Preparation Process and Quality Characterization of High Density Fine Grain Osmium Target for Coated Cathode

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Abstract—High quality osmium targets are the key influence in improving the emission performance, lifetime and reliability of M-type cathodes. In this experiment, oxidative distillation was used to prepare osmium powder with a purity greater than 99.99%. The effect of hydrogen sintering and hot pressing sintering processes on the densities and grain size of the targets was investigated. The results show that the oxidation distillation process can effectively separate Os from Si, Fe, Ni, Zn and other impurity elements, and the purity of osmium powder prepared by multiple oxidation distillation was not less than 99.99%. Both hydrogen sintering and hot pressing sintering processes can be used to obtain osmium targets with a density of not less than 95%. However, the sintering temperature and time used in the hot pressing sintering process under pressure assistance are significantly lower than those of hydrogen sintering, which is more conducive to inhibiting grain growth during the high densification sintering process. By optimizing the parameters of the hot pressing sintering process, the sintering temperature of 1500°C and the holding time of 1.5h resulted in an osmium target with a density of 99.11% and a grain size of ≤12. XPS analysis of the highly dense fine crystalline osmium targets prepared by hot pressing sintering showed that the C and O mass fractions on the surface of the targets were 0.85% and 4.43% respectively, and the C and O contents gradually decreased with increasing etching depth. The above highly dense and fine crystalline osmium targets can be used in the M-type cathode standard coating process to obtain high purity, dense and strong bonded osmium films.

1. Introduction
Millimeter-wave electric vacuum devices have the advantages of high resolution, high precision and high energy density, and are widely used in military and civil applications such as 5G communications, integrated air-space communications and high-resolution radar. The cathode is the "heart" of the electric vacuum device, its life and reliability directly determine the performance and reliability of the traveling wave tube[1,2]. With China's high detection accuracy, wide width, lightness and deep space exploration and other air and space science and technology development needs, there is an urgent need for centimeter wave and millimeter wave high-power and high-pulse space traveling wave tubes.
The M-type cathodes by depositing a thin metal or alloy film (Os, Ir, Re or Os-Ir) on the surface of B or S type impregnated cathodes to reduce cathode surface fugitive work, increase cathode emission current density, cathode life and reliability[3-5]. The actual work function of the surface osmium coated cathode is 0.2 eV lower than that of the conventional barium tungsten cathode, and the emission current densities of the osmium coated cathode and the tungsten coated cathode are 8.04 A/cm² and 3.02 A/cm² respectively at 1000°C. The emission performance of the Os film cathode is much better than that of the W film[6,7].

Osmium (Os) is the densest metal with a density of 22.59 g/cm³. Pure osmium melts at 3027°C, second only to tungsten and rhenium. Its crystal structure is dense and hexagonal, hard and brittle, not easily machined, furthermore, osmium is easily oxidized, generating OsO₄ which is highly toxic.

Osmium targets for magnetron sputtering are mostly prepared by powder metallurgy due to their high melting point and difficulty in shaping. The quality of the osmium targets for coating directly limits the performance of the M-type cathodes. A large number of domestic and abroad studies have shown that the factors that have the greatest impact on the quality of sputtering targets are purity, density, grain size, dimensional accuracy, weave and so on. For a long time, most of the domestic demand for osmium targets relies on imports, the product performance of the target purity, grain size, density and other important information requirements of the index is basically lacking. In recent years, the domestic demand for cathode material batch stability and high quality requirements highlighted, can not be prepared to meet the needs of high-power tube development.

The purity of osmium powder is about 99.9% due to the scarcity of osmium raw materials and dependence on imports. In this paper, a high purity osmium powder was prepared from crude osmium by oxidative distillation and precipitation reduction processes. The osmium targets were prepared by cold isostatic pressing-hydrogen sintering (CIP-H₂) and hot-pressing sintering (HP) processes, respectively. Their properties such as density, purity and grain size were analyzed and characterized by drainage, GDMS and metallographic analysis in order to control the fine crystalline and high density process of the osmium targets. At the same time, it is difficult to detect the C element content of osmium powder or targets by conventional high-frequency combustion-IR absorption methods due to the chemical nature of Os, which is easily oxidized and volatile at low temperatures. The experiments are aimed at detecting the composition and distribution of C, O, N, S and other impurities in the osmium targets by means of XPS analysis, in order to provide guidance data for the applications of the osmium target coating and the performance of the cathode.

2. Experiment.

The purity of the raw osmium powder is approximately 99.9%. Osmium is separated from other impurities by oxidative distillation through self-made purification device, and is prepared by alkaline absorption and multi-stage hydrogen reduction, with a median particle size of 0.6 μm and a normal uniform distribution. The osmium target was prepared by powder metallurgy, and the effects of CIP-H₂ and HP on the density and grain size of osmium target were studied. The CIP-H₂ sintering in tungsten boat, sintering temperature 2100~2300°C, sintering time 6~12 h. HP sintering process using high purity graphite mold, sintering pressure 20~40 MPa, sintering temperature 1400~1700°C, sintering time 0.5~2 h.

The density of the osmium target was tested by using the Archimedes drainage method and the grain size of the target was tested by metallographic analysis. For the characterization of metallic impurities in osmium powder and targets by GDMS, a Nu Astrum-ES low pressure source DC glow discharge mass spectrometer with a dual focus mass analyzer consisting of an electrostatic field analyzer and a magnetic field mass analyzer was used. The compositional and structural analysis was carried out on the surface of the osmium target up to a certain depth from the surface by XPS. The XPS inspection equipment is a NEXSA X-ray photoelectron spectrometer system from Thermo Scientific, USA, with an incident light source of 1486.68 eV monochromate Al Kα rays and an energy resolution of ∆E ≤ 0.5 eV. The etching rate for Ta₂O₅ at this etching power was 0.56 nm/s. Since the etching rate is inversely proportional to the hardness (Mohs hardness: Ta₂O₅ = 6, Os = 7), the etching rate for the osmium target was calculated to be...
0.48 nm/s. High purity osmium powder specimens and osmium targets were transferred to the sample chamber and vacuum desorbed for 2 hours when the vacuum level reached $10^{-7}$ Pa. The purpose was to use the high vacuum environment to remove the impurities adsorbed on the surface of the samples. Photoelectron spectra of the elements on the target surface and inside the target were collected to characterize the content and distribution of elements such as C and O in the target material.

3. Result and discussion

3.1 Purity

Os can produce volatile OsO$_4$ vapor under the action of strong oxidizing agents, and this feature can be used to separate Os from other metallic elements[8,9]. The type and content of impurity elements of osmium powder are closely related to the purification process. At present, only the standard 《YS/T681-2008 Osmium Powder》 specifies 99.90% and 99.95% impurity elements of the osmium powder, and there is no national or industry standards for higher purity osmium products.

In this experiment, the impurity content of the osmium was determined by GDMS method and the purity of the osmium targets was calculated using the subtraction method, involving impurity elements such as Au, Mg, Si, Fe, Pt, Ni, Al, Ir, Pd, Cu, Ag, Rh, Zn and Ru.

Table 1 shows the GDMS analysis results of crude osmium powder, and the osmium powder purified by oxidative distillation. It can be seen that the oxidative distillation process can effectively reduce the content of impurity elements such as Si, Fe, Ni and Zn, and the purity of osmium powder can be increased to 99.99% after purification by multiple oxidative distillation. The GDMS analysis results of hydrogen sintered osmium targets and hot press sintered osmium targets are shown in Table 2, and the purity of the targets is not less than 99.99%.

| Project          | Impurity element content / $10^{-6}$ | Purity / % |
|------------------|-------------------------------------|------------|
|                  | Au       | Mg       | Si       | Fe     | Pt     | Ni     | Al     | Ir     | Pd     | Cu     | Ag     | Rh     | Zn     | Purity / % |
| Crude            | >0.005   | 20.4     | 352.1    | 81.1   | 0.9    | 40.1   | 5.26   | <10    | 0.035  | 6.48   | 1.2    | 0.017  | 11.4   | 99.90333 |
| Purified 1       | >0.005   | 0.64     | 31.9     | 8.34   | 0.14   | 2      | 0.63   | $<5$   | $<0.005$ | 2.53   | 0.03   | $<0.005$ | 0.21   | 99.9954   |
| Purified 2       | >0.005   | 0.45     | 30.5     | 10.7   | 0.11   | 2.68   | 1.06   | $<5$   | $<0.005$ | 2.89   | 0.05   | $<0.005$ | 0.16   | 99.9951   |

Table 2 Composition of CIP-H$_2$ sintering and HP sintering osmium target analyzed by GDMS

| Project | Impurity element content / $10^{-6}$ | Purity / % |
|---------|-------------------------------------|------------|
|         | Au       | Mg       | Si       | Fe     | Pt     | Ni     | Al     | Ir     | Pd     | Cu     | Ag     | Rh     | Zn     | Purity / % |
| CIP-H$_2$ | <0.005   | 1.77     | 32.7     | 10.1   | 0.42   | 1.21   | 2.58   | 2.29   | $<0.005$ | 1.93   | $<0.005$ | $<0.005$ | 5.59   | 99.9922   |
| HP      | <0.005   | 2.26     | 22.7     | 11.8   | 0.76   | 3.5    | 2.74   | 1.45   | $<0.005$ | 2.04   | $<0.005$ | $<0.005$ | 3.20   | 99.9999   |

3.2 Effect of sintering process on target density and grain size

For powder metallurgy sintered block materials, their high density and fine grain size indicators are contradictory. This is because the powder metallurgy sintered block materials are usually not high density. To improve the density, it is necessary to increase the sintering temperature or extend the sintering time, which will lead to grain growth[10-12].

The CIP-H$_2$ sintering and the HP sintering processes have been investigated and optimized in order to obtain the finest possible grain size of the target with a high density. Fig.1 shows the variation of density with the osmium targets prepared by different sintering processes, and Fig.2 shows the metallographic of the osmium targets prepared by different sintering processes at different sintering temperatures. As can be seen from Fig.1 and 2, the density of the osmium targets prepared by both the CIP-H$_2$ sintering and the HP sintering processes gradually increases as the sintering temperature rises, and decreases slightly
when the CIP-H$_2$ sintering temperature exceeds 2400°C and the HP sintering temperature exceeds 1700°C. This may be due to the fact that the crystal grains grow fast and the gas is not discharged in time as the sintering temperature increases. As a result closed pores are formed within the grains, leading to a reduction in density. Comparing the metallography of the osmium target grains prepared by the two processes with a similar density. It can be seen that at a target density of approximately 95%, the HP sintering process produces a target with a grain size of grade 12 and a grain size of ≤5.6 μm, while the CIP-H$_2$ sintering process produces a target with a grain size of grade 1.5 and a grain size of ≤213 μm. The grain size of the targets prepared by HP sintering is significantly smaller than that of the CIP-H$_2$ sintering process, which is due to the fact that the sintering temperature and sintering time of the HP sintering process are significantly lower than those of the CIP-H$_2$ sintering process under pressure assisted action. Admittedly HP is more conducive to promoting the densification of osmium sintered blanks and suppressing the grain size. After optimization of the HP sintering process, the densities of the prepared osmium targets are not less than 99%, while the grain size reaches grade 12.

![Graph](image1.png)

**Fig.1** The influence of sintering process on the density of osmium target

![Images](image2.png)

**Fig.2** The influence of sintering process on the grain size of osmium target

(a) CIP-H$_2$, 2300°C, 6 h, grain size number 4; (b) CIP-H$_2$, 2400°C, 6 h, grain size number 3.5; (c) CIP-H$_2$, 2450°C, 6 h, grain size number 1.5; (d) HP, 1600°C, 1.5 h, grain size number 12; (e) HP, 1700°C, 1.5 h, grain size number 8.5; (f) HP, 1750°C, 1.5 h, grain size number 6.5;
The fracture morphology analysis of the target with 99% density in the HP sintering, microstructure morphology as shown in Fig.3. The osmium target grains are uniformly small, with an average grain size of less than 10 μm, and the grain structure is closely connected. There is obviously no grain boundary melting phenomenon at the grain boundary, and only in the multi-grain contact position appears tiny holes.

![Microstructure of dense osmium target sintered by hot pressing](image)

**Fig.3** Microstructure of dense osmium target sintered by hot pressing (a)X2000 (b)X10000

### 3.3 XPS analysis of osmium target composition

The impurity elements such as carbon and oxygen in the target material have a great influence on the cathodic coating process and the activation of the ageing process. Too high a content will lead to a large amount of outgassing during the cathodic coating, which is not conducive to the adhesion of the osmium film to the porous tungsten substrate and the cathodic emission performance [13,14]. In this experiment, the GDMS method was used to detect the content of impurity elements in osmium, but due to the poor detection limits of nonmetallic element, the content of C and O in osmium targets could not be accurately evaluated. To solve this problem, the analytical technique of X-ray photoelectron spectroscopy was used to analyze the C and O elements in osmium targets.

Fig.4 shows the full XPS spectrum of an Ar⁺ etched osmium target prepared by the hot press sintering, with etch depths ranging from 0 to 86.4 nm. The identification of the peaks shows that the presence of peaks for Os, C, O, N and S. The intensity of the spectral bands can reflect the amount of elemental content. As can be seen in Fig.4, there are strong spectral bands in the region of binding energy 500-600 eV, 250-300 eV and 0-60 eV, corresponding to higher content of O, C and Os and lower content of N and S.

![Full XPS spectra of osmium targets](image)

**Fig.4** Full XPS spectra of osmium targets
The relative spectral intensities of the other elements were measured by the sensitivity factor method by using the spectral intensities of specific elements as a reference standard, and the curve of the osmium target element content and etching depth is shown in Figure 4. As can be seen from Table 3, the mass fractions of Os, C and O on the surface of the osmium target were 93.98%, 0.85% and 4.43%, respectively, when the target was not etched. This indicates that there is some carbon and oxygen present on the surface of the hot-press sintered osmium target. With the increase of etching depth, the mass fraction of C and O gradually decreases and the mass fraction of Os gradually increases.

### Table 3 Percentage of element mass in osmium target at different etching depths / %

| Etch depth (nm) | Os    | C     | N     | O     | S     |
|----------------|-------|-------|-------|-------|-------|
| 0              | 93.9815 | 0.8507 | 0.3041 | 4.4341 | 0.4294 |
| 28.82          | 98.8894 | 0.1180 | 0.0598 | 0.8605 | 0.0721 |
| 48.0           | 99.1358 | 0.0609 | 0.0533 | 0.6955 | 0.0544 |
| 67.3           | 99.2103 | 0.0392 | 0.0442 | 0.6441 | 0.0619 |
| 86.4           | 99.2251 | 0.0379 | 0.0472 | 0.6256 | 0.0639 |

The existing M-type cathode preparation process usually etches the coating target before coating, and the etching depth is usually 5-6 μm[15]. Therefore, the etching process can completely remove the C and O impurities from the surface of the osmium target, improve the coating performance and effectively enhance the bonding force of the film[16]. The results of the XPS analysis of the osmium targets also indirectly show that the hot-press sintering process can fully meet the requirements of impurity control for M-type cathode coating.

### 4. Conclusion
1. Oxidation distillation purification of osmium can effectively reduce the content of Si, Fe, Ni, Zn and other impurity elements, after several times of oxidation distillation purification can obtain the purity of not less than 99.99% of osmium powder. Not only does it successfully solve the problem of lower purity and quality of imported osmium powder, but it also enables industrial scale-up and stable batch production.
2. CIP-H₂ and HP sintering can be used to obtain osmium targets with a density of not less than 95%. The HP sintering process is beneficial to obtain the osmium targets with a better combination of density and grain size. After optimization of the hot-press sintering process, 99.99% purity, 99.11% density, less than 12 grain size and less than 5.6 μm grain size were achieved.
3. The C and O content of the osmium target of HP gradually decreases with the increasing of the etch depth. When the etch depth of Ar⁺ ion exceeds 67.3 nm, it tends to be stable, and the target mainly composed of Os. This depth is less than the etch depth of the cathodic coating process specification, and can be completely removed before the cathodic magnetron sputtering, ensuring a high purity, dense and strongly bonded osmium film.
4. After powder property repair and optimization of sintering process parameters, the osmium target reached high standards in terms of purity, density and grain size. We successfully realize the completely independent development and mass production of osmium targets for laminating cathodes, freeing itself from import dependence.

### References
[1] Wang J, Wu G, Yang M H, Su X G. Development Status of High Power Millimeter Wave Traveling Wave Tube [J]. Vacuum Electronics, 2010, (03): 38-42.
[2] Shao W S, Li J, Yu Z Q, Cheng C, Zhang K, Wang H, Wang L S. Experimental study on cathode life of space traveling wave tube [J]. Chinese Space Science and Technology, 2017, 037(002):103-107.
[3] Green M C, Skinner H B, Tuck R A. Osmium-tungsten alloys and their relevance to improved M-type cathodes [J]. Applications of Surface Science, 1981, 8(1): 13-35.

[4] Fang C. Surface studies of Os/Re/W alloy - coated impregnated tungsten cathodes [J]. Journal of Vacuum Science & Technology A Vacuum Surfaces & Films, 1990, 8(3): 2329-2332.

[5] Chaharsoughi M S, Hadianfard M J, Shiezadeh M M. Study the Effect of Nanoemissive Materials on M-Type Cathode Performance [J]. Advanced Materials Research, 2014, 829: 772-777.

[6] Yin S Y, Zhang H L, Yang J X, Qian H J, Wang J X, Wang Y, Wang X X. Study on Surface Synchrotron Radiation Photoelectron Spectra of Cathode Coated with Osmium Film [J]. Journal of Electronics & Information Technology, 2011, (12): 250-255.

[7] Yin S, Yang J, Zhang H, Wang Y, Wang X. SPRES study on surface of barium tungsten cathodes coated with os film [J]. IEEE, 2010.

[8] Griffith W P. Osmium and its compounds [J]. Quarterly Reviews Chemical Society, 1965, 19(3): 254-273.

[9] Alexander I , Alan M. Method for the production of high purity osmium: US, US3536479 A[P]. 1970.

[10] Wang H, Xia M X, Li Y C, Liu X F, Cai X M, Bai R, Zhang X. Application and preparation technology of refractory metal sputtering target [J]. China Tungsten Industry, 2019(1):64-69.

[11] Wang S M, Zuo Y T, Du F Z, Zhang Z H, Wen M, Guo J M. Microstructure and sintering mechanism of high purity ruthenium target sintering process [J]. Precious Metals, 2019(S01): 1-5.

[12] Wang G D, Xiong N, Liu G H, Chen F G. Effect of powder properties on sintering density of pure rhenium [J]. Chinese Journal of Rare Metals, 2021, 45(04): 507-512.

[13] Yu Z Q, Gao Y J, Shao W S, Li J, Zhang K. Summary of poisoning characteristics of barium tungsten diffusion cathode[J]. Vacuum Electronics, 2017(01): 22-27.

[14] Shao W S, Zhang K, Li J, Yan S Q, Chen Q L, Gas poisoning investigations of scandate and M-type dispenser cathodes [J]. Applied Surface Science, 2003, 215(1-4): 54-58.

[15] Ma J, Wang Y C, Xie Q H, Lu W Y. Application of Cathode Etching and Coating [C]. Article series of the Eleventh Vacuum Academic Exchange Meeting of Jiangsu province. 2007.

[16] Wang P, Li J. A Novel Nanocomposite Scandia-Tungsten Coated Dispenser Cathode [J]. Vacuum Electronics, 2009, (03): 17-22.