Research on the sintered microspheres of high purity molybdenum powders

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Abstract. The process of preparation of the sintered microspheres of high purity molybdenum powders was investigated. The results indicate that the process include spray granulation, degreasing and sintering(spray granulation- degreasing -sintering). And in the process, spray granulation is the key step of deciding the morphology and size of the powders, degreasing temperature is the important parameter to control the purity of the powder and sintering is the necessary process to control the morphology and physical properties of the final microsphere products. The higher of the sintering temperature is, the higher of the bulk density and flowability of sintered microspheres are. And the higher of the sintering temperature is, the lower of the O content of the powder is. The sintered microspheres of high purity molybdenum can be used not only in coating industry, but also in manufacturing industry of precision parts.

1. Introduction
With the development of modern technology, such as electronic information and astronauts aviation industry, some miniature or special-shaped molybdenum parts are in great needs. For example, LCD backlight source of molybdenum electrode, microwave oven magnetron cathode assembly, high performance and molybdenum alloy nozzle and throat with a new generation of aerospace engine. All these parts have complex shape, processing and difficult. Powder (near) net forming is a new technology for preparation of those parts is complicated, long processing cycle. In powder net forming, powder molding is the key technology.

Conventional hydrogen reduction of molybdenum powders are featured with irregular morphology, small bulk density, poor mobility, which are difficult to fulfill powder uniform filling, and can not meet the powder (nearly) net shaping demand. Therefore, the preparation of microspheres molybdenum powder with round morphology, large bulk density, good flowability has become an urgent problem. At present, the main methods to improve the propertied of powders are plasma spherical, sol-gel method, spray drying and spray drying and sintering[1-11]. Plasma spherical has the defect of high cost and low yield, sol-gel process is complex and long production cycle, spray granulation technology can improve the bulk density and flow velocity to some extent, but introduce high impurity. Spray granulation+sintering can not only improve the bulk density and flow velocity greatly, but also lower the impurity of the powder, and more importantly, spray granulation+sintering has the advantages of simple process, low cost, and easy to achieve industrialization.

2. Experimental Results and discussion
The molybdenum powders used are hydrogen reduced by nomal procedures, their Fisher particle sizes are about 3.1μm, and bulk density are 1.0g/cm³. The morphology of original molybdenum powders are as Figure 1, and their chemical compositions are as table 1. The binder used is PVA(Polyvinyl alcohol) with molecular weight of about 15000~25000.
The procedures of the experiment are as follows: Firstly, PVA is dissolved in the pure water completely, and molybdenum powders are added into the PVA solution as 68% solid content and stirred well to make slurry. Secondly the slurry is spray dried by centrifugal spray dryer with the rotation rate of atomizing disc about 12000 r/min. Thirdly, the spray dried molybdenum powders are degreased in the mono pipe hydrogen furnace at 800-900℃. Finally, the degreased molybdenum powders are sintered at 1100℃ - 1500℃ in a muffle furnace with hydrogen atmosphere. Bulk density of the powders are determined by funnel method, their flowability are detected by hall flowmeter, and the morphologies of the powders are observed by scanning electron microscope(SEM). The content of C in the powders is detected by infrared carbon and sulphur analyser, and the content of O is detected by oxygen analyzer.

### Table 1 Chemical composition of original molybdenum powders (wt%)

| Element | Fe     | Ni     | Ca   | Mg     | Si   |
|---------|--------|--------|------|--------|------|
| Content (wt%) | 0.0040 | 0.0014 | ≤0.0008 | 0.0001 | ≤0.0015 |
| Element | Al     | Cu     | Cr   | Mn     | Pb   |
| Content (wt%) | ≤0.0010 | 0.0003 | ≤0.0012 | ≤0.0001 | 0.002 |
| Element | Sn     | K      | C    | O      | Mo   |
| Content (wt%) | 0.002  | 0.0018 | 0.005 | 0.08   | balance |

3. Results and discussion

3.1. Morphology and physical properties of the microspheres of molybdenum powders

Morphology of the microspheres of molybdenum powders at spray granulation, degreasing and sintering states are shown in Figure 2. It can be seen that the morphology of the microspheres at
different states are relatively ideal ball type. Spray granulation powders are smooth spherical which are bonded by fine molybdenum powders as raw material (Figure 2(a)), and spray granulation powders after degreasing are rough loose microspheres (Figure 2(b)). Spray granulation powders after sintering at 1100 °C, 1200 °C are rough but a little shrink (Figure 2(c),(d)) compared with the degreasing powders (Figure 2(b)), and spray granulation powders after sintering at 1300 °C, 1400 °C, 1500 °C are compacted microspheres with much sintering neck between the original raw powders (Figure. 2(e),(f),(g)). The physical properties of the spray granulation microspheres of molybdenum powders after degreasing and sintering at different temperatures are shown in Figure 3. It can be seen that the physical properties of the spray granulation microspheres of powders after degreasing will be worse than that of spray granulation microspheres, while it will be better after sintering. And the higher the sintering temperature is, the higher of bulk density and flowability of the microspheres powders are. But at different sintering temperature ranges, the degree of improvement of the physical properties is different as well. At the sintering temperate between 1100 °C -1200 °C, the bulk density and flowability of the microsphere powders are improved a little, while at the sintering temperature between 1300 °C-1500 °C, the bulk density and flowability of the microsphere powders are improved a lot. The process of sintering is the migration of substance, and to fill the pore between the particles. The sintering of molybdenum powders can be explained by diffusion and mass transfer[11]. Self-diffusion coefficient expression of the atomic is described as by formula (1)

\[ D = D_0 \exp \left( -\frac{\Delta G}{RT} \right) \]  

where \( D \) denotes the diffusion coefficient, \( D_0 \) is the so called pre-exponential factors, \( R \) the gas constant and \( T \) the thermodynamic temperature. From formula (1), it can be seen that the diffusion coefficient in the particles increases according to the index law with the rising of the sintering temperature. Therefore, with the rising of the sintering temperature, thermal diffusion velocity is increased, the molybdenum powders are bonded to each other and formed necking. And at the same time, hollows between particles are decreased, the size of the microsphere particles reduced, which
lead to the density of the microsphere particles improved, thus the bulk density of the microspheres of powders is increased.

Generally speaking, the flowability is proportional to the bulk density of the powders. It can be explained as follows: powders with large bulk density are more conducive to slip created by the gravity on itself, which conquer the frictions and adhesion between the particles of the powder. Hence with the rising of the sintering temperature, the flowability of the powders is increased. Size distribution curves of the microsphere powders sintered at different temperatures are shown in Figure 4. It can be seen that with the increasing of the sintering temperature, the peak size of the microspheres of powders decreases. Which are consistent with the conclusion from formula (1).

3.2. The chemical constitution of the agglomerated microspheres of molybdenum powders

During our research, in addition of PVA, no other impurities are introduced. As it is known, PVA is a kind of high molecular polymer with chemical formula of \((\text{C}_3\text{H}_4\text{O})_n\), so C, O are the main impurities elements in the molybdenum powders we should consider. Figure 5 shows C content of the powders at different states. From Figure 5, we can see that the content of C in the spray drying powders is much higher than that in the original powders(as table 1 illustrated), and after degreasing, the content of C are tend to be the same. The high content of C in the spray drying powders is attribute to the adding of PVA, and the lower content of C in the degreased and sintered powders is due to the decomposing of PVA. Generally speaking, PVA began to decompose into water, acetic acid, acetaldehyde and crotonaldehyde at about 300 °C, and between 700 °C - 800 °C, it decompose completely. Consequently, after degreasing at 800-900°C, PVA in the spray drying powders decomposed completely, and the contents of C in the powders is as much as in the original molybdenum powders.

Relationship between O content and sintering temperature of microsphere molybdenum powders are illustrated in Figure 6. From Figure 6, we find that the higher of the sintering temperature is, the lower of the O content of the powder is. Which can be explained as following[12]: Some O exist deeply in the molybdenum particles which are bounded firmly after hydrogen reduction (the nominal reduction temperature of molybdenum powder is about 1000 °C), and it will be released only at a higher temperature. accordingly after heating at 1100°C ~ 1500°C, the contents of O is lower than that of original powders.

4. Summary

The sintered microspheres of high purity molybdenum powders can be prepared by spray drying-degreasing-sintering process. And the physical properties and O content of the microsphere powders are various when the sintering temperature changed. The higher of the sintering temperature is, the higher of the bulk density and the flowability of the powders are. And the higher of the sintering temperature is, the lower of the O content of the powders is.
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