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Hot-pressed AlN-Cu metal matrix composites and their thermal properties

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AlN-Cu metal matrix composites containing AlN volume fractions between 0.1 and 0.5 were fabricated firstly by liquid phase sintering of AlN using Y_2O_3 as a sintering aid and then by hot pressing the powder mixtures of sintered AlN and Cu at 1050°C with a pressure of 40 MPa under flowing nitrogen. With Y_2O_3 additions of 1.5 to 10 wt%, the densification of AlN could be achieved by liquid phase sintering at 1900°C for 3 h and subsequently slow cooling. The sintered AlN showed a maximum thermal conductivity of 166 W/m/K at a Y_2O_3 level of 6 wt%. Dense AlN-Cu composites with AlN contents up to 40 vol% were achieved by hot pressing. The thermal conductivity and the coefficient of the thermal expansion (CTE) of the composites decreased with increasing AlN volume fractions, giving typical values of 235 W/m/K and 12.6×10^{-6}/K at an AlN content of 40 vol%.

1. Introduction

As two of the most important ceramic and metal materials, both aluminum nitride (AlN) and copper (Cu) have been broadly used in the electronics industry for many years. For electronic packaging applications, AlN is attractive due to its high thermal conductivity enable it to remove the heat rapidly from a chip, its good electrical and mechanical properties, and a low coefficient of thermal expansion (CTE) that can match semiconductors well to avoid thermal stresses. This is important as most failures in microelectronic circuits are caused by thermal fatigue due to the thermal mismatch between the substrate and the circuits [1, 2]. However, the thermal conductivity of polycrystalline AlN reported in the literature is not as high as that of pure AlN single crystal (estimated to be 319 W/m/K by Slack [3]) but usually below 200 W/m/K [4–10]. This has been attributed to impurities, particularly oxygen, in the raw materials that becomes incorporated into the lattice of AlN by forming aluminum vacancies, thereby lowering the thermal conductivity of the material by phonon scattering [8, 9], and to secondary phases at the grain boundaries that have a very poor thermal conductivity as low as 10 W/m/K [5, 6, 10]. Cu also has a very high thermal conductivity, up to 400 W/m/K [11], and thus is very attractive for electronic packaging applications. Unfortunately, pure Cu has a very high CTE (16.5×10^{-6}/K [11]). However, the CTE of Cu can be reduced to some extent by forming composites containing appropriate volume fractions of low CTE materials. AlN is a preferred choice. Since much progress has been achieved in recent years in the electronics industry through system miniaturization and such progress has a demand for packaging materials with a very high thermal conductivity and a low coefficient of thermal expansion (CTE) [12, 13], the combination of AlN and Cu to form AlN-Cu metal matrix composites is quite attractive to meet this demand. With regard to the AlN-Cu metal matrix composites, up to now no previous work has been reported in the literature.

This work was focused on the fabrication of AlN-Cu metal matrix composites and investigations of the thermal properties of the composites. Fabrications of the composites were achieved firstly by liquid phase sintering of AlN using Y_2O_3 as a sintering aid to obtain sintered AlN and then hot pressing the powder mixtures of sintered AlN and Cu. The thermal properties of the composites were investigated by measuring the thermal conductivity at room temperature and the CTE of the composites in a temperature range of 50–300°C.

2. Experimental procedure

2.1. Processing

Commercially available high purity AlN powder (99.9% pure, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan, with an average particle size ∼1 μm), Y_2O_3 powder (99.9% pure, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan, with an average particle size ∼1 μm), and Cu powder (99.9% pure, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan, with an average particale size ∼15 μm) were used as the

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raw materials. Powders of AlN with different levels of Y_2O_3 additions, from 1.5 to 10 wt% as a sintering aid, were ball milled for 24 h in ethyl alcohol and then dried at 80°C in an oven. The dried powders were cold pressed into cylindrical samples (12 mm in diameter and 5–15 mm in height). The samples were then placed in a covered boron nitride (BN) crucible and heated from 1000 to 1900°C at a heating rate of 10°C/min in a graphite furnace under flowing nitrogen. After being held at 1900°C for 3 h, the sample was slowly cooled to 1800°C at a rate of 3°C/min, held for 30 min at 1800°C, and then slowly cooled to 1600°C at a rate of 3°C/min and to 1000°C at a rate of 10°C/min. The sintered AlN body was pulverized and sieved to a particle size range of 75–150 μm. The sieved AlN powder was then manually mixed with Cu powder and hot pressed in a carbon crucible at 1050°C under a pressure of 40 MPa under flowing nitrogen. After hot pressing, the sample was annealed at 900°C for 1 h in nitrogen.

2.2. Characterization

The microstructures of the sintered AlN and the hot pressed AlN-Cu composites were investigated using scanning electric microscopy (SEM). The volume fractions of the secondary phases in the sintered AlN bodies were determined from the SEM micrographs. At least three SEM micrographs were used for each sintered AlN sample. The phases present in the sintered AlN body and the AlN-Cu composites were determined by X-ray diffraction (XRD) analysis.

The thermal conductivity (k, W/m/K) of the sintered AlN and the AlN-Cu composites was determined by Equation 1:

$$k = \alpha \cdot \rho \cdot c_p \tag{1}$$

where α is the thermal diffusivity of the sample, ρ is the density, and c_p is the heat capacity. The density was measured using the Archimedes method. The thermal diffusivity and the heat capacity were measured at room temperature by the laser flash method (Thermal constant analyzer TC-7000, ULVAC-RIKO, Japan). Typically a cylindrical sample with a diameter of 10 mm and a thickness of 3–4 mm was made and then ground to 2 mm in thickness. The sintered AlN sample used for the thermal diffusivity measurements was coated with carbon on both sides by carbon spraying to prevent direct transmission of the laser beam. A sapphire standard was used to determine the laser energy before the heat capacity measurements. All the measurements were performed at least three times, and the reported values are the averages.

The CTE of the sintered AlN and the AlN-Cu composites was measured by the differential expansion method (Thermomechanical analyzer TMA-50, Thermal analyzer TA-60WS, Shimadzu, Japan) using a SiO_2 standard. Typically a sample with dimensions of 6 mm × 4 mm × 4 mm was placed in the furnace and held at 50°C for 10 min to stabilize the system and then heated to 300°C at a heating rate of 10°C/min. The differential expansion between the sample and the SiO_2 standard was recorded by a personal computer and corrected to give the CTE of the sample. For each sample at least three measurements,were performed, and the average is reported.

3. Results and discussion

3.1. AlN sintering

Densification of AlN could be easily achieved by liquid phase sintering using a Y_2O_3 sintering aid. Table I shows the data obtained for sintered AlN with different levels of Y_2O_3 addition. With Y_2O_3 additions between 1.5 and 10 wt%, all the AlN samples, after sintering, showed linear shrinkages of 17–19% and relative densities over 99.5%, indicating good densification during sintering. Aluminum yttrium oxide, $Y_4Al_2O_9$, was found to be present as a secondary phase, using XRD, in all the samples. Some unreacted Y_2O_3 appeared in the 8 and 10 wt% Y_2O_3 samples. The amount of the secondary phases increased proportionally with the increasing Y_2O_3 levels. The measured thermal diffusivity, however, did not show a continuous increase with increasing Y_2O_3 but reached a maximum at a Y_2O_3 level of 6 wt% and then decreased. The measured heat capacity was almost independent of the Y_2O_3 amount.

The thermal conductivity was calculated and graphically shown in Fig. 1 as a function of the Y_2O_3 addition amount. In Fig. 1, with a Y_2O_3 addition amount ranging from 1.5 to 10 wt%, the sintered AlN showed a thermal conductivity of 140–170 W/m/K with a maximum of 166 W/m/K at a Y_2O_3 level of 6 wt%. AlN single crystals can have a very high thermal conductivity, estimated to be 319 W/m/K by Slack [3]. The reported values for polycrystalline AlN in the literature, however, were not as high and mainly in the range of 100–200 W/m/K. Oxygen, the most important impurity in the raw material, can incorporate into the lattice of AlN by forming aluminum vacancies, which can scatter phonons and thereby lower the thermal conductivity of the material. The residual secondary phase after liquid

TABLE I AlN sintering behaviors and thermal properties

Y_2O_3 addition		Secondary phase		Density		Thermal properties		
Amount (wt%)	Linear shrinkage (%)	Secondary phase	Amount (vol%)	Sintered (g/cm^3)	Relative (%)	Diffusivity (cm^2/s)	Capacity (J/g/K)	Conductivity (W/m/K)
1.5	17.8	$Y_4Al_2O_9$	1.7	3.27	99.8	0.626	0.703	144
3	17.7	$Y_4Al_2O_9$	3.1	3.29	99.8	0.654	0.692	149
4.5	18.5	$Y_4Al_2O_9$	4.3	3.30	99.7	0.677	0.706	158
6	17.8	$Y_4Al_2O_9$	6.1	3.32	99.6	0.705	0.709	166
8	17.8	$Y_4Al_2O_9$, Y_2O_3	8.2	3.34	99.6	0.679	0.700	159
10	18.8	$Y_4Al_2O_9$, Y_2O_3	10.2	3.36	99.5	0.634	0.703	150

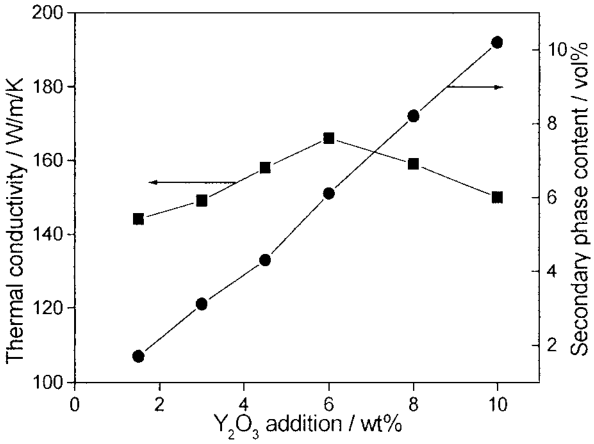

Figure 1 Thermal conductivity of sintered AlN at room temperature.

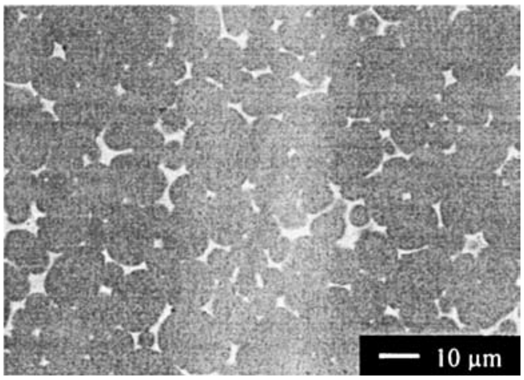

Figure 2 Typical SEM microstructure of sintered AlN (6 wt%Y_2O_3). Gray: AlN; white: secondary phase.

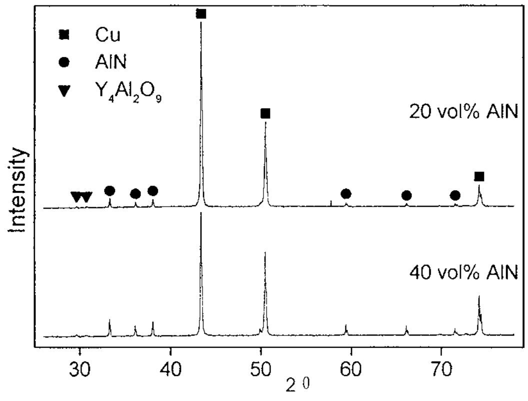

Figure 3 Typical XRD patterns of hot pressed AlN-Cu composites.

phase sintering, which has a thermal conductivity as low as 10 W/m/K, can decrease the thermal conductivity. In addition, the morphology of the secondary phase can also greatly affect the thermal conductivity of polycrystalline AlN. It is clear that a secondary phase isolated at the corners of the AlN grains is less harmful than an elongated and interconnected one. In our experiments, the AlN samples were sintered at a relatively high temperature of 1900°C. This was expected to be beneficial to the diffusional removal of oxygen from the AlN grains [7]. After sintering, the AlN samples were cooled slowly as described previously. This was expected to be beneficial to the formation of isolated secondary phases [7]. The microstructure of the sintered AlN is shown in Fig. 2. Some secondary phases were present in an elongated form while others were all at the corners of the AlN grains. The obtained thermal conductivity was moderately high, compared to those in the literature [4–10]. The maximum thermal conductivity was around a Y_2O_3 level of 6 wt%. This was also in good agreement with the results reported in the literature [6].

3.2. AlN-Cu composites

Because it showed a maximum thermal conductivity, the sintered AlN body with a Y_2O_3 addition of 6 wt% was selected and crushed to a powder with a particle size range of 75–150 μm for the fabrication of the AlN-Cu metal matrix composites. The composites after hot pressing were quite dense, having a relative density of 98.4% for 40 vol% AlN addition. As AlN addition increased to 50 vol%, the composite was not as dense and showed a relative density of ~96%. Further densification of the composite was quite difficult by hot pressing. The XRD examination of the composites indicated that the composites consisted of only crystalline AlN and Cu with a small amount of $Y_4Al_2O_9$. Typical XRD patterns and microstructures of the composites with AlN contents of 20 and 40 vol% are shown in Figs 3 and 4. As shown in Fig. 4, the AlN particles were dispersed homogeneously in a continuous matrix of Cu.

The thermal diffusivity and the heat capacity of the composites were measured and the thermal conductivity was calculated and the results are shown in Fig. 5. The thermal conductivity of a composite could also be predicted by considering the random distribution of spherical reinforcement in a matrix using the Rayleigh model as shown in Equation 2 [14]:

$$k_c = k_m \cdot \frac{1 + 2V_r \cdot \frac{1-k}{1+2k}}{1 - V_r \cdot \frac{1-k}{1+k}}, \quad \left(k = \frac{k_m}{k_r}\right) \qquad (2)$$

where k_c, k_m, and k_r were the thermal conductivity of the composite, the matrix, and the reinforcement phase, and V_r was the volume fraction of the reinforcement phase in the composite. The thermal conductivity of the AlN-Cu composites was predicted using the Rayleigh model and the results are also shown in Fig. 5 (dashed line). As seen in Fig. 5, the thermal conductivity of the AlN-Cu composites decreased with increasing AlN content. The measured values were somewhat lower than the predicted values. The composite with an AlN content of 40 vol% showed a thermal conductivity of 235 W/m/K. With an AlN content of 50 vol%, the thermal conductivity decreased sharply, giving a value much lower than the prediction. This could be understood by considering the relative density of the composites after hot pressing, as shown in Fig. 5. The composites with AlN contents up to 40 vol% were quite dense after hot pressing, while in the case of an AlN content of 50 vol% the sample was not as dense but showed a relative density as low as ~96%. Some visible pores were present in the samples. The presence of pores could extensively decrease the thermal conductivity of the composite.

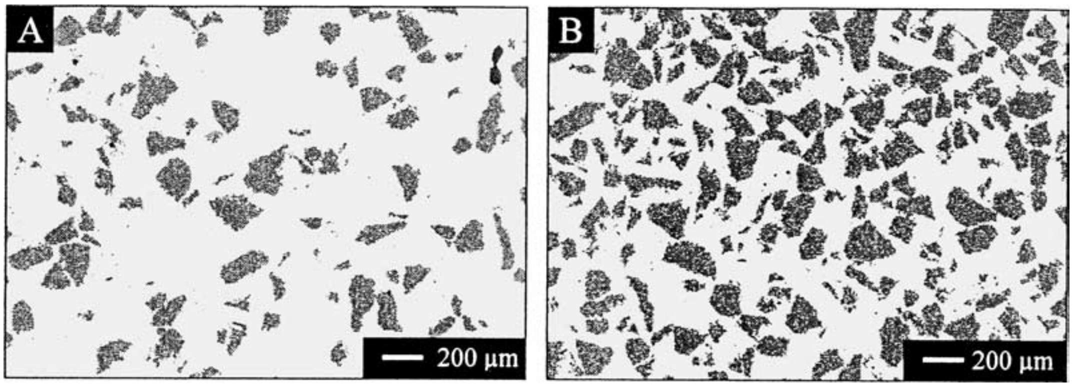

Figure 4 Typical SEM microstructures of hot pressed AlN-Cu composites. The AlN contents in the composites were A: 20 vol% and B: 40 vol%. The measured values were 20.3 vol% for A and 41.3vol% for B. Black phase was sintered AlN and white phase was Cu.

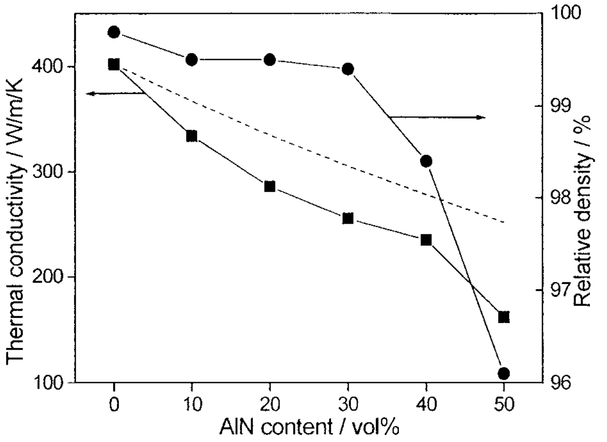

Figure 5 Thermal conductivity of hot pressed AlN-Cu composites at room temperature. Dashed line represents the prediction of the thermal conductivity of the composite using the Rayleigh model [14].

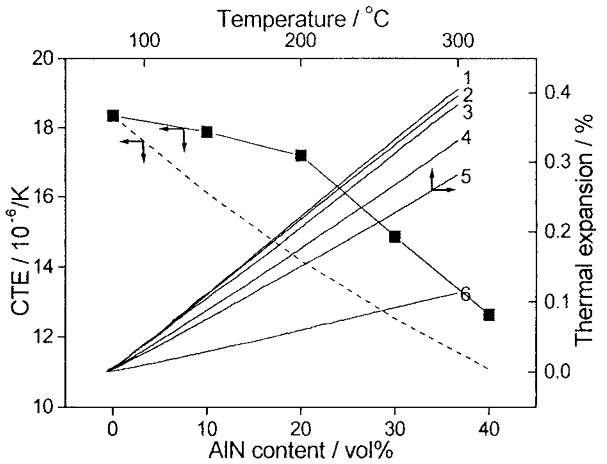

Figure 6 Typical thermal expansion and CTE of sintered AlN and hot pressed AlN-Cu composites. Details for the thermal expansions are: 1. Pure Cu; 2. 10vol%AlN-Cu; 3. 20vol%AlN-Cu; 4. 30vol%AlN-Cu; 5. 40vol%AlN-Cu; 6. AlN.Dashed line represents the prediction of the CTE of the materials using the Turner model [15].

The coefficient of thermal expansion (CTE) of the hot pressed AlN-Cu composites as well as the sintered AlN with a Y_2O_3 addition of 6 wt% were measured in the temperature range of 50–300°C in air. The results are shown in Fig. 6. As indicated in Fig. 6, the thermal expansion increased with increasing temperature for both the hot pressed AlN-Cu composites and the sintered AlN body. The obtained curves fitted straight lines very well, indicating a constant CTE in this temperature range. The measured CTE for the composites decreased with increasing AlN content. The composite with an AlN content of 40 vol% showed a CTE of 12.6×10^{-6}/K.

Typically for a composite consisting of two constituents, the CTE of the composite can be predicted theoretically by considering the constraint due to the dimensional change of each constituent using the Turner model as shown in Equation 3 [15]:

$$\alpha = \frac{\alpha_1 \cdot V_1 \cdot B_1 + \alpha_2 \cdot V_2 \cdot B_2}{V_1 \cdot B_1 + V_2 \cdot B_2} \tag{3}$$

where α is the CTE of the composite, α_1 and α_2 are the CTE of the two constituents, V_1 and V_2 the volume fractions of the constituents, and B_1 and B_2 the bulk modulus of the constituents. With the CTE obtained for pure Cu and sintered AlN from this work, as well as the elastic modulus and Poisson's ratio in the literature [11, 16, 17], the CTE of the hot pressed AlN-Cu composites was predicted and the results are shown in Fig. 6 as a dashed line. As seen in Fig. 6, the experimental CTE values for the composites were larger than the predicted values, especially at low Cu contents. It was proposed that such large difference was due to the microstructure of the composite itself. In the Turner model, the microstructure of a composite was poorly treated. In fact, with the same volume fraction of the reinforcement phase in the composite, it is clear that a composite with a dispersed reinforcement in a matrix can have a CTE larger than a composite with an interconnected reinforcement phase. The hot pressed AlN-Cu composites were similar to the former and thus showed CTE values larger than the predictions.

4. Conclusions

The fabrication and thermal properties of the AlN-Cu metal matrix composites have been investigated in the present study. The major conclusions were summarized below.

1. With a Y_2O_3 sintering aid between 1.5 and 10 wt%, the densification of AlN could be achieved by liquid phase sintering at 1900°C for 3 h followed by

subsequently slow cooling. The sintered AlN showed a maximum thermal conductivity of 166 W/m/K at a Y_2O_3 level of 6 wt%.

2. AlN-Cu composites containing AlN volume percent of 10–50% were fabricated by hot pressing powder mixtures of Cu and sintered AlN with a 6 wt% Y_2O_3 addition at 1050°C under a pressure of 40 MPa under a flowing nitrogen atmosphere. Dense composites could be achieved with AlN volume fractions up to 40 vol%. For an AlN content of 50 vol%, the composite was not as dense, having a relative density of ~96%.

3. The thermal conductivity of the AlN-Cu composites decreased with increasing AlN contents. The composite with an AlN content of 40 vol% showed a thermal conductivity of 235 W/m/K.

4. The CTE of the composites decreased with increasing AlN contents. The composite with an AlN content of 40 vol% showed a CTE of 12.6×10^{-6}/K. The experimental values were larger than the predicted values, especially at low AlN contents. This could be attributed to the fact that the composites had microstructures of dispersed reinforcement phase rather than interconnected one.

Acknowledgments

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