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PREPARATION OF W-Cu COMPOSITE POWDERS BY HYDROGEN REDUCTION OF WO_3 AND COPPER NITRATE MIXTURE

The synthesis of fine W composite powder with homogeneously dispersed Cu particles was investigated. Commercial or ultrasonic spray pyrolysis WO_3 powders were used as source materials of W, and copper nitrate was added and hydrogen-reduced to finally fabricate W-Cu composite powder. The reduced powder prepared using ultrasonic spray pyrolysis WO_3 powder exhibited a spherical agglomerate composed of fine particles and pores, whereas that using commercial WO_3 showed relatively fine particles with a size of about 200 nm. TEM analysis revealed that Cu elements were uniformly distributed in the composite powder. These results help to optimize the synthesis process of homogeneous W-Cu nanocomposite powders.

Keywords: W-Cu powder; WO_3 and copper nitrate; hydrogen reduction; microstructure

1. Introduction

Tungsten-copper (W-Cu) composites are widely used in electronic packaging, heat sink, and welding electrode materials due to the low coefficient of thermal expansion and excellent mechanical properties of W, and the excellent electrical and thermal conductivity of Cu [1,2]. However, the W-Cu system has many difficulties in fabricating homogeneous and dense composite due to its poor mutual solubility and wettability [3]. Considering that the main densification mechanism in the liquid phase sintering of the W-Cu system is particle rearrangement, the use of nanocomposite powder is expected to effectively improve the sinterability and microstructural homogeneity [4]. Therefore, several approaches have been proposed to prepare homogeneous and fine composite powders.

One approach is high energy ball milling of W and Cu powders [5]. However, it is difficult to produce a uniform composite powder because the mixing of ductile Cu and brittle W particles results in plate-like Cu sheets containing fine W particles after ball milling. To overcome this problem, ball milling of metal oxide powders followed by hydrogen reduction is considered an attractive process for the synthesis of nanocomposite powders with enhanced sinterability [2,6]. However, ball milling using oxide powders has limitations in uniform mixing between the component powders, so a new process is needed to fabricate homogeneous composite powders.

In this study, we focus on the synthesis of fine W composite powders with homogeneously dispersed Cu particles using the solution chemistry route [7]. The composite powders were prepared by ball milling of WO_3 combined with the copper nitrate solution and hydrogen reduction process. Also, the effect of the characteristics of the initial WO_3 powders on the microstructure of the final W-Cu composite powder was investigated.

2. Materials and methods

Two different WO_3 powders were applied to obtain the W-Cu composite powders. The first one is a powder prepared by ultrasonic spray pyrolysis (USP) as reported in a previous work [8], and the second one is the use of commercial WO_3 (99.9%, 0.2 µm, Kojundo Chemical Lab. Co.) powder. High-purity copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, 99.9%) was used as source material for Cu. Weighted nitrate powder, corresponding to 5 wt.% of Cu in the final composite, was initially dissolved in distilled water. Subsequently, two types of WO_3 powders were mixed with the above-mentioned solution and vigorously stirred for 30 min. Dried mixtures were calcined at 300°C for 5 h in air to obtain WO_3/CuO mixed powders. The powder mixtures were kept in an alumina boat and reduced by flowing hydrogen gas at 800°C for 1 h. Phase identification was carried out by X-ray diffraction (XRD) analysis. The microstructure was characterized

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by field-emission scan electron microscopy (FE-SEM) and transmission electron microscopy (TEM) equipped with energy-dispersive X-ray spectroscopy (EDS).

3. Results and discussion

The morphology of calcined powder mixture of WO_3 and copper nitrate was observed by FE-SEM. As shown in Fig. 1(a), the composite powders prepared using USPed WO_3 exhibited a spherical shape with a size of about 1 μm, and CuO particles were unevenly distributed in the form of islands on the surface of the WO_3 particles. Conversely, the calcined powders using commercial WO_3 were composed of relatively fine particles, as shown in Fig. 1(b). Also, as shown in Fig. 2(a), XRD pattern of the calcined powder contains the characteristic peaks for the mixture of WO_3 and CuO phases. These results indicated that the starting materials strongly influenced the morphology of calcined powder, and copper nitrate can be completely transformed to CuO powder by the calcination at 300°C for 5 h in air.

Fig. 2(b) shows the XRD pattern of the mixed powder using commercial WO_3 obtained by hydrogen reduction at 800°C. The reduced powder mixture was composed entirely of W and Cu phases, where the Cu peak represented weak intensity due to its low content. Neither residual metal oxides nor reaction phase was observed. In general, it is reported that CuO is converted to metallic Cu by hydrogen reduction below 300°C, and WO_3 is completely reduced to W near 800°C, via the formation of $WO_{2.9}$, $WO_{2.72}$ and WO_2 as intermediate phases [9,10]. Therefore, considering the reported reduction behavior of metal oxides, it is suggested that WO_3-CuO can be reduced to W-Cu composite under the reduction condition used in this study.

Fig. 3 represents typical morphologies of reduced composite powders using different starting WO_3 powders. As shown in Fig. 3(a), the hydrogen-reduced W-Cu powder prepared from USPed WO_3 exhibited a very similar morphology to the calcined state of Fig. 1(a). The composite powder existed as a spherical aggregate composed of nano-sized particles and pores shown in magnified image due to the volume change accompanying the hydrogen reduction process [11]. However, as clearly seen in the magnified

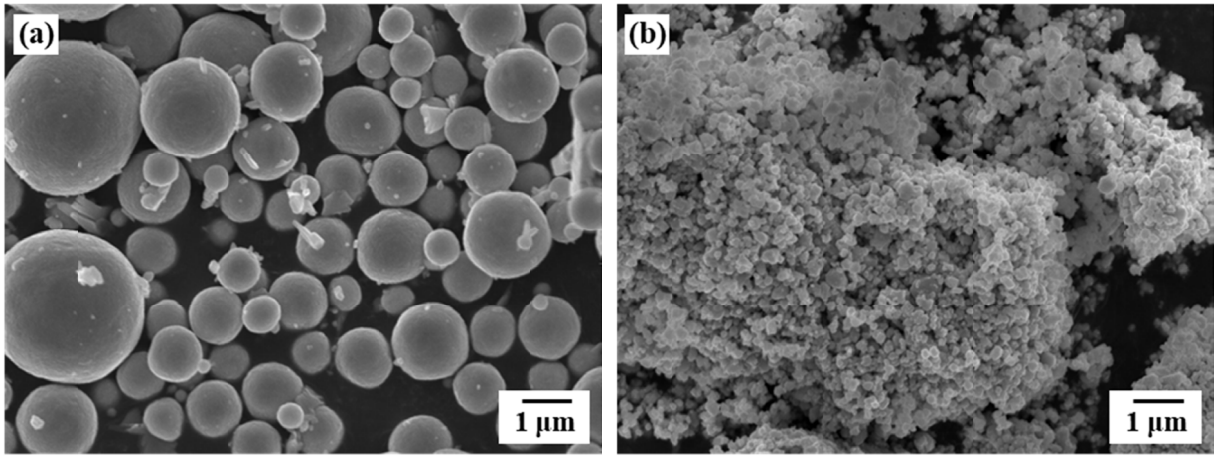

Fig. 1. SEM micrographs of calcined composite powders using (a) USP and (b) commercial WO_3 as raw powders

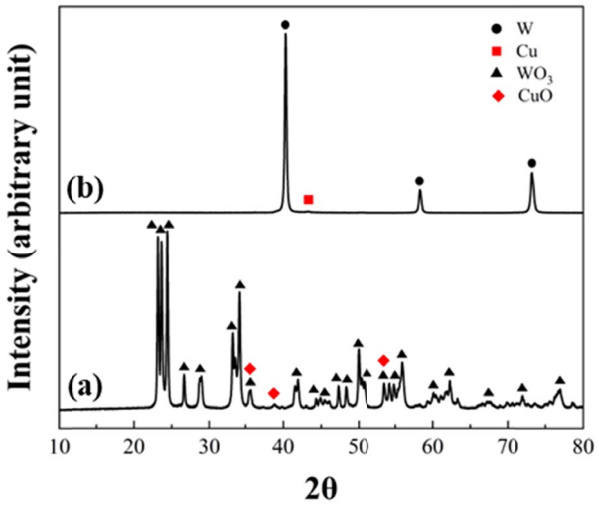

Fig. 2. XRD profiles for the powder mixture of commercial WO_3 and copper nitrate after (a) calcination at 300°C in air and (b) reduction at 800°C in hydrogen atmosphere

image of Fig. 3(b), relatively fine particles with a size of about 200 nm were observed in the reduced powder using commercial WO_3. For detailed phase analysis of W and Cu, the composite powder was examined by TEM accompanied by the selected area electron diffraction (SAED) and EDS mapping.

As shown in TEM image in Fig. 4, the hydrogen-reduced W-Cu composite powder is composed of nano-sized particles, and the SAED pattern reveals the existence of W and Cu phases. Pure W spots were observed well-fitted with XRD results corresponding to (110), (211) and (220) planes, and Cu phase was also identified. Additionally, EDS mapping clearly shows that Cu element is uniformly distributed in the composite powder. From these observations, it was found that the process of WO_3 powder coupled with the solution chemistry method using copper nitrate was useful for preparing W nanocomposite powders with uniformly dispersed Cu particles.

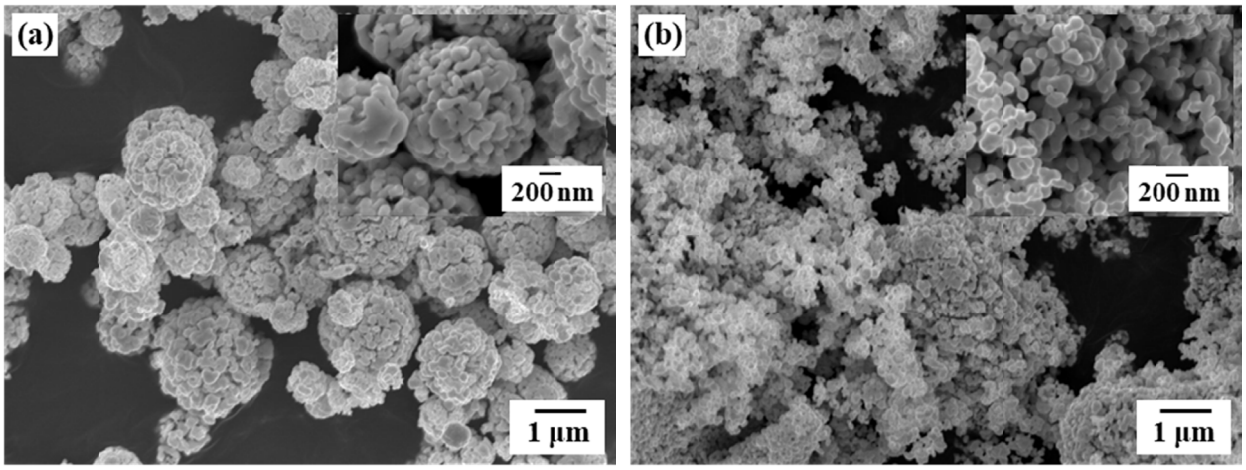

Fig. 3. SEM micrographs of hydrogen-reduced W-Cu composite powders using (a) USP and (b) commercial WO_3 as raw powders

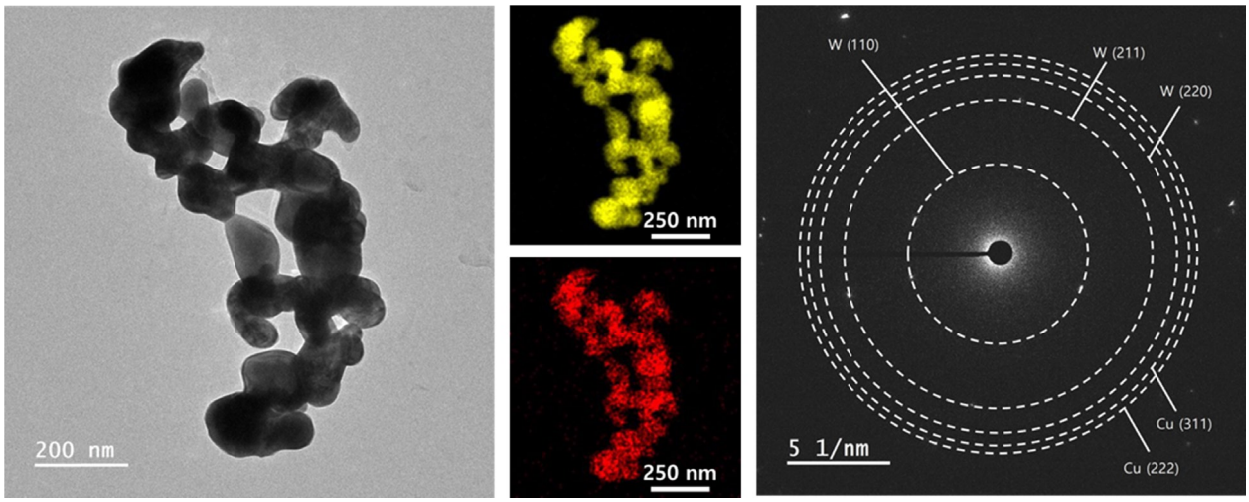

Fig. 4. TEM-EDS-SAED results of hydrogen-reduced W-5 wt.% Cu composite powder

4. Conclusions

Fine W powders with homogeneous dispersion of Cu particles were prepared by the solution chemistry route using WO_3 and copper nitrate. Microstructural observation revealed that the calcined mixtures prepared using USPed WO_3 powder exhibited a spherical shape with a size of about 1 µm, and CuO particles were unevenly distributed on the surface of the WO_3 particles. Conversely, relatively fine particles in the calcined powders using commercial WO_3 were observed. XRD analysis showed that the oxide powder can be completely transformed to W-Cu composite powder by the hydrogen reduction at 800°C for 1 h. The reduced composite powder using commercial WO_3 exhibited fine particles of about 200 nm in size. In addition, it was confirmed through TEM analysis and EDS mapping that W and Cu elements were uniformly distributed within the composite powder. These results suggest that the solution chemistry route can be used to synthesize W nanocomposite powders with uniformly dispersed metal particles, and more detailed quantitative analysis of the synthesis behavior is required for applications in various nanocomposite powder systems.

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