

莫来石助剂对氧氮化铝透明陶瓷显微结构及光学性能的影响

史镭玮^{1,2}, 安丽琼¹, 毛小建², 张步豪^{2,3}, 李建民², 章 健², 王士维²

(1. 上海海事大学海洋科学与工程学院, 上海, 201306, 中国; 2. 中国科学院上海硅酸盐研究所国家重点实验室, 上海 200050, 中国; 3. 英国诺丁汉大学工程学院, 诺丁汉, NG7 2RD, 英国)

摘 要: 以自制 AION 粉体为原料、莫来石为烧结助剂, 结合无压烧结与热等静压烧结在相对较低的温度下(分别为 1 880 °C 和 1 800 °C)制备了 AION 透明陶瓷, 研究了莫来石含量对无压烧结和热等静压烧结 AION 陶瓷的显微结构以及光学性能的影响。结果表明, 莫来石含量在 0.02%~0.20%(质量分数)时, 无压烧结 AION 陶瓷为纯 AION 相, 其 Raman 光谱相似。随着莫来石含量增加, AION 陶瓷无压预烧体的致密度先增加后减小, 而其晶粒尺寸逐渐变大。热等静压烧结后, 所有样品的致密度均高于理论密度的 99.2%且晶粒长大; 其致密度、晶粒和透过率随莫来石含量增加呈现出先增大后减小的趋势。最终, 0.05% 莫来石 AION 透明陶瓷致密度为 3.67 g/cm³, 平均晶粒尺寸为 80.4 μm, 其透过率最高, 4 mm 厚样品在 2 000 nm 处达到 81.9%。

关键词: 氧氮化铝; 透明陶瓷; 烧结助剂; 莫来石; 热等静压

中图分类号: TQ174 文献标志码: A 文章编号: 0454-5648(2024)03-0845-08

网络出版时间: 2024-02-06



氧氮化铝(γ -AION, 即 AION)透明陶瓷具有优异的紫外-可见-红外波段透光性和力学性能, 被广泛应用于光学校镜、透明装甲、红外窗口等领域, 特别是在防御大口径、高速冲击源和严苛工况应用具有显著优势, 是一种重要的国防材料^[1-2]。

为获得性能优异的 AION 透明陶瓷, 其制备过程包括粉体制备、成型、烧结和后处理均需精确控制, 如控制 AION 粉体颗粒大小及分布、采用干压或凝胶注等成型工艺、调节烧结温度和保温时间等。目前, 比较常用的制备方法为两步法, 即采用碳热还原氮化反应法制备 AION 粉体、采用无压预烧结和热等静压后处理烧结相结合来获得高性能 AION 透明陶瓷。该方法中除了优化制备工艺之外, 烧结助剂也是降低烧结温度、获得高性能 AION 透明陶瓷的有效办法。AION 体系已报道的烧结助剂有 Y_2O_3 ^[3-5] 和其他稀土元素^[6]、 $CaCO_3$ ^[7]、 $LiAl_5O_8$ ^[8-9]、 $Y_2O_3-La_2O_3$ ^[10-12]、 Y_2O_3-MgO ^[13]、 $Y_2O_3-MgAl_2O_4-H_3BO_3$ ^[14] 等多种, 均起到提高致密

度和样品透过率的效果。然而, 烧结温度依旧比较高, 如无压烧结温度在 1 860~1 940 °C, 热等静压烧结温度在 1 825~2 000 °C, 这使得制备成本偏高。此外, 烧结助剂的添加会对材料本征的力学性能带来影响。因此, 烧结助剂的选择及用量以低成本制备高性能 AION 透明陶瓷仍然是一个巨大挑战。

SiO_2 是一种优异的烧结助剂, 广泛应用于石榴石透明陶瓷中, 如 $Y_3Al_5O_{12}$ (YAG)^[15-16]、 $Lu_3Al_5O_{12}$ (LuAG)^[17] 等, 同时也被证明在 AION 体系中有效^[18-19]。Feng 等采用 SiO_2 作为烧结助剂、无压烧结与热等静压烧结(1 880 °C)相结合制备了 AION 透明陶瓷, 3.5 mm 厚样品在 2 000 nm 处的透过率为 86%^[18]。Li 等采用类似制备方法获得在 2 000 nm 处透过率为 85.9% (4 mm 厚)的 AION 透明陶瓷, 并成功将热等静压烧结温度降低至 1 810 °C, 有利于降低制备成本^[19]。然而, 在还原气氛的高温烧结过程中 SiO_2 容易分解生成 SiO 气体, 导致预烧体中微气

收稿日期: 2023-08-28。 修订日期: 2023-10-09。

基金项目: 国家自然科学基金(51902330)资助。

第一作者: 史镭玮(1997—), 男, 硕士研究生。

通信作者: 安丽琼(1979—), 女, 博士, 副教授;

毛小建(1980—), 男, 博士, 研究员。

Received date: 2023-08-28. Revised date: 2023-10-09.

First author: SHI Rongwei (1997—), male, Master candidate.

E-mail: srw1997@163.com

Correspondent author: AN Liqiong (1979—), female, Ph.D., Associate Professor;

MAO Xiaojian (1980—), male, Ph.D., Professor.

E-mail: anlq@shmtu.edu.cn; maoxiaojian@mail.sic.ac.cn

孔增多, 从而引起样品内外密度的不均匀以及随后热等静样品的光学不均匀。因此, 探索一种不易分解挥发的含硅助剂以获得高性能 AION 透明陶瓷很有必要。采用 Si_3N_4 作固相烧结助剂、1900 °C 无压烧结和 1800 °C 热等静压烧结 8 h 获得了 AION 透明陶瓷, 4 mm 厚样品在 2 000 nm 处的透过率为 85.6%^[20]。莫来石($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)作为含有 Si、Al 为 AION 主相的氧化物, 具有优异的高温热稳定性^[21–22], 有作为 AION 陶瓷烧结助剂的潜力。本工作以莫来石烧结助剂、采用无压烧结和热等静压烧结相结合来制备 AION 透明陶瓷, 研究了莫来石含量对无压烧结和热等静压烧结 AION 陶瓷的微观形貌以及光学性能的影响。

1 实验

1.1 样品制备

以实验室自制 AION 粉体为原料、0.02%~0.20% (质量分数)莫来石为烧结助剂、采用湿法球磨法将 2 种粉体混合 20 h, 其中, 球磨介质为无水乙醇, 磨球为高纯氧化铝球。对球磨后的浆料干燥、过筛、煅烧, 即获得含莫来石烧结助剂的 AION 粉体。使用该粉体干压和冷等静压成型成素坯, 置于流动氮气气氛中、1880 °C 温度下进行无压预烧结, 保温时间为 4 h; 然后将无压预烧结样品在流动氩气气氛中进行热等静压烧结(HIP), 烧结温度、压力和保温时间分别为 1800 °C、200 MPa 和 6 h, 即获得 AION 透明陶瓷。

1.2 样品表征

用 Bruker 公司 D8 Advance 型 X 射线衍射仪(XRD)进行物相分析, 采用 $\text{Cu-K}\alpha$ 射线, $\lambda=1.5406\text{Å}$, 扫描范围 $10^\circ\sim 80^\circ(2\theta)$, 扫描步长 0.02° 。用 Archimedes 排水法测量并计算无压和热等加压烧结陶瓷的密度。对无压和热等静压烧结陶瓷进行表面抛光、300 °C H_3PO_4 溶液中化学腐蚀 10 min 和喷金处理后, 用 Hitachi 公司 TM3000 台式扫描电子显微镜进行抛光腐蚀表面和断口形貌表征。用 Nano Measurer 软件, 通过校正系数为 1.56 的线性截距法测定晶粒尺寸。用 Horiba 公司 XploRA One-532 型 Raman 光谱量 AION 陶瓷的 Raman 光谱, 测试采用 532 nm Ar^+ 激光器, 室温测试, 测试范围 $200\sim 1200\text{cm}^{-1}$ 。用 JASCO 公司 V770 型紫外/可见光/近红外分光光度计和 FT/IR-4600 Fourier 红外光谱仪分别对热等静压样品在 $190\sim 2500\text{nm}$ 和 $2500\sim 6000\text{nm}$ 波长范围进行透过率测试, 测试样品厚度

为 4 mm。

2 结果与讨论

2.1 球磨后含莫来石 AION 粉体微观形貌及粒径分布

图 1 给出了球磨后含莫来石 AION 粉体的微观形貌及粒径分布。由图 1a 可以看出, 球磨后的 AION 粉体颗粒尺寸均匀, 呈不规则形状。粉体颗粒大小在 $0.2\sim 1.6\mu\text{m}$ 之间(图 1b); 粒径呈单模分布, 平均值为 $0.7\mu\text{m}$ 。

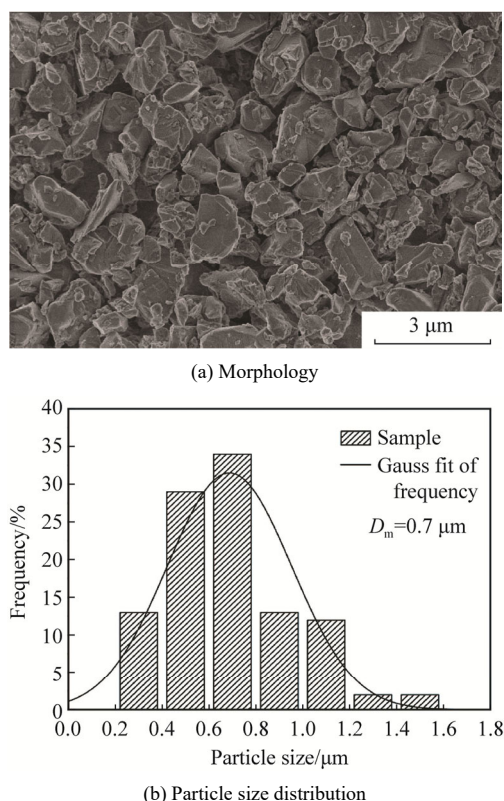


图 1 球磨后含莫来石 AION 粉体的微观形貌和粒径分布
Fig. 1 Morphology and particle size distribution of ball-milled AION powders doped with mullite

2.2 无压预烧结 AION 陶瓷的物相和显微结构

图 2 为无压预烧结含不同量莫来石 AION 陶瓷的 XRD 谱。由图 2 可以看出, 所有 XRD 谱均与标准立方 AION 相(JCPDS 48-0686)匹配良好, 且没有观察到其他杂峰。这意味着莫来石在无压烧结过程全部固溶进入 AION 晶格。考虑到 AION 相图^[23]、AION 中 O/N 比^[24–26]以及含烧结助剂 AION 陶瓷烧结过程中相的演变^[19–20, 26], Al_2O_3 和 SiO_2 均能固溶进入 AION 晶格。Li 等^[19]观察到了 SiO_2 助剂烧结的 AION 陶瓷晶格常数减小, 这归因于离子半径小的 Si^{4+} 进入 AION 晶格取代离子半径大的 Al^{3+} ; 同

时, 取代过程中为保持电中性形成铝空位和 Al_2O_3 , 生成的 Al_2O_3 固溶进入 AION 晶格, 也会促使晶格常数减小^[24]。

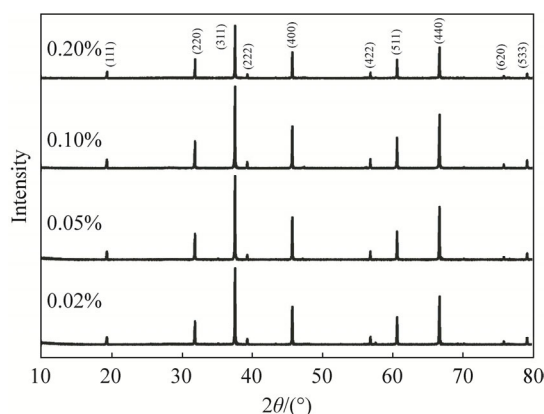


图 2 无压预烧结合含 0.02%~0.20%莫来石 AION 陶瓷的 XRD 谱

Fig. 2 XRD patterns of the pre-sintered AION ceramics doped with 0.02%~0.20% mullite

为了进一步探明莫来石掺杂后 AION 结构的变化, 图 3 给出了含不同量莫来石 AION 陶瓷无压预烧体的归一化 Raman 光谱。由图 3 可见, 在 316、372、628、764 和 920 cm^{-1} 处均有声子振动, 这被认为与尖晶石的 3T_{2g} 、 E_g 和 A_{1g} 模式有关^[27], 并与文献报道一致^[20, 25, 28]。随着莫来石含量的增加, Raman 谱带峰值没有明显偏移且没有出现新峰, 这说明莫来石含量对 AION 结构和相没有明显影响。此外, 所有样品的最大声子频率几乎不变, 这意味着所有样品具有相同的红外截止波长^[25], 这将在随后的透光率光谱中体现。

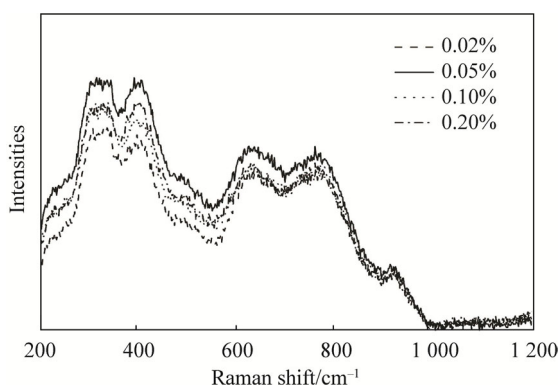


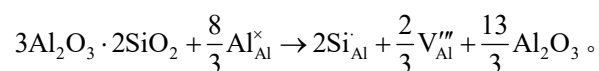
图 3 无压预烧结合含 0.02%~0.20%莫来石 AION 陶瓷的归一化 Raman 光谱

Fig. 3 Normalized Raman spectra of the pre-sintered AION ceramics doped with 0.02%~0.20% mullite

经过无压预烧得到的 AION 预烧体呈乳白

色、不透明状。图 4 是含不同量莫来石 AION 陶瓷预烧体的断口形貌和晶粒尺寸分布图。所有预烧体样品均观测到大量气孔, 均匀分布在晶粒及晶界上, 气孔尺寸远小于晶粒尺寸。随着莫来石含量增加至 0.10%~0.20%, 样品中有大气孔出现(图 4e 和图 4g)。晶粒尺寸随着莫来石含量增加呈现出单调递增的趋势, 由 23.5 μm 逐渐增加到 31.9 μm 。表 1 给出了 AION 陶瓷预烧体的体密度和晶粒尺寸随莫来石含量变化数据。随着莫来石含量从 0.02%增加到 0.20%, 体密度呈现先增大后减小的趋势, 在 0.05%时密度最高, 为 3.61 g/cm^3 。

SiO_2 作为石榴石透明陶瓷体系中广泛使用的一种烧结助剂, 被认为在低浓度时起到固相烧结的作用; 在高浓度时, 起到液相烧结的作用^[17]。Li 等^[19]认为 SiO_2 在真空高温下分解成 SiO 气体导致 AION 陶瓷无压预烧体的密度降低且气孔增多, SiO 气体填充到气孔中, 能在热等静压过程中固化并吸收进入 AION 晶格, 从而样品在退火后也能保持高透过率。在本研究中, 莫来石用量(0.02%~0.20%)相比于文献报道 SiO_2 用量(0.20%~0.90%)^[19]较小, 且微观形貌演变规律不同于 SiO_2 烧结 AION 陶瓷^[19]; 同时考虑到莫来石具有优异的高温稳定性^[21-22], 莫来石与 AION 粉体间反应主要以固相反应为主,



此外, AION 相形成过程中先形成富氧 AION 相, 然后残留的 AIN 固溶进入富氧 AION 晶格^[29], 且 Al—N 的共价键力强于 Al—O^[30]和烧结过程中氧原子扩散速度高于氮原子扩散速度^[26, 29], 因而 Al_2O_3 含量高的 AION 更容易烧结, 晶粒也容易长大。因此, 随着莫来石含量增大, Al_2O_3 含量增大, AION 陶瓷晶粒逐渐变大。当莫来石含量高时, 晶粒生长速度过快, 导致气孔排出时间不够充分而被包裹在晶粒内部, 从而导致预烧体致密度降低, 大气孔出现。

2.3 热等静压烧结 AION 陶瓷的显微结构

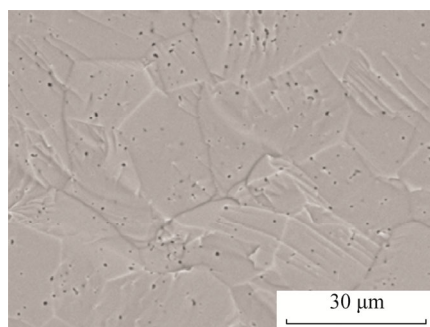
图 5 是含不同量莫来石 AION 陶瓷在 1 800 $^{\circ}\text{C}$ 热等静压的断面照片和晶粒尺寸分布。由图 5 可以看出, 热等静压烧结 AION 陶瓷样品呈致密状态, 达到理论密度的 99.2%以上, 但仍可观察到微量气孔; 断口呈现出穿晶和沿晶 2 种断裂模式。随着莫来石含量从 0.02%增加到 0.05%, 样品的平均晶粒尺寸从 71.2 μm 增加到 80.4 μm ; 进一步增加莫来石含量至 0.20%, 晶粒尺寸则下降至 74.8 μm (如表 1

所示)。这可能是因为预烧阶段形成较多的晶内气孔在热等静压烧结阶段无法排除,起到钉扎效应抑制了晶粒生长^[10]。

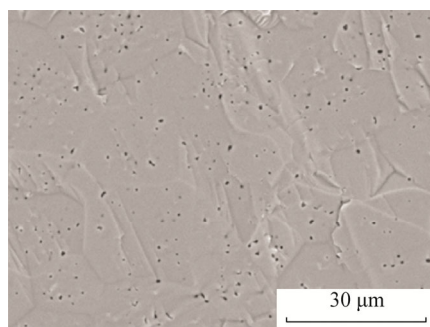
2.4 热等静压烧结 AION 陶瓷的透过率

图 6 是热等静压后 4 mm 厚、含不同量莫来石

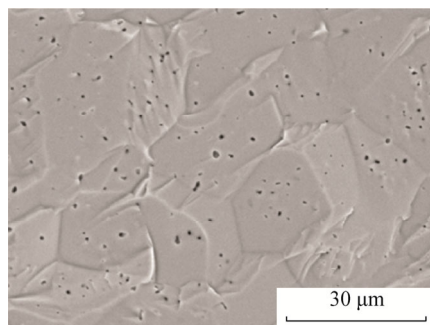
AION 陶瓷在 200~6 000 nm 波长范围内的透过率曲线。由图 6 可以看出,样品的透过率在较宽的波长范围均有较高透过率。随着莫来石含量的增加,透过率先上升后降低,在含量为 0.05% 时最高,2 000 nm 处达到 81.9%。该透过率达到理论值的



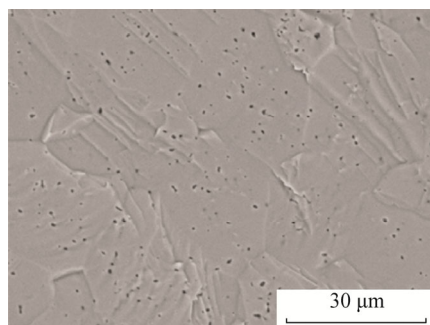
(a) SEM image of sample with 0.02% mullite



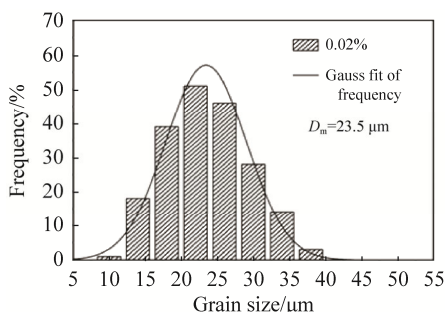
(c) SEM image of sample with 0.05% mullite



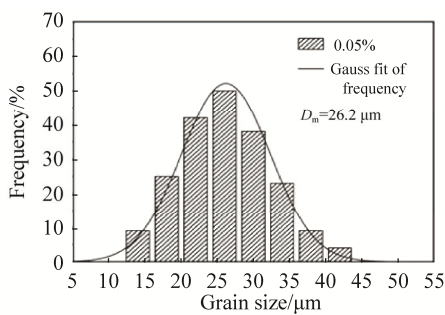
(e) SEM image of sample with 0.10% mullite



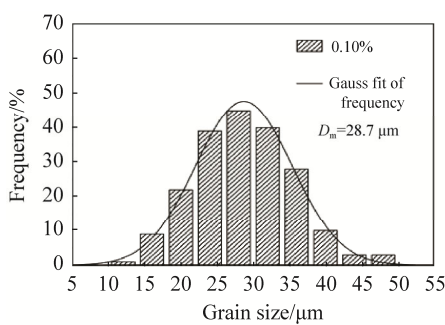
(g) SEM image of sample with 0.20% mullite



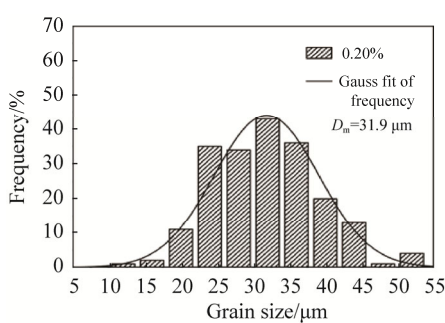
(b) Grain size distribution of sample in Fig.4 (a)



(d) Grain size distribution of sample in Fig.4 (c)



(f) Grain size distribution of sample in Fig.4 (e)



(h) Grain size distribution of sample in Fig.4 (g)

图 4 无压预烧结含 0.02%~0.20%莫来石 AION 陶瓷的断口形貌和晶粒尺寸分布图

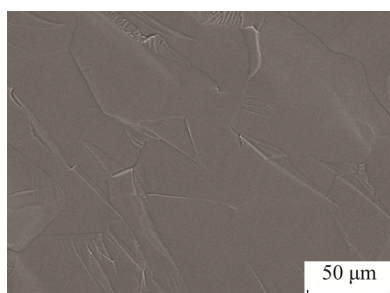
Fig. 4 SEM images of fracture surfaces and grain size distribution of the pre-sintered AION ceramics doped with 0.02%–0.20% mullite

表 1 无压预烧结和热等静压烧结合 0.02%~0.20%莫来石 AION 陶瓷的密度和平均晶粒尺寸

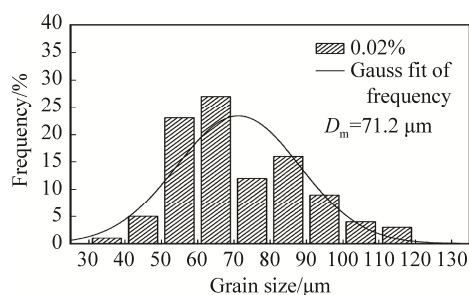
Table 1 Density and average grain size of the pre-sintered and HIPed AION ceramics doped with 0.02%–0.20% mullite

w(mullite)/%	Pressureless pre-sintered AION		HIPed AION	
	Density/(g·cm ⁻³)	Average grain size/μm	Density/(g·cm ⁻³)	Average grain size/μm
0.02	3.60±0.01	23.5±1.7	3.66±0.01	71.2±3.1
0.05	3.61±0.01	26.2±1.9	3.67±0.01	80.4±3.4
0.10	3.59±0.01	28.7±2.6	3.66±0.01	77.1±4.5
0.20	3.58±0.01	31.9±3.1	3.65±0.01	74.8±4.9

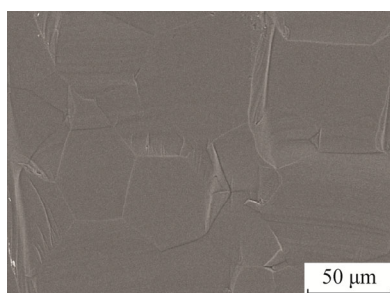
w—Mass fraction.



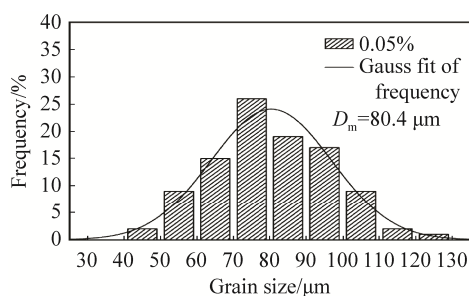
(a) SEM image of sample with 0.02% mullite



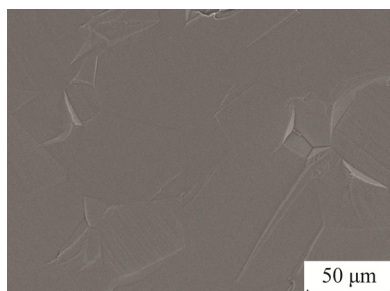
(b) Grain size distribution of sample in Fig.5 (a)



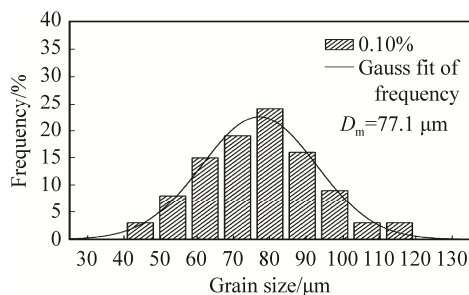
(c) SEM image of sample with 0.05% mullite



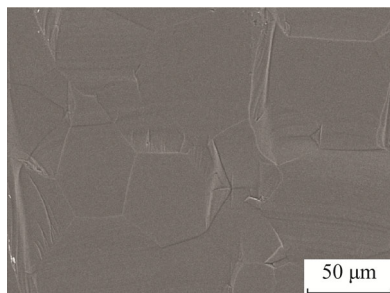
(d) Grain size distribution of sample in Fig.5 (c)



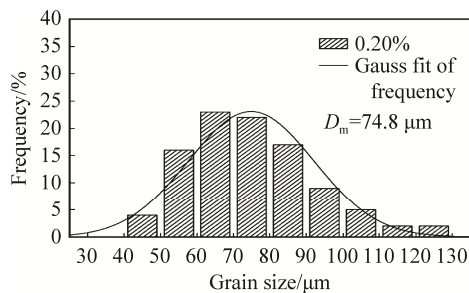
(e) SEM image of sample with 0.10% mullite



(f) Grain size distribution of sample in Fig.5 (e)



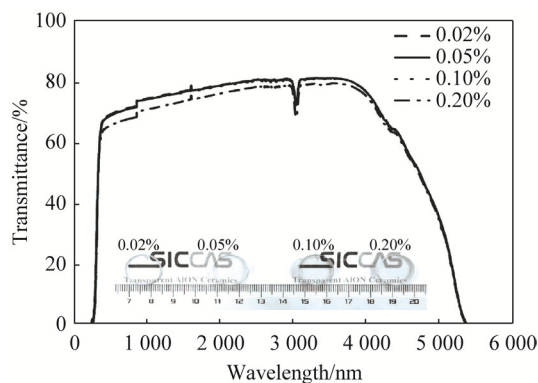
(g) SEM image of sample with 0.20% mullite



(h) Grain size distribution of sample in Fig.5 (g)

图 5 热等静压烧结合 0.02%~0.20%莫来石 AION 陶瓷的断面形貌和晶粒尺寸分布图

Fig. 5 SEM images of fracture surfaces and grain size distribution of the HIPed AION ceramics doped with 0.02%–0.20% mullite



Insert is photographs of the samples.

图 6 热等静压烧结合 0.02%~0.20%莫来石 AlON 陶瓷 (4 mm 厚)的透过率曲线和宏观样品照片

Fig. 6 Transmittance spectra and photos of HIPed AlON ceramics (4 mm thickness) doped with 0.02%–0.20% mullite

95%，比以类似制备工艺、含硅类烧结助剂 SiO_2 ^[19] 和 Si_3N_4 ^[20] 样品的透过率略低 (4 mm 厚样品在 2 000 nm 处值分别为 85.9%和 85.6%)，但与其它烧结助剂，如 Y_2O_3 ^[4]、 LiAl_5O_8 ^[9] 所制备样品的透过率接近。采用热等静压烧结温度相对较低 (1 800 °C)，与以 Si_3N_4 ^[20] 为烧结助剂的烧结温度相同 (1 800 °C)，但比以其他烧结助剂，如 $\text{Y}_2\text{O}_3\text{--MgO}$ (1 825 °C)^[13]、 Y_2O_3 (1 850 °C)^[4]、 LiAl_5O_8 (1 880 °C)^[9] 的烧结温度低。所有样品在 3 μm 左右均检测到 1 个弱吸收峰，这是来自于物理吸附的水所产生的 OH 拉伸振动峰^[20, 25]。所有样品具有相同的红外截止波长，这与 Raman 光谱结果一致 (图 3)。Hostasa 等报道了高 SiO_2 含量无压烧结 YAG 陶瓷的微观形貌发生明显晶粒生长，且有晶内气孔^[17]；而热等静压烧结能够容易消除晶间气孔，而难以消除晶内气孔^[31–32]。本研究中，热等静压高莫来石含量样品存在微量晶间气孔 (图 5)，这是 AlON 陶瓷透过率降低的主要原因。因此，需要控制好烧结助剂用量、避免形成晶内气孔来获得高透过率 AlON 透明陶瓷。

3 结论

1) 莫来石在 0.02%~0.20% 含量所获得的 AlON 陶瓷保持原有结构。

2) 采用莫来石烧结助剂、在相对较低热等静压温度下 (1 800 °C) 可以获得 AlON 透明陶瓷，透过率在 0.05% 时最高，2 000 nm 处达到 81.9% (4 mm 厚)。

3) 莫来石含量高于 0.10% 时，发现无压烧结 AlON 陶瓷中有晶间气孔形成，抑制了热等静压烧

结过程中的晶粒生长。

参考文献:

- [1] MCCAULEY J W, PATEL P, CHEN M W, et al. AlON: a brief history of its emergence and evolution[J]. J Eur Ceram Soc, 2009, 29(2): 223–236.
- [2] WU J, WANG Z J, HU Z C, et al. Recent progress and challenges of transparent AlON ceramics[J]. Trans Nonferrous Met Soc China, 2023, 33(3): 653–667.
- [3] WANG Y, XIE X M, QI J Q, et al. Two-step preparation of AlON transparent ceramics with powder synthesized by aluminothermic reduction and nitridation method[J]. J Mater Res, 2014, 29(19): 2325–2331.
- [4] SHAN Y C, MA L Y, SUN X N, et al. Fast fabrication of AlON ceramics with ultra-high transmittance by the assistance of hot isostatic pressing treatment[J]. J Eur Ceram Soc, 2022, 42(13): 5538–5544.
- [5] MIN P, LI H L, FENG Z, et al. Pressureless sintering of highly transparent aluminum oxynitride ceramic by precipitation-coating with sintering aid[J]. J Eur Ceram Soc, 2023, 43(4): 1663–1670.
- [6] TSABIT A M, KIM M D, YOON D H. Effects of various rare-earth additives on the sintering and transmittance of γ -AlON[J]. J Eur Ceram Soc, 2020, 40(8): 3235–3243.
- [7] SHAN Y C, SUN X N, REN B L, et al. Pressureless sintering of highly transparent AlON ceramics with CaCO_3 doping[J]. Scr Mater, 2018, 157: 148–151.
- [8] CLAY D, POSLUSNY D, FLINDERS M, et al. Effect of LiAl_5O_8 additions on the sintering and optical transparency of LiAlON[J]. J Eur Ceram Soc, 2006, 26(8): 1351–1362.
- [9] YANG G J, SUN P, WANG Y Z, et al. Effects of Y_2O_3 and LiAl_5O_8 on the microstructure and optical properties of reactively sintered AlON based transparent ceramics[J]. Materials, 2022, 15(22): 8036.
- [10] CHEN F, ZHANG F, WANG J, et al. Microstructure and optical properties of transparent aluminum oxynitride ceramics by hot isostatic pressing[J]. Scr Mater, 2014, 81: 20–23.
- [11] CHEN F, ZHANG F, WANG J, et al. Hot isostatic pressing of transparent AlON ceramics with $\text{Y}_2\text{O}_3/\text{La}_2\text{O}_3$ additives[J]. J Alloys Compd, 2015, 650: 753–757.
- [12] WANG J, ZHANG F, CHEN F, et al. Effect of Y_2O_3 and La_2O_3 on the sinterability of γ -AlON transparent ceramics[J]. J Eur Ceram Soc, 2015, 35(1): 23–28.
- [13] JIANG N, LIU Q, XIE T F, et al. Fabrication of highly transparent AlON ceramics by hot isostatic pressing post-treatment[J]. J Eur Ceram Soc, 2017, 37(13): 4213–4216.
- [14] YANG S X, LI J M, GUO H, et al. Reactive sintered highly transparent AlON ceramics with $\text{Y}_2\text{O}_3\text{--MgAl}_2\text{O}_4\text{--H}_3\text{BO}_3$ ternary additive[J]. J Am Ceram Soc, 2021, 104(9): 4304–4308.
- [15] BOULESTEIX R, MAÎTRE A, BAUMARD J F, et al. The effect of silica doping on neodymium diffusion in yttrium aluminum garnet ceramics: Implications for sintering mechanisms[J]. J Eur Ceram Soc, 2009, 29(12): 2517–2526.
- [16] STEVENSON A J, LI X, MARTINEZ M A, et al. Effect of SiO_2 on densification and microstructure development in Nd: YAG transparent ceramics[J]. J Am Ceram Soc, 2011, 94(5): 1380–1387.
- [17] HOSTAŠA J, PICELLI F, HRÍBALOVÁ S, et al. Sintering aids, their role and behaviour in the production of transparent ceramics[J]. Open Ceram, 2021, 7: 100137.

- [18] FENG Z, QI J Q, GUO X F, et al. A new and highly active sintering additive: SiO_2 for highly-transparent AlON ceramic[J]. *J Alloys Compd*, 2019, 787: 254–259.
- [19] LI J M, ZHANG B H, TIAN R, et al. Hot isostatic pressing of transparent AlON ceramics assisted by dissolution of gas inclusions[J]. *J Eur Ceram Soc*, 2021, 41(7): 4327–4336.
- [20] AN L Q, SHI R W, MAO X J, et al. Fabrication of AlON transparent ceramics with Si_3N_4 sintering additive[J]. *J Adv Ceram*, 2023, 12(7): 1361–1370.
- [21] DAVIS R F, PASK J A. Diffusion and reaction studies in the system Al_2O_3 – SiO_2 [J]. *J Am Ceram Soc*, 1972, 55(10): 525–531.
- [22] TORRECILLAS R, CALDERÓN J M, MOYA J S, et al. Suitability of mullite for high temperature applications[J]. *J Eur Ceram Soc*, 1999, 19(13/14): 2519–2527.
- [23] WILLEMS H X, HENDRIX M M R M, DE WITH G, et al. Thermodynamics of alon II: phase relations[J]. *J Eur Ceram Soc*, 1992, 10(4): 339–346.
- [24] GUO H, YANG S X, CHEN H T, et al. Effects of AlN content on mechanical and optical properties of AlON transparent ceramics[J]. *Ceram Int*, 2020, 46(10): 16677–16683.
- [25] ZHENG K P, WANG H, XU P Y, et al. Effect of nitrogen content on optical properties of transparent γ -AlON polycrystalline ceramics[J]. *J Eur Ceram Soc*, 2021, 41(7): 4319–4326.
- [26] FENG Z, HUANG X, CHEN D, et al. Pressureless sintering of transparent AlON ceramic with assimilable γ - Al_2O_3 as sintering promoting additives[J]. *J Am Ceram Soc*, 2022, 105(5): 3189–3196.
- [27] BATYREV I G, TAYLOR D E, GAZONAS G A, et al. Density functional theory and evolution algorithm calculations of elastic properties of AlON[J]. *J Appl Phys*, 2014, 115(2): 023505.
- [28] GUO J J, WANG K, FUJITA T, et al. Nanoindentation characterization of deformation and failure of aluminum oxynitride[J]. *Acta Mater*, 2011, 59(4): 1671–1679.
- [29] BANDYOPADHYAY S, RIXECKER G, ALDINGER F, et al. Effect of reaction parameters on γ -AlON formation from Al_2O_3 and AlN[J]. *J Am Ceram Soc*, 2004, 85(4): 1010–1012.
- [30] TU B T, WANG H, LIU X A, et al. First-principles study on site preference of aluminum vacancy and nitrogen atoms in γ -alon[J]. *J Am Ceram Soc*, 2013, 96(6): 1937–1943.
- [31] WANG S F, ZHANG J, LUO D W, et al. Transparent ceramics: processing, materials and applications[J]. *Prog Solid State Chem*, 2013, 41(1–2): 20–54.
- [32] SHAHBAZI H, TATAEI M, ENAYATI M H, et al. Structure-transmittance relationship in transparent ceramics[J]. *J Alloys Compd*, 2019, 785: 260–285.

Effect of Mullite Addition on Microstructure and Optical Property of AlON Transparent Ceramics

SHI Rongwei^{1,2}, AN Liqiong¹, MAO Xiaojian², ZHANG Buhao^{2,3}, LI Jianmin², ZHANG Jian², WANG Shiwei²

(1. College of Ocean Science and Engineering, Shanghai Maritime University, Shanghai, 201306, China; 2. State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, China; 3. Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, United Kingdom)

Extended Abstract

Introduction γ -aluminum oxynitride (γ -AlON) is widely used for optical lens, transparent arms, and infrared windows due to its high transparency from the ultraviolet to mid-infrared range. To obtain a high-performance AlON transparent ceramic, each stage of its manufacture process should be controlled with cares, i.e., powder synthesis, forming, sintering and annealing. Sintering aid (i.e., Y_2O_3 , CaCO_3 , Y_2O_3 – La_2O_3 , etc.) is also used to improve the property of AlON transparent ceramic. However, the sintering temperature is still rather high, resulting in a high production cost. Recently, SiO_2 is used in AlON system, leading to a decreased temperature of hot isostatic pressing (HIP) (i.e., 1 810 °C). Unfortunately, however, the evaporation of SiO decomposed from SiO_2 could increase the micro-pores in pre-sintered bodies, leading to the density variations and then optical inhomogeneity after HIP. It is thus necessary to explore new Si-contained additive that is stable at a high temperature for the preparation of high-performance AlON transparent ceramics. Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) as a main phase of AlON has a superior high-temperature thermal stability, which is a promising application in AlON system. In this paper, AlON transparent ceramics were fabricated via pressureless sintering and hot isostatic pressing. In addition, the effect of mullite content on the microstructure of pre-sintered and hot isostatic pressed AlON ceramics and their corresponding optical property was also investigated.

Materials and method An γ -AlON powder with 0.02%–0.20% mullite in alcohol was ground by a planetary mill with high-purity alumina balls. After drying, sieving and then calcining, the mixed powder was pressed into pellets and then cold isostatic pressed to obtain AlON green bodies. The green bodies were pressureless-sintered in a flowing N_2 atmosphere at 1 880 °C for 4 h, and further hot isostatic pressed in a flowing Ar atmosphere at 1 800 °C and 200 MPa for 6 h to obtain AlON transparent ceramics.

The phase analysis of specimens was identified by a model D8 Advance X-ray diffractometer (XRD, Bruker Co., Germany) using nickel-filtered Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The bulk density of AlON ceramics was determined by a water immersion method based on Archimedes' principle. The chemically-etched and fracture surfaces of AlON ceramics were characterized by a model TM3000 scanning electron microscope (SEM, Hitachi Co., Japan). The average grain size was determined by a linear intercept line method with a correction factor of 1.56 via a software named Nano Measurer. The Raman spectra were recorded by a model

XploRA One-532 Raman spectrometer (Horiba Co., Japan) using a 532 nm Ar⁺ laser. The optical in-line transmittance spectra of HIPed AlON ceramics were measured by a model V-770 UV-Vis-NIR spectrophotometer (JASCO Co., Japan) and a model FT/IR-4600 Fourier transform infrared spectrometer (FTIR, JASCO Co., Japan).

Results and discussion The ground AlON powder mixed with mullite has a homogeneous distribution and the particle sizes are in the range of 0.2–1.6 μm with an average value of 0.7 μm. After pressureless sintering, all the XRD patterns of AlON ceramics with 0.02%–0.20% mullite match well with the standard cubic AlON phase (JCPDS 48-0686), and no extra peaks appear, indicating the dissolution of mullite in AlON lattice. The Raman spectra indicate the effect of the mullite content on the structure of the pre-sintered AlON ceramics. The phonon modes located at 316, 372, 628, 764 cm⁻¹ and 920 cm⁻¹ appear in all the samples, which are corresponded to the 3T_{2g}, E_g and A_{1g} modes of spinel. No shift of the Raman bands occurs and new bands do not appear, indicating the same structure and phases in AlON with different mullite contents.

All the pre-sintered AlON ceramics have a milk-white color and are opaque. The microstructure of fracture surfaces indicates that pores easily appear in all the samples. Large pores appear and density decreases in AlON ceramics with 0.10%–0.20% mullite. The grain size increases steadily with increasing mullite content. For the low content and high-temperature stability of mullite, a reaction of solid-state sintering is proposed as $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \frac{8}{3}\text{Al}_{\text{Al}}^{\times} \rightarrow 2\text{Si}_{\text{Al}}''' + \frac{2}{3}\text{V}_{\text{Al}}''' + \frac{13}{3}\text{Al}_2\text{O}_3$. Furthermore, for an oxygen-rich

AlON phase in the formation of AlON, the covalent bond strength of Al-N is higher than that of Al-O, and the diffusivity of oxygen is faster than that of nitrogen. AlON with a higher Al₂O₃ content is easy to sintering, leading to the grain growth. Al₂O₃ content increases and grains grow with increasing mullite content. The grains grow fast at a high mullite content, resulting in some trapped pores within the grains.

All the hot isostatic pressed AlON ceramics have a density of > 99.2% of the theoretical value and a high transparency. The density, grain size and transmittance of hot isostatic pressed AlON ceramic firstly increase and then decrease with increasing mullite content. AlON transparent ceramic doped with 0.05% mullite exhibits the maximum transmittance of 81.9% (4 mm thickness) at 2000 nm, with a density of 3.67 g/cm³ and an average grain size of 80.4 μm. Some pores in the grains appear in pre-sintered bodies at a higher mullite content, inhibiting the grain growth during the HIP process and decreasing the grain size. Also, some pores in the grains cannot eliminate and remain after HIP, degrading the transmittance.

Conclusions AlON transparent ceramics were fabricated via pressureless sintering at 1880 °C and hot isostatic pressing (HIP) at 1800 °C, respectively, with AlON powder and mullite. The same structure of AlON with different mullite contents of 0.02%–0.20% could be obtained. AlON transparent ceramic with 0.05% mullite exhibited the maximum transmittance of 81.9% (4 mm thickness) at 2000 nm. At a mullite content of > 0.10%, some pores in grains appeared in pre-sintered bodies, inhibiting the grain growth in the HIP process.

Keywords aluminum oxynitride; transparent ceramic; sintering aid; mullite; hot isostatic pressing