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Synthesis of ultra-fine Mo–Cu nanocomposites by coreduction of mechanical-activated $CuMoO_4$–MoO_3 mixtures at low temperature

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ABSTRACT

We report the low temperature synthesis of Mo–Cu composite powders by mechanical-activation (ball-milling) of $CuMoO_4$ and MoO_3 mixtures followed by subsequent coreduction process. The phases and microstructures of the Mo–Cu composites were systematically examined by X-ray diffractometer, scanning electron microscope and transmission electron microscope, and correlated with the ball-milling time and reduction temperature. It was shown that mechanical-activation (ball-milling) can significantly enhance the reduction activity by reducing the particle size of powders and hence increasing the reaction surface area, therefore giving rise to the synthesis of Mo–Cu composite powders at relatively low temperature (650 °C). By optimizing the experimental parameters, Mo–25 wt.%Cu nanocomposite powders with superfine particles with size ranging from 100 nm to 200 nm could be successfully obtained by ball-milling for 20 h followed by reduction in hydrogen at 650 °C.

1. Introduction

Mo–Cu alloys are of special interest because of their excellent physical and electronic properties, such as high thermal and electrical conductivity, low and alterable thermal expansion coefficient, low weight, nonmagnetic and well high-temperature behavior [1–5]. Compared with their partners (e.g. W–Cu alloys), Mo–Cu alloys are easier to sinter and process due to the small density difference between Mo and Cu and low melting point of Mo [6]. These properties render Mo–Cu alloys widespread applications in electronic packing devices [7], heat sink materials [8], vacuum technology [6], aeronautics [5] and so on. In most of the applications, high-dense Mo–Cu materials with homogeneous microstructure are required for high performance, which has led in turn to attempts to prepare ultra-fine and well-dispersed Mo–Cu powders in different ways, such as spray drying and reduction process [9], metal injection molding [10], electroless plating technique [11], mechanical alloying process [12] and gelatification-reduction process [6]. However, most of these methods were accomplished at high temperature (typically 900 °C), resulting in undesirable growth of large Cu phases; furthermore, these methods usually require complicated experimental facilities and procedure. As such, it is highly desirable to develop a simple process to fabricate ultra-fine and well-dispersed Mo–Cu powders.

In present paper, we report a simple route to synthesize ultra-fine and well-dispersed Mo–Cu nanocomposites, which consists of mechanical-activation (ball-milling) of $CuMoO_4$ and MoO_3 mixtures followed by subsequent coreduction process, referred to as "mechanical-activation-coreduction" process. The influence of the ball-milling time and reduction temperature on the microstructure of the Mo–Cu powders will be studied by combined techniques: X-ray diffractometer (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM).

2. Experimental procedure

MoO_3 powder with mean particle size of 1 μm and purity of 99.95% (Tianjin Sifang Chemical Development Co., Ltd., China) and CuO powder with mean particle size of 5 μm and purity of 99.0% (Sinopharm Chemical Reagent Co., Ltd., China) were used as precursors for the synthesis of Mo–Cu alloy powders. MoO_3 and CuO powders with a ratio of 3.6:1 were homogeneously mixed and calcined in air atmosphere at 530 °C to get $CuMoO_4$–MoO_3 mixtures. The $CuMoO_4$–MoO_3 mixtures were then ball-milled at 400 rpm over a range of time from 1 h to 20 h in air atmosphere using a Planet-Ball-Grinding machine. The ball-milled $CuMoO_4$–MoO_3 mixtures were finally reduced in the hydrogen atmosphere at different temperatures of 200 °C, 400 °C and 650 °C to obtain Mo–Cu alloys. The dew point of H_2 gas was −30 °C to −40 °C; the flow rate was 0.8 L min^{-1}, and the height of powder bed was 12 mm. XRD was used to study the structure and composite phases of the powers. SEM and TEM were employed to investigate the influence of the ball-milling time and reduction temperature on microstructure of the powders.

3. Results and discussion

Fig. 1 shows SEM images of the microstructures of $CuMoO_4$–MoO_3 powders ball-milled at different time. It is

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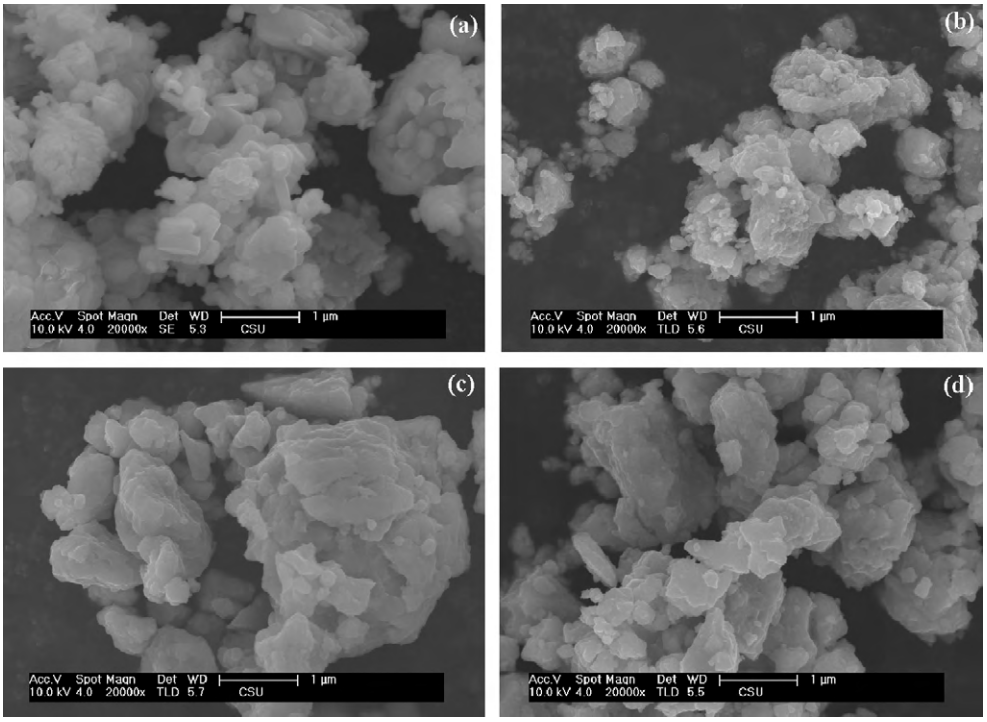

Fig. 1. SEM images of $CuMoO_4$–MoO_3 powders: (a) before milling; (b) milled for 1 h; (c) milled for 10 h; (d) milled for 20 h.

observed in Fig. 1(a) that the $CuMoO_4$–MoO_3 powder mixtures without milling are composed of short rods and spherical particles. These short rods and spherical particles are quite compact, which may reduce the reaction surface area between the $CuMoO_4$–MoO_3 powders and hydrogen during the reduction process. Obviously, this may bring negative effect to the reduction process. Fig. 1(b) and (c) shows the microstructures of the $CuMoO_4$–MoO_3 powders ball-milled for 1 h and 10 h, respectively. We can clearly observe that the rod-like structures and spherical particles of the initial powders disappear and the milled powders show irregularly shaped features. After milling for 20 h, as shown in Fig. 1(d), the lamellar structures begin to appear and the crystalline size decreases compared with that of the powders milled for 1 h.

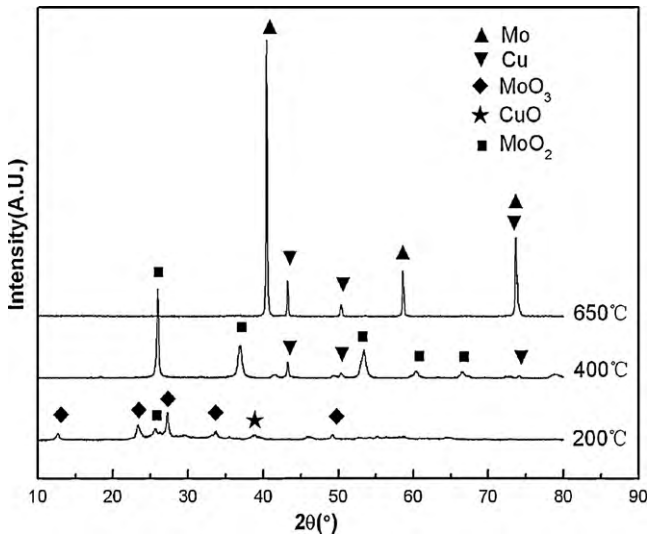

Fig. 2. XRD diffraction patterns of Mo–Cu powders reduced from 20 h ball-milled $CuMoO_4$–MoO_3 mixtures at 200 °C, 400 °C and 650 °C.

Fig. 2 shows XRD diffraction patterns of the Mo–Cu powders obtained by reducing the 20 h ball-milling $CuMoO_4$–MoO_3 powders at a temperature of 200 °C, 400 °C and 650 °C, respectively. For the powders reduced at 200 °C, diffraction peaks attributed to MoO_3, MoO_2 and CuO phases can be identified and no peaks from $CuMoO_4$ phase can be found, indicating that the $CuMoO_4$ completely decompose into MoO_2, CuO and H_2O (evaporated) under the action of hydrogen. The initial MoO_3 phase keeps intact during the reduction process at this temperature. Nonetheless, the MoO_3 phase disappear when the powders are reduced at 400 °C and only diffraction peaks from MoO_2 and Cu phases can be observed. This is consistent with the fact that MoO_2 have an autocatalytic effect in the reduction of MoO_3 [13], which promotes MoO_3 to reduce into MoO_2 at the temperature below 400 °C. Indeed it has been recently reported by Chen et al. that the reduction of MoO_3 in the presence of MoO_2 could occur at 300 °C [9]. Reducing the powders at 650 °C gives rise to the complete reduction of $CuMoO_4$–MoO_3 powders into pure Mo and Cu phases. As shown in the XRD patterns at 650 °C, only intense peaks from Mo and Cu phases can be observed and there is no indication of other oxides. It is worth noting that the reduction temperature in present work is much lower compared with those reported in literature, e.g. 950 °C [14].

Two possible mechanisms may ascribe to the complete reduction of $CuMoO_4$–MoO_3 powders at such a low temperature: firstly, our XRD diffraction results show that MoO_3 have a phase transition from monoclinic structure into hexagonal structure during the heating process of the $CuMoO_4$–MoO_3 powders, as shown in Fig. 3. It has been reported that hexagonal MoO_3 has higher reduction activity than that of monoclinic MoO_3 in the presence of Cu, therefore promoting the reduction of MoO_3 into pure Mo at a low temperature; [15] secondly, the ball-milling may play an important role in increasing the reduction activity of the powders. As shown in Fig. 1(d), the irregular-shaped small size particles resulting from ball-milling increase the reaction surface area for the hydrogen reduction. As such, the reduction activity of the powers is expected to be significantly enhanced by the mechanical activation effect compared with the powders without ball-milling. To verify

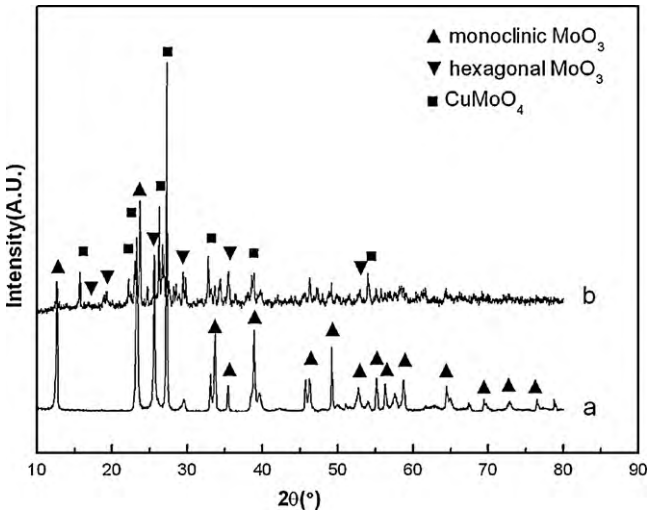

Fig. 3. XRD diffraction patterns of: (a) MoO_3 powders without heating; (b) $CuMoO_4$–MoO_3 mixtures from calcining MoO_3 and CuO powders.

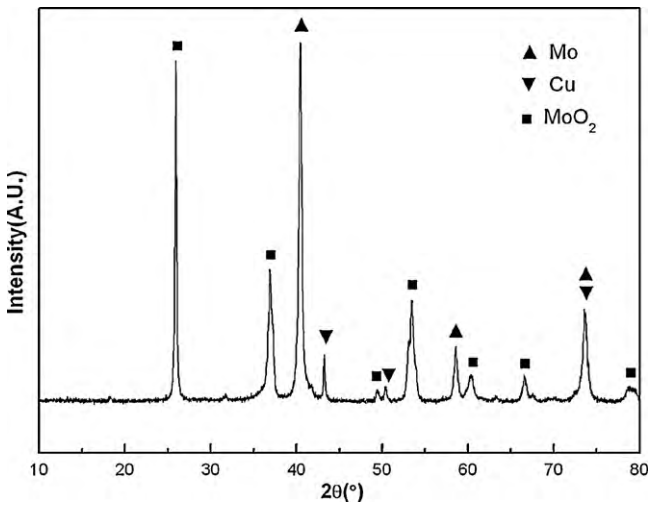

Fig. 4. XRD diffraction patterns of Mo–Cu powders obtained by reducing the $CuMoO_4$–MoO_3 powders without milling at 650 °C.

this statement, we investigate the XRD diffraction of the un-milled powders reduced at 650 °C, as shown in Fig. 4. Indeed, the powders are not able to be reduced completely and a great quantity of MoO_2 can still be observed.

To further gain insight into the effect of mechanical activation on the reduction of the Mo–Cu powders, we study the evolution of the microstructures of Mo–Cu powders with different ball-milling time of 0 h, 1 h, 10 h and 20 h. As shown in Fig. 5(a), the Mo–Cu powders reduced from un-milled $CuMoO_4$–MoO_3 mixtures have a great quantity of large composite particles. However, the particle grain sizes can be gradually reduced with increasing ball-milling time. Fig. 5(b) and (c) shows that the Mo–Cu powders with 1 h and 10 h ball-milling have smaller particles than that of without milling. Nonetheless, we can still observe the appearance of large particles, which may be formed by the agglomeration of small compact particles. These large agglomerations may reduce the reaction surface area and play a negative role in the subsequent sintering process of Mo–Cu powders. The Mo–Cu powders reduced from 20 h milled $CuMoO_4$–MoO_3 mixtures exhibit homogonous cellular microstructures [see Fig. 5(d)]. Fig. 6 shows corresponding magnified TEM images. It can be seen that the Mo–Cu powders consists of superfine spherical nanoparticles, with particle size ranging from 100 nm to 200 nm. These spherical particles exhibit smooth surfaces as shown in Fig. 6(b). According to the model by Chen et al. [9], pure Cu phase, formed at the beginning stage of reduction, can act as the nucleation cores for the following deposition of Mo phase reduced at a low temperature. Since this reduction model can control the growth of Cu effectively, the two phases of Mo–Cu powders can

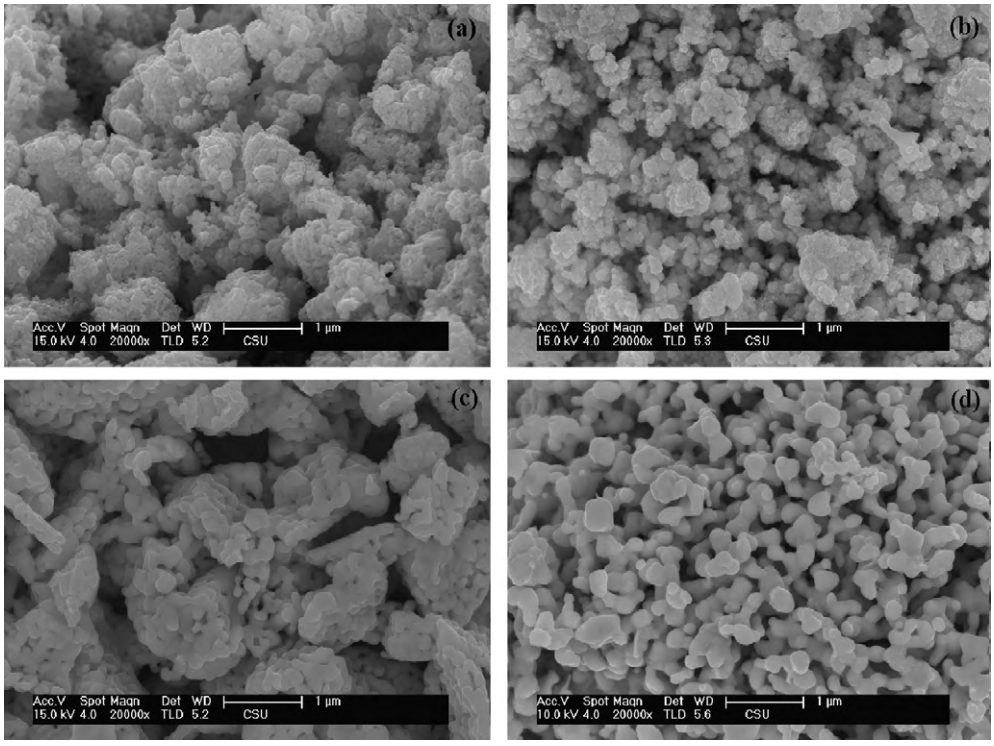

Fig. 5. SEM images of the microstructures of Mo–Cu powders reduced from $CuMoO_4$–MoO_3 powder with different ball-milling time: (a) 0 h; (b) 1 h; (c) 10 h; (d) 20 h.

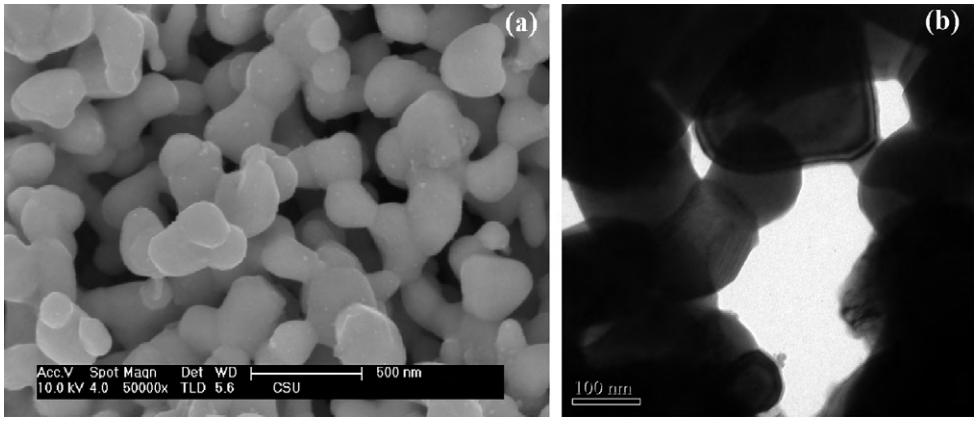

Fig. 6. (a) and (b) Magnified TEM microstructures of powders ball-milled for 20 h and hydrogen-reduced at 650 °C.

disperse homogeneously, playing a beneficial role to the sintering process of Mo–Cu powders. Further detailed study is under way to unravel the exact activation and reduction mechanisms and will be reported elsewhere.

4. Conclusions

In summary, we have demonstrated that a simple way to synthesize Mo–Cu composite powders by mechanical-activation (ball-milling) of $CuMoO_4$ and MoO_3 mixtures followed by subsequent coreduction process. The mechanical-activation (ball-milling) plays a important role in enhancing the reduction activity by reducing the particle size of powders and therefore promotes the complete reduction of $CuMoO_4$ and MoO_3 mixtures at a relatively low temperature (650 °C). Mo–25 wt.%Cu nanocomposite powders with superfine particles with size ranging from 100 nm to 200 nm could be successfully obtained by ball-milling for 20 h followed by reduction in hydrogen at 650 °C.

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