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Preparation of AlN/Cu composites through a reactive infiltration process

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ABSTRACT

The wetting of copper (Cu) melt on aluminum nitride (AlN) is very poor. In the present study, a reactive infiltration process is developed to prepare AlN/Cu composites. With the help of a sulfur-containing atmosphere, the Cu–S and Cu–O compounds are formed at elevated temperatures. Due to the presence of these reaction phases, the infiltration of copper melt into a powder compact of aluminum nitride and yttrium oxide becomes possible. After infiltration, the sulfur within the powder compact is absorbed by the yttrium oxide. Dense AlN/Cu composite with a thermal conductivity of 100 W/m K can be prepared at a temperature as low as 1400 °C.

1. Introduction

Aluminum nitride (AlN) is known for its superb thermal conductivity; it has thus been widely used as the substrate for power IC chips. However, densification of AlN is difficult due to its covalent bonding nature. Temperatures above 1700 °C are usually needed to achieve full densification [1]. Such high processing temperatures can raise the cost of AlN substrates. In the present study, a reactive infiltration process is developed which can be carried out at temperatures as low as 1400 °C.

The thermal conductivity of metallic copper can reach 400 W/m K [2]; it is an ideal candidate for an infiltrating component for AlN. However, the wetting of copper melt on AlN, the key requirement for successful infiltration, is very poor. For example, the contact angle of copper melt on AlN ranges from 139° to 160° [3,4]. Such poor wetting makes the infiltration of Cu melt into AlN an unworkable approach. Furthermore, the bonding between AlN and Cu is challenging due to the same poor wetting problem. The problem may be solved by using an AlN/Cu interlayer. Nevertheless, the thermal conductivity of AlN/Cu interlayer should be high enough for its possible application for thermal management. In the present study, a novel process is developed to prepare the AlN/Cu composite. The thermal conductivities of the AlN/Cu composites are then determined.

2. Experimental

The starting materials used in the present study were AlN powder (TAN-2, particle size: 11.5 μm; TAIYEN Co., Ltd., Tainan, Taiwan), copper powder (particle size: 106 μm, purity: 99%, Acros Organics Co., Ltd., USA); yttrium oxide powder (Y_2O_3, purity: 99.99%, Alfa Aesar Co., UK) and calcium sulfate hemihydrate powder ($CaSO_4{\cdot}0.5H_2O$, J.T. Baker, New Jersey, USA). AlN, Cu and $CaSO_4$ discs with diameters of 13 mm were prepared by die-pressing. In the AlN powder compact, 3 wt.% Y_2O_3 powder was pre-mixed. In the $CaSO_4$ powder compact, 16.7 wt.% AlN powder was added.

Fig. 1 shows the schematic for the infiltration process. The Cu powder compact was placed on the top of AlN (+3 wt.% Y_2O_3) powder compact. The powder compact of $CaSO_4$ (+16.7 wt.% AlN) was used as the bottom layer. A graphite powder bed was also employed. The infiltration was carried out in a tube furnace flowing N_2–5%H_2 gas. The peak temperature varied from 1200 °C to 1400 °C, and time at peak temperature was 1 h. After infiltration, the surfaces were ground with SiC papers, and analysis of the specimens was carried out.

The densities of the specimens were estimated using their dimensions and weights. X-ray diffraction (XRD, TTRAX III, Rigaku Co., Japan) was used to detect the phases in the resulting composites. An electronic probe microanalyzer (EPMA, JXA-8200, JOEL Co., Japan) was used to determine the composition of each phase. The

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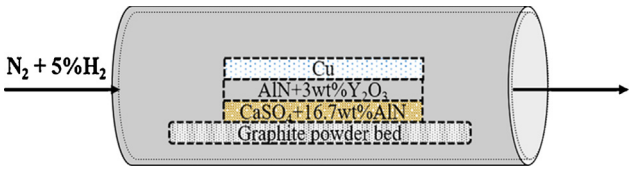

Fig. 1. Schematic for the infiltration process.

Table 1
Phases in the AlN/Cu composites and their densities after infiltration.

Temperature (°C)	Crystalline phases* in the composites	Density (g/cm^3)
1200	AlN, Cu, Al_2O_3, CuS, Cu_2S, Cu_2O	3.66 ± 0.15
1300	AlN, Cu, Al_2O_3, $Cu_{1.8}S$, Cu_2O	4.04 ± 0.38
1400	AlN, Cu, Al_2O_3, $CuAlS_2$, $CuAlO_2$	4.49 ± 0.27

* *Note*: AlN: JCPDS# 08-0262; Cu: JCPDS# 04-0836; Al_2O_3: JCPDS# 46-1212; CuS: JCPDS# 06-0464; $Cu_{1.8}S$: JCPDS# 24-0061; Cu_2S: JCPDS# 53-0622; Cu_2O: JCPDS# 78-2076; $CuAlO_2$: JCPDS# 75-1988; $CuAlS_2$: JCPDS# 25-0014.

thermal diffusivity (α) and heat capacity (C_p) of the composites were determined with the flash method (LFA 447, NETZSCH Co., Germany). The thermal conductivity (k) was calculated using the values of density (ρ), heat capacity (C_p) and thermal diffusivity (α), as follows [5]:

$$k = \rho \times C_p \times \alpha \quad (1)$$

3. Results

The porosity in the AlN powder compact was 38%. Our preliminary tests indicated that the infiltration of copper melt into the AlN powder compact was not possible without the presence of the $CaSO_4$ powder compact. Using the arrangement shown in Fig. 1, the infiltration of Cu melt into the AlN (+3 wt.% Y_2O_3) compact took place at a temperature above 1200 °C. The densities of the AlN/Cu composites after infiltration are shown in Table 1. Fig. 2 shows the XRD patterns for infiltrated discs after firing at 1200 °C, 1300 °C and 1400 °C. The resulting phases in the discs are summarized in Table 1. Apart from the major phases of AlN and Cu, small amounts of Al_2O_3, Cu–S, and Cu–O compounds were found. The reaction phases of $CuAlS_2$ and $CuAlO_2$ were detected in the composite prepared at 1400 °C. However, yttrium oxide was not observed.

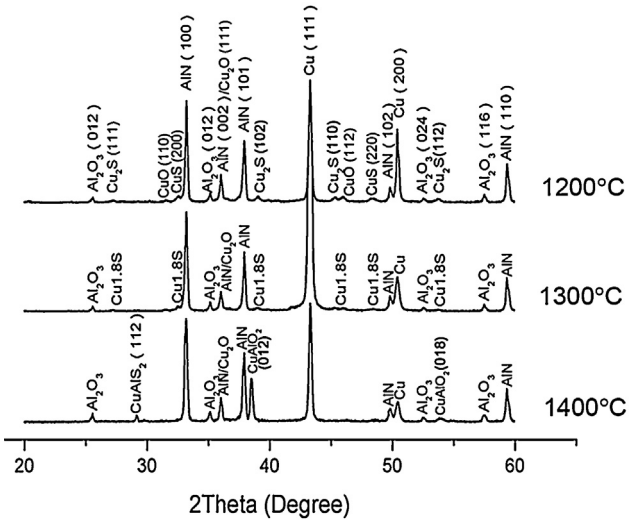

Fig. 2. XRD patterns for AlN/Cu composites prepared by infiltration at 1200–1400 °C.

Fig. 3 shows a typical micrograph for the AlN/Cu composite prepared by infiltration at 1400 °C; the residual porosity in the composite is less than 10%. The corresponding distributions of copper, aluminum, nitrogen, oxygen, yttrium and sulfur in the cross-section are also shown in the figure. The oxygen was found to surround the AlN particles; the sulfur was always found in the same locations as yttrium. Fig. 4 shows the thermal conductivity for all the composites as a function of density; a strong dependence on density can be discerned.

4. Discussion

After infiltration, a weight loss of around 40% was found for the $CaSO_4$ + AlN powder compact. Calcium sulfide (CaS) was found on the $CaSO_4$ powder compact through XRD analysis. Though the infiltration of Cu melt into AlN compact is takes place, no infiltration of copper into the calcium sulfate compact was observed. The calcium sulfate hemihydrate ($CaSO_4{\cdot}0.5H_2O$) changes to anhydrite ($CaSO_4$) after heating to a temperature above 150 °C [6]. The densification of anhydrite can take place above 1100 °C [7] but the addition of AlN can prevent this densification. The anhydrite powder compact thus remains porous during the infiltration process. The decomposition of anhydrite compact can take place throughout the infiltration process. The decomposition of $CaSO_4$ is a reaction involving the release of sulfur dioxide (SO_2) as shown in the following reaction [8]:

$$CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2 \quad (2)$$

The solubility of sulfur in copper is extremely low: 0.012 wt.% at 1067 °C [9]. The XRD patterns (Fig. 2) show the formation of Cu–S and Cu–O compounds above 1200 °C during infiltration. This suggests that the SO_2 reacts with Cu to form Cu–S compounds as in the reaction shown below [8]:

$$2Cu + SO_2 \rightarrow Cu_2S + O_2 \quad (3)$$

The oxidation of copper has also taken place, as shown in the following:

$$2Cu + \frac{1}{2}O_2 \rightarrow Cu_2O \quad (4)$$

There is a eutectic liquid for the Cu_2S–Cu [9] and Cu_2O–Cu systems [10]. The eutectic temperatures are 1067 °C and 1065 °C, respectively. These temperatures are lower than the melting point of copper (1083 °C). The wetting of Cu melt on AlN is improved due to the presence of these eutectic liquids. The reactions forming Cu–S and Cu–O compounds are helpful. The infiltration of Cu melt into the porous AlN compact is then possible. Since the thermal conductivities of AlN and Cu are high and the excess sulfur is consumed by Y_2O_3, the thermal conductivity of the AlN/Cu composite can reach 100 W/m K when its density is high (Fig. 4).

A value for the thermal conductivity of Cu_2S is not available; it is likely as low as the thermal conductivity of Cu_2O (k = 6) [10]. The presence of Cu–S and Cu–O compounds is detrimental to the thermal conductivity of the composite. From the EPMA mapping (Fig. 3), the sulfur is always found to associate with yttrium. This implies that some sulfur is absorbed by the yttrium oxide. Nevertheless, the amount of Y–S–O compounds is below the detection limit of our XRD technique (Fig. 2). It suggests that either the amount of Y–S–O compound is low or a Y–S–O glass is formed instead.

Some minor reaction phases, $CuAlS_2$ and $CuAlO_2$, are also found (Fig. 2). Possible reactions during infiltration are proposed in Fig. 5. The Cu_2S forms due to the reaction between SO_2 and Cu (Eq. (3)). The Cu_2O forms due to the oxidation of Cu (Eq. (4)). The oxidation of AlN may also take place before and/or during infiltration. The Cu_2S can react with Al_2O_3 to form $CuAlS_2$ [11]; the Cu_2O can react with Al_2O_3 to form $CuAlO_2$ at 1400 °C [10].