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Durability experiment on anti-electron-bombardment of RE_2O_3-Mo secondary emission material ①

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Abstract: A durability test to determine anti-bombardment sensitivity of multi-RE_2O_3-Mo secondary emission material was carried out and the variation of maximum secondary emission coefficient (δ_{max}) was monitored at regular intervals. After the experiment, the cathode was analyzed with SEM, EDS and XRD techniques. The results show that δ_{max} of multi-RE_2O_3-Mo cermets cathode heated to 1 100 ℃ under electron bombardment of 300 W/cm^2 reaches the peak of 3.35 at 200 h. After 500 h of bombardment, the maximum secondary-electron-yield curve stabilizes. The δ_{max} value of the cathode remains at about 2.5 after 1 000 h and represents a good anti-bombardment property. The high δ_{max} value of the cathode is related with formation of an enriched Y_2O_3 layer on the surface under high temperature and with the amount of La_2O_3 particles in the shape of nanometer distributed on the surface. Under the experimental conditions, the drop of δ_{max} value may be caused by the reduction of La_2O_3 content and the porous layer resulted from evaporation of MoO_2, which is formed when Mo at the surface is oxidized.

Key words: rare earth oxide; molybdenum; anti-electron-bombardment property; secondary emission

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1 INTRODUCTION

Rare-earth oxides cathode, abbreviated to RE_2O_3-Mo, as a new kind of cermets cathode, has shown good properties in thermion emission, secondary electron emission, anti-exposure in atmosphere and in molding[1-5]. It is simple in processing and low in cost with no radioactivity compared with Ba-W that is now widely in use in high power magnetron tubes and with Ir-La and Th-Re cathodes which are developed in recent years[6, 7]. Since the electron at adverse phase position in high frequency field is to bombard back the cathode when the magnetron tube is at work, the power of back bombardment accounts for about 2 - 10 percent of the DC input power of which 2 - 6 percent is released in the form of heat on the pulse magnetron tube. Thus, the cathode must have enhanced secondary electron emission properties, and work steadily under high temperature with good anti-electron-bombardment property. To understand the changes of secondary emission coefficient under continuous electron bombardment is of great significance for the research on the emitter property and its application in the apparatus. To verify the anti-electron-bombardment property of RE_2O_3-Mo cermets cathode under high temperature, a simulation on working conditions of the cathode is made in this paper where a durability test on anti-electron-bombardment of RE_2O_3-Mo cermets cathode is carried out over a period of 1 000 h under 1 100 ℃. The cathode after durability experiment is studied with SEM, EDS and XRD techniques and the emission mechanism of the cathode is discussed.

2 EXPERIMENTAL

2.1 Preparation of RE_2O_3-Mo cathode

Mix RE_2O_3 in the form of rare earth nitrates in water solution with MoO_2. The addition of rare earth nitrates is calculated at 30% of the RE_2O_3 in the total amount of RE_2O_3-Mo. The mass ratio of La_2O_3 to Y_2O_3 in RE_2O_3 is 1∶3. The mixture is insulated for 6 h in dry hydrogen atmosphere and deoxidized into La_2O_3-Y_2O_3-Mo powder after decomposition process. Then mold the powders under iso-hydrostatic pressure of 200 MPa and sinter it in molybdenum wire furnace in dry hydrogen atmosphere at 1 800 ℃ for 2.5 h, finally we get the multi- RE_2O_3-Mo sinter.

2.2 Durability test of anti-electron-bombardment

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Fig. 1 shows the structure of the test tube containing two parts. The upper part includes an electron gun and a secondary electron collecting pole made of nickel plate. The lower part is the RE_2O_3-Mo cathode, which is welded on the Mo sleeve with the size of 10 mm in diameter and 1.5 mm in thickness. The cathode is heated by heater welded inside the Mo sleeve and is surrounded by a heat screen sheet made of Tl. After exhaustion and activation (heating at 1 200 ℃ for 17 h), the test tube is encapsulated with a vacuum degree of 5×10^{-6} Pa. The cathode is continuously heated up to 1 100 ℃ while constant bombardment is maintained at primary electronic current. The capacity of electron bombardment is 1 keV and its current density is 3 mA/cm^2; and the beam diameter is 1 mm. The secondary-electron-yield curve is monitored at regular intervals at 600 ℃ under 2 V of target pressure.

Fig. 1 Structure of cathode tube for anti-bombardment test

2.3 Microcosmic analyses

An observation is conducted on SEM (HITACHI-S3500N) on the micro-image of the surface of secondary emitter and the collecting pole after the durability test. Meantime, analysis of the surface composition and structure of the cathode is also carried out by applying EDS and XRD (D/MAX-3C).

3 RESULTS AND DISCUSSION

3.1 Anti-electron-bombardment property of RE_2O_3-Mo cermets cathode

Fig. 2 shows the change of δ_{max} of RE_2O_3-Mo cermets cathode with electron bombardment time. Under high temperature of 1 100 ℃ and continuous electron bombardment for 1 000 h, the change of δ_{max} value can be divided mainly into three stages. At its first 200 h, δ_{max} value increases gradually from 2.7 to 3.35, reaching its peak. Then it drops to 2.5, 20% down in its second stage which is between 200 and 500 h. After 500 h of bombardment, δ_{max} value drops steadily and becomes stabilized at about 2.5.

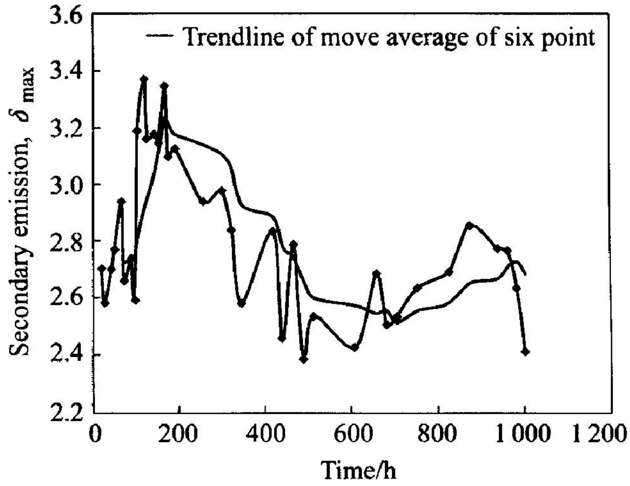

Fig. 2 Variation of maximum yield δ_{max} of RE_2O_3-Mo cermets cathode with duration of bombardment

From this we can see that RE_2O_3-Mo cermets cathode possesses very good properties in high temperature resistance and anti-electron bombardment.

3.2 Microcosmic analyses of RE_2O_3-Mo cermets cathode

The photograph of the surface of the cathode after 1 000 h of the durability experiment is shown in Fig. 3. The dark area *A* in the center of the cathode is primary electron bombardment area. According to the formula of $P = P_{total}/S$ (where P is bombardment power and S is the area of beam spot), the actual bombardment power is about 300 W/cm^2. It is observed that the surface of the cathode turns dark gradually during the first 200 h. At the same time, some dark sediment is found in the secondary electron collecting pole. XRD analytical results on the surface of cathode and collecting pole are shown in Figs. 4 and 5.

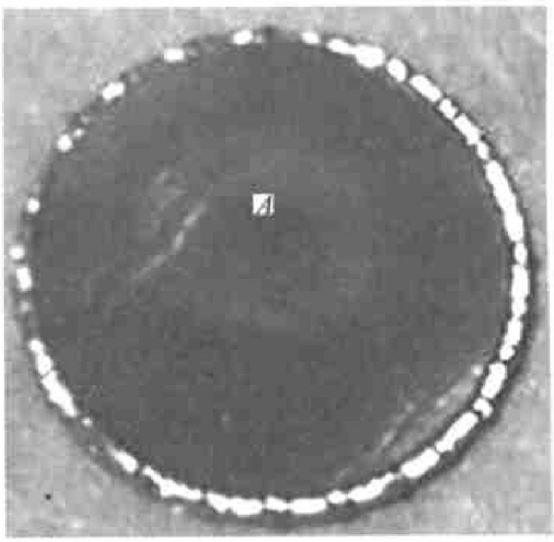

Fig. 3 Photograph of cathode after durability experiment

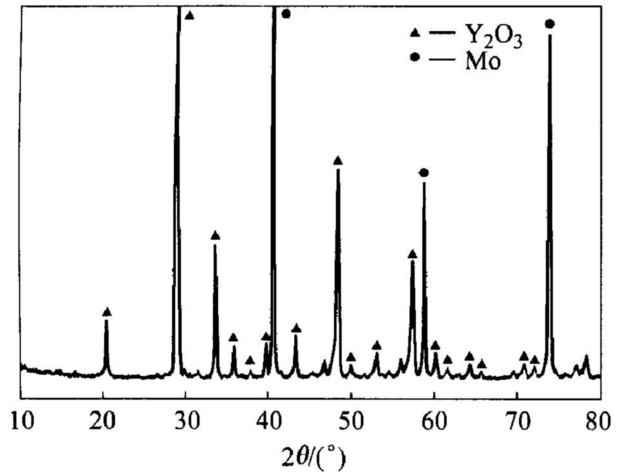

Fig. 4 XRD pattern of cathode after durability experiment

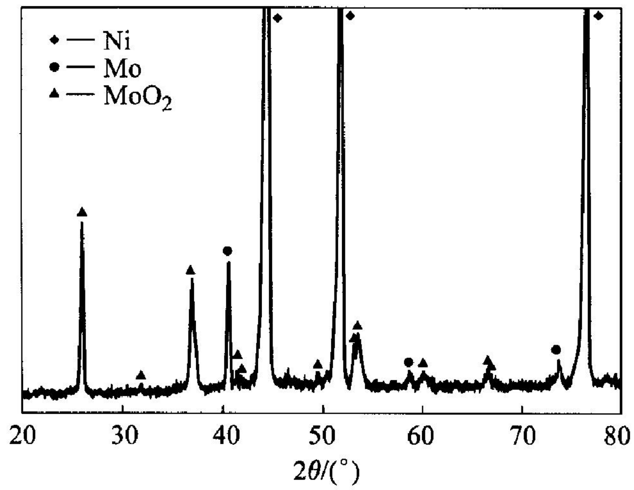

Fig. 5 XRD pattern of collector pole after durability experiment

According to Fig. 4, the cathode consists mainly of Mo and Y_2O_3 where the reflection peaks of Y_2O_3 are very strong, but that of La fails to be detected. This indicates that there is a high content of Y_2O_3 in the surface after 1 000 h of heating and electron bombardment. In Fig. 5, the result shows that Ni, Mo and MoO_2 exist in the surface of collecting pole. The presence of Mo could probably be the result of evaporation sediment of Mo under continuous electron bombardment. And MoO_2 could be the result of evaporation under high temperature. The appearance of MoO_2 will be discussed later.

The BSEM image of primary bombarded area and EDS patterns for Area *A* and *B* are shown in Fig. 6. The BSEM image indicates that the surface of cathode is composed of a network and particles. EDS results show that the composition of Area *A* is mainly Mo, and that of Area *B* is the rare earth elements Y and La. It can be determined from the results of XRD that the network phase is Y_2O_3 while the particles within the network are La_2O_3 with sizes much smaller than 100 nm. Judging from the network phase in

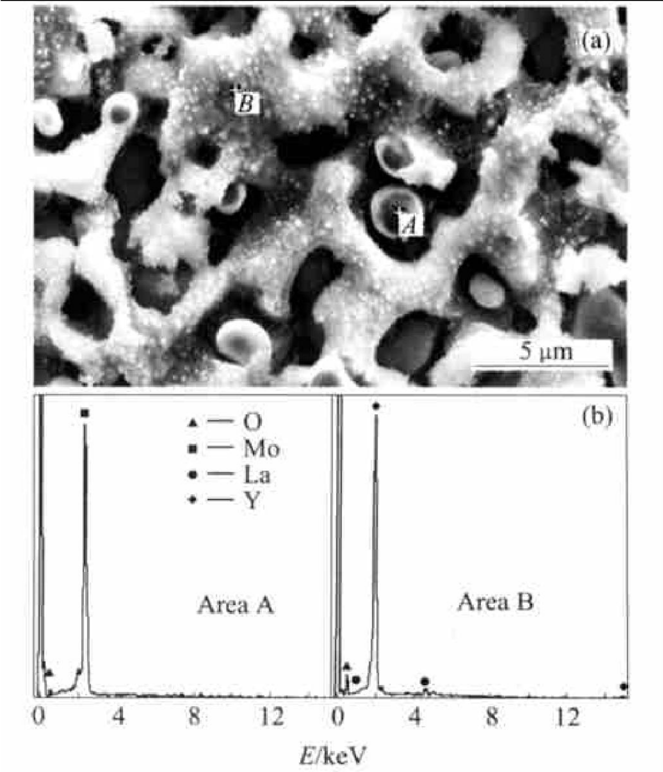

Fig. 6 BSEM image of primary bombarded area(a) and EDS patterns for Area *A* and *B*(b)

Area *B* and the contrast difference of BSEM image of nano-particles, they are not the same kind of matters. In this case, the nano-particles should be the oxide of La.

Analysis is made on sample surfaces before and after the durability test with EDS. The results indicate that the molar ratios of Mo/RE and Y/La on the sample surfaces change from 1.89 and 3.51 to 0.46 and 13.11 respectively after the experiment, which shows an evident change of surface compositions due to continuous electron bombardment for 1 000 h at 1 100 ℃ where the relative quantity of Mo increases rapidly and the ratio of La to Y drops dramatically. According to the analysis, under high temperature, high degree of vacuum and continuous electron bombardment, rare earth oxide especially La_2O_3 changes to LaO by losing part of lattice oxygen[8-10]. The separated O ions oxidize Mo and forms MoO_2, which evaporates at high temperature. Metallic Mo particles take up spherical shape due to the high speed of oxidation along lattice grain boundary to lower the surface free energy. Meantime, the formation of free interface provides a favorable condition for RE diffusing from free boundary to surface so that the relative quantity of surface RE oxide increases. All of the above leads to the relative enrichment of Y_2O_3, which results in the increase of δ_{max} at the first stage in Fig. 2. However, the facts that evaporation results in enhanced porous surfaces will again cause decrease of δ_{max} value at the second stage. EDS result shows that there is very small quantity of La on the surface of the collecting pole. This proves that evaporation results in La loss at area of electronic bombardment since evaporation ratio of La_2O_3 is one order larger than that of Y_2O_3 at high temperature[11, 12]. Thus, under the temperature of 1 100 ℃ and within the range of 300 W/cm^2 power of the primary electron bombardment, La_2O_3 will diffuse and evaporate, but Y_2O_3 stays stable. As the process of oxidization and evaporation of Mo become slow, the diffusion of La_2O_3 and Mo to the surface reach dynamic equilibrium with its decomposition and evaporation ratio, δ_{max} value will tend to become stable and now comes the third stage where a 2.5 μm thick film of RE oxide is built after 1 000 h of the durability test, as seen in Fig. 7.

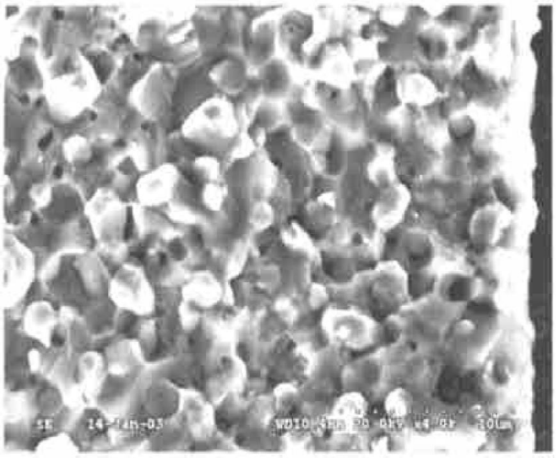

Fig. 7 SEM micrograph of fractured surface of cathode after durability experiment

RE_2O_3-Mo cathode, which differs from a pure oxide cathode, is a cermets cathode where both Mo and RE oxide are secondary emitter. Therefore, δ_{max} value is the result of comprehensive contribution by both of them. It is known that δ_{max} of clean Mo is 1.38, and those of Y_2O_3 and La_2O_3 are about 2.5[13]. Even Y_2O_3 is deposited on Mo by the electrophoresis method, its δ_{max} = 3.0, all of which are lower than 3.35 of the δ_{max} of Y_2O_3-La_2O_3-Mo cathode. After the durability experiment, the cathode is covered by Y_2O_3. This large δ_{max} value should be related with both of the enriched layer of rare earth oxides formed on the surface under high temperature and the quantity of dispersion of La_2O_3 in nano-particles on Y_2O_3 surface as shown in Fig. 6. The dispersed nano-particles of La_2O_3 lead to a large amount of dangled bonds within the interface, which are not well configured, unsaturated and lack of oxygen. This results in existence of positive charge on the interface, which attracts the secondary electrons from inside and enhances the production of secondary electron. Detailed consideration however needs further discussion.

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