ELSEVIER

Journal of Alloys and Compounds 454 (2008) 327–330

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Consolidation behavior of Mo powder fabricated from milled Mo oxide by hydrogen-reduction

Gil-Su Kim, Young Jung Lee, Dae-Gun Kim, Young Do Kim *

Division of Materials Science and Engineering, Hanyang University, Seoul 133-791, Republic of Korea

Received 29 September 2006; received in revised form 6 December 2006; accepted 10 December 2006

Available online 24 January 2007

Abstract

Nano-sized Mo powder was synthesized by ball-milling and subsequent hydrogen-reduction of MoO_3 powder. The crystalline size of the MoO_3 powder was decreased to below 10 nm by a 20 h ball-milling process. Hygrometric measurement was performed to understand hydrogen-reduction behavior of MoO_3 with different milling time. The peak temperature for the reduction was shifted to lower temperatures by increasing the milling time. The peak for the reaction of $MoO_3 \rightarrow MoO_2$ was more effective than that for the reaction of $MoO_2 \rightarrow Mo$. This result is due to the transformation steps for the reaction of $MoO_3 \rightarrow MoO_2$ take place via chemical vapor transport (CVT) by generation of a gaseous transport phase. After hydrogen-reduction at 800 °C, the crystalline size of the Mo powder was about 60 nm. The sinterability of the nano-sized Mo powder was considerably enhanced compared with that of a commercial Mo power.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Molybdenum; High-energy ball-milling; Hydrogen-reduction; Sintering

1. Introduction

Molybdenum (Mo), as one of the refractory metals, has been applied in high temperature industrial fields [1–4]. Powder metallurgy (P/M) is a general process for the production of bulk Mo components because of its high melting point, 2610 °C [2]. Generally, sintering of commercial Mo powder with a particle size of several micrometers is performed at elevated temperatures for a long time. It has been reported that a Mo sintered body above 90% of theoretical density could be obtained over a sintering temperature range of 1800–2000 °C for several hours [2]. There have been some efforts to reduce the processing cost for a fully densified bulk component with an activated sintering that lowers the sintering temperature to 1200–1400 °C through the addition of a small amount of Ni, Pt, Pd, and Co [2,5–11]. These sintering aids, however, induce a deterioration of the electrical and thermal conductivity, as well as several mechanical properties.

Generally, it has been reported that fine particle size induces enhanced sinterability because diffusion in solid state sintering is very sensitive to particle size [12–14]. Based on this sintering behavior, the synthesis of nano-sized Mo powders and their densification are investigated in this work. In order to improve the sinterability of the Mo powder, a nano-sized powder was used for enhanced densification, due to particle size reduction and extended surface area. A nano-sized Mo metallic powder was synthesized by ball-milling and a subsequent hydrogen-reduction process using MoO_3 powder. The hydrogen-reduction behavior of the ball-milled MoO_3 powder was characterized by measuring the humidity of the outlet gas in the hydrogen-reduction process. The sinterability of the nano-sized Mo powder was evaluated by dilatometric analysis and compared with that of a commercial Mo powder.

2. Experimental procedure

A commercial MoO_3 (1–10 μm, 99.9%, JunTec) powder was used as a raw material and was high-energetically ball-milled at a milling speed of 400 rpm in an Ar atmosphere for up to 50 h with a Simoloyer, which is a horizontal-typed attrition mill. Stainless steel balls were used as the milling media, and the ball to powder weight ratio was 16:1. The ball-milled MoO_3 powder was reduced under non-isothermal conditions up to a temperature of 800 °C with a heating rate of 10 °C/min in a H_2 atmosphere with a dew point of −76 °C. The content of water vapor in the outlet gas, which formed through the hydrogen-reduction of the oxides, was measured by an in situ humidity measuring system, the hygrometer.

Commercial Mo powder (1 μm, 99.99%, JunTec) was also used for the comparison of sinterability. The hydrogen-reduced Mo and a commercial Mo powder

---

* Corresponding author. Tel.: +82 2 2220 0408; fax: +82 2 2282 1976.
E-mail address: ydkim1@hanyang.ac.kr (Y.D. Kim).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.12.039

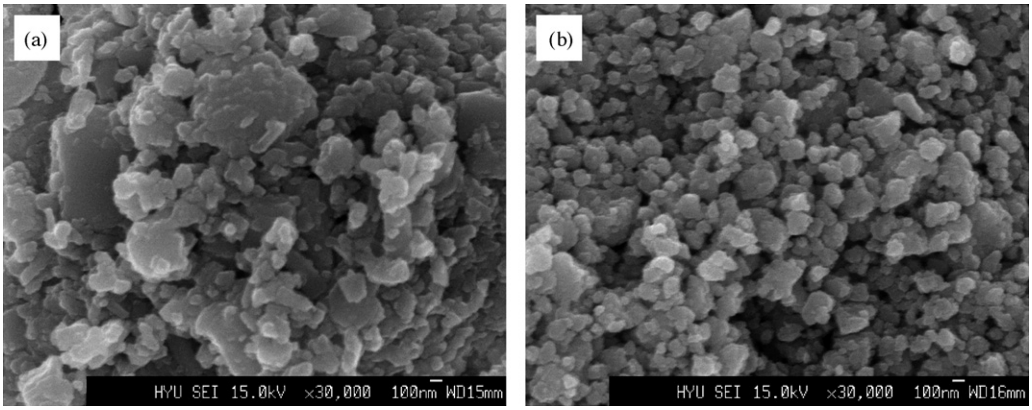

Fig. 1. Micrographs of MoO_3 powder ball-milled for 1 h (a) and 20 h (b).

were compacted under a pressure of 250 MPa, with green densities of about 40 and 60% of the theoretical density, respectively. The two kinds of green compact were sintered under a constant heating rate of 10 °C/min up to 1400 °C in a H_2 atmosphere using a push-rod type Harrop dilatometer (TDA-H-AP6). Densities of the sintered Mo samples were calculated by Archimedes' principle. The microstructures of the milled and the hydrogen-reduced Mo powder were observed by a field emission scanning electron microscope (FE-SEM). X-ray diffractometry (XRD) was employed for phase analysis and the calculation of the Mo crystalline size.

3. Results and discussion

The SEM microstructures of the milled MoO_3 powder are shown in Fig. 1 at various milling times. In the initial stage of the milling process Fig. 1(a), the MoO_3 particles were inhomogeneously pulverized and remained as large particles in the aggregate. After milling for 20 h Fig. 1(b), the MoO_3 particles were homogeneously refined. The crystalline size of MoO_3 powder had decreased as a result of the milling process. After milling for 20 h, the crystalline size of the milled powder had decreased to below 10 nm, which was calculated from XRD data.

Fig. 2 shows the non-isothermal humidity curves for the hydrogen-reduction process of the MoO_3 powder with various milling times. There are two reactions for the hydrogen-reduction of the MoO_3 [15,16]. The first reaction is assigned to the reduction process of $MoO_3 \rightarrow MoO_2$. This reaction occurs over a temperature range of 450–650 °C. Below 450 °C, the reduction process proceeds very slowly, yielding intermediate oxides of Mo_4O_{11} between MoO_3 and MoO_2. Intermediate oxides were confirmed by XRD. The second reaction, which occurs at a temperature range of 650–800 °C, is assigned to the reduction process of $MoO_2 \rightarrow Mo$. Both reactions take place in two distinct stages, viz. [4,15,16]:

$$MoO_3 + H_2 \rightarrow MoO_2 + H_2O \tag{1}$$

and

$$MoO_2 + 2H_2 \rightarrow Mo + 2H_2O. \tag{2}$$

It is interesting to note that the peaks in Fig. 2 were shifted to lower temperatures by increasing the milling time, and thereby decreased the particle size by the ball-milling process. The temperatures of two peaks relating to the reaction of (a) $MoO_3 \rightarrow MoO_2$ and (b) $MoO_2 \rightarrow Mo$ from the humidity curves of the MoO_3 powder are plotted in Fig. 3. The reduction of peak temperature for the $MoO_3 \rightarrow MoO_2$ process was more effective than that for the process of $MoO_2 \rightarrow Mo$. It is reported that the transformation steps for the reaction of $MoO_3 \rightarrow MoO_2$ take place via chemical vapor transport (CVT) by generation of a gaseous transport phase [16]. Considering that the CVT pro-

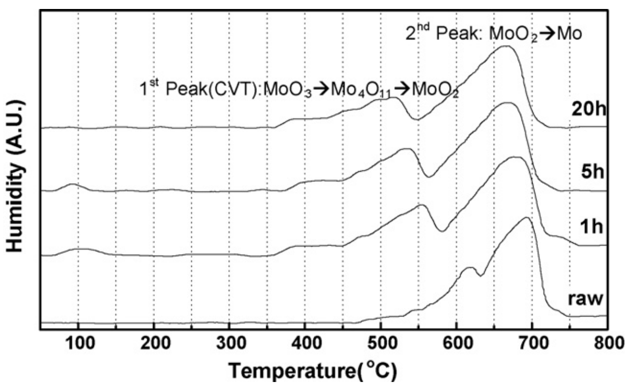

Fig. 2. Non-isothermal humidity curves obtained during the heating of MoO_3 powder at 10 °C/min in a hydrogen atmosphere at various milling times.

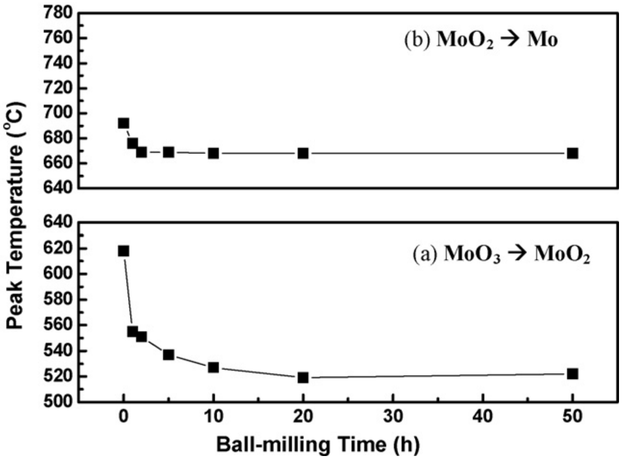

Fig. 3. The peak temperatures of (a) $MoO_3 \rightarrow MoO_2$ and (b) $MoO_2 \rightarrow Mo$ during the reduction process obtained from humidity curves of MoO_3 shown in Fig. 2.

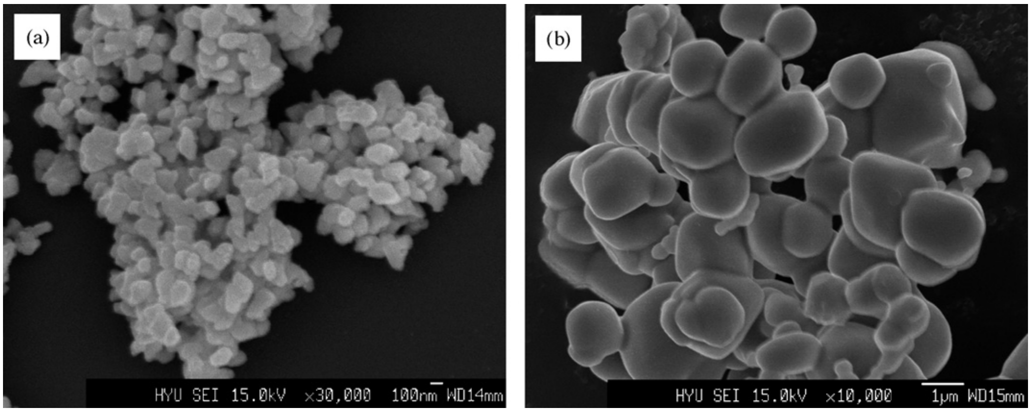

Fig. 4. Micrograph of (a) Mo powder hydrogen reduced at 800 °C without holding time and (b) Mo commercial powder.

cess is related to gas flow, which determines the local humidity by changing particle sizes and porosities in aggregates of oxide powder, it is reasonably expected that the hydrogen-reduction behavior was strongly affected by the powder characteristics. Thus, it is plausible that the diminution of peak temperature for the $MoO_3 \rightarrow MoO_2$ reaction with respect to increasing milling time was due to the acceleration of CVT by the refinement of particle size and enhanced porosities in aggregates of the oxide powder through the milling process. On the other hand, the reduction process from MoO_2 to Mo primarily occurs by oxygen transport and is partially dependent on the CVT process, which in turn is dependent on the dew point of the hydrogen gas [16]. Considering that the particles had already grown as a result of the high reduction temperature, the reaction of $MoO_2 \rightarrow Mo$ was only slightly dependent on the initial particle size, as plotted in Fig. 3(b).

On the basis of the above results, the optimum synthesis conditions for generating Mo powder from MoO_3 was found to be a milling time of 20 h followed by hydrogen-reduction at 800 °C for 20 h. Fig. 4 shows the morphologies of the reduced Mo powder with a particle size of about 100 nm and commercial Mo powder with relatively coarse particle size of 1 μm. The XRD analysis of the reduced Mo powder revealed that the oxide peaks completely disappeared and that the mean crystalline size was about 60 nm calculated from peak broadening. This result suggested that a nano-sized Mo powder could be successfully fabricated by ball-milling and hydrogen-reduction of MoO_3 powder.

To evaluate the sintering behavior of two different kind powders, a dilatometric analysis was employed up to 1400 °C with a heating rate of 10 °C/min in a H_2 atmosphere. As clearly shown in Fig. 5, the linear shrinkage behavior of the nano-sized Mo powder was quite different from that of the commercial Mo powder. In the case of the nano-sized Mo powder, shrinkage started at a lower temperature, about 600 °C, compared with the commercial Mo powder which shrank at a temperature of 1000 °C. Also, the linear shrinkage of the compacts showed large difference values: 22% for the nano-sized Mo powder and 4% for the commercial powder at a sintering temperature of 1400 °C. Relative densities of the sintered compacts using nano-sized and commercial Mo powders were measured as 94 and 74%, respectively. Based on the theory of the particle size effect [14], a reduction in sintering temperature is desired in order to achieve an equivalent degree of sintering, assuming that the sintering time is constant. The new sintering temperature, based upon the change of particle size, may be given as $T_2 = 1/[(1/T_1) - (km/Q \ln(D_2/D_1))]$, where Q is the activation energy, k the gas constant, m the constant depending on the transport process, D_1 and D_2 the particle sizes and sintering temperatures are T_1 and T_2, respectively. If particle size D_2 is smaller than D_1, there is a reduction in the sintering temperature, where $T_2 < T_1$. In this experiment, sintering temperature of commercial Mo powder to have sintered density of 74% is about 1400 °C. In case of the nano-sized Mo powder, sintering temperature to have the same density was calculated about 1079 °C by equation. Constants m and Q were 3 and 405 kJ/mol for volume diffusion, respectively [2]. Actually, sintered density of 74% for nano-sized Mo powder was obtained around 1075 °C during non-isothermal sintering. This result is in good agreement with relationship between particle size and sintering temperature.

It is expected that a nano-sized powder exhibits a greater reduction in the sintering temperature. Therefore, the enhanced sinterability of the nano-sized Mo is due to the particle size reduction achieved by the high-energy milling process. From

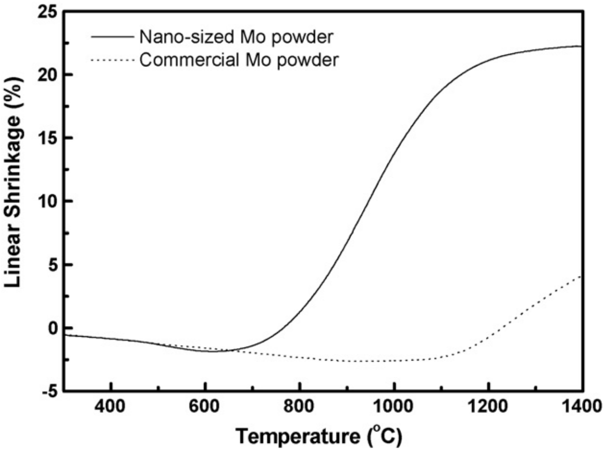

Fig. 5. Linear shrinkage of nano-sized and commercial Mo powder with a heating rate of 10 °C/min.

these results, it may be suggested that a nano-sized Mo powder with excellent sinterability can be successfully synthesized by ball-milling and a hydrogen-reduction process using MoO_3 powder.

4. Conclusions

To fabricate a nano-sized Mo powder, MoO_3 powder was ball-milled and then hydrogen reduced at 800 °C. The crystalline size of the MoO_3 powder decreased with increasing milling time. For a milling time of 20 h, the crystalline size of the MoO_3 powder was measured to be below 10 nm. After hydrogen-reduction at 800 °C, the crystalline size of Mo was calculated to be 60 nm. Dilatometric analysis revealed that the nano-sized Mo powder had a lower starting temperature for densification and a higher value for linear shrinkage at 1400 °C than the commercial powder. The enhanced sinterability of the Mo powder prepared from MoO_3 is explained by a decrease in the particle size.

Acknowledgment

This work was supported by the research fund of Hanyang University (HY-2005-I).

References

[1] E.F. Baroch, M. Ostermann, G. Patrick, Adv. Powder Metall. 5 (1991) 321.

[2] P. Garg, S.J. Park, R.M. German, Int. J. Refract. Met. Hard Mater. 25 (2007) 16.

[3] T.S. Srivatsan, B.G. Ravi, A.S. Naruka, L. Riester, M. Petraroli, T.S. Sudarshan, Powder Technol. 114 (2001) 136.

[4] E.R. Braithwaite, J. Haber, Molybdenum: An Outline of its Chemistry and Uses, Elsevier, New York, 1994.

[5] R.M. German, C.A. Labombard, Int. J. Powder Metall. Powder Technol. 18 (1982) 147.

[6] P.E. Zovas, R.M. German, Metall. Trans. A 15A (1983) 1103.

[7] H. Hofmann, M. Grosskopf, M. Hofmann-Amtenbrink, G. Petzow, Powder Metall. 29 (1986) 201.

[8] Y. Hiraoka, T. Ogusu, N. Yoshizawa, J. Alloys Compd. 381 (2004) 192.

[9] K.S. Hwang, H.S. Huang, Acta Mater. 51 (2003) 3915.

[10] K.S. Hwang, H.S. Huang, Int. J. Refract. Hard Mater. 22 (2004) 185.

[11] R.M. German, Z.A. Munir, J. Less-Common Met. 58 (1878) 61.

[12] W.J. Huppmann, W. Bauer, Powder Metall. 19 (1976) 249.

[13] S.S. Ryu, Y.D. Kim, I.H. Moon, J. Alloys Compd. 335 (2002) 233.

[14] R.M. German, Sintering Theory and Practice, The Pennsylvania State University/John Wiley & Sons, 1996.

[15] M.J. Kennedy, S.C. Bevan, J. Less-Common Met. 36 (1974) 23.

[16] V.S. Werner, M.O. Hugo, Int. J. Refract. Met. Hard Mater. 20 (2002) 261.