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Letter

Mechanochemical synthesis of Mo–Cu nanocomposite powders

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ABSTRACT

Mo–Cu nanocomposite powders were successfully synthesized by the mechanochemical (high energy ball-milling) and hydrogen-reduction process at low temperature (650 °C). MoO_3 and CuO powders were used as precursors, which were calcined in air atmosphere to get $CuMoO_4$–MoO_3 mixtures. The mechanochemical treatment of the $CuMoO_4$–MoO_3 powder mixtures caused a substantial increase of both the reduction activity of powder mixtures in hydrogen and the refinement of powders. It was accompanied by a transformation from $CuMoO_4$ to $Cu_3Mo_2O_9$, playing a critical role in hydrogen reduction process. By optimizing the experimental parameters, Mo–30 wt.% Cu nanocomposite powders with superfine particles with size ranging from 100 to 200 nm could be successfully obtained by mechanochemical-reduction method.

1. Introduction

Mo–Cu alloys have been widely used for electronic packing devices, heat sink materials, vacuum technology, aeronautics and many other applications [1–5] due to 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 [6–8]. 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], electroless plating technique [10], mechanical alloying process [11], and gelatification–reduction process [12]. 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. Recently, a mechanochemical process, which consists of ball-milling or jet-milling and subsequent hydrogen-reduction with oxides mixture, has been suggested as a fabrication method of the Mo–Cu nanocomposite powders or their partners (e.g. W–Cu powders) [12–15]. Nevertheless, few details have been reported about the influence of chemical change during the milling process on the subsequent reduction process.

In this study, we report a simple route to synthesize ultra-fine and well-dispersed Mo–Cu nanocomposites, which consists of mechanochemical (ball-milling) of $CuMoO_4$ and MoO_3 mixtures followed by subsequent reduction process. The chemical change during the mechanochemical process was discussed. Also, the effect of the newly formed substance in this process on hydrogen-reduction was described.

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 weight ratio of 2.8:1 were homogeneously mixed and calcined in air atmosphere at 530 °C to get $CuMoO_4$–MoO_3 mixtures. 50 g $CuMoO_4$–MoO_3 mixtures and 1000 g stainless steel ball with diameter of 10 mm were added into each stainless steel tank with volume of 1 L. The $CuMoO_4$–MoO_3 mixtures were then high-energetically ball-milled at 450 rpm for 1 h and 5 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, 400, 600 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 10 mm. XRD and SEM were employed to investigate the composite phases and microstructure of the powers, respectively.

3. Results and discussion

Fig. 1 shows the XRD diffraction patterns of the ball-milled $CuMoO_4$–MoO_3 mixtures with various ball-milling times. Fig. 1(a) shows that the powder mixtures before milling are comprised of MoO_3 and $CuMoO_4$ and no other phase is found. For the powders milled for 1 h, diffraction peaks attributed to MoO_3, $CuMoO_4$ and

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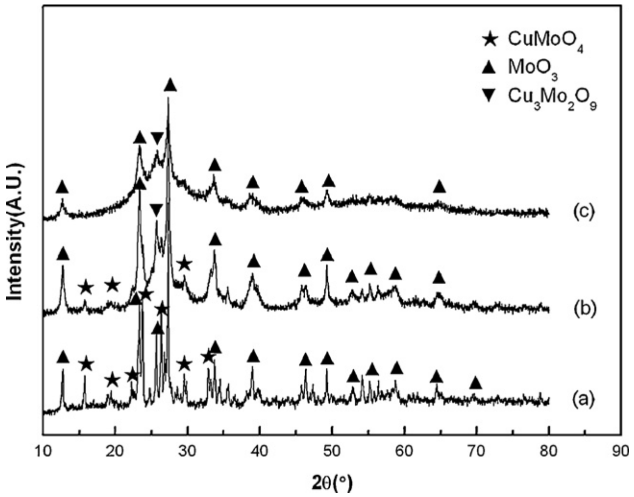

Fig. 1. XRD diffraction patterns of $CuMoO_4$–MoO_3 powders ball-milled for: (a) 0 h, (b) 1 h, and (c) 5 h.

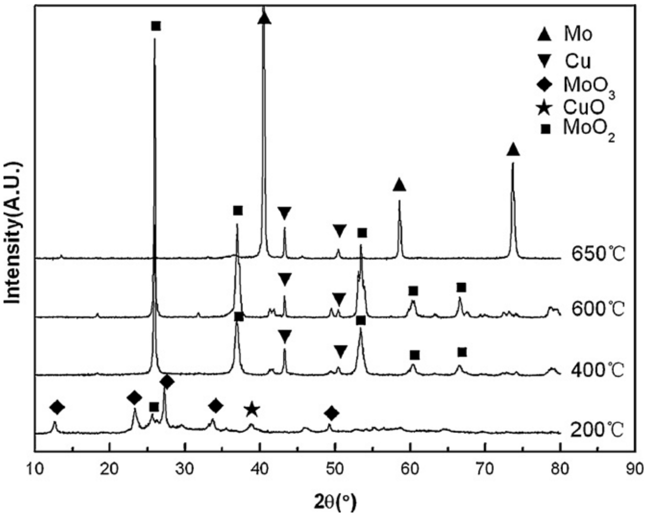

Fig. 3. XRD diffraction patterns of Mo–Cu powders reduced from 5 h ball-milled $CuMoO_4$–MoO_3 mixtures at 200, 400, 600 and 650 °C.

$Cu_3Mo_2O_9$ phases can be identified, indicating that mechanochemical treatment of the $CuMoO_4$–MoO_3 powder mixtures causes a chemical change, which leads to a transformation from $CuMoO_4$ to $Cu_3Mo_2O_9$. This transformation is not completely for there is $CuMoO_4$ left. Nonetheless, the $CuMoO_4$ phase disappear when the powders are milled for 5 h and only diffraction peaks from MoO_3 and $Cu_3Mo_2O_9$ phases can be observed. Increasing the ball-milling time, the MoO_3 peak is broadened and its intensity decreases due to the grain size refinement by high-energy ball-milling.

Typical microstructures of the ball-milled $CuMoO_4$–MoO_3 mixtures are shown in Fig. 2. It is observed in Fig. 2(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. In the initial stage of the ball-milling process (Fig. 2(b)), 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, and the particles are still very large. After ball-milling for 5 h, as shown in Fig. 2(c), plenty of superfine particles are observed in the aggregate.

Fig. 3 shows XRD diffraction patterns of the Mo–Cu powders obtained by reducing the 5 h ball-milling $CuMoO_4$–MoO_3 powders at a temperature of 200, 400, 600 and 650 °C, respectively. As previously described, $CuMoO_4$ phase is converted into $Cu_3Mo_2O_9$ completely after ball-milling for 5 h. 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 $Cu_3Mo_2O_9$ phase can be found.

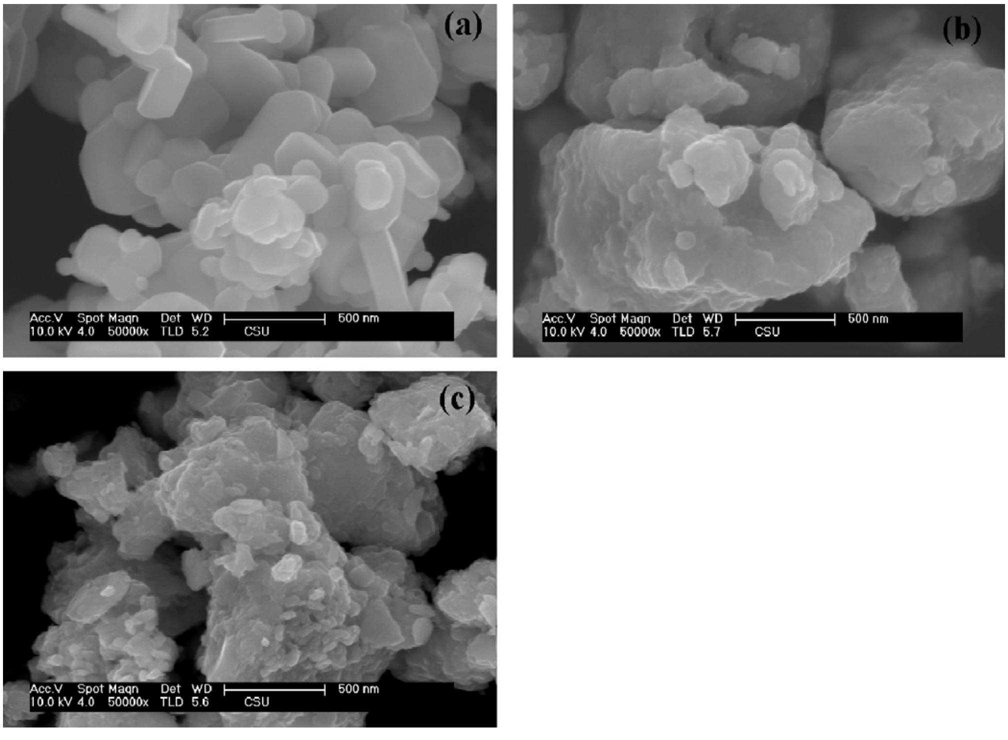

Fig. 2. SEM images of $CuMoO_4$–MoO_3 powders: (a) before milling, (b) milled for 1 h, and (c) milled for 5 h.

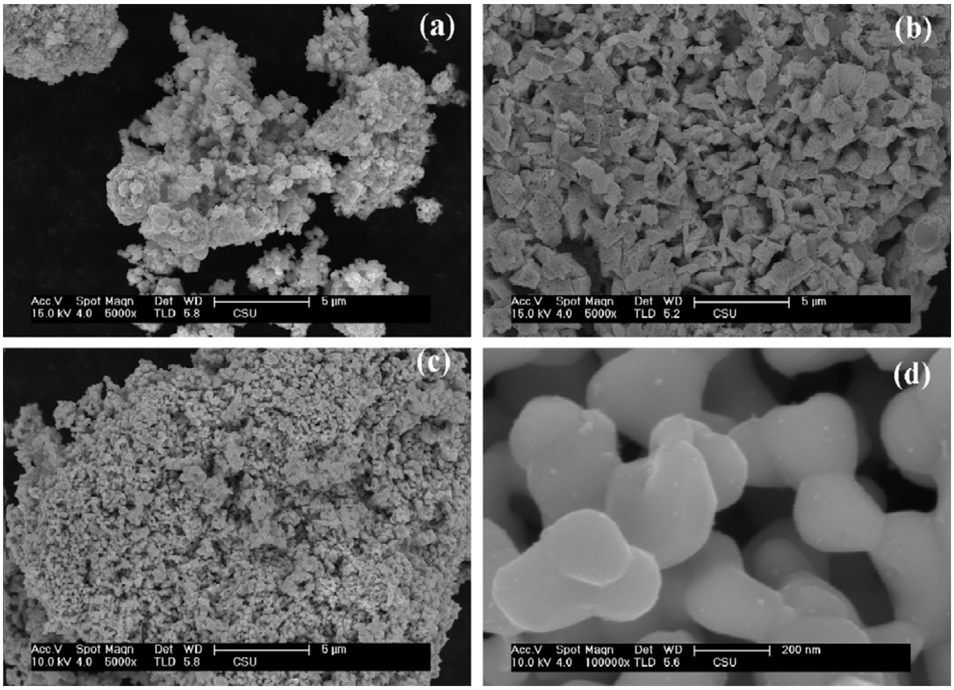

Fig. 4. SEM images of the microstructures of Mo–Cu powders reduced from $CuMoO_4$–MoO_3 powder with different ball-milling times: (a) 0 h, (b) 1 h, (c) 5 h, and (d) higher magnification SEM image of (c).

As we all know, MoO_3 cannot be reduced to MoO_2 at 200 °C [16], demonstrating that the MoO_2 is produced by decomposition of $Cu_3Mo_2O_9$. This is inconsistent with the study result reported by Chen et al. that $CuMoO_4$–MoO_3 mixtures remain the same and no MoO_2 is observed after being reduced at 200 °C [9]. This difference may be caused by the fact that the structure of $Cu_3Mo_2O_9$ formed during the mechanochemical process is thermally unstable [17,18], making it decompose into MoO_2, CuO and H_2O (evaporated) at 200 °C under the action of hydrogen. The initial MoO_3 phase keeps intact during the reduction process at this temperature. Nonetheless, the MoO_3 phase disappears when the powders are reduced at 400 °C and only diffraction peaks from MoO_2 and Cu phases can be observed. The powders reduced at 600 °C have the same phases with these powders reduced at 400 °C. 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 the literatures, e.g. 950 °C [19]. One mechanism may ascribe to the complete reduction of $CuMoO_4$–MoO_3 powders at such a low temperature: mechanochemical treatment of the $CuMoO_4$–MoO_3 gives rise to the formation of $Cu_3Mo_2O_9$, which decompose into MoO_2 at 200 °C. It has been reported that MoO_2 have an autocatalytic effect in the reduction of MoO_3 [20], which promotes MoO_3 to reduce into MoO_2 at the temperature below 400 °C.

To further gain insight into the effect of mechanochemical treatment on the reduction of the Mo–Cu powders, we study the evolution of the microstructures of Mo–Cu powders with different ball-milling times of 0 h, 1 h and 5 h. As shown in Fig. 4(a), the Mo–Cu powders reduced from un-milled $CuMoO_4$–MoO_3 mixtures have a great quantity of large composite particles with irregular shape. Fig. 4(b) shows that the Mo–Cu powders with 1 h ball-milling have particles with more regular shape than that of without milling. It can be observed that the powders are formed by the agglomeration of many flake-like particles with size ranging from 1 to 3 μm.

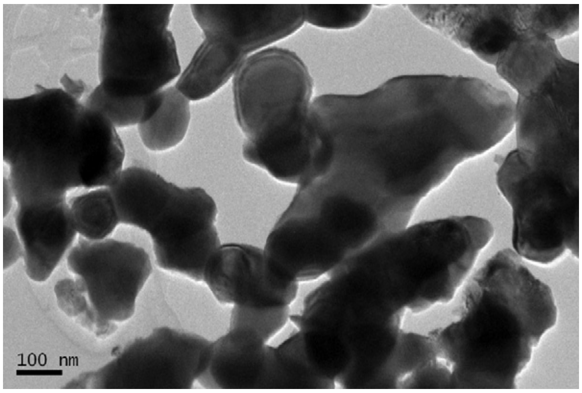

Fig. 5. TEM images of the microstructures of Mo–Cu powders.

The Mo–Cu powders reduced from 5 h milled $CuMoO_4$–MoO_3 mixtures exhibit homogonous cellular microstructures [see Fig. 4(c)]. Figs. 4(d) and 5 show corresponding magnified SEM and TEM images. It can be seen that the Mo–Cu powders consist of superfine spherical nanoparticles, with particle size ranging from 100 to 200 nm. These spherical particles exhibit smooth surfaces, regular shape and uniform size distribution, which make the Mo–Cu powders have excellent capability in pressing and sintering.

4. Conclusions

To conclude, we have demonstrated that a simple way to synthesize Mo–Cu composite powders by mechanochemical of $CuMoO_4$ and MoO_3 mixtures followed by subsequent hydrogen-reduction process. $Cu_3Mo_2O_9$ forms during the mechanochemical process and it promotes the complete reduction of $CuMoO_4$ and MoO_3 mixtures at a relatively low temperature (650 °C). Mo–30 wt.% Cu nanocomposite powders with superfine particles with size ranging from 100 to 200 nm could be successfully obtained by ball-milling for 5 h followed by reduction in hydrogen at 650 °C.

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