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Reduction property of rare earth oxide doped molybdenum oxide*

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Abstract: Rare earth oxide doped molybdenum powders were prepared by the reduction of rare earth nitrites doped MoO_3. The effect of rare earth oxide on the reduction behavior of molybdenum oxide had been studied by means of Temperature Programmed Reduction (TPR), thermal analysis, X-ray diffraction. Doping rare earth oxide in the powder could lower the reduction temperature of molybdenum oxide and decrease the particle size of molybdenum. The mechanism for the effects had been discussed in this paper.

Key words: RE_2O_3; molybdenum; reduction; doping

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1 Introduction

Magnetron tubes have a wide application in the fields of communication, medical treatment, heat apparatus and military uses. The cathodes in the magnetron tubes should have better secondary emission property, the capabilities of working at high temperature, anti-bombing insentivity and long life[1]. Among them, secondary emission property is the most important factor for the application of this kind of cathode. Our former studies on rare earth oxide (RE_2O_3 in brief) doped molybdenum cathodes showed that the secondary emission coefficient increased with the decrease of grain size of the cathode material and increase of the cathode density[2,3]. It is well known that the grain size and density of the cathode are correlated with the particle size of the raw material. In order to obtain the optimum reduction technique for the preparation of rare earth oxide doped molybdenum powder with small grain size, the reduction property of rare earth oxide doped molybdenum oxide has been studied in this paper.

2 Experimental method

Either a single rare earth oxide or a mixture of rare earth oxides of La_2O_3, Y_2O_3 or Gd_2O_3 (the total content is 25%, mass fraction) has been added in the molybdenum oxide in the form of rare earth nitrites. La_2O_3, La_2O_3-Y_2O_3 (mass ratio of $La_2O_3 : Y_2O_3$ is 1 : 3) co-doped and La_2O_3-Y_2O_3-Gd_2O_3 (mass ratio of $La_2O_3 : Y_2O_3 : Gd_2O_3$ is 1 : 2 : 1) co-doped molybdenum oxide could be assigned to Sample 1, Sample 2

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and Sample 3, respectively. The thermal analysis was carried out on STA-449-Jupiter thermal analysis apparatus. The reduction property of the powder was done by Temperature Programmed Reduction (TPR) method. In this experiment, the mixed gas of 95% (volume fraction) argon and 5% (volume fraction) hydrogen was introduced into the apparatus with an effective heating rate of 10K/min and the exhausted gas was dehydrated using $Mg(ClO_4)_2$. The composition and morphology of the powder was analyzed by D/MAX-3C X-ray diffraction apparatus and Hitachi scanning electron microscope.

3 Results and discussion

After heating the mixture of MoO_2 powder and water solution of $La(NO_3)_3$, $Y(NO_3)_3$ in water bathing, the main compositions of the powder are MoO_2, two rare earth nitrites shown above and several kinds of rare earth molybdate. Since there are a lot of nitrites in the sample, the doped powder should be decomposed in air to remove NO_2 (the decomposition product of nitrites produced during the reduction process) before the reduction treatment. In order to determine the appropriate decomposition temperature, TG-DTA analysis was carried out in the experiment, and the result is shown in Fig. 1. In Fig. 1, an obvious change was found in the DTA and TG curves. In three stages A, B, C, exothermal reactions took place, accompanied by the weight loss of the sample. When the temperature was lower than 200℃ (stage A), $La(NO_3)_3 \cdot 6H_2O$, $Y(NO_3)_3 \cdot 6H_2O$ and other substance gradually lost the absorbed water, leading to the weight loss. In the temperature range 200-310℃ (stage B), $La(NO_3)_3 \cdot 6H_2O, Y(NO_3)_3 \cdot 6H_2O$ and other products lost the crystal water. The weight loss in TG curve and endothermal peak in the DTA curve in stage C (400-540℃) could be assigned to the nitrite decomposition. When the temperature was higher than 550℃, no weight loss was found in the TG curve, indicating that nitrites had decomposed completely. Therefore, the maximum decomposition temperature could be assigned as 550℃. When the temperature was higher than 550℃, several endothermal peaks appeared in the DTA curve, indicating that the chemical reactions between rare earth oxides and MoO_2 might take place to form rare earth molybdates.

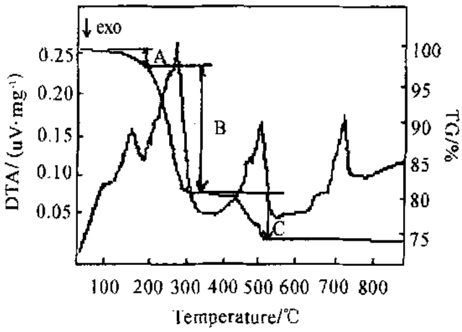

Fig. 1 Thermal analysis result of $La(NO_3)_3$, $Y(NO_3)_3$ co-doped MoO_2 powder

Fig. 2 depicts the XRD patterns of the powders decomposed at 550℃. It showed that molybdenum existed as MoO_3, the oxidation product of the raw material MoO_2. On the other hand, lanthanum and yttrium existed as rare earth oxides, $La_2Mo_4O_{15}$ and Y_2MoO_5 which are the reaction products of La_2O_3, MoO_3 and Y_2O_3, MoO_3.

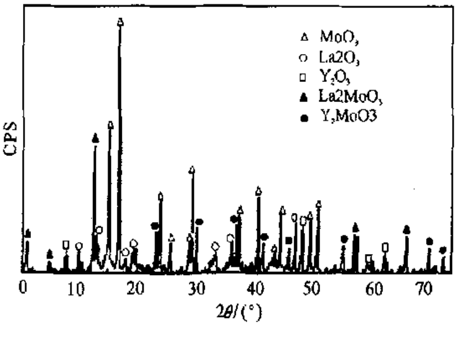

Fig. 2 XRD patterns of $La(NO_3)_3$, $Y(NO_3)_3$ co-doped MoO_2 decomposed at 550℃

The effect of rare earth oxide on the reduction property of the molybdenum oxide was studied by temperature programmed reduction method. Fig. 3 shows the TPR spectra of pure MoO_3 (a), lanthanum nitrite doped molybdenum oxide powder decomposed at 550℃(b), lanthanum nitrite, yttrium nitrite co-doped MoO_3 decomposed at 550℃(c) and lanthanum nitrite, yttrium nitrite, gadolinium nitrite co-doped MoO_3(c) decomposed at 550℃(d).

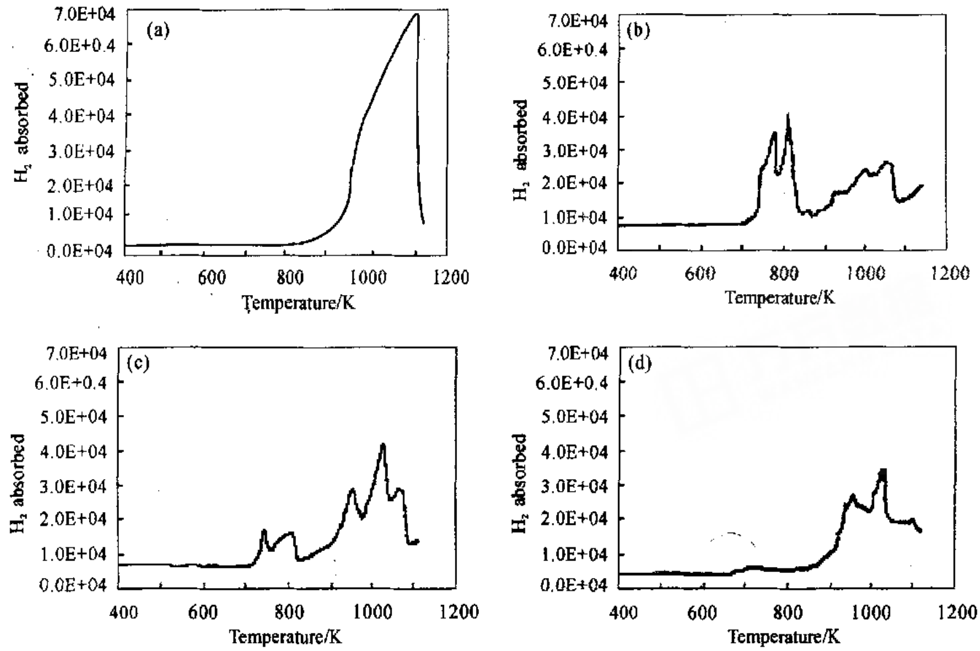

Fig. 3 The TPR spectra of different samples

(a)—pure MoO_3; (b)—Sample 1; (c)—Sample 2; (d)—Sample 3

It showed that doping rare earth oxide has a remarkable influence on the reduction behavior of the powders. Only one peak of hydrogen consumed appeared in the TPR spectra of pure MoO_3 at the temperature of 1123K, see Fig. 3(a), indicating that the peaks of hydrogen consumed involved in the two steps reduction of $Mo^{6+} \longrightarrow Mo^{4+} \longrightarrow Mo^0$ merged into one peak. On the other hand, it showed clearly in Fig. 2(b)-(d) that the reduction process of doped MoO_3 had divided into two stages. In each stage, there are several peaks of hydrogen consumed corresponding to the oxygen active centers and the TPR peaks shift to the lower temperature side. The evident change in the peak area of hydrogen consumed (the peak area is proportional to the number of oxygen active centers) could be ascribed to the effect of different kinds of rare earth oxide in the samples. It is clear to see the effect of La_2O_3 on the reduction behavior of MoO_3 by comparing curves in Fig. 2(b)-(d), in which adding La_2O_3 in the sample was favorable for the formation of oxygen active center with high activation energy and low consumed hydrogen peak temperature. Decreasing the content of La_2O_3 from 25% (mass fraction) (b) to 6.25% (mass fraction) (c), no change in the peak temperature of the samples in the low temperature range was found, indicating that the species of the oxygen active center formed in these two samples are the same. However, the peak area of Sample 2 was much smaller than that of Sample 1. Although Sample 2 and Sample 3 had the same content of La_2O_3 (6.25%, mass fraction) in the raw material, the peak of hydrogen consumed of Sample 3 in the low temperature range almost disappeared, see Fig. 3(d). By combination with XRD analysis result of Sample 3 (see Fig. 4) in which La_2O_3 patterns were not detected in the spectra, it confirmed that the oxygen active centers in the low temperature range were formed by the addition of La_2O_3. In this sample, La went into the crystal lattice of $Gd_{1.26}Y_{0.74}O_3$ compound and formed substitutional solid solution (which will be introduced in another paper) since La^{3+}, Y^{3+} and Gd^{3+} have nearly the same ionic radius, resulting in the decrease in the formation probability of oxygen active centers. The phenomenon on the smaller peak area of sample 2 described above could also be explained by the effect of La_2O_3. Fig. 5 shows the XRD patterns of La_2O_3, Y_2O_3 co-doped Mo prepared (Sample 2). $LaYO_3$ diffraction peaks were observed. In Sample 2, apart from the lower content of La_2O_3 (6.25%, mass fraction) in the original design, the reaction product $LaYO_3$ also caused the consumption of La_2O_3. As a result, only a certain number of oxygen active centers could be formed. On the other hand, the doped MoO_3 exhibited different reduction behavior in the high temperature range compared with pure MoO_3. The strong interactions between rare earth ions and molybdenum ions in the samples led to the changes in the chemical environment of molybdenum and Mo-O bonds. As a consequence, different oxygen active centers were formed and, thus the continuous reduction process split up and the peak temperature of hydrogen consumed shifted to the lower temperature side[4], see Fig. 3.

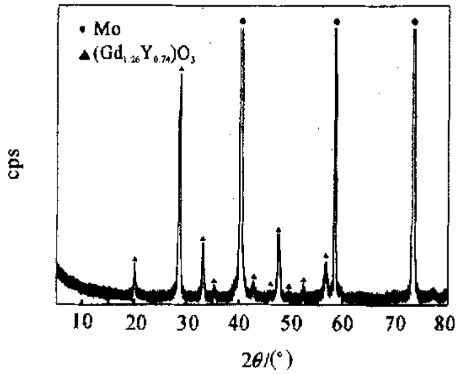

Fig. 4 XRD patterns of La_2O_3, Y_2O_3, Gd_2O_3 co-doped Mo prepared

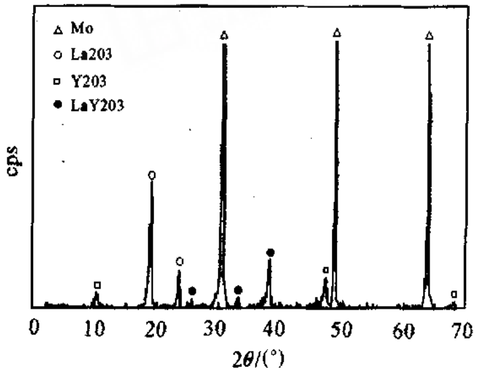

Fig. 5 XRD patterns of La_2O_3, Y_2O_3 co-doped Mo prepared

It is evident from Fig. 3 that the addition of rare earth oxide could decrease the reduction temperature in the high temperature range. As we know, the reduction at low temperature can avoid the growth of the particles. So, we could deduce that this kind of reduced powder would have smaller particle size than those prepared from pure MoO_3. Moreover, the particle size of the powder varied with the amount of rare earth oxide. Figs. 6(a) and (b) show the morphology of La_2O_3 and Y_2O_3 co-doped Mo powder with the total content of 10% and 30% (mass fraction) (the ratio of La_2O_3 and Y_2O_3 is kept at 1:3), respectively. As shown in Fig. 6(a), when the content of rare earth oxide is low (10%, mass fraction), the particles have polygon shape with larger size and distributed in a wide size range. We also found that some small particles attached to the large particles. EDS result shows that these small particles contain the elements of La and Y, indicating that these particles can be assigned to rare earth oxide particles. Increasing the content of rare earth oxide to 30% (mass fraction), the particle size decreased greatly and the particles distributed in a narrow size range. Rare earth oxide changed the chemical environment of molybdenum and Mo-O bands in MoO_3, resulting in the decrease of the content of MoO_3 taken in the reduction reaction and, thus the evaporation rate of MoO_3 at high temperature slowed down. As a result, the vapor transfer during the reduction process could be hampered and the particle size of molybdenum was small[5]. In addition, the tiny rare earth oxide particles that attached to the surface of molybdenum hindered the growth of molybdenum particles. The more the content of rare earth oxide, the finer the particles and the more uniform the particle size.

4 Conclusions

(1) MoO_3, La_2O_3, Y_2O_3, $La_2Mo_4O_{15}$ and Y_2MoO_5 existed in the sample prepared by heating the mix-

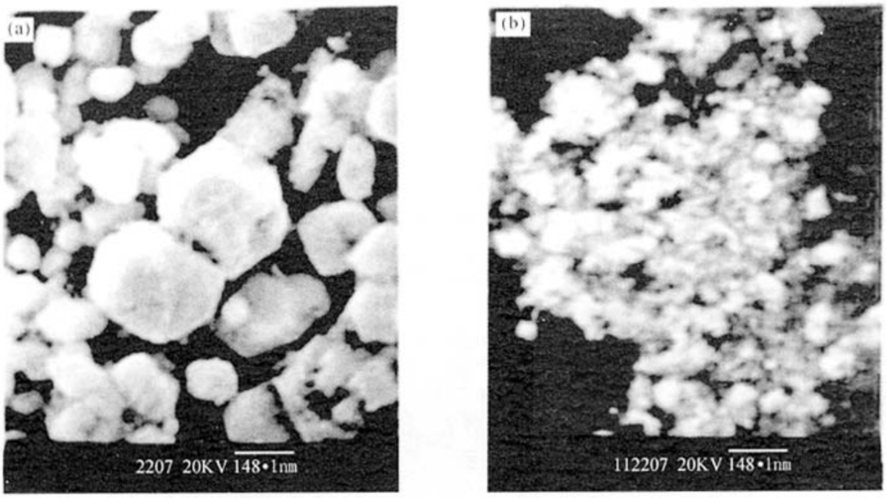

Fig. 6 Morphology of RE_2O_3 doped molybdenum powder with the content of RE_2O_3 10% (a) and 30% (b)

ture of MoO_2 powder and water solution of $La(NO_3)_3$, $Y(NO_3)_3$ in water bathing followed by decomposition in air at 550℃.

(2) Temperature programmed reduction (TPR) results show that the reduction behavior of rare earth oxide doped MoO_3 is different from that of pure MoO_3. The reduction peak shifts to the lower temperature side.

(3) Doping rare earth oxide in the powder could decrease the particle size of molybdenum. The more the content of rare earth oxide, the finer the particle size of molybdenum.

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