

煤矸石基高强度泡沫陶瓷的制备与性能

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摘 要: 以煤矸石为主要原料, 硅藻土粉、滑石粉及发泡剂 SiC 为辅料制备出高强度泡沫陶瓷, 研究了煤矸石掺入量(质量分数)、SiC 添加量(质量分数)和混合原料粒度对制备的泡沫陶瓷性能的影响。当煤矸石掺入量增加时, 混合原料的硅铝质量比逐渐减小, 样品抗压强度先增大后减小, 煤矸石掺入量为 70% (质量分数)时, 制备出的样品具有均匀的孔结构; 增加 SiC 加入量使得烧结过程中发泡产生的气体增多, 样品抗压强度及表观密度随气孔率的增大而减小, SiC 加入量为 0.6%时, 制备的泡沫陶瓷的性能最佳; 样品平均孔径和开孔率随着混合原料的粒度的减小而降低, 此时较小的孔径和均匀孔结构提高了泡沫陶瓷抗压强度, 混合原料体积平均粒径为 $5.4\ \mu\text{m}$ 时, 总气孔率为 80.6%, 此时抗压强度达到 6.1 MPa。本工作中煤矸石利用率高, 制备的高气孔率高强度泡沫陶瓷为煤基固废的综合利用提供了借鉴与指导。

关键词: 泡沫陶瓷; 煤矸石; 抗压强度; 孔结构; 碳化硅发泡剂; 颗粒粒径

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泡沫陶瓷是一种经高温烧结后具有三维网状结构的无机非金属材料, 具有密度低、韧性高、比表面积大、介电常数低等优点^[1], 作为过滤、催化剂载体、生物陶瓷等材料广泛应用于各种领域, 同时, 其优异的隔热性能和耐高温等特性还可作为保温和耐火材料应用于建筑领域^[2-3]。常见泡沫陶瓷制备方法有添加造孔剂法^[4]和直接发泡法^[5]等, 此类方法在制备过程中气孔易发生团聚, 泡沫陶瓷的气孔率较低。有机泡沫浸渍法^[6]可通过选择泡沫模板调控气孔结构, 但是排塑时间长、陶瓷骨架易产生裂纹, 力学性能较差。因此, 采用简单的工艺, 降低生产成本, 强化泡沫陶瓷性能逐渐成为当前研究热点。

煤矸石是煤炭开采和洗选加工过程中产生的固体废弃物, 是目前中国排放量最大的固体废弃物之一, 煤矸石库存量大、利用率低, 长期堆放占用大量土地, 造成严重环境污染^[7]。煤矸石主要由 SiO_2 和 Al_2O_3 组成, 通常以石英、高岭石、伊利石、长石等物相存在, 可代替黏土来制备泡沫陶瓷^[8-9]。在烧结过程中, SiO_2 和 Al_2O_3 形成泡沫陶瓷的骨架, 同时含有一定量的 Na_2O 、 K_2O 、 MgO 、 CaO 等金属

氧化物, 可以降低烧结温度^[10-11]。Li 等^[12]以煤矸石为原料制备了高闭孔率泡沫陶瓷, 在 $1\ 200\ ^\circ\text{C}$ 最佳烧结温度条件下制备出体积密度、抗压强度、总气孔率分别为 $0.22\ \text{g}/\text{cm}^3$ 、1.51 MPa、91.38%的泡沫陶瓷, 可作为一种高性价比的无机保温材料应用于建筑行业。Ge 等^[13]研究了 Na_2O 及 MgO 对泡沫陶瓷性能及孔结构的影响, 发现在混合原料中加入适量的 Na_2O 及 MgO 时, 在 $1\ 200\ ^\circ\text{C}$ 烧成的泡沫陶瓷具有良好孔隙结构, 样品的体积密度为 $0.28\ \text{g}/\text{cm}^3$, 抗压强度为 1.04 MPa。本课题组最近研究发现, 以煤矸石为原料, 添加不同含量的 Na_3PO_4 可制成气孔率为 49.4%~77.1%、抗压强度为 1.17~10.76 MPa 的泡沫陶瓷材料^[14]。此外, 在制备泡沫陶瓷过程中提高煤矸石的比例不仅可降低成本、提高收益, 同时还可实现煤矸石的高值化利用^[15-16]。

目前, 对泡沫陶瓷的研究主要集中在提高孔隙率、降低体积密度^[17-19], 同时力学性能是评价泡沫陶瓷的重要指标, 根据 Rice 模型^[20], 高孔隙率将降低泡沫陶瓷的承载能力^[21], 限制其应用。因此, 研究侧重点是如何平衡泡沫陶瓷的孔隙率和抗压强

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度。泡沫陶瓷的抗压强度受孔隙率、气孔大小、孔隙分布和骨架结构等因素的影响,减小气孔尺寸或使其孔径分布变窄、或形成闭孔结构等,均可有效提高泡沫陶瓷的抗压强度^[22]。但以煤矸石为原料制备泡沫陶瓷时,仍存在煤矸石利用率低、能耗较高、发泡原理不明确等问题^[23–24]。泡沫陶瓷发泡的关键在于形成具有适当黏度的熔融基体和熔融基体中产生适量的发泡气体^[25],但由于煤矸石的成分复杂,很难控制高温熔融坯体的黏度,且高温时液相包裹产生的气体使得泡沫陶瓷制品的孔结构分布不均匀,降低了泡沫陶瓷的力学性能。

本工作以煤矸石为主要原料,添加硅藻土粉、滑石粉及少量发泡剂 SiC,采用粉末堆积法制备高强度泡沫陶瓷,考察原料组成、SiC 添加量(质量分数)、原料粒度对泡沫陶瓷物相变化、气孔结构、表观密度及抗压强度等性能的影响。采用的煤矸石基泡沫陶瓷的制备方法简单,且煤矸石利用率较高,为煤矸石的高值化利用提供了借鉴和指导,同时可减少煤矸石堆积造成的环境污染,为固体废弃物

转化成性能优异的新型建筑材料提供了一种可行的方法。

1 实验

1.1 制备方法

先将煤矸石破碎筛分至 200 目(筛孔尺寸为 74 μm),并将所有原料在 100 °C 干燥 12 h 脱除吸附水。为保证高温烧结过程中形成具有适当黏度的熔融基体,以 SiO₂–Al₂O₃–MgO 三元体系为基础,根据原材料的化学组成,将煤矸石、硅藻土粉、滑石粉以不同质量比混合制成 5 种配方,发泡剂 SiC 的添加量(质量分数)为 1%,分别标记为样品 CG1~样品 CG5,实验配方如表 1 所示。配料完成后将混合物放入玛瑙研磨罐中,按照原料与玛瑙球质量比为 1:1 充分球磨 8 h,球磨转速 300 r/min。采用粉末堆积法,将混合原料置于刚玉瓷舟中,在高温炉中以 5 °C/min 先升温至 1 100 °C 保温 20 min,然后以 1 °C/min 升温至 1 190 °C 保温 25 min 后自然冷却至室温得泡沫陶瓷。

表 1 泡沫陶瓷实验配方
Table 1 Experimental proportions of ceramic foams

Sample No.	w(Coal gangue)/%	w(Diatomite)/%	w(Talc)/%	m(SiO ₂)/m(Al ₂ O ₃)
CG1	60	30	10	2.66
CG2	70	20	10	2.38
CG3	75	15	10	2.26
CG4	80	10	10	2.15
CG5	85	5	10	2.05

w—Mass fraction. m—Mass.

1.2 样品表征

用岛津 EDX-7000 型 X 射线荧光光谱仪(XRF)测定原料的灰成分化学组成。用理学 SmartLab SE X 射线衍射仪(XRD)测定原料及泡沫陶瓷的物相组成,测试条件: Cu K_α 射线为辐射源,管电压 40 kV,管电流 40 mA,扫描速率 10(°)/min。用美国 PE STA-8000 型同步热分析仪(TG-DSC)在空气气氛下对混合原料进行热失重分析,升温速率为 20 °C/min。用 Bettersize 2600 激光粒度仪对不同球磨时间混合后的原料分析其粒径(体积加权平均粒径 $D[4,3]$);用光学数码相机和体视显微镜记录样品的宏观形貌,利用 Nano Measurer 1.2 对样品进行孔径分布统计,在照片中选取至少 100 个孔进行孔径分布统计。采用电脑全自动恒应力试验机 DYE-300 测试样品的抗压强度,每个变量选取 3 个泡沫陶瓷样品进行测试,取 3 次测试结果的平均值为该样品的抗压强度值。

利用 Archimedes 排水法、比重瓶法测定泡沫陶瓷的吸水率及总气孔率、开孔率,每个样品重复 3 次取平均值分析数据变化规律。

2 结果与讨论

2.1 原料分析

煤矸石、硅藻土粉和滑石粉的灰成分的 XRF 分析结果见表 2。由表 2 可以看出,煤矸石的主要化学组成为 SiO₂ 和 Al₂O₃。硅藻土粉和滑石粉中含有较多的 SiO₂,可为混合物料提供更多的 SiO₂,有利于在高温形成更加均匀的硅酸盐网络结构。同时,硅藻土粉和滑石粉中还分别含有较多的碱土金属氧化物 CaO 和 MgO,可破坏熔融坯体中的 Si—O 键,降低熔融硅铝酸盐的黏度^[26]。不同原料的物相组成如图 1 所示。由图 1 可见,煤矸石主要晶相由室温时的石英(SiO₂, PDF 79-1906)和高岭石

($2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, PDF 78-2109) 及少量云母 ($\text{KAl}_2[\text{Si}_3\text{AlO}_{10}](\text{OH})_2$, PDF 07-0025) 转变为高温时的石英及莫来石 ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, PDF 79-1275); 硅藻土粉的主要晶相由室温时的石英、云母和方解石 (CaCO_3 , PDF 99-0022) 及少量钠长石 ($\text{NaAlSi}_3\text{O}_8$, PDF 19-1184) 转变为高温时的石英和鳞石英 (SiO_2 ,

PDF 42-1401); 滑石粉的主要晶相由室温时的滑石 ($\text{Mg}_3[\text{Si}_4\text{O}_{10}](\text{OH})_2$, PDF 29-1493) 转变为高温时生成的顽火辉石 ($\text{Mg}_2(\text{Si}_2\text{O}_6)$, PDF 86-0432); 碳化硅经高温焙烧后的碳化硅 (SiC , PDF 74-1302) 物相仍存在, 但高温焙烧后出现了较弱的石英相 (PDF 74-0201), 表明 SiC 氧化生成了 SiO_2 。

表 2 不同原材料灰成分的化学组成
Table 2 Ash components of different raw materials

Composition	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2	CaO	Na_2O	MgO	Others	LOI
Coal gangue	45.94	26.33	3.39	1.84	0.75	1.26	0.84	0.85	1.19	17.6
Diatomite powder	64.31	10.71	1.93	1.99	0.23	7.68	1.21	3.70	0.44	7.8
Talc powder	55.17	0.66	1.15	0.01	0.04	4.01	0	28.92	0.84	9.2

LOI is loss on ignition.

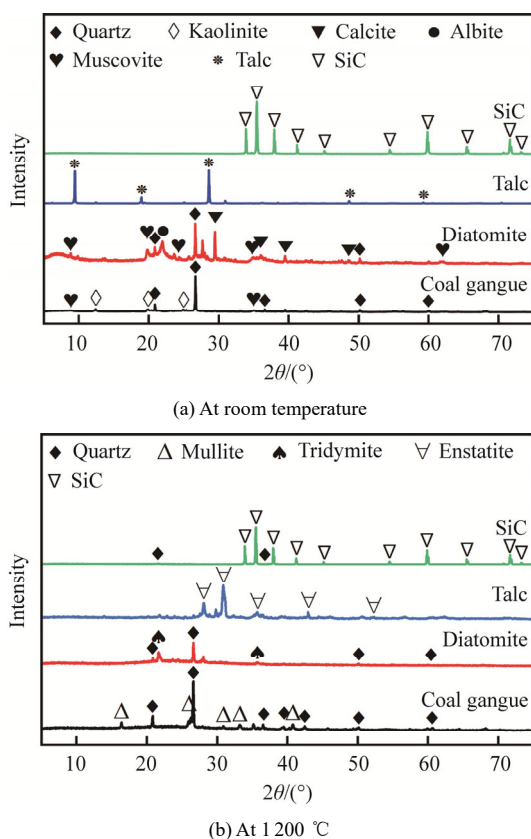


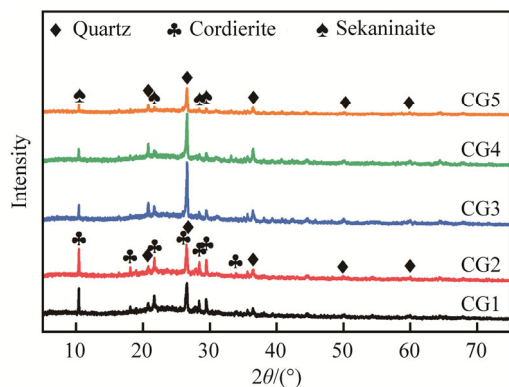
图 1 不同原料在室温和 1200 °C 焙烧后的 XRD 谱
Fig. 1 XRD patterns of different raw materials at room temperature and 1200 °C

2.2 煤矸石含量的影响

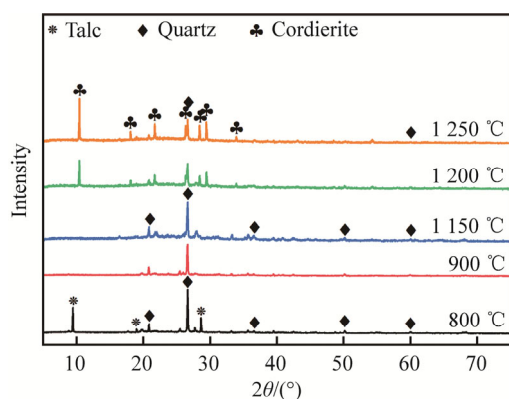
图 2 为不同组成样品在 1190 °C、样品 CG2 在不同温度焙烧后的 XRD 谱及样品 CG2 的 TG-DSC 曲线。由图 2a 可以看出, 不同组成的原料在焙烧后的主要物相为堇青石 ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, PDF 82-1543) 和石英。在 SiO_2 - Al_2O_3 - MgO 体系中, 随着煤矸石掺量的增加, CG1 到 CG3 配比组成点向着堇

青石初晶区内部移动, 样品 CG2 硅铝质量比为 2.38, 此时原料的组成更接近堇青石的理论化学组成, 有利于堇青石相的生成, 这与图 2 中出现的堇青石特征衍射峰的结果相一致^[27]。煤矸石掺入量超过 75% 时, 石英相的特征衍射峰强度逐渐增强, 原料中的 Fe_2O_3 含量增多, 堇青石相逐渐转变为铁堇青石相 ($(\text{Fe}, \text{Mg})_2\text{Al}_3[\text{AlSi}_5\text{O}_{18}]$, PDF 83-1599)。针对样品 CG2, 考察其在不同焙烧温度下样品晶相组成的变化规律。由图 2b 可见当焙烧温度为 800 °C 时, 样品的物相组成主要为石英和滑石; 随着温度升高至 1150 °C, 滑石相衍射峰消失, 此时主要物相为石英; 达到 1200 °C 后, 石英相衍射峰明显减弱, 并出现堇青石相。这是由于 SiO_2 是构成泡沫陶瓷的骨架结构, 部分石英溶入熔融硅酸盐液相促进了堇青石相的形成^[28], 同时加入的滑石作为烧结助剂降低了制备堇青石陶瓷所需的烧结温度, 有利于堇青石的生成^[29]。进一步升高温度, 石英相衍射峰减弱, 堇青石相衍射峰增强。由图 2c 可见, 样品的总质量损失量为 26.2%。在 30~250 °C 之间, 样品的质量损失量为 3.5%, 主要归因于样品的自由水及煤矸石的部分有机物的质量损失。在 250~900 °C 范围内观察到明显的质量损失 (19.5%), 主要是由于煤矸石中的挥发分和含碳物质的氧化导致^[30], 在 546 °C 时出现的较宽的吸热峰是高岭石吸热发生脱羟基反应, 使得晶体层状结构被破坏, 转变为无序非晶态的偏高岭石; 在 625 °C 左右出现 DTG 峰值同时出现较大的放热峰, 归因于煤矸石中碳和有机质的剧烈氧化反应^[31]。在 900~1200 °C 范围内的质量损失为 3.1%, 这是由于硅藻土和滑石分解等造成的^[32]。

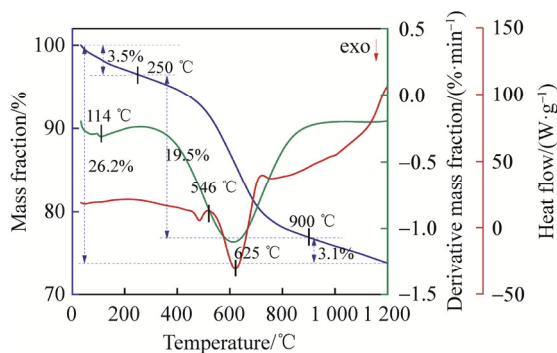
为研究煤矸石掺入量对泡沫陶瓷孔结构的影



(a) XRD patterns of samples with different compositions



(b) XRD patterns of CG2 samples at different calcination temperatures



(c) TG-DSC curves of CG2 samples

图2 不同组成样品在 1 190 °C 和样品 CG2 在不同温度焙烧后的 XRD 谱及样品 CG2 的 TG-DTG-DSC 曲线

Fig. 2 XRD patterns of samples with different compositions at 1 190 °C, XRD patterns of sample CG2 at different calcination temperatures and TG-DTG-DSC curves of CG2 samples

响, 对不同煤矸石掺量的样品进行孔径分布统计, 样品照片及孔径分布统计如图 3 所示。由图 3a~图 3e 可见, 随着煤矸石掺入量的增加, 泡沫陶瓷的气孔结构发生了明显的变化: 当煤矸石添加量为 60% 和 70% 时, 样品的孔径分布均匀, 气孔结构独立且完整; 当煤矸石含量大于 70% 时, 样品平均孔径减小, 孔隙相互连接, 气孔形状变为不规则多边形, 气孔的连通孔隙增多; 当煤矸石含量为 85% 时,

样品 CG5 孔隙明显减小且孔径分布不均匀。这是由于煤矸石掺量的增加使得坯体中的 SiO_2 和 Al_2O_3 质量比减小, 增多的 Al_2O_3 提高了坯体熔融温度, 导致高温下生成的硅酸盐熔融物质减少且黏度增大、黏度分布不均, 从而产生了分布不均的孔隙结构^[33]。由图 3f 可见, 当煤矸石含量从 60% 增加至 85%, 即硅铝质量比从 2.66 降低至 2.05 时, 样品的平均孔径从 2.01 mm 减小至 0.80 mm, 表观密度从 0.28 g/cm^3 增大至 0.66 g/cm^3 , 不均匀的气孔结构降低了孔壁的承载能力, 抗压强度先增大后减小, 煤矸石含量为 75% 时达到最大值 2.2 MPa。

2.3 SiC 发泡剂含量的影响

在 CG2 配比的基础上, 将样品球磨 8 h, 然后在 1 190 °C 焙烧, 考察 SiC 加入量对泡沫陶瓷孔隙结构和孔径分布的影响, 结果如图 4 所示。由图 4a 可见坯体表面存在细小的气孔, 堆密度较大。随着发泡剂 SiC 含量的增加, 高温时 SiC 与空气中氧气反应产生的气体量增多, 坯体中产生了更多的孔隙^[34]。当 SiC 含量从 0.4% 增加到 1.4% 时, 样品的平均孔径从 0.94 mm 增大至 3.33 mm; SiC 含量在 0.4%~0.8% 范围内时, 样品的孔径主要集中在 0~2 mm 内, SiC 含量继续增大时气孔尺寸变得不均匀。当 SiC 含量为 1.2% 或 1.4% 时, 产生的气体量增多, 坯体内的气体压力大于液相的表面张力, 气体冲破液相包裹导致气孔破裂, 使得连通孔增加。

图 5 为不同 SiC 加入量对制备的泡沫陶瓷的性能影响及 SiC 高温发泡反应示意图。由图 5a 可以看出, 随着 SiC 加入的增加, 样品的抗压强度、表观密度逐渐减小, 气孔率逐渐增大。当 SiC 含量从 0.4% 增加到 1.4% 时, 样品的气孔率从 77.8% 增加到 89.9%, 表观密度从 0.56 g/cm^3 减小到 0.23 g/cm^3 , 抗压强度从 2.9 MPa 减小到 0.8 MPa, 这主要是因为高温焙烧过程中, 增加 SiC 的含量使得产生的气体量增多, 产生了更多的孔隙, 并使得小孔隙连通形成大孔隙, 样品的孔径逐渐增大, 导致总气孔率增大、抗压强度和表观密度减小^[35]。由图 5b 可见, 增加 SiC 的加入量使得样品的闭孔率先增大后减小, 总气孔率逐渐增大, 吸水率显著提高。当 SiC 加入量为 0.4% 和 0.6% 时, 样品的总气孔率差别不大; SiC 含量大于 0.8% 时, 此时过量的 SiC 无法充分与液相中的碱性氧化物接触, 导致氧化反应不能继续发生产生发泡气体, 减弱了 SiC 的发泡作用^[36]; SiC 加入量增加到 1.4% 时, 产生的过多气泡使得连通孔增多形成缺陷孔, 开孔率增大, 高

孔隙率使得样品的吸水率增大。由图 5c 可见。在高温焙烧时, 坯料中的 SiC 表面优先被氧化, 形成致密的 SiO_2 保护层, 导致氧气在 SiO_2 保护层中的扩散速率非常低, 阻碍了氧化反应的进一步发生^[37]。当焙烧温度升高时, 样品晶相的变化和碱

性硅酸盐腐蚀作用破坏了 SiO_2 保护层, 氧气在熔融基体内部的扩散速率增大, 使得氧化反应可持续发生^[34]。高温液相的存在使得熔体的黏度低, 液相内包裹的气体扩散压力大于表面张力, 产生的孔隙不断增大。

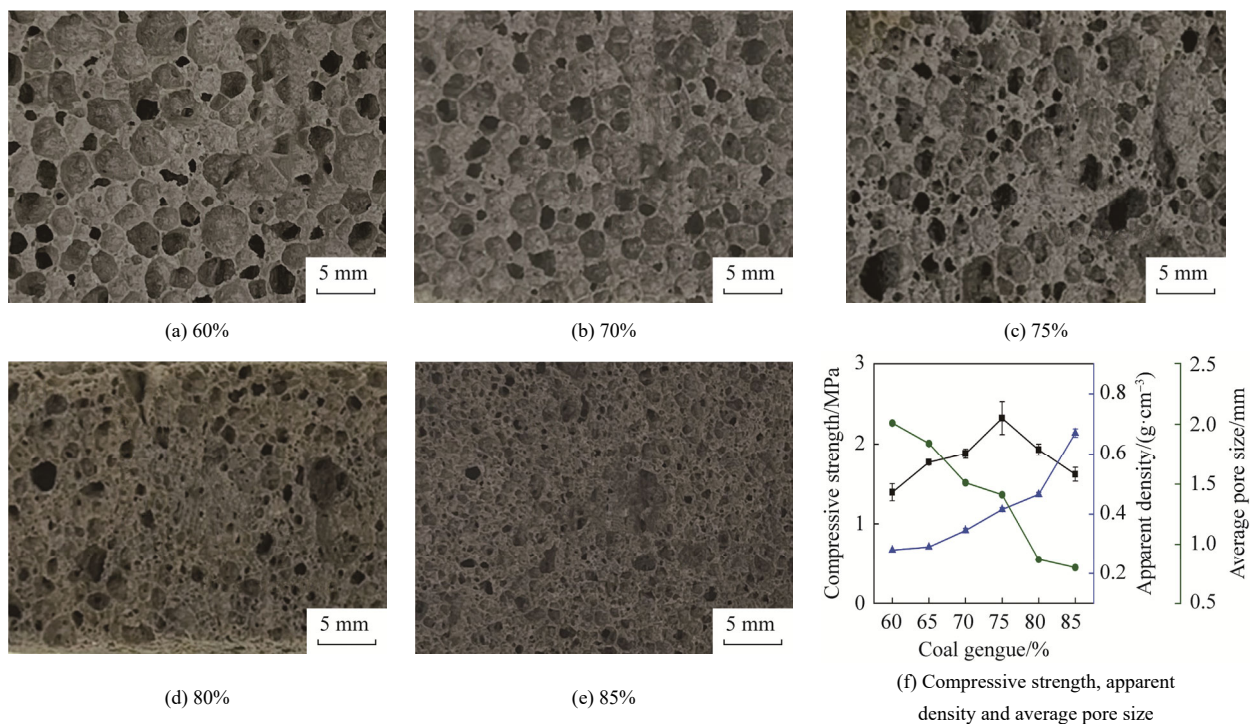


图 3 不同煤矸石含量制备的泡沫陶瓷样品的孔径分布及性能

Fig. 3 Pore size distribution and properties of ceramic foams prepared with different coal gangue contents

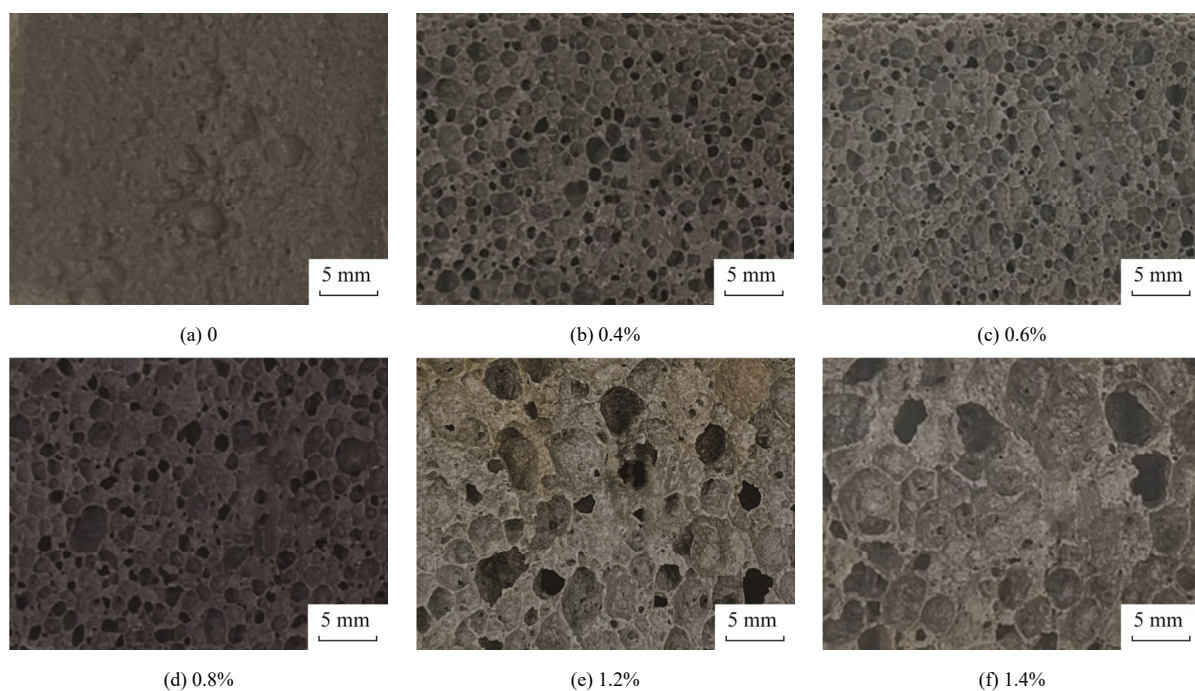
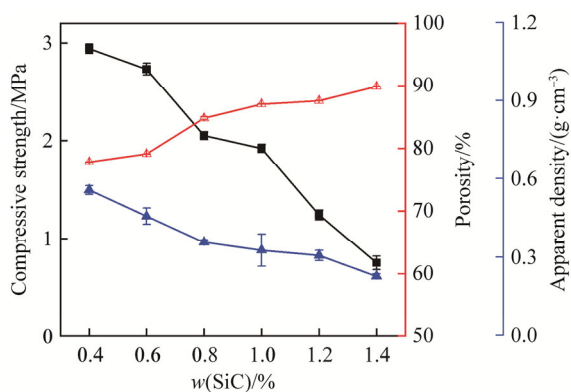
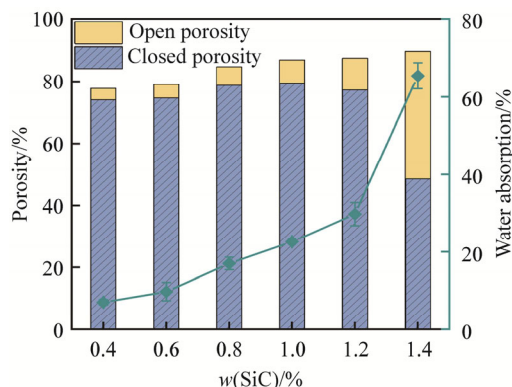


图 4 不同 SiC 添加量下制备的泡沫陶瓷孔径分布图

Fig. 4 Pore size distribution of ceramic foams prepared with different SiC addition amounts



(a) Compressive strength, porosity and apparent density



(b) Porosity and water absorption



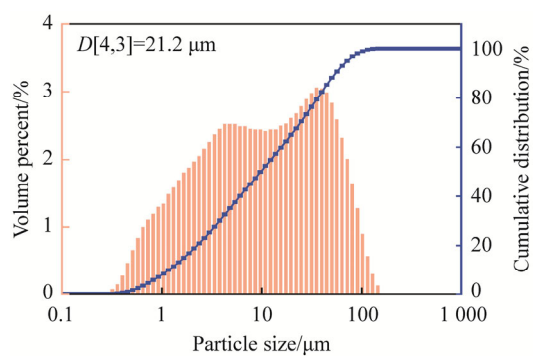
(c) Schematic diagram of SiC foaming reaction process at high temperature

图 5 不同 SiC 加入量对制备的泡沫陶瓷的性能影响及 SiC 高温发泡反应示意图

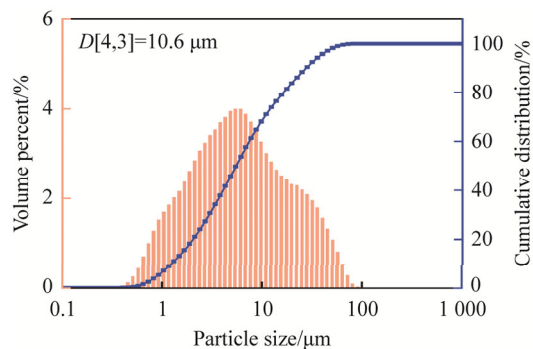
Fig. 5 Effects of SiC addition amounts on properties of ceramic foams and schematic diagram of SiC foaming reaction process at high temperature

2.4 原料粒度的影响

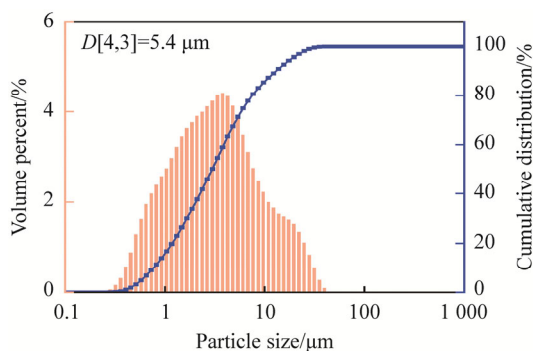
在煤矸石添加量为 70%, SiC 添加量为 0.6% 时, 考察样品的球磨时间对原料粒度及原料粒度对制备样品的性能的影响。图 6 为球磨时间对混合原料粒度的影响及不同粒径制备泡沫陶瓷的 XRD 谱。由图 6a~图 6c 可见, 随着球磨时间的增加, 原料的粒径分布更加集中, 球磨 4、8、16、24、32 h 的体积加权平均粒径 $D[4,3]$ 分别为 21.2、16.9、10.6、7.0、5.4 μm 。当样品的球磨时间短时, 原料混合不均匀, 增加球磨时间后, 球磨机械活化使得混合原料粒度小, 颗粒粒径分布集中, 且有利于增大样品的表面



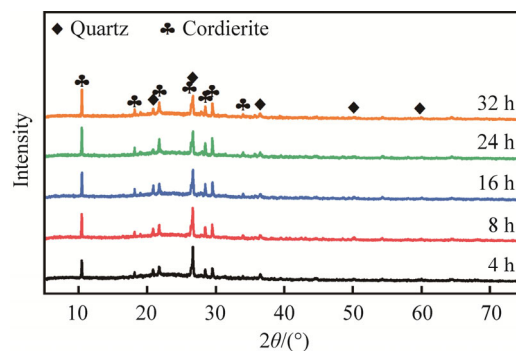
(a) 4 h



(b) 16 h



(c) 32 h



(d) XRD patterns of ceramic foams with different milling time

图 6 球磨时间对混合原料粒度的影响及不同粒径制备泡沫陶瓷的 XRD 谱

Fig. 6 Effects of milling time on particle size of feed mixture and XRD patterns of prepared ceramic foams

接触面, 从而有利于泡沫陶瓷的制备^[38], 这是因为混合料的粒径减小时, 颗粒趋向于球体, 此时细小

的颗粒有利于原料中的 SiO_2 在较低温度下实现团聚和烧结, 增大熔融坯体的黏度。由图 6d 可见, 随着混合原料粒度的减小, 样品中的堇青石相的特征衍射峰逐渐增强, 石英的衍射峰逐渐减弱, 表明细小的颗粒提高了粉末的反应活性, 降低了体系的自由能, 促进了中间相向堇青石相的转变, 同时使得粉末颗粒之间的接触面积增大, 有利于 Si^{4+} 、 Al^{3+} 、 Mg^{2+} 等离子在焙烧过程中的扩散而发生固相反应生成堇青石。

图 7 为不同原料粒度制备样品的微观形貌。由图 7 可以看出, 混合原料的粒度减小, 样品的孔径逐渐减小, 气孔的孔径分布更加均匀。体积平均粒径为 $21.2\ \mu\text{m}$ 的样品粉料的分散性差, 发泡剂聚集形成的超大孔多; 体积平均粒径为 $10.6\ \mu\text{m}$ 时, 样品的孔径分布集中, 细小的孔隙和均匀的气孔结构有效地提高了泡沫陶瓷抗压强度^[39], 颗粒粒度继续减小, 对样品孔径的影响减小。

图 8 为原料粒度对泡沫陶瓷性能的影响。由图 8a 可见, 随着混合原料粒度的减小, 样品的表观密度及气孔率变化不大, 表观密度在 $0.45\sim 0.47\ \text{g}/\text{cm}^3$ 范围内波动, 总气孔率在 $79.1\%\sim 83.0\%$ 范围内波动。但样品的开孔率逐渐减小, 吸水率从 21.9% 减小至 4.4% , 这是由于颗粒粒度大时, 制备的样品具有较大的孔隙形成开孔结构使得总气孔率高, 导致表观密度低而吸水率高, 颗粒粒度减小到 $10.6\ \mu\text{m}$ 时, 高温下生成的熔融物质包裹均匀分散的发泡剂, 样品的气孔结构分布均匀, 对气孔率及表观密度的影响减小。由图 8b 可见, 减小颗粒粒度显著增强了样品的抗压强度, 混合原料的颗粒粒度为 $5.4\ \mu\text{m}$ 时, 样品的抗压强度达到 $6.1\ \text{MPa}$, 这是因为原料中细小的 SiO_2 颗粒提高了孔壁的致密性, 从而提高了泡沫陶瓷的承载能力^[40]。

表 3 与文献中泡沫陶瓷性能比较如所示。由表 3 可见, 以煤矸石为主要原料制备泡沫陶瓷主要

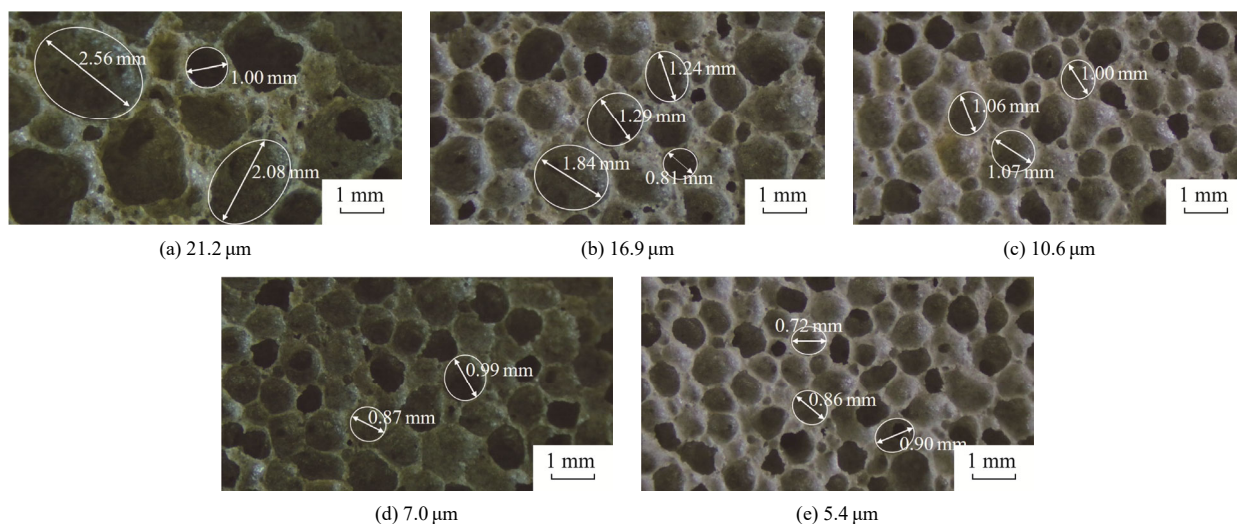


图 7 不同原料粒度制备泡沫陶瓷的微观形貌

Fig. 7 Microstructure of ceramic foams prepared by feed mixture with different particle sizes

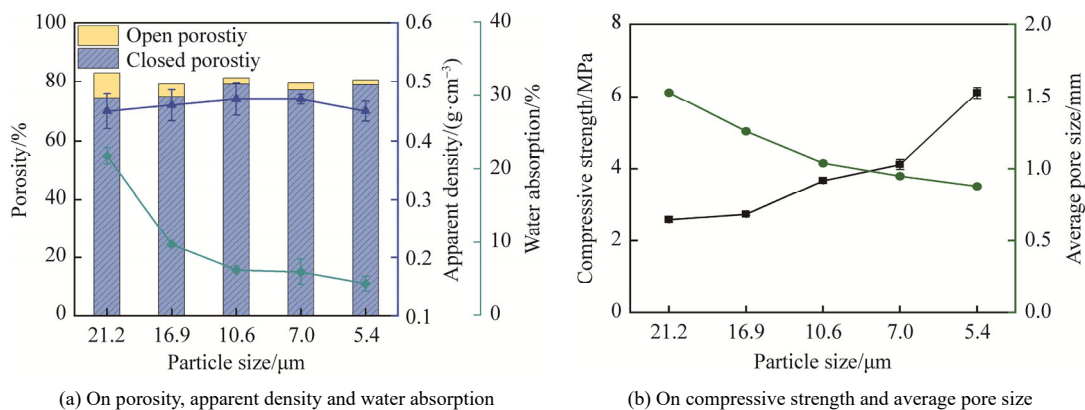


图 8 原料颗粒粒度对泡沫陶瓷性能的影响

Fig. 8 Effects of particle size of feed mixture on properties of ceramic foams

表 3 文献中泡沫陶瓷性能比较
Table 3 Comparison of properties of ceramic foams in literature

w(Raw materials)/%	w(Additive)/%	Calcination temperature/ ℃	Holding time/min	Porosity/%	Apparent density/ (g·cm ⁻³)	Compressive strength/ MPa	Reference
Coal gangue (53.8), high alumina refractory solid wastes (46.2)		1 500	180	15.6	2.52	71.8	[10]
Coal gangue (40), phosphorus tailing (60)	Dextrin (5), deionized water	1 150		61.3		2.95	[11]
Coal gangue (66.2), basic magnesium carbonate (22.7), bauxite (11.1)	Hydrochloric acid, sulfuric acid, NaOH (20), CMC (1), silica sol	1 200		73.7		2.23	[41]
Coal gangue (20), granite waste (70), waste cullet (10)	SiC, CaO, MgO, Na ₂ HPO ₄ and Na ₃ PO ₄	1 150	30		1.22	12.58	[42]
					0.45	5	T/CBCSA 12-2019 Industry standard
Coal gangue (70), diatomite (20), talc (10)	SiC (0.6)	1 190	25	80.6	0.45	6.1	This work

存在煤矸石掺量较低，表观密度大的问题，本工作制备的泡沫陶瓷煤矸石利用率高且具有较高的综合性能，可以用作保温隔热材料。

3 结论

1) 本工作以 SiO₂–Al₂O₃–MgO 体系为基础，煤矸石为主要原料，加入硅藻土粉、滑石粉及少量发泡剂 SiC 制备出了堇青石基泡沫陶瓷。在 1 190 ℃焙烧 25 min 条件下，煤矸石含量为 70%时制备出了气孔结构较好的泡沫陶瓷，主要物相为堇青石和石英。随着煤矸石含量的增加，硅铝质量比从 2.66 降低至 2.05，样品的气孔结构逐渐变差，抗压强度先增大后减小。

2) 发泡剂 SiC 含量的增加使得高温下产生的气体量增加，总气孔率从 77.8%增加到 89.9%，表观密度从 0.56 g/cm³ 减小到 0.23 g/cm³，SiC 含量大于 0.8%时，过量的 SiC 使得开孔率增大，降低了泡沫陶瓷抗压强度。

3) 减小原料的粒度提高了泡沫陶瓷的力学性能和反应活性，促进了烧结过程中石英相向堇青石相的转变，细小的孔隙和均匀的气孔结构有效地提高了泡沫陶瓷抗压强度。使用最优配比煤矸石:硅藻土粉:滑石粉(质量比)为 7:2:1，添加 0.6%的 SiC 发泡剂，混合原料体积平均粒径为 5.4 μm 制备的样品表观密度、气孔率和抗压强度分别为 0.45 g/cm³、80.6%和 6.1 MPa，在保温墙体材料具有广阔的应用前景。

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Preparation and Properties of Coal Gangue-Based High Strength Ceramic Foams

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Extended Abstract

Introduction Ceramic foams is a kind of inorganic non-metallic material with a three-dimensional porous network structure after calcination at high temperatures. The mechanical properties are one of the important factor to evaluate the application of ceramic foams, which affected by the porosity, pore size, pore distribution and skeleton structure, *etc.* High porosity would reduce the bearing capacity of ceramic foams and limit its application fields. Therefore, this research is mainly focused on how to balance porosity and strength of ceramic foams, as compressive strength could be improved effectively by reducing the pore size, narrowing the pore size distribution or forming a closed pore structure.

When coal gangue is used as raw materials to prepare ceramic foams, it still exists some problems, such as the low utilization, high energy consumption and unclear foaming principle. The key to producing a ceramic foam is to form a melt matrix with appropriate viscosity and to generate a certain amount of foaming gas in the matrix. Due to the complex composition of coal gangue, it is difficult to control the viscosity of the melt matrix at high temperatures, resulting in the pore structure distribution uneven and reducing the mechanical properties of ceramic foams.

In this work, coal gangue was used as the main raw materials, and diatomite powder, talc powder, a small amount of silicon carbide (SiC) foaming agent were added to prepare the ceramic foams with high compressive strength. The effects of raw materials composition, SiC content (mass fraction) and particle size of feed mixture on the pore structure, apparent density and compressive strength and other properties of ceramic foams were investigated.

Methods The coal gangue was crushed and sieved to less than 74 μm . Based on the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$ ternary system, the coal gangue, diatomite powder and talc powder were mixed at different mass ratios, and then SiC powders were added as the foaming agent, the mixture and agate balls in a mass ratio of 1:1 were milled with a speed of 300 r/min. After ball milling, the powders were placed in a corundum boat and heated at 1 190 $^\circ\text{C}$ for 25 min, then cooled to room temperature in furnace. The chemical compositions of the raw materials were determined by X-ray fluorescence spectrometer (XRF). The crystalline structure of raw materials and ceramic foams was determined by X-ray diffraction (XRD). The thermogravimetric analyzer (TG–DSC) was used to analyze the mass change and thermal analysis of raw materials. The particle size of mixed materials was analyzed via a laser particle size analyzer. The compressive strength of ceramic foams was measured *via* a pressure test machine. The pore size distribution of the sample was measured by Nano Measurer 1.2, and the water absorption and porosity of ceramic foams were measured by Archimedeian method.

Results and discussion When amount of coal gangue reached 60% and 70%, the main phases of ceramic foams were cordierite and quartz, and when content of coal gangue exceeded 75%, sekaninaite phase appeared. When content of coal gangue reached 85%, the average pore size of the ceramic foams decreased from 2.01 mm to 0.80 mm, and the distribution of pore size became uneven as the increase of coal gangue could reduce the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mass ratio, which would lead to an increase of melting temperature of the matrix, and thus the generated silicate molten material at high temperature decreased and the viscosity increased. As a result, the pore structure with uneven distribution would decrease the bearing capacity. Compressive strength reached the maximum value of 2.2 MPa at the coal gangue content of 75%. When content of SiC foaming agent increased, more small pores were generated in the matrix, these pores could connect to form large pores during sintered process, resulting in a gradual increase in pore size. When content of SiC increased from 0.4% to 1.4%, the compressive strength of ceramic foams decreased from 2.9 MPa to 0.8 MPa, the reduction of particle size of the feed materials could be benefit to the agglomeration and sintering behavior of SiO_2 at low temperature. When the average particle size decreased from 21.1 μm to 5.4 μm , the apparent density and porosity of ceramic foams changed slightly, while the compressive strength gradually increased from 2.6 MPa to 6.1 MPa, being due that the small particle size of SiO_2 in feed mixtures could improve the densification of the pore wall and finally improve the bearing capacity of the ceramic foams.

Conclusion The main conclusions of this work can be summarized as follows: With the increase of coal gangue content in the feed materials, $\text{SiO}_2/\text{Al}_2\text{O}_3$ mass ratio decreased from 2.66 to 2.05, the pore structure of the sample deteriorated, and the compressive strength first increased and then decreased. When the content of SiC increased, more gases were released during calcination process, and thus increasing the porosity. When it exceeded 0.8%, the excess SiC should increase the open porosity and thus reduces the compressive strength of ceramic foams. Reducing the particle size of the feed mixture could improve the reaction activity of powders during the high temperature foaming process, the small pores and uniform pore structure could obviously improve the compressive strength of ceramic foams. When mass ratio of coal gangue: diatomaceous earth powder: talc was 7 : 2 : 1, content of SiC was 0.6%, the average particle size of the mixed materials was 5.4 μm , the apparent density, porosity and compressive strength of the prepared samples were 0.45 g/cm^3 , 80.6%, and 6.1 MPa, respectively, expected to be applied in the field of heat preservation wall.

Keywords ceramic foams; coal gangue; compressive strength; pore structure; silicon carbide foaming agent; particle size