

含烧结助剂氮化硅陶瓷粉体的先驱体法制备及其烧结

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摘 要: 将金属钪和镁接枝三甲基硅基取代聚硅氮烷先驱体中, 先驱体在热解过程中就可以原位生成金属氮化物烧结助剂, 烧结助剂含量可通过钪、镁的接枝量进行精准调控。热解陶瓷为高纯氮化硅陶瓷, 碳元素含量低于 0.1% (质量分数), 氧元素含量低于 1.6%。含烧结助剂的氮化硅陶瓷可直接低温烧结制备高纯多孔氮化硅陶瓷块体, 相对密度可达到 99.4%, 具有良好的硬度和导热性能。原位生成烧结助剂避免了额外添加烧结助剂造成的杂质引入和混合不均匀的问题, 在高纯陶瓷烧结领域具有独特的优势。

关键词: 氮化硅; 先驱体; 烧结助剂; 原位; 多孔陶瓷

中图分类号: TQ12 文献标志码: A 文章编号: 0454-5648(2024)09-2767-06

网络出版时间: 2024-09-02



先驱体法是指通过化学合成方法制得高分子先驱体, 对先驱体进行热处理获得陶瓷材料的方法, 该方法可以从分子层面上实现陶瓷内部原子的均匀分布, 通过分子结构设计对先驱体组成结构进行设计和优化, 实现对材料微观结构和纯度的有效控制, 从而达到陶瓷材料的结构与性能可控的目的^[1]。由于先驱体转化陶瓷内部分布均匀, 相比于其他方法微观结构内晶种较少, 陶瓷更难结晶, 往往烧结温度更高, 烧结更困难^[2]。目前, 先驱体在陶瓷材料制备工艺中更多以陶瓷黏接剂或填孔剂形式参与^[3], 先驱体转化陶瓷直接烧结的报道相对较少^[4-6]。

氮化硅陶瓷是重要的结构陶瓷材料, 具有优异的耐高温、抗氧化、抗热震、高强度、耐磨损性能, 目前广泛应用于航空航天、机械加工、汽车制造及微电子领域中^[7]。氮化硅共价键程度高、扩散系数低, 因此烧结驱动力小, 难以实现烧结致密化, 需要在烧结过程中添加烧结助剂, 降低材料的烧结温度, 改善陶瓷内部的微观结构, 提高烧结材料的性能参数^[8-9]。比较常见的氮化硅烧结助剂包括氧化

镁、氧化铝、氧化钪等, 为获得更好的烧结效果, 复合烧结助剂的研究报道较多, 包括: 1) $\text{MgO}/\text{Y}_2\text{O}_3$ 体系^[10]及 $\text{MgO}/\text{Y}_2\text{O}_3/\text{ZrO}_2$ 体系^[11]; 2) $\text{MgO}/\text{Al}_2\text{O}_3$ 体系^[12]、 $\text{MgO}/\text{Al}_2\text{O}_3/\text{CeO}_2$ 体系^[13]及 MgO/AlPO_4 体系^[14]; 3) $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ 体系^[15]; 4) $\text{Al}_2\text{O}_3/\text{Yb}_2\text{O}_3$ 体系^[16]等。

高温下金属氧化物与氮化硅表面的氧化膜形成共熔液相, 促进氮化硅的扩散及晶型转变, 从而实现氮化硅的致密化烧结^[17]。同时, 金属氧化物烧结助剂的引入造成氮化硅晶粒中掺杂氧原子形成缺陷, 影响氮化硅陶瓷材料性能。现阶段控制氧含量主要采用如下几种方法: 1) 使用高纯氮化硅原料粉体; 2) 通过预处理除去氮化硅表面的氧化层; 3) 使用非氧化物烧结助剂如氮化物^[18]、氢化物^[19]等。

本工作针对先驱体转化陶瓷难烧结和添加烧结助剂引入氧元素影响性能的问题, 将金属元素接枝在先驱体上, 在先驱体热解过程中原位生成金属氮化物烧结助剂, 实现烧结助剂在陶瓷粉体中的原位无氧添加和均匀混合, 实现先驱体转化高纯氮化硅陶瓷的低温烧结。

收稿日期: 2022-02-22。 修订日期: 2024-03-16。

基金项目: 国家重点研发计划(2021YFB3200500); 宁波 3315 计划(2018 A-03-A); 先进能源科学与技术广东省实验室(HND20TDTH GC00)。

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Received date: 2022-02-22. Revised date: 2024-03-16.

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1 实验

1.1 含烧结助剂氮化硅陶瓷粉体的制备

将 14 g 三甲基硅基氯硅烷单体(Me_3SiNH) $_2\text{SiCl}_2$ 、0.14 g 氯化钇和 0.085 g 氯化镁溶于 20 mL 吡啶中,充分搅拌,加入 4 mL 丙胺,氮气氛下加热至 120 °C 反应 2 d。将混合物置于管式炉中,氮气氛下以 10 °C/min 加热至 400 °C 反应 4 h,再以 10 °C/min 加热至 1 000 °C 热解 4 h,冷却至室温,得到白色氮化硅粉体样品 SiN-1。氮化硅粉体样品 SiN-2 与样品 SiN-3 制备方法同上,样品 SiN-2 添加 0.055 g 氯化镁,样品 SiN-3 不添加氯化镁(见表 1)。

表 1 含烧结助剂氮化硅陶瓷粉体各组分理论含量

Table 1 Theoretical contents of components in silicon nitride ceramic powders with sintering additives

Sample No.	x/%		
	Si_3N_4	YN	Mg_3N_2
SiN-1	94	4	2
SiN-2	95	4	1
SiN-3	96	4	0

x—Mole fraction.

1.2 氮化硅陶瓷粉体的烧结

将氮化硅粉体研磨过筛,置于石墨模具中,进行放电等离子体烧结,烧结温度 1 450 °C,烧结压力 45 MPa,保温时间 30 min。烧结后得到的块体经研磨、抛光,进行材料性能测试与分析表征。

1.3 样品表征

使用 LECO ON836 型氧氮分析仪测定氮化硅粉体氮、氧元素含量。使用 LECO CS844 型碳硫分析仪测定氮化硅粉体的碳元素含量。使用 Bruker AXS D8 ADVANCE DAVINCI 型 X 射线粉末衍射仪测定氮化硅粉末和氮化硅块体的晶型。使用 Axiolab 5 型金相显微镜和 Regulus 8230 型高分辨冷场发射扫描电镜表征氮化硅块体表面形态和微观形貌。使用 Archimedes 排水法测定氮化硅块体的密度,根据测试密度与理论密度的比值,计算出氮化硅块体的相对密度。使用浸润法测定氮化硅块体的孔隙率。使用 Bruker TI980 型纳米压痕仪测定氮化硅块体的显微硬度。使用 Tukon2500 型 Vickers 硬度计测定氮化硅块体的 Vickers 硬度。使用 NETZSCH LFA467 型号激光导热仪测定氮化硅块体的热导率、比热容和热扩散系数。使用 NETZSCH DIL402C 型热膨胀仪测定氮化硅块体的热膨胀系数。

2 结果与讨论

2.1 接枝金属对氮化硅陶瓷性质的影响

图 1 为接枝金属聚硅氮烷先驱体分子结构示意图。由图 1 可见,以三甲基硅基取代聚硅氮烷先驱体为基础,通过氮原子对金属的配位及 N—H 与 M—Cl 键的反应实现金属对聚硅氮烷分子的接枝。通过红外光谱对先驱体进行表征,并未观察到金属—氮键,观察到金属—氧键,这是由于金属—氮键活性极高,暴露在空气中就发生快速地水解和氧化,金属—氮键快速转化为金属—氧键。

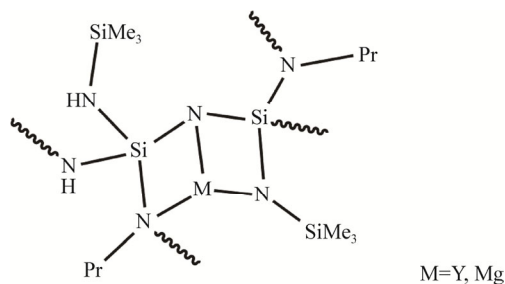


图 1 接枝金属聚硅氮烷先驱体分子结构示意图

Fig. 1 Molecular structure diagram of polysilazane precursor with metal elements

表 2 为烧结助剂含量不同的 3 种氮化硅陶瓷粉体碳、氧、氮元素含量。由表 2 可知,金属元素接枝量对热解陶瓷的杂质元素含量影响不大,与未接枝金属的热解氮化硅相比[C 为 0.06%(质量分数),O 为 1.20%]^[20],杂质氧元素含量提高,这是由于热解原位生成金属氮化物(氮化钇、氮化镁)活性极高,容易氧化水解,引入杂质氧元素。随着金属氮化物烧结助剂含量降低,样品 SiN-1 到样品 SiN-3 氧元素有略微降低,同时,含烧结助剂的氮化硅粉体暴露在空气中会观察到明显的放热,氧元素含量极大提高,以上现象也证明金属氮化物烧结助剂在热解过程中的原位生成。

表 2 含烧结助剂氮化硅陶瓷粉体碳、氧、氮元素含量

Table 2 Carbon, oxygen, nitrogen element contents of silicon nitride ceramic powders with sintering additives

Sample No.	w/%		
	C	O	N
SiN-1	0.05	1.65	34.32
SiN-2	0.05	1.60	34.91
SiN-3	0.06	1.46	35.61

w—Mass fraction.

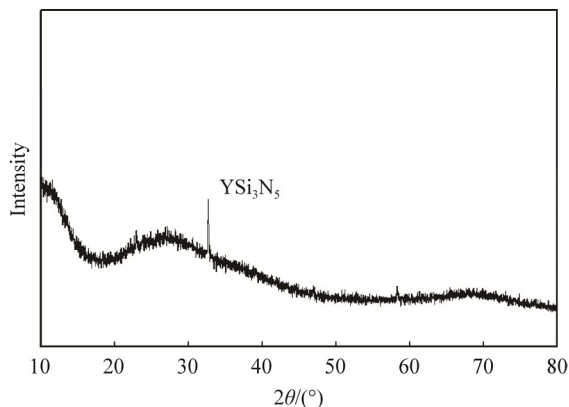
图 2 为含烧结助剂氮化硅陶瓷粉体的 X 射线粉末衍射谱。由图 2a 可见,大量的氮化硅以无定形态

存在, 镁原子以无定型氮化物形式掺杂在氮化硅中, 钇原子与氮化硅形成 YSi_3N_5 晶体。当氮化硅粉体加热至 $1\,500\text{ }^\circ\text{C}$ 时, 主体氮化硅开始结晶, 不添加镁原子的 SiN-3 只有 $\alpha\text{-Si}_3\text{N}_4$ 晶体, 随着镁原子添加量不断增加, $\beta\text{-Si}_3\text{N}_4$ 晶体含量逐渐增加(样品 SiN-2 中 $\beta\text{-Si}_3\text{N}_4$ 含量 3.71%, 样品 SiN-1 中 $\beta\text{-Si}_3\text{N}_4$ 含量 34.79%, 图 2b)。以上结果证明, 在氮化硅陶瓷中,

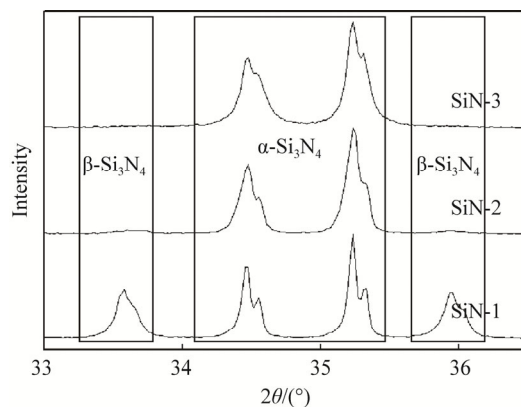
氮化镁主要起促进 $\alpha\text{-Si}_3\text{N}_4$ 到 $\beta\text{-Si}_3\text{N}_4$ 晶型转变的作用, 氮化钇与氮化硅形成 YSi_3N_5 , 起到活化晶格作用。

2.2 含烧结助剂氮化硅陶瓷的直接烧结

图 3 为样品 SiN-1 烧结氮化硅块体微观结构, 3 种含烧结助剂氮化硅陶瓷都可以通过放电等离子体烧结制备氮化硅块体, 但只有含镁量最高的样品 SiN-1

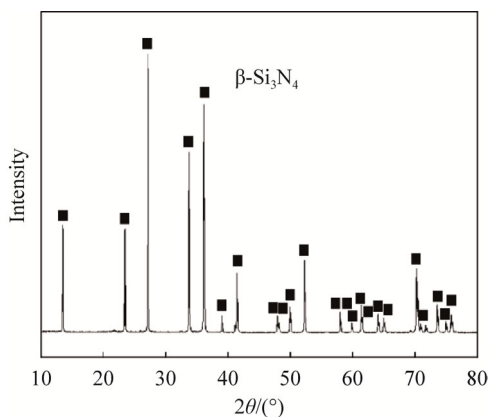


(a) SiN-1

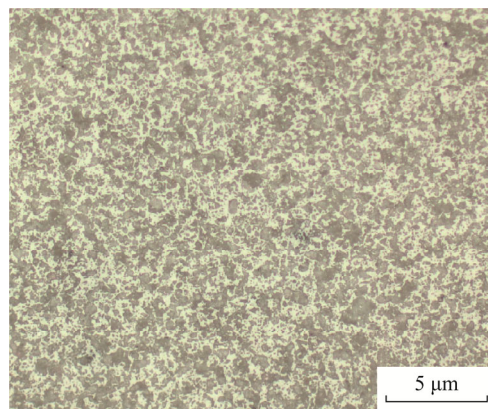


(b) Partial enlarged view of samples SiN-1, SiN-2 and SiN-3 in $1\,500\text{ }^\circ\text{C}$

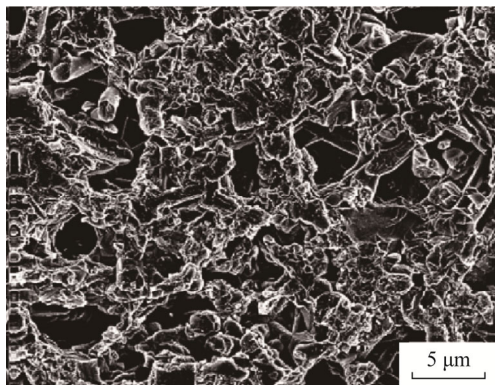
图 2 含烧结助剂氮化硅陶瓷粉体的 X 射线粉末衍射谱
Fig. 2 X-ray powder diffraction spectrum of silicon nitride ceramic powders with sintering additives



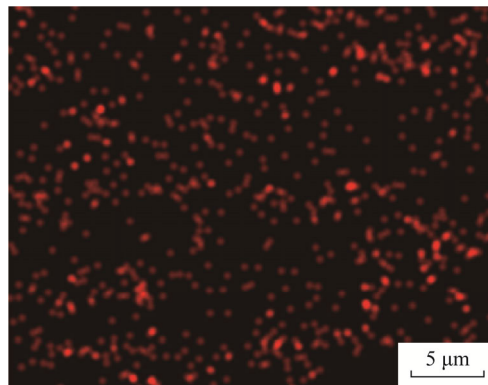
(a) X-ray powder diffraction spectrum



(b) Microscopic optical photo



(c) High resolution cold field emission scanning electron microscopy image



(d) X-ray nitrogen element energy spectrum

图 3 样品 SiN-1 烧结氮化硅块体微观结构
Fig. 3 Microstructure of SiN-1 sample sintered silicon nitride block

可以制备纯 β - Si_3N_4 晶型的块体(图 3a), 对样品 SiN-1 制备的块体进行表征和研究。通过金相显微镜观察块体呈现多孔形态(图 3b), 孔大小约为 $0.5\ \mu\text{m}$ 。测量块体密度为 $3.172\ \text{g}/\text{cm}^3$, 计算相对密度为 99.4%, 证明该多孔块体中, 孔主要以通孔形式存在, 不存在或存在极少量闭孔, 测量孔隙率为 30.6%。通过高分辨冷场发射扫描电子显微镜表征氮化硅块体微观形貌, 观察到大量棒状晶体存在, 棒状晶体为 β - Si_3N_4 , 框架由棒状晶体堆叠组成, 孔隙不规则且分布不规律(图 3c~图 3d)。金属氮化物烧结助剂与金属氧化物差异较大, 即使高温条件下仍保持固态, 无法与氮化硅形成高温熔体, 不能增加陶瓷流动性或发挥填隙功能, 金属氮化物只起到促进晶型转变和活化晶格促进晶粒增长的功能, 所以该方法制备的含烧结助剂氮化硅陶瓷烧结得到框架致密的多孔块体。

图 4 为样品 SiN-1 烧结氮化硅块体力学性能。使用纳米压痕仪对多孔氮化硅块体框架的硬度进行表征(图 4a), 框架平均硬度为 29.1 GPa, 平均弹性模量 229.1 GPa, 证明该多孔块体的框架部分致密度非常高, 为块体提供较高强度。使用 Vickers 硬度计对多孔氮化硅块体的整体硬度进行表征(图 4b), 硬度

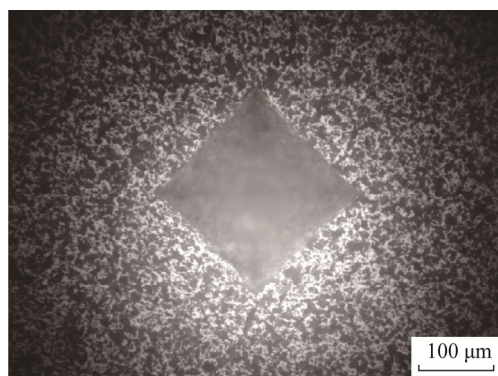
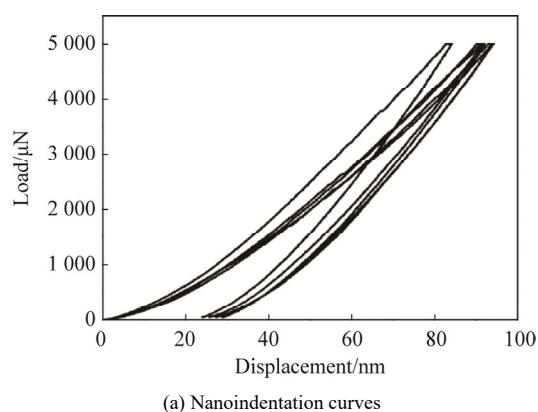


图 4 样品 SiN-1 烧结氮化硅块体力学性能

Fig. 4 Mechanical property of sample SiN-1 sintered silicon nitride block

为 2.51 GPa, 尽管该多孔块体有较强的框架, 但由于孔隙存在, 整体强度降低, 相比于其他多孔氮化硅块体仍体现出较高的硬度^[21]。

对多孔氮化硅块体的热性能进行表征, 25 °C 条件下热导率为 $20.451\ (\text{W}/\text{m}\cdot\text{K})$, 比热容为 $0.355\ \text{J}/(\text{g}\cdot\text{K})$, 热扩散系数为 $18.169\ \text{mm}^2/\text{s}$, 热膨胀系数在 $1200\ ^\circ\text{C}$ 以下整体低于 $4\times 10^{-6}/\text{K}$ (图 5)。由于孔隙存在, 热导率和热扩散系数出现明显的降低, 热膨胀系数仍维持较低的水平。

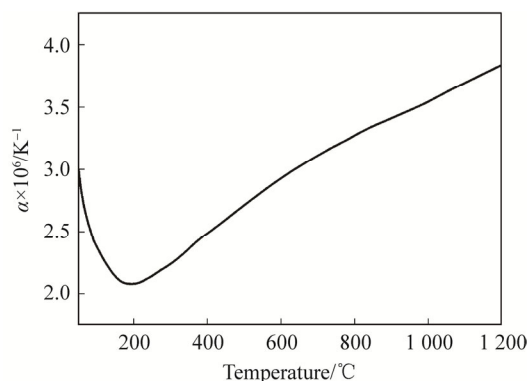


图 5 样品 SiN-1 烧结氮化硅块体热膨胀系数曲线

Fig. 5 Thermal expansion coefficient curve of sample SiN-1 sintered silicon nitride block

3 结论

本工作在三甲基硅基聚硅氮烷先驱体分子中接枝金属钇、镁元素, 金属元素含量可以按需调控, 该先驱体可以在热解过程中原位生成金属氮化物烧结助剂, 制备含烧结助剂的高纯氮化硅陶瓷粉体。该方法充分发挥了先驱体法的优势, 既实现了烧结助剂的原位无氧添加, 又实现了烧结助剂在陶瓷粉体中分子级别的均匀混合。同时, 这种含烧结助剂的氮化硅陶瓷粉体可以直接进行低温烧结制备多孔氮化硅陶瓷块体, 块体为纯 β - Si_3N_4 晶型, 具有良好的力学和热学性能, 硬度为 2.51 GPa, 25 °C 条件下热导率为 $20.451\ [\text{W}/(\text{m}\cdot\text{K})]$, 比热容为 $0.355\ \text{J}/(\text{g}\cdot\text{K})$, 热扩散系数为 $18.169\ \text{mm}^2/\text{s}$, 热膨胀系数在 $1200\ ^\circ\text{C}$ 以下整体低于 $4\times 10^{-6}\ \text{K}^{-1}$, 证明了该方法在陶瓷烧结工艺的可行性和潜在应用价值。

参考文献:

- [1] BIROT M, PILLOT J P, DUNOGUES J. Comprehensive chemistry of polycarbosilanes, polysilazanes, and polycarbosilazanes as precursors of ceramics[J]. Chem Rev, 1995, 95(5): 1443–1477.
- [2] WYNNE K. Ceramics via polymer pyrolysis[J]. Annu Rev Mater Res, 1984, 14(1): 297–334.
- [3] SCHWAB S T, BLANCHARD C R, GRAEF R C. The influence of

- preceramic binders on the microstructural development of silicon nitride[J]. *J Mater Sci*, 1994, 29(23): 6320–6328.
- [4] WAN J L, GASCH M J, MUKHERJEE A K. *In situ* densification behavior in the pyrolysis consolidation of amorphous Si–N–C bulk ceramics from polymer precursors[J]. *J Am Ceram Soc*, 2001, 84(10): 2165–2169.
- [5] VIARD A, FONBLANC D, LOPEZ-FERBER D, et al. Polymer derived Si–B–C–N ceramics: 30 years of research[J]. *Adv Eng Mater*, 2018, 20(10): 100969.
- [6] CHAUDHARY R P, PARAMESWARAN C, IDREES M, et al. Additive manufacturing of polymer-derived ceramics: Materials, technologies, properties and potential applications[J]. *Prog Mater Sci*, 2022, 128: 100969.
- [7] RILEY F L. Silicon nitride and related materials[J]. *J Am Ceram Soc*, 2000, 83(2): 245–265.
- [8] ZIEGLER G, HEINRICH J, WÖTTING G. Relationships between processing, microstructure and properties of dense and reaction-bonded silicon nitride[J]. *J Mater Sci*, 1987, 22(9): 3041–3086.
- [9] NISHIMURA T, XU X, KIMOTO K, et al. Fabrication of silicon nitride nanoceramics—Powder preparation and sintering: A review[J]. *Sci Technol Adv Mater*, 2007, 8(7–8): 635–643.
- [10] LIN Y B, NING X S, ZHOU H P, et al. Study on the thermal conductivity of silicon nitride ceramics with magnesia and yttria as sintering additives[J]. *Mater Lett*, 2002, 57(1): 15–19.
- [11] FENG Q Q, CHOCKALINGAM S, EARL D A. Microstructures of microwave-sintered silicon nitride with zirconia as secondary particulates[J]. *J Am Ceram Soc*, 2006, 89(12): 3770–3777.
- [12] 刘学建, 黄智勇, 黄莉萍, 等. 无压烧结氮化硅陶瓷的力学性能和显微结构[J]. *无机材料学报*, 2004, 19(6): 1282–1286.
LIU Xuejian, HUANG Zhiyong, HUANG Liping, et al. *J Inorg Mater*, 2004, 19(6): 1282–1286.
- [13] 杨亮亮, 谢志鹏, 李双. MgO–Al₂O₃–CeO₂复合烧结助剂对放电等离子烧结氮化硅陶瓷致密化和性能的影响[J]. *硅酸盐学报*, 2015, 43(12): 1712–1718.
YANG Liangliang, XIE Zhipeng, LI Shuang. *J Chin Ceram Soc*, 2015, 43(12): 1712–1718.
- [14] 李家亮, 陈斐, 牛金叶. 氮化硅陶瓷的低温常压烧结及其力学性能[J]. *硅酸盐通报*, 2011, 30(6): 1309–1313.
LI Jialiang, CHEN Fei, NIU Jinye. *Bull Chin Ceram Soc*, 2011, 30(6): 1309–1313.
- [15] 唐翠霞, 唐敬友, 姚怀, 等. 添加Y₂O₃–Al₂O₃烧结助剂的氮化硅陶瓷的超高压烧结[J]. *硅酸盐学报*, 2007, 35(7): 828–831.
TANG Cuixia, TANG Jingyou, YAO Huai, et al. *J Chin Ceram Soc*, 2007, 35(7): 828–831.
- [16] YANG L L, DITTA A, FENG B, et al. Study of the comparative effect of sintering methods and sintering additives on the microstructure and performance of Si₃N₄ ceramic[J]. *Materials*, 2019, 12(13): 2142.
- [17] MIR A H, AHMAD S N. A study on fabrication of silicon nitride-based advanced ceramic composite materials *via* spark plasma sintering[J]. *Proc Inst Mech Eng Part L J Mater Des Appl*, 2021, 235(8): 1739–1756.
- [18] EKSTRÖM T C, J D MACKENZIE K, J RYAN M, et al. Phases occurring in the Si₃N₄–YN system[J]. *J Mater Chem*, 1997, 7(3): 505–509.
- [19] 王为得, 陈寰贝, 李世帅, 等. 以YbH₂–MgO体系为烧结助剂制备高热导率高强度氮化硅陶瓷[J]. *无机材料学报*, 2021, 36(9): 959–966.
WANG Weide, CHEN Huanbei, LI Shishuai, et al. *J Inorg Mater*, 2021, 36(9): 959–966.
- [20] LI T H, ZHANG W, DUAN L T, et al. High-purity stoichiometric Si₃N₄ ceramics through trimethylsilyl-substituted polysilazanes[J]. *J Am Ceram Soc*, 2023, 106(6): 3329–3335.
- [21] CHEN F, YAN K, ZHOU J P, et al. Multilayer graphene and β-Si₃N₄ whisker-reinforced porous Si₃N₄ ceramics by spark plasma incomplete sintering[J]. *Mater Sci Eng A*, 2021, 823: 141770.

Preparation and Sintering of Silicon Nitride Ceramic Powders with Sintering Additives *via* Precursor Method

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Extended Abstract

Introduction Uniform distribution in molecular level of ceramics could be achieved by polymer-derived method. Comparing to other methods, fewer crystal seeds existed in microstructure of polymer-derived ceramics, which made it more difficult to sinter. Up to now, few reports focused on the direct sintering of the polymer-derived ceramics. For silicon nitride sintering, the introduction of metal oxide additives caused defects in the lattice of silicon nitride because of oxygen atoms, which could affect the properties of the material. This work focused on the sintering behavior of polymer-derived ceramics and the issue of performance degradation caused by introducing oxygen elements in sintering additives. The metal elements were connected to the precursor molecule and formed the metal nitride sintering additives during pyrolysis process. The method could help to achieve the *in-situ* non-oxygen addition and uniformly mixing of sintering additives, and the followed low-temperature sintering could achieve the high-purity silicon nitride ceramics.

Methods 4 mL of propylamine was added into a solution of trimethylsilyl chlorosilane monomer (14 g), yttrium chloride (0.14 g) and magnesium chloride (0.085 g) in pyridine (20 mL) at room temperature in N₂ atmosphere. The mixture was warmed up to 120 °C

and stirred for 2 d. The mixture was then heated to 400 °C for 4 h in N₂ atmosphere and further heated to 1 000 °C with the rate of 10 °C/min, finally the mixture were holding at 1 000 °C for 4 h and then cooled to room temperature naturally. A white silicon nitride powder SiN-1 was obtained. Silicon nitride powders SiN-2 and SiN-3 were prepared by the same method, in which 0.055 g magnesium chloride was added in SiN-2 and no magnesium chloride was added in sample SiN-3. Silicon nitride ceramics was prepared through spark plasma sintering of silicon nitride powders in 1 450 °C, 45 MPa for 30 min. Before characterization of the silicon nitride ceramics, surface of it was pre-polished.

Results and discussion Based on trimethylsilyl-substituted polysilazane precursors, the Y and Mg elements were successfully connected to N with the reaction of M-Cl to N-H and coordination. Through pyrolysis process, three kinds of ceramic powders SiN-1, SiN-2 and SiN-3 were obtained. The main component of these powders was silicon nitride, and content of C was below 0.1%, that of O was below 1.6%. As the content of metal decreased, there is a slight decrease in oxygen contents, being due to the high reactivity of metal nitrides. When treated at 1 000 °C, a large amount of amorphous silicon nitrides with small amount of magnesium nitrides via the dope of magnesium. Small amount of YSi₃N₅ with Si₃N₄ via the dope of yttrium. When ceramics were heated to 1 500 °C, amorphous silicon nitride began to crystallize, and sample SiN-3 only contained α -Si₃N₄. As the amount of magnesium increased, the content of β -Si₃N₄ crystal gradually increased. These results demonstrate that magnesium nitrides could promoted the transformation of amorphous Si₃N₄ to β -Si₃N₄ crystalline, while yttrium nitrides activated the lattice of Si₃N₄ crystal.

Silicon nitride ceramics were prepared by spark plasma sintering when three types of silicon nitride ceramic powders acted as main raw materials, but only SiN-1 powders with the highest magnesium content could obtain pure β -Si₃N₄. The frame of the obtained ceramics was mainly composed of stacked rod-shaped β -Si₃N₄ crystals. These results prove that the pores in porous ceramics were mainly through-pores, and few closed-pores. The porous ceramics showed a hardness of 29.1 GPa, an elastic modulus of 229.1 GPa, which attributed to the speical porous structure. At 25 °C, the ceramics possessed a thermal conductivity of 20.451 (W/m·K), a specific heat capacity of 0.355 J/(g·K), a thermal diffusion coefficient of 18.169 mm²/s, and an overall thermal expansion coefficient less than 4×10⁻⁶/K in the range of room temperature to 1 200 °C. Due to the presence of pores, a significant decrease in thermal conductivity and thermal diffusion coefficient can be obtained, while the coefficient of thermal expansion remained relatively low.

Conclusions Metal element Y and Mg were successfully connected to trimethylsilyl-substituted polysilazane precursors and contents could be adjusted as needed. Metal nitride sintering additives were *in-situ* generated during pyrolysis process and polymer-derived high-purity silicon nitride ceramics with sintering additives were prepared. This method could help to achieve both *in-situ* non- oxygen addition and molecular level uniform mixing of sintering additives in ceramic powders. Low-temperature sintering could help to achieve the silicon nitride ceramic powders which resulting in the obtained silicon nitride ceramics with good mechanical and thermal properties.

Keywords silicon nitride; precursor; sintering additive; *in situ*; porous