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Fabrication of fine-grained W-Cu composites with high hardness

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ABSTRACT

W-Cu composite powders were prepared by ball milling method using quasi-spherical tungsten nanopowders as starting materials, and further used to fabricate W-Cu composites. The sintering behavior of obtained composite powders was investigated and experimental results reveal that composite powders exhibit high sintering activity and nanosized tungsten spheres could effectively suppress the grain growth of prepared W-Cu compacts. Importantly, composite compacts with high hardness of 409 ± 9 Hv are obtained when sintered at 1200 °C for 1.5 h, which could be attributed to the fine grain size and homogeneous constituents distribution of sintered composites. Furthermore, 96.5% of theoretical density (TD) of obtained compacts could be achieved by liquid phase sintering process due to enhanced grain rearrangement. Kinetic analysis indicates that liquid phase diffusion is the dominant mass transfer mechanism during liquid phase sintering. The grain size comparison of products prepared by pure tungsten nanopowders and W-Cu composite powders confirms fine-grained W-Cu composites could be obtained using quasi-spherical tungsten nanopowders.

1. Introduction

W-Cu composites with 5–20 wt% Cu are widely used in electrical and mechanical engineering such as heat sink materials for microelectronic packaging and warhead materials owe to combining the low thermal expansion coefficient, good mechanical strength of tungsten and brilliant thermal and electrical properties of copper [1–3]. Generally, high dense and fine-grained W-Cu composites with homogeneous microstructure are significant to obtain products with outstanding mechanical properties such as high hardness. Conventionally, liquid phase sintering and infiltration of porous tungsten matrix by liquid copper are two mainly adopted methods to fabricate W-Cu composites [4–6]. However, fine-grained W-Cu composites with high densification and homogeneous microstructure are difficult to be obtained because of poor wettability between W and Cu [7,8]. To improve the sinterability of composite powders, adding group VIII transition elements such as Ni, Pd as activators and decreasing particle size into nanoscale have been widely researched [3,9,10]. However, adding additives would suffer uncontrolled grain growth during sintering process and activators would also deteriorate the thermal properties of obtained composites [10–12]. In addition, it has been reported that composite powders with fine tungsten particle size could facilitate solid state sintering and enhance grain rearrangement during liquid phase sintering [13]. The sintering process of nanosized composite powders prepared by mechanical alloying or spray drying has been widely investigated [14–17]. For example, Maneshian et al. have reported the sintering of nanostructured W-Cu composite powders prepared by mechanical alloying, and the compacts with 85–98% of TD could be achieved by adjusting milling time [18]. Fine particles could be obtained with long milling time and tend to get W-Cu composites with high densification during sintering process. However, in these works, irregular nanoparticles with serious agglomeration and broad particle size distribution were used as starting materials and the grain size of sintered products grew up abnormally to micron level, which would worsen the mechanical properties of obtained W-Cu composites.

To suppress the tungsten grain growth during sintering process, many methods have been put forward, such as oxide dispersion strengthened (ODS) mechanism [19–21], special sintering techniques [22,23]. The average tungsten grain size could be decreased to 1.29 μm from 4.41 μm when 2.0 wt% Al_2O_3 powders were added into tungsten matrix, which would contribute to obtaining samples with high hardness [24]. In addition, fabrication compacts by

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sparking plasma sintering process could inhibit the grain growth effectively because of its fast sintering and short holding time [22]. Nevertheless, oxide dispersion process would do harm to the thermal conductivity of pure compacts and special sintering techniques are too demanding on device and sample [25]. In our previous work, the sintering behavior of well-dispersed spherical particles was studied and the results revealed that uniform pores packed by spherical particles could inhibit the grain growth efficiently in initial sintering stage [26,27]. As a result, it is reasonable to assume that W-Cu composites with high densification and fine grain size could be obtained using spherical tungsten nanopowders as starting materials.

In this work, W-Cu composite powders with well distributed W and Cu were prepared using quasi-spherical tungsten nanopowders as starting materials, and the sintering behavior of composite powders was further investigated. The influence of sintering conditions on the microstructure and microhardness of obtained composites was analyzed. In addition, the optimal sintering conditions and grain size comparison between tungsten nanopowders and W-Cu composite powders were reported.

2. Experimental

2.1. Materials

Quasi-spherical tungsten nanopowders (>99.8 purity) used in this study were synthesized by Radio-Frequency induction thermal plasma and the synthesis process and sintering behavior were exhibited in our previous work [27,28]. The average particle size of quasi-spherical tungsten nanopowders is 58.6 nm. Copper powders (99.7% purity) with the particle size of <53 μm were provided by Sinopharm Chemical Reagent Co., Ltd.

2.2. Fabrication of W-Cu composites

W-20 wt% Cu (W-20Cu) composite powders were fabricated by mixing quasi-spherical tungsten nanopowders and copper powders using a planetary ball mill (Nanjing Nanda Instrument Plant, QM-QX, China). The ball-to-powder weight ratio was 10:1 and the milling rate kept at 150 rpm for 10 h. Such obtained W-Cu composite powders were pressed into green compacts under a pressure of 250 MPa and holding for 1 min without a binder or any other pretreatment. The green samples were firstly sintered at 400 °C for 30 min with a constant heating rate of 5 °C/min and then up to the specific temperature with 10 °C/min in a tube furnace under flowing hydrogen atmosphere. Finally, the tube furnace was naturally-cooled under hydrogen atmosphere. Different sintering temperatures including 1050 °C, 1100 °C, 1150 °C, 1200 °C, 1250 °C, 1300 °C were selected to investigate the influence of sintering temperature on the microstructure and properties of W-Cu composites (holding for 1.5 h). Different holding time including 0.5 h, 1.0 h, 1.5 h, 2.0 h were selected to investigate the influence of holding time on the microstructure and properties of W-Cu composites (sintered at 1100 °C, 1150 °C and 1200 °C).

2.3. Characterization

The structures of tungsten and composite powders were analyzed by X-ray diffractometer (XRD, Philips X'Pert PRO MPD). The morphologies of composite powders and sintered products were examined by transmission electron microscope (TEM, JEM-2100) and field-emission scanning electron microscopy (FESEM, JEOL JSM-7001F). Energy dispersive spectrometer (EDS, INCA Microanalysis Suite) was applied to characterize the distribution and compositional analysis of tungsten and copper. The purity of initial W nanopowders was analyzed based on X-ray fluorescence (XRF, PANalytical, AXIOS-MAX) spectrum techniques. The melting point of copper in composite powders was determined based on Differential Thermal Analysis (DTA) curve. The particle size distribution of tungsten nanopowders and grain size of sintered samples were quantitatively measured by particle size analysis software of Nano-measurer and three different micrographs were taken into account at least. A total of more than 300 grains were measured for each compacts and grain size distribution was also displayed. The average grain size value was used as the grain size for this specimen. The error bar for each grain size data was calculated by the difference between the average grain size for this specimen and mean grain size for each field of view. Linear shrinkage of sintered compacts was based on samples' diameter variation. The density of green samples was calculated directly from the ratio of weight to volume, and densities of sintered W-Cu composites were measured according to the Archimedes principle and relative densities of sintered samples were obtained using the TD of composites ρ_c,

$$\frac{1}{\rho_c} = \frac{w_W}{\rho_W} + \frac{w_{Cu}}{\rho_{Cu}} \quad (1)$$

where w_i and ρ_i (i = W, Cu) represent the weight ratio and density of components, ρ_c means the TD of composites. In this work, w_W and w_{Cu} theoretically equal 80 wt% and 20 wt%, respectively. Therefore, the TD of W-20Cu composites (ρ_c) is determined to be 15.68 g/cm^3. The Vickers microhardness test was conducted on polished samples using microhardness tester (Shanghai Tai Ming Optical Instrument Co., Ltd, HX-1000TM, China) under 1.96 N loading and 10 s duration.

3. Results and discussion

3.1. Powder characterization

Fig. 1 displays the morphology and structure of tungsten powders used in this work. SEM and TEM images shown in Fig. 1a and b indicate that nanoparticles are well dispersed and exhibit as quasi-spherical shape. Fig. 1c presents the XRD pattern of tungsten powders, and all peaks could be well indexed to α-W with small amounts of non-equilibrium β-W and tungsten oxides. β-W could be transformed to α-W by annealing to 900 K [29]. The particle size of quasi-spherical tungsten powders is normally distributed, as presented in Fig. 1d, and the average particle size is determined to be 55.8 nm and more than 90% particles are smaller than 100 nm.

W-Cu composite powders were prepared by admixed method, and the characterization of as-obtained composite powders is exhibited in Fig. 2. The SEM image shown in Fig. 2a reveals the uniform particle size distribution of as-obtained composite powders after milling for 10 h. Importantly, the tungsten size of composite powders still keeps at the nanoscale (the inset of Fig. 2a), which ensures high sintering activity of composite powders [30]. Cu content is determined to be 19.8 wt% and 20.3 wt% based on EDS analysis and XRF technique, respectively, and these are closed to the theoretical copper content of composite powders (20.0 wt%), which indicates that W-20Cu composite powders could be effectively prepared by ball milling. The TEM image of composite powders shown in Fig. 2b reveals that tungsten particles still keep quasi-spherical shape after milling and mainly embed in copper particles. The corresponding elements distribution of obtained composite powders is shown in Fig. 2c, and quasi-spherical tungsten nanopowders are surrounded by copper in composite powders after milling. The XRD pattern of composite powders presented in Fig. 2d indicates that no other impurities exist except small amounts of tungsten oxides, which could be reduced under