

## Reduction and sintering of WO<sub>3</sub>-CuO nanocomposite powders produced by high energy ball milling process

Woo-Seok Shim\*, Dae-Gun Kim, Tohru Sekino<sup>a</sup>, Joon Woong Noh<sup>b</sup>, Young Do Kim and In-Hyung Moon

Division of Materials Science and Engineering, Hanyang University, Seoul 133-791, Korea

<sup>a</sup>Institute of Scientific and Industrial Research, Osaka University, Ibaraki 567-0047, Japan

<sup>b</sup>Agency for Defense Development, Materials Research and Development Center, Yuseong, Daejeon 305-600, Korea

In the fabrication of W-Cu nanocomposite powders, it is important to consider the design of the alloying content and microstructure to get optimal thermal properties. However, W and Cu have mutual insolubility and their contact angle is very large, thus it is difficult to fabricate homogeneous and fully dense composite materials. Therefore, in recent years studies have been made of the fabrication of W-Cu nanocomposites through the reduction of WO<sub>3</sub>-CuO powders. In the present study, WO<sub>3</sub> and CuO powders were ball-milled with high energy at 400 rpm for 1-50h in Ar atmosphere. They were examined using XRD, SEM and TEM. After the sieved WO<sub>3</sub>-CuO powders were reduced in dry hydrogen, the reduced W-Cu powders were liquid-phase sintered at 1200 and 1300°C for 1h in dry hydrogen. After ball-milling of 1h, the reduced powder had a cored structure and the W particles were faceted. However, after ball-milling of 20h, the powder had a "homogeneously mixed structure" and the W particles were smaller than from the reduced powder ball-milled for 1h. After sintering at 1200°C, the W grain size was finest and most homogeneous with 20h of milling time and a reduction treatment at 980°C.

**Key words:** W-Cu composite, nanocomposite, mechanical alloying, high energy ball milling, reduction, liquid phase sintering, mechano chemical process.

### Introduction

W-Cu composite materials have been applied in various fields of industry, for example ultrahigh-voltage electric contact materials, microelectronic applications like blocking materials for microwave packages and heat-sink materials for high density integrated circuit, due to the properties of excellent wear and arc resistance, high electric and thermal conductivity and a similar thermal expansion coefficient to IC-substrates such as Al<sub>2</sub>O<sub>3</sub>, BeO and AlN. In the case of heat-sink materials, it is important to consider the design of the alloying content and microstructure to get optimal thermal properties [1-4].

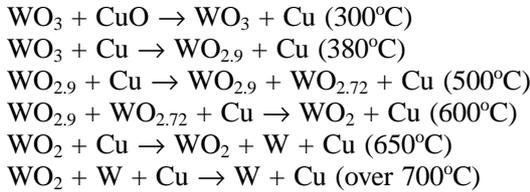
W-Cu composite materials are primarily produced by infiltration or a liquid phase sintering process. In the case of infiltration, although the W-Cu composite can be easily densified, it is difficult to control the composition and to obtain a fine microstructure. By contrast, W and Cu homogeneously distributed with exact and controlled compositions of each of them may be achieved through a liquid phase sintering process. However, because W and Cu are mutual insoluble and their contact angle is very large, it is difficult to fabricate homogeneous and fully dense composite

materials [5-6]. For the fabrication of fully dense W-Cu composites, two alternative approaches have been researched. One is the activated-sintering process [7]. It is reported that activators promote the solution-precipitation of W, leading to the formation of intermetallic compounds with W and diminish the contact angle between Cu and W [8-10]. The other approach involves mechanical alloying (MA) or high energy ball milling [11-12]. Both of these approaches improve the sinterability of W-Cu with increasing rearrangement of finer and more homogeneous W after milling. Incidentally, it is difficult to mix W and Cu homogeneously because of the difference of density between W (19.3 g/cm<sup>3</sup>) and Cu (8.9 g/cm<sup>3</sup>) which is large. More recently, a reduction method of ball-milled W and Cu oxide powders (a mechanochemical process, MCP) has been investigated [6, 13]. WO<sub>3</sub> and CuO powders are easy to mix and crush because they have nearly the same density (WO<sub>3</sub>: 7.2 g/cm<sup>3</sup>, CuO: 6.3 g/cm<sup>3</sup>) and a brittleness surpassing that of metal powders.

First of all, the W-Cu oxide powders are homogeneously mixed and refined through wet or dry ball milling with the chosen composition. The ball-milled WO<sub>3</sub>-CuO powders are completely reduced over 700°C and the characteristics of the reduced W-Cu powders change with the various reduction conditions. WO<sub>3</sub> powders are reduced in a series of steps, as nuclei on the surface of metallic Cu which has been already reduced under 300°C. The optimum reduction temper-

\*Corresponding author:  
Tel : +82-2-2282-1976  
Fax: +82-2-2282-1976  
E-mail: sws@ihanyang.ac.kr

ature would be changed by reduction conditions such as dew point and flow rate of  $H_2$  gas, bed height, grain and agglomerated particle size of ball-milled powder and so on. Their reduction steps are :



In these experiments,  $WO_3$ -CuO composite powders, fabricated through a high energy ball milling process, were reduced at various temperature and the microstructures at each reduction step were observed. Also, the reduction process was estimated through evaluation of sintered microstructures and densities.

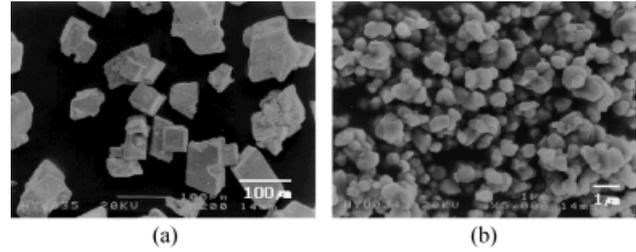
### Experimental Procedure

The characteristics of the  $WO_3$  and CuO powders are given in Table 1 and the morphologies of them were shown in Fig. 1.  $WO_3$  and CuO (W-25 wt%Cu) powders were ball-milled with high energy at 400 rpm for 1-50 hour in a Simoloyer (Zoz GmbH, CM101), which is a horizontal type ball-mill. The balls used were made of stainless steel and of 5 mm diameter. The ball to powder ratio was 16 : 1 and the atmosphere in the grinding unit was Ar. To prevent contamination due to the stainless steel balls and grinding tank, a pre-milling for about 100 hour was accomplished.

The properties of  $WO_3$ -CuO powders ball-milled

**Table 1.** Characteristics of elemental powders

	$WO_3$	CuO
Mean particle size	20 $\mu m$	10 $\mu m$
Grain size	<100 $\mu m$	1-2 $\mu m$
Purity	99.94%	99.9%
Vendor	Korea Tungsten TaeguTec. Ltd.	Japan High Purity Chemicals



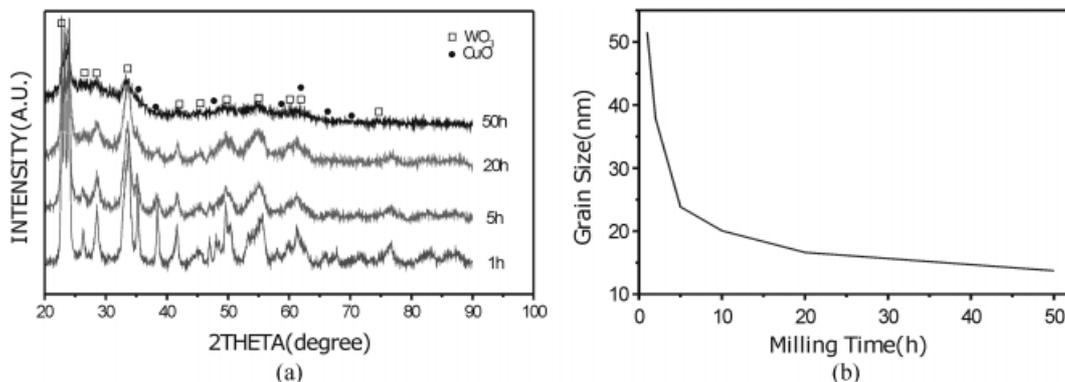
**Fig. 1.** SEM morphologies of (a)  $WO_3$  and (b) CuO.

with high energy were examined by XRD, SEM, TEM and TG. The  $WO_3$ -CuO powders sieved with a 325 mesh grid were reduced at  $980^\circ C$  for 30 minutes in dry hydrogen, with a flow rate of 1 l/min and with the holding steps at 250 and  $650^\circ C$  for 30 minutes respectively. SEM, EDS and XRD analyses of reduced powders were made with the purpose of observing the effect of the high energy ball milling on the composite powders. To observe the reduction behavior, quenching in Ar gas was accomplished at 250, 450, 650 and  $850^\circ C$  during the reduction process.

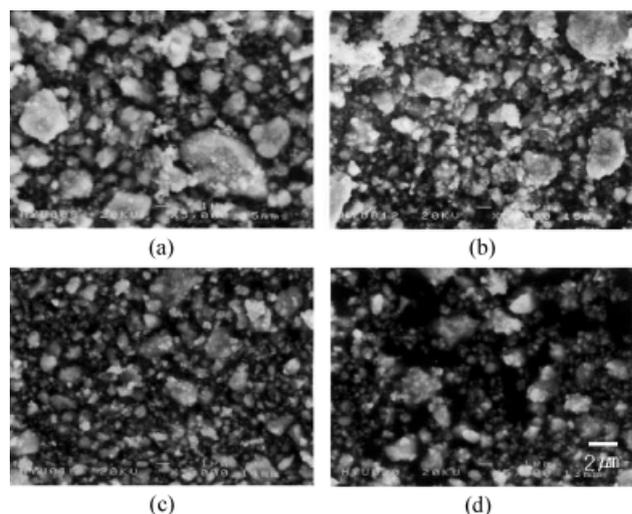
The reduced W-Cu powders were cold compacted at 200 MPa in a cylindrical shaped mold to  $40 \pm 5\%$  of theoretical density. Then the compacted parts were liquid-phase sintered at 1200 and  $1300^\circ C$  for 1h in dry hydrogen, with a flow rate of 1 l/min. The heating and cooling rates were  $10^\circ C/min$ . The sintered density was measured using Archimedes principle and the sintered microstructures were observed through SEM. To observe the relative densities during the sintering process, quenching in Ar gas was accomplished at 800, 900, 1000 and  $1100^\circ C$  during the sintering process.

### Results and Discussion

The  $WO_3$  powder was not agglomerated and the grain size distribution was broad comparatively. By contrast the CuO powder was very agglomerated and the grain size distribution was narrow. Figure 1 shows that the shape of the  $WO_3$  powder is faceted polygons and that of the CuO powder is irregular. The grain size

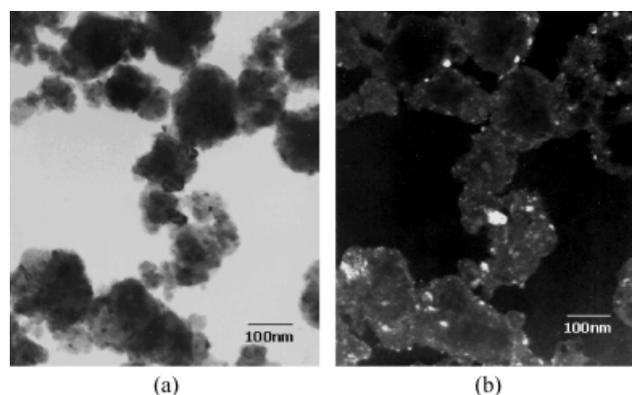


**Fig. 2.** (a) XRD patterns and (b) calculated grain size of ball-milled  $WO_3$ -CuO powders.

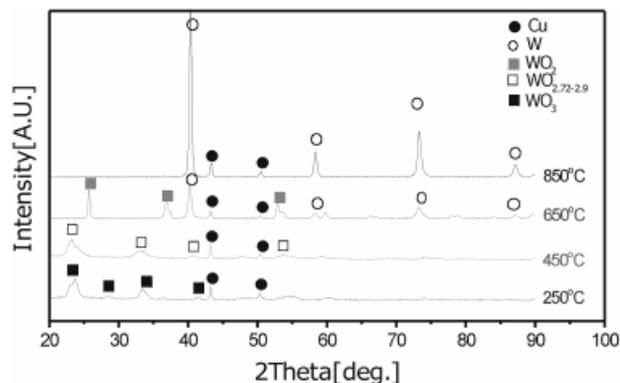


**Fig. 3.** SEM morphologies of powders ball-milled for (a) 1h (b) 5h (c) 20h (d) 50h.

of the ball-milled  $WO_3$ -CuO powder was around 15-50 nm as calculated through the Hall-Williamson equation from the full width at half maximum of the XRD peaks. However, the grains of the ball-milled  $WO_3$ -CuO powder was below 20 nm and these grains were distributed and agglomerated. Figure 2 shows the XRD patterns and grain sizes of the ball-milled  $WO_3$ -CuO powder calculated by the Hall-Williamson equation. The XRD peaks of the  $WO_3$ -CuO powders ball-milled with high energy were remarkably broadened with increase of milling time, the calculated grain sizes of the  $WO_3$ -CuO powders rapidly decreased after 1h milling. Figure 3 gives the SEM morphologies of ball-milled  $WO_3$ -CuO powders with high energy during 1-50 hour. These show that the  $WO_3$ -CuO powders were refined and became more homogeneously distributed with increase of milling time. Figure 4 shows that ball-milled  $WO_3$ -CuO powders became agglomerated as seen by TEM. The mean grain size of the ball-milled  $WO_3$ -CuO powder after 20h was about 15-20 nm. In our pre-experiment, we found that the grain size of the



**Fig. 4.** TEM morphologies of powder ball-milled for 20h. (a) bright field image (b) dark field image.



**Fig. 5.** XRD patterns of W-25 wt%Cu reduced at various temperatures after ball milling with high energy of 20h.

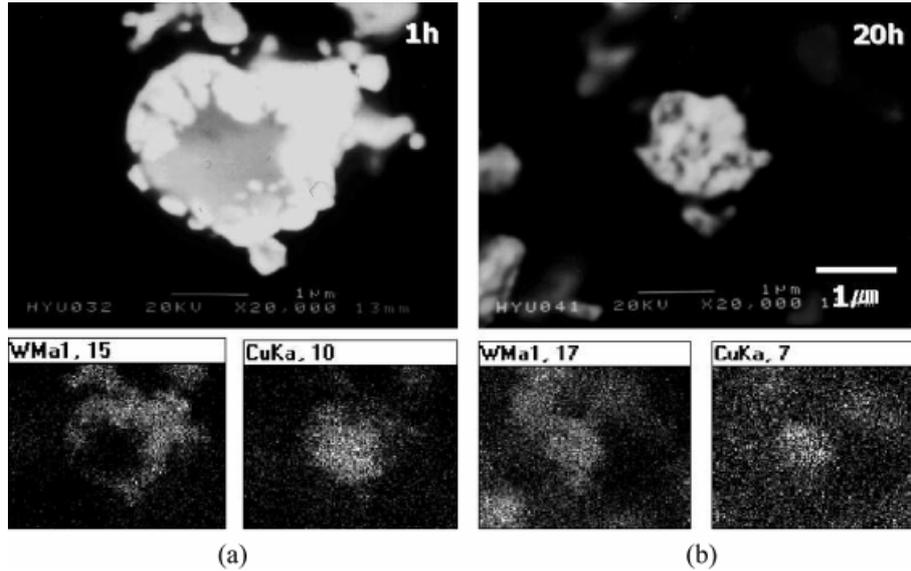
ball-milled  $WO_3$ -CuO powder decreased to about 15 nm after milling for 20h. It was shown that the calculated grain size from the Hall-Williamson equation on the XRD results agreed with the actual grain size observed by TEM.

Figure 5 gives XRD patterns of quenched W-Cu powders at various temperatures during the reduction process after 20h ball milling. It is shown that the oxide peaks disappear as the temperature increased. By comparison with figure 2, it is also shown that the oxide peaks disappear after reducing and the only W and Cu peaks are present. Figure 6 shows back-scattered electron images of W-25 wt%Cu powders reduced at 980°C for 30 minutes and the distribution of W and Cu analyzed by EDS mapping of cross-sectioned W-Cu composites. The W-Cu powder ball-milled for 1h was larger than that ball-milled for 20h and showed a cored structure, the agglomerates of Cu located in the center were surrounded by refined W powders. Otherwise, the ball-milled W-Cu powder for 20h appeared the homogeneously mixed structure, W and Cu powders were homogeneously distributed and agglomerated.

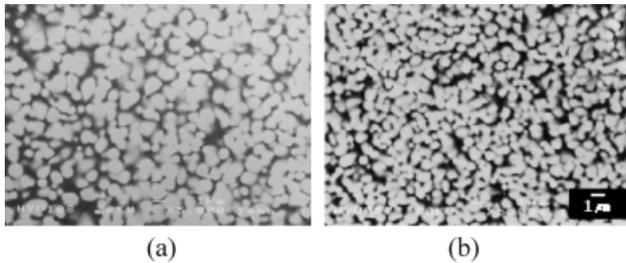
In case of being the around 15 nano-sized grain distributed through the high energy ball milling, it was thought that the preferentially reduced Cu refined homogeneously and reduced W was distributed homogeneously with metal Cu, and then metal Cu was agglomerated with drawing W powder as the temperature was increased. The size of the composite powder shown in Fig. 6 was 1-2  $\mu\text{m}$ . If the reduction temperature was lower, the reduced powder should be finer. However, in Lee's work reduced powder was finest at 980°C, between 780 and 1060°C due to the  $H_2/H_2O$  partial pressure, which affects the chemical vapor transport and diffusion-controlled mechanism [13].

The first step of the reduction of the  $WO_3$ -CuO powders was  $CuO \rightarrow Cu + O$  below 300°C and  $WO_3$  was reduced around metallic Cu like a core in a series of steps between 300 and 700°C.

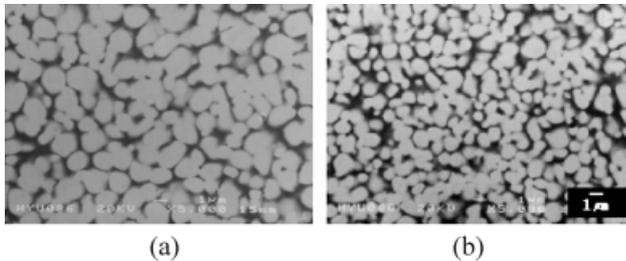
Figures 7 and 8 show the SEM morphologies of sintered parts at 1200 and 1300°C. As the temperature



**Fig. 6.** Back-scattered electron images of W-25 wt%Cu powders reduced at 980°C for 30 minutes and EDS mapping (a) 1h (b) 20h ball-milled powder.

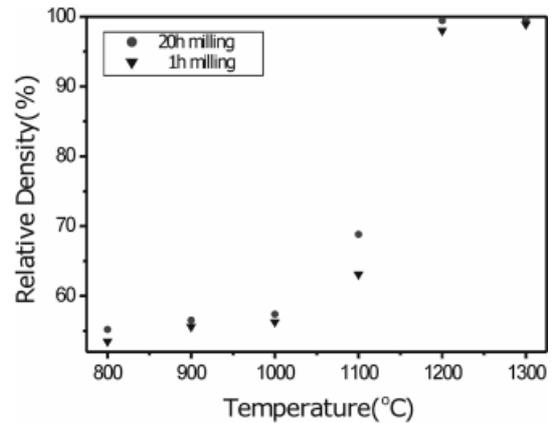


**Fig. 7.** SEM morphologies of parts sintered at 1200°C. (a) high energy ball-milled for 1h (b) high energy ball-milled for 20h.



**Fig. 8.** SEM morphologies of parts sintered at 1300°C. (a) high energy ball-milled for 1h (b) high energy ball-milled for 20h.

increased, W particles grew in the liquid Cu matrix. Also, as the ball-milling time increased from 1h to 20h, it was observed that finer W particles were distributed homogeneously. When the W particle size of the reduced powder was finest, the W grain size of the sintered microstructure was densest and most homogeneous. The grain growth of W and densification was considered to be more active with finer reduced W particles because the Cu liquid was insufficient for separation between the W particles in the W-25 wt%Cu system. Figure 9 shows that the relative density of sintered parts increased exponentially with increase in temper-



**Fig. 9.** Relative density of the parts sintered at various temperatures.

ature. Moreover, the relative density of sintered parts increased with milling time increasing.

## Conclusions

1. W-Cu nanocomposite powders could be fabricated by high energy ball milling in Ar and reduction in hydrogen.
2. The grain size of the ball-milled  $\text{WO}_3\text{-CuO}$  powder decreased as milling time increased. In particular, the grain size of the powder ball-milled for 20h was below 20 nm.
3. The cross-sectioned morphology of the reduced powder after high energy ball milling for 1h differed from that of the powder after high energy ball milling for 20h.
4. The reduced powder lost its “cored structure” as the milling time increased and a very fine W particle was distribution in the inside of reduced Cu agglomerate.

rates became, what is called, a homogeneously mixed structure.

5. The relative densities of sintered parts at solid-state temperatures were just below 60%. However, the density increased rapidly at temperatures above 1083°C because Cu started to melt at 1083°C.

6. In the part sintered at 1200°C, the W grain size was the finest and the most homogeneous microstructures were achieved after ball milling for 20h and reducing at 980°C.

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