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# Fabrication of homogeneous Mo-Cu composites using spherical molybdenum powders prepared by thermal plasma spheroidization process

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ABSTRACT

In this work, spherical and dense molybdenum particles with the average particle size of 16.6 μm were synthesized by thermal plasma spheroidization process, and further used to fabricate homogeneous Mo-25 wt% Cu composites by infiltration method. The influence of infiltration temperature and holding time on the microstructure and properties of obtained Mo-Cu composites was investigated, and experimental results show that homogeneous Mo-Cu composites with high densification are obtained and the smooth surface of pores could facilitate the infiltration process. Specially, 98.6% of relative density of Mo-Cu composites is achieved and less than 10% irregular particles existing in spherical powders induce closed or half-connected pores in porous Mo skeleton, which shows adverse effect on full dense Mo-Cu composites obtaining. In addition, the highest microhardness of Mo-Cu composites (199 ± 3.6 Hv) is obtained when infiltrated at 1300 °C for 1 h. Moreover, the maximum value of thermal conductivity (TC) of Mo-Cu composites is 154 W/(m·K), and this is lower than that predicted by theoretical models, which may be due to the small amounts of carbon in Mo-Cu composites and non-full dense of Mo-Cu composites. Furthermore, the carbon in porous skeleton could be well removed by controlling the atmosphere of sintering process. Importantly, Mo-25 wt% Cu composites fabricated by irregular particles exhibit non-uniform microstructure and low TC compared to that prepared by spherical particles, which would be due to the uneven pore distribution and closed pores in porous skeleton fabricated by irregular particles. These results well illustrate the superiority of spherical molybdenum particles on fabrication homogeneous Mo-Cu composites.

## 1. Introduction

Mo-Cu composites with 20–40 wt% Cu have been used in industry as electrical contact materials owe to combining brilliant mechanical properties, low coefficient of thermal expansion of molybdenum and prominent thermal and electrical properties of copper [1–5]. Generally, Mo-Cu composites with homogeneous microstructure and high densification are necessary to achieve outstanding properties. Conventionally, liquid phase sintering of Mo-Cu composite powders and the infiltration of porous Mo skeleton by liquid copper are two main methods to fabricate Mo-Cu composites [6–9]. However, homogeneous Mo-Cu composites with high densification are difficult to be obtained by liquid phase sintering because of the negligible mutual solubility and poor wettability between Mo and Cu [3,10–12]. Adding transition elements such as Fe, Ni to Mo-Cu composite powders has improved their sinterability and decreased the sintering temperature, which would introduce impurities undesirably and deteriorate the thermal properties of obtained products [13–16].

Liquid copper infiltration technique is an effective method to fabricate Mo-Cu composites with high densification, which is pre-sintering Mo skeleton with proper porosity and then infiltrates molten copper into the open pores of porous Mo skeleton [17,18]. It has been reported that the pore structure of porous Mo skeleton has a notable influence on the infiltration liquid copper for Mo-Cu composites, and it is necessary to make the pores in porous Mo skeleton open and prepare Mo skeleton with uniform pore distribution and smooth pore surface, which would contribute to infiltrating copper into pores and improving the infiltration efficiency [2,7]. However, most of researches on fabrication porous Mo skeleton focus on irregular molybdenum particles, and this would induce uneven pore distribution and closed or half-connected pores, which would deteriorate the densification and thermal properties of Mo-Cu composites [19,20]. It is worth mentioning that spherical particles with dense internal structure allow regular packing compared to irregular particles. The regular packing of spherical particles shows an advantage of preparing homogeneous skeleton with interlinked pores for infiltration [20–23]. Nevertheless, spherical and dense molybdenum

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particles are difficult to be synthesized due to their high melting point and few studies focus on fabrication Mo-Cu composites by infiltration method using spherical molybdenum particles as starting materials. As a result, it is possible to obtain homogeneous Mo-Cu composites with high densification using spherical molybdenum particles.

In this work, homogenous Mo-25 wt% Cu composites with high densification were fabricated by infiltration method using spherical molybdenum particles as starting materials. The influence of infiltration conditions on the densification and properties of Mo-Cu composites was further investigated. The results indicate that the uniform porous Mo skeleton with interlinked pores is obtained, which contributes to obtaining Mo-Cu composites with homogeneous and high dense microstructure. The TC of obtained products is lower than that predicted by theoretical models, which may attribute to the small amounts of carbon existing in porous Mo skeleton and non-full dense of Mo-Cu composites. Importantly, Mo-Cu composites fabricated by spherical powders exhibit superiority on the densification and TC compared to that made by irregular powders, and smooth pore channels prepared by spherical particles with smooth surface contribute to facilitating the infiltration process.

## 2. Experimental

### 2.1. Spherical molybdenum powders prepared by plasma spheroidization process

Spherical molybdenum particles used in this study were prepared by Radio-Frequency (RF) induction thermal plasma and the detailed description of spheroidization process was displayed elsewhere [24]. In a typical spheroidization process, irregular powders were fed into the plasma system by a carrier gas and the surface of original particles melted in the plasma zone. Then the melted particles solidified under the atmosphere of quenching gas and formed spherical particles due to the surface tension effect.

### 2.2. Fabrication of Mo-Cu composites

In the part of preparing porous Mo skeleton, spherical molybdenum powders obtained in Section 2.1 were pressed into green compacts under a pressure of 220 MPa and holding for 1 min using a stainless die of 13.0 mm diameter with 2.0 wt% stearic acid assistance. Stearic acid granules were dissolved in absolute ethyl alcohol and mixed with powders and then completely-dried at 80 °C using water bath while stirring with a spoon continuously. The green samples were treated at 400 °C for 2 h with a constant heating rate of 2 °C/min to remove the stearic acid, and then up to 1500 °C with 10 °C/min and sintered for 1 h to manufacture porous Mo skeleton. In the part of preparing Mo-Cu composites, copper powders (99.7% purity, Sinopharm Chemical Reagent Co., Ltd) were compacted and placed on the top of the sintered porous matrix. Different infiltration temperatures including 1100 °C, 1200 °C, 1300 °C and 1400 °C were selected and holding time was 1.0 h to investigate the influence of infiltration temperatures on the properties of obtained composites. In addition, different dwelling time including 0.5 h, 1.0 h, 1.5 h and 2.0 h was selected at the temperature of 1300 °C to investigate the influence of dwelling time on the properties of obtained composites. All experiments were carried out under hydrogen atmosphere.

### 2.3. Characterization

The morphologies of Mo powders and Mo-Cu composites were characterized by optical microscope and Scanning Electron Microscopy (SEM, MLA250, FEI company, USA). The structure of Mo powders was analyzed by X-ray diffractometer (XRD, Philips X'Pert PRO MPD). Spherical Mo particle size was quantitatively measured by particle size analysis software of Nano-measurer. Six different optical micrographs were used to determine the particle size distribution of Mo powders and a total of more than 1500 particles were measured. $N_2$ adsorption measurement (Builder, SSA-7300) was applied to measure the Brunauer-Emmett-teller (BET) specific surface area of powders. The heating treatment of powders was analyzed by thermal analysis instrument (TG-DTA 6300, NSK, Japan). The apparent density and flow time of irregular and spherical powders were measured based on funnel method (GB/T 1479.1-2011) and hall flowmeter (GB/T 1482-2010). The carbon and oxygen contents of raw powders and obtained skeleton were measured by C/S analyzer (CS-2800, NCS, China) and O/N analyzer (ON-3000, NCS, China). The pore size distribution of porous Mo skeleton was determined by mercury porosimetry (Micromeritics, AutoPore IV 9510). The linear shrinkage of porous Mo skeleton was calculated based on the radial diameter variation ($\triangle D/D_0$). The green density of Mo compacts was calculated directly by the ratio of weight to volume. The densities of sintered Mo skeleton and obtained Mo-Cu composites were measured according Archimedes principle. The relative densities of obtained composites were obtained using the theoretical density of composites $\rho_c$,

$$\frac{1}{\rho_c} = \frac{w_{Mo}}{\rho_{Mo}} + \frac{w_{Cu}}{\rho_{Cu}} \tag{1}$$

$\rho_{Mo}$ and $\rho_{Cu}$ are the density of Mo (10.22 g/cm$^3$ [25]) and Cu (8.96 g/cm$^3$ [26]), $w_{Mo}$ and $w_{Cu}$ mean the weight ratio of Mo and Cu. In this work, $w_{Mo}$ and $w_{Cu}$ theoretically equal to 75 wt% and 25 wt%. Therefore, the theoretical density of Mo-Cu composites is calculated to be 9.87 g/cm$^3$. The open porosity of porous Mo skeleton was evaluated by Archimedes replacement method after 15 min pretreatment in deionized water with ultrasonic assistance. Energy Dispersive Spectrometer (EDS, INCA Microanalysis Suite) was applied to analyze the distribution of molybdenum, copper and carbon. The Vickers microhardness of obtained Mo-Cu composites was conducted on the polished samples using microhardness tester under a 1.96 N loading and 10 s duration, and an average of ten readings with standard deviations was used as the final value. Thermal diffusivity ($\alpha$) of Mo-Cu composites was measured by LFA 427 Nanoflash (NETZSCH, Germany) according to ASTM E1461. The thermal conductivity ($\lambda$) was determined by the thermal diffusivity ($\alpha$), specific heat ($C_p$) and density ($\rho$) of obtained Mo-Cu composites according to the relation $\lambda = \alpha \cdot C_p \cdot \rho$, and stainless steel 310 was used as the standard sample and an average of three sets of data was used as the final value.

## 3. Results and discussion

### 3.1. Powder characterization

The typical morphologies and structure of Mo powders before and after thermal plasma spheroidization are exhibited in Fig. 1. Fig. 1a shows the SEM image of irregular raw molybdenum powders, and many small particles are agglomerates to big aggregates. The SEM image of spherical Mo powders after spheroidization process is shown in Fig. 1b, and monodispersed spherical particles with smooth surface could be observed. The optical micrograph shown in Fig. 1c further confirms the obtained powders have a good spherical shape and the rate of spheroidization exceeds 90% after thermal plasma process. The cross-section image of spherical Mo particles under the background of epoxy resin is exhibited in Fig. 1d, which indicates the dense internal structure of obtained spherical Mo particles. The XRD pattern shown in Fig. 1e reveals that the obtained spherical powders could be well indexed to Mo phase (Reference code: 00-042-1120). The obtained spherical particles have an average particle size of 16.6 μm with uniform particle size distribution, as exhibited in Fig. 1f. As a result, homogeneous spherical Mo particles with dense internal structure and smooth surface could be well prepared by thermal plasma spheroidization process.

The basic physical parameters of spherical and irregular Mo powders are exhibited in Table 1 and the result is listed as follows: *a*) The