Sintering Behavior and Properties of Mo-Cu Composites

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1.Introduction

Owing to the outstanding physical and mechanical properties (e.g., satisfactory electrical and thermal conductivity, low and adjustable coefficient of thermal expansion, wear resistance, and high temperature strength) of Mo-Cu composites with different copper contents, they are now broadly used for the heavy duty service contacts [1]. Infiltration of molten/liquid copper into the preformed molybdenum skeleton is a conventional process to fabricate the Mo-Cu composites. Nevertheless, Mo-Cu composites with high density can be obtained in this way on account of the mutual insolubility between molybdenum and copper or the high contact angle between liquid copper and molybdenum [2, 3]. In the last few years, a chemical-activated sintering process has been conducted to improve the sinterability by adding a certain amount of the metal activator into Mo-Cu powders. Nevertheless, these activators (such as Co, Ni, or Fe) exhibit a passive effect on the electrical and thermal properties of the M-Cu composites (M=W, Mo) [4–7].

Considering that the sintering activity of most powders can be modified by decreasing the particle size and enhancing the homogeneity of the starting powders, many researches have been performed recently to prepare superfine (even nanoscale) Mo-Cu powders [8–11]. Many attempts have been tried to prepare these powder systems in different ways, such as the heterogeneous precipitation process [12], gas-phase synthesis [13], mechanical alloying process [14, 15], and nitridation-denitridation method [16]. However, the quantity and content of published works in this area do not seem sufficient to draw a plausible conclusion about successfully preparing Mo-Cu powders with good sinterability and Mo-Cu composite compacts with excellent performance.

In our previous study [17], well-dispersed Mo-Cu nanopowders were synthesized by a simple and time-saving route. The densification behavior and properties of Mo-Cu powders obtained in this way are investigated in the present research. Effects of temperature on the microstructures and properties are also systemically studied in this work.
2. Experimental Procedure

Initially, hexaammonium heptamolybdate tetrahydrate and copper(II) nitrate trihydrate at a designed weight ratio were dissolved in deionized water to obtain mixed salt solution. After that, excessive ammonia solution was instilled into the salt solution till no precipitate and gel left. This obtained solution was heated in a microwave oven to evaporate all liquid, and then, the dry precipitates were collected and reduced at 650 °C for 2 h to obtain Mo-Cu composite powders. The as-prepared Mo-Cu composite powders were compacted in a steel die under the pressure of 250 MPa to produce green parts. The compacts were sintered at 900 ∼ 1300 °C under reducing atmosphere of Ar-20 vol.% H₂ in a tube-type resistance furnace for 2 hours, and the heating rate is 10 ± 6% °C·min⁻¹. Then, the sintered samples were cooled to the room temperature (20 °C) through free cooling.

The actual density of sintered Mo-Cu composites was measured using Archimedes’ principle. The samples were weighed in air and when immersed in distilled water, and the masses of the thoroughly wetted sample were also measured. An AR5120 electronic balance with an accuracy of 0.0001 g was used for recording the weights. Theoretical densities of the samples were calculated using the rule-of-mixture principle. Microscopic morphology observations were conducted on an FEI Sirion 200 scanning electron microscope (SEM). The electrical conductivity was measured by the four-point probe method on the HL5500PC Hall effect measurement system. Hardness was measured using an HVD-1000 Vickers hardness tester (by LaiZhou Hardness Tester Corp., China). Bending strength was examined using a mechanics tester of materials (Instron 3369, US). The thermal conductivity was calculated through the following formula:

\[ \lambda = \alpha \rho C_p, \]

where \( \rho \) and \( C_p \) are the density and specific heat capacity of the sample, respectively, and \( \alpha \) is the thermal diffusivity of the sample and was measured by the thermal diffusivity analyzer (STA449C/3/MFC/G, Netzsch Corporation, Germany). The \( C_p \) values were calculated based on the rule-of-mixture principle. The detailed equation is as follows:

\[ C_p = \omega_{\text{Cu}} \cdot C_{\text{Cu}} + \omega_{\text{Mo}} \cdot C_{\text{Mo}}, \]

where \( \omega_{\text{Cu}} \) and \( \omega_{\text{Mo}} \) are the mass fractions of Cu and Mo in Mo-Cu composites, respectively. \( C_{\text{Cu}} \) (0.38 J·g⁻¹·K⁻¹) and \( C_{\text{Mo}} \) (0.25 J·g⁻¹·K⁻¹) are specific heat capacities at a constant pressure of Cu and Mo, respectively [18].

3. Results and Discussion

3.1. Sintering Behavior. Figure 1 shows the influence of sintering temperature on shrinkage of sintered compacts. It is well known that as sintering temperature rises, the contact area between particles increases, evolving into the sintering neck. Continuous growth of the sintering neck leads to diminishment or vanishment of pores between particles and the increase of shrinkages. It is worth noting that the radial shrinkage of Mo-Cu composites is always higher than the axial shrinkage. This is because one-direction compacting is used to obtain the green compacts, so the radial pressure is invariably lower than the axial pressure during the uniaxial pressing process, causing that the shrinkage along radial direction is always easier to be accomplished than that of axial direction.

Figure 2 depicts the effect of sintering temperature on density and relative density of sintered compacts. It can be clearly seen that both the density and the relative density of the sintered samples are dramatically increased by increasing the sintering temperature at the anterior half segment of the whole sintering process. However, when the temperature goes beyond 1100°C, the growth in density and relative density becomes slow. The solid-phase sintering is conducted
at 900°C and 1000°C because the sintering temperatures are below the melting point of copper (1083°C). During this process, atomic diffusion ability is enhanced, resulting in the increase of the contact area between particles, the decrease of pores, and the formation and growing of sintering necks, and then, all the above phenomena lead to the increase of the density and the relative density of specimens. When the temperature exceeds the melting point of copper (1100°C), a bridged copper network all over the structure is gradually formed by bonding and linking of the liquid Cu phase from different composite particles. Formation of this network can improve the densification [8, 19]. As a consequence, a significant growth of the densification can be observed as the temperature increased. Nevertheless, the increase in density becomes slow when sintered at 1200°C and 1300°C (liquid-phase sintering), even though remarkable shrinkage of the Mo-Cu samples can be noticed (Figure 1). Reasons for this phenomenon are concluded as follows: Firstly, there are some impurities in Mo-Cu composite powders, and some of them vaporize into gases during

Figure 3: Cross-sectional microstructure of Mo-Cu compacts at different sintering temperatures: (a) 900°C, (b) 1000°C, (c) 1100°C, (d) 1200°C, and (e) 1300°C.
sintering at the temperatures. These gases are encapsulated in the samples under the compacting pressure, and volume of them is getting bigger and bigger when the sintering temperature rises, leading to reverse densification. Secondly, when the sintering temperature is higher than the melting point of copper, the large seepage of liquid copper will give birth to many pores, resulting in the decrease in density growth.

In some researches [20, 21], the relative density of Mo-Cu composites is ranging from 92 to 97% (relatively low), even though the compacts are sintered at a higher temperature with more sintering time than those in this research. In contrast, the relative density of Mo-Cu composites reaches up to 98% after sintering at 1200°C for 2 h from Figure 2. One possible reason may ascribe to the excellent sintering ability of Mo-Cu powders obtained from the microwave-assisted method: Mo-Cu powders are synthesized at a very low temperature, and the small grain size and uniform size distribution give birth to the good powder activity for Mo-Cu powders; furthermore, the distinctive copper-core/molybdenum-shell structure of powders obtained by the microwave-assisted method can effectively

Figure 4: Fractograph of Mo-Cu compacts at different sintering temperatures: (a) 900°C, (b) 1000°C, (c) 1100°C, (d) 1200°C, and (e) 1300°C.
prevent the growth of Cu grain and agglomeration of Cu, which further facilitates the densification [17].

3.2. Microstructure. The Cross-sectional microstructure of Mo-Cu compacts sintered for 2 h at temperatures ranging from 900°C to 1300°C is shown in Figure 3. The results demonstrate that the temperature has a significant effect on the sintering response of the Mo-Cu composites studied here. From Figure 3(a), it can be clearly seen that there are plenty of large interparticle pores on the cross section of the specimen sintered at 900°C, and even some particle-like structures can be observed, indicating insufficient sintering reaction at this temperature. As the temperature rises, the porosity of Mo-Cu composites is significantly decreased and the microstructure becomes more homogeneous (Figures 3(b)–3(d)). When the sintering temperature rises up to 1200°C, the diffusion of the Cu phase is enhanced because of the good liquidity of molten copper. Furthermore, the bonding and linking of the liquid Cu phase makes the distribution of Cu more uniform. However, too high sintering temperature (1300°C) gives rise to serious copper evaporation and generation of massive pores and bigger particles (Figure 3(e)).

To further gain insight into the microstructure of Mo-Cu composites, the fractograph of the samples is studied, as shown in Figure 4. One can notice that the particle size is particularly small when sintered at low temperatures (Figures 4(a) and 4(b)). The grain size increases obviously as the sintering temperature increases, as shown in Figures 4(c) and 4(d). Additionally, an interconnected network of copper can be seen apparently because the liquid copper phasediffuses easily between Mo particles when sintered at 1100°C and 1200°C. By and large, every Mo particle is capsulated in the continuous network structure of Cu. This network structure, an ideal sintering state, is beneficial to the overall performance of Mo-Cu composites, including hardness, strength, electrical conductivity, and thermal conductivity. Nevertheless, a mass of defects, such as pores and uneven distribution of the Cu phase, are resulted from too high sintering temperature (1300°C; Figure 4(e)), which is consistent with the aforementioned result from Figure 3(e).

3.3. Properties

3.3.1. Hardness. Figure 5 presents the influence of sintering temperature on the hardness of Mo-Cu composites. It is evident that the Vickers hardness is dramatically increased by increasing the sintering temperature at the beginning of the sintering process, but too high temperature has slowed down the growth of hardness. This variation trend is extremely similar to that of density (Figure 2). Evidently, the high density of the sintered samples is the main reason for high hardness. The decrease in porosity of the specimens and the increase in grain size make the Vickers hardness reach up to 219 HV when sintered at 1200°C.

3.3.2. Electrical Conductivity and Thermal Conductivity. Figure 6 depicts the variation of electrical conductivity (EC) and thermal conductivity (TC) of Mo-Cu composites with different temperatures. The results show that both the electrical conductivity and the thermal conductivity increase gradually from 900°C to 1200°C, while a slight decrease can be found in both of them when the sintering temperature rises to 1300°C. It is known that the Cu phase inherently has a much higher electrical conductivity and thermal conductivity than molybdenum; hence, a continuous network structure of Cu formed at 1200°C (Figure 4(d)) makes the electricity and heat transfer promptly between Mo and Cu. However, too high sintering temperature (1300°C) results in serious copper evaporation and generation of massive pores, which causes the decrease in both the electrical conductivity and the thermal conductivity. The highest values for EC and TC are obtained when the sintering temperature reaches
1200°C, which are $23.9 \times 10^6 \text{ S} \cdot \text{m}^{-1}$ and $172.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively.

### 3.3.3. Bending Strength

Figure 7 shows the bending strength of composites prepared at different temperatures. At the beginning, the bending strength increases gradually with the increase of sintering temperature and reaches the maximum value of 847 MPa at 1200°C. Nevertheless, a sharp decline in bending strength can be evidently observed when the temperature climbs above 1200°C. Therefore, it can be seen that the bending strength, EC, and TC of Mo-Cu composites have almost the same trend. As is known, the improvement of relative density leads to the bending strength enhancement with the processing parameter optimization [22]. From Figure 2, it can be seen that composites obtained at 1300°C show higher relative density than that at 1200°C. But losses of the copper network structure and emergence of pores (Figure 4(e)) lead to the decrease of bending strength.

### 4. Conclusion

In summary, Mo-Cu composites with excellent properties are prepared by sintering Mo-Cu nanoparticles synthesized from a microwave-assisted method. The results show that the sintering temperature is a critical factor in the densification process of Mo-Cu composites. The shrinkage, density, relative density, hardness, electrical conductivity, thermal conductivity, and bending strength increase with the rise of sintering temperatures. However, too high temperature results in the decrease in electrical conductivity, thermal conductivity, and bending strength. As a consequence, Mo-Cu composites sintered at 1200°C have the optimal microstructure and desired properties. The relative density, hardness, electrical conductivity, thermal conductivity, and bending strength of composites obtained at this temperature are 98%, 219 HV, $23.9 \times 10^6 \text{ S} \cdot \text{m}^{-1}$, $172.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, and 847 MPa, respectively.

### Data Availability

All the data used to support the findings of this study are available from the corresponding author upon request (aksun@hut.edu.cn).

### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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