase of Y_2O_3 content in the samples. The maximum secondary emission yield δ_{max} of the cathode with 15% amount of Y_2O_3 can reach 2.92. Furthermore, the cathode shows a certain thermionic emission performance. The zero field emission current density J_0 of 4.18A/cm^2 has reached at 1050 °C$_b$ for this kind of cathode after being activated at 1200 °C$_b$, which are much higher than that of rare earth oxide doped molybdenum (REO-Mo) cathode reported in the previous work.

1. Introduction

As one important kind of high power microwave devices, magnetrons have a wide range of applications in civil, medical and military fields, such as microwave oven, radiology and radar system [1,2]. Cathodes which are the heart component of the magnetrons play a very important role in the operation of the devices [3]. Different from the thermionic cathodes applied in traveling wave tubes and klystrons, the cathodes are needed to have a certain thermionic emission property and excellent secondary electron emission performance in the high-power and high-frequency magnetrons [4,5].

Oxide cathodes (e.g. Ni sponge oxide cathode and reservoir oxide cathode) are widely applied in magnetrons, electric light sources, CRTs, transmitter–receiver tubes, grid control tubes and high-power klystrons because of its low operating temperature, large pulsed emission current density and simple manufacturing technology [6,7]. However, the application of oxide cathode in the high power magnetron still needs challenges since the strong bombardment of the electrons in the high power magnetron could result in the increase of cathode temperature which cause the high evaporation rate of active elements in the oxide cathode and short life. Alloy cathode (e.g. $IrLa_5$, BaPt and BaPd) have many advantages for application such as low wok function, low operating temperature and high secondary emission yield [8,9], whereas there is a severe problem in removing surface contamination when processing the cathode after exhaust or during operation of the device [10]. In addition, high price of the raw noble materials is the main block for their large scale applications. Recently, researchers have found that scandia doped tungsten nano-particle cathodes which are able to deliver more than 100A/cm^2 current density show great promise for use in the high power terahertz vacuum electron devices [11–14]. But different from Ba–W dispenser cathode which

* Corresponding author.
E-mail address: wangjsh@bjut.edu.cn (J. Wang).

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shows good performance in some commercial magnetrons [15], scandate dispenser cathodes can not meet the requirement of the high power magnetrons owing to its bad anti-bombarding insensitivity and moderate secondary emission yield which remains to be enhanced. Rare earth oxide (REO in brief) -Mo cathode has aroused great attention in recent years due to its optimal secondary emission property and good anti-bombarding insensitivity [16–18]. However, it is difficult for such an emitter to get the practical application because of its lower thermionic emission property. Therefore, it is desirable to develop a novel cathode to meet the requirement of the high power magnetrons.

Impregnated cathode consists of a porous tungsten matrix and active substance. To obtain an impregnated cathode, a series of complicated procedures have to be taken including pressing, sintering, impregnating and surface treatment [19]. As for a pressed cathode, its simple fabrication process shows great advantage since we can get a pressed cathode easily only after pressing and sintering. As reported by our previous work, the secondary emission property of the cathode is enhanced by the rare earth oxide [20]. In order to choose what kind of rare earth oxide is suitable for the improvement of emission property, three kinds of rare earth oxide, Y_2O_3, light rare earth oxide such as La_2O_3 and heavy rare earth oxide Lu_2O_3, were chosen to calculate the work function. Based on the calculation results, rare earth oxide-W dispenser cathode was prepared and both the thermionic emission property and secondary emission property were studied. To the best of our knowledge, this is the first report on this kind of secondary emitter.

2. Theoretical calculation

The work functions of La_2O_3, Y_2O_3 and Lu_2O_3 have been calculated using first principles calculations based on the density functional theory (DFT). All the first principle calculations are performed within DFT formalism, using the Cambridge Serial Total Energy Package (CASTEP). The plan-wave basis set cut-off is set at 340 eV, the exchange and correlation energy is treated using the generalized gradient approximation (GGA) and the Monkhorst–Pack special K-points scheme is used with $4 \times 4 \times 4$ points for the Brillouin zone sampling. Based on these accuracy settings, the convergence tolerance of energy, maximum force, and maximum displacement become 1.0×10^{-4} eV/atom, 0.05 eV/Å, and 2.0×10^{-3} Å, respectively. A uniform vacuum width of 15 Å is employed. As shown in Table 1, the secondary electrons of Y_2O_3 tend to escape from the O(111) surface (O atoms as the terminations) into the vacuum since the work function has the lowest value of 2.75 eV among the three kinds of rare earth oxides, indicating that the secondary electrons only have to overcome 2.75 eV of potential energy to escape from Y_2O_3. It is assumed that Y_2O_3 is the optimal rare earth oxide to improve the emission property of the cathode among these three kinds of rare earth oxide. So in this work, pressed yttrium oxide-tungsten matrix dispenser cathode has been prepared by a sol–gel method combined with two-step reduction in dry hydrogen.

Table 1
The work function (φ) of different rare earth oxide (φ_1-La_2O_3, φ_2-Y_2O_3 and φ_3-Lu_2O_3) calculated using GGA function.

Cleave Plane	(100)		(110)	(111)	
	RE(100)	O(100)	–	RE (111)	O(111)
La_2O_3-φ_1(eV)	3.29	4.95	3.40	3.48	3.44
Y_2O_3-φ_2(eV)	3.52	5.54	3.92	4.03	2.75
Lu_2O_3-φ_3(eV)	3.70	5.59	4.05	4.11	2.90

3. Microstructure and composition analysis

The Y_2O_3 and barium–calcium aluminates co-doped tungsten powders were prepared by a sol–gel method using $Y(NO_3)_3 \cdot 6H_2O$, $Ba(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and ammonium metatungstate (AMT) as the raw materials. The total content of Y_2O_3 were 5%, 10%, 15% and 20% by weight (Y5, Y10, Y15 and Y20) respectively, and the content of barium–calcium aluminates with the molar ratio of $BaO:CaO:Al_2O_3 = 4:1:1$ in all the samples was 10% by weight and balanced with tungsten. After calcined at 600 °C for 2 h in air to remove the organics, the Y_2O_3 and barium–calcium aluminates co-doped tungsten powders were reduced in dry hydrogen atmosphere at 880 °C_b for 2 h. Fig. 1 represents the XRD patterns of Y_2O_3 and barium–calcium aluminates co-doped reduced powders with different content of Y_2O_3. The results show that the powders are mainly consisted of W, $BaWO_4$ and Y_2O_3, wherein the intensity of diffraction peaks of Y_2O_3 which is produced by the decomposition of Y_2WO_6 increases with the increase of yttrium concentration in the samples (as shown in the inset in Fig. 1). The tungsten oxide has been entirely reduced into metallic tungsten after the two-step reduction. $BaWO_4$ is produced by the reaction between $BaO \cdot Al_2O_3$ and W. Peaks of $BaAl_2O_4$, BaO and Ba are not detected in the diffraction patterns due to the low content. The chemical reactions involved during the reduction process are expressed as follows:

$$Y_2WO_6 = Y_2O_3 + WO_3 \quad (1)$$

$$WO_3 + H_2 = WO_2 + H_2O \quad (2)$$

$$WO_2 + 2H_2 = W + 2H_2O \quad (3)$$

$$(4BaO) \cdot Al_2O_3 + \frac{1}{2}W = \frac{1}{2}BaWO_4 + BaAl_2O_4 + BaO + \frac{3}{2}Ba \quad (4)$$

Granularity analysis is carried out by using the Malvern Laser granularity analysis equipment to investigate the particle size of the reduced powder. The median sizes D ($n = 50$) of Y_2O_3 and barium–calcium aluminates co-doped reduced powders are shown in Table 2. It can be seen that the grain sizes of the co-doped tungsten powders decrease with the increase of Y_2O_3 content in the materials, wherein the median size of the co-doped tungsten

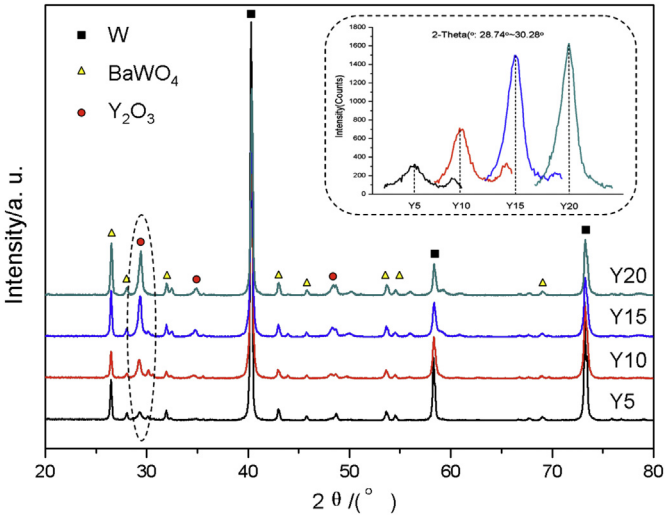

Fig. 1. XRD patterns of yttrium barium–calcium aluminates co-doped reduced tungsten powders. Inset is the main peak pattern of Y_2O_3 of different powders.