

高温透波材料在微波烧结领域的应用及研究进展

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摘 要: 微波烧结技术凭借选择性加热、均匀加热及省时高效等优势得以飞速发展。为进一步提升微波烧结设备的能源利用效率和使用寿命, 开发适用于微波烧结设备的结构功能一体化材料已成为当下的重点。介绍了微波烧结技术的工作原理及发展现状, 综合评述了高温陶瓷透波复合材料的研究进展, 提出了氧化物陶瓷基透波复合材料在微波烧结技术发展中的关键科学技术问题。最后, 讨论了陶瓷基透波材料未来的发展趋势。

关键词: 微波烧结技术; 高温透波材料; 耐火材料; 多孔氧化物陶瓷

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中国制造业、典型流程工业等的发展在加快了国民经济发展的同时也产生了较高的碳排放, 引起严重的环境污染, 而且传统工业窑炉平均热效率相比西方先进工业国家有一定差距, 造成中国单位 GDP 能耗达世界平均水平的 130%^[1-2]。为此, 促进工业窑炉逐渐向绿色、智能化方向发展已成为双碳大背景下的必然趋势。以陶瓷行业为例, 相关发达国家陶瓷窑热效率已到 50% 以上, 中国国内仅有 28% 左右^[3], 除窑炉结构设计、耐火材料的保温性能等因素外, 影响窑炉能耗的很大一部分原因是传统高温窑炉工作时加热源与物料间能量传递过程中产生的能量损失。因此, 研发清洁能源的新型烧结技术, 实现制备技术的高效、绿色化发展也是减污降碳环节中的一个重要途径。区别于传统烧结的温度梯度式热传递加热方式, 微波烧结技术体现出快速烧结的特点^[4], 已成为一种用于矿物加工、粉体及陶瓷制备等多领域的既高效又环保的方法, 常被称作“21 世纪新一代烧结技术”^[5]。由于微波与物料间相互作用, 烧结过程中有效热源大多位于材料内部且不需

要将整个炉膛加热到烧结温度, 这不仅反映出微波烧结潜在的节能性, 同时也赋予其低能耗、选择性加热及体积加热等优势^[6-7]。例如, 研究表明微波烧结可降低材料烧结所需温度、提高烧结效率^[8-9], 即使在较低温度(1300 °C)也能获得性能良好、显微组织正常的硬质合金^[10]; 采取热压和传统烧结法需在 2000~2300 °C 范围内完成致密化烧结的 ZrB₂ 基复合材料, 通过微波烧结可将温度降至 1 850 °C, 所得 ZrB₂-SiC 复合材料的弯曲强度和断裂韧性最高可达 625 MPa 和 7.18 MPa·m^{1/2}^[11]等, 同时, 相比常规方法, 微波烧结能够加速材料的致密化和晶粒生长, 更有利于优化材料性能^[12-14], 且借助不同材料与微波耦合能力间的差异, 微波选择性加热在材料结构设计、矿物提纯等领域也展示出很重要的作用^[15-17]。基于此烧结原理, 对炉体材料也提出了更高的要求: 1) 耐高温; 2) 工作温度范围内的高强度低导热性; 3) 高透波率及稳定的介电性能, 以此保证炉体的使用寿命及烧结时微波利用效率最大化。目前, 已有多种高温透波材料,

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如 β -SiAlON 陶瓷、氮化硅陶瓷、 $\text{Si}_2\text{N}_2\text{O}$ 陶瓷、氧化铝陶瓷、莫来石及相关复合材料等^[18-24], 但研究多集中于飞机天线罩领域, 关于微波烧结炉用透波材料仍缺乏系统介绍。

本文总结了不同类型高温透波材料研究现状, 结合微波烧结工作原理及应用需求对比了各类材料的优缺点, 讨论了透波材料在微波烧结领域未来的发展趋势和应用前景。

1 微波烧结技术概述

微波烧结概念于 20 世纪 60 年代末提出, 设备主要包括微波发生器、波导管和加热腔体 3 部分(图 1a), 烧结过程中由微波发生器产生的微波经波导管传输穿过内外多层保温隔热体进入烧结腔内, 最后, 透过坩埚与物料相互作用, 在物料内部产生介电损耗进而将微波能转化为热能, 电

磁波与材料之间的相互作用包括反射、吸收和传输 3 种^[25], 如图 1b 所示。其中, 与炉衬材料不同的是, 窑具吸收电磁波能量自身被加热后, 有利于延长被煅烧物料或烧成制品的烧成保温时间、达到保温与节能目的, 因此, 可具有一定吸波性。微波烧结炉的工作频率包括 915 MHz、2.45 GHz、6 GHz、28 GHz 及 60 GHz 等多种, 其中, 不同工作频率的选择与微波发生器相匹配, 市售微波烧结设备用频率多为 2.45 GHz, 对应微波发生器为磁控管, 而空腔类型主要包括单模和多模腔^[26], 单模腔尺寸可以调整以接近谐振条件, 电场分布对应于稳定的平稳波(图 1c 左), 而多模腔是一种大腔, 通常是平行六面体, 由于波在 2 侧多次反射导致多种传播模式和复杂的场分布(图 1c 右), 多模腔内的样品常放置在旋转板上, 以获得更为均匀的周围场。

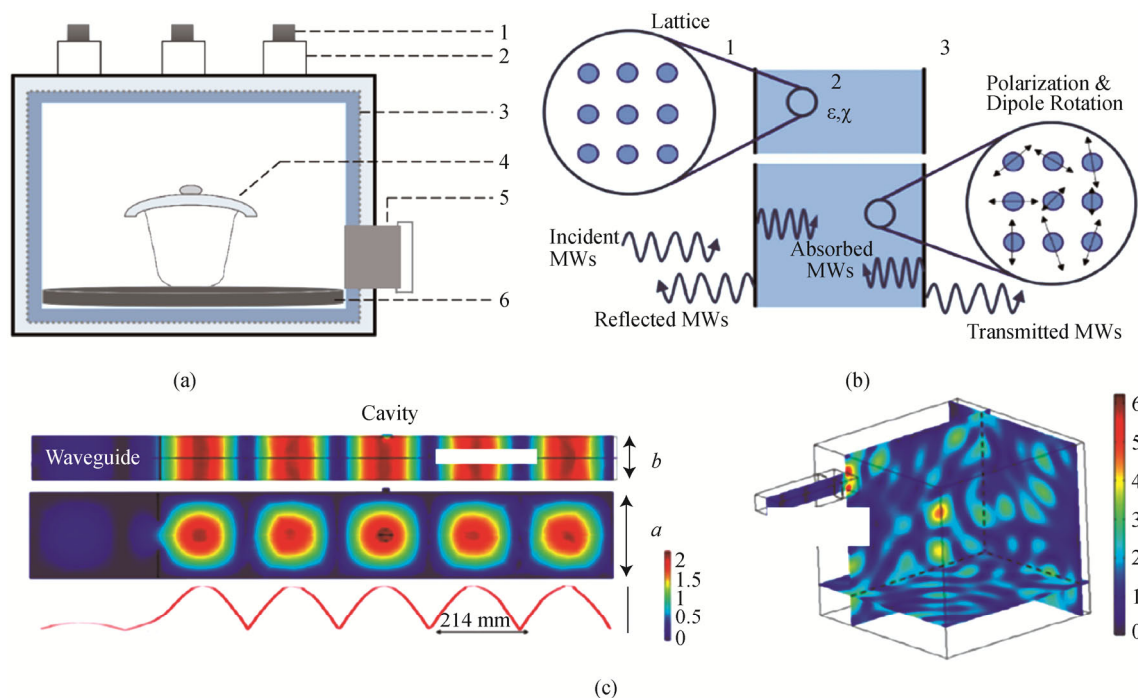


图 1 (a)微波烧结腔体结构(1-微波发生器 2-波导管 3-保温隔热体 4-坩埚 5-炉门 6-物料承载台); (b)微波与陶瓷材料相互作用机制^[25]; (c)微波烧结腔体几何形状和电场: 单模腔(左)多模腔(右)^[26]

Fig. 1 (a) Microwave sintering chamber structure (1-microwave generator, 2-waveguide, 3-thermal insulation body, 4-crucible, 5-furnace door, 6-material bearing platform); (b) Interaction mechanism between microwave and ceramic materials^[25]; (c) Geometry and electric field used in MWS: single-mode(left) and multimode cavities(right)^[26]

表 1 整理了国内外部分微波高温设备生产企业、经营设备类型及微波高温设备相关参数, 其中, 微波实验设备代表微波干燥箱、微波马弗炉、微波管式炉、烧结炉、热解炉、气氛炉及微波催化合成、萃取、消解等设备, 工业微波设备则代

表用于食品或药品等行业的加热、杀菌或干燥设备, 微波超声系列指超声波清洗、超声波材料气蚀及超声波破碎等设备, 微波设备配件为环形器、磁控管及漏磁变压器等零部件。目前, 使用微波烧结设备也已成功制备出 Al_2O_3 、 B_4C 及 Si_3N_4 等

多种材料,微波烧结技术也凭借快速加热等诸多优势吸引了广泛关注,尤其对于常规烧结温度需达到 2 000 °C 以上的材料展现出较好的应用前景。然而,尽管由理论层面出发,直接微波耦合效果可能更好,但为了避免直接微波加热出现升温制度的不可控甚至形成破坏性热点,而且该方法无法在不形成等离子体的情况下达到高温,大多数实验工作往往使用基座辅助微波加热^[27–29],其中,较为常见的是 SiC 基座^[30]。此外,现已衍生出微波辅助热压烧结^[31]、微波辅助碳还原^[32]、微波辅助辐射混合烧结^[33]及微波烧结超声辅助^[34]等多种烧结方法。例如, Kerbart 等^[35]利用如图 2a 所示的微波压力辅助系统,无需特定气氛在 1100 °C 保温 8 min 获得镁铝尖晶石陶瓷,且 1600 nm 处其

透过率可高达 83%,如图 2b 所示。Li 等^[36]通过微波辅助碳热还原法以 TiO₂、B₄C 和炭黑为原料在 1450 °C 合成高纯 TiB₂,实验流程如图 2c 所示,所得材料平均晶粒尺寸为 0.75 μm,利用火花等离子烧结将 TiB₂ 粉末在 2000 °C、50 MPa 压力下保持 15 min 后相对密度为 97.9%,明显高于市售 TiB₂ 粉末(约为 90.2%)。Li 等^[37]利用微波辅助烧结技术得到 Y₂O₃ 稳定 ZrO₂。结果表明,微波烧结后样品结晶度和稳定性显著提高, Huang 等^[38]将微波技术用于烧结 Al₂O₃–ZrO₂ 粉末也得到了类似结果。然而,受限于大尺寸微波场的稳定性、不同材料间的介电性能差异以及高频率设备造价等多重因素,如何实现微波烧结大规模的工业化应用仍是今后需解决的一个重点问题。

表 1 国内外微波高温设备生产企业及设备信息

Table 1 Domestic and foreign enterprises of microwave high-temperature equipment and production innformation

Company(website)	Equipment type	Equipment parameters
HUNAN HUAIE MICROWAVE TECHNOLOGY CO.,LTD. http://www.huaemw.com/	Microwave experimental equipment	2.45GHz, 1550°C 3/5kW
Hunan Changyi microwave technology Co., LTD http://www.changemw.com/	Microwave experimental equipment and microwave equipment accessories	2.45GHz, 1630°C 3/5kW
Nanjing Sanle Microwave Technology development Co., LTD https://www.sanlemicrowave.com/	Industrial microwave equipment and microwave equipment accessories and microwave equipment accessories	2.45GHz, 1200°C 3/9/12/25kW
HUNAN THERSUN THERMAL ENERGY TECHNOLOGY CO., LTD http://www.thersun.com/	Industrial microwave equipment and microwave equipment accessories	2.45GHz, 1650°C 1.5/3/6/12kW
Changsha Longtai microwave thermal engineering Co., LTD	Industrial microwave equipment and microwave equipment accessories	2.45GHz, 1600°C 3/4/6/8kW
NANJING XIANOU INSTRUMENT MANUFACTURING CO.,LTD http://www.xokeji.com/	Microwave experimental equipment and microwave ultrasonic series	2.45GHz, 1500°C 1.5/3/5kW
Qingdao anix microwave automation equipment Co., LTD http://www.qdanks.cn/	Industrial microwave equipment and microwave equipment accessories	2.45GHz, 1500°C 1/2kW
Yantai Baoguang microwave machinery Equipment Co., LTD http://www.ytbaoguang.com/	Industrial microwave equipment and microwave equipment accessories	2.45GHz 3/9/18/150kW
JIANGSU NELE INSTRUMENT EQUIPMENT MANUFACTURING CO.,LTD http://www.jsnele.cn/	Microwave experimental equipment and microwave ultrasonic series	3/5/8/15kW 1800°C
Tangshan Renshi Juyuan Microwave Instrument Co., LTD http://www.rsjywb.com	Microwave experimental equipment	2.45GHz, 1550°C 2/4kW
SAIREM(France) https://www.sairem.com/	Industrial microwave equipment and microwave equipment accessories	-
VB Ceramic Consultants(India) https://www.vbceramics.com/	Microwave experimental equipment	2.45GHz, 1600°C 10kW
CEM(America)	Microwave experimental equipment	-

Note: This table can only provide the reader with the type of equipment, the detailed equipment information and model still need to enter the official website of the enterprise.

2 微波传输机理及性能表征

2.1 微波传输机理

透波材料是指能够透过特定频率或频段电磁波

的介质材料,但“透波”这一概念往往是相对的,电磁波在通过介质时会存在不同程度的能量损失,如图 1b 所示,其中电磁波反射主要发生在介质与空气之间的界面上,电磁波吸收常发生在介质内部,主

要为外部电场存在时介质极化现象引起的电磁波能量损失。与吸波材料类似，透波材料的波传输系数由介电常数和损耗正切值决定，介电常数可反映介质极化程度及其对电磁波的存储能力，介质的极化包括电子极化、离子极化、取向极化及界面极化等多种，不同类型介电极化现象已在图 3 中展示。其中，电子极化与离子极化均属于位移式极化，是一种弹性的、瞬间完成的极化，过程中不消耗能量；

取向极化也叫偶极极化，属于非弹性极化，该过程与分子热运动有关，消耗一定能量；界面极化是指在外加电场作用下，介质中电荷分布不均匀，产生电偶极矩，这种极化通常需要较长时间，也是非均匀相介质中极化的主要形式^[39-41]。介电损耗则是指电磁波通过介质传输时被消耗，转化为热能的能力。简单来说，电磁波入射至材料后，反射及损耗越小，材料的波传输效果越好。

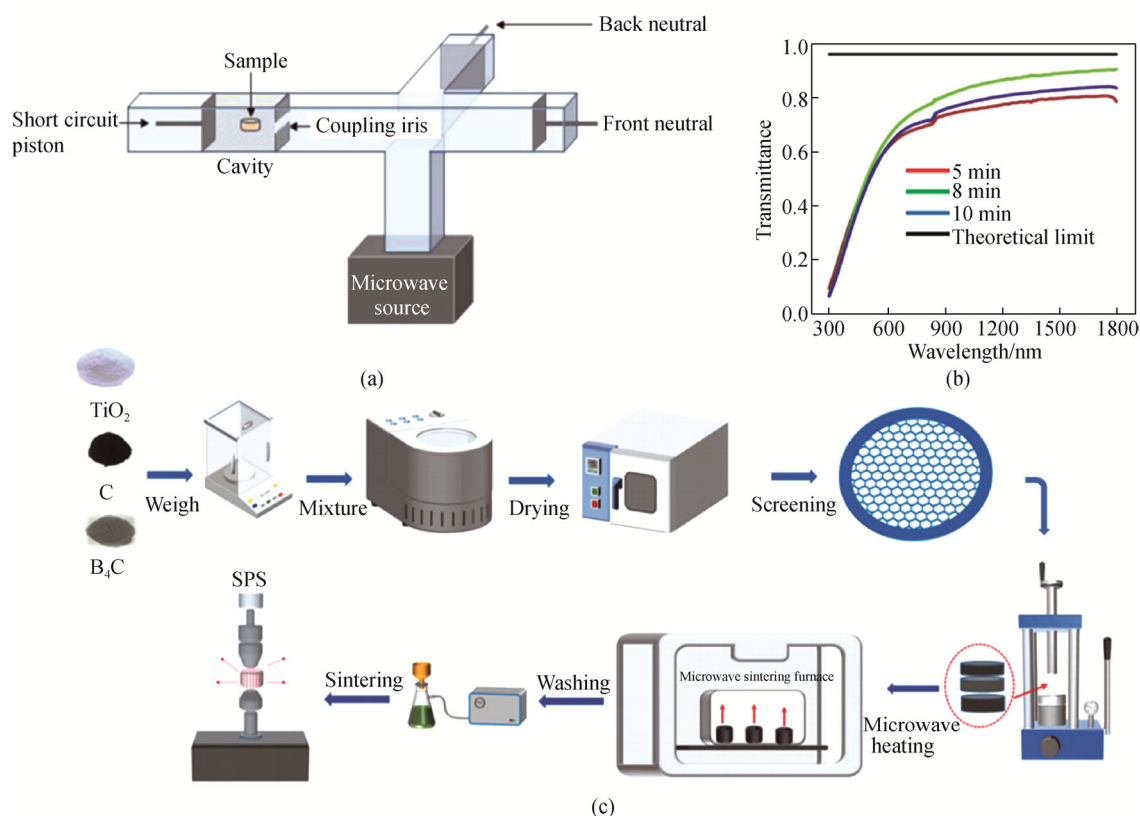


图 2 (a)2.45 GHz 微波炉方案俯视图；(b)不同停留时间下材料透过率随波长的变化关系曲线^[35]；(c)微波辅助碳热还原技术合成 TiB_2 实验流程图^[36]

Fig. 2 (a) Top view of the 2.45 GHz microwave oven scheme; (b) The relationship between material transmittance and wavelength at different residence times^[35]; (c) Experimental flow chart of synthesizing TiB_2 by microwave assisted carbothermal reduction^[36]

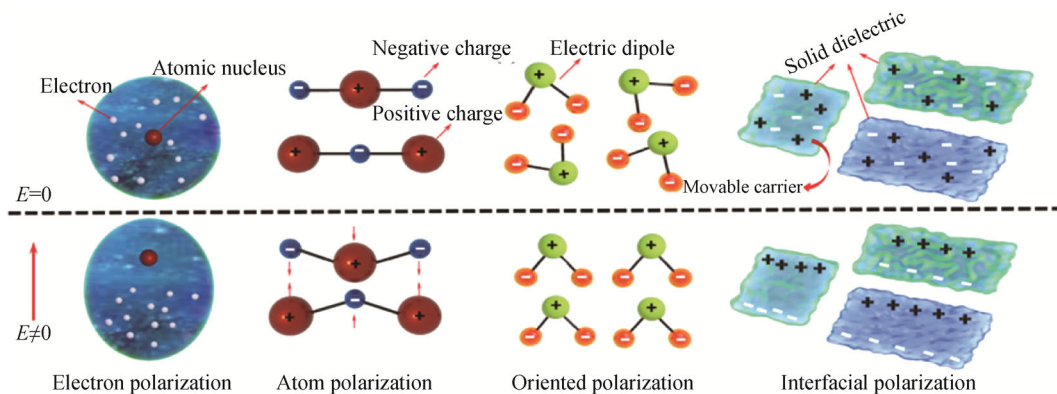


图 3 介电极化原理图^[39]

Fig. 3 Schematic diagram of dielectric polarization^[39]

依据能量守恒原理, 发射出的电磁波能量包括透射、反射和功率损耗, 可以用式(1)表示^[42]:

$$|\Gamma|^2 + R^2 + L = 1 \quad (1)$$

$$R = \frac{1-n}{1+n} \quad (2)$$

$$n = \frac{\varepsilon \cos \theta}{(\varepsilon - \sin^2 \theta)^{1/2}} \quad (3)$$

$$L = \left(\frac{2\pi d}{\lambda} \right) \left[\frac{\varepsilon \tan \delta}{(\tan \delta - \sin^2 \theta)^{1/2}} \right] \quad (4)$$

式中: $|\Gamma|^2$ 为功率传输系数; R^2 为功率反射系数; L 为功率损耗; n 为材料的折射率; Γ 为微波透射率; ε 为相对复介电常数; d 为样品厚度; λ 为电磁波长; θ 为电磁波入射角(波垂直入射时, $\theta=0$)。透波材料是指对波长在 1~1000 mm、频率在 0.3~300.0 GHz 范围的电磁波的透过率大于 70% 的材料^[43], 即 $\Gamma > 70\%$ 。材料的波传输性能与其化学组成、微观结构以及环境条件等因素有关。

2.2 微波传输性能表征

1) 介电常数、介电损耗

耐火材料透波性能的强弱主要通过介电常数 ε 及介电损耗 $\tan \delta$ 衡量, 表 2 列出了微波烧结合耐火材料介电性能评价参考标准。由于透波类材料介电损耗较低, ε 、 $\tan \delta$ 通常使用谐振腔法测量, 公式如下:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad (5)$$

式中: ε' 、 ε'' 分别为介电常数实部和虚部, 代表储存、消耗电磁能的能力。通常 0.3~300.0 GHz 频率范围内, $\varepsilon < 10$ 、 $\tan \delta$ 在 $10^{-1} \sim 10^{-3}$ 数量级范围内时有利于更大的电磁波透过。介电常数 ε 、介电损耗正切值 $\tan \delta$ 大小常与频率及温度变化密切相关^[41], 频率升高时, ε 不断降低最终趋于稳定, $\tan \delta$ 呈波动式变化。 ε 随温度的变化较为复杂, 低温范围内 ε 的变化程度较小, 但随着温度升高、分子的热运动加快, 削弱了物质的结合力, 所以在外电场的作用下, 材料更易被极化, ε 呈指数式规律上升, 而当温度升高到一定数值后, ε 值反而会出现下降的趋势。

2) 穿透深度

穿透深度 D_p 也可用于表征材料波传输性能, 它是指当电磁波入射到材料上时, 能量衰减到原始入射波 $1/e(36.8\%)$ 时的厚度, 计算公式如下^[45]:

$$D_p = \frac{\lambda_0}{2\pi \cdot (2\varepsilon')^{1/2}} \left\{ \left[1 + \left(\frac{\varepsilon''}{\varepsilon'} \right)^2 \right]^{1/2} - 1 \right\}^{-1/2} \quad (6)$$

式中: ε' 、 ε'' 分别为介电常数实部和虚部; λ_0 为入射波长。材料穿透深度越大, 其微波传输性能越好。对于微波窑炉内衬材料, 更大的穿透深度有利于材料厚度及力学性能的调控。由式(6)可知, 除材料本身特性外, 穿透深度与波长变化有关, 频率越高, 波长越短, 其穿透力也越弱。

表 2 微波烧结合耐火材料介电性能评价参考标准^[44]

Table 2 Reference standard for evaluating the dielectric properties of microwave refractory materials^[44]

Evaluation parameters	Dielectric constant(ε)	Dielectric loss factor(ε'')	Dielectric loss tangent($\tan \delta$)
Wave-transmitting material	1–10	0.001–0.1	0.0001–0.01
Wave-absorbing material	10–30	0.3–12	0.1–1
Wave-reflecting material	10–30	0.004–0.01	0.001–0.01

由于高温下(>1000 °C)耐火材料的透波性能暂无国家标准测试方法, 王佳等^[44]将所得样品置于微波马弗炉中, 利用样品升温速率反映其透波性能: 升温速率越小, 则表明材料透波性能越好, 该方法可用于比较不同材料间透波性能的好坏, 但无法直观体现材料具体的透波率大小, 在实际应用中仍存在一定的局限性。

3 用于微波窑炉内衬的高温透波材料研究进展

耐火材料的微波传输性能与温度密切相关, 特别是高温下材料介电性能的变化会严重影响微波烧

结设备的工作效率。对高温环境下材料波传输性能的研究主要集中在国防和军事航天领域, 主要包括氮化物、氧化物、硅酸盐及磷酸盐等陶瓷材料, 但关于此类材料在工业微波频率范围内高温介电性能的研究仍十分欠缺, 这也侧面反映了这一领域的研究价值。本文从上述几种高温透波材料类型出发, 参照现有文献资料中其他频段下材料的介电性能, 同时依据微波烧结合耐火材料所需的抗热震、耐高温及良好的隔热等基本性能条件, 对不同类型透波材料的优缺点整理比对, 并对其用于窑炉衬体材料的可行性加以分析, 希望为今后透波类耐火材料的研究提供一定的借鉴意义。

3.1 陶瓷耐火砖

在窑炉衬体材料的实际应用中,对具有多孔结构材料的研究更加广泛,一方面,孔隙的存在可以降低材料的导热系数,使其具有更好的保温隔热效果^[46];另一方面,由于空气具有最低的介电常数($\epsilon=1.0000\ 5$),多孔陶瓷结构有利于获得更低的介电常数^[24]。尽管多孔氮化物及其衍生物陶瓷(如 Si_3N_4 、 SiAlON 及 $\text{Si}_2\text{N}_2\text{O}$ 等)曾被认为是很有前途的透波材料,其介电常数可以在 2~8 的范围内进行调整,同时具有优异的机械性能^[47-49]。然而,对于微波窑炉衬体材料,长期高温工作是材料应用的基础,多孔氮化物材料由于其固有的开放孔隙率和高比面积导致温度高于 900 °C 时出现氧化现象,机械和介电性能变差,加之复杂的技术及昂贵的成本等因素极大地限制了氮化物陶瓷的大规模应用^[42, 50]。因此,低成本多孔氧化物陶瓷的发展仍然是高温波传输领域的重要热点。

3.1.1 氧化硅系列 熔融石英陶瓷具有较为稳定的介电常数(3~4)和较低介电损耗(4×10^{-4}),当温度低于 500 °C 时,石英陶瓷在 915 MHz 和 2.45 GHz 频率下的相对介电常数几乎保持不变,500~1000 °C 温度范围内介电常数增加约 2%,温度高于 500 °C 时相对介电损耗系数增加 5~7 倍,仍为 10^{-2} 量级,在电磁波透明材料领域显示出较好的应用前景。图 4a 与图 4b 分别为不同频率下熔融石英陶瓷的功率传输系数(PTC)随厚度变化的温度依赖性曲线,由此可以看出,熔融石英陶瓷在 2360 MHz 频率下存在多个微波传输峰,对应厚度分别为 0.033、0.065 m 及 0.098 m 左右,表明通过选择传输峰对应的厚度值,可以获得良好的微波传输效果^[51]。Bergmann 等^[52]提出一种利用共面波导传输线技术对熔融石英材料介电性能进行检测的方法,所得复合材料在 320 MHz~325 GHz 范围内介电常数为 3.87 ± 0.03 ,损耗正切 $\tan\delta < 5\times 10^{-3}$ 。

此外,石英陶瓷的导热系数和热膨胀系数($0.54\times 10^{-6}\text{ K}^{-1}$)均较低、抗热冲击性良好,尽管其机械强度相对较差(约为 50 MPa),但目前已有大量研究表明,可通过向原料中引入 BN、氮化硅、石英纤维、石墨烯或二氧化锆等加以改善,例如 Sun 等^[53]在熔融石英陶瓷中添加 0.5%BN 纳米片后发现复合材料的弯曲强度和断裂韧性分别提高了 53% 和 32%。Huang 等^[54]制备晶须含量为 10%的 $\text{Si}_3\text{N}_4/\text{SiO}_2$ 陶瓷的抗弯强度比纯 SiO_2 增加了 7.75%,10 GHz 处 ϵ 与 $\tan\delta$ 分别为 3.37 和 1.10×10^{-3} 。

Wan 等^[55]在熔融石英陶瓷中加入 10% ZrO_2 后材料弯曲强度提高了 31.5%,达到 97.6 MPa,1 MHz 处其介电常数及介电损耗分别为 4.63 和 1.55×10^{-3} 。Yin 等^[56]研究发现,固体负载的增多可以提升力学性能(62.2~72.3 MPa),材料在 2~18 GHz 频率范围的介电常数和介电损耗切线还保持在 2.52~4.36 及 $0.19\sim 1.71\times 10^{-2}$ 之间,以上结果均表明,熔融石英陶瓷是作用于高温透波领域的结构功能一体化材料。然而,尽管 BN_w/SiO_2 复合材料弯曲强度高于 100 MPa,热膨胀系数 $1.34\times 10^{-6}\text{ K}^{-1}$,且具有优异的透波性能,在 20~40 GHz 范围内具有低介电常数为 3.77,损耗切线为 1.25×10^{-3} ,但如图 4c 和图 4d 所示,孔隙率的增大在优化介电性能的同时也会导致材料弯曲强度下降^[57],且该体系在高温下(1050 °C 以上)会发生相转变^[6],在基体与晶界处形成微裂纹,导致其使用温度受限,Tong 等^[58]采用低温化学气相沉积、模板和等静压 3 种工艺相结合的高效干法制备了 $\text{Si}_3\text{N}_4/\text{SiO}_2$ 泡沫陶瓷,该材料具有低密度($0.38\text{ g}\cdot\text{cm}^{-3}$)、高抗压强度(7.5 MPa)、低热导率($0.081\text{ W}/(\text{m}\cdot\text{K})$)和优异的介电性能($\epsilon < 1.32$, $\tan\delta < 9\times 10^{-3}$, 8~18 GHz),但在空气中的最高工作温度为 1100 °C。而关于方石英结晶导致材料机械性能下降的问题,Huang 等^[59]采用注浆法制备了添加 $\beta\text{-Si}_3\text{N}_4$ 晶须的熔融石英陶瓷,与纯熔融石英陶瓷相比活化能提高了 23.6%,为 506.2 kJ/mol,有效延缓了方石英的结晶。Liu 等^[60]研究指出 $\alpha\text{-Si}_3\text{N}_4$ 的引入可以有效抑制 SiO_2 陶瓷在 1450 °C 以上温度下的结晶。Sun 等^[61]指出 BN 纳米片的加入有效提高熔融石英的机械性能,并且可以在高温使用期间保持。Liang 等^[62]发现在 1180~1220 °C 的烧结过程中,氧化铝的加入促进了熔融二氧化硅的结晶,增加了方石英的含量,导致更大的热膨胀。测试对比室温和 1500 °C 条件下的弯曲强度,结果表明添加氧化铝不会影响室温强度,但会降低 1500 °C 的弯曲强度。Sui 等^[63]通过将 B 和 N 掺入熔融石英陶瓷中,利用 B 和 N 的结合使玻璃晶格结构杂化,显著提高了材料的抗结晶及机械性能,室温下, SiBON 陶瓷的弯曲强度达到 104 MPa。

3.1.2 氧化铝系列 Al_2O_3 陶瓷作为一种重要的介电材料,具有耐腐蚀、良好的导热性和优异的微波介电性能,已被广泛应用于谐振器、陶瓷基板和卫星通信等领域。室温下, Al_2O_3 介电常数 8~10,介电损耗 10^{-4} ^[44],图 5 为不同条件下熔融石英、莫来石及氧化铝陶瓷的 PTC 随厚度的变化关系。由图

5a 和图 5b 可以看出, 低温下 Al_2O_3 陶瓷的功率传输系数与石英相比存在一定差距, 但其机械强度高, 具有良好的绝缘能力和化学稳定性, 同时也是目前工业中应用最广泛、最成熟的耐火材料之一, 空气中最高使用温度可达 $1900\text{ }^\circ\text{C}$, 因此可作为微波加热的耐火材料^[64–65]。Geng 等^[66]制备了具有闭孔结构的氧化铝陶瓷, 在样品中加入 $5\%\text{B}_2\text{O}_3$ 和 6% 莫来石纤维, 抗压强度可达 11.97 MPa , 总孔隙率为 62.5% , 在高温保温、抗冲击和轻型承重结构等领域具有较好的应用前景。Marco 等^[67]对氧化铝在 $8\sim 73\text{ GHz}$ 之间的介电性能研究发现, 对于 25 GHz 以下的低频, 获得低损耗正切值最重要的是对密度的调控, 其次是平均晶粒尺寸, 最后是杂质的影响。Jenkel 等^[68]研究了烧结温度对 3d 打印氧化铝陶瓷 W 波段介电性能的影响, 结果表明, 介电性能主要依赖于孔隙率的变化, 随着烧结温度由 $1250\text{ }^\circ\text{C}$ 升高到 $1650\text{ }^\circ\text{C}$, 材料的相对介电常数从 4.4 增至 9.2 , 介电损耗正切同时保持在 3×10^{-3} 范围内。Yan 等^[69]将 $\text{CeMgAl}_{11}\text{O}_{19}$ 作为增强相引入到氧

化铝陶瓷中, 研究发现 $\text{CeMgAl}_{11}\text{O}_{19}$ 显著提高了材料力学性能, 且所有样品介电常数 ε 均介于 $9\sim 11$ 间, $\tan\delta < 1.20\times 10^{-3}$ 。尚小标等^[70–71]通过计算发现氧化铝陶瓷的传输性能随厚度的增加而动态波动, 当温度升高至 $1379\text{ }^\circ\text{C}$ 时, 功率传输系数高于 70% 时对应材料厚度约在 $16.5\sim 19.0\text{ mm}$ 范围内。然而, Chatterjee 等^[72]对氧化铝材料在不同温度下的介电常数和损耗因子研究发现, 氧化铝的介电常数和损耗因子均会随温度的升高而增大, 且损耗因子的温度依赖性在较高温度下的表现更为明显。如图 5c 和图 5d 所示, 当温度达到 $1050\text{ }^\circ\text{C}$ 甚至更高时, 波传输系数显著下降, 由此许多研究人员认为氧化铝体系材料不适合用作高温微波加热领域^[70]。尽管 Florio 等^[73]指出, 由于固有电导率的存在, 氧化铝的介电损耗存在下限, 但缺乏关于这些变量的详细知识, 观察到的差异现象没有得到进一步的解释。此外, 氧化铝陶瓷热膨胀系数较大($8.10\times 10^{-6}\text{ K}^{-1}$)、抗热震性能差, 因此, 关于氧化铝高温介电性能的变化仍有待进一步探索。

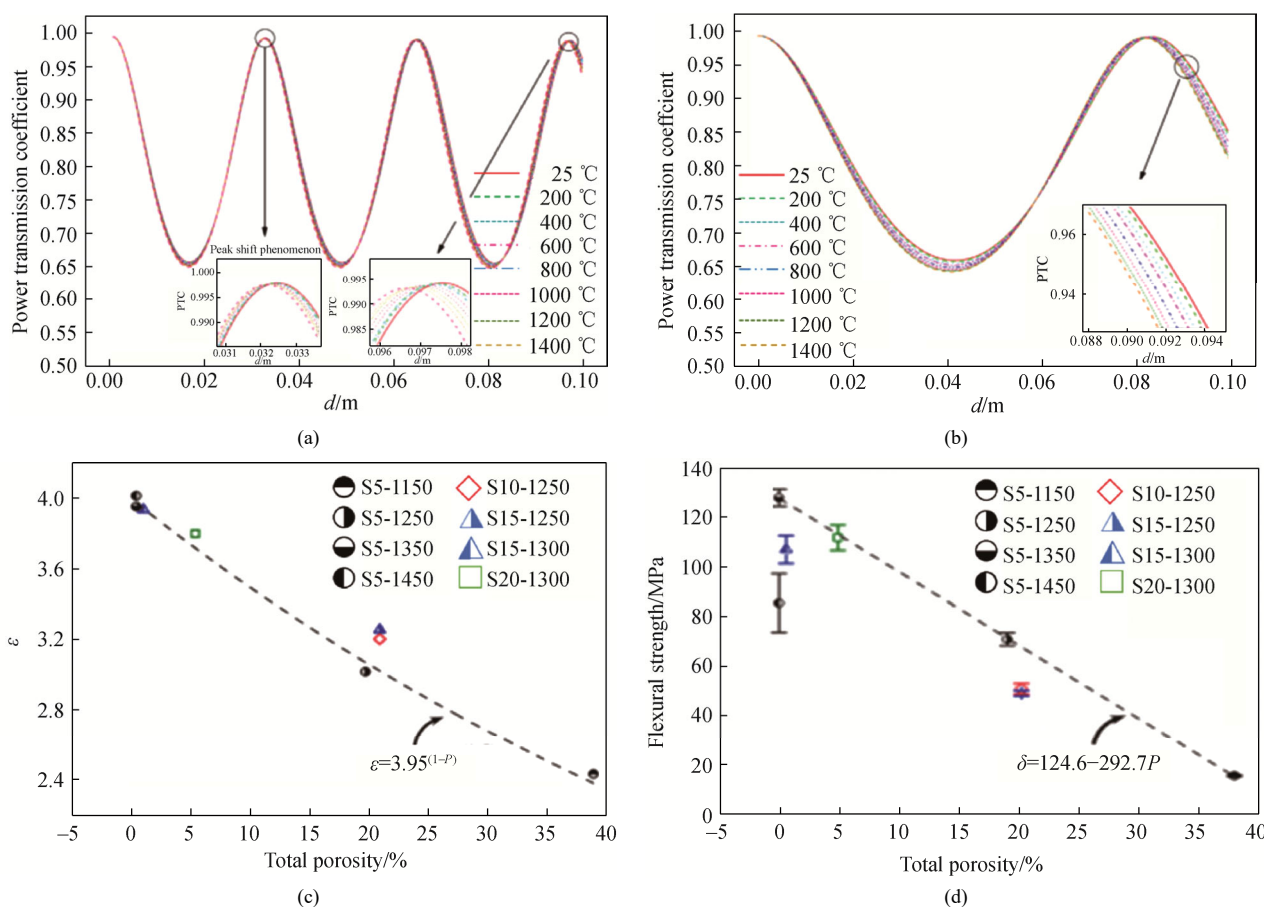


图 4 不同频率(a)2360 MHz(b)915 MHz 熔融石英陶瓷 PTC 随厚度变化的温度依赖性^[51]; BN_w/SiO_2 陶瓷的(c)弯曲强度及(d)介电常数随孔隙率的变化曲线^[57]

Fig. 4 Temperature dependence of PTC with thickness of fused quartz ceramics at different frequencies (a) 2360 MHz and (b) 915 MHz^[51]; Curves of (c) bending strength and (d) permittivity with porosity of BN_w/SiO_2 ceramics^[57]

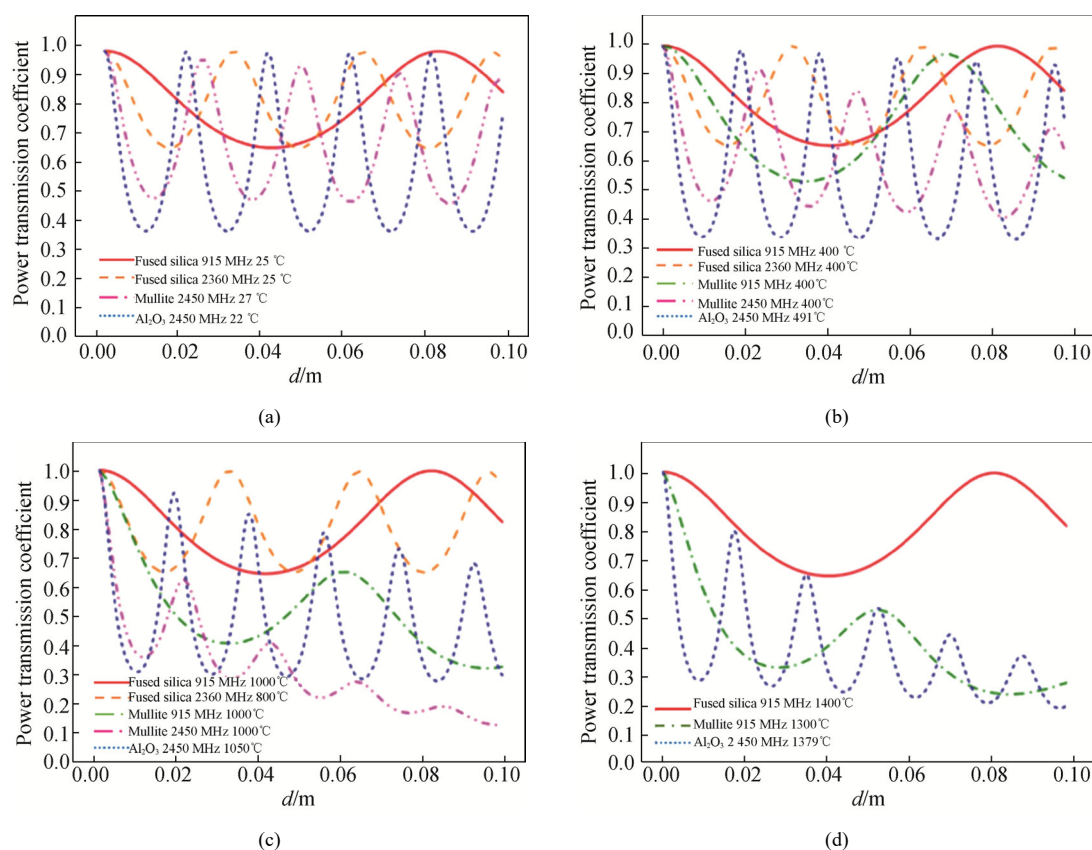


图 5 不同条件下熔融石英、莫来石及氧化铝陶瓷的 PTC 随厚度变化的温度依赖性^[51]

Fig. 5 Temperature dependence of PTC of the fused silica, mullite and Al_2O_3 ceramics as the thickness varies under different conditions^[51]

3.1.3 硅酸盐系列 莫来石和堇青石透波性良好。堇青石($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$)属于镁铝硅酸盐矿物, 据报道纯堇青石的介电常数约为 5 左右^[74], 低于氧化铝陶瓷, 最初由康宁公司在 50 年代开发出的 Mg-Al-Si 系微晶玻璃(9606)具有较好的热稳定性, 已应用于美国第一款主动雷达制导的先进中程空对空导弹^[75], 但微晶玻璃的析晶现象使其在高温环境应用时存在一定的局限性, 此外, 堇青石密度为 $2.53 \sim 2.78 \text{ g} \cdot \text{cm}^{-3}$, 莫氏硬度约为 7.0~7.5, 具有较低的热膨胀系数($1.0 \sim 2.0 \times 10^{-6} \text{ K}^{-1}$)、高化学稳定性和抗热震性以及一定的机械强度, 六方结构 α -堇青石为高温稳定相^[76], 因此, 常被用于制作窑具。Silva 等^[77]以黏土、氧化镁、高岭土残渣和氧化铝为原料, 在 $950 \sim 1400 \text{ }^\circ\text{C}$ 条件下烧结后发现以堇青石为主要成分的配方中 $\tan\delta$ 仍可低至 $3.0 \sim 9.0 \times 10^{-3}$ 。Okamura 等^[78]研究发现室温下, Yb_2O_3 掺杂堇青石在 18 GHz 频率下的介电常数和介电损耗正切分别为 4.9 和 1.60×10^{-4} , 59 GHz 时分别为 4.9 和 2.60×10^{-4} , 表明了其用于微波领域的可行性。堇青石具有优异的抗热震性能, 然而较难烧结、且使用温度常低于 $1400 \text{ }^\circ\text{C}$, 常与其他材料复合以提升其应用范围。例

如, Zhang 等^[24]制备得到具有较低热膨胀系数 (CTE) ($3.2 \sim 4.2 \times 10^{-6} \text{ K}^{-1}$) 的堇青石-莫来石-氧化铝陶瓷, 室温至 $600 \text{ }^\circ\text{C}$ 范围内材料在 1 MHz 频率下的介电常数和介电损耗因子分别为 5~10 和 $<4 \times 10^{-2}$ 。

室温下致密莫来石陶瓷的介电常数略高于石英陶瓷, 约为 6.7, 且作为 Al_2O_3 - SiO_2 二元体系中唯一稳定的化合物, 莫来石陶瓷($\text{Al}_6\text{Si}_2\text{O}_{13}$)具有较高的熔点($1830 \text{ }^\circ\text{C}$)、低热膨胀系数($4.5 \times 10^{-6} \text{ K}^{-1}$)及低导热系数(4.5)等优异特性^[79], 在空气中最高使用温度可达 $1750 \text{ }^\circ\text{C}$ ^[75]且不发生高温氧化行为, 以莫来石为主要成分的耐火材料也是当今高温加热设备中常用的内衬材料^[45]。与氮化硅基陶瓷类似, 莫来石晶粒具有独特的自增韧结构(长棒状晶粒), 且烧结过程中容易形成具有针状的晶粒, 使其强度和韧性在高孔隙度下仍可保持相对较高的水平。Zhang 等^[80]研究发现, 室温下不同聚苯乙烯微球含量的多孔莫来石复合材料的介电常数和损耗切线分别低于 2.61 和 5.90×10^{-3} , 对 10 GHz 频率下材料介电常数的温度依赖性研究发现, 室温至 $1000 \text{ }^\circ\text{C}$ 范围内介电常数增加缓慢, 介电损耗由约 10^{-3} 增至约 10^{-2} 。Ren 等^[50]制备了多孔莫来石陶瓷, 孔隙度 62.10%~67.54%,

且 7~17 GHz 频率范围内具有良好的介电性能 ($\epsilon < 2.96$, $\tan\delta < 5.55 \times 10^{-3}$)。Ren 等^[81]通过水合氧化铝凝胶注模法结合碳纤维作为造孔剂的方法制备了极高孔隙率的莫来石陶瓷, 所制备的莫来石陶瓷孔径小于 10 μm , 孔隙率在 90.6%~78.1% 范围内可控, 抗压强度高 (1.41 ± 0.21)~(16.30 ± 0.20) MPa, 30 GHz 时介电常数为 1.34~1.79, 介电损耗角正切小于 3×10^{-3} , 热导率为 ($0.083 \sim 0.305$) W/(m·K)。Ren 等^[82]通过原位反应和部分烧结法成功制备含 B 莫来石 (Al_5BO_9) 陶瓷, 研究发现室温至 1273 K, 孔隙率为 43.2% 的 Al_5BO_9 陶瓷在 7~19 GHz 频率范围内的介电常数小于 3.2, 介电损耗正切值低于 7×10^{-3} 。潘建中等^[83]以刚玉、莫来石、 $\alpha\text{-Al}_2\text{O}_3$ 粉、有机结合剂及稀土氧化物等为原料, 得到一种工业微波窑炉用耐火材料, 具有良好的耐温性 (1100~1730 $^{\circ}\text{C}$) 及透波性。2015 年, 李光亚等^[84]结合凝胶注模技术与发泡法工艺制备了刚玉-莫来石多孔陶瓷, 结果表明氧化铝含量为 50% 时, 材料热膨胀系数为 $6.5 \times 10^{-6} \text{ K}^{-1}$, 7~18 GHz 频率内介电常数和介电损耗分别为 3.20~3.25 和 $1.7 \sim 2.2 \times 10^{-3}$ 。其次, 作为需长期服役于高温环境的微波窑炉衬体材料, 莫来石陶瓷具有优异的高温体积稳定性, 如郭会师^[85]、殷波^[86]制备的莫来石陶瓷重烧线变化仅为 -0.1% (1500 $^{\circ}\text{C}$ /24 h) 和 -0.9% (1620 $^{\circ}\text{C}$ /12 h)。然而, Shang 等^[45, 71]对莫来

石陶瓷的微波传输性能研究发现 915 MHz 频率下的其微波传输性能优于 2.45 GHz, 对于厚度较大的介质低频加热更有利于微波传输。随着温度由 400 $^{\circ}\text{C}$ 升高到 1300 $^{\circ}\text{C}$ 时, 915 MHz 频率下最佳微波传输对应材料厚度从 71 mm 降至 53 mm, PTC 从 0.9705 下降到 0.5229, 材料微波穿透深度降低, 因此多孔莫来石陶瓷的综合性能仍有待进一步探索。而且, 对窑炉内衬材料, 常加入 SiC、 TiO_2 、 ZrO_2 等遮光剂抑制高温辐射传热, 但此类材料往往具有较高的介电常数, 高温电导损耗较大, 例如温度超过 973 K, ZrO_2 颗粒的介电损耗增大了几个数量级, 这表明, 材料的高温隔热性能和介电性能之间存在矛盾, 为此, 高孔隙率成为隔热透波材料较为显著的特征之一, 但由此导致材料机械性能的下降又是另一大难题, 因此, 探索合适的遮光剂、协同调控孔隙大小及其微观结构的变化对材料各项性能的作用机制成为今后研究中的重点课题。目前, 已有多个研究报告表明, 多孔陶瓷材料透波及机械性能与其微观结构 (如杂质、晶界、气孔等) 的变化密切相关^[43, 87-88], 表 3 为不同因素引起的材料介电性能参数变化。然而, 同一因素引起的材料介电常数及损耗的变化不完全一致, 其中的机理有待研究, 且如图 6 所示, 引入添加剂导致材料孔隙及微观结构演变对其机械性能及热导率的影响不可忽视。

表 3 不同因素对透波材料介电性能参数影响

Table 3 Influence of different factors on dielectric properties of wave-transmitting materials

Material	Variate	Variable parameter	ϵ	$\tan\delta$	Frequency	Reference
Mullite	Heating rate	5 $^{\circ}\text{C}/\text{min}$	~32	0.10	1.5 GHz	[89]
		30 $^{\circ}\text{C}/\text{min}$	~37	0.16		
Mullite-hBN	Additive	Er_2O_3	~8	5.82×10^{-3}	1 MHz	[90]
		La_2O_3	5.63	$\sim 7 \times 10^{-3}$		
$\beta\text{-Si}_3\text{N}_4$	Hole orientation	Gel-casting	4.9	1.5×10^{-3}	~21 GHz	[91]
		Freeze-drying	3.6	2.0×10^{-3}		
MgAl_2O_4	Porosity	76.08%	1.91	~0	8–12 GHz	[92]
		83.51%	1.68			
Si_3N_4	$\beta\text{-Si}_3\text{N}_{4\text{w}}$ content	5%	~3.8	$\sim 4.5 \times 10^{-3}$	20–36 GHz	[93]
		25%	~4.1	$\sim 3.2 \times 10^{-3}$		
Si_3N_4	coating		3.61	1.41×10^{-3}	14 GHz	[94]
		Si_3N_4	3.81–4.34	$1.65 \sim 2.35 \times 10^{-3}$		
		BN	3.68–3.72	$1.45 \sim 1.49 \times 10^{-3}$		
hBN	Grain orientation	Random-BN		11.2×10^{-3}	14.5 GHz	[95]
		Oriented-BN		6.1×10^{-3}		
AlPO_4	Whisker content	30%	3.89–4.24	$1.6 \sim 2.8 \times 10^{-3}$	10 GHz	[96]
		70%	2.71–3.02	$0.8 \sim 1.3 \times 10^{-3}$		
$\alpha\text{-Sialon Y}_{m/3}\text{Si}_{11-m}\text{Al}_{m+1}\text{ON}_{15}$	Composition	$m=1.1$	8.4002	2.38×10^{-2}	10 GHz	[19]
		$m=1.5$	8.7129	2.17×10^{-2}		
Al_2O_3	Grain size	0.86 μm		5.7×10^{-4}	1 MHz	[97]
		0.73 μm		10^{-3}		

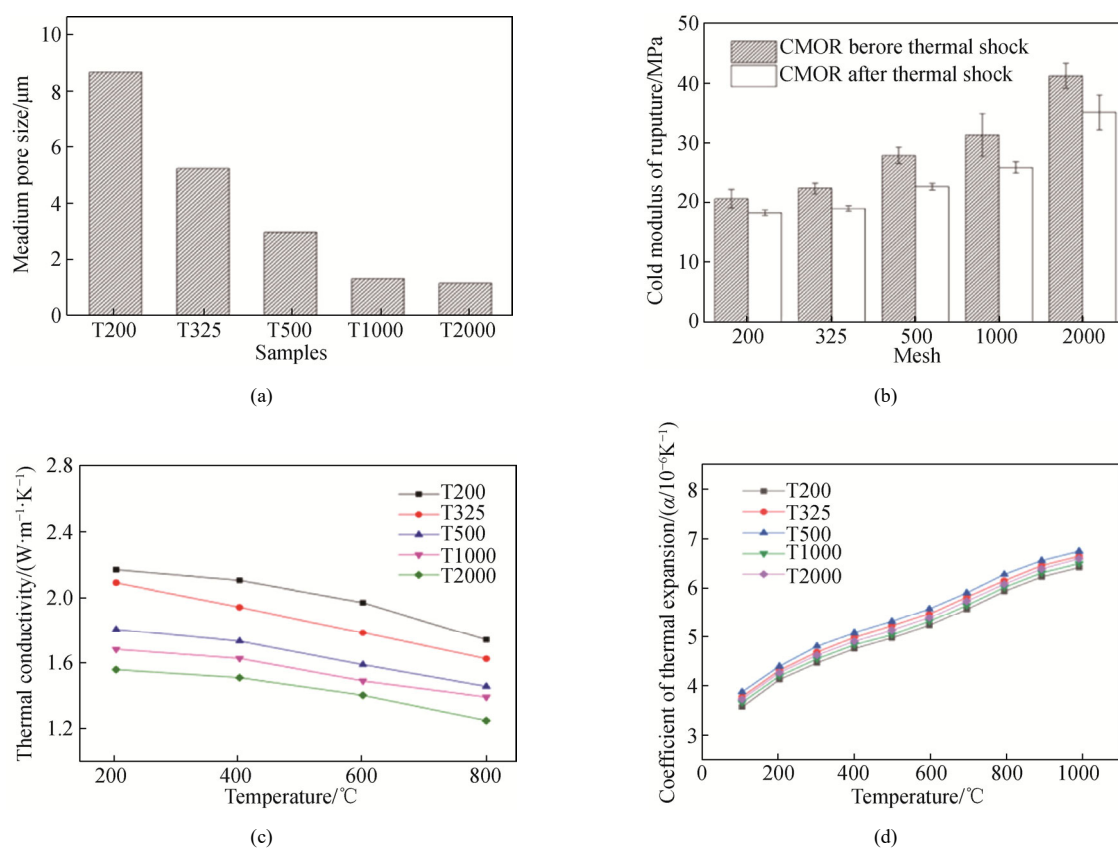


图 6 不同目数片状石墨制备的 SiC-莫来石陶瓷的(a)平均孔径; (b)热冲击前后的 CMOR; (c)导热系数和(d)热膨胀系数随温度的变化^[88]

Fig. 6 (a) Average pore size and (b) CMOR before and after thermal shock of SiC-Mullite ceramics prepared by flake graphite with different mesh numbers; The change of (c) Thermal conductivity and (d) Thermal expansion coefficient with temperature of SiC-Mullite ceramics^[88]

3.1.4 磷酸盐系列 磷酸盐体系材料在 $800\text{ }^{\circ}\text{C}$ 以下具有良好的力学和介电性能, 磷酸盐陶瓷复合材料的弯曲强度 (120 MPa) 优于氧化硅基体复合材料 (50 MPa), 介电性能相当 (介电常数为 3.65 , 介电损耗正切值 0.01), 是较理想的低介电损耗材料, 早期俄罗斯的研究集中于纤维织物增强磷酸盐复合材料, 如连续碳化硅纤维、石英纤维等增强磷酸铬铝等, 但纤维的抗氧化、材料耐温及机械强度等限制了高温结构材料的应用^[98-100]。Chen 等^[100]制备并研究了莫来石晶须原位生长对磷酸铬铝透波陶瓷的影响, 结果表明, 陶瓷的室温抗弯强度、 $1000\text{ }^{\circ}\text{C}$ 抗弯强度和断裂韧性分别为 135.60 MPa 、 121.71 MPa 和 $4.52\text{ MPa}\cdot\text{m}^{1/2}$ 。 $1500\text{ }^{\circ}\text{C}$ 烧结后, 材料在 $8\sim 12\text{ GHz}$ 范围内的 ϵ 、 $\tan\delta$ 和透波率对应的最佳性能分别为 <3.6 、 $<3\times 10^{-2}$ 和 $>80\%$ 。Lu 等^[96]发现硼酸铝晶须可有效抑制硼酸铝晶须增强磷酸铝复合材料中磷酸铝的结晶, 10 GHz 时介电常数和损耗角正切为 4.23 和 2.40×10^{-3} 。Zhao 等^[101]研究发现, 多孔 ZrP_2O_7 陶瓷介电常数对频率和温度不敏感, 19 GHz 频率下当温度由 298 K 升高到 1273 K 时, 孔隙率为 60% 的

ZrP_2O_7 介电常数仅由 2.4 变化为 2.5 , 热导率低于孔隙率为 67% 的莫来石陶瓷。Li 等^[102]通过直接发泡和热处理相结合制备了 $\text{ZrP}_2\text{O}_7\text{-CePO}_4$ 复合多孔陶瓷, 发现在 $15.3\sim 18.2\text{ GHz}$ 频率范围内其介电常数和介电损耗分别为 $1.64\sim 2.72$ 和 $0.88\sim 1.99\times 10^{-3}$ 。除此之外, 磷酸盐在高温下不熔融而成为胶体的性能, 在陶瓷和耐火材料生产过程中常用作黏结剂, 且磷酸盐胶黏剂作为一种无机胶黏剂具有高温稳定性、低温固化、优异的强度和耐磨性等性能。Lu 等^[103]对比了引入磷酸铝 (PA) 或磷酸铬铝 (PCA) 后氮化硅陶瓷的性能变化, 发现添加量相同时, $\text{Si}_3\text{N}_4\text{-PA}$ 材料的体积密度、表观孔隙率和力学性能均优于 $\text{Si}_3\text{N}_4\text{-PCA}$, 但介电常数和介电损耗恰好相反。室温下, $\text{Si}_3\text{N}_4\text{-}10\%\text{PCA}$ 在 20 MHz 处的介电常数为 2.06 , 介电损耗正切约为 2×10^{-3} 。Sun 等^[104]对气化炉衬里含磷酸盐和不含磷酸盐的 2 种高铬砖在其整个使用寿命期间进行了分析, 结果表明高氧化铬砖中的磷酸盐降低了由于渗透引起的剥落频率, 这将导致较低的早期磨损率和较长的使用寿命。Cao 等^[105]在莫来石纤维表面涂覆高强度耐高温磷酸盐涂层后发

现复合材料抗压强度提高了约 9 倍, 达到 4.1 MPa, 且导热系数仅为 0.090 W/(m·K), 展现出优异的机械及隔热性能。

表 4 比较了各类高温透波材料的优缺点。由表 4 可以看出, 硅酸铝体系耐火陶瓷在微波烧结领域具有不错的前景, 且目前关于多孔陶瓷的制备方法多样, 但仍需注意以下问题: 1) 选取造孔

剂时应注意残留碳对材料透波性能的影响; 2) 较大的孔隙率会导致材料强度显著下降, 所承受振动冲击的潜在风险增大。因此, 掌握孔隙引起的材料介电常数和力学性能变化间的关系, 并由此采取合理的制备方法对材料孔隙及微观结构进行调控仍是微波窑炉衬体材料设计中一个巨大的挑战。

表 4 各类高温透波材料优缺点对比表

Table 4 Comparison of advantages and disadvantages of various high temperature wave transmitting materials

Material	Advantage	Disadvantage	Reference
Fused quartz	Fused quartz has stable dielectric properties ($\epsilon \sim 3-5$, $\tan\delta$ is about $10^{-4}-10^{-6}$), low coefficient of thermal expansion ($0.54 \times 10^{-6} \text{ K}^{-1}$), its mechanical properties can be improved to more than 130 MPa by adding reinforcement	The preparation of porous materials will further reduce the mechanical properties of quartz ceramics, the occurrence of phase transformation at high temperature will limit the maximum working temperature of quartz ceramics	[50, 56, 106–107]
Alumina ceramics	Alumina ceramic has excellent mechanical properties and the air atmosphere temperature reaches 1900 °C, which is one of the commonly used refractory materials	Its thermal shock resistance should be improved, and the dielectric property at room temperature is slightly higher than that of quartz ceramics (ϵ about 8–10, $\tan\delta$ is about 10^{-4}), and the temperature dependence is strong	[67], [108]
Silicate ceramics	Cordierite ceramics have excellent dielectric properties ($\epsilon \sim 5$), low thermal expansion coefficient ($1.5 \times 10^{-6} \text{ K}^{-1}$) and good thermal shock resistance. Mullite ceramics have relatively high temperature resistance, excellent dielectric properties (ϵ about 3–6, $\tan\delta$ is about 10^{-3}), mature preparation process and low cost	Cordierite ceramics have low temperature resistance and are commonly used as kiln furniture. The strength, thermal conductivity and thermal shock resistance of mullite ceramics are not ideal, and the dielectric properties of mullite ceramics are excellent at low frequency	[23,47,50], [77,81,109–111]
Phosphate ceramics	The preparation process is simple and the dielectric properties are excellent. The common materials are chromium phosphate and aluminum phosphate, which are often used as adhesives in the field of refractory materials	Chromium phosphate will decompose at high temperatures, and the workig temperature is limited	[96,100,112]

3.2 陶瓷纤维板

除上述各类材料制得的耐火砖外, 陶瓷纤维板也逐渐吸引了广泛关注, 因为其既能够克服多孔陶瓷的脆性, 同时又保持了优越的力学性能, 且陶瓷纤维板的高孔隙率导致了较低的密度和更好的保温性能^[113]。如图 7 所示, 尚小标等^[114–117]整理了硅酸铝系列纤维板在不同频率下的波传输系数随厚度的变化趋势, 为微波烧结设备炉衬的选材以及工艺参数的优化提供了参考, 其中, 当频率为 2.45 GHz 时, 含锆型硅酸铝纤维板在 25~1000 °C 范围内的介电常数呈非线性变化, 由 1.40 升高至 1.57, 而介电损耗在 25~900 °C 范围内变化较为缓慢, 当温度大于 900 °C 后开始极速增长, 增长幅度达 152.3%。肖利平等^[118]在介电性能数据基础上建立三维模型对高铝型硅酸铝纤维板加热效果进行仿真研究, 指出合理设计微波加热设备的工艺参数, 有助于提高微波加热效果。Cheng 等^[113]对莫来石中空

纤维板研究发现, 材料密度低至 0.10~0.20 g·cm⁻³, 500 °C 导热系数约为 0.0988~0.1230 W/(m·K), 随着重烧结(1 300 °C/10 h)次数增加, 纤维板抗压强度增大, 每次体积收缩系数小于 2%, 但与传统莫来石纤维板相比体积收缩系数增大, 如图 8 所示。王佳等^[44]制得氧化铝纤维制品用于工业微波窑炉内衬材料, 研究了杂质对材料透波性的影响, 结果表明, Fe₂O₃、CaO 及 Na₂O 的含量应控制在 0.05% 以内。王佳等^[119]研究了 Al₂O₃ 及相组成对纤维板透波性能的影响, 发现以 72 氧化铝纤维棉为原料, 当氧化铝含量为 80%(质量分数)时, 材料中莫来石相含量最高, 透波性最好。此外, 目前微波烧结领域多个研究报道使用陶瓷纤维板作为衬体材料, 包括氧化铝、硅酸铝及氧化锆纤维等, 同时利用 SiC 为辅助烧结体增强物料受热均匀性^[120–123]。但是, 按照 GOST 23619—79 《耐火绝热莫来石-硅石玻璃纤维材料及产品规格》生产的纤维制品的最高

温度范围仅为 1150~1300 °C^[124], 且使用耐火陶瓷纤维板过程中, 材料结晶和烧结时的收缩现象是

关键问题, 否则会导致炉衬的剥落^[125], 影响窑炉使用寿命。

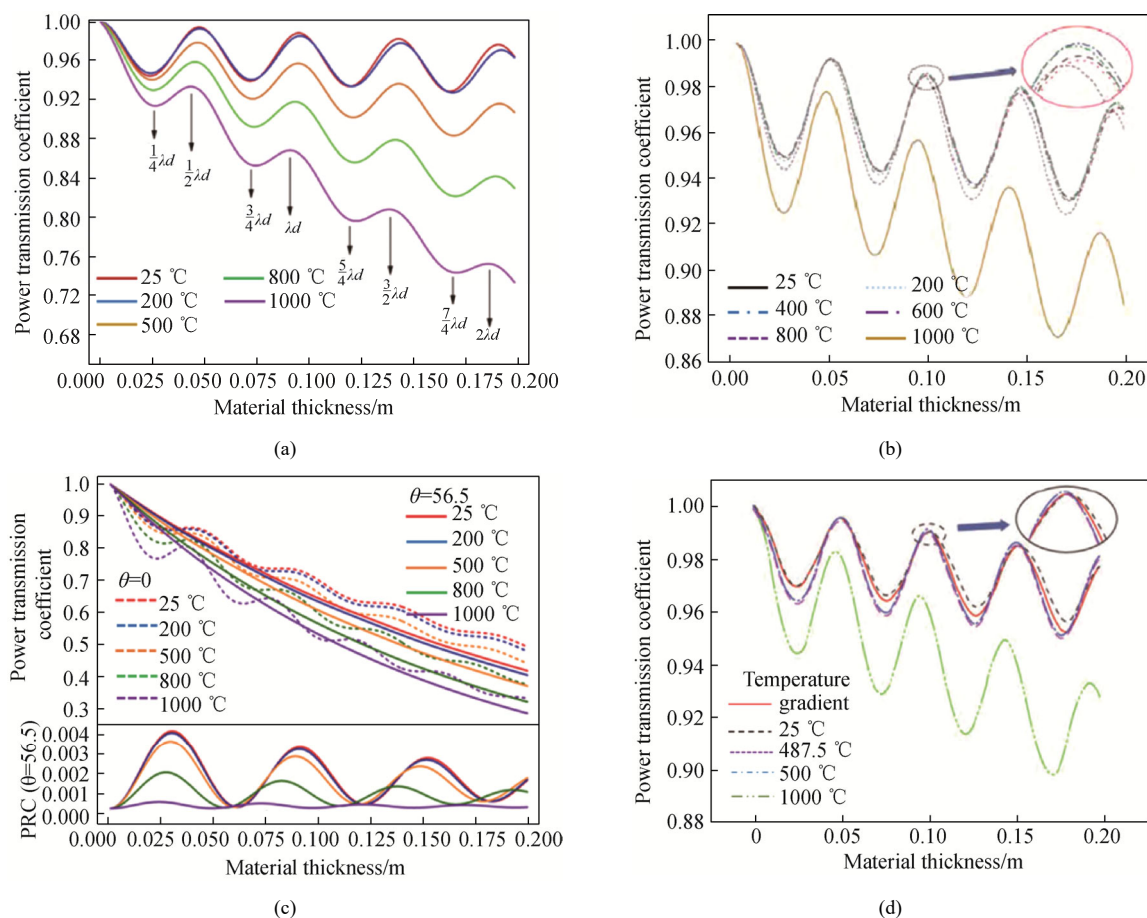


图 7 2.45 GHz 下(a)多晶莫来石纤维板(b)高铝型硅酸铝纤维板(c)硅酸铝纤维板(d)含锆型硅酸铝纤维板的波传输系数随厚度的变化曲线^[114-117]

Fig. 7 Thickness dependence of power transmission coefficient of (a)polycrystalline mullite fiberboard (b)high-Al aluminium silicate fibreboard (c)aluminium silicate fibreboard (d)zirconium aluminum silicate fiberboard at 2.45 GHz^[114-117]

3.3 陶瓷气凝胶

为解决现有的氮化物及氧化物透波陶瓷表现出的高蓄热性、高温下低微波透过率及氧化、抗热冲击性差等问题, 气凝胶材料得以迅速发展, 其低密度、高孔隙率(>90%)和纳米孔径的特点使其在隔热领域的应用一直受到研究人员的关注^[126-127]。得益于较高的孔隙率, SiO₂ 气凝胶常温热导率只有 0.013 W/(m·K), 介电常数在 1.1~3.5 之间可调^[128], 但气凝胶材料的高温稳定性较差, 长期使用温度仅为 650~800 °C^[129], 加之其在力学性能上的欠缺, 常通过引入第二相进行增韧。Song 等^[130]通过在 BN 纤维表面原位生长 SiO₂ 获得了密度为 0.07 g·cm⁻³ 的 BN@SiO₂ 复合气凝胶, 在 2~10 GHz 频率范围内, 其 ϵ 为 2.58~2.80, $\tan\delta$ 低至 $5.13\sim7.98\times10^{-3}$ 。Wang 等^[126]合成了 BN 纳米气凝胶, 该材料展现出良好的

高温稳定性(惰性气氛下 1400 °C, 空气气氛下 750 °C)、宽带透波性(ϵ 为 1.03, $\tan\delta$ 为 1.6×10^{-2} , 4~18 GHz)和隔热性能(0.073 W/(m·K), 600 °C)。Zhang 等^[131]采用溶胶-凝胶和超临界干燥法制备 SiBN_{0.5}/SiO₂ 气凝胶复合材料, 在空气中可稳定至 1100 °C 且具有低热导率(0.051 W/(m·K), 1100 °C)和良好的透波性能($\epsilon<1.45$, $\tan\delta<10^{-2}$, 4~18 GHz)。Yang 等^[132]对 Si₃N₄/SiO₂ 气凝胶复合材料研究发现嵌入纳米网络结构中的 Si₃N₄ 颗粒提供了有效的支撑并阻碍了 SiO₂ 气凝胶在高温下的结晶, 且掺杂适量 TiO₂ 可以提高材料的隔热性能, 测得的介电常数为 2.85。Song 等^[133]通过静电纺丝、冷冻干燥和高温热解制备了 Si₃N₄/PAN/SiZrOCN 陶瓷气凝胶复合材料, 样品的介电常数在 3.1 至 3.7 之间, 介电损耗角正切值在 2.6×10^{-3} 至 1.6×10^{-2} 之间。Yang 等^[134]通过溶胶

凝胶常压干燥法制备了 Si_3N_4 颗粒增强二氧化硅气凝胶复合材料, 所得介孔复合材料具有低介电常数(1.55~1.85)、低损耗角正切($5.0\sim 7.0\times 10^{-3}$)和低热导率($0.024\sim 0.072\text{ W}/(\text{m}\cdot\text{K})$)。Yang^[135]通过冷冻浇注和溶胶-凝胶浸渍制备了二氧化硅气凝胶浸渍多孔 Si_3N_4 复合材料, 测试结果表明, 室温热导率显著降低, 为 $0.043\text{ W}/(\text{m}\cdot\text{K})$, 抗压强度提高, 低介电常数约为 1.6, 损耗角正切约为 1.8×10^{-3} 。然而, 尽管理论上 SiO_2 气凝胶可在 $1000\sim 1200\text{ }^\circ\text{C}$ 工作, 但相关研究表明, 其耐高温时间小于 120 min ^[136], 无法满足微

波烧结炉衬材料的工作要求, 且 SiO_2 气凝胶不能直接使用, 而低密度的介孔 SiO_2 气凝胶在现实应用中很脆, 甚至无法加工, 这导致大规模加工复合材料(如纤维增强硅气凝胶毯或颗粒与黏合剂相结合)过程十分艰难; 另一方面, 以高成本为代价换取材料性能的提升不是合适的选择, 例如在保温性能方面, 硅气凝胶产品零售价约为 $400\sim 6000\text{ } \$/\text{m}^3$, 而聚苯乙烯和岩棉仅为 $25\sim 180$ 和 $40\sim 350\text{ } \$/\text{m}^3$ ^[137], 加之实际工业化生产过程中气凝胶的制备涉及到的环境问题及有机溶剂的回收等都是阻碍该材料应用的关键。

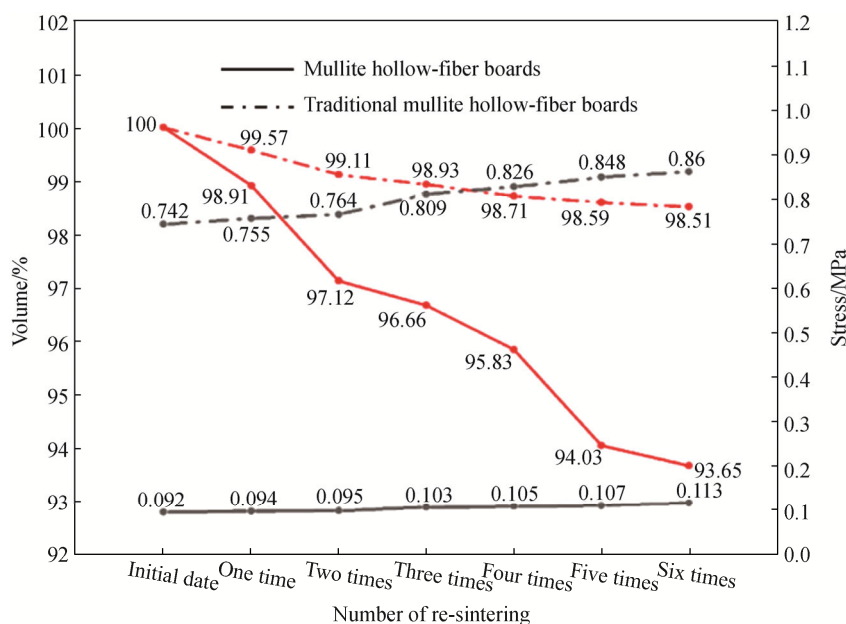


图8 莫来石中空纤维板与传统莫来石纤维板在不同重烧循环后的体积收缩和抗压强度比较^[113]

Fig. 8 Comparison of volume shrinkage and compressive strength of mullite hollow-fiber board and traditional mullite solid-fiber board after various resintering cycles^[113]

4 总结与展望

关于高温透波材料的研究已取得一定的进展, 多集中于航空天线罩、通信等领域, 但对于微波烧结所需的兼具保温隔热、抗热震及稳定介电性能的材料仍有待进一步探索。本文结合微波烧结条件对各类材料进行了简要对比, 其中氧化硅、氧化铝及莫来石陶瓷/陶瓷纤维板/陶瓷气凝胶等材料均在透波领域展现出广阔的应用前景, 且由于空气具有最低的介电常数(ϵ 约为 1.0), 多孔材料成为微波窑炉内衬材料发展的必然趋势。然而, 结合目前高温多孔透波陶瓷材料的研究现状, 仍有多个问题亟待解决: 1)按照理论分析, 为保证材料基础力学性能, 其孔隙率的增大存在极值, 因此应加强等效孔隙率情况下, 材料孔隙的形状、大小等因素与介电及机

械性能参数间的协同调控; 2)目前关于高温介电性能的研究多局限于 $1200\text{ }^\circ\text{C}$ 以下, 但对于微波窑炉内衬材料, 工作温度可达 $1700\text{ }^\circ\text{C}$, 为此, 应加强材料在更高温度下的透波率变化情况的研究和高温下介电常数测试系统的研发; 3)为确保实际应用中材料在高温环境下长期使用的稳定性, 应强化对材料重烧线变化的研究; 4)持续加强结构功能一体化材料的研发, 探索结构与性能间的关联机制, 进一步加快陶瓷基透波材料在微波烧结技术领域的升级和应用, 为推动国家减污降碳、早日实现“碳中和”目标奠定基础。

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Progress on High-Temperature Wave-Transmitting Materials in Microwave Sintering

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Extended Abstract

Industrial operations lead to energy consumption and environmental pollution with the economy development. In developed countries, the thermal efficiency of ceramic kilns in ceramic industry reaches over 50%, while in China it is only about 28%. Combined with the pollution reduction and carbon reduction in recent years, the gradual development of industrial kilns towards green and intelligent direction becomes an inevitable trend in the context of dual carbon. As is well known, microwave energy can reduce energy consumption and greenhouse gas emissions in drying processes. Microwave sintering technology is also regarded as a 'new generation sintering technology of the 21st century'. This technology is an efficient and environmentally friendly method used in metallurgy, powder and ceramics preparation due to its advantages such as volumetric heating, selective heating, time-saving and high efficiency. Compared with conventional sintering methods, a coupling effect between microwaves and materials is utilized in microwave sintering process, thereby producing dielectric loss, converting microwave energy into thermal energy. The microwave sintering furnace mainly involves microwave generator, waveguide tube and sintering chamber. In the operation, the microwave generated by the microwave generator is transmitted through a wave guide, thus entering the sintering chamber after passing through multiple layers of insulation, interacting with the material in the crucible, generating dielectric loss inside the material and converting microwave energy into thermal energy. For this purpose, some imperative requirements put forward for the selection of furnace lining materials. In addition to conventional fire resistance, the lining material used for microwave sintering furnaces also has good wave transmission properties. However, the existing research on transparent materials mostly focus on aircraft radome, and there is still a lack of systematic introduction on wave-transparent materials used in microwave sintering furnaces.

This review briefly introduces the working principle of microwave sintering technology and the wave transmission mechanism of materials, and summarizes several common types of high-temperature wave transmitting materials like ceramic firebrick, ceramic fiberboard, ceramic aerogel. Among them, ceramic aerogels have typically nano-pores of up to 90%, which can reduce the dielectric constant of the material significantly. Ceramic fiberboard has a low density and thermal conductivity. However, the application of these two materials is limited due to their lower operating temperatures. Ceramic firebrick with its superior mechanical properties and high-temperature stability shows a broad application prospect in fused silica, alumina, silicate and phosphate ceramics, and these materials with porous structures are more widely used because of the lower dielectric constant of air. Some influencing factors on the dielectric properties of materials are described. Combination with the mechanical properties and dielectric properties of materials, the performance of each ceramic is analyzed, and the advantages and disadvantages of different high-temperature wave transmitting materials are given. Among them, aluminum silicate ceramic shows a promising application prospect in the lining materials for microwave furnace. However, the comprehensive properties of the material in the industrial microwave frequency range still need to be further investigated.

Summary and prospects Although the favourable dielectric property of ceramic aerogel and fiberboard is proved in the selection of lining materials for microwave sintering, some problems of operating temperature still remain in the practical application. For ceramic firebrick, compared with nitride ceramics (*i.e.*, Si_3N_4 , SiAlON and $\text{Si}_2\text{N}_2\text{O}$), some porous oxides ceramics (*i.e.*, fused quartz, alumina, silicate and phosphate ceramics) become a research hotspot because of the lower cost and better antioxidant properties. All the materials show some advantages in mechanical properties and dielectric properties. For instance, fused quartz with relatively stable dielectric properties has a lower operating temperature. Alumina ceramics have a higher operating temperature, but their thermal shock resistance needs to be improved and its dielectric properties have a temperature dependence. Mullite ceramics have excellent characteristics such as high melting point (*i.e.*, $1830\text{ }^\circ\text{C}$), low thermal expansion coefficient (*i.e.*, $4.5 \times 10^{-6}\text{ K}^{-1}$), and low thermal conductivity, which can be used in air at $1750\text{ }^\circ\text{C}$ without high temperature oxidation. In addition, mullite ceramics also have the superior dielectric properties (*i.e.*, ϵ is about 3–6, $\tan\delta$ is about 10^{-3}). Some refractory materials with mullite as a main component are commonly used as lining materials in conventional high-temperature furnace. Furthermore, according to the existing studies, the increase of porosity can effectively reduce the dielectric constant of materials, and has a negative impact on the mechanical properties of materials. In this case, mullite ceramics are easy to form grains with acicular morphology during sintering, which is beneficial to maintaining high mechanical properties of the material at a high porosity. However, some challenges still remain in the scientific researches and practical application, such as some related studies on the dielectric properties at high temperatures are limited at $<1200\text{ }^\circ\text{C}$, but it is far from enough for the lining materials of microwave kiln, in which the working temperature can often reach $1700\text{ }^\circ\text{C}$. The change of the transmittance of materials at higher temperatures is still of great research value. Also, it is necessary to optimize the dielectric constant test system at high temperatures. Finally, some novel material systems of oxides ceramic in a largescale need to be further explored for the microwave sintering application. Meanwhile, exploring the relevance between microstructure and properties and further accelerating the upgrading and application of ceramic based wave-transmitted materials in microwave sintering technology become some research hotspots, which can reduce the pollution and carbon emissions caused by the use of industrial kilns and lay a foundation for the realization of 'carbon neutrality'.

Keywords microwave sintering technology; high-temperature wave-transmitting material; refractory materials; porous oxide ceramics