

Preparation of High Specific Surface Area Micro/Meso-porous SiOC Ceramics by the Low Temperature Phase Separation Method

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Abstract: Micro/meso-porous SiOC ceramics with high surface area and narrow pore size distribution were prepared by the low temperature phase separation method (namely water vapor assisted pyrolysis) followed by etching in hydrofluoric acid (HF) solution. The cross-linked body was made from hydrogen-containing polysiloxane (PHMS), tetramethyl-tetravinylcyclotetrasiloxane (D_4^{Vi}) and Pt-complex by thermal cross-linking. Phase compositions, chemical bonds, microstructures, and specific surface area of the prepared SiOC ceramic were investigated by XRD, FT-IR, SEM, and BET, *etc.* Water vapor can promote the precursor to produce Si–O–Si bonds, SiO_2 -rich clusters, and SiO_2 nanocrystals in SiOC ceramics. All of these species act as pore-forming substrate and can be etched away by HF. Water vapor injection and pyrolysis temperature have important effects on phase compositions, microstructures and specific surface area of SiOC porous ceramics, which have a maximum specific surface area of $1845.5\text{ m}^2/\text{g}$ and pore size distribution of 2.0–10 nm at pyrolysis temperature of 1300°C .

Key words: micro/meso-porous SiOC; low temperature phase separation; phase composition; microstructure; etching

In recent years, porous SiOC ceramics have attracted a lot of interest due to their higher specific surface area, thermal stability and good electric conductivity. They have wide application potentials in the field of catalyst support, solar cells, solid oxygen fuel cells, and super capacitors, *etc.*^[1-2]

Various strategies have been used to prepare porous SiOC materials from polymers, including replica^[3], sacrificial template^[4], direct foaming^[5], reactions^[6], and high temperature phase separation^[7]. Out of these approaches, only SiOC porous ceramic prepared by high temperature phase separation can offer uniform micro-/meso-pore sizes, large pore volumes, and higher specific surface area.

High temperature phase separation can occur during pyrolysis above 1200°C and produce SiO_2 nanodomains, SiC, and free carbon. The SiO_2 nanodomains may be eliminated by HF, so the pores are left behind by SiO_2 nanodomains^[8-9]. Due to carbothermal reaction is accompanied by high temperature phase separation reaction during pyrolysis^[10-11], and it consumes SiO_2 nanodomains and free carbon ($SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)}$) which are produced from high temperature phase separation, and the rate of carbothermal reaction will be accelerated with the increase of pyrolysis temperature, thus

carbothermal reaction will hinder further increase of specific surface area of SiOC. In order to prevent or decrease carbothermal reaction, some researchers have done a lot of work. Main study focuses on the adjustment of batch formula or adding dopants^[9,12].

In this work, a versatile method, water vapor assisted pyrolysis, is used to promote phase separation of the precursor at a low temperature (below 1000°C). Porous SiOC ceramics with micro-/meso-pore sizes are prepared with HF etching for SiOC ceramics. Effects of water vapor and pyrolysis temperature on SiOC ceramic phase compositions, chemical bonds, microstructures and porosity are investigated before and after etching.

1 Experimental

1.1 Preparation of samples

Commercially available hydrogen-containing polysiloxane (PHMS) was used as the preceramic polymer, tetramethyltetravinylcyclotetrasiloxane (D_4^{Vi}) as the cross-linking agent and Pt-complex as catalyst. PHMS and D_4^{Vi} (mass ratio 2:1) with adding Pt-complex (0.5wt% based on PHMS content) were mixed by ball milling. The cross-linking process was carried in an oven

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at 80°C for 10 h.

The green bodies were pyrolyzed in an alumina tube furnace in Ar. The furnace temperature was raised at rate of 3°C/min and cooled at rate of 2°C/min. The temperature range of water injection was chosen at 500°C–800°C^[13]. As temperature arrived at 500°C, deionized water was injected into the furnace with rate of 0.25 g/min. When temperature arrived at 800°C, water injection was stopped. The temperature was then raised to 900°C–1500°C for 60 min, and then cooled down. Comparable experiments were carried out by pyrolysis of the green bodies without water injection using the same pyrolysis conditions.

1.2 Characterization

The etching process was performed on SiOC ceramics using HF solution (20wt%) until there was no distinct mass loss. Then, SiOC ceramics were rinsed with deionized water and dried at 120°C. Phase compositions of the pyrolyzed samples were analyzed by XRD (D8 Advance). The step size was 0.03°/s with Cu K α radiation ($\lambda = 0.15406$ nm). FT-IR (Nicolet 8700) was recorded between 400 cm⁻¹ and 4000 cm⁻¹ wavenumber for SiOC ceramics analysis. Specific surface area and pore size distribution of the pyrolyzed samples were studied by BET method with a Quantachrome Autosorb-1 analyzer.

A field emission SEM (JSM-6700, JEOL) was used to characterize morphology of the pyrolyzed samples.

2 Results and Discussion

2.1 Phase evolution

Fig. 1 shows XRD patterns of SiOC ceramics pyrolyzed in Ar + H₂O at different temperatures before and after etching. For SiOC ceramic before etching (Fig. 1(a)), XRD pattern at 900°C shows an amorphous structure with only the presence of the silica halo centered at $\sim 22.5^\circ$ and a weak carbon diffraction peak (43.6°). This means that phase separation in SiOC ceramic just starts to occur (compared Fig. 1(a) and Fig. 1(b)). When pyrolysis temperature is increased to 1000°C, such tendency is more visible. At 1300°C, new XRD peaks appear at 22.5°, 36.3° and 60.5°, indicating that SiO₂ and SiC crystal start to form along with carbon formation. With the increase of pyrolysis temperature to 1500°C, XRD peaks of SiO₂ and SiC continue to strengthen.

Fig. 1(b) shows XRD patterns of SiOC ceramic pyrolyzed in Ar+H₂O at different temperatures after etching. Compared with XRD patterns before etching (Fig. 1(a)), SiO₂ peaks disappear. At 1000°C, the preceramic has obviously happened phase separation to form β -SiC and

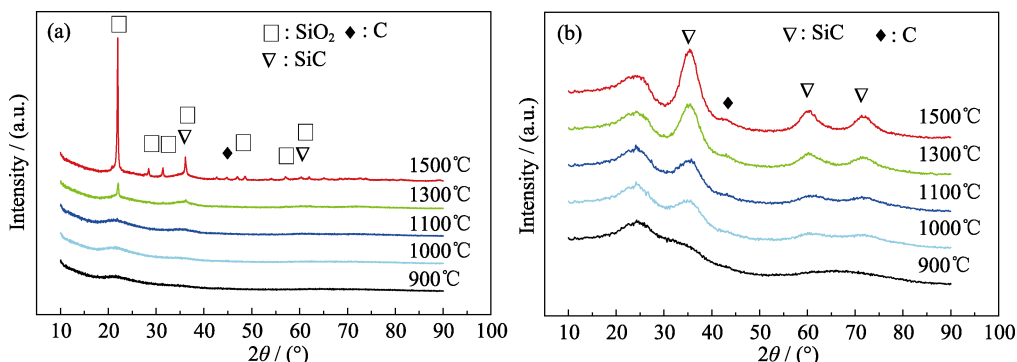


Fig. 1 XRD patterns of SiOC ceramics pyrolyzed in Ar + H₂O at different temperatures
(a) Before etching; (b) After etching

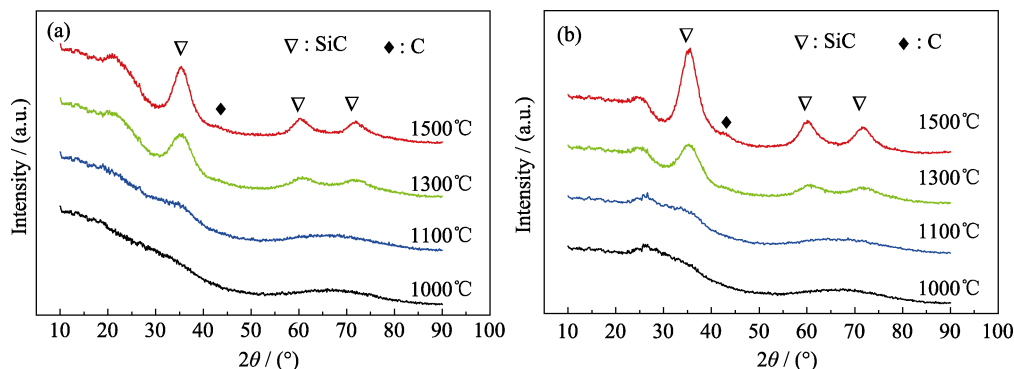


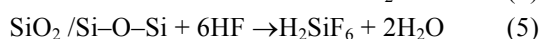
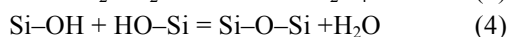
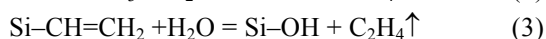
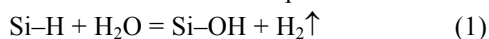
Fig. 2 XRD patterns of SiOC ceramics pyrolyzed in Ar at different temperatures
(a) Before etching; (b) After etching

carbon. Intensities of XRD peaks for β -SiC and carbon increase after etching for the same sample, and obviously increase with the increase of pyrolysis temperature.

Compared with SiOC ceramics pyrolyzed only in Ar (see Fig. 2 (a)), the difference is that a completely amorphous structure is present at 1100°C pyrolysis temperature. At 1200°C and higher, the SiOC starts to undergo phase separation and forms SiC, carbon, and SiO₂ nanodomains (see Fig. 2 (b)). In the range of 1100°C-1500°C, SiO₂ crystal is not observed for the samples pyrolyzed in Ar.

Fig. 3 shows FT-IR spectra of the pyrolyzed SiOC ceramic in Ar+H₂O and Ar at 1300°C before and after etching. Intensity of Si-O-Si peak is much higher for the sample pyrolyzed in Ar+H₂O than those in Ar. This means that water vapor greatly favors Si-O-Si bonds formation. Moreover, it may be seen from Fig. 3 that the intensity of Si-O-Si peak obviously decreases after etching. This indicates that Si-O-Si bonds has been etched away by HF.

This difference can be understood as follows. For pyrolysis reactions in Ar, C-H, Si-H and C=C bonds cleavage in organic groups occur, leading to SiOC ceramics consisting of amorphous SiOC with Si-O, Si-C and C-C bonds. For pyrolysis reactions in Ar+H₂O, except for the above reactions, the reactions between organic groups and H₂O produce Si-OH bonds (Eq. (1)-(3)), and Si-OH bonds are subsequently condensed into Si-O-Si through dehydrogenation reaction (Eq. (4))^[14]. SiO₂ nanodomains, Si-O-Si bonds and SiO₂ nanocrystals in SiOC ceramic are etched away by HF (Eq. (5)), these will be helpful to increase specific surface area of SiOC porous ceramic.



2.2 Microstructure analysis

Fig. 4 shows SEM cross section images of SiOC ceramic pyrolyzed at 1300°C in Ar+H₂O and in Ar before and after etching. The samples are dense and have no pores before etching (Fig. 4(a) and (c)). This means that the samples are sintered during pyrolysis, and the other samples also have dense structure which are pyrolyzed at 900°C-1500°C. After etching, the samples have porous structure (Fig. 4(b) and (d)). These pores are left behind after phase separated SiO₂ nanodomains/crystals and Si-O-Si bonds are etched away by HF (Eq. (5)). Moreover, it may be seen from Fig. 4(b) and (d), the sample pyrolyzed in Ar+H₂O owns much more porosity than that of the sample pyrolyzed in Ar. These are due to the fact that water may react with the precursors and promote their phase separation at low temperature (Eq. (1-4)), produce

SiO₂ nanodomains, Si-O-Si bonds and SiO₂ nanocrystals, so the samples own much more porosity after etching.

2.3 Specific surface area and pore size

BET adsorption-desorption isotherms of SiOC ceramics pyrolyzed in Ar +H₂O and in Ar at 1300°C after etching are shown in Fig. 5. The hysteresis loops are very narrow and adsorption-desorption branches almost overlap with each other, and there is a plateau at higher relative pressure region of the isotherms. These indicate that SiOC ceramics contain narrow micro-/meso-pores. The insets in Fig. 5(a) and (b) show that pore size distribution is 2 nm-10 nm and 2 nm-6 nm, respectively. In addition, it can be seen from Fig. 5(a) and (b) that N₂ maximum adsorbed volume and pore volume for the sample pyrolyzed in Ar+H₂O is higher than that of the sample pyrolyzed in Ar. Cumulative and interval specific surface area for SiOC are shown in Fig. 6. It may be seen from Fig. 6(a) and (b) that specific surface area arrives at 1845.50 m²/g for SiOC ceramics pyrolyzed in Ar +H₂O, and it is 2.91 times than that of SiOC pyrolyzed in Ar.

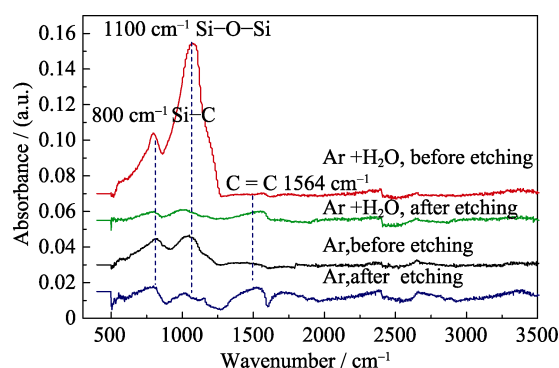


Fig. 3 FT-IR spectra of SiOC ceramics pyrolyzed in Ar+ H₂O and Ar at 1300°C before and after etching

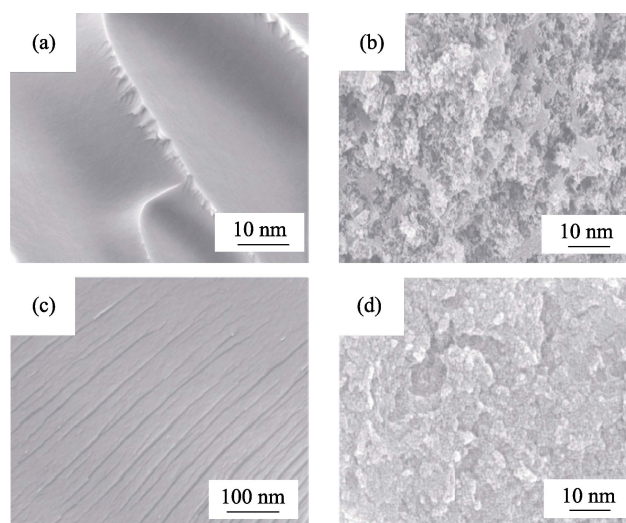


Fig. 4 SEM cross section images of SiOC pyrolyzed at 1300°C in Ar+H₂O before (a) and after (b) etching, in Ar before (c) and after (d) etching

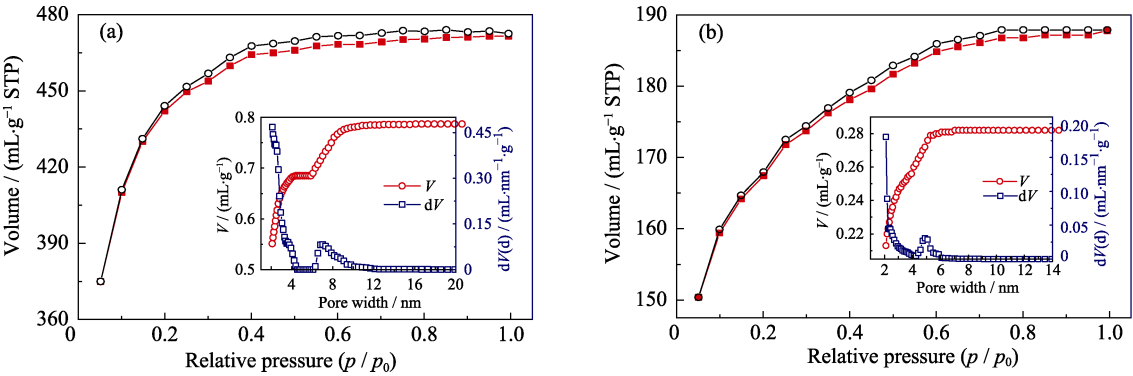


Fig. 5 N₂ adsorption (solid symbols) and desorption (open symbols) isotherms for the samples obtained from SiOC ceramics pyrolyzed in (a) Ar +H₂O and (b) Ar at 1300°C after etching

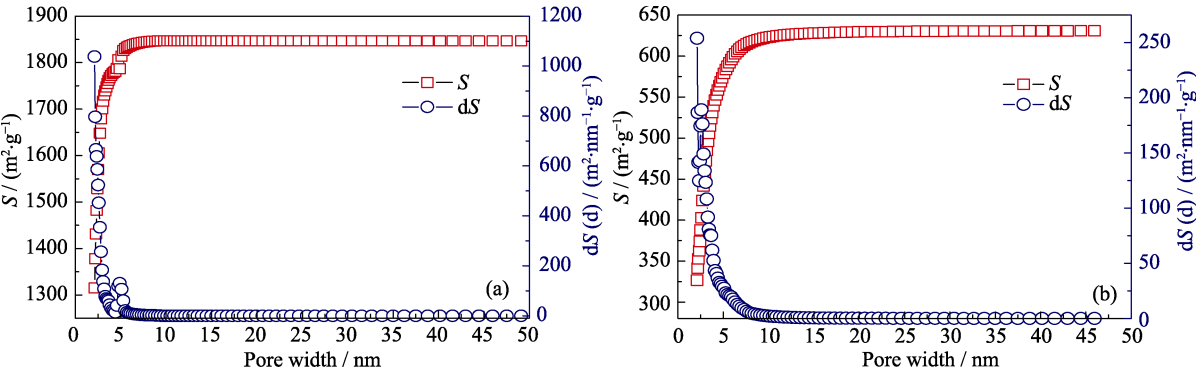


Fig. 6 Cumulative specific surface area (S), interval specific surface area (dS) and pore size distribution (PSD) for SiOC ceramics pyrolyzed in Ar +H₂O (a) and in Ar (b) at 1300°C after etching

Table 1 BET results of SiOC ceramics after etching with different pyrolysis temperatures in Ar and Ar+H₂O

Temperature/°C	Specific surface area/ (m ² ·g ⁻¹)		Average pore size/nm		Pore volume/(cm ³ ·g ⁻¹)	
	Ar	Ar +H ₂ O	Ar	Ar +H ₂ O	Ar	Ar +H ₂ O
900	—	58.6	—	2.05	—	0.105
1100	—	435.23	—	2.16	—	0.142
1200	53.65	654.16	1.43	2.23	0.015	0.202
1300	635.13	1845.50	2.25	2.83	0.282	0.788
1400	632.24	1817.20	2.18	2.75	0.286	0.764
1500	633.52	1805.60	2.15	2.77	0.288	0.756

Note: The samples pyrolyzed in Ar at 900°C and 1100°C are not listed in Table 1, because they are fully dense before and after HF etching.

BET results of SiOC ceramics pyrolyzed at different temperatures after etching are shown in Table 1. For SiOC ceramics pyrolyzed in Ar+H₂O, at 900°C, SiOC shows a little porous after etching. Moreover, at the same temperature, the samples pyrolyzed in Ar+H₂O have higher specific surface area than those of the samples pyrolyzed in Ar. These results are consistent with XRD, FT-IR and SEM analysis.

3 Conclusions

SiOC porous ceramics with high specific surface area and micro-/meso-pores are prepared by pyrolysis

of the precursors in Ar + H₂O and subsequent HF etching. Water vapor reacts with organic groups to promote phase separation at 500°C-800°C and produces Si–O–Si bonds. Above 1100°C, Si–O–Si bonds gradually crystallize into SiO₂ nanocrystals. The Si–O–Si bonds, SiO₂ nanodomains and SiO₂ nanocrystals in SiOC ceramic can be etched away by HF and leave behind micro-/meso-pores. Therefore, SiOC porous ceramics shows higher specific surface area than those of pyrolyzed only in Ar. A maximum specific surface area of 1845.50 m²/g, average pore size of 2.83 nm, pore volume of 0.788 cm³/g can be obtained at pyrolysis temperature of 1300°C in Ar+H₂O.

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低温分相法制备高比表面积微/介孔 SiOC 陶瓷

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摘要: 以含氢聚硅氧烷(PHMS)、四甲基四乙烯基环四硅氧烷(D_4^{vi})和铂络合物为原料, 采用热交联成交联体, 通过水蒸汽辅助热解促进前驱体低温分相及后续 HF 对 SiOC 陶瓷侵蚀基础上, 获得高比表面积微/介孔 SiOC 陶瓷。采用 XRD、FT-IR、SEM 和 BET 等测试技术对试样的物相组成、化学键、微观结构、比表面积和孔径分布等进行了表征。实验结果表明, 水蒸气能够促进前驱体低温分相, 使 SiOC 陶瓷中生成 Si—O—Si 键、 SiO_2 纳米畴和 SiO_2 纳米晶, 这些可以作为造孔剂而被 HF 侵蚀, 从而提高了 SiOC 陶瓷的比表面积。在热解温度 1300°C 条件下, 微/介孔 SiOC 陶瓷具有最大比表面积 $1845.5\text{ m}^2/\text{g}$, 孔径分布 $2.0\sim 10\text{ nm}$ 。

关键词: 微/介孔 SiOC 陶瓷; 低温分相; 物相组成; 微观结构; 侵蚀

中图分类号: TQ174 **文献标识码:** A