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Synthesis of SiC precursors by a two-step sol–gel process and their conversion to SiC powders

Jinwang Li *, Jiemo Tian, Limin Dong

Beijing Fine Ceramic Lab, Tsinghua University, PO Box 1021, Beijing 102201, PR China

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Abstract

A two-step sol–gel processing was developed to synthesize phenolic resin–SiO_2 hybrid gels as SiC precursors, with tetraethoxysilane (TEOS) and novolac phenolic resin being the starting materials, and oxalic acid (OA) and hexamethylenetetramine (HMTA) being the catalysts. At the first step TEOS was prehydrolyzed under the catalysis of OA. At the second step HMTA was added to facilitate gelation. The influences of the molar ratio of OA/TEOS and prehydrolysis time on the sol–gel reaction were investigated. There existed an optimum OA/TEOS ratio where prehydrolysis time needed to form transparent gels was the shortest. The increase of temperature could accelerate sol–gel reaction. The dried hybrid gels were yellowish transparent glassy solids, with uniform microstructure composed of nanometer-sized particles. The conversion of the gels to silicon carbide powders was complete when heated at 1650°C for 30 min in vacuum. The oxygen and free carbon were 0.43 and 0.50 wt%, respectively, in the powder produced from the gel prepared with starting resin/TEOS being 0.143 g/ml. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Powders-solid state reaction; Precursors-organic; SiC; Sol–gel processes

1. Introduction

SiC ceramics are important wear and high-temperature structural materials. It has been recognized that the characteristics of the starting SiC powders have great influences on the properties of SiC ceramics sintered. To obtain high-performance SiC ceramics, fine powder with a narrow particles-size distribution are required. For this purpose, many effective methods have been developed, such as laser or plasma driven chemical vapor deposition[1–3] and thermal decomposition of organic silicon compounds.[4] However, carbothermal reduction of SiO_2 is industrially extensively used to produce SiC powders for its relatively low cost.[5] In this method, the mixing condition of the two reactants, SiO_2 and carbon, greatly influences the properties of the powder produced. Homogeneous mixing condition is expected to accelerate reaction rate and to lower reaction temperature. Lower reaction temperature is preferable for producing fine powders. Tanaka et al.[6] developed a sol–gel processing to mix the reactants in liquid phase, with ethylsilicate liquid and liquid phenolic resin as the sources of SiO_2 and carbon, respectively, and toluensulfonic acid as the catalyst. The powders obtained after carbothermal reduction of the gel were sinterable cubic SiC (β-SiC), containing no residual SiO_2 and carbon at proper starting resin content. Similar sol–gel route has also been used to fabricate β-SiC fibers, with hydrochloric acid as the catalyst.[7]

In this study we developed a two-step sol–gel processing to synthesize phenolic resin-SiO_2 hybrid gels with oxalic acid (OA) and hexamethylenetetramine (HMTA) as the catalysts, and synthesized SiC powders by carbothermal reduction of the obtained gels. In their molecules, OA and HMTA contain no sulfur and chlorine, which are detrimental to mechanical properties of SiC ceramics. Furthermore, OA and HMTA are benign to human body and not volatile, making the sol–gel processing easier to operate and control.

2. Experimental

The chemical reagents used in the experiments, tetraethoxysilane (TEOS), OA, HMTA, and ethanol were all

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* Corresponding author at present address: Institute of Chemical Metallurgy, Chinese Academy of Sciences, Beijing 100080, PR China. Tel.: +86-10-8261-0244.

E-mail address: jinwangl@hotmail.com (J. Li).

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of analytical grade. The water was deioned. The phenolic resin was novolac type, which was synthesized in the lab following a published procedure,[8] in the course of which the catalyst, OA, was removed by sublimation during drying of the resin in vacuum at 120°C. OA was not only the catalyst in synthesizing the phenolic resin, but also the catalyst in the sol–gel processing. HMTA acted both as the catalyst in the sol–gel reaction and as the curing agent of the resin. Mixing with HMTA in the mass ratio of HMTA/resin = 0.09, cured at 150°C in air, and pyrolyzed at 1000°C in nitrogen, the resin yielded approximately 50 wt% carbon.

A typical two-step sol–gel processing was as following. At the first step (prehydrolysis), the solution of 1.2 g phenolic resin, 0.8 ml water, and OA in 3.3 ml ethanol was prepared. 5 ml TEOS was then added with stirring. The molar ratio of OA/TEOS (denoted as R hereafter) varied from 0.0025 to 0.02. The resulted solution was held at 20–60°C for prehydrolysis. At the second step (gelation), the solution of 0.11 g HMTA in 0.2 ml water was added into the prehydrolyzed mixture with stirring, and the resulted mixture was kept at 20°C for gelation. The ratio of the mass of phenolic resin to the volume of TEOS (hereafter denoted as S, g/ml) was used to indicate resin content. The S value of the gels prepared as described above was 0.240 g/ml. By changing the amount of phenolic resin used in the preparation and varying the amount of HMTA correspondingly so that the mass ratio of HMTA/resin was 0.09, gels of S values ranging from 0.107 to 0.322 g/ml were prepared. The gel obtained was aged for 2 days and then dried at 150°C in air, during which the resin was cured by HMTA.

The carbothermal reduction of the cured gel was conducted in a graphite resistor-heated furnace. The gel was crushed into blocks of the size smaller than one centimeter, loaded with a graphite crucible, and put into the furnace. The furnace was kept being evacuated while it was firstly heated at 10°C /min, then held at 1550–1650°C for 30 min for reduction to proceed, and at last cooled down at 20°C /min.

The gels were observed by scanning electronic microscopy (SEM). The powders obtained after reduction were characterized via SEM and X-ray diffraction (XRD) with Cu K_α radiation. Free carbon content of the reduced sample was measured by firing the sample to constant weight in air at 600°C. Oxygen content after reduction was analyzed with a TC-136 oxygen-nitrogen determinator (Leco Co. Ltd., USA).

3. Results and Discussion

3.1. Condition for obtaining gels

OA content and prehydrolysis time determined whether gels could be obtained. Table 1 shows that only when prehydrolysis time was longer than a certain period could gels form. If prehydrolysis time was insufficient, for example, shorter than 2 h at 20°C, precipitates instead of gels were produced at the beginning of the second step when HMTA was added. The prehydrolysis time needed for forming gels varied with R value, and there existed an R value where the prehydrolysis time needed to form gel was the shortest. In the case showing in Table 1, this R value was around 0.005. Deviation from this R value led to longer necessary prehydrolysis time for forming gels. Especially noted was that the doubling of R from 0.01 to 0.02 led to the increase of the necessary prehydrolysis time for forming gels by more than five times.

Table 1
Products under different prehydrolysis conditions (S = 0.240 g/ml)[a]

Prehydrolysis condition		R = 0.0025	R = 0.005	R = 0.01	R = 0.02
Temperature (°C)	Time (h)				
20	2	p	p	p	p
	4	p	g	cg	p
	7	g	g	cg	p
	20	g	g	g	p
	120	–	–	–	cg
	300	–	–	–	g
60	20	g[b]	g	g	g

[a] p, Large amount of precipitate appeared upon adding HMTA; g, transparent gel; cg, cloudy gel, indicating partial precipitation.

[b] Gelated before adding HMTA.

Increase of temperature could accelerate reaction rate, thus reducing the necessary prehydrolysis time to form gel. For example, with the prehydrolysis temperature of 60°C gel formed after 20 h of prehydrolysis when R was 0.02, while with the prehydrolysis temperature of 20°C only cloudy gel was obtained even after 120 h of prehydrolysis. The sample with R = 0.0025 even gelated within 20 h during prehydrolysis at 60°C.

Varying of the S value from 0.107 to 0.322 g/ml had not significant influence on gel-forming condition.

3.2. Gelation time after adding HMTA

OA content and prehydrolysis condition influenced the time required for the liquid samples to convert to gels after adding HMTA (Table 2). Increase of prehydrolysis time or temperature, or decrease of R, could reduce gelation time after adding HMTA.

3.3. Effect of HMTA on gel formation

HMTA could greatly shorten gelation time. For example, 11 days were needed to form gel when R was 0.01 and S was 0.240 g/ml, if the water–HMTA solution was not added. Nevertheless, only 1.5 h were required to form gel at the second step for the same sample, if the

Table 2
Gelation time after adding HMTA (S = 0.240 g/ml)[a]

Prehydrolysis condition		Gelation time after adding HMTA (min)			
Temperature (°C)	Time (h)	R = 0.0025	R = 0.005	R = 0.01	R = 0.02
20	4	p	40	130	p
20	20	10	30	90	p
60	20	g[b]	10	30	90

[a] p, Large amount of precipitate appeared upon adding HMTA; g, transparent gel.

[b] Gelated before adding HMTA.

water–HMTA solution was added after 20 h of prehydrolysis.

3.4. Mechanism of the sol–gel reaction

In gel formation from TEOS, Si–OH groups are firstly produced by hydrolysis of Si–OC_2H_5 groups. Then Si–O-Si chains are formed by condensation between two Si–OH groups or between a Si–OH group and a Si–OC_2H_5 group. Finally the chains cross-link and/or entangle with each other in the whole liquid to form gel.

It was believed that the hydrolysis and condensation rates of TEOS were greatly dependent upon the catalyst and the pH value.[9,10] Generally when pH was below 7, hydrolysis rate increased with decreasing pH, but condensation rate decreased and reached its lowest point at pH = 2, the isoelectric point for silica.

In the present study, OA was used at the first step to promote the hydrolysis of TEOS, and a weak alkali, HMTA, was added at the second step to promote condensation and gelation. Measurements indicated that during both steps the pH values were below 7 and decreased with increasing OA content. Typically when S was 0.240 g/ml, the pH values ranged between 1.8 and 3.3 at the beginning of the first step, and between 4.5 and 5.7 at the beginning of the second step.

Hydrolysis and condensation occurred at both steps, and played important roles for gel formation at the first step. If Si–O–Si chains produced at the first step were too small or too few, it would be difficult for them to cross-link and/or entangle with each other, and precipitate was likely to form when HMTA was added and the pH increased respondingly away from the isoelectric point of silica. This was the reason why precipitates were formed if prehydrolysis time was not enough. At the first step, low R value resulted in low hydrolysis rate, and high R value led to low condensation rate. Because Si–O–Si chains were produced by condensation following hydrolysis, the slower one of hydrolysis and condensation determined their forming rate. Therefore, there was an optimum R value where the forming rate of Si–O–Si chains were the highest and prehydrolysis time needed for producing Si–O–Si chains sufficient to form gel was the shortest.

After sufficient hydrolysis, condensation rate decided the time needed for the Si–O–Si chains to cross-link and/or entangle to form gel. Longer prehydrolysis time and higher prehydrolysis temperature made reactions more complete at the first step, thus shortening gelation time at the second step. With R increasing, condensation rate decreased at both steps, so longer time was needed for gel to form at the second step.

3.5. Morphology of the gel

All transparent gels were yellowish glassy solids after dried and cured at 150°C. SEM microscopy shown that their microstructures were uniform, composed of particles of tens of nanometers. Prehydrolysis condition had no significant influence on the particle size. A typical SEM image is shown in Fig. 1. The transparent yellowish glassy appearance and the uniform microstructure of the gel indicated that the resin distributed uniformly.

3.6. Reduction of the gel

The appearance of the reduced gel is shown in Table 3. Most of the products after reduction remained the shapes of the gel blocks before reduction, and had a loose greenish outer layer as part of every block of some samples. The loose greenish layer of the block became

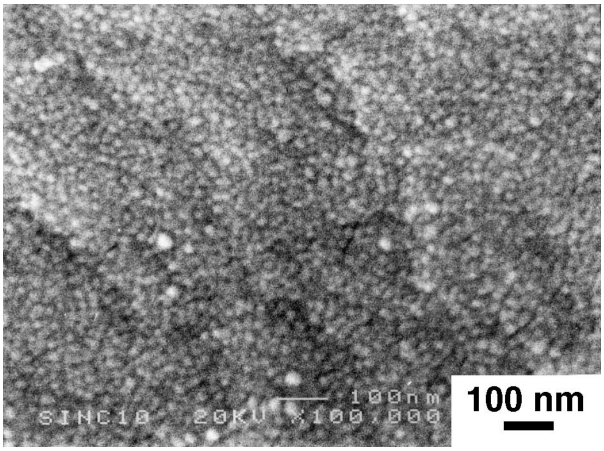

Fig. 1. SEM image of a phenolic resin–SiO_2 hybrid gel (S = 0.240 g/ml; prehydrolysis condition: 20°C, 7 h, R = 0.0025).

Table 3
Appearances of the products after reduction

Reducing temperature (°C)	S = 0.143 g/ml	S = 0.179 g/ml	S = 0.215 g/ml
1550	Greenish and black blocks[a]	Greenish and black blocks[a]	Black blocks
1650	Greenish powder	Greenish and black blocks[a]	Black blocks

[a] The surface and near-surface part of the block was loose and greenish, while the inner part of the block was relatively hard and black.

thicker with increasing reducing temperature and decreasing S value. In two extreme cases, loose greenish powders (S = 0.143 g/ml, 1650°C) and black blocks without greenish layer (S = 0.215 g/ml) were respectively obtained. XRD analysis of the greenish powder obtained by reducing the gel with S = 0.143 g/ml at 1650°C revealed that this powder was pure β-SiC. Evidently the greenish color and the black color in other products were shown by β-SiC and free carbon, respectively. From the apparent difference in appearances it was deduced that the reducing reaction was more complete at 1650°C than at 1550°C.

Table 4 shows the oxygen and nitrogen contents of two products after reduction. In the reduced samples, oxygen existed in the form of SiO_2. At 1650°C the reducing reaction was complete, and almost pure SiC powder was obtained when S was 0.143 g/ml. Much excessive free carbon remained when S was increased to 0.179 g/lm. Apparently when S was 0.215 g/ml, more excessive free carbon existed and the greenish color of β-SiC was completely hidden by the black color of free carbon.

Fig. 2 shows the microstructure of the as produced powder after reducing the gel of S = 0.143 g/ml at 1650°C. The powder was composed of submicron particles forming large agglomerates.

The formation of a greenish outer layer as part of every block of some samples was related to the mechanism of the reducing reaction. In the reduction the overall reaction

$$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g) \quad (1)$$

was commonly believed to proceed through the following two steps:[11]

$$SiO_2(s) + C(s) = SiO(g) + CO(g) \quad (2)$$

$$SiO(g) + 2C(s) = SiC(s) + CO(g) \quad (3)$$

Table 4
Oxygen and nitrogen contents for the samples reduced at 1650°C

S = 0.143 g/ml		S = 0.179 g/ml	
Oxygen (wt%)	Nitrogen (wt%)	Oxygen (wt%)	Nitrogen (wt%)
0.43	0.50	0.30	9.59

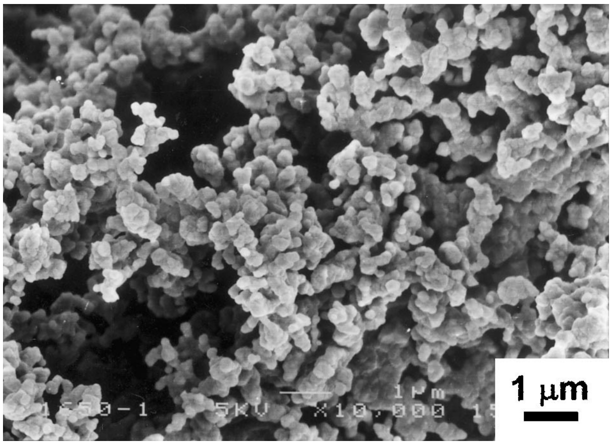

Fig. 2. SEM image of the as produced SiC powder after reduction of the gel with S = 0.143 g/ml at 1650°C.

The SiO gas produced by reaction (2) throughout every sample block would diffuse toward the outside of the block. Therefore the carbon in the outer part of the block had the greatest opportunity to react with SiO gas to form SiC by reaction (3), and would be depleted quicker than that in the inner part. An outer greenish layer would form if the carbon in the outer part of the block was all converted to SiC while that in the inner part remained much.

4. Conclusions

A two-step sol–gel processing under the catalysis of oxalic acid (OA) and hexamethylenetetramine (HMTA) was developed to prepare SiO_2-phenolic resin hybrid gels used as SiC precursors, with tetraethoxysilane (TEOS) and novolac type phenolic resin as the starting materials. The gels were transparent yellowish glassy solids, with uniform microstructure composed of particles of tens of nanometers. OA content and prehydrolysis time determined whether gel instead of precipitate could form. OA was considered promoting hydrolysis of TEOS, and HMTA promoting condensation and gelation. The increase of temperature could accelerate sol–gel reaction. By reducing the gel of proper resin content at 1650°C for 30 min in vacuum, almost pure β-SiC powder was obtained.

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