Preparation of Mo nanoparticles through hydrogen reduction of commercial MoO$_2$ with the assistance of molten salt

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ABSTRACT

In the present work, the hydrogen reduction of commercial MoO$_2$ with the assistance of molten salt has been investigated at 720–850 °C. In the case of no salt addition, the prepared Mo particles maintained the big platelet shape of raw MoO$_2$ powders. However, after adding a small amount of salt (0.1% NaCl−KCl binary salt, MgCl$_2$−KCl binary salt, or LiCl mono salt), Mo nanoparticles were prepared successfully. It was found that a small amount of molten salt can help Mo to nucleate dispersedly and its growth via chemical vapor transport (CVT) mechanism can be controlled by reducing temperature. At 750 °C, when the NaCl−KCl binary salt was used, the obtained Mo nanoparticles had both good dispersion and small average size of about 70 nm. Kinetics analyses indicated that the rate controlling step for the hydrogen reduction of MoO$_2$ was the interface chemical reaction, and after adding salt, the reaction rate constant decreased dramatically, relative to that without salt. The extracted activation energies for pure MoO$_2$, MoO$_2$ with 0.1% NaCl−KCl binary salt and MoO$_2$ with 0.1% LiCl mono salt were 76.13 kJ/mol, 117.45 kJ/mol and 97.23 kJ/mol, respectively.

1. Introduction

Molybdenum (Mo) is a extensively used refractory metal that keeps its body-centered cubic (bcc) crystal structure from room temperature to its molting temperature of 2610 °C [1]. Mo and its alloys are attractive in many critical fields such as aerospace, military, chemical, metallurgical and nuclear applications due to its excellent properties including high molting point, moderate density (10.23 g/cm^3), low thermal expansion coefficient, high stability, high creep and corrosion resistance, high thermal and electrical conductivities [1–5].

Nanopowders are particulate materials that display dominant structural features on size scales from 1 to 100 nm, containing many unique properties such as extremely high specific surface area, enhanced chemical activity of atoms and molecules at an interface, and high absorptive capabilities, which may significantly alter their physical, mechanical, and chemical properties [6–10]. Nanopowders could be sintered to actual nanostructured materials with high density at much lower temperatures than micrometer powders, which could avoid the coarsening of grain [1,5,11–13]. Refining grains of metal into the nanoscale can dramatically improve its mechanical properties such as strength, hardness, toughness and wear resistance [6–10]. In order to manufacture compact materials with dramatically improved mechanical properties for aerospace, military, chemical and metallurgical

applications, refractory nanometals have been the subject of interest [8].

The manufacture of Mo nanopowders is a critical step to prepare nanocrystalline Mo metal or its alloy products. A lot of methods have been developed to synthesis Mo nanoparticles. Lamprey and Ripley [14] prepared Mo nanopowders with the particle size of 10–100 nm via the reduction of molybdenum chloride by hydrogen. Hoseinpur et al. [3] reported a method of synthesizing elemental Mo nanoparticles by zincothermic reduction of MoO$_3$. Nersisyan et al. [15] synthesized nanostructured metallic molybdenum from the MoO$_3$−NaBH$_4$−kNaCl system. Liu et al. [16] successfully synthesized nanosized metal Mo powder by the microwave plasma chemical vapor deposition (MPCVD) method. Saghafi et al. [17] prepared molybdenum nanopowders by the hydrogen reduction of mechanically activated MoO$_3$. Huang et al. [18] synthesized molybdenum nanopowders by a molten salt technique using Na$_2$MoO$_4$ and Al as the starting materials. In the authors' previous work [19], ultrafine metal Mo powder with a high purity was successfully prepared by one step direct reduction of MoO$_3$ vapor with H$_2$.

Even though a lot of methods have been developed to prepare Mo nanopowders, nowadays, hydrogen reduction of commercial molybdenum oxides is still an important and well-established industrial process for the manufacturing of high-quality Mo powder [20–22]. That contains two steps, the hydrogen reduction of MoO$_3$ to MoO$_2$ and

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further reduction of MoO_2 to Mo [21]. However, it is hard to obtain Mo nanoparticles by this method. In the process of reducing MoO_2 by H_2, the pseudomorphic transformation mechanism takes effect at low local concentration of water vapor, while a chemical vapor transport (CVT) mechanism takes effect at high local concentration of water vapor [23]. In the case of the pseudomorphic transformation mechanism, Mo product keeps the size of starting material (MoO_2), which is usually a few microns. Under the condition of high concentration of water vapor, the growth of Mo particles can be promoted due to the high concentration of volatile molybdenum oxide, $MoO_2(OH)_2$, which facilitates the transport of Mo through the gas phase, and the size of Mo particles would be always large. Therefore, it is difficult to refine the size of Mo powders into nanoscale successfully in hydrogen reduction of commercial molybdenum oxides by adjusting of the reduction temperature, concentration of water vapor, hydrogen content, and the flow rate of hydrogen gas [20,24].

For the preparation of nanoparticles, the control of nucleation and growth of grains is a crucial issue. In the present study, a new mechanism was proposed to prepared Mo nanoparticles via hydrogen reduction of MoO_2 with the assistance of molten salt. A small amount of molten salt was used to control the nucleation and growth of Mo grains. The mechanisms and reduction kinetics after adding the salt were investigated.

2. Experimental section

Raw materials for this work include commercial MoO_2 powder (99.9% purity; Jinduicheng Molybdenum Co., Ltd., Xi'an, China), NaCl, KCl, LiCl and $MgCl_2$ salts (99.5% purity, Sinopharm Chemical Reagent Co., Ltd.). Fig. 1 shows the XRD patterns and FE-SEM micrographs of the raw MoO_2 powder. It can be seen that the XRD patterns are well coincided with MoO_2 (PDF card no. 32–671), and the MoO_2 has a platelet shape with the particle size in the range of 1-2 μm. NaCl−KCl (50 mol%) binary salt (melting point, 657 °C), $MgCl_2$−KCl (65.3 mol%) binary salt (melting point, 429 °C), and LiCl mono salt (melting point, 605 °C) were dissolved in deionized water respectively, which were mixed with MoO_2 powder into uniformly by the solution spraying method. Then, the mixtures were dried at 100 °C for 6 h. Mixed powders of MoO_2 with different salts (0.1 mass%) were prepared, respectively.

To monitor the weight loss continuously during the reduction process, a thermal analysis system (HTC-2, Beijing Hengju Instrument Ltd., Beijing), which includes a thermo-gravimetry (TG) microbalance with a precision of ± 0.1 μg, was used. The schematic diagram of the

experimental apparatus was described in the previous paper [25]. In each experiment run, samples of about 100 mg were used. Then, the furnace was heated from room temperature to the desired reduction temperature with a heating rate of 20 °C/min in the protection of flowing argon (60 ml/min). After the temperature was increased to the desired temperature and held for 15 min, the argon gas was switched to H_2 (60 ml/min) to start the reduction reaction. When the experiment was finished, H_2 was switched to Ar again and the sample was cooled to the room temperature.

The phase composition of reduction product was determined by XRD (TTR III, Rigaku Corporation, Japan). The morphology and size of particles were detected by FE-SEM (ZEISS SUPRA 55, Oberkochen, Germany) and transmission electron microscopy (TEM).

3. Results

The reaction extent (α) of the hydrogen reduction of MoO_2 was calculated by the following equation

$$\alpha = \frac{W_t}{W_{max}} \tag{1}$$

where W_t is the weight loss ratio of raw material after reacting for a period of time t, which is defined as the ratio of mass loss at time t to the total mass of the initial sample, and W_{max} is defined as the weight loss ratio when the MoO_2 is completely reduced to Mo, which is 25%.

3.1. TG analyses

When the experiments were finished, the mass loss rates of all the samples maintained at about 25%, which is equal to the theoretical mass loss ratio of reducing MoO_2 to Mo, indicating that samples were reduced completely in all cases. Fig. 2 shows the TG reduction curves of MoO_2 powders with and without the assistance of salts at different temperatures from 720 °C to 850 °C. From Figs. 2 (a), (b) and (c), it can be found that the temperature had a significant influence on the reduction rate of MoO_2 with H_2 regardless of with and without the assistance of salts. With the increase of temperature, the time of complete reduction was reduced gradually. Besides, it can be seen that adding a small amount salts had a significant influence on the reduction of MoO_2 by H_2. Taking the reduction at 750 °C for example, as shown in Fig. 2 (d), the reaction time of MoO_2 samples at a fixed reacted fraction with the addition of different salts were close, but much slow than the case without salt addition, indicating that a pretty small amount of molten salts can remarkably decrease the reduction rate of MoO_2 by H_2. The mechanism for this phenomenon will be discussed in the following section.

3.2. Phase compositions analyses

It has been known from the mass loss ratios that all molybdenum oxide powders were completely reduced within 75 min. The phase compositions of the Mo products were characterized by X-ray diffraction t (XRD) and the results are shown in Figs. 3 (a) and (b), from which it can be seen that the only phase was Mo metal in all the products. Fig. 3 (c) shows the XRD patterns of products after reducing pure MoO_2 and MoO_2 with 0.1% NaCl−KCl binary salt at 750 °C with the reaction extents of 0.39 and 0.37, respectively. It can be seen that MoO_2 was reduced into metal Mo powder directly without any intermediate oxides whether the salt exists or not.

3.3. Morphology and size analyses

Fig. 4 shows the FE-SEM images of Mo products obtained by completely reducing commercial MoO_2 with H_2 without salt addition at different temperatures. It can be seen that the Mo products obtained at temperatures had a similar morphology, which maintained the platelet
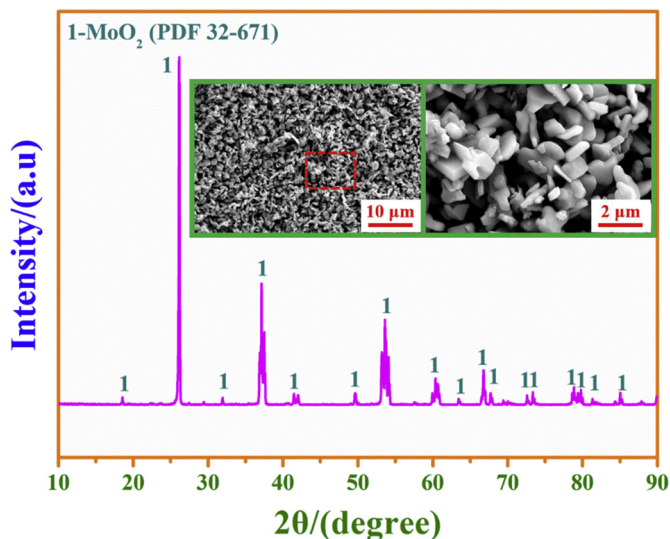

Fig. 1. XRD pattern and FE-SEM images of MoO_2 powder.