

$\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量对碳化硅晶须自增强多孔陶瓷性能的影响

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摘 要: 以碳化硅粉为主要原料、硅粉和炭黑为碳化硅自结合相粉体、 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 为添加剂, 采用发泡结合反应烧结法制备了碳化硅晶须自增强多孔陶瓷。研究了 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量(质量分数)对碳化硅晶须自增强多孔陶瓷的物相组成、显微结构和力学性能等的影响。结果表明: 添加适量的 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 可以促进碳化硅晶须的形成, 并提高多孔陶瓷样品的强度。当 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量为 2% 时, 所制备孔隙率为 76.9% 的碳化硅晶须自增强多孔陶瓷样品的常温抗折强度和耐压强度分别为 2.6 MPa 和 3.7 MPa, 样品中生成的 SiC_w 晶须的长度约为 4 μm , 直径约为 62 nm, 其生长是由气-固反应机理控制。

关键词: 碳化硅多孔陶瓷; 碳化硅晶须; 三水氟化铝; 力学性能

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碳化硅多孔陶瓷因具有耐腐蚀、耐高温、比表面积大、抗热震性好、力学性能优异等特点^[1-5], 被广泛地应用于气液过滤、催化载体、保温材料、燃烧器材料等领域^[6-8]。

碳化硅多孔陶瓷的制备方法主要有添加造孔剂法^[9-10]、有机泡沫浸渍法^[11-12]、冷冻干燥法^[13-14]、溶胶-凝胶法^[15-16]、发泡法^[17-18]等, 其中, 发泡法因操作简单、制品密度和形状可控, 成为制备高孔隙率碳化硅多孔陶瓷常用的方法之一。Zhao 等^[19]以碳化硅粉为原料、 H_2O_2 为发泡剂、十二烷基硫酸钠为表面活性剂, 采用发泡法经 2000 $^\circ\text{C}$ 烧结后制备了孔隙率为 56.3% 和抗压强度为 24.3 MPa 的碳化硅多孔陶瓷。Wu 等^[20]以碳化硅粉为原料、十二烷基三甲基溴化胺为发泡剂, 采用发泡结合 3D 打印法经 1650 $^\circ\text{C}$ 烧结后制备了孔隙率为 65.4%、抗压强度为 7.9 MPa 的碳化硅多孔陶瓷。Jing 等^[21]以可膨胀聚甲基丙烯酸甲酯微球为发泡剂和模板, 采用发泡法结合牺牲模板法制备了孔隙率高达 90.3%, 抗压强度为 3.9 MPa 的碳化硅多孔陶

瓷。虽然上述研究都取得了较好的结果, 但仍存在烧结温度高、力学性能低等缺点, 限制了其应用领域。

反应烧结法不仅具有工艺简单、烧结温度低等优点, 而且新生成的结合相可使最终制品具有较高的强度, 同时还可以通过反应结合相的生成来调控最终制品的收缩率。因此, 反应烧结法被广泛地应用于碳化硅多孔陶瓷的制备^[22-23]。Ren 等^[24]以硅屑和活性炭为原料, 采用反应烧结法经 1500 $^\circ\text{C}$ 制备了孔隙率为 59.6%、抗压强度为 34.7 MPa 的碳化硅多孔陶瓷。Xing 等^[25]以硅废料为原料, 采用反应烧结法制备了孔隙率为 45.4%、抗折强度为 66.0 MPa 的多孔碳化硅-莫来石陶瓷。Zhu 等^[26]以 $\alpha\text{-SiC}$ 和聚碳硅烷为原料, 经 1100 $^\circ\text{C}$ 保温 2 h 氩气条件下反应烧结后制备了体积密度为 1.66 g/cm^3 、孔隙率为 44.7%、抗折强度为 15.8 MPa 的碳化硅自结合多孔陶瓷。Kennedy 等^[27]以不同粒径的碳化硅粉、硅粉及炭黑为原料, 硼粉为烧结助剂, 经 1750 $^\circ\text{C}$ 保温 1 h 氩气氛烧结制备了孔隙率为 46.0%、抗折强度为

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35.5 MPa 的碳化硅自结合多孔陶瓷, 原位新生成的碳化硅相增强了碳化硅颗粒间的结合强度, 从而提高了碳化硅多孔陶瓷的力学性能。

研究表明^[28–29], 在碳化硅多孔陶瓷中原位生成晶须/柱晶可以大幅度地提高材料的力学性能。碳化硅晶须是优异的增强体, 不仅具有碳化硅材料的优异性能, 而且可以显著提高材料的综合性能。Eom 等^[30]以氧化钙为添加剂, 经 1650~1900 °C 制备了抗折强度高达 628.0 MPa 的碳化硅多孔陶瓷。氧化钙的加入促进了碳化硅晶须的形成, 碳化硅晶须的桥接和拔出机制阻止了裂纹的扩展, 从而提高多孔陶瓷的抗折强度。Wang 等^[31]以硝酸铁为催化剂前驱体, 经 1300 °C 保温 3 h 制备了断裂模量为 21.2 MPa 的碳化硅多孔陶瓷, 比未添加硝酸铁样品的断裂模量提高了 2.3 倍。Zhang 等^[32]采用泡沫浸渍法制备了体积密度为 0.72 g/cm³ 和抗压强度为 1.5 MPa 的碳化硅晶须自增强多孔陶瓷, 原位形成的碳化硅晶须消除了涂层表面的裂纹, 优化了多孔陶瓷的显微结构, 从而提高了碳化硅多孔陶瓷的强度和抗热震性能。上述结果表明: 氧化钙、硝酸铁等添加剂在碳化硅晶须的原位合成过程中起着重要的作用; 但仍存在着生成的碳化硅晶须的数量少、长度短等问题。因此, 急需一种可以形成大量大长度碳化硅晶须的添加剂。

本工作以 70%(质量分数)的碳化硅粉为原料、30%的硅粉和炭黑为碳化硅自结合相粉体、三水氧化铝($\text{AlF}_3 \cdot 3\text{H}_2\text{O}$)为添加剂, 采用发泡结合反应烧结法制备了碳化硅晶须自增强多孔陶瓷。研究了 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量对碳化硅晶须自增强多孔陶瓷的物相组成、显微结构和力学性能等的影响。

1 实验

1.1 原料

碳化硅粉[99%(质量分数), d_{50} 为 5 μm , 中国安阳市远达硅业有限公司]、硅粉(99.5%, d_{50} 为 3.5 μm , 中国山东博肯硅材料有限公司)、炭黑(99%, d_{50} 为 0.4 μm , 中国天津天一世纪化工产品科技发展有限公司)、三水氟化铝(化学纯, 中国上海山浦化工有限公司)、十二烷基硫酸三乙醇胺(分析纯, 中国山东优索化工科技有限公司)、羧甲基纤维素钠(化学纯, 中国山东力宏宝冠纤维素有限公司)、Isobam 104(工业级, 日本可乐丽株式会社)。所用原料的 X 射线衍射(XRD)谱如图 1 所示。由图 1 可见, 碳化硅粉主要为 α -SiC、硅粉为硅相、炭黑为无定形相。

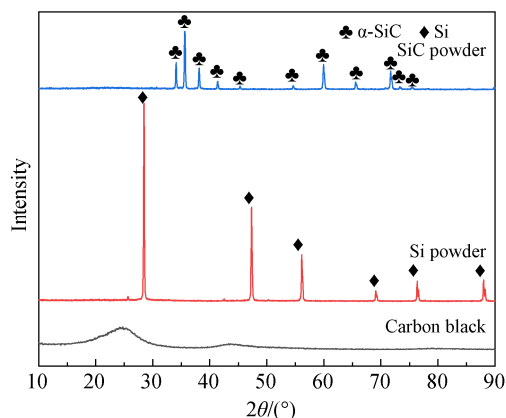


图 1 原料的 XRD 谱

Fig. 1 XRD patterns of raw materials

1.2 样品制备

将刚玉球、预混合粉体(碳化硅粉、硅粉和炭黑)和去离子水按质量比为 4:2:1 放入球磨罐中, 以 300 r/min 在行星球磨机中球磨 3 h, 所得浆料置于 120 °C 烘箱中干燥至恒定质量, 并过 100 目筛制得所需混合粉体。然后控制混合粉体的固含量为 50%(体积分数), 将其逐渐加入至含有 0.5%(质量分数)的 Isobam 104 和 0.15% 的羧甲基纤维素钠的溶液中, 经机械快速搅拌 5 min 后, 向浆料中加入 1.0%(体积分数)的十二烷基硫酸三乙醇胺, 再快速机械搅拌 3 min 制得泡沫浆料, 将其注入 160 mm×80 mm×40 mm 的模具中, 常温静置 48 h 脱模, 脱模后的坯体于常温干燥 72 h 后, 再置于 40~100 °C 的烘箱中干燥至恒定质量。最后将干燥的坯体置于 1600 °C 的氩气中烧结 2 h, 冷却至室温制得所需样品。

1.3 样品表征

采用 Bruker D8 Advance 型 X 射线衍射仪分析样品的物相组成。使用 Nano SEM 430 型扫描电子显微镜观察多孔陶瓷的显微形貌, 基于 SEM 照片, 采用 Image-Pro Plus 软件统计计算 100 个近球形的大气孔和环形小气孔的平均尺寸。采用微米 X 射线 CT(Micro-CT, GE Vtomexs, 美国)表征多孔陶瓷样品的三维孔隙结构特征。采用 GX-8011-A 型电子万能材料试验机表征多孔陶瓷样品的常温抗折和抗压强度。

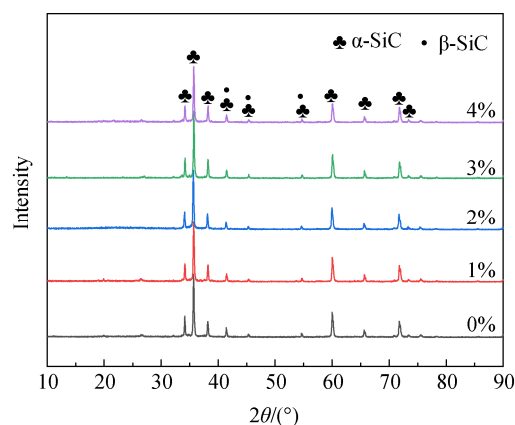
2 结果与讨论

2.1 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量对多孔陶瓷样品物相组成的影响

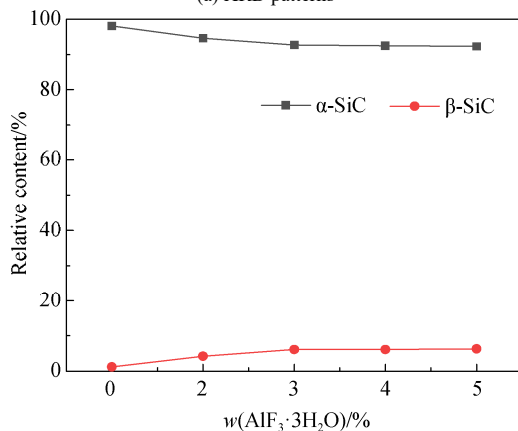
图 2 为 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量对所制备碳化硅晶须自增强多孔陶瓷样品 XRD 谱和物相含量的影响。

由图 2a 可见, 所制备样品的主晶相为 α -SiC 相, 次晶相为 β -SiC 相。随着 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量从 0% 增加到 4% 时, α -SiC 的衍射峰强度先略有降低而后基本保持不变, 而 β -SiC 的衍射峰强度先略有升高而后基本保持不变。

由图 2b 可见, 随着 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量从 0% 增至 4% 时, 所制备多孔陶瓷样品中 α -SiC 的含量先略有减小而后趋于稳定, β -SiC 的含量先略有增加而后基本保持不变。当 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量为 4% 时, 所制备的样品中 α -SiC 的含量为 93.7%, β -SiC 的含量为 6.3%。



(a) XRD patterns



(b) Phase contents

w—Mass fraction.

图 2 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量对碳化硅晶须自增强多孔陶瓷样品 XRD 谱和物相含量的影响

Fig. 2 Effect of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ contents on XRD patterns and crystalline phase content of silicon carbide whiskers self-reinforced porous ceramics

2.2 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量对多孔陶瓷样品显微结构的影响

图 3 为 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量不同时所制备具有相同孔隙率(76.9%)多孔陶瓷样品的 SEM 照片。由图 3 可见, 所制备的多孔陶瓷样品中均存在近似球形的大气孔

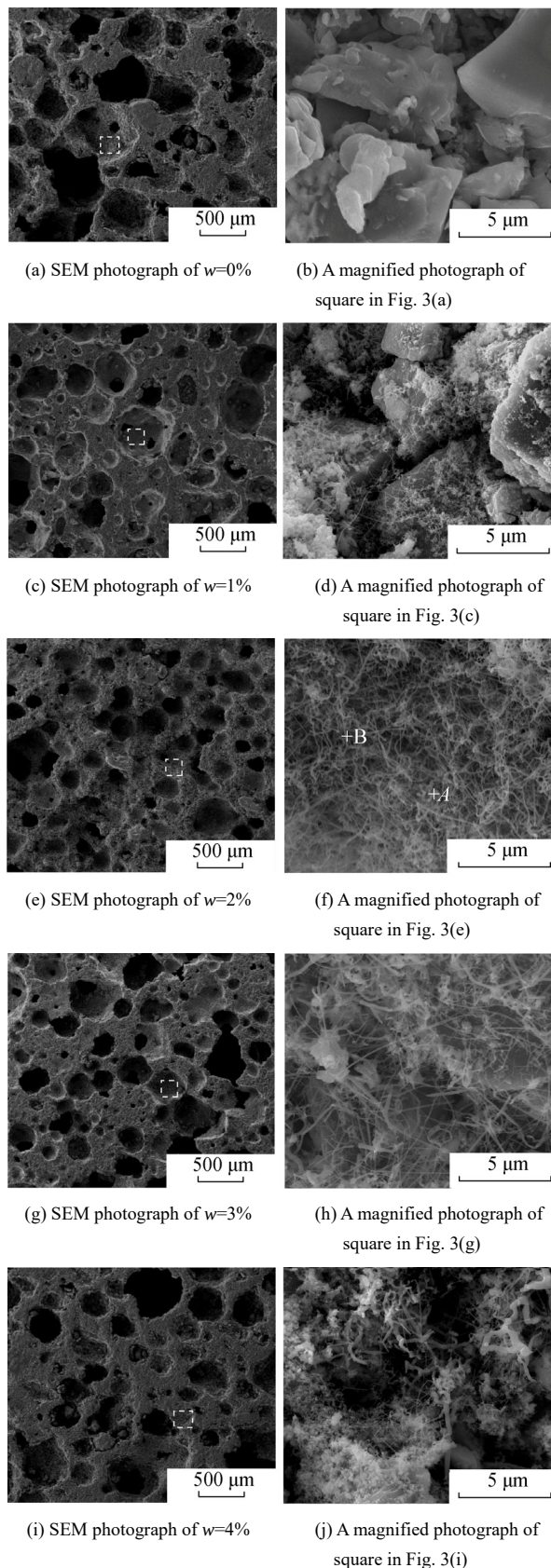


图 3 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量不同时所制备碳化硅晶须自增强多孔陶瓷样品的 SEM 照片

Fig. 3 SEM images of silicon carbide whiskers self-reinforced porous ceramics prepared with different contents of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$

和环形的小气孔。当 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量从 0% 增至 2% 时, 所制备的多孔陶瓷样品中气孔的数量逐渐增多, 孔径逐渐变小。当 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量从 2% 增至 4% 时, 多孔陶瓷样品中气孔的数量略有减少, 孔径略有增大。这可能是当 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量为 2% 时, 所制备陶瓷浆料的表面自由能最小, 使气泡能稳定地存在于浆料中, 从而使多孔陶瓷的孔径较小^[33–34]。

图 4 为基于图 3a、图 3c、图 3e、图 3g 和图 3i 统计计算得出的平均孔径分布图。由图 4 可知, 当 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量从 0 增至 4% 时, 所制备多孔陶瓷的近球形大气孔和环形小气孔的平均孔径均呈现先减小后增大的趋势。当 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量为 2% 时, 所制备碳化硅晶须自增强多孔陶瓷的球形大气孔和环形小气孔的平均孔径为最小, 分别为 206 μm 和 50 μm 。

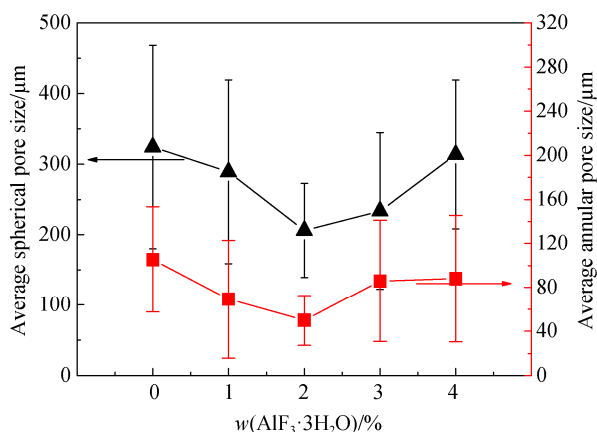


图 4 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量对碳化硅晶须自增强多孔陶瓷样品平均孔径的影响

Fig. 4 Effect of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ contents on the average pore size of silicon carbide whiskers self-reinforced porous ceramics

图 5 为 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 的添加量为 2% 时所制备碳化硅晶须自增强多孔陶瓷样品的显微 CT 图像。由图 5 可知, 所制备的碳化硅晶须自增强多孔陶瓷样品中由许多近球形的气孔构成, 部分气孔之间相互连通, 这与 SEM 所观察到的结果相一致。

由图 3 可知, 未添加 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 时, 所制备多孔陶瓷的样品中只有颗粒状的碳化硅(图 3b)。当 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量为 1% 时, 所制备的多孔陶瓷样品中出现了少量的晶须(图 3d)。提高 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量至 2% 时, 所制备多孔陶瓷样品中晶须的数量明显增多(图 3f)。继续提高 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量至 3%~4% 时, 多孔陶瓷样品中晶须的直径明显变大(图 3h~图 3j)。这是 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量较多时, 体系中生成的氟化物气体浓度超过晶须生长所需, 导致晶

须横向生长所致^[35]。同时, 采用能量色散 X 射线谱(EDS)能对图 3f 中晶须的成分进行了检测(如图 6 和表 1)。由图 6 和表 1 可知, 晶须中只有 Si 和 C 2 种元素, 其摩尔比约为 1:1, 结合 XRD 谱结果可以确定样品中生成的晶须为碳化硅晶须。

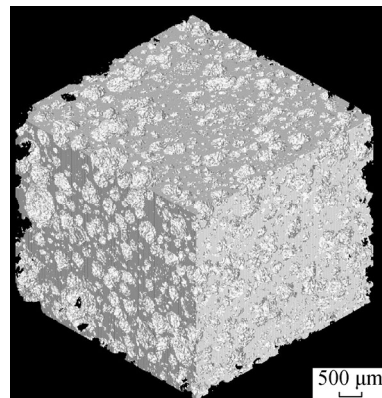
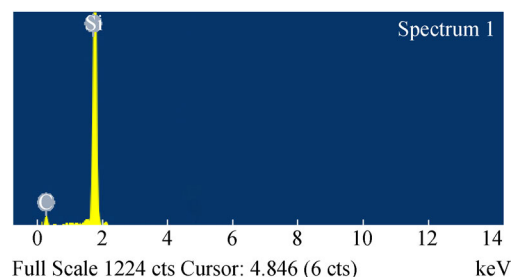
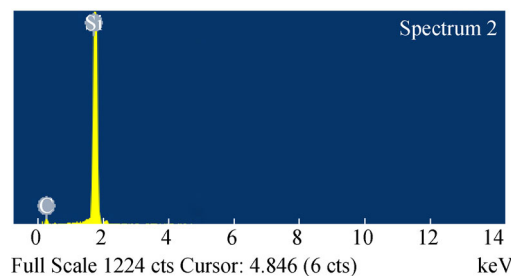


图 5 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量为 2% 时所制备碳化硅晶须自增强多孔陶瓷样品的显微 CT 图像

Fig. 5 Micro-CT image of silicon carbide whiskers self-reinforced porous ceramics prepared with 2% $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$



(a) EDS spectrum of point A in Fig. 3(f)



(b) EDS spectrum of point B in Fig. 3(f)

图 6 图 3f 中样品选取点的 EDS 结果

Fig. 6 EDS results of the selected points in Fig. 3(f)

表 1 图 3f 中晶须选取点的 EDS 结果

Table 1 EDS results of the selected points in Fig. 3(f) whiskers

Points	Mole fraction/%		
	C	Si	Total
A	53.4	46.6	100
B	49.3	50.7	100

图 7 为基于图 3b、图 3d、图 3f、图 3h 和图 3j 统计计算所得碳化硅晶须长度和直径的分布图。由图 7 可见,随着 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量的增多,所制备多孔陶瓷样品中碳化硅晶须的长度呈先增大后减小的趋势,而直径则呈现先逐渐增大而后基本保持不变的趋势。当 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量为 2% 时,所制备多孔陶瓷样品中的 SiC_w 长度约为 $4 \mu\text{m}$,直径约为 62 nm 。

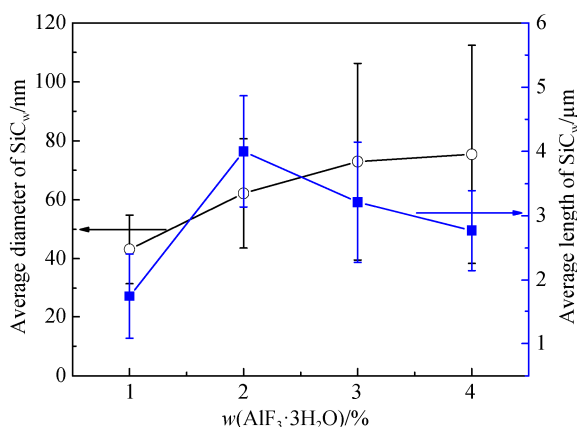


图 7 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量对多孔陶瓷中碳化硅晶须平均长度和直径的影响

Fig. 7 Effect of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ contents on average length and diameter of SiC whiskers in porous ceramics

为进一步确定样品中生成晶须的显微结构,又采用透射电子显微镜(TEM)及高分辨透射电子显微镜(HRTEM)对其进行了表征,结果如图 8($\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量为 2%)所示。由图 8a 可知,所合成晶须的直径约为 69 nm ,与根据 SEM 照片统计计算所得晶须的直径基本一致。由图 8b 可知,晶须生长发育良好,可见整齐的晶格条纹,其间距为 0.25 nm ,与 $\beta\text{-SiC}$ (111)面的晶面间距 0.25 nm 基本一致,表明样品中生成的晶须为 $\beta\text{-SiC}$,也表明平行于 $\beta\text{-SiC}$ 晶须生长方向的晶面为(111)面。

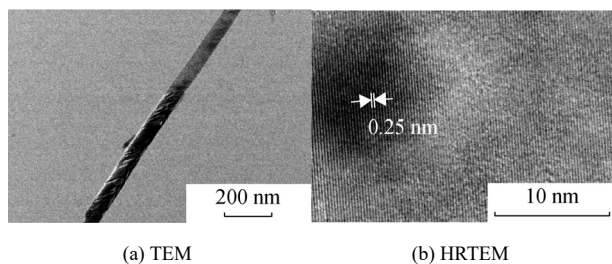


图 8 碳化硅晶须自结合多孔陶瓷样品中所生成晶须的 TEM 和 HRTEM 照片

Fig. 8 TEM and HRTEM images of whiskers in silicon carbide whiskers self-reinforced porous ceramics

2.3 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量对多孔陶瓷样品常温强度的影响

图 9 为 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量(0%~4%)对多孔陶瓷常温强度的影响。由图 9 可知,随着 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量的逐渐增加,所制备多孔陶瓷样品的常温抗折强度和耐压强度均呈先增大而后略有下降的趋势。当 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量为 2% 时,所制备多孔陶瓷样品的常温抗折强度和耐压强度达最大,分别为 2.6 MPa 和 3.7 MPa ,明显高于未添加 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 所制备多孔陶瓷样品的抗折强度(1.1 MPa)和耐压强度(1.4 MPa),这一方面是添加 2% 的 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 所制备多孔陶瓷样品中的球形大气孔和环形小气孔的平均孔径最小,且气孔分布均匀,提高了碳化硅晶须自增强多孔陶瓷样品的常温强度^[36];另一方面, $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 为 2% 时所制备的多孔陶瓷样品中生成了大量的 SiC_w (图 3f),其长度最长, SiC 晶须不仅可以使裂纹桥联和裂纹偏转来阻止裂纹的扩展,而且 SiC 晶须的拔出和断裂会消耗大量的能量,从而使碳化硅晶须自增强多孔陶瓷样品的常温强度进一步提高^[37]。

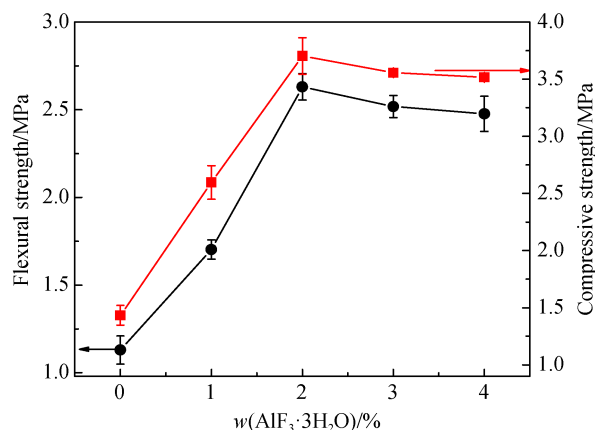
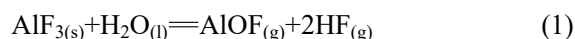


图 9 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量对碳化硅晶须自增强多孔陶瓷样品常温强度的影响

Fig. 9 Effect of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ contents on strength of silicon carbide whiskers self-reinforced porous ceramics

2.4 自增强多孔陶瓷中碳化硅晶须的生长机理

基于图 2、图 3 和已有研究结果^[38-39],在 $\text{SiC-Si-C-AlF}_3 \cdot 3\text{H}_2\text{O}$ 体系中存在如下反应:



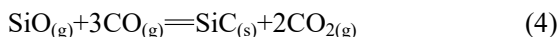
$$\Delta_r G_1^\theta = 522.7 - 0.367T \text{ (kJ/mol)}$$



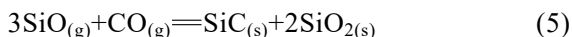
$$\Delta_r G_2^\theta = -272.6 - 0.174T \text{ (kJ/mol)}$$



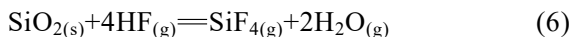
$$\Delta_r G^\theta_3 = -342.6 - 0.118T \text{ (kJ/mol)}$$



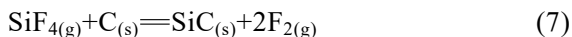
$$\Delta_r G^\theta_4 = -323.3 + 0.348T \text{ (kJ/mol)}$$



$$\Delta_r G^\theta_5 = -1293.2 + 3.401T \text{ (kJ/mol)}$$



$$\Delta_r G^\theta_6 = -68.8 + 0.069T \text{ (kJ/mol)}$$



$$\Delta_r G^\theta_7 = 1507.8 - 0.136T \text{ (kJ/mol)}$$



$$\Delta_r G^\theta_8 = -113.6 + 0.030T \text{ (kJ/mol)}$$

图 10 为反应(1)~反应(8)的 $\Delta_r G^\theta$ 随反应温度的变化曲线。由图 10 可见, 标准状态下, 反应(1)在 1425~1800 °C 条件下其 $\Delta_r G^\theta$ 为负值, 表明高于 1425 °C 能发生反应。反应(4)和反应(6)在低温下其 $\Delta_r G^\theta$ 为负值, 高温下其 $\Delta_r G^\theta$ 为正值, 表明该反应在低温时能自发反应, 高温时可发生逆向反应。反应(7)在 100~1800 °C, 其 $\Delta_r G^\theta$ 为正值, 说明该反应在此温度下不发生反应。反应(2)、反应(3)、反应(5) 和反应(8)在 100~1800 °C, 其 $\Delta_r G^\theta$ 均为负值, 表明在此温度下均能自发反应。因此, 碳化硅晶须的形成涉及除反应(7)外的所有反应。

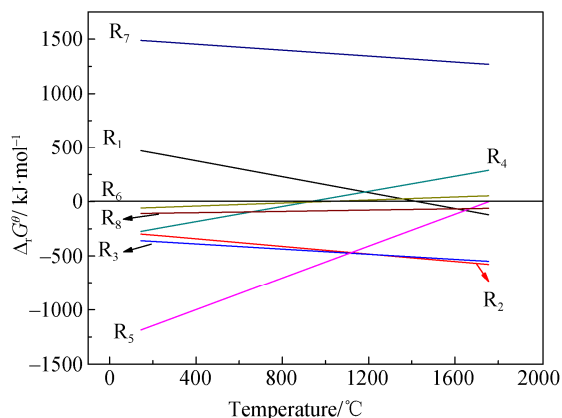


图 10 反应式(1)~反应式(8)(R₁~R₈)的标准 Gibbs 自由能 $\Delta_r G^\theta$ 与反应温度关系曲线

Fig. 10 Relationship between standard Gibbs free energy $\Delta_r G^\theta$ and temperature of reactions (1)–(8) (R₁–R₈)

由图 3d、图 3f、图 3h、图 3j 及图 8a 可知, 所制备多孔碳化硅陶瓷样品中生成的碳化硅晶须表面光滑平整, 顶端无液滴状物质形成, 表明碳化硅晶须的形成过程无液相的参与。而图 3b 和图 10 的结果表明, 气相参与了碳化硅晶须合成。

为验证烧结过程中 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 产生的气相物质对多孔陶瓷内碳化硅晶须生成的作用, 实验采用相

同的工艺条件($\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量为 2%, 1600 °C 保温 2 h), 在开放气氛下制备了多孔陶瓷, 其高倍 SEM 照片如图 11 所示。由图 11 可知, 多孔陶瓷中均为颗粒状物质, 没有晶须形成, 表明在烧结过程中 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 产生的气相物质是生成碳化硅晶须的关键。因此, 可认为碳化硅晶须的生长是由气–固反应机理控制。而图 10 和已有研究结果^[38]表明, 烧结过程中形成的 $\text{SiO}_{(\text{g})}$ 和 $\text{CO}_{(\text{g})}$ 参与了碳化硅晶须的生成, 推测其生长机理示意图如图 12 所示。首先, 在 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 的作用下, Si 与体系中的 O_2 反应形成气相 $\text{SiO}_{(\text{g})}$, C 与体系中的 O_2 反应生产 $\text{CO}_{(\text{g})}$ 。然后, $\text{SiO}_{(\text{g})}$ 与 $\text{CO}_{(\text{g})}$ 反应生成 SiC 晶核, 晶核形成后, 通过气相反应生成的碳化硅分子优先吸附于晶核具有高表面能的晶面, 随着反应的进行, 该晶面吸附沉积的碳化硅分子越来越多, 最终形成了大长径比的碳化硅晶须^[40]。

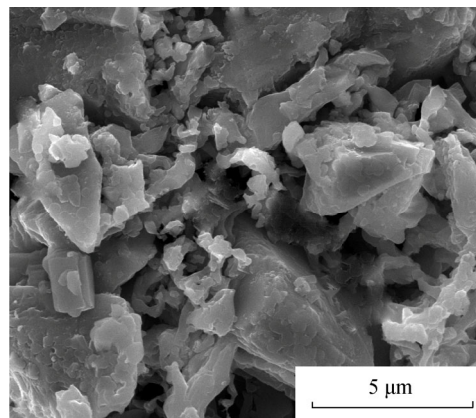


图 11 开放气氛下所制备多孔陶瓷样品的 SEM 照片
Fig. 11 SEM image of porous ceramics sample sintering under flowing atmosphere

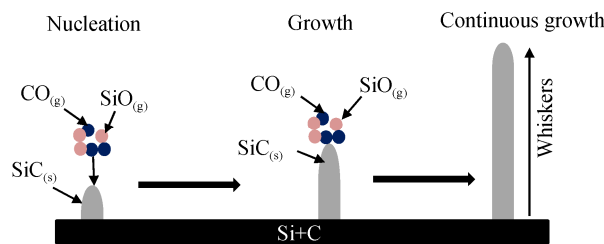


图 12 SiC_w 气固生长机理示意图

Fig. 12 Schematic diagram of SiC_w gas-solid growth mechanism

3 结论

1) 以 70% 的碳化硅粉为主要原料, 30% 的硅粉和炭黑为碳化硅自结合相粉体, $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 为添加剂, 采用发泡结合反应烧结法经 1600 °C 保温 2 h 烧结后制备了碳化硅晶须自增强多孔陶瓷。

2) 添加适量 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 可以显著提高碳化硅晶须自增强多孔陶瓷的常温力学性能。当 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 添加量为 2% 时, 所制备碳化硅晶须自增强多孔陶瓷的常温抗折强度和耐压强度分别达 2.6 MPa 和 3.7 MPa, 明显高于未添加 $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 所制备碳化硅多孔陶瓷样品的常温抗折强度和耐压强度。

3) $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ 的加入促进了多孔陶瓷样品中形成了大量的碳化硅晶须, 其生长由气-固反应机理控制。

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Effect of AlF₃·3H₂O Content on Properties of Silicon Carbide Whiskers Self-Reinforced Porous Ceramics

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Extended Abstract

Introduction Silicon carbide porous ceramics are widely used in many fields because of their corrosion resistance, good thermal shock resistance, large specific surface area and superior mechanical properties. Silicon carbide porous ceramics are mainly prepared by different methods (i.e., pore-forming agent method, organic foam impregnation method, freeze-drying method, and foaming method). Among these, the foaming method with simple operation and controllable density and shape of the products is a common approach to prepare silicon carbide porous ceramics with a high porosity. However, silicon carbide porous ceramics still have the disadvantage of low mechanical properties. The *In-situ* generation of SiC whiskers can greatly improve the mechanical properties of the materials. Therefore, in this paper, silicon carbide whiskers self-reinforced porous ceramics were prepared by foaming method and reactive sintering with silicon carbide powder of 70% (in mass fraction) as a raw material, 30% silicon powder and carbon black as a self-bonding phase, AlF₃·3H₂O as an additive. In addition, the effect of AlF₃·3H₂O content on the phase composition, microstructure and mechanical properties of silicon carbide whiskers self-reinforced porous ceramics was also investigated.

Methods In this work, silicon carbide powders were used as raw materials. Silicon powders and carbon black were used as self-bonding phase materials. AlF₃·3H₂O was selected as an additive. Triethanolamine dodecyl sulfate was used as a blowing agent. The ground powders were slowly added to a solution containing 0.5% Isobam 104 and 0.15% sodium carboxymethylcellulose, which was vigorously stirred in a mechanical stirrer to produce a slurry containing 50% (in volume fraction) of ground powders. Subsequently, 1.0% (in volume fraction) triethanolamine dodecyl sulphate was added to the obtained slurry and then vigorously stirred to prepare a homogeneous wet foam, which was rapidly poured into moulds with the dimensions of 160 mm × 80 mm × 40 mm and dried at ambient temperature for 48 h. Afterwards, the demoulded foam green bodies were dried at 40–100 °C. Finally, the dried foam green bodies were fired in argon atmosphere furnace at 1600 °C for 2 h to obtain porous ceramics.

Results and discussion , The average large spherical pore size and annular pore size in as-prepared silicon carbide whiskers self-reinforced porous ceramics both firstly decrease and then increase with increasing the content of AlF₃·3H₂O from 0 to 4%. These results are due to the minimum surface free energy of the slurry with 2% AlF₃·3H₂O, leading to the stable bubbles existing in the slurry. Adding an appropriate amount of AlF₃·3H₂O can promote the formation of silicon carbide whiskers and improve the strength of as-prepared silicon carbide whiskers self-reinforced porous ceramics. At AlF₃·3H₂O content of 2%, the flexural and compressive strengths of porous ceramic samples with a porosity of 76.9% are 2.6 MPa and 3.7 MPa, respectively, which are significantly higher than those of the porous ceramic samples prepared without AlF₃·3H₂O (i.e., 1.1 MPa and 1.4 MPa). The enhanced mechanical properties can be related to the microstructure of the porous samples. The more uniform pore distribution and smallest average

spherical pores and annular pores in porous sample with $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ addition of 2% are formed, resulting in improved mechanical properties of porous sample. Also, a large number of silicon carbide whiskers with the largest length are generated, which act as a reinforcing phase for further improving the mechanical properties of porous samples.

Conclusions Adding an appropriate amount of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ could promote the formation of silicon carbide whiskers and improve the strength of porous ceramic specimens. At $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ content of 2%, the flexural and compressive strengths of as-prepared silicon carbide whisker self-reinforced porous ceramic samples with a porosity of 76.9% were 2.6 MPa and 3.7 MPa, respectively. The length and the diameter of SiC_w whiskers generated in the samples were 4 μm and 62 nm, respectively, and their growth was controlled due to the gas-solid reaction mechanism.

Keywords silicon carbide porous ceramics; silicon carbide whiskers; aluminum fluoride trihydrate; mechanical properties