Preparation and reduction behavior of Mo-Cu powders by Sol-Gel

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Abstract. Mo-Cu composite powders were prepared by the Sol-Gel method using citric acid as chelating reagent. The composition, morphology and particle size of the powders were studied by the XRD and TEM. TEM observation result shows the particle size of Mo-Cu powders is about 150nm after reduction and the Mo grains are covered homogeneously by Cu on the surface. The reduction behavior and mechanism were analyzed systematically. Temperature programmed reduction (TPR) results indicate that the appropriate two-step reduction temperatures are 500°C and 700°C, respectively. The results from FT-IR show that the bond of Mo=O is weakened due to the bond of Cu-O-Mo, which leads to the increase of the reduction capability of the Mo-Cu composite oxide powders.

1. Introduction

Due to the excellent properties of high electrical and thermal conductivities, arc erosion resistance and low thermal expansion coefficient, Mo-Cu alloy is extensively used as heavy-duty electronic contacts, welding electrodes, and other parts used in electronic packaging and military fields [1-4].

In general, full densification for Mo-Cu compact is difficult to achieve by liquid phase sintering. The low solubility of Mo in Cu makes the contribution of grain-shape accommodation by solution-re-precipitation negligible, so densification can be attributed to either particle rearrangement due to capillary forces or sintering of the Mo skeletal structure by solid state diffusion. Consequently, the particle size and mixing uniformity of the Mo and Cu raw powders make a great impact on the densification behavior and final microstructure owing to the lack of homogenization during sintering [5,6]. Recently, mechanical alloying [7-9] which has been successfully used to fabricate Mo-Cu alloy possessing high mechanical property aroused great attention. Homogenization of the ingredients occurs by a process involving repeated extrusion, cold welding and crush of the powder particles during milling, accompanied by the gradual refinement of the mixed powder particles. At the same time, the formation of a large amount of dislocation, lattice distortion and the nano-grain boundaries increase the activity of powders, which is beneficial to the sintering process [10]. Unfortunately, high energy ball milling includes long time for achieving ultra-fine particle size and involves introduction of impurities. Therefore, Sol-Gel as a chemical procedure [11-13] has been explored to prepare homogeneously dispersed ultra-fine Mo-Cu powders, possessing the advantages of good uniformity of

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different substances, small particle size and high purity. However, little attention has been focused on
the reduction process. Reduction temperature is very important since it should be higher than that for
the reduction reaction taken place but as low as possible to prevent grain growth during the reduction
period. In this study, Mo-Cu composite powders were successfully produced by the Sol-Gel method
followed by reduction. In order to get the optimum reduction technique for the preparation of Mo-Cu
powders with small particle size, the reduction behavior was analyzed using temperature programmed
reduction (TPR) and infrared spectrum (IR).

2. Experimental
To produce the Mo-30wt.%Cu composite powders, Cu(NO$_3$)$_2$·3H$_2$O and (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O as
starting materials were dissolved in distilled water, and citric acid was used as chelating reagent in the
precursor solution. The mixed solution was adjusted to pH=1 by adding ammonia or dilute nitric acid
solution. Afterwards the solution was evaporated to composite sol by heating at 80°C in water bath
with continuous stirring. Then the xerogel was formed at 120°C and was calcined at 500°C in air.
Finally, the obtained metal oxide powders were reduced by a two-step reduction at temperatures of
500°C and 700°C for 90min, respectively.

The phase analysis was conducted by X-ray diffraction (XRD) using Cu Kα radiation
(SHIMADZU XRD-7000). The Microstructure was characterized by TEM (JEM-2010) and SEM
(S4800). The particle size was evaluated by laser particle size analyzer (LA-920). The fourier
transform infrared (FT-IR) spectrum was measured by BRUKER VERTEX 70 infrared spectrometer
(squashed with KBr). TPR was performed in Ar+5%H$_2$ of flow rate 35mL·min$^{-1}$. Heating rate was
10K·min$^{-1}$ and the bridge current was 120mA.

3. Result and discussion
3.1. Analysis of calcined product
In order to obtain composite oxide powders, the xerogel was calcined under air to remove impurities
such as C and N elements. The samples were calcined at different temperatures and the XRD results
are shown in Figure 1. Figure 1(a) presents XRD pattern of xerogel calcined at 400°C. Both
amorphous peaks caused by the residue of organic substance and XRD peaks identified as CuMoO$_4$,
CuO and MoO$_3$ phases, were observed in the XRD patterns. Figure 1(b) is XRD patterns of calcined
products at 500°C. No amorphous peak is found, indicating that organic substance has been
decomposed completely. Therefore, 500°C was chosen as the appropriate calcination temperature.

Figure 2 shows the TEM micrograph of the samples calcined at 500°C. Direct TEM observation
shows that Mo-Cu oxides agglomerate and single particle size is about 200nm.

![Figure 1. XRD patterns of xerogel calcined by different temperatures :](image-url)
(a) 400°C; (b) 500°C.
3.2. Reduction process

TPR was applied to determine the appropriate reduction process of calcined product. Figure 3 shows the TPR spectra of pure MoO$_3$ and Mo-Cu composite oxide powders prepared by Sol-Gel methods. The reduction of pure MoO$_3$ to Mo consists of two reduction stages, namely, $\text{MoO}_6^{6+} \rightarrow \text{MoO}_4^{4+} \rightarrow \text{Mo}_0^0$. However, only one peak of hydrogen consumption appears in the TPR spectra of pure MoO$_3$ at a temperature of 655°C (see Figure 3(a)), indicating that the hydrogen consumption corresponding to the two-step reduction of $\text{MoO}_6^{6+} \rightarrow \text{MoO}_4^{4+} \rightarrow \text{Mo}_0^0$ has been merged into one peak. On the other hand, Figure 3(b) indicates clearly that the Mo-Cu composite oxide powders show different reduction behavior. The reduction process of the oxides is divided into three stages. The hydrogen consumption peak at 250°C corresponds to the oxygen active site of the Cu-O bond for hydrogen consumption. The other two peaks appearing at 380°C and 620°C might be caused by reduction of two stages for $\text{MoO}_3 \rightarrow \text{MoO}_2$ and $\text{MoO}_2 \rightarrow \text{Mo}$. The relevant chemical equations are listed as follows:

$$\text{CuMoO}_4(s) + \text{H}_2(g) = \text{Cu}(s) + \text{MoO}_2(s) + \text{H}_2\text{O}(g)$$  \hspace{1cm} (1)

$$\text{MoO}_3(s) + \text{H}_2(g) = \text{MoO}_2(s) + \text{H}_2\text{O}(g)$$  \hspace{1cm} (2)

$$\text{MoO}_2(s) + 2\text{H}_2(g) = \text{Mo}(s) + 2\text{H}_2\text{O}(g)$$  \hspace{1cm} (3)

Each peak of hydrogen consumption for the composite oxides is associated with a different oxygen active site. The peaks move towards lower temperatures side compared with pure MoO$_3$. From Fig.3, it can be seen that additive Cu is favorable for the formation of active oxygen centers with high activation energy, leading to a low temperature of the hydrogen consumption peak. It may be assumed the interaction between Cu and Mo atoms have significant influence on coordination environment for Mo and bond of Mo-O, which can form the different oxygen active sites to separate continuous reduction into different processes.

Based on the TPR result, 500°C and 700°C are determined as the optimum two-step reduction temperatures for Mo-Cu powders in this work in order to get fully reduced metallic Mo-Cu powder.

**Figure 3.** TPR spectra of MoO$_3$ and Mo-Cu composite oxides: (a) MoO$_3$; (b) Mo-Cu.
3.3. Characterization of reduced powders

Figure 4 shows the XRD patterns of the samples reduced by a two-step of 500°C and 700°C. The patterns exhibit well-defined crystalline peaks completely identified as Mo and Cu phase, indicating that MoO$_3$ and CuMoO$_4$ composite powders have been reduced completely above 700°C.

TEM micrographs of the Mo-Cu powders after reduction at 700°C are shown in Figure 5. From Figure 5(a), it can be seen that the powders has uniform particle size with the mean of around 150nm. In addition, the single particle observation (Figure 5(b)) indicates that the Mo grains are homogeneously covered by copper phase since a thin layer is found on the particle surface. This kind of particle is the key point to obtain Mo-Cu alloy with homogeneous structure and good properties.

In order to further characterize the particle size, particle size analysis for the powder mixtures was employed. The particle size distribution of Mo-Cu powders reduced at 700°C is presented in Figure 6. The result shows that the average powder particle size D(n,50) is 407nm, much larger than the result of TEM observation. This difference results from the particle agglomeration because ultra-fine particles with high specific surface area and specific surface energy caused a relatively unstable thermodynamic state. The aggregation between particles could reduce free energy of the system. However, this aggregation is a kind of soft agglomeration caused by physical interaction, which is generally believed that this will not affect either the uniformity of powders or the densification during sintering process.
3.4. Reduction behavior

TPR results illustrate the reducibility of Mo-Cu composite oxides is enhanced compared with pure MoO₃. Copper is easy to be reduced in Mo-Cu composite oxides, and the reduction behavior of Mo is closely related to the nature of Mo-O bond, which is dependent on the coordination environment and interaction with other components for Mo atom. Figure 7 shows IR spectra of MoO₃ and Mo-Cu composite oxides. There are distinct absorption peaks in both MoO₃ and Mo-Cu oxides located in 800~1000 cm⁻¹ range. It is reported that the absorption peak in 800~900 cm⁻¹ corresponds to expansion vibration of metal-oxide-metal band (M-O-M), and the absorption peak in 900~1000 cm⁻¹ is attributed to the terminal metal=oxide band (M=O) [14]. In this study, The absorption peak of Mo-Cu oxides defined as Mo-O-Mo and Cu-O-Mo bands is located at 863 cm⁻¹, which is nearly the same with the result of MoO₃ (862 cm⁻¹). Moreover, the Mo=O band of Mo-Cu oxides at 954 cm⁻¹ is lower than that of MoO₃ samples (993 cm⁻¹). This red shift indicates that the bond of Cu-O-Mo makes the Mo=O bond weakened and the activity for terminal oxygen atoms increased, which leads to the increase of the reduction capability of the Mo-Cu composite oxide powders. Therefore the reduction temperature of Mo-Cu composite oxide powders is lower than that of pure molybdenum oxides.

![Figure 7. IR spectra of MoO₃ and Mo-Cu composite oxides: (a) MoO₃; (b) Mo-Cu.](image)

Based on the crackling core model for the reaction of solid particles [15], a simple model is proposed to describe the reduction process of Mo-Cu particles under hydrogen gas. Figure 8 shows the schematic diagram of reduction process for Mo-Cu oxides. A lot of cracks and micropores form on the Mo-Cu oxide particle from the surface to the interior in initial reduction stage. Cu phase possessing low melting point, is reduced firstly, then it will be soften and precipitated onto the surface of reduced Mo particles by capillary action with the increase of reduction temperature. After cooling, a copper layer coated on Mo particles will be formed. Since the composition of Mo-Cu oxides is well-mixed by Sol-Gel, Mo grains are covered homogeneously by Cu phase after reduction.

Metallic Mo-Cu particles are smaller than Mo-Cu oxides in size, which is also caused by the reduction process. During the first reduction period of MoO₃, cracks and micropores are extend to the
center of particle with the decrease of oxygen content and the increase of vacancies. A great deal of MoO₂ nuclei and an intermediate gaseous transport phase are formed. This transport phase is deposited on MoO₂ nuclei, which leads to grain growth. The grain size of the final product is determined by the growth of MoO₂ grain.

In addition, the addition of Cu element also plays a significant role in obtaining ultra-fine Mo-Cu powders. On the one hand, precipitated copper phase are favorable for the formation of micropores and cracks. On the other hand, during the reduction period, many defects such as dislocations and crystal deformation are formed by the enlargement of either phase interface between reduced Mo and MoO₂ phases or contact surface between the crystallites formed in incubation period and MoO₂. The reduced Cu deposits around MoO₂ grain could pin these dislocations and prevent the grain growth.

![Mo-Cu oxide particle](image)

**Figure 8.** The reduction process of Mo-Cu composite oxides.

### 4. Conclusion

Mo-Cu composite powders have been successfully produced by the Sol-Gel method followed by two-step hydrogen reduction. Obtained Mo-Cu powders consist of metallic Mo-Cu composite particles about 150nm in size in which the Mo grains are homogeneously dispersed in copper phase. The optimum two-step reduction temperatures are 500°C and 700°C. The bond of Mo=O is weakened due to the bond of Cu-O-Mo, which leads to the increase of the reduction capability of the Mo-Cu composite oxide powders.

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