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High-strength AlN ceramics by low-temperature sintering with $CaZrO_3$–Y_2O_3 co-additives

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Abstract

Aluminum nitride (AlN) ceramics with the concurrent addition of $CaZrO_3$ and Y_2O_3 were sintered at 1450-1700 °C. The degree of densification, microstructure, flexural strength, and thermal conductivity of the resulting ceramics were evaluated with respect to their composition and sintering temperature. Specimens prepared using both additives could be sintered to almost full density at relatively low temperature (3 h at 1550 °C under nitrogen at ambient pressure); grain growth was suppressed by grain-boundary pinning, and high flexural strength over 630 MPa could be obtained. With two-step sintering process, the morphology of second phase was changed from interconnected structure to isolated structure; this two-step process limited grain growth and increased thermal conductivity. The highest thermal conductivity (156 $Wm^{-1} K^{-1}$) was achieved by two-step sintering, and the ceramic showed moderate flexural strength (560 MPa).

Keywords: Aluminum nitride; $CaZrO_3$; Strength; Thermal conductivity; Sintering

1. Introduction

Aluminum nitride (AlN) is a useful ceramic material for many technical applications like substrate, heat sinks, refractive materials in metallurgical industry, packaging materials for high power integrated circuits for electronic devices, due to its combination of high thermal conductivity, low dielectric constant, high electrical resistance, wide band gap (E_g = 6.2 eV at room temperature), chemical inertness, and thermal expansion coefficient (which is close to that of silicon).[1–6] The thermal conductivity of AlN and the factors affected by it have received much attention for several decades.[7–10] The high power-density required in many applications can cause crack propagation in ceramic substrates owing to high thermal stresses arising at the joints with circuits. Therefore, for AlN ceramics to be widely useful, they must show high thermal conductivity and good mechanical properties. A few studies have focused on the mechanical properties of AlN. Watari and Hwang investigated the thermal conductivity and flexural strength of $LiYO_2$–CaO-doped AlN ceramics,[11] finding respective values of 170 $Wm^{-1} K^{-1}$ and 440 MPa. They concluded that both properties were influenced by AlN grain size and the number of grain boundaries.

The flexural strength of AlN ceramics can be improved by eliminating pores and by having smaller grains. However, decreasing the grain size reduces the thermal conductivity of the sintered material. Therefore, new fabrication techniques are sought that produce ceramic substrates with high thermal conductivity and good mechanical properties.

The primary objective of this work is the fabrication of AlN ceramics with both high flexural strength and high thermal conductivity. The AlN ceramics were pressureless sintered at 1450–1700 °C for 3 h with $CaZrO_3$ and Y_2O_3 additives. CaO–Y_2O_3 is the most popular additive system for the low-temperature sintering of AlN ceramics due to its low eutectic temperature.[12,13] However, large grains tend to form in the resulting sintered AlN, leading to poor flexural strength. The inhibition of grain growth is therefore desirable, because it would lead to smaller grains and stronger ceramics. Secondary phase inclusions can inhibit grain growth, and are frequently used for this purpose in sintered ceramics. Lange and Hirlinger used ZrO_2

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to inhibit grain growth for Al_2O_3 sintering.[14,15] The secondary phases were located at the grain boundaries and they hindered grain growth by exerting a dragging force and by pinning the grain boundary.[14]

$CaZrO_3$ is a phase between CaO–ZrO_2 that is stable at high temperature.[16] This sintering additive plays a double role during the sintering process. One is to promote the densification by forming a liquid phase when it is in contact with Al_2O_3 in presence of certain impurities. Mostly, AlN raw powder contains a small amount of oxygen impurity which is Al_2O_3 existed on the surface of AlN. The other is to suppress grain growth, keeping the grains small via grain-boundary pinning from the secondary phase. The resulting small grains can yield AlN ceramics with high flexural strength. The addition of CaO can also promote the secondary phase to be located at the boundaries of the AlN grains during sintering.[17]

Sintering in two-steps can produce AlN ceramics that are both strong and highly thermal conductive.[18,19] Chen and Wang introduced this technique to suppress grain growth during the final stage of sintering.[19] The thermal conductivity of AlN ceramics is affected by phonon-defect scattering caused by oxygen-related defects and secondary phases.

This work reports the two-step sintering of AlN ceramics with $CaZrO_3$ and Y_2O_3 additives. The additives suppressed grain growth, and the two-step sintering process provided high thermal conductivity without reducing flexural strength. The second step of the sintering was conducted at temperatures that allowed active grain boundary diffusion but hindered grain boundary migration. Consequently, densification and purification of the AlN lattice were able to continue without significant grain growth.[20,21]

2. Experimental procedure

2.1. Powders and processing

Green AlN specimens were prepared using commercial high-purity AlN power (particle size 1.0 μm, specific surface area 3.27 $m^2\,g^{-1}$; E grade, Tokuyama Corp., Tokyo, Japan) with additives of $CaZrO_3$ (particle size <50 nm, Aldrich, USA) and Y_2O_3 (particle size 30 nm, Aldrich, USA). Three systems employing both additives were tested: both additives were each used at 1 wt. % (system CzY), 2 wt. % (Cz2Y2), and 3 wt. % (Cz3Y3). The AlN powder and the additives were ball milled using zirconia balls for 24 h in a polyethylene bottle with 2-propanol as liquid medium. After mixing, the slurry was dried on a hot plate with stirring. The dried powder was sieved through a 100-mesh sieve and then shaped into 20 mm diameter disk under a pressure of 30 $kg\,cm^{-2}$, and was cold isostatic pressed (CIP) at 200 MPa. A similarly prepared system of only Y_2O_3-doped AlN (system Y) was also tested for comparison.

2.2. Sintering

All the systems were sintered using both one-step and two-step regimes. The green bodies shaped through CIP were sintered between two boron nitride (BN) plates. Sintering was at 1450–1700 °C for 3 h under a nitrogen atmosphere in a graphite furnace (ASTRO, Thermal Technology, Santa Barbara, CA). The heating rate during sintering was 10 °C/min; the cooling rate was 25 °C/min.

Two-step sintering was conducted using different temperatures to minimize grain growth. The second sintering temperature was selected to promote densification and purification of the AlN lattice without allowing grain growth. During the first step, specimens were heated to T_1 with rate of 10 °C/min and held for 3 h at T_1. They were cooled at 25 °C/min to a lower sintering temperature T_2, which was then maintained for 2 h.

2.3. Characterization

Bulk density was measured by Archimedes' method. The microstructure of facture surfaces and the mean diameter of the grains were characterized by scanning electron microscopy (FE-SEM; Philips XL30 FEG, Eindhoven, Netherlands) and transmission electron microscopy (TEM; Tecnai G^2 F30 S-twin FEI, Eindhoven, The Netherlands). The thermal conductivity at room temperature was measured by the laser flash method with a glass–Nd laser and an InSb infrared sensor using a Xenon Flash instrument (LFA 447 Nanoflash, Netzsch Instruments Inc., Burlington, USA).[22] The precision of this apparatus is estimated to be ±3 %. Each reported thermal conductivity is an average of three measurements.

The flexural strength of 1.5 mm × 2.0 mm × 15 mm rectangular bars was tested using a 10 mm support span and a crosshead speed of 0.2 mm/min. Sintered disks were cut into bars for the measurements. The bars were polished with 6 μm diamond paste in alcohol-based slurry (Blue Lube, Struers) and flaws on either side of each bar were removed. The reported flexural strength is an average of the test results of ten bending bars.

3. Result and discussion

3.1. Densification behavior

The AlN ceramics sintered with various additive concentrations showed bulk density values that depended on the sintering temperature (Fig. 1). The green densities of the powder compacts were approximately 57–60 % of theoretical density (TD). The density of each specimen increased as the sintering temperature increased from room temperature to 1550 °C. The theoretical density of AlN was reached by each sample, with the exception of sample Y, when sintered at over 1550 °C. Sample Y, which lacked $CaZrO_3$, achieved only 81 % of the TD after sintering at 1550 °C for 3 h (Fig. 1). Overall, the bulk density comparison shows that the use of both $CaZrO_3$ and Y_2O_3 additives greatly improved the sinterability of AlN ceramics and achieved the lower temperature sintering process. The densification was achieved by means of liquid-phase sintering. The $CaZrO_3$–Y_2O_3–Al_2O_3 additive system formed a liquid phase by eutectic melting, which promoted densification at lower temperatures.