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Sintering behavior of aluminum nitride ceramics with $MgO–CaO–Al_2O_3–SiO_2$ glass additive

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ABSTRACT

In this study, $MgO–CaO–Al_2O_3–SiO_2$ (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.

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. Y_2O_3 is known to be the most common and effective additive to achieve the densified AlN ceramics. This additive reacts with the Al_2O_3 layer on the surface of the AlN particles, thus forming secondary phases that promote the densification at lower temperatures than AlN without additive [9–14].

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 $Y_2O_3–CaO–Li_2O$ 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.% CaF_2 and 2 wt.% Y_2O_3 [17].

In addition to the sintering aids 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 $MgO–CaO–Al_2O_3–SiO_2$ (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 SiO_2 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. $MgO–CaO–Al_2O_3–SiO_2$ (MCAS) glass was prepared using a conventional melting process. Reagent

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oxides of MgO, $CaCO_3$, Al_2O_3, and SiO_2 were used as the starting raw materials to prepare the glass frits. The glass composition (in wt.%) consisted of 5% MgO, 19% CaO, 26% Al_2O_3, and 50% SiO_2, 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 it 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 shrinkage was measured in the axial direction by a linear variable differential transducer. The temperature was measured using a thermocouple, which was placed directly above the sample in a flowing N_2 atmosphere. The temperature was maintained to within 5 °C every minute. Additionally, isothermal sintering in a W element furnace was also carried out over a temperature range of 1300 °C to 1700 °C for 4 h at a heating rate of 5 °C/min in a flowing N_2 atmosphere.

The density of the sintered sample was measured by the Archimedes displacement method and the sintered microstructure was observed by FE-SEM (JSM-9701, JEOL, Japan). The crystalline phases of the sintered specimen were identified using X-ray diffractometry analysis (XRD, RINT-2000, RIGAKU Corp., Japan). The thermal conductivity was determined from thermal diffusivity and heat capacity measured using a laser flash technique.

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.

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 N_2 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 of 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 N_2 atmosphere. It is well known that the addition of rare earth oxides such as Y_2O_3 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 Y_2O_3 or CaO additives and the Al_2O_3 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 ($3Y_2O_3 \cdot 5Al_2O_3$, $2Y_2O_3 \cdot Al_2O_3$, $Y_2O_3 \cdot Al_2O_3$) or Ca–Al compounds

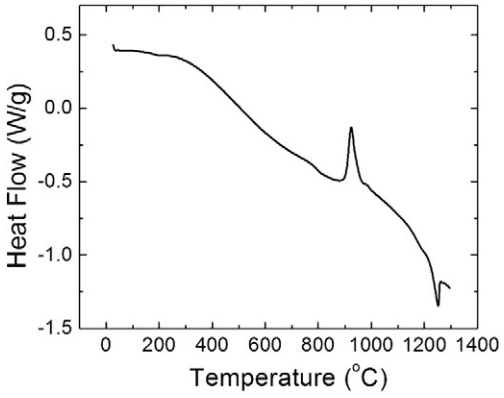

Fig. 1. DTA scans of MCAS glass oxide powder used as a sintering additive of AlN in this study.

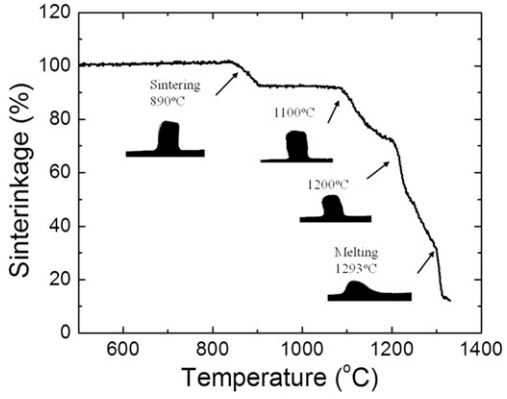

Fig. 2. Variation in shrinkage for MCAS glass powder compact. Images on its morphological change are also inserted inside this plot.