Sintering behavior of aluminum nitride ceramics with MgO–CaO–Al2O3–SiO2 glass additive

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A B S T R A C T
In this study, MgO–CaO–Al2O3–SiO2 (MCAS) glass oxide fabricated by a conventional melting process was used as a sintering additive to prepare dense AlN ceramics at lower temperatures. AlN specimen with 5 wt.% MCAS glass oxide was produced by sintering in a dilatometer and a conventional furnace. The sintering behavior of the glass-doped AlN was investigated by means of dilatometric analysis, X-ray diffraction analysis, and field-emission scanning electron microscopy microstructural observation. Results revealed that the melted glass phase had a significant effect on the densification of the AlN ceramics by a liquid-phase sintering. This led to a reduction in the sintering temperature by 200 °C from the 1800 °C required for conventional AlN–rare earth or –alkaline earth oxide system.

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1. Introduction

Aluminum nitride (AlN) is considered to be a promising substrate and package material for high-power integrated circuits owing to its high thermal conductivity, low dielectric constant, high electrical resistivity, high dielectric breakdown strength, non-toxicity, and thermal expansion coefficient which is close to that of silicon [1,2]. However, AlN is difficult to sinter due to its highly covalent bonding and because it requires a high sintering temperature (≥ 1900 °C) to achieve full density. For full densification, rare earth and/or alkaline earth oxides are often added as sintering aids in the fabrication of AlN ceramics [3–8]. These sintering aids play a double role during the sintering process. One is to help form an aluminate liquid phase that promotes densification through the liquid-phase sintering (LPS) process. The other is to improve the thermal conductivity by decreasing the oxygen contents in solution in the AlN lattice. Y2O3 is known to be the most common and effective additive to achieve the densification of AlN ceramics [3–8]. These sintering aids play a double role during the sintering process. One is to help form an aluminate liquid phase that promotes densification through the liquid-phase sintering (LPS) process. The other is to improve the thermal conductivity by decreasing the oxygen contents in solution in the AlN lattice. Y2O3 is known to be the most common and effective additive to achieve the densification of AlN ceramics [3–8].

Recently, more and more attention has been given to the low-temperature sintering of AlN ceramics as a way of reducing manufacturing costs and benefiting from the co-firing of multilayer substrates [15–17]. Watari et al. showed an effective sintering aid in the Y2O3–CaO–Li2O system, which promotes full densification at 1600 °C and high thermal conductivity values (~100–172 W/mK) [16]. Qiao et al. have reported that after sintering at 1650 °C, dense AlN ceramics with a thermal conductivity of 148 W/mK were prepared by the simultaneous addition of 2 wt.% CaF2 and 2 wt.% Y2O3 [17].

In addition to the sintering aid mentioned above, several attempts have been made to reduce the sintering temperature using glass ceramic with low melting temperatures [18–21]. For example, Yang et al. [21] reported that the densification of AlN could be achieved using MgO–CaO–Al2O3–SiO2 (MCAS, fabricated by sol-gel method) glass as a sintering aid at lower temperature. However, this report focused on the dielectric properties of the sintered AlN specimen; it did not investigate the sintering behavior of AlN based on the role of the glass oxide as a sintering additive.

Glass oxide addition could decrease the thermal conductivity of AlN since SiO2 element contained in a glass oxide composition deteriorated the thermal conductivity of AlN. However, this work aimed mainly to investigate the effect of the MCAS glass addition on the sintering characteristics of the AlN powder rather than on its thermal conductivity by means of dilatometric analysis, which is useful for studying the kinetics of densification during sintering [14,22–24]. X-ray diffraction analysis, and field-emission scanning electron microscopy (FE-SEM) microstructural observation. MCAS glass oxide, which was prepared by a conventional melting process, was used to fabricate dense AlN ceramics at lower temperature.

2. Experimental procedure

Commercially available AlN powder (Grade H, Tokuyama Soda, Japan) was used as a starting material. MgO–CaO–Al2O3–SiO2 (MCAS) glass was prepared using a conventional melting process. Reagent...
oxidies of MgO, CaCO3, Al2O3, and SiO2 were used as the starting raw materials to prepare the glass frits. The glass composition (in wt.%) consisted of 5% MgO, 19% CaO, 26% Al2O3, and 50% SiO2, as given in the literature [21]. Stoichiometric amounts of the constituents were melted in an alumina crucible after being mixed in a TURBULA® mixer for 1 h. The melting temperature was 1500°C and the melting duration was 1 h. The molten glass was quenched to form a glass frit. The glass frit was milled in a planetary mill for 2 h to obtain a fine glass powder with a particle size of approximately 5 μm. The obtained glass powder was characterized by high-temperature microscopy (Misura HSM1400-5008, Expert System Solutions, Italy) and differential thermal analysis (DTA, SDT Q600, TA Instruments, USA). High-temperature microscopy was employed to investigate the wetting behavior of the cylindrical MCAS glass powder compact on a commercial AlN substrate during heating. The shrinkage data and morphological changes were recorded during heating up to 1300°C at a constant heating rate of 40°C/min.

AlN powder doped with 5 wt.% of the glass powder was pressed at 10 MPa by the die compaction method, followed by cold isostatic pressing at 300 MPa in order to minimize the shrinkage anisotropy. The sintering behavior of the AlN powder compact was investigated by heating the sample up to 1600°C at a constant heating rate of 5°C/min and holding at this temperature for 4 h in a push-rod dilatometer (DIL-402C, NETZSCH, Germany). For comparison, a pure AlN sample without additive was prepared following the same processing route. The sintering behavior of the cylindrical MCAS glass powder compact on a commercial AlN substrate during heating. The shrinkage data and morphological changes were recorded during heating up to 1300°C at a constant heating rate of 40°C/min.

High-temperature microscopy was used to investigate the wetting behavior of the cylindrical MCAS glass powder compact on a commercial AlN substrate during heating. The shrinkage data and morphological changes were recorded using a high-temperature microscope during heating up to 1300°C. Fig. 2 shows the variation in shrinkage for the MCAS glass powder compact. Images of changes in the thermal properties of the glass oxide such as the flowing point are also included in this shrinkage plot. As shown in this figure, the initial shrinkage occurred between 800°C and 900°C. More significant shrinkage occurred beginning at 1100°C, accompanied by morphological changes, i.e., the cylindrical powder compact began to melt into a spherical or semispherical shape with increasing temperature, indicating that the glass viscosity significantly decreased during heating [20]. During the initial shrinkage stage, a decrease in the height of the compact was only observed without its shape change. The flow point of this glass was 1293°C, meaning that the glass melted when the temperature reached 1293°C, which is similar to the DTA results. This temperature for glass melting was observed to be roughly comparable to the temperature at the trailing foot of the endothermic peak in the DTA diagram of Fig. 1.

Fig. 3 shows the linear sintering shrinkage and shrinkage rate versus temperature curve for the glass-doped AlN powder compact and the AlN specimen without additive obtained by heating the samples to 1600°C at a constant heating rate of 5°C/min and holding for 4 h in a N2 atmosphere. In the case of the AlN specimen without additive, shrinkage increased slowly even after 1600°C, whereas the sintering shrinkage of the glass-doped AlN powder compact increased steeply at approximately 1400°C. In order to investigate the shrinkage behavior of the glass-doped AlN powder in detail, the sintering shrinkage rate curve as shown in Fig. 3(b) was plotted on the basis of the dilatometric data given in Fig. 3(a). As shown in Fig. 3(b), a shrinkage rate of the glass-doped AlN increased significantly at 1300°C after the MCAS glass additive melted at 1251°C and a maximum shrinkage rate occurred at 1575°C. This peak in shrinkage rate curve corresponds to the increased densification due to liquid-phase sintering (LPS), which is characterized by the rearrangement of AlN particles and the viscous flow of the melted MCAS glass [20]. Yang et al. reported that during the sintering process, according to the LPS principle, the MCAS glass will produce a liquid phase on the surface of the AlN ceramics [21].

Fig. 4 shows the XRD patterns for the glass-doped AlN specimens sintered at different sintering temperatures for 4 h in N2 atmosphere. It is well known that the addition of rare earth oxides such as Y2O3 and alkaline earth oxides such as CaO as sintering aids can promote the densification of AlN by LPS at high temperatures close to 1760°C based on the liquid-phase formation of aluminates by a reaction between the Y2O3 or CaO additives and the Al2O3 layer on the surface of the AlN particles [25]. As a result, in addition to AlN peaks, crystalline peaks of secondary phases such as Y–Al compounds (3Y2O3·5Al2O3, 2Y2O3·Al2O3, Y2O3·Al2O3) or Ca–Al compounds

3. Results and discussion

Fig. 1 shows the DTA scans of the synthesized MCAS glass oxide powder used as a sintering additive in this study. As shown in Fig. 1, an exothermic reaction occurred at 922°C and an endothermic peak appeared at 1251°C. The exothermic reaction corresponded to the typical crystallization peak temperature of glass and the endothermic reaction was attributed to the glass melting.
crystallization of the glass phase and the reaction between the oxide did not react with the Al2O3 layer on the AlN particles. Minor crystalline peaks corresponding to a Ca-Al compound (Ca₂Al₃O₁₀) due to the crystallization of the glass phase and the reaction between the oxide phase and Al₂O₃ began to appear at 1600 °C. However, this compound did not seem to affect the densification of AlN as in the AlN-Y₂O₃ and AlN-CaO systems since most densification occurred below 1600 °C. On the other hand, according to Yang et al. [21], after sintering AlN doped by MCAS glass at temperatures over 1400 °C, crystalline phases such as corderite and Al₂O₃ were identified in the XRD pattern, and it was suggested that the Al₂O₃ phase appeared as the result of a reaction between the AlN particles and oxygen. However, this result was completely different from ours, as mentioned above. Based on dilatometric and XRD analyses, it was found that the melted glass phase played a key role in promoting the densification of AlN at temperatures below 1600 °C via LPS without a reaction between the glass phase and the AlN particles, especially during the shrinkage process resulting from the melting of the glass.

Fig. 5 shows FE-SEM micrographs of AlN specimens sintered at temperatures between 1400 °C and 1700 °C at a heating rate of 5 °C/min in an N₂ atmosphere. As shown in this figure, the pores decreased and AlN grain growth was clearly observed with increasing temperature. After sintering at 1600 °C, a fully densified microstructure was achieved and the pores almost disappeared. It is noted that the sample sintered at 1400 °C, shown in Fig. 5(a), exhibited fine particles of a secondary glass phase and that at temperatures over 1500 °C, a secondary phase was not observed. Molisani et al. [14] reported that the spreading rate of a liquid phase with a higher viscosity among the primary AlN particles was low, resulting in the formation of secondary-phase particles. When the liquid phase has a lower viscosity, the liquid phase tends to spread between the AlN grains, distributing uniformly along AlN grain boundaries. Generally, since the viscosity of glass oxide decreases with increasing temperature after its melting, the melted glass phase can spread rapidly simultaneously with the rearrangement of the AlN particles. The good spreading and wetting characteristics of the glass phase on the AlN particles contributed to the densification of the glass-doped AlN sample at lower temperatures.

On the other hand, at 1700 °C [Fig. 5(e)], the morphology of the AlN particles changed from polygonal to needle-like and pores were observed again. This seems to be associated with the crystallization of the glass phase and the reaction between the AlN particles and the glass phase, as shown in the XRD patterns of Fig. 4.

Fig. 6 shows the relative sintered density of the glass-doped AlN specimens as increased significantly beginning at 1400 °C. Outstanding densification at a relative density of 96.7% and 97.6% occurred after sintering at 1600 °C, which was 200 °C lower than the temperature needed to sinter conventional AlN ceramics with additives of rare earth or alkali earth oxides. The decrease in the sintered density when sintered at 1700 °C was caused by pores that could be formed due to a chemical reaction between the glass phase and the AlN particles [25], as can be seen in the microstructure of Fig. 5(e).

Fig. 7 shows the variation in thermal conductivity of the glass-doped AlN samples after isothermal sintering at 1400, 1500, and 1600 °C for 4 h in a N₂ atmosphere. Unfortunately, it was found that the sample at 1400 °C attained a thermal conductivity of only 46 W/mK and with increasing temperature thermal conductivity decreased. The decrease in thermal conductivity seemed to be associated with the distribution of the glass phase, the formation of a crystalline secondary phase of low thermal conductivity value, and the incorporation of SiO₂ into the AlN lattice. Further investigation concerning the effect of glass additive on the thermal conductivity of AlN is required in the future. On the other hand, we can improve the thermal conductivity of AlN up to around 80 W/mK by controlling the amount of glass addition, glass size, or sintering condition, which will be described in a separate paper.

Fig. 3. Change in (a) linear shrinkage and (b) linear shrinkage rate as a function of time for pure AlN and 5 wt.% glass-doped AlN powder compacts.

Fig. 4. XRD patterns for 5 wt.% glass-doped AlN specimens sintered at different sintering temperatures.
4. Conclusions

A MgO–CaO–Al₂O₃–SiO₂ (MCAS) glass oxide powder, which was produced by a conventional melting process, was used as a sintering additive to AlN ceramics. The small addition of 5 wt.% MCAS glass powder significantly promoted the densification of the AlN ceramics, even at lower temperatures. Dilatometric analysis showed that the shrinkage of the AlN specimen with the glass additive increased steeply at approximately 1400 °C as a result of the melting of the glass, and the maximum shrinkage rate occurred at 1575 °C. Full densification could be obtained when the sample was sintered at 1600 °C for 4 h. The sintering temperature was 200 °C lower than that of conventional AlN–Y₂O₃ and AlN–CaO.

Fig. 5. FE-SEM micrographs of 5 wt.% glass-doped AlN specimens sintered at temperatures of (a) 1300 °C, (b) 1400 °C, (c) 1500 °C, (d) 1600 °C and (e) 1700 °C.

Fig. 6. The relative sintered density of pure AlN and 5 wt.% glass-doped AlN specimens sintered at different temperatures for 4 h in a N₂ atmosphere at a heating rate of 5 °C/min.

Fig. 7. Thermal conductivity of 5 wt.% glass-doped AlN specimens sintered at different temperatures for 4 h in a N₂ atmosphere at a heating rate of 5 °C/min.
systems. Based on dilatometric analysis, X-ray diffraction analysis, and FE-SEM microstructural observation, it was found that the sintering of the glass-doped AlN specimen was promoted by the liquid-phase sintering of the melted glass phase.

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References