Synthesis of molybdenum nanopowders by RF plasma combustion

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ABSTRACT

Molybdenum nanopowders have been synthesized in a RF plasma by controlling the various process parameters. The obtained Mo nanopowders are characterized by SEM, TEM, and XRD. Mo nanopowders are sintered to a pellet with ultra-fine grain by two step sintering process. Mechanical properties of ultra-fine grained Mo with relative density of above 90% were significantly improved at room and high temperatures comparing to commercial bulk Mo of 99% relative density.

Keywords: nanoparticles, molybdenum, plasma

1 INTRODUCTION

Text Molybdenum, which is a silvery metal, has the sixth-highest melting point of any element. It readily forms hard, stable carbides, and for this reason it is often used in high strength steel alloys. The ability of molybdenum to withstand extreme temperatures without significantly expanding or softening makes it useful in applications that involve intense heat, including the manufacture of aircraft parts, electrical contacts, industrial motors and filaments. [1]

Molybdenum metal is usually produced by powder metallurgy techniques in which Mo powder is hydrostratically compacted and sintered at high temperatures in the range of 1,800°C to 2100°C. [2] Therefore, because of molybdenum's high cost compared to more common engineering materials, it is not widely used unless it is required. Now a day, molybdenum is utilized to meet specific needs with respect to elevated temperature strength, chemical compatibility, tribological properties, or physical properties like thermal expansion, thermal conductivity, and electrical conductivity. The examples are heat sinks with thermal expansivity matching silicon for semiconductor chip mounts and sputtered layers for gates and interconnects on integrated circuit chips. These applications use the molybdenum as a form of sputtering target with dense and ultrafine crystalline.

To make a dense target with lowering the sintering temperature, there are two approaches. The first approach is activated sintering using aiding elements such as Ni, Pt, Pd, and Co.[3-6] Although these sintering aids are very effective for the densification of the Mo powder, they cause deterioration of the electrical properties of Mo. The second method to enhance sinterability is using powder size refinement like nano-sized powders [7-11].

In this paper, we report the synthetic approach to molybdenum nanoparticles by using the RF plasma reduction and the sintering results with high strength at low temperature sintering.

2 EXPERIMENTALS

The experimental apparatus for powder synthesis mainly consists of a water-cooled induction plasma torch, a 2-MHz radio frequency power supply system, a water-cooled stainless steel reactor, and a stainless steel filter connecting the reactor and a vacuum pump. Details of the experimental setup are shown in Figure 1.

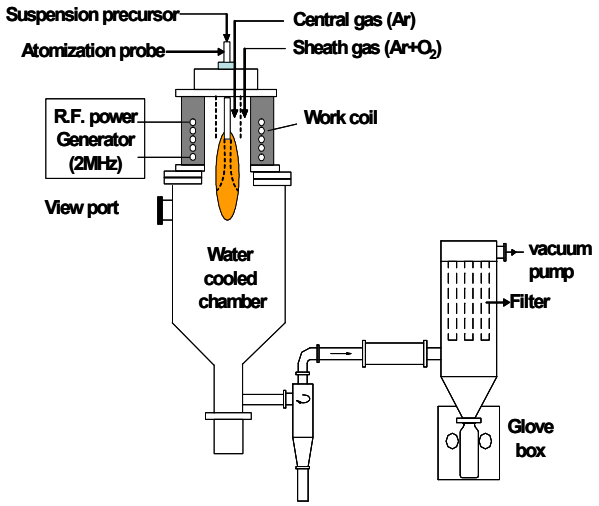

Figure 1: A schematic illustration showing the experimental setup.

For the synthesis of Mo nanopowders, the micro-sized MoO_3 precursor powders were delivered by a vibrating powder feeder into the center of the plasma flame through an atomization probe. Flow rate of the MoO_3 precursor was controlled at 1.5g/min. The atomization was water-cooled to resist the extreme temperature of the plasma, and the precursor was atomized by argon carrier gas flowing through the probe at 10 L/min. The Ar/H_2 thermal plasma was generated by mixing H_2 gas to the Ar sheath. Total flow rate of the sheath gas ($Ar + H_2$) was set at 120 L/min. Other details of the processing parameters were summarized in Table 1.

Table 1: Experimental conditions for preparing Mo nanoparticles by RF plasma.

Parameter	Value
Central gas & flow rate	Ar, 30 L/min
Rate sheath gas & flow rate	Ar+H_2, 120 L/min in total
Atomization gas & flow rate	Ar, 20 L/min
Precursor feeding rate	1.5g/min
Induction power	30~60kw
Chamber pressure	720 torr

The morphology of Mo nanopowders was investigated with transmission electron microscopy (TEM, JEOL-2100F). The X-ray diffraction (XRD, DMAX 1400, Rigaku) patterns were recorded using Cu Kα radiation with a tube voltage of 40 mV and current of 40 mA. Scans were stepwise from 10° to 90° with a step of 0.08°(2θ) and a dwelling time of 6 s.

The Mo nanopowders and commercial Mo powders were pressed into pellets in one direction under the pressure of 250 kg/cm^2, at which green densities of approximately 40% and 60% of of the theoretical density were obtained, repectively. The green compacts were heated to 1070℃ at a constant heating rate of 10℃/min in 1.5%H_2/Ar atmosphere and then continuously sintered at 970℃ for 5hr.

3 RESULTS AND DISCUSSION

The Mo nanopowders formed via rapid thermal reduction of sublimated MoO_3 precursor by Ar/H_2 thermal plasma mainly deposit on the filter and the inner walls of the reactor. The crystallinity and phase of as synthesized Mo nanopowders were examined by XRD. Fig. 2. shows XRD patterns of the nanopowders synthesized with 120 L/min of Ar/H_2 flow in the plasma sheath. The diffraction peaks shown in Fig. 2 can be indexed to the standard pattern for the pure bcc phase of Mo, which are in good agreement with the reported data (JCPDS No. 42-1120). The result from XRD revealed that the nanopowders obtained is reduced metal cubic Mo. The strong intensities relative to the background signal indicate a high purity of the Mo cubic phase of the resulting products.

The obtained Mo nanopowders are black in color and these morphology is shown in Fig. 3. The SEM image shown in Fig. 3 indicates the typical Mo nanopowders with the various sizes less than 200 nm are approximately sheperical in morphology. The experiments carried out to study the influence of generator plate power on the synthesized powder size. The results indicated that generator plate power from 30 to 60 kw has less effect on powder size.

The formation of nanopowders was further confirmed by TEM. From the TEM data, the particle size histograms can be drawn and the mean diameter of the particles is determined. Fig.4 shows the particle size distribution of Mo nanopowders. It can be seen that the particle sizes range from 40 nm to 200 nm, and the mean diameter (taken as average particle diameter) is about 90 nm, being measured from the laser particle size analyzer, which shows a relatively narrow size distribution.

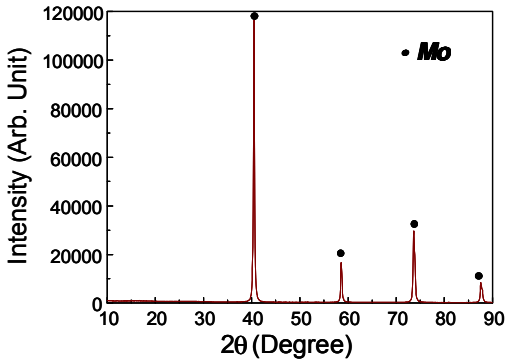

Figure 2: XRD patterns of the Mo nanoparticles

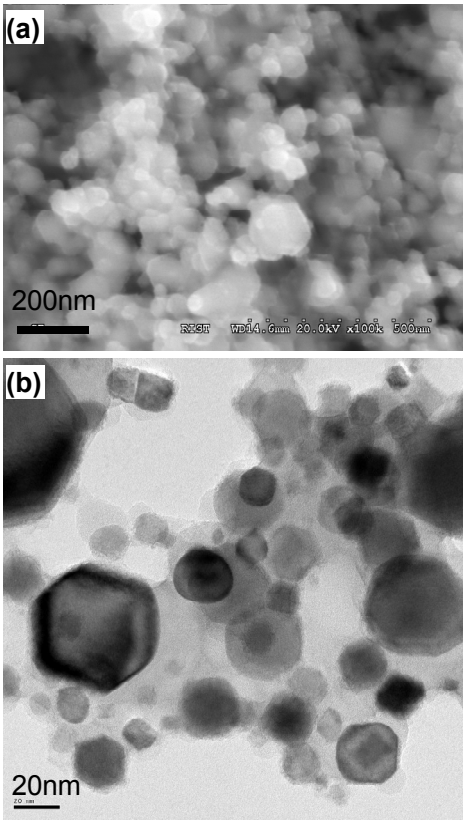

Figure 3: (a) SEM and (b) TEM micrograph of the Mo nanoparticles.

The obtained Mo nanopowders and commercial Mo powders were pressed into pellets in one direction under the pressure of 250 kg/cm^2, and sintered to a pellet with ultra-fine grain by two step sintering process.

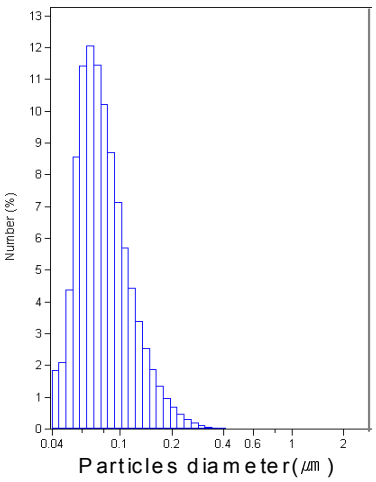

Figure 4: The particle size distribution of Mo nanopowders by laser particle size analyzer.

For the Mo nanopowder, the linear shrinkage attained at 1070℃ was 10%, which is comparable to the 0.8% value of commercial powder. This sharikage results demostrate the enhanced sinterability of the Mo nanopowder compared with that of the commercial powder. Vickers hardness for the sintered nanopowder was 3.1GPa, which value is much larger than the 1.5GPa for the commercial Mo. Mechanical properties of ultra-fine grained Mo pellet by sintering of nanopowders were significantly improved comparing to commercial bulk Mo of 99% relative density.

4 CONCLUSION

The Mo nanopowders with the average size less than 100 nm were successfully prepared by RF plasma reduction of molybdenum trioxide. Mechanical properties of the sintered pellet of Mo nanopowder were significantly improved comparing to commercial bulk Mo of 99% relative density.

5 ACKNOWLEDGEMENT

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