MECHANOCHEMISTRY AND MECHANICAL ALLOYING 2003

JOURNAL OF MATERIALS SCIENCE **39** (2004) 5235– 5238

Microstructural and chemical properties of AlN-Cu nanocomposite powders prepared by planetary ball milling

KWANG-MIN LEE*
Department of Materials Science and Engineering, Chonnam National University, Gwangju 500-757, Korea
E-mail: kmlee@chonnam.ac.kr

T. WEISSGÄRBER, B. KIEBACK
Department for Powder Metallurgy and Composite Materials, Fraunhofer Institute for Applied Materials Research, Dresden 01277, Germany

Microelectronic circuits require contact with a high thermal conductivity, and controlled low coefficients of thermal expansion packaging materials for the high performance and reliability of the semiconductor chips. The present study was carried out to investigate the microstructural and chemical properties of AlN-Cu nanocomposite powders created by planetary ball milling. X-ray diffraction and scanning electron microscopy analysis of the obtained powders were performed. The residual oxygen and carbon in ball milled AlN-Cu powders were analyzed. AlN-Cu composite powders of 15 μm size and copper crystallites of 25 nm were obtained after milling for 8 h. The amount of residual oxygen was considerably reduced after exposure to hydrogen reduction treatment at 600°C for 2 h. More significantly, 97% of the residual carbon was removed regardless of milling time and alloy composition. Furthermore, residual carbon was removed as a gaseous mixture of carbon monoxide and carbon dioxide. *© 2004 Kluwer Academic Publishers*

1. Introduction

The miniaturization of semiconductor devices has resulted in enhanced speed and computational performance. However, with such progress, there arise problems with heat generation on the computer chip. The heat must be effectively removed from the microelectronic circuits because the generated heat is directly related to the high performance and reliability of the chip [1, 2]. Accordingly, the new heat dissipation materials must be thermally compatible with the semiconductor and substrate materials [3, 4]. One approach to meet these demands is to create new composite materials with properties tailored specifically for electronic packaging. Metal matrix composites are particularly attractive. W-Cu is a popular thermal management material, largely because of its availability resulting from previous work on electrical contacts. Most of the other potential thermal management composites are not as well developed as W-Cu.

Planetary ball milling has the ability to make alloys, via solid state processing from normally incompatible components, with excellent composition and grain size control. The ball milling process also provides an attractive method of preparing Cu based ceramic composites, due to a low wettability between solid and liquid phases and the significantly different melting points of the constituent elements. The thermal conductivity of AlN-Cu heat sink materials is greatly affected by alloy purity. Therefore, it is very important to minimize the content of oxygen and carbon in ball milled powders to the lower limit as much as possible. Heat transfer by free electrons is greatly disrupted by impurities such as oxygen and carbon, which are easily incorporated into the ball-milled powder through a process control agent (PCA), such as stearic acid or through the processing atmosphere.

The present study investigates the microstructural and chemical properties of AlN-Cu nanocomposite powders created by planetary ball milling for the application of heat sink materials.

2. Experimental

2.1. Planetary ball milling processing

Planetary ball milling was carried out with four different compositions: AlN-40 vol%Cu (AlN-64.5 wt%Cu), AlN-60 vol%Cu (AlN-80.3 wt%Cu), AlN-70 vol%Cu (AlN-86.4 wt%Cu), and AlN-80 vol%Cu (AlN-91.6 wt%Cu). Copper powder used for the experiment has an average particle size of 25 μm with dendrite morphology. Aluminum nitride powder has an average size of 60 μm or less with a purity of 99%. Planetary ball

---

*Author to whom all correspondence should be addressed.

milling (Fritsch Pulverisette) was accomplished using a chamber with 250 cm^3 capacity with an argon atmosphere maintained at room temperature and a milling velocity of 200 rpm. The ratio of the stainless steel ball to powder was kept at 10 to 1.5 wt% of stearic acid was used as a process control agent and added to the powder mixture to prevent the powder from sticking to the milling tools throughout the process.

2.2. Microstructural and chemical properties of AlN-Cu composite powders

The ball milled AlN-Cu composite powders were reduced at 600°C for 2 h in a hydrogen atmosphere containing less than 5 ppm water content. The residual oxygen and carbon levels in ball milled AlN-Cu powders were analyzed using a LECO N/O analyzer (TC-436) and LECO C/S analyzer (CS-300). A JSM-5200 microscope was used to conduct scanning electron microscopy (SEM) allowing us to observe the morphology of the ball-milled powder and the hydrogen reduced powder particles. X-ray diffraction (XRD) analysis was performed using a Siemens X-ray diffractometer (D-5000) with Cu K_α radiation and a scan speed of 10 degree/min in a 20° to 130° range. Crystallite sizes were calculated from peak broadening using the Sherrer equation [5]:

$$D = \frac{0.9\lambda}{\beta\cos(\theta)}, \tag{1}$$

where D is the crystallite size, β is the full width at half-maximum (FWHM) of the Bragg peaks, λ is the wave length of the Cu K_α radiation and θ is the Bragg angle.

3. Results and discussion

3.1. Microstructural characteristics of ball milled AlN-Cu composite powders

Fig. 1 shows SEM morphology of AlN-60 vol%Cu powders ball milled at 200 rpm for 32 h. As shown in this figure, rounded composite powders with the size of about 15 μm were obtained. This resulted from the repeated action between cold welding and fracture during the ball milling processing.

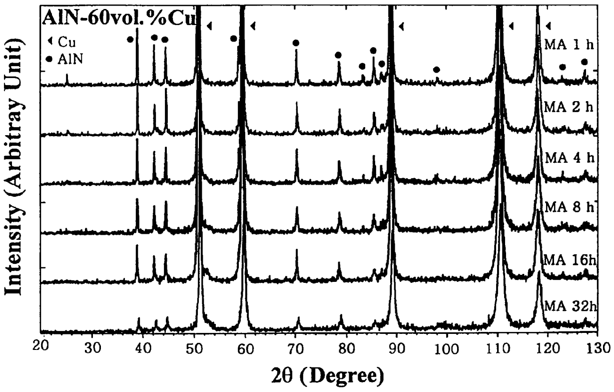

Figure 2 X-ray powder diffraction patterns for AlN-60 vol%Cu powders as a function of milling time.

Fig. 2 shows XRD patterns of AlN-60 vol%Cu powders as a function of milling time. As the milling time increased, the diffraction peaks of copper and aluminum nitride were broadened and decreased due to the refinement of the crystallite size and an increase in atomic-level strains. XRD patterns were quite similar to those with a lower amount of metallic copper components such as AlN-40 vol%Cu powders. Due to a very thermodynamically stable aluminum nitride, new phases or amorphization were not detected even after 32 h of milling time.

Fig. 3 shows the copper crystallite sizes of AlN-40 vol%Cu and AlN-60 vol%Cu as a result of milling time. Measurements indicate that the copper crystallite size decreased with increase of milling time. In the early stage of milling, the crystallite size rapidly decreased and it approached a steady-state value of about 25 nm after MA for 8 h. The nanometer-sized copper was identified by transmission electron microscopy observation. As shown in Fig. 3, the copper crystallite size of AlN-60 vol%Cu was slightly larger than that of AlN-40 vol%Cu.

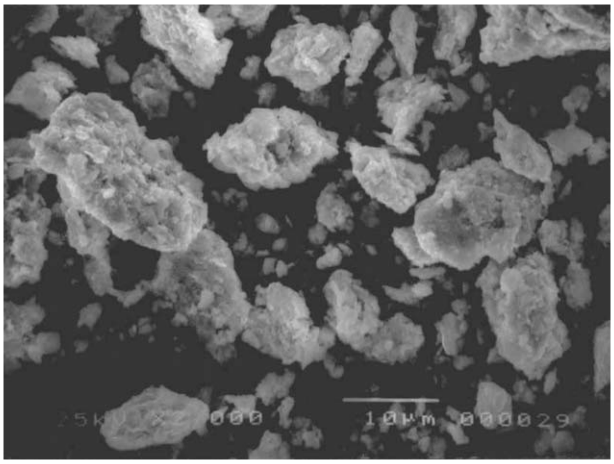

Figure 1 SEM morphology for AlN-60 vol%Cu powders ball milled for 32 h at 200 rpm.

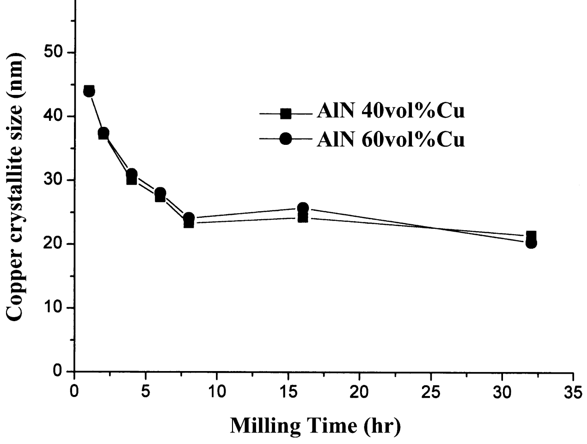

Figure 3 Copper crystallite size for AlN-40 vol%Cu and AlN-60 vol%Cu powders as a function of milling time.

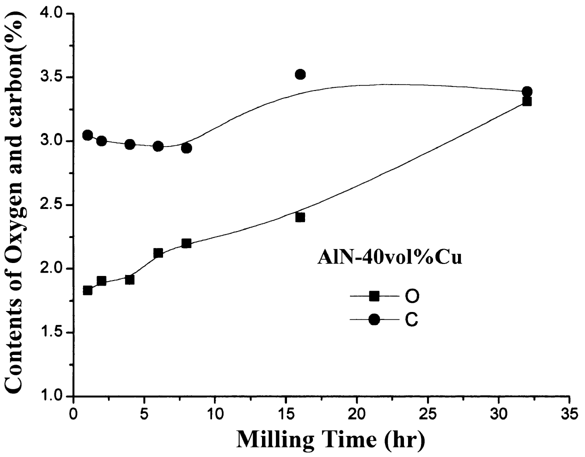

Figure 4 Content of oxygen and carbon in AlN-40 vol%Cu powders as a function of milling time.

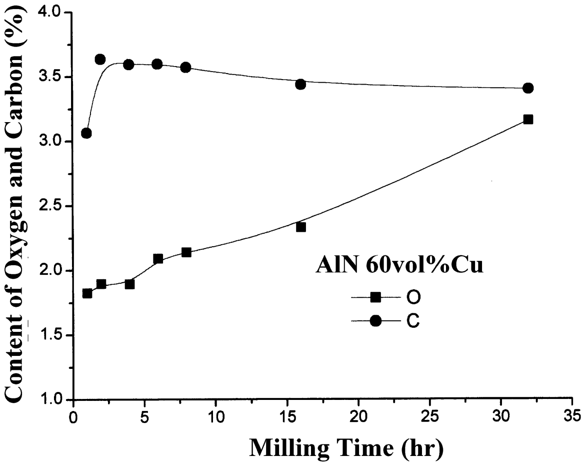

Figure 5 Content of oxygen and carbon in AlN-60 vol%Cu powders as a function of milling time.

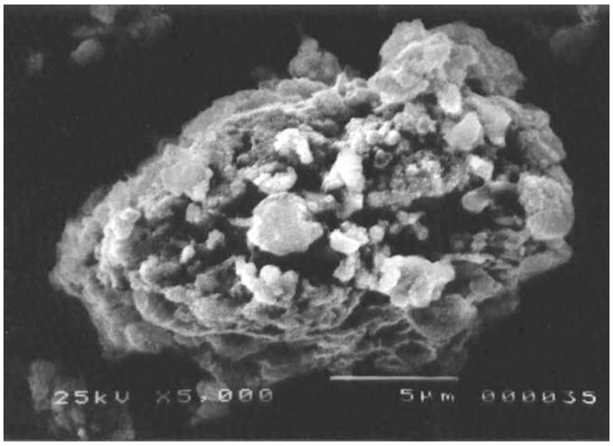

Figure 6 SEM morphology for AlN-60 vol%Cu powder after hydrogen reduction at 600°C for 2 h.

3.2. Effect of hydrogen reduction on ball milled AlN-Cu composite powders

Figs 4 and 5 show the residual oxygen and carbon in AlN-40 vol%Cu and AlN-60 vol%Cu as a function of milling time, respectively. The residual oxygen content in powders in the early stage of milling was approximately 1.8 wt%. It increases with milling time to the value of about 3.5 wt% (at 32 h of milling). However, the residual carbon content in the powders was kept within a 2.9 to 3.5 wt% range regardless of the milling time. The residual oxygen and carbon contents according to the alloy compositions were not greatly changed (compare Figs 4 and 5).

Table I shows the residual oxygen and carbon content in AlN-40 vol%Cu, AlN-60 vol%Cu, AlN-70 vol%Cu and AlN-80 vol%Cu after hydrogen reduction treatment at 600°C for 2 h. The hydrogen reduction treatment greatly reduced the impurity of oxygen and carbon. As the copper content increased, a larger amount of oxygen was removed due to the easy reduction of copper oxide in this state. For example, up to 70% of the existing 0.64 wt% oxygen in AlN-80 vol%Cu powders was removed, and 97% of the residual carbon was removed regardless of the milling time or alloy compositions. It is worth noting the significant reduction of residual carbon even though the water content in the hydrogen atmosphere was constantly kept within 5 ppm. A chemical reaction for decarburization is as follows:

$$MO + H_2 \xrightarrow{600^\circ C} M + H_2O \qquad (2)$$

$$(C_xH_y) + H_2O \xrightarrow{600^\circ C} CO + CO_2 + H_2 \qquad (3)$$

Metal oxides (MO) are reduced to metal (M) primarily by the hydrogen component of the atmosphere. Although the reducing atmosphere contains small amount of water (5 ppm), much more H_2O vapor can be generated through the reduction of copper oxide (Equation 2). If a suitable oxidant is present, a chemical reaction (oxidation) rather than thermal decomposition occurs. The residual carbon, resulting from the process control agent, combines with the oxidant and is removed as a gaseous mixture comprised of carbon monoxide and carbon dioxide.

Fig. 6 shows SEM morphology of ball milled AlN-Cu powders (32 h) after hydrogen reduction at 600°C for 2 h. The size and shape of the powders did not change after hydrogen treatment, but aluminum nitride and copper were much more agglomerated, with very

TABLE I Effect of hydrogen reduction on residual content of oxygen and carbon in ball milled AlN-Cu powders

		Oxygen (wt%)			Carbon (wt%)		
Composition (vol%)	Milling time (h)	Before	After	Decrement (%)	Before	After	Decrement (%)
AlN-40Cu	8	2.197	1.587	27.8	2.944	0.085	97.1
AlN-60Cu	8	2.138	1.332	37.7	3.570	0.078	97.9
AlN-70Cu	16	2.636	1.012	61.6	3.428	0.063	98.2
AlN-80Cu	16	2.138	0.642	70.0	3.413	0.051	98.5

small clusters. Additionally, the agglomerated powders were very porous because of reduction in oxides and decarburization.

4. Conclusions

AlN-Cu composite powders of 15 μm size and copper crystallites of 25 nm were obtained after milling for 8 h. The amount of residual oxygen was considerably reduced after exposure to hydrogen reduction treatment at 600°C for 2 h. More significantly, 97% of the residual carbon was removed regardless of milling time and alloy composition. Furthermore, residual carbon combined with the oxidant, and was removed as a gaseous mixture of carbon monoxide and carbon dioxide.

References

1. A. H. KUMAR and R. R. TUMMALA, *J. Met.* **44** (1992) 10.
2. C. ZWEBEN, *ibid.* **44** (1992) 15.
3. R. M. GERMAN, K. F. HENS and J. L. JOHNSON, *Intern. J. Powder Metall.* **30** (1994) 205.
4. S. FUCHS and P. G. BARNWELL, *Intern. J. Microcirc. Electr. Packag.* **20** (1997) 61.
5. B. D. CULLITY, "Elements of X-ray Diffraction," 2nd ed. (Addision-Wiesly Pub. Co. Inc., New York, 1978) p. 356.

Received 11 September 2003
and accepted 27 February 2004