STRUCTURE AND PROPERTY OF SINTERED MOLYBDENUM DOPED WITH La_2O_3 ①

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ABSTRACT The effect of La_2O_3 on the microstructure and property of sintered molybdenum has been investigated. It was shown that the sintering density of molybdenum increased, the grain structure was fined obviously and the bending strength and ductility of molybdenum were improved greatly with the addition of La_2O_3. Moreover, its linear expansion coefficient of sintered molybdenum decreased as well.

Key words molybdenum La_2O_3 microstructure mechanical property

1 INTRODUCTION

Sintered molybdenum has a wide application. It can be used as the nozzles of rocket, the dies for hot working, the thimbles for producing seamless steel tube and the electrode for smelting furnace of glass and refractory. It is also used as substrate of thyristor extensively. In all its applications, the density, grain structure, strength and ductility of material have much influence on its performance. For the use of substrate of thyristor, the linear expansion coefficient is of critics.

Usually, sintered molybdenum has the shortage of low density and brittleness. In order to solve these problems, in particular the brittleness, a lot of attempts have been made. "The effect of rhenium" had ever been used to improve the brittleness of molybdenum effectively by the addition of rhenium[1], but this can not be widely applied due to the cost of rhenium. In some recent research, it has been found that the property of molybdenum can be improved by the addition of trace rare earth elements.[2]

In this paper, the effect of La_2O_3 on the structure and property are investigated.

2 EXPERIMENTAL

The lanthanum nitrate liquid was added to molybdenum powder, reduced and acquired powder contained 0.5%～3.0% La_2O_3. The pure molybdenum powder and the Mo-La_2O_3 powders were pressed into billets with the same size, then sintered at 1 800 ℃ for 4 h in hydrogen, thus seven kind of samples of different La_2O_3 contents were acquired.

The density of these samples were tested and the bending strength of them were measured with three-point bending test. The results are listed in Table 1.

Table 1 The sintering density and bending strength of pure Mo and Mo-La_2O_3

samples series	content of La_2O_3 /%	density /$g\cdot cm^{-3}$	bending strength /MPa
1	0	9.50	752
2	0.5	9.64	789
3	1.0	9.70	815
4	1.5	9.78	827
5	2.0	9.88	835
6	2.5	9.92	841
7	3.0	9.76	794

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The microstructure of samples were observed by scanning electron microscope (SEM). The phase structure of the addition were determined by X-ray diffraction and energy dispersive spectroscopy (EDX). In addition, the linear expansion coefficient of 0# and 3# were measured.

3 RESULTS AND DISCUSSIONS

3. 1 *Effect of* La_2O_3 *on Structure of Sintered Molybdenum*

Fig. 1 shows a SEM fractograph of sintered molybdenum doped with La_2O_3. A large number of dispersed particles are observed and the EDX analysis indicates that these particles are compound of Lanthanum. The corresponding data of X-ray diffraction indicates that La_2O_3 is in existential form of Lanthanum.

Because La_2O_3 particles neither decompose nor dissolve in molybdenum when sintered at 1 800 ℃ and they distribute dispersely along grain boundaries in the form of secondary phase. The migration of grain boundaries are dragged strongly by these particles during sintering, and this restrains grain growth and results in obovious fining of grain structure of molybdenum, as seen in Fig. 2. The higher the content of La_2O_3 is, the finer the grain structure is.

It can be seen from Fig. 2 and Table 1 that the sintering pores on molybdenum structure become less and smaller, and the sintering density increase with the addition of La_2O_3. That is mainly due to the fining of grain structure of molybdenum doped with La_2O_3 and as a result the grain boundary increases greatly. The grain boundary can be regarded as "trap" for the absorption of cavities and the path of cavity diffusion. The cavities, which are of high concentration around the sintering pores, move to grain boundary and are absorbed by it or are transmited to the surface of sintered body through the diffusion path. Therefore, the sintering pores shrink gradually and close even, lead to the increasing of sintering density.

In addition, from Fig. 3 it can be seen that La_2O_3 particles locate mainly on grain boundary or at the convergence polycyclic boundaries, where several grains meet each other, and the sites are often the locations of sintering pores. With the occupation of La_2O_3 particles on the locations of sintering pores, the sintering pores decrease and the sintering density increases.

Normally sintering density of molybdenum increases with the increasing of La_2O_3. However when La_2O_3 particles are over a certain number, they not only occupy the locations of sintering pores, but also increase the volume of the materials. Because the density of La_2O_3 is lower than that of molybdenum, the density of sintered molybdenum may decrease when the content of La_2O_3 is too high, as seen in Table 1.

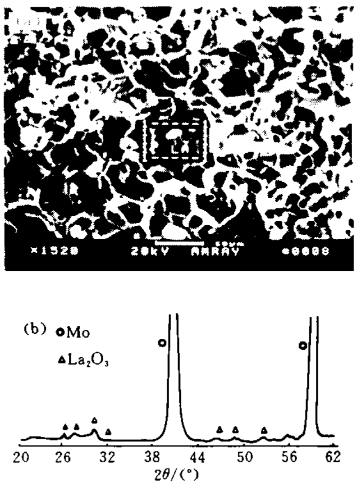

Fig. 1 SEM fractograph of sintered Mo-La_2O_3 alloy and X-ray diffraction analysis

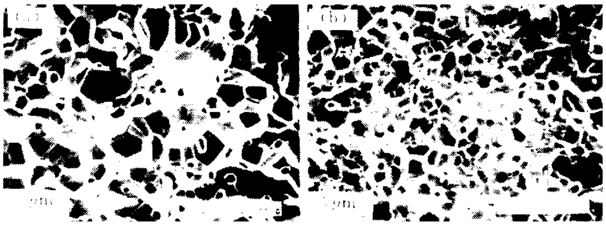

Fig. 2 SEM fractograph of Pure Mo and $Mo\text{-}La_2O_3$ alloy
(a)—Pure Mo; (b)—$Mo\text{-}La_2O_3$

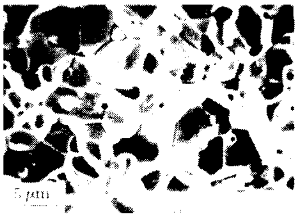

Fig. 3 The condition of La_2O_3 particles dispersed in sintered molybdenum

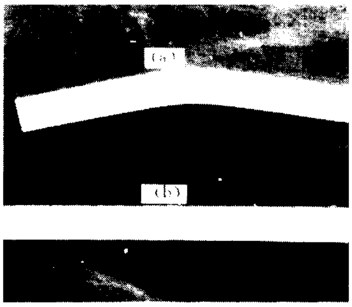

Fig. 4 The objects after three-point bending test
(a)—$Mo\text{-}La_2O_3$; (b)—Pure Mo

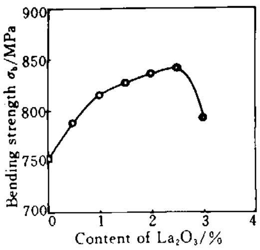

Fig. 5 Bending strength of sintered molybdenum versus content of La_2O_3

3.2 *Effect of* La_2O_3 *on Property of Sintered Molybdenum*

It can be observed from the three-point bending test that there isn't any bend deformation for pure molybdenum sample from loading to fracture and it fractures quickly. When the fracture parts are put together there is still a straight line. But for the sample doped with La_2O_3, an obvious bend can be observed when it is loaded to a certain degree. A noticeable bend deformation can be seen when the fracture parts, which have stood a maximum bend deforming, are put together, as seen in Fig. 4. It is clear that the room temperature plasticity of sintered molybdenum is improved greatly when it is doped with a proper quantity of La_2O_3.

Fig. 5 shows that bending strength of sintered molybdenum versus the content of La_2O_3. At the beginning, the bending strength of sintered molybdenum rises rapidly with increasing La_2O_3 content, but drops abruptly when La_2O_3 content exceeds 2. 5%. It is clear that the ductility of sintered molybdenum can be improved greatly when it is doped with a proper quantity of La_2O_3.

The improvement of the ductility is relevant to the fining of grain structure doped with La_2O_3. Some study discovered that the brittleness of sintered molybdenum is increased linearly to the coarsing of grain[3], moreover, grain boundary segregation of interstitial impurities is a main reason for the brittleness of molybdenum[4]. The fining of grain structure of molybdenum doped with La_2O_3 leads to the increasing of grain boundary, thus the concentration of interstitial impurties on the per unit grain boundary decreases, the ductility of the material improves.

Fig. 6 shows linear expansion coefficient versus temperature for pure molybdenum and Mo-La_2O_3 alloy. The linear expansion coefficient of material decreases by the addition of La_2O_3, which is very important for the use of substrate of thyristor. The change of temperature is great in the process of manufacture or operation of thyristor, in particular, the change of temperature can reach several hundred degree centigrades during welding silicon wafer onto substrate. The linear expansion coefficient of silicon is 4.2×10^{-6} 1/K, much less than that of normal metal material. The bigger of the difference of the linear expansion coefficient between silicon and substrate, the higher bend tensile stress yieldes on silicon wafer and this makes wafer damage easily. The decrease of the linear expansion coefficient of sintered molybdenum doped with La_2O_3 just meets the demand that the linear expansion coefficient of thyristor substrate be as close to that of silicon wafer as possible.

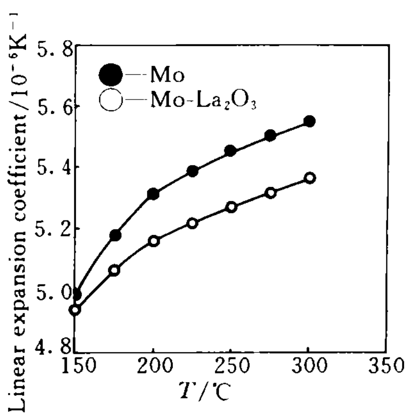

Fig. 6 Comparison of linear expansion coefficient of pure molybdenum with Mo-La_2O_3

4 CONCLUSIONS

(1) With the addition of La_2O_3, the sintering density of molybdenum increases highly and its grain fines greatly.

(2) The strength and the plasticity of sintered molybdenum are improved obviously when it is doped with a proper quantity of La_2O_3.

(3) The linear expansion coefficient of sintered molybdenum is decreased by the addition of La_2O_3 and that makes it more suitable to the use of thyristor substrate.

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