

轻质高强硅氧碳气凝胶的制备及其高温隔热性能

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摘 要: 陶瓷气凝胶因其优异的隔热性能和高温稳定性而成为新型的高性能热防护材料, 但是低的强度限制了其应用和发展。本工作以聚甲基氢硅氧烷作为前驱体、四乙烯基环四硅氧烷为交联剂, 通过水热反应和冷冻成型, 再经热解过程制备出轻质高强、耐高温的硅氧碳(SiOC)陶瓷气凝胶。多孔的蜂窝结构赋予 SiOC 气凝胶低的密度($0.13 \text{ g}\cdot\text{cm}^{-3}$)和热导率($0.0655 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)以及高的抗压强度(0.96 MPa)。同时, SiOC 气凝胶表现出优异的高温稳定性, 在 1400°C 热处理和 800°C 氧化处理后未出现结构的坍塌, 热导率和抗压强度基本保持不变。

关键词: 硅氧碳陶瓷; 隔热性能; 高温稳定性; 抗氧化性能

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随着航空航天、军事国防和工业生产等领域的迅速发展, 一些航空发动机、导弹、运输管道等设备对新型耐高温、轻质、高效热防护材料的需求日益强烈^[1]。气凝胶材料因具有低的密度($0.01\sim 0.50 \text{ g}\cdot\text{cm}^{-3}$), 高的气孔率($80\%\sim 90\%$)和低的热导率($0.02\sim 0.09 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)而在结构和功能领域受到广泛关注^[2]。另外, 为满足飞行器热防护系统、换热器、工业炉隔热层等设备在高温环境的使用要求, 高性能的气凝胶材料在具有优异的隔热性能的同时, 应具有一定的高温稳定性^[3-4]。

硅氧碳(SiOC)陶瓷作为前驱体陶瓷(PDCs)的典型代表, 通常被认为是 SiO_2 四面体中 O 原子被部分 C 原子取代所形成。因此, 相较于 SiO_2 气凝胶, SiOC 气凝胶具有更好的热稳定性和化学稳定性以及高的机械性能^[5]。目前, 已经报道的 SiOC 气凝胶一般通过溶胶凝胶路线和 PDCs 路线合成, 主要表现出颗粒堆积结构^[3,6]。但是, 与传统的 SiO_2 气凝胶相比, SiOC 气凝胶由于制备方法的限制难以实现较低的密度, 从而影响了其在轻质隔热领域的应用。同时, 高温环境下气凝胶粒子之间较弱的连接会导致孔结构的坍塌, 先前关于 SiOC 气凝胶的报道大部分集

中于其制备方法和热解过程中结构演变的探究, 关于其高温稳定性和抗氧化性能的报道极少^[7-8]。YANG 等^[8]报道的 BN/SiOC 气凝胶材料在 1300°C 氩气环境中热处理后已表现出明显的结构坍塌。我们课题组报道的采用溶剂热和冷冻干燥法制备蜂窝状的 SiOC 气凝胶密度低至 $0.14 \text{ g}\cdot\text{cm}^{-3}$, 热导率为 $0.0577 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, 但是制备过程中使用的交联剂二乙烯苯(DVB)在该气凝胶内部引入较多的游离碳相, 导致该气凝胶在 1400°C 氩气环境和 800°C 氧气环境中处理后其隔热性能和机械强度均表现出一定程度的降低^[9]。

为了解决以上问题, 本工作以成本较低的聚甲基氢硅氧烷作为前驱体、四甲基四乙烯基环四硅氧烷(D_4Vi)为交联剂, 经溶剂热、冷冻干燥和热解等过程制备 SiOC 气凝胶。与原先的 DVB 相比, D_4Vi 交联度更高, 碳含量较少, 制备的气凝胶材料在保持低密度和高孔隙率的同时, 表现出较低的热导率和较高的机械强度。另外, D_4Vi 在 SiOC 气凝胶中形成稳定的蜂窝孔结构, 并引入较少的游离碳相, 使得该气凝胶在 1400°C 氩气环境和 800°C 氧气环境中表现出结构和性能的稳定。

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1 实验

1.1 SiOC 气凝胶的制备

聚甲基氢硅氧烷(PHMS)作为前驱体、四乙烯基环四硅氧烷(D₄Vi)作为交联剂、铂络合物为催化剂制备 SiOC 气凝胶。

1.5 g 的 D₄Vi 和 1.0 g 的 PHMS (质量比为 1: 1) 加入 52.4 g 环己烷中搅拌 30 min, 加入 1%(质量分数)的 Pt 催化剂搅拌 15 min 得到聚硅氧烷(PSO) 溶液。将 PSO 溶液转移至 80 mL 的聚四氟乙烯水热釜内胆中, 在 150 °C 交联 20 h 后得到 PSO 溶胶, 接着在 -50 °C 冰箱中预冷 3 h 进行冷冻成型, 再在 -50 °C 真空条件下干燥 48 h 得到 PSO 气凝胶。最后, PSO 气凝胶在 1000 °C 氩气中热解 2 h 得到 SiOC 气凝胶, 升温速率和降温速率均为 5 °C/min。

再将 D₄Vi: PHMS 的质量比设定为 1.5: 1.0 和 2: 1, 样品命名为 SiOC-X, X 为 D₄Vi 和 PHMS 的质量比值。将其分别在 1400 °C 氩气环境和 800 °C 空气环境中热处理 2 h, 探究 SiOC 气凝胶的高温稳定性和抗氧化性能。

1.2 样品表征

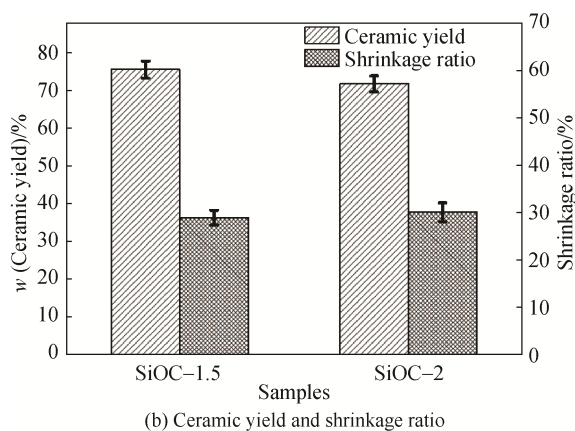
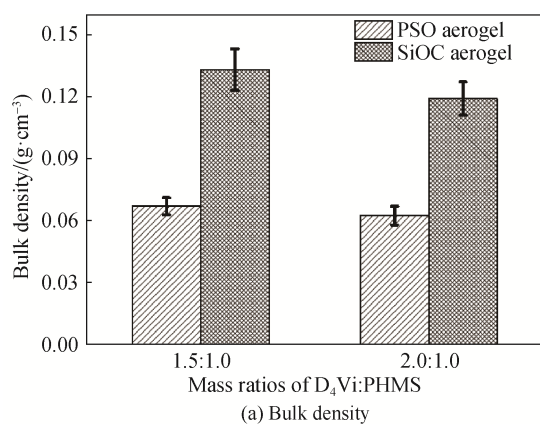
采用称量样品质量和测量尺寸的方法计算

SiOC 气凝胶的体积密度。采用 AutoPore IV 9500 型压汞测试仪表征其孔径分布。采用 D/MAX-2500 型 X 射线衍射仪表征其晶体结构。采用 S-4800 型冷场发射扫描电子显微镜表征其微观结构。采用 iD7 型 Fourier 变换红外光谱仪表征气凝胶热解前后分子结构的变化。采用 TPS2500S 型热常数分析仪测试 SiOC 气凝胶的热导率。采用 LD24.204 微机控制电子万能试验机研究其机械强度, 测试样品尺寸为 $\phi 15\text{ mm} \times 20\text{ mm}$, 压缩速率为 0.1 mm/s。

2 结果与讨论

2.1 SiOC 气凝胶的结构与组成

图 1 为 SiOC 气凝胶的体积密度、陶瓷产率和收缩率。由图 1 可见, 热解前 PSO 气凝胶的密度在 0.063~0.067 g·cm⁻³ 范围内, 热解后出现 30% 的线收缩, 密度上升至 0.12~0.13 g·cm⁻³ 范围内, 明显低于先前报道的 SiOC 气凝胶材料 (0.23~0.62 g·cm⁻³) [3,5-9]。随着 D₄Vi 含量的增加, SiOC 气凝胶的陶瓷产率有所降低, 从 75.49%(质量分数)降至 71.68%, 这是由于 D₄Vi 的增加导致气凝胶内部交联程度的降低。



w—Mass fraction.

图 1 SiOC 气凝胶的体积密度、陶瓷产率和收缩率

Fig. 1 Density, ceramic yield and shrinkage of SiOC aerogels

图 2 为 SiOC 气凝胶热解前后的红外光谱和 X 射线衍射(XRD)谱。由图 2a 和图 2b 可见, 热解前, PSO 在 1039、1257、1597、2160 cm⁻¹ 和 3000~3100 cm⁻¹ 处表现出明显的吸收峰, 分别对应于 Si—O—Si、—CH₃、—CH=CH₂、Si—H 和 C—H 键的伸缩振动。热解后, SiOC 气凝胶中 —CH₃、—CH=CH₂ 和 —Si—H 键的吸收峰消失, 而在 1039 cm⁻¹ 处的 Si—O—Si 峰强度增加, 并在 788 cm⁻¹ 处出现 Si—C 键的伸缩振动峰, 说明该气凝胶内部完

成了有机 PSO 网络向无机 Si—O—C 陶瓷结构的转变。由图 2c 可见, 热解后 SiOC 气凝胶在 26.5° 呈现出较宽的衍射峰, 对应于无定形的 SiOC 相和游离碳相^[10]。

图 3 为不同 D₄Vi 含量的 SiOC 气凝胶微观形貌和孔径分布图。由图 3 可见, 样品 SiOC-1.5 和样品 SiOC-2 均表现出较高的孔隙率和均匀大孔结构, 但两者的结构略有区别。样品 SiOC-1.5 呈现出相互连通的蛛网状结构, 孔的大小在 15~30 μm 之间, 孔的

形状和排列规则度较低。这主要是因为 D_4Vi 含量较低时形成的 PSO 溶液交联度高, 溶液黏度大, 冷冻过程中环己烷冰晶生长阻力增加, 降低冰晶生长的连续性, 从而影响孔的均匀性。随着 D_4Vi 含量的升高, PSO 溶液交联度降低, 冰晶生长阻力减小, 因此, 样品 SiOC-2 气凝胶呈现出典型的蜂窝孔结构, 孔径增大至 $40\sim 60\ \mu\text{m}$, 孔的排列更为规则, 形状接近六边形。另外, 样品 SiOC-2 表现出致密的孔壁, 孔壁厚度约为 $5\ \mu\text{m}$, 不同于之前报道的颗粒堆积结构^[11-13]。致密的孔壁为 SiOC 气凝胶高的机械强度和优异的高温稳定性的实现提供了可能。由图 3c 可见, 样品 SiOC-2 的孔径主要集中在 $40\sim 100\ \mu\text{m}$ 范

围内, 平均孔径为 $55.7\ \mu\text{m}$, 与 SEM 结果一致; 气凝胶的孔隙率为 91.9%, 高于已经报道的 SiOC 气凝胶和多孔 SiOC 陶瓷, 为良好的隔热性能的实现提供基础^[6,14]。

表 1 为热常数分析仪和万能试验机测得的 SiOC 气凝胶的热导率和抗压强度。由表 1 可见, 样品 SiOC-1.5 在室温下的热导率为 $0.0655\ \text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, 接近先前报道的 SiOC、SiBOC 等聚合物前驱体陶瓷气凝胶 ($0.05\sim 0.75\ \text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [6,12,15-17])。另外, 样品 SiOC-1.5 表现出较高的抗压强度($0.96\ \text{MPa}$), 而随着 D_4Vi 含量的升高, 抗压强度呈现出轻微的降低, 与样品 SiOC-2 具有更低密度和更疏松的网络骨架有关。

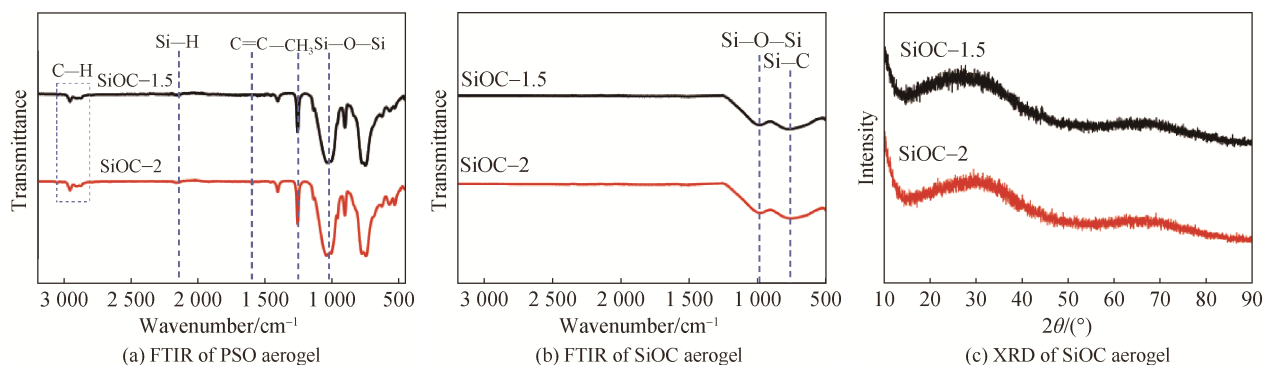


图 2 PSO 和 SiOC 气凝胶的红外光谱和 SiOC 气凝胶的 XRD 谱

Fig. 2 FT-IR spectra of PSO and SiOC aerogels and XRD patterns of SiOC aerogels

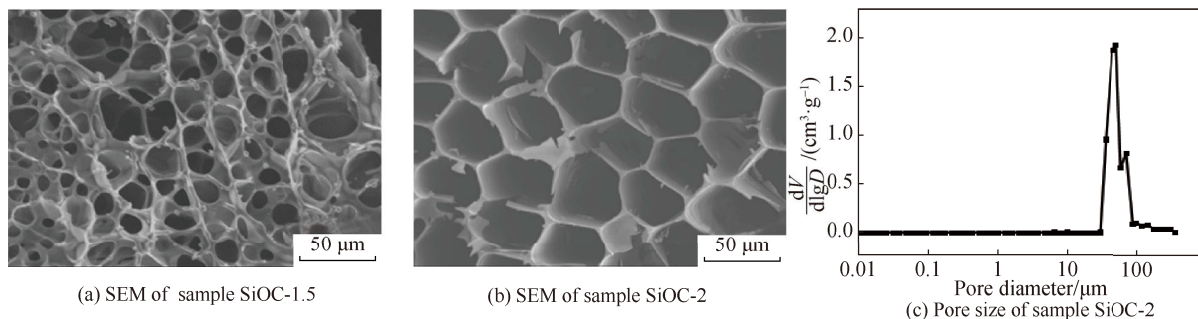


图 3 SiOC 气凝胶微观形貌和孔径分布图

Fig. 3 Microstructure and pore size distribution of SiOC aerogels.

表 1 SiOC 气凝胶的热导率和抗压强度

Table 1 Thermal conductivity and compressive strength of SiOC aerogels

Sample No.	Thermal conductivity/ ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	Compressive strength/MPa
SiOC-1.5	0.065 5	0.96
SiOC-2	0.061 9	0.60
SiOC-1.5 (1 400 °C, Ar)	0.070 3	0.95
SiOC-2 (1 400 °C, Ar)	0.066 7	0.56
SiOC-1.5 (800 °C, Air)	0.064 3	0.91
SiOC-2 (800 °C, Air)	0.060 7	0.58

2.2 SiOC 气凝胶的高温稳定性

为了进一步研究 SiOC 气凝胶的高温稳定

性, 将样品 SiOC-1.5 和样品 SiOC-2 在 $1\ 400\ ^\circ\text{C}$ 氩气环境中热处理 2 h, 并探究其结构和性能的变化。

图 4 为样品 SiOC-1.5 和样品 SiOC-2 热处理后的体积密度、质量损失和收缩率。由图 4 可见, 与热处理前相比, 热处理后 SiOC 气凝胶的密度未发生明显改变。样品 SiOC-1.5 的质量损失仅为 2.57%, 并伴随有较低的线收缩($<3\%$)。随着 D_4Vi 含量的升高, 该气凝胶交联程度降低, 质量损失上升至 4.7%。SiOC 气凝胶良好的高温性能主要来源于 D_4Vi 中较低的游离碳含量和稳定的蜂窝孔结构。

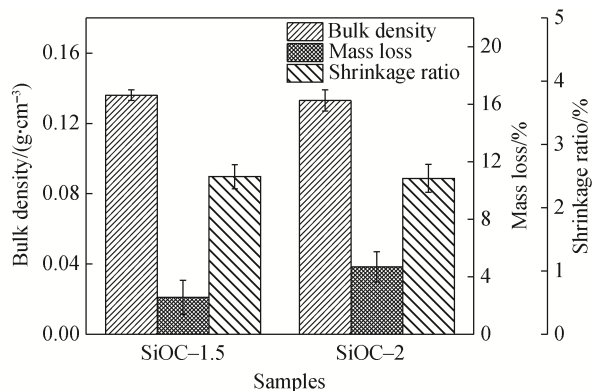


图4 热处理后的SiOC气凝胶体积密度、质量损失和收缩率
Fig. 4 Bulk density, weight loss and shrinkage ratio of SiOC aerogels after heat treatment

图5为SiOC气凝胶高温热处理后的XRD谱。由图5可见,样品SiOC-1.5和样品SiOC-2经1400℃热处理2h后在35.6°、60.1°和71.9°处显示出明显的衍射峰,对应于 β -SiC晶相的(1 1 1)、(2 2 0)和(3 1 1)晶面。其生成是由于高温下碳热还原反应的发生导致Si—O—C基体中的部分游离碳相被转化成SiC纳米晶。

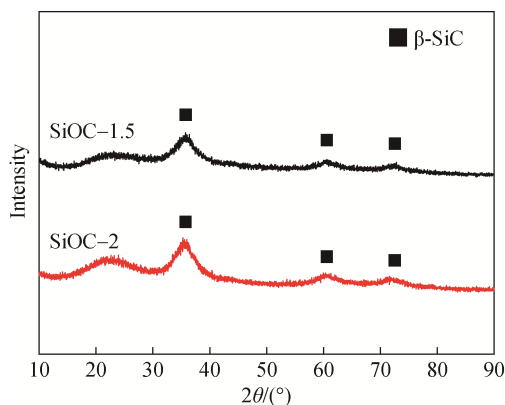
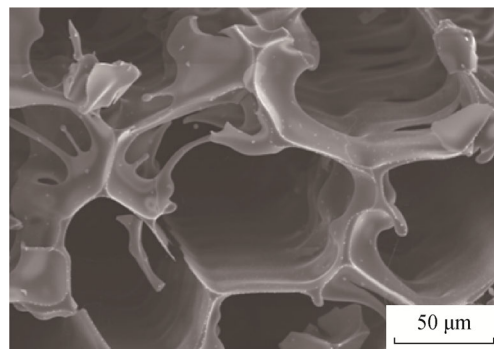


图5 SiOC气凝胶经高温热处理后的XRD谱
Fig. 5 XRD results of SiOC aerogels after heat treatment

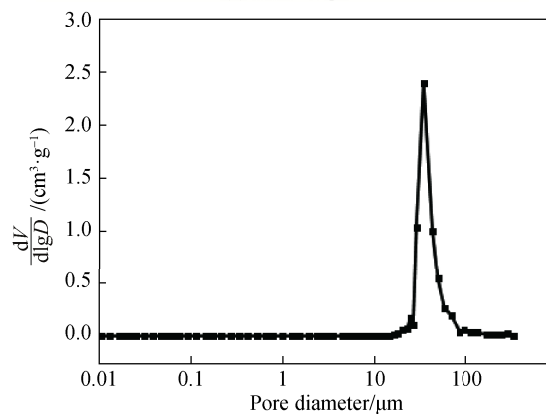
图6为样品SiOC-2在1400℃氩气气氛中热处理2h后的微观形貌图和孔隙分布曲线。由图6a可见,样品SiOC-2保持了原来稳定的蜂窝孔结构,孔径分布在40~100 μm范围内,孔的形状、大小、均匀性以及孔壁厚度未发生明显改变。由图6b可见,样品SiOC-2经热处理后孔隙尺寸主要集中在30~100 μm范围内,且分布均匀,表明该SiOC气凝胶具有良好的高温稳定性。

由表1还可以看出,相较于高温热处理前,热处理后样品SiOC-1.5和样品SiOC-2的热导率表现出轻微的增加趋势,分别为 $0.0703 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ 和 $0.0667 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ 。力学性能分析显示其热处理后的抗压强度分别保持在0.95 MPa和0.56 MPa,未呈现

出明显的降低。与先前报道的DVB作交联剂制备的SiOC气凝胶相比,其具有更优异的高温稳定性^[9]。



(a) SEM image



(b) Pore size of distribution

图6 样品SiOC-2经高温热处理后的SEM照片和孔隙分布曲线
Fig. 6 SEM image and pore size distribution of sample SiOC-2 after heat treatment

2.3 SiOC气凝胶的抗氧化性

图7为样品SiOC-1.5和样品SiOC-2经氧化处理后的体积密度、质量损失和收缩率。由图7可见,处理后的SiOC气凝胶密度保持在 $0.12 \sim 0.13 \text{ g} \cdot \text{cm}^{-3}$ 范围内,与氧化前相比未呈现出明显的变化,质量损失低于1.5%,线收缩低于2%,证明SiOC气凝胶具有优异的抗氧化性。

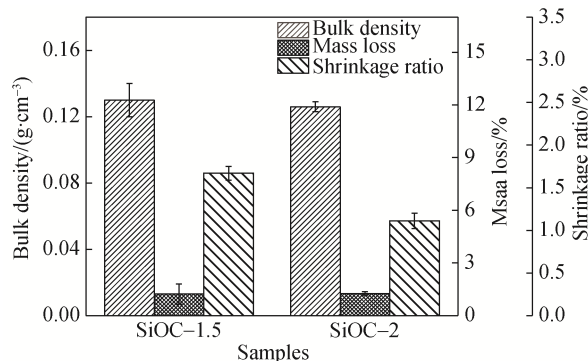


图7 SiOC气凝胶在800℃氧化处理2h的密度、质量损失和收缩率
Fig. 7 Density, mass loss and shrinkage ratio of SiOC aerogels after oxidation at 800 °C for 2 h

图8为氧化处理后的SiOC气凝胶相组成的变化。由图8可见,样品SiOC-1.5和样品SiOC-2经氧化处理后在 23° 处有1个较宽的衍射峰,对应于无定形的SiOC相和Si-O-C网络部分氧化产生的 SiO_2 相^[18]。

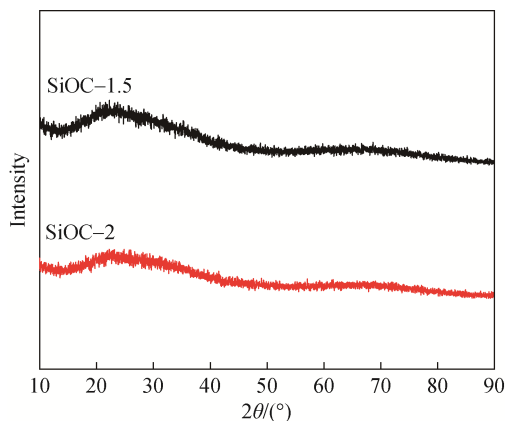
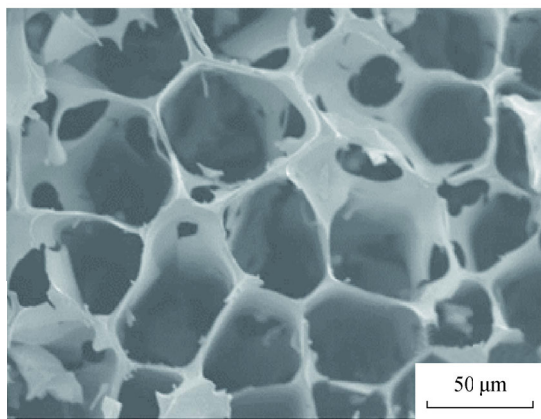


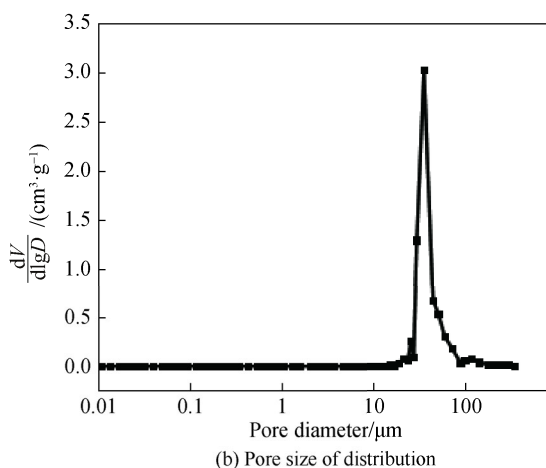
图8 氧化处理后的SiOC气凝胶的XRD谱
Fig. 8 XRD patterns of SiOC aerogels after oxidation



(a) SEM image

图9为样品SiOC-2气凝胶经氧化处理后的微观结构和孔隙分布曲线。由图9可见,该气凝胶在 800°C 氧化后保持了原先的蜂窝孔结构,未观察到明显的孔隙坍塌。孔的大小主要集中在 $40\sim 60\mu\text{m}$ 范围内,孔的形状、均匀性、孔壁厚度没有呈现出较明显的变化。压汞结果显示样品SiOC-2的孔径分布略微向低尺寸方向移动,平均孔径由 $55.71\mu\text{m}$ 降低至 $40.84\mu\text{m}$,这是由氧化过程中SiOC基体轻微的收缩导致。

由表1可见,氧化后样品SiOC-1.5和样品SiOC-2的热导率分别为 $0.0643\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 和 $0.0607\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$,抗压强度保持在 0.91 MPa 和 0.58 MPa ,与氧化前相比热导率和抗压强度均未发生明显的变化。与之前探究的DVB作为交联剂制备的SiOC气凝胶相比,本工作所得到的气凝胶材料优异的抗氧化能力主要来源于稳定的蜂窝孔结构和内部较少的游离碳含量。



(b) Pore size of distribution

图9 样品SiOC-2氧化处理后的微观形貌和孔隙分布曲线

Fig. 9 Microstructure and pore size distribution curve of sample SiOC-2 after oxidation treatment

3 结论

以PHMS和 D_4Vi 作为前驱体,通过水热、冷冻干燥和热解过程制备轻质隔热的SiOC气凝胶。相较于先前报道的SiOC气凝胶和多孔的SiOC陶瓷,该气凝胶具有较低的密度($0.12\sim 0.13\text{ g}\cdot\text{cm}^{-3}$),稳定的蜂窝孔结构使其表现出低的热导率($0.0619\sim 0.0655\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)和高的抗压强度($0.60\sim 0.96\text{ MPa}$)。

另外,SiOC气凝胶具有优异的高温稳定性和抗氧化性能,在 1400°C 的Ar气氛和 800°C 的空气气氛中处理后隔热性能和机械强度均未发生明显的改变,为其在极端环境中的使用提供了可能。

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Preparation of Lightweight and High-Strength Silicon Oxycarbide Aerogels and Their Thermal Insulation Performance

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Extended Abstract

Introduction With the rapid development of high-technology fields, advanced aerogel acts as the thermal insulation materials under high-temperature environment attracted extensive attention. Polymer derived ceramic (PDC) aerogels were considered to be a promising thermal protection materials due to its low density, high porosity, excellent thermal insulation performance and high-temperature stability. Silicon oxycarbide (SiOC) ceramic aerogels, one kind of typical representative PDC materials, were mainly formed by partial substitution of C atoms for O atoms in SiO₂ tetrahedra. Compared the traditional silica aerogels, silicon oxycarbide (SiOC) aerogels exhibited better thermal and chemical stability as well as higher mechanical strength. Previously research reported that SiOC aerogels were mainly prepared by sol-gel method and PDC route, exhibited a higher density, which limited its applications and development in lightweight thermal insulation filed. Moreover, the obtained SiOC aerogels exhibited a necklace-like structure, poor high-temperature stability and mechanical strength due to the weak contact between nanoparticles. And most researches on SiOC aerogels focused on its high-temperature pyrolysis behavior. In this paper, a lightweight and high-strength SiOC aerogel were prepared using polyhydromethylsiloxane (PHMS) as precursor and tetramethyltetravinylcyclotetrasiloxane (D₄Vi) as crosslinker through solvothermal, freeze casting and pyrolysis. The influence of D₄Vi content on the microstructure and thermal stability of SiOC aerogels were discussed. The evolution of phase composition, mechanical strength and thermal insulation performance was further explored via high-temperature heat treatment and oxidation treatment.

Methods In a typical process, 1.5 g D₄Vi and 1.0 g PHMS were added into 52.4 g cyclohexane solvent and mixed uniformly by magnetic stirring for 30 min. Then, 1% Pt catalyst was added into the mixture for another 15 min stirring to obtain the transparent polysiloxane (PSO) solution. The PSO solution was then poured into an 80 ml Teflon-lined autoclave and underwent hydrothermal treatment at 150 °C for 20 h. Subsequently, the sample was freeze-dried at –50 °C for 48 h to obtain PSO aerogels. Finally, the PSO aerogels were pyrolyzed at 1 000 °C for 2 h with a heating rate of 5 °C/min in Ar atmosphere. The pyrolyzed SiOC aerogels were further treated at 1 400 °C in Ar and 800 °C in air to explore their high-temperature stability and anti-oxidation.

The bulk density of SiOC aerogels was calculated by the measurement of the mass and dimension of the samples. The pore size distribution of SiOC aerogels was characterized using mercury intrusion porosimetry. The chemical structure and phase composition of SiOC aerogels was explored by Fourier transform infrared spectrometer and X-ray diffractometer. The microstructure of SiOC aerogels was characterized by scanning electron microscopy. The thermal conductivity of SiOC aerogels was measured by the hot-disk method using a thermal constant analyzer with the sample's dimension of $\phi 15\text{ mm} \times 20\text{ mm}$. The compressive strength of SiOC aerogels was investigated by an electronic universal testing machine using the samples with a dimension of $\phi 15\text{ mm} \times 20\text{ mm}$.

Results and discussion lightweight SiOC aerogels were prepared by solution-based freeze-drying method under the mass ratio of D_4Vi : PHMS of 1.5 and 2. Both kinds of obtained aerogels exhibited low density of $0.12\text{--}0.13\text{ g}\cdot\text{cm}^{-3}$, much lower than that of previously reported SiOC aerogels and porous SiOC ceramics ($0.23\text{--}0.62\text{ g}\cdot\text{cm}^{-3}$). With the increase in DVB content, the ceramic yield of SiOC aerogels decreased from 75.40% to 71.68% as the decreased crosslinking degree of PSO precursor, further leading to the transition from relatively disordered spider-web structure to ordered honeycomb-like structure. The stable porous structure endowed SiOC aerogels with low thermal conductivity of $0.0619\text{--}0.0655\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and high compressive strength of $0.60\text{--}0.96\text{ MPa}$.

Moreover, the SiOC aerogels possessed excellent high-temperature stability, when heat treatment at $1400\text{ }^{\circ}\text{C}$ in Ar, density of it was still ranged between 0.12 and $0.13\text{ g}\cdot\text{cm}^{-3}$ with original honeycomb-like structure. Meanwhile, the SiOC aerogels remained low thermal conductivity of $0.0667\text{--}0.0703\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and high compressive strength of $0.56\text{--}0.95\text{ MPa}$. When oxidation at $800\text{ }^{\circ}\text{C}$ in air, the SiOC aerogels still maintained porous structure and a density of $0.12\text{--}0.13\text{ g}\cdot\text{cm}^{-3}$ with a low mass loss of about 1.2%. The related thermal conductivity showed a minor variation of $0.0607\text{--}0.0643\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and the compressive strength lightly decreased to $0.58\text{--}0.91\text{ MPa}$, indicating a good anti-oxidation performance.

Conclusions In this work, SiOC aerogels with lightweight, high-strength and thermal performance were prepared using PHMS as precursor and D_4Vi as crosslinker through solvothermal, freeze casting and pyrolysis. Porous honeycomb-like structure endowed SiOC aerogels with low density ($0.13\text{ g}\cdot\text{cm}^{-3}$) and thermal conductivity ($0.0655\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) as well as high compressive strength (0.96 MPa). Meanwhile, SiOC aerogels exhibited excellent high-temperature stability and oxidation resistance. The corresponding bulk density, phase composition, thermal conductivity and compressive strength still remained and without any structural collapse even heat treatment at $1400\text{ }^{\circ}\text{C}$ in Ar, which could be an ideal candidate for lightweight, high strength, and high-temperature stability materials.

Keywords silicon oxycarbide ceramics; thermal insulation; high-temperature stability; oxidation resistance