Materials Research Proceedings 38 (2023) 113-119 https://doi.org/10.21741/9781644902837-17

Preparation of High-Quality Mo-Nb (Ti/Ni-Ti) Sputtering Target by Hot Isostatic Pressing

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Keywords: Hot Isostatic Pressing; High Quality Sputtering Target; Powder Metallurgy; Density; Grain Size

Abstract. Mo-Nb, Mo-Ti, Mo-Ni-Ti sputtering target samples were prepared using Mo powder, Nb powder,Ni powder and Ti powder as raw materials by hot isostatic pressing (near net forming). The density, phase composition, microstructure and element distribution of Mo-Nb, Mo-Ti, Mo-Ni-Ti sputtered target samples were measured by optical microscope, scanning electron microscope and energy dispersive spectrometer. The experimental results show that hot isostatic pressing can prepare Mo-Nb target at lower temperature, and the obtained samples have finer grains, higher density and more uniform element distribution than that of non-pressure sintering. High-quality Mo-Nb, Mo-Ti, Mo-Ni-Ti sputtering targets (density>99%, grain size<100 μm) were obtained by hot isostatic pressing.

Introduction

With the rapid development of electronic information and related industries, the market demand for high-quality sputtering targets is increasing. Sputtering targets are widely used in many fields, such as plane display backplane, semiconductor, integrated circuit, recording medium and energy battery[1-4]. With the continuous expansion of application fields, the added value of sputtered targets is constantly improving. Therefore, the requirements for its performance and technical indicators are more stringent. The refractory metal Mo sputtering target has the advantages of high melting point, high elastic modulus, low thermal expansion coefficient, low resistivity and good thermal stability. It is widely used in the sputtering coating industry and occupies an important position. It is an indispensable raw material for products such as flat panel displays, semiconductors (gate electrodes, connecting wiring, diffusion barrier layers), microelectronics, solar cells, etc., and has broad market prospects[5]. In the electronics and information industries, such as semiconductors, integrated circuits and liquid crystal displays, which require high target quality, have strict requirements on the purity, density, grain size and ingredient uniformity of the target[6]. The films sputtered from pure Mo targets have some problems in terms of corrosion resistance (discoloration) and adhesion (film peeling). A large number of studies show that adding Nb, Ti, Ni and other metals to molybdenum can make its specific impedance, stress, corrosion resistance and other properties balanced[7-9].

There are many disadvantages in the production of Mo alloy targets by the traditional sintering method, such as high target porosity, low yield, coarse grains, and poor organizational uniformity, which makes it difficult to guarantee product quality. Hot isostatic pressing (HIP) is a kind of technology that takes inert gas as the pressure medium, places the product in a closed container, and applies equal pressure to the product under the joint action of high temperature (~2000°C) and high pressure (~200MPa) to sinter the product [10]. In this study, Mo-Nb, Mo-Ti and Mo-Ni-Ti

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alloy targets will be prepared by hot isostatic pressing, the effects of preparation methods on the microstructure, density and element distribution of Mo-Nb, Mo-Ti and Mo-Ni-Ti alloy targets will be studied, so as to provide process references for the preparation of high-quality Mo alloy targets.

Test materials and methods

Test materials

The average powder particle diameter of Mo powder selected in this test is 3.3 μm~5.0 μm, Nb powder is 45 μm~75 μm, Ni powder is 15 μm~45 μm and Ti powder is 45 μm~75 μm. The specific components of the powder are shown in Table 1, and the purity of all powders is above 99.95%. The powder morphologies of Mo powder, Nb powder, Ni powder and Ti powder are shown in Fig. 1. It can be seen from Fig. 1 that under the observation of the scanning electron microscope, the morphology of Mo powder is relatively uniform, and the particles are spherical or nearly spherical. The morphology of the Nb powder particles is relatively non-uniform in size, and most of them are irregular blocks or prismatic structures. The Ni powder particles are agglomerated, which requires reduction heat treatment before mechanical mixing. The morphology of the Ti powder particles is similar to that of the Nb powder particles, and the size is relatively non-uniform and irregular prismatic structure.

Table 1. Impurity element content of test metal powder / ($\times 10^{-6}$)

Powder	C	O	N	H	Fe	Si	Cu	Al	Ca	Mg	S
Mo	17	120	5	12	29	7	1	3	2	2	/
Nb	105	750	108	11	36	15	4	11	/	/	11
Ni	50	610	150	10	50	5	1	1	/	/	/
Ti	110	960	120	15	40	3	/	/	/	10	/

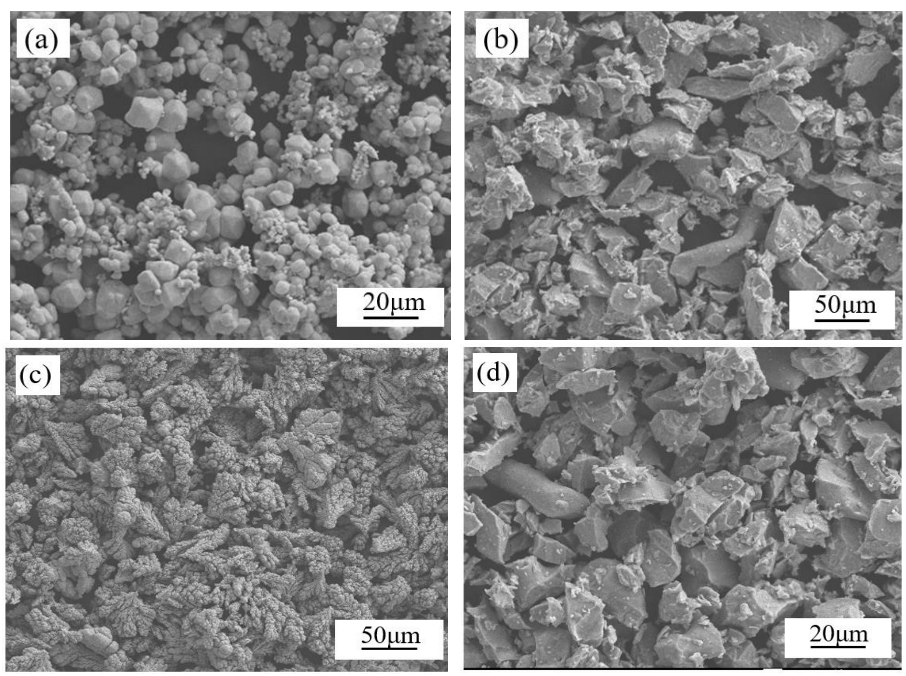

Figure 1. Powder morphologies by SEM
Mo powder; (b) Nb powder; (c) Ni powder; (d)Ti powder

Sample preparation method and process

The first step is mixing the powder of Mo+Nb, Mo+Ti, Mo+Ti+Ni according to the specified weight ratio. Then load the mixed powder into a vertical V-type mixer, where the three-dimensional mixing is carried out under the protection of argon. The stirring power is 1.1 KW, the stirring speed is 30 rpm~40 rpm, and the three-dimensional mixing time is 4 h. The oxygen in the air sucked by the metal powder shall be strictly controlled during the whole mixing process. The mixed Mo-Nb powder is divided into two groups, one group is used for non-pressure sintering, the other group is used for hot isostatic pressing. The specific preparation process of all samples is shown in Table 2. The sintering temperature of Mo-Nb sample is 1600 ℃~1800 ℃, and sintering in reducing atmosphere for 6~8 h. The hot isostatic pressing process of Mo-Nb sample is to put the mixed powder into a soft steel capsule, preheat the powder at 400 ℃~500 ℃, and conduct degassing sealing welding to make the vacuum degree less than 6×10^{-3} Pa. Put the capsule (after degassing sealing welding) into the furnace for hot isostatic pressing. The hot isostatic pressing pressure is 120 ~180 MPa, temperature is 1150~1300 ℃, and holding time is 2~4 h. The hot isostatic pressing process of Mo-Ti sample is as follows: the hot isostatic pressing temperature is 950 ~1100 ℃, pressure is 120 ~180 MPa, and holding time is 2~4h. The hot isostatic pressing temperature for Mo-Ni-Ti sample is 900~1050℃, the pressure is 120 ~180 MPa, and holding time is 2"4 h. After the preparation of the samples, the metallographic and density tests are carried out on all samples. The metallographic samples are polished with 400, 600, 800, 1000 and1200 mesh water abrasive paper, then cleaned with alcohol, dried and finish polish. The microstructure observation and energy spectrum analysis of the samples are carried out with optical microscope and Zeiss SUPER55 scanning electron microscope.

Table 2. Preparation Process of Samples

Sample	Process	Process parameters
Mo-Nb	Non-pressure sintering	Sintering temperature: 1600℃-1800℃, sintering in reducing atmosphere: 6~8h.
	HIP	Soft steel for capsule with a thickness of 3mm, hot isostatic pressing temperature is 1150℃~1300℃, pressure is 120MPa~180MPa, holding time is 2~4h.
Mo-Ti	HIP	Capsule thickness: 3mm, hot isostatic pressing temperature is 950℃~1100℃, pressure is 120MPa~180 MPa, holding time is 2~4h.
Mo-Ni-Ti	HIP	Capsule thickness: 3mm, hot isostatic pressing temperature is 900℃~1050℃, pressure is 120MPa~180 MPa, holding time is 2~4h.

Results and discussion

Density and oxygen content

Figure 2 shows the density test results of the samples. It can be seen from the figure that the density of Mo-Nb sample obtained by non-pressure sintering is only 96.5%, which does not meet the requirement (⩾99%) for high-quality sputtering targets. The density of the Mo-Nb sample prepared by hot isostatic pressing is 99.8%. The density of the Mo-Ti obtained by hot isostatic pressing is 99.8%, which is close to the theoretical density of the sample. The density of Mo-Ni-Ti obtained by hot isostatic pressing is 99.1%, which is relatively low, but it has also reached the density requirement for high quality sputtering target. By analyzing and comparing the densification degree of these samples, it is shown that hot isostatic pressing can greatly reduce the porosity and increase the density. Table 3 shows the detection values of oxygen content of the

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samples. It can be seen from the table that the oxygen content of the sample prepared by non-pressure sintering reaches 1380 ppm, exceeding the required range. The reason may be related to the fact that the samples were not protected by reducing atmosphere in time during high temperature sintering for a long time.

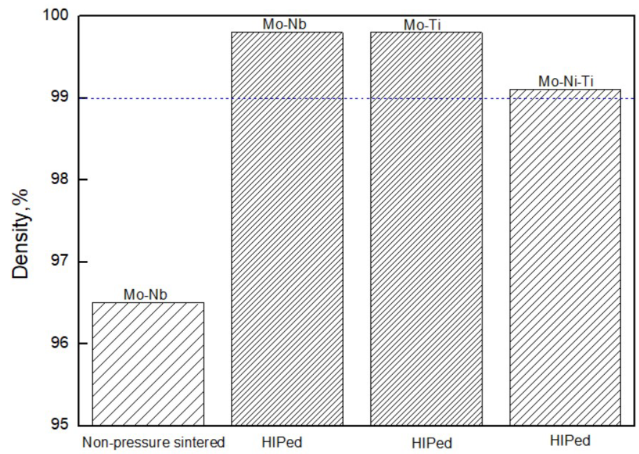

Figure 2. Results of sample density

Table 3. Oxygen content of samples

Sample	Oxygen content /(×10^{-6})
Mo-Nb（non-pressure sintered）	1380
Mo-Nb（HIPed）	790
Mo-Ti（HIPed）	860
Mo-Ni-Ti（HIPed）	760

Microstructure

Figure 3 shows the metallographic micrographs of Mo-Nb, Mo-Ti and Mo-Ni-Ti samples. It can be seen from Fig. 3 (a) that the grain size distribution of Mo-Nb sample prepared by non-pressure sintering is wide, the larger grain size reaches 200 μm, and the smaller grain size is less than 50 μm. Fig. 3 (b) shows the microstructure of the Mo-Nb sample prepared by hot isostatic pressing. It can be seen from the figure that the grain size is small and evenly distributed, and the grain size is 20 μm~100 μm, the original size of the powder is basically maintained. Mo-Ti and Mo-Ni-Ti samples prepared by the hot isostatic pressing process have uniform microstructure and no obvious pores and oxide inclusions, which are shown in Fig. 3 (c) and Fig. 3 (d). Compared with these metallographic micrographs, it can be found that the samples prepared by non-pressure sintering have more pores and larger grain size. In Fig. 3 (a), many particles and pores (black part) are distributed along the grain boundary. Referring to the measurement results of the oxygen content of the sample in Table 3, it can be preliminarily determined that the oxide in the sintered body is the main reason for the low density. In order to find the reason for the low density of non-pressure sintering, the internal factors of the low density of Mo-Nb sample prepared by non-pressure sintering process will be determined by scanning electron microscope and energy spectroscopic analysis.

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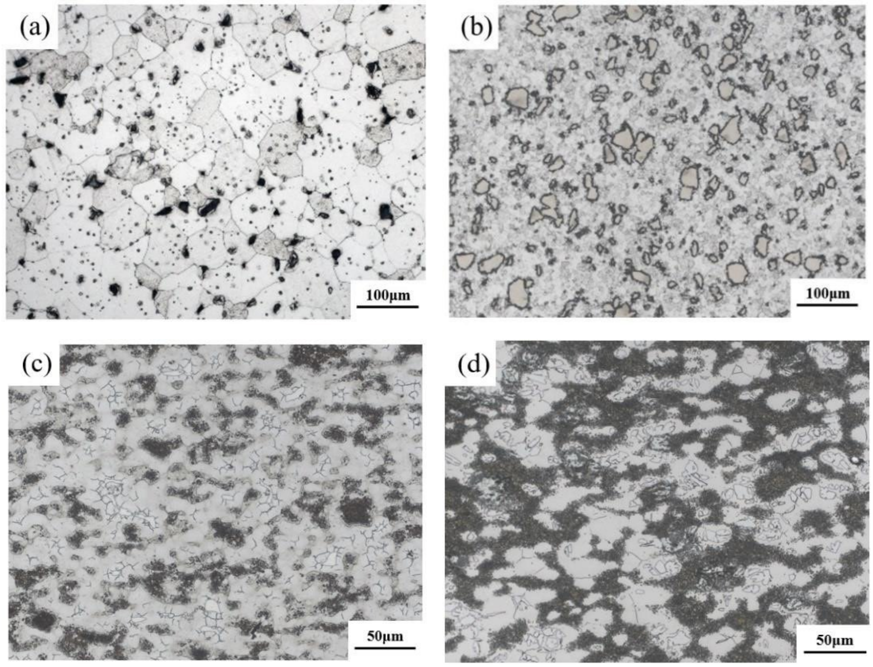

Figure 3. Metallographic micrographs of samples (a) Mo-Nb (non-pressure sintered); (b) Mo-Nb (HIPed); (c) Mo-Ti (HIPed); (d) Mo-Ni-Ti (HIPed)

Distribution of chemical elements

Figure 4 shows the SEM analysis results of Mo-Nb sample prepared by non-pressure sintering. It can be seen from Fig. 4 that there is obvious aggregation of Nb elements in the Mo-Nb alloy sample. From the energy spectrum analysis results in the figure, it shows that Nb elements aggregate at the grain boundaries in the form of NbO*x*. The fine niobium powder is easy to absorb oxygen, and it is difficult to control the oxygen content. Therefore, these oxides may be brought into the powder particles or generated during the sintering process. According to relevant literature reports[11], the deoxidation of niobium oxide in the sintering process is divided into two stages: the first stage has only a small amount of weight loss, and the second stage starts at 1995 K, a large amount of weight loss occurs in this stage. The formation of NbO is better than that of NbO_2 under high temperature and low oxygen conditions. If the high temperature hydrogen reduction sintering method is used, due to the moisture contained in the hydrogen, the free Nb is easily combined with it to form NbO_2 during the heating process. Therefore, this explains the phenomenon that a large amount of NbO*x* accumulates at the grain boundary during the sintering process of Mo-Nb to reduce the density. Figure 5 shows the element distribution of the Mo-Nb sample prepared by hot isostatic pressing. It can be seen that the element distribution of the Mo-Nb sample prepared by the hot isostatic pressing process is uniform. Figure 6 is the scanning electron microscope analysis of the fractures of Mo-Ti and Mo-Ni-Ti samples. It can be seen that the fracture of Mo-Ti sample is flush and there is no obvious pore. While the fracture of Mo-Ni- and there is an obvious hole embedded inside, which is about 10 μm in length and 2~3 μm in width. The reason for the formation of voids is probably due to the reaction between Mo and Ni to form Mo-Ni brittle phase at high temperature during hot isostatic pressing, which is also the reason for the relatively low density of Mo-Ni-Ti. Therefore, the research results show that the hot isostatic pressing parameters for Mo-Ni-Ti need to be optimized.

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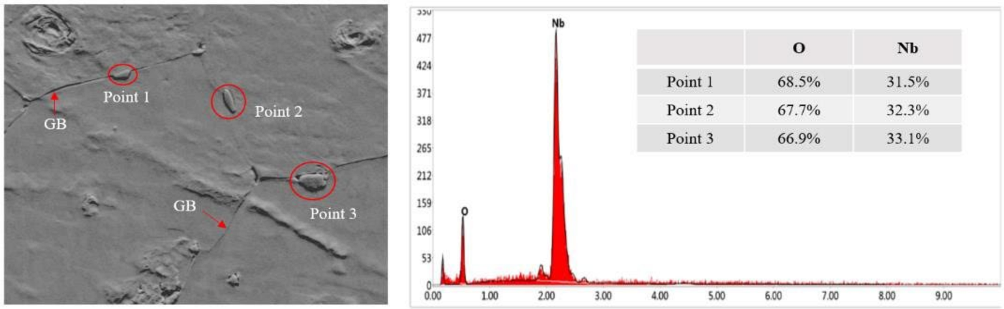

Figure. 4 SEM-EDS analysis of Mo-Nb (non-pressure sintered)

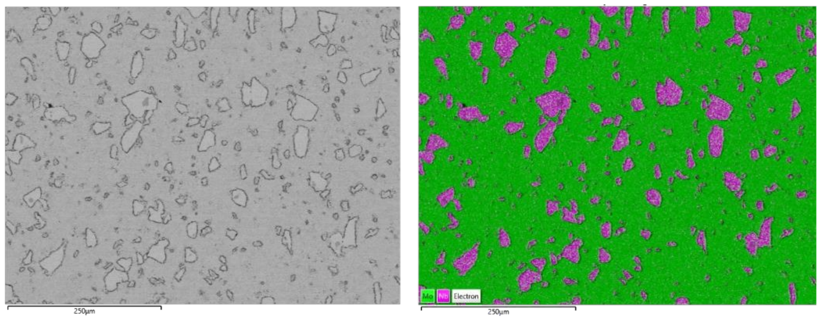

Figure. 5 SEM-EDS analysis Mo-Nb (HIPed)

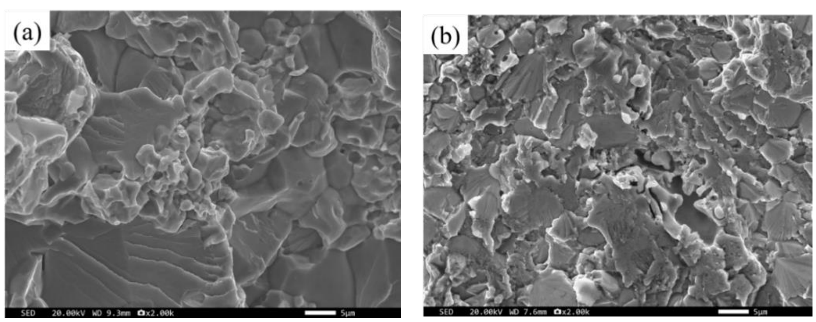

Figure. 6 SEM analysis of sample fracture
(a) Mo-Ti (HIPed); (b) Mo-Ni-Ti (HIPed)

There are some studies on the influence of microstructure and density on the sputtering performance of Mo target. Huang H S *et al.* [12] studied the effect of the preparation process on the microstructure and sputtering performance of the Mo target by using several preparation methods. The research results show that hot isostatic pressing can prepare Mo targets with a density close to the theoretical density. In contrast, through hydrogen sintering, the density of the Mo target reaches only 95%. In addition, due to the lower hot isostatic pressing temperature, grain growth is not obvious after densification. Therefore, the microstructure of the Mo target processed by HIP is very fine, and the average grain size is below 100 μm. The study of sputtering performance shows that the Mo target produced by hot isostatic pressing has the highest deposition rate, followed by the hydrogen reduction sintered Mo target, and the asrolled Mo has the lowest deposition rate. Researchers have carried out relevant research on the microstructure and sputtering performance of Mo target, but there are few detailed reports on the preparation method, microstructure analysis and phase analysis. In particular, the rapid development of hot isostatic pressing technology in recent years has opened up a new way to prepare Mo and most refractory metal targets by using this technology to produce high-quality targets.

Conclusion

In this study, the effects of preparation methods on the microstructure, density and element distribution of Mo-Nb, Mo-Ti and Mo-Ni-Ti targets are analyzed by means of optical microscope, scanning electron microscope and energy spectrometer. The conclusions are as follows:

(i) Hot isostatic pressing can prepare Mo-Nb target with finer grain, higher density and more uniform element distribution than non-pressure sintering at lower temperature.
(ii) A large number of niobium oxide particles gather at the grain boundary of MoNb alloy prepared by non-pressure sintering, which is the main reason for the insufficient density. An important source of niobium oxide is the moisture in hydrogen during sintering.
(iii) High-quality Mo-Nb, Mo-Ti and Mo-Ni-Ti sputtering targets with density >99% and grain size <100μm can be prepared by hot isostatic pressing.

Acknowledgements

The authors thank CISRI HIPEX for providing the hot isostatic pressing equipment. This work was supported by China Iron & Steel Research Institute Group, and Project No. 2020018.

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