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# Microstructure and optical properties of transparent aluminum oxynitride ceramics by hot isostatic pressing

Feng Chen,[a] Fang Zhang,[a] Jun Wang,[a] Hailong Zhang,[a] Run Tian,[a] Jian Zhang,[a] Zhao Zhang,[a] Feng Sun[b,*] and Shiwei Wang[a,*]

[a]*Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai, People's Republic of China*
[b]*School of Materials Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai, People's Republic of China*

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Highly transparent aluminum oxynitride ceramic was fabricated by presintering at 1900 °C and further sintering by hot isostatic pressing (HIP) at 1900 °C under a 190 MPa argon atmosphere. For a 4.2 mm thick specimen doped with 0.1 wt.% $Y_2O_3$–$La_2O_3$, the inline light transmittance reached 78.8% at 600 nm and 84.4% at 1084 nm, respectively. Unlike the inhomogeneous microstructure of pressureless sintered specimen (grain size ~150 μm), which contained substructure and twinning grains, the HIPed specimen had a homogeneous and refined microstructure with average grain size of ~45 μm.


*Keywords:* Aluminum oxynitride; Hot isostatic pressing; Optical property; Microstructure

Transparent aluminum oxynitride (γ-AlON) ceramics are being investigated due to their excellent optical and mechanical properties, which render them suitable for transparent media in hostile environments such as IR/visible windows, electron microscope domes and transparent armor [1,2]. Most AlON materials developed to date exhibit a grain size of ~100–200 μm, explaining the disappointing optical and mechanical properties reported [3,4]. Small grain size and high density is the key to extending the applications of AlON ceramics. To simultaneously limit grain growth and obtain maximum densification, hot isostatic pressing (HIP) has proved to be a good candidate for materials such as $Y_2O_3$, $MgAl_2O_4$ and yttrium aluminum garnet (YAG) [5–7]. With the assistance of three-dimensional pressure, HIP offers the possibility to consolidate ceramic powders to be fully dense within a short time at comparatively lower temperatures, with the preservation of a relatively fine microstructure. However, to date only a few papers have addressed the use of HIP for fabricating transparent AlON ceramic. Fujii and Shibata [8] fabricated AlON ceramics by hot pressing AlON powders at 1650 °C and further HIP-sintering (200 MPa) at 1700 °C for 2.5 h in a $N_2$/1% $O_2$ atmosphere. The obtained 5 mm thick AlON ceramic exhibited a transmittance of ~81% in the 0.4–2 μm range, with a final grain size of 30 μm. Clay et al. [9] reported using pressureless sintering plus HIP to obtain AlON ceramics at 2000 °C for 2 h with α-$Al_2O_3$/AlN as starting powders and $LiAl_5O_8$ as sintering aid. With a final grain size of 78 ± 18 μm the obtained 6.2 mm thick specimen exhibited a maximum transmittance of ~65% in the 3–33 μm range. The present study was undertaken to fabricate fine-grained and highly transparent AlON ceramic using an HIP-sintering technique.

The laboratory-synthesized AlON powder was pure $Al_5O_6N$ phase with high crystalline quality, characterized by X-ray diffractometry (D/MAX-RBX, Rigaku Co., Tokyo, Japan). The powder exhibited a log-normal particle size distribution with average size of 0.5 μm, measured using a particle size analyzer (H43-MaterSizer 2000, Malvern, UK). The sintering additive $Y_2O_3$–$La_2O_3$ (99.9% purity, Baotou Rare-Earth Institute, PR China) was mixed sufficiently with AlON powder by a ball-milling process. The obtained slurry was dried and

* Corresponding authors. +86 21 5241 5219; e-mail addresses: fsun@sjtu.edu.cn; swwang51@mail.sic.ac.cn

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pressed into 20 mm diameter × 6 mm disks, followed by cold isostatic pressing (CIP) under 200 MPa. After CIP, green bodies were presintered to the closed pore state. The presintering temperature was designed based on the shrinkage behavior of the AlON green body measured by a thermal dilatometer (DIL 402C, Germany). HIP sintering was then carried out in Ar (190 MPa). For comparison, pressureless sintering was also employed at 1930 °C for 15 h to prepare AlON ceramic. Densities were determined following the Archimedes principle. Inline transmission ($T_{in}$) was measured with a spectrophotometer (Cary 5000, Varian, USA). Microstructural evolution was observed by scanning electron microscopy (JSM-6360LV, JEOL, Tokyo, Japan). Grain sizes were measured from the average linear intercept length multiplied by 1.56. Acquisition of electron backscattered diffraction (EBSD) was done using an FEI Sirion field-emission gun scanning electron microscope equipped with a fully automatic HKL Technology EBSD attachment.

Figure 1 shows the shrinkage curve of the AlON green body. Shrinkage started at ~1300 °C and ended at ~1600 °C. Then, a sudden expansion happened between 1650 and 1750 °C. After the expansion, significant shrinkage occurred at ~1800 °C and ended at ~2000 °C. The shrinkage between 1300 and 1600 °C may be caused by the formation of YAG liquid phase, because the green body contained a small amount of $Al_2O_3$ introduced by alumina grinding balls, which can react with $Y_2O_3$ to form YAG eutectoid. According to the phase diagram of the $Al_2O_3$–AlN pseudo-binary system by Willems et al. [10], AlON was at equilibrium at ~1650 °C. Therefore, the expansion between 1650 and 1750 °C was attributed to the reaction between $Al_2O_3$, AlN and AlON in the $Al_2O_3$–AlN equilibrium system. The densification process started at ~1800 °C. Based on the dilatometry above, 1800, 1850 and 1900 °C have been selected as presintering temperatures. All the presintered specimens were then HIPed at 1900 °C for 2 h.

Figure 2 (inset) shows photographs of presintered and HIPed specimens. The 1900 °C presintered specimen was opaque with a white appearance. After HIPing at 1900 °C, the specimen exhibited a blackish color but the background words can be seen clearly. Darkening discoloration is common in HIPing due to carbon contamination from the graphite crucible. After annealing at 1200 °C in air, the specimen exhibited better transparency. Figure 2 shows the transmittance curves comparing the HIPed specimens to a pressureless sintered specimen. The transmission of HIPed specimens was superior to that of the pressureless sintered one in the IR and visible regions. For HIPed specimens, increasing the presintering temperature led to a dramatic improvement in transmittance over the entire range of wavelengths studied. The 1900 °C presintered specimen showed superior transmittance over the others, achieving 78.8% at 600 nm and 84.4% at 1084 nm. The present data are comparable to those reported by Fujii and Shibata, and much higher than most of the previous reported results [11,12].

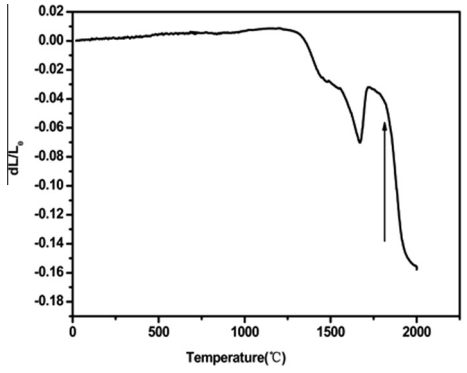


**Figure 1.** The relation between shrinkage rate and temperature of AlON green body.

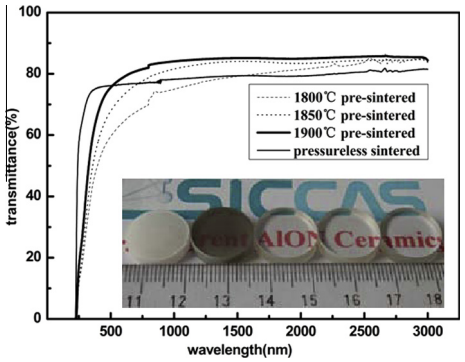


**Figure 2.** Transmittance for 1900 °C HIPed AlON (4.2 mm thick, presintered at 1800, 1850 and 1900 °C) compared to pressureless sintered AlON (4.2 mm thick, sintered at 1930 °C for 15 h). Insert: photographs of AlON presintered at 1900 °C in $N_2$ (white disk), HIPed at 1900 °C in Ar (black disk), and annealed at 1200 °C in air (transparent disk), respectively.

Grain size, pore diameter and density evolution are listed in Table 1. During the presintering stage, increasing the presintering temperature resulted in larger grain size, reduced pore diameter and higher density. The pore diameter/grain diameter ratio decreased from 0.83 to 0.03 when the presintering temperature increased from 1800 to 1900 °C. According to Bagwell and Messing [13], if the pore diameter/grain diameter ratio is <1, the pores will shrink at a dihedral angle near 120°. Here, the pore diameter/grain diameter ratio was in the range of 0.03–0.83, which was assisted the removal of residual pores during HIP. Comparing the grain size before and after HIPing, it was found that a smaller grain size after presintering resulted in a smaller grain size after HIPing. The initial presintering grain size may be the key factor in determining the final grain size after HIPing. Moreover, according to a report on pressure-assisted liquid-phase densification, the grain size before HIPing is inversely proportional to the densification rate during the final stage of sintering [14]. To obtain a fine grain size and high-density ceramic, the grain size must be controlled during the presintering stage using a rigorously controlled sintering system. As expected, the grain size of the presintered specimen was controlled at 20 μm by presintering at 1900 °C, achieving a final grain size of 45 μm and a relative density (RD) of 99.99% after HIPing.

Figure 3a–c shows that the AlON green body was transformed into a closed pore state after presintering, meeting the prerequisite for non-encapsulating