PREPARATION OF FLUXIBLE Mo PARTICLES BY HYDROGEN PLASMA

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The molybdenum flexible powder were prepared by radio frequency(RF) plasma using irregular molybdenum powder as precursor, plasma process parameters were optimized. The effects of the carrier gas flow rate and molybdenum powder feeding rate on the shape and size of the final products were studied. The morphology of molybdenum powder was observed by high resolution scanning electron microscopy. The powder phases were analyzed by X-ray diffraction. The tap density and apparent density of molybdenum powder were investigated by the Hall flow meter and the Scott volumeter. The optimal process parameters for the spherical molybdenum powders preparation are: 50 g/min powder feeding rate and 0.6 m^3/h the carrier gas rate. At the same time, pure spherical molybdenum powders can be obtained from irregular powder, and the tap density is enhanced after plasma processing. The average size is reduced from 72 μm to 62 μm and the tap density is increased from 2.7 g/cm^3 to 6.2 g/cm^3. Thus, RF plasma is a promising method for preparation of spherical powders with high density and purity.

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1. Introduction

Molybdenum and molybdenum based alloys have attracted wide interests for their various applications at high temperature circumstances due to its outstanding properties, such as highest melting temperature among metals, low thermal expansion, high thermal conductivity, etc [1-3]. For example, molybdenum based alloys are regarded as promising plasma facing materials (PFMs) candidates in fusion reactors, which should sustain extremely severe working conditions, such as high flux plasma etching, high energy neutron irradiation and high transient heat loads up to 1 GW/m 2 , etc[6-10]. However, the properties of tungsten-based alloys still need to be further optimized to meet the needs of actual applications[4,5]. Especially, cracking caused by transient heat loads would seriously shorten the lifetime of materials and devices [6,7]. Therefore, the thermal shock resistance is one of the most important properties to accommodate the special working conditions.

Spherical molybdenum powder is a kind of high-tech material applied in thermal spraying, powder metallurgy and other industrial applications, due to the unique nature of its preparation technology and excellent performance. It has attracted attention of domestic and international markets, causing further research and development[8]. Currently, spray granulation method, rotating electrode method, or the like, can prepare spherical molybdenum powder. However, these

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methods have some shortcomings, such as high oxygen content, quasi-spherical shape, powder particle adhesion, too large particle size, wide particle size distribution and low preparation efficiency. In China, there is still no adequate research and development of the high performance spherical molybdenum powder with low oxygen content.

Thermal plasma technology has drawn considerable attention over the last few decades because of its wide range of operating conditions, and various industrial applications[9-11]. For instance, thermal plasma technology has been developed to synthesize metals and ceramics [12-14]. Compared with DC thermal plasma, radio frequency (RF) thermal plasma produced by an RF electric field without electrodes has particular advantages of clean high energy, large volume, and suitability for the synthesis of high purity materials. RF thermal plasma has been extensively used for the spheroidization of refractory metals, ceramics and powders[15-18]. RF thermal plasma has been successfully utilized to prepare spherical tantalum powder and spherical tungsten powder. However, there are few reports using radio frequency plasma to prepare spherical molybdenum powder. In this paper, molybdenum powder particles with irregular shape carried by powder feeding gas into the RF plasma torch, whose temperature was up to 10,000 K, were rapidly heated, melted and then quenched to form micro-spherical molybdenum powder particles, and the influence of process parameters on the final powder properties was also discussed. This method can also be extended to spheroidization and densification of other refractory metals or ceramics [19-23].

2. Experiment

2.1. RF thermal plasma setup

The spheroidization and densification of molybdenum powder was carried out in the RF thermal plasma system under atmospheric pressure. The schematic illustration of the setup is asthis：the plasma reactor system consisted of an RF generator (100 kW, 4 MHz), a plasma generator with a downward plasma torch, a power supply unit, a cylindrical reactor, a precursor feeding system, a powder collector, a quenching chamber, a gas delivery system, and an off-gas exhaust system. The plasma torch consisted of three main parts: a four-turn induction coil, cooled by water, an injection probe, also cooled by water, and a confinement tube. The reactor consisted of the 25 cm inner diameter vertical quartz tube, 200 cm long. The quenching chamber, connected to the bottom of the reactor, was a water-cooled dual layer stainless steel box, which cooled the outgoing gas to less than 200 °C. The precursor feeding system could feed the molybdenum powder precursor with a controlled feeding rate into the plasma flame. The resulting products were collected at the bottom of the chamber.

2.2. Preparation of spherical molybdenum powders

Irregularly shaped molybdenum powder (99.9% pure, -200 to 325 mesh) produced by the Jinduicheng Molybdenum Co. Ltd. was used as the precursor. Argon (Ar, 99.99% pure) was used as the plasma gas (central gas and sheath gas) and hydrogen (H_2, 99.99% pure) was used as the carrier gas. Both argon and hydrogen were provided by the Yatai Gas Company. Before delivering the precursor into the plasma flame, the reactor was heated by the plasma flame for 8 min until the system temperature reached a steady level. Hydrogen gas flowed through the precursor feeding system to carry the precursor molybdenum powder into the plasma flame. The spherical molybdenum powders produced were collected at the bottom of the chamber. The reactor was purged with Ar at 5 L/min flow rate for 10 min before and after each experiment. In order to operate the RF plasma torch stably, the plasma processing parameters were very important. The detailed parameters of the plasma processing in this work is Center gas flow rate, argon 0.6m3/h；Sheath gas flow rate, argon 0.9m3/h ；Carrier gas flow rate, hydrogen 0.5-1.2m3/h；Powder feed rate 45-90g/min； Raw molybdenum powder 200 to 325 mesh；Plasma power 30kW。

2.3 Characterization of the molybdenum powders before and after spheroidization

The product phases were analyzed by the X-ray diffractometer (XRD, Rigaku

D/MAX-2400) with the 2θ angle ranged from 20° to 80° at a scan rate of 0.02 deg/s operated at 40 kV and 30 mA with Cu K□ radiation. Both the raw materials and the produced powders were characterized by high-resolution scanning electron microscopy (HRSEM, JSM-6700F) for particle morphology. The tap density of the molybdenum powder before and after plasma treatment was measured by the Hall flowmeter and the apparent density was determined by the Scott volumeter. The flowability was investigated by means of a calibrated funnel (the Hall flowmeter).

2.4 Statistics of spheroidization efficiency

The percentage of spherical particles in the sample after spheroidization was calculated from the SEM images. Each sample was randomly counted 3 times and the mean value was taken as the spheroidization efficiency of the sample.

3. Results and Discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the X-ray diffraction patterns of the molybdenum powder after spheroidization. The results showed that there was no intervention of oxides and other impurities during the preparation of the spherical molybdenum powder. The plasma gas did not come in contact with the electrodes, which eliminated additional sources of contamination. Furthermore, hydrogen, as carrier gas, also provided reducing atmosphere, which ensured that the final product was high purity molybdenum metal powder. Studies had shown that plasma treatment can effectively remove impurity elements in the molybdenum powder. Due to the space limitations, this aspect is not elaborated in this article.

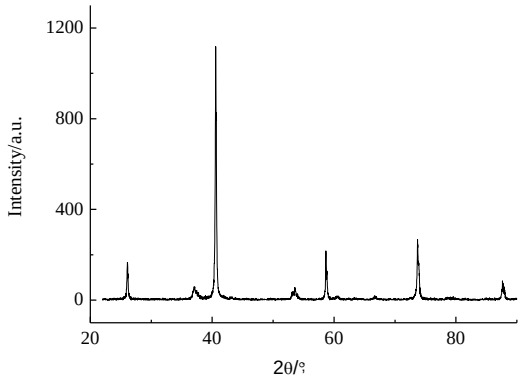

Fig. 1. X-Ray diffraction pattern of the spherical Mo powder after plasma processing.

3.2. Morphology, particle size and tap density before and after plasma spheroidization

Fig. 2 shows high-resolution SEM images of molybdenum powders before and after plasma spheroidization. The SEM image of the feedstock molybdenum powder with the average particle size of 70 μm is seen in Fig. 2(a), presenting aggregates of irregular shape powders. After the RF plasma processing, Fig. 2(b) presents typical SEM images of the synthesized molybdenum powders with high sphericity and smooth surface, which were obtained under the following conditions: carrier gas flow rate of 0.6 m3/h, and a powder feed rate of 50 g/min. The laser particle size distribution of the molybdenum powders before and after spheroidization is shown in Fig. 3. It can be clearly seen that the curve of the particle size distribution after spheroidization narrowed down. The powder particle size distribution becomes more uniform, and particle size of more than 80% molybdenum powder after spheroidization was between 44 μm and 86 μm, whose d(0.5) was 62.22 μm. Compared with the feedstock molybdenum powder, whose d(0.5) was 72.243 μm, the

powder size after plasma treatment obviously decreased. It was illustrated that plasma processing also caused powder refinement in addition to spheroidization. There may be two reasons for the refinement. First, because the feedstock molybdenum powder may be made up of porous molybdenum powder with low density, or aggregates of many small particles. These aggregates or loose particles will be cracked quickly and refined. Further, molybdenum powder went through the gasification-condensation processing, which was another reason of the refinement.

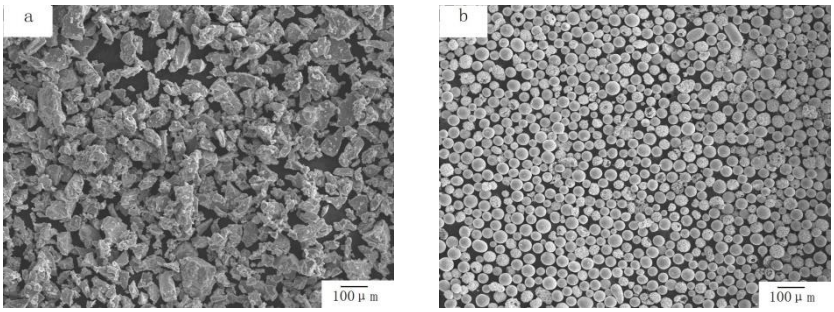

Fig. 2. High resolution SEM images of the molybdenum powders: (a) before and (b) after spheroidization

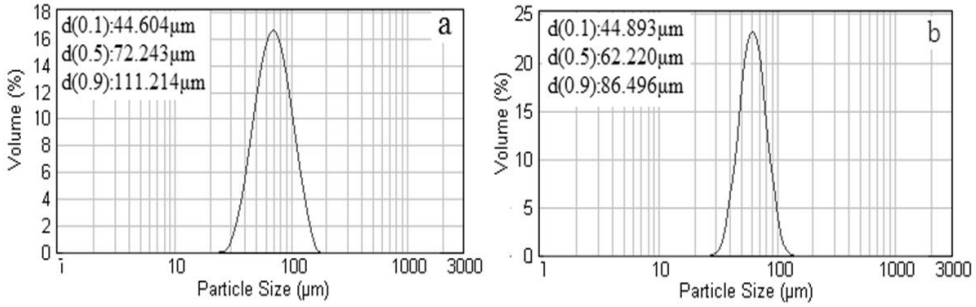

Fig. 3. Particle size distribution of the molybdenum powders in Fig. 3: (a) before and (b) after spheriodization

The tap densities of molybdenum powder before and after plasma treatment in Fig. 3 were determined by the Hall flowmeter, which were 2.7 g/cm3 and 6.2 g/cm3, respectively. The tap density of the molybdenum powder after spheroidization was greater than the raw molybdenum powder. The fact that the molybdenum powder in this study had large tap density is related to their sphericity. The higher the spherical efficiency, the larger the tap density is.

3.3 Effect of powder feed rate on spheroidization

In the complicated plasma processing, the powder feed rate plays an important role in the spheroidization of molybdenum powders. Under otherwise identical conditions, different feed rate will lead to different spherical effects. Fig. 4 shows the plasma-processed powders morphology obtained with different powder feed rates. The percentage of spheroidization with the feed rate of 50 g/min was 98%, while the feed rate of 70 g/min decreased spheroidization to 90%, and with the feed rate of 110 g/min the spheroidization was only 30%. The reason for this phenomenon might be that much more powders meaned much little heat energy single powder could gain under the specific conditions. When precursor powders were fed into plasma flame at a fixed feed rate less than 50 g/min, every single powder could gain sufficient heat energy for melting itself entirely.But when more than 50 g/min, every single power can not，resulting in reducing in spheroidization efficiency. Of course, too slow powder feed rate also brings a series of shortcomings, such as poor flowability and low apparent density, because every single powder particle absorbs too much heat, leading to too smaller molybdenum particles and greater surface tension. Therefore, controlling the

powder feed rate is very important to ensure spheroidization efficiency. In this paper, 50 g/min was chosen as the optimal powder feed rate.

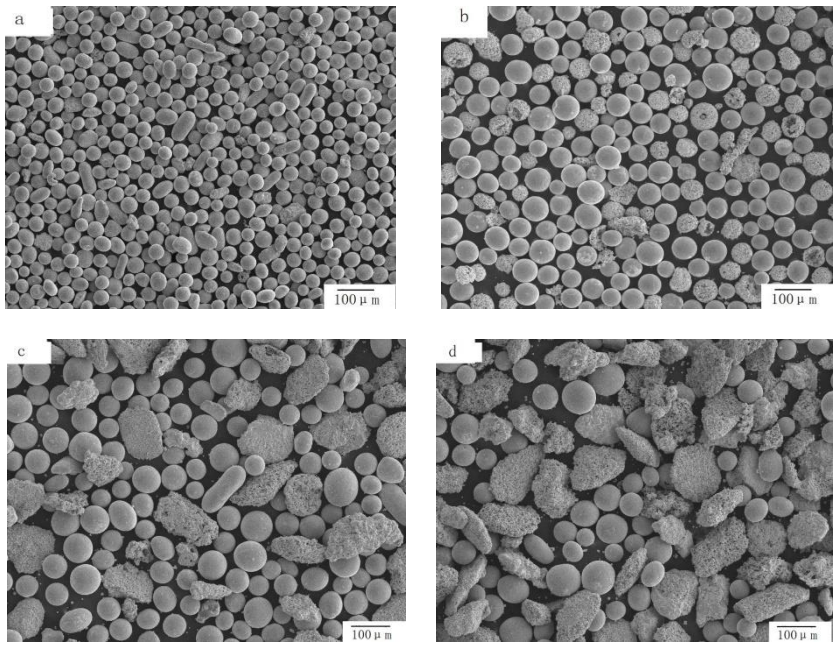

Fig. 4. High resolution SEM images of Mo products obtained with different powder feeding rates:(a) 50 g/min; (b) 70 g/min; (c) 90 g/min; (d) 110 g/min

3.4. Carrier gas flow rate effect on spheroidization

The experiment used hydrogen as the carrier gas to inject the raw material of molybdenum powders into the plasma torch. Reducing atmosphere of the hydrogen plasma torch ensured that the molybdenum powders didn't get oxidized, resulting in high purity. The carrier gas flow rate affects the molybdenum powder dispersed state, along with the residence time in the plasma torch. The greater the carrier gas flow rate, the better the dispersed properties are, which would result in higher thermal efficiency of the plasma torch and much higher uniformity of the produced spherical particles. The residence time in the plasma torch was shortened with increasing the carrier gas flow rate, while melting or vaporization of molybdenum powder in the plasma torch required absorbing enough heat. Therefore, too high carrier gas flow rate will also affect the quality of spheroidization.

4. Conclusions

Using RF thermal plasma, dense spherical molybdenum powder with high purity can be prepared. In addition to spheroidization, RF plasma can purify, densify and refine the molybdenum powder. Under optimal conditions, tap density of molybdenum powder increased from 2.7 g/cm3 to 6.2 g/cm3.

The effects of powder feed rate and carrier gas flow rate on the morphology and particle size of the product had been studied. The optimal parameters are: 50 g/min powder feed rate and 0.6 m3/h carrier gas flow rate.

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