Synthesis of SiC–TiC Powders by Pyrolysis of Phenolic Resin–Alkoxides Hybrid Precursors

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フェノール樹脂–アルコキシドハイブリッド前駆体の熱分解による SiC–TiC 複合粉末の合成

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Hybrid gels were synthesized from liquid mixtures composed of tetraethyl orthosilicate, titanium tetraisopropoxide and phenolic resin with an acid catalyst addition and a continuous stirring. The gels, prepared with various Ti/Si ratios, were dried, crushed and finally pyrolyzed at 1873 K to yield SiC–TiC powders. Infrared (IR) and nuclear magnetic resonance (NMR) spectra suggested the existence of Si–O–Ti in the precursors pyrolyzed at 773 K, while the precursor before the pyrolysis contained a considerable amount of Si–O–H in addition to Si–O–Ti. The addition of titanium alkoxide in the starting mixture accelerated the final carbothermic reduction rate at 1873 K. A diminished stacking fault structure in the formed SiC crystallites was revealed in SiC–TiC mixed powders.

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1. Introduction

Carbothermic reduction process of silica by carbon has been widely used to produce silicon carbide powders. The mechanism of such carbothermic reduction is, however, not simple, because the material carbon and silica particles merely contact by points on surface in usual cases.^{1)–7)} We have investigated the simultaneous condensation reaction of water soluble liquid phenol resin and tetraethyl orthosilicate (TEOS) in concentrated mixtures and their pyrolysis process to overcome such heterogeneous mixing between the carbon sources and silica sources.^{8)–11)} This process is based on the method developed by Kurachi in 1991.^{12),13)} This method, in addition, allows the mixing of various alkoxides in the starting mixtures, which will be incorporated into organic-inorganic network during the condensation reaction. Effect of borate addition into the resin-TEOS starting precursor has been investigated from the viewpoint of the SiC crystallite growth during the carbothermic reduction process at 1873 K.

It is known that titanium oxide (TiO_2) yields carbide by carbothermic reduction at lower temperature than SiO_2 .^{5)–7),14)–17)} and the combination of SiC and TiC have been investigated as a promising ceramic composite with the controlled high toughness and electrical resistivity.^{18)–21)} In this article, the precursors for SiC–TiC powders were synthesized from the resin–tetraethyl orthosilicate (TEOS)–titanium tetraisopropoxide (TTIP) mixtures to be investigated by FT-IR, solid state NMR and small angle X-ray scattering in their pyrolysis process. The SiC–TiC powders obtained at 1873 K were characterized by SEM, X-ray diffraction and solid state NMR.

2. Experimental

On the basis of the process reported in the previous study,^{8)–11)} the liquid mixtures of tetraethyl orthosilicate (TEOS; Wako Chemicals), titanium tetraisopropoxide (TTIP; Tokyo Kasei) and phenolic resin (Sumiliteresin

PR-50781, Sumitomo Durez Co., Ltd.) were prepared. The compounding ratio of each material is shown in Table 1. After the continuous stirring of the mixtures, the acid catalyst (30 mass% of toluenesulfonic acid solution in water) was added and stirred up to the gelation. The obtained gels were dried in vacuum, crushed and pyrolyzed at various temperatures up to 1273 K (heating rate: 5 K/min, holding time: 1 h) in a nitrogen atmosphere (flowing rate: 1 l/min). The precursor pyrolyzed at 1273 K was put into the graphite furnace preheated at 1873 K under an Ar flow rate of 1 l/min to yield the SiC–TiC powders by carbothermic reduction.

Infrared (IR) spectra of the starting gels and the pyrolyzed precursors were measured with a FT-IR 1650 (Perkin Elmer). ^{13}C NMR and ^{29}Si MAS NMR in solid state were measured by MSL-400 (Bruker). CP-MAS technique was used for ^{13}C NMR, and single pulse method (100 s of delay time) was used for ^{29}Si NMR. The small angle X-ray scattering (SAXS) measurements were performed by using

Table 1. Compositions of the Starting Mixtures

Sample Ti/Si	Phenolic Resin /g	TEOS /g	TTIP /g
0	47.0	132.0	0
0.125	50.0	132.0	22.5
0.2	54.0	132.0	36.0
0.3	58.5	132.0	54.0
0.4	63.0	132.0	72.0

TEOS: Tetraethyl orthosilicate
TTIP: Titanium tetraisopropoxide

a point beam instrument with an imaging-plate. The large angle XRD measurement was performed by RINT-1100 (Cu K α , Rigaku).

Mass loss during the carbothermic reduction process at 1873 K was monitored by automatic balance attached with the vertical graphite furnace. The powders obtained after the carbothermic reduction were investigated by XRD measurements, scanning electron microscope (SEM; S-4500, Hitachi) and transmission electron microscope (TEM; JEM-2000FX, JEOL) and solid state NMR.

Electron probe microanalyses (Electron Probe Micro-analyzer, JXA-870, JEOL) using a WDX detector was performed on the precursors and the resulting powders. Intensity of the characteristic X-ray, Ti K α , Si K α , O K α and C K α was measured. Since this elemental analysis method is rough in general for light elements, the precise carbon contents in the samples are reconfirmed by carbon combustion tests at 1573 K with a CuO oxidizing agent using a CSA-1 C-S estimation apparatus (Kawatetsu Keiryosya). The oxygen contents are calculated as residue.

3. Results and discussion

The starting mixtures showed turbid appearance with resin dispersions in liquid TEOS-TTIP. After the catalyst addition, exothermic reaction was observed (Maximum temperature: 493 K in 0.5–1 min). The solution with TTIP showed the turbid appearance as compared with the undoped solution. The mixture with Ti/Si ratio of 0.4 was rapidly gelled in 1 min after the catalyst addition, while the undoped mixture needed 12 h for gelation.

IR spectra of the undoped gels pyrolyzed at various temperatures are shown in Fig. 1 (a). The spectrum of the dried gel indicates the existence of O–H (broad absorption at 3400 cm⁻¹ with a shoulder at 3600 cm⁻¹), C–H (aliphatic bridges: 3100–2900 cm⁻¹), C=O (1700–1600 cm⁻¹), CH₂ (1500–1400 cm⁻¹), C–O (shoulder at 1250 cm⁻¹), Si–O–Si (1250–1050 cm⁻¹) and Si–O–H (960 cm⁻¹).^{22)–24)} As the pyrolysis temperature increases, intensity of these absorption peaks decreases except the Si–O–Si absorption. Figure 1 (b) indicates IR spectra of the precursors pyrolyzed at 773 K with various amount of TTIP addition. IR spectra of these precursors at 773 K show the broad absorption of Si–O–Si and a characteristic shoulder at 960 cm⁻¹, which is increased with the TTIP addition even in the 0.125Ti precursor with TTIP/TEOS molar ratio of 0.125. This shoulder is assigned to Si–O–Ti absorption,^{25),26)} because the stretching bands of hydroxyl group around at 3400 cm⁻¹ is absent at 773 K.

On the other hand, the IR spectra of the merely dried gels with TTIP addition in the range of 0.125–0.4 Ti/Si show no remarkable difference from that of the dried undoped gel. This should be due to the similar wavenumber of the Si–O–Ti band to that of the Si–O–H band.

Figure 2 shows the ²⁹Si NMR spectra of the undoped gels after pyrolysis at various temperatures. The ²⁹Si NMR shows 3 peaks assigned to Q₄ (–110 ppm: Si(OSi)₄), Q₃ (–101 ppm: Si(OSi)₃(OH) or Si(OSi)₃(OC)) and Q₂ (–92 ppm: Si(OSi)₂(OH)₂, Si(OSi)₂(OH)(OC) or Si(OSi)₂(OC)₂).^{27),28)} The dried gel contains quite large amount of Q₃ and Q₂ even by the single pulse method, which is larger than Q₃ and Q₂ ratios in the foregoing phenolic resin-silica hybrid gels synthesized by Haraguchi.²⁹⁾ As the heat treatment temperature increases, the contents of Q₃ and Q₂ decrease that probably corresponds to the formation of complete silica network from the original network containing large amounts of Si–O–H or Si–O–C (Fig. 3(a)). When the TTIP was added in the starting mixture, the peak intensity of Q₃ in the dried gels increases in appearance. This is probably due to the existence of TiQ₃ (–104 ppm, Si(OSi)₃

Fig. 1. IR spectra of the pyrolyzed precursors: (a) undoped precursors pyrolyzed at various temperatures, (b) precursors pyrolyzed at 773 K with various TTIP amount of addition.

(OTi)) in the dried gels.^{26),30)} Our try to estimate TiQ₃ contribution on the dried gel spectra quantitatively, however, gave ambiguous results, due to the quite similar chemical shifts between TiQ₃ and Q₃ and many parameters about the assumed 4 peaks. We try to estimate the contribution TiQ₃ after the pyrolysis of the gels at 773 K. After the pyrolysis at 773 K, the peaks are unified to one broad peak (Fig. 2(b)). The peak position, however, shifts to lower field with the addition of TTIP. We assumed that the observed peaks are

Fig. 2. ^{29}Si NMR spectra of the pyrolyzed precursors: (a) undoped precursors pyrolyzed at various temperatures, (b) precursors pyrolyzed at 773 K with various TTIP amount of addition.

composed of the Q_4 main peak (-110 ppm) with perturbation of the Q_3 (-101 ppm) and TiQ_3 (-104.0 ppm). The results of our quantitative estimation indicate the contribution of TiQ_3 has been saturated beyond Ti/Si ratio of 0.2 (Fig. 3(b)). Thus, titanium in the pyrolyzed gels are considered to be incorporated into silica network in the form of Si-O-Ti up to Ti/Si ratio of 0.125. The contribution of TiQ_3 , however, does not exceed 10% even under the high TTIP addition.

In the solid state ^{13}C NMR spectra of the undoped gel with merely drying, the signals assigned to phenolic C-OH (155 ppm), aromatic CH (130 ppm) Ph-CH₂-OH (65–60 ppm) and methyl-methylene mixture (25–15 ppm) were observed.³¹⁾ The signals of Ph-CH₂-OH and methyl-methy-

Fig. 3. Quantitative estimation of the silicon atom 1st coordination in the pyrolyzed precursors from their ^{29}Si NMR spectra: (a) undoped precursors pyrolyzed at various temperatures, (b) precursors pyrolyzed at 773 K with various TTIP addition.

lene mixture have disappeared up to 523 K. The broad signal of phenolic C-OH has disappeared beyond 673 K. Only the signal of aromatic CH remains after high temperature pyrolysis. Fairly sharp profile of the signals of methyl-methylene mixture may reveal the existence of Si-OC₂H₅ in the dried gel, which were not perfectly hydrolyzed during the gelation and the drying processes. The overlapping of the spinning side bands on the measured signals, however, makes the detailed assignments difficult.³²⁾ The addition of TTIP in the starting mixture seemed to have no influence on the observed spectra.

Figure 4 shows SAXS patterns of the pyrolyzed gels at 1073 and 1273 K. Up to 1073 K, the SAXS patterns showed broad tails without shoulders. The SAXS patterns began to show shoulders at 1073 K. The constant radii of the domains calculated on the basis of Guinier law were about 1.5–2 nm for the precursors with 1073 K pyrolysis, and 2–3 nm for the precursors with 1273 K pyrolysis.³³⁾ The TTIP addition, however, has no large influence on the domain size in any Ti/Si ratios. The observed SAXS pattern suggests the existence of the controlled microstructure in the prepared precursors, and such structure continues to evolve even at the temperature range where the IR or NMR spectra show

Fig. 4. Results of SAXS analyses: (a) 1073 K, (b) 1273 K.

Table 2. Compositions of the Precursors Pyrolyzed at 1273 K

Sample Ti/Si	SiO ₂ (molar ratio)	TiO ₂ (molar ratio)	C (molar ratio)
0	1	0	3.06
0.125	1	0.125	3.56
0.2	1	0.2	3.81
0.3	1	0.3	4.17
0.4	1	0.4	4.23

no remarkable changes.

Table 2 shows the estimated compositions of the precursors pyrolyzed at 1273 K. TiO₂/SiO₂ ratios were estimated from the original TTIP/TEOS ratios. Some of these values were reconfirmed by electron microprobe analyses on the precursors about Ti/Si atomic ratios. Carbon contents were estimated from high temperature combustion method on the finely ground samples. In this table, all the titanium in the system is assumed to exist in the form of TiO₂. A part of titanium is, however, considered to exist in the form of Si-O-Ti on the basis of ²⁹Si NMR spectra. In addition, the large angle X-ray scattering of the pyrolyzed precursors

Fig. 5. Isothermal mass loss curves of the precursors at 1873 K.

Table 3. Compositions of the SiC-TiC Powders Obtained at 1873 K (4.5 ks)

Sample Ti/Si	Si /mol%	Ti /mol%	C /mol%
0	40.5	0	59.5
0.125	44.1	5.5	50.4
0.4	38.8	15.5	45.7

XRD patterns suggested Ti₃O₅ existence in the 0.125 Ti and the 0.4 Ti powders. The oxygen, however, was not captured in the electron microprobe analyses.

shows broad peaks of TiO₂ (anatase) beyond Ti/Si ratio of 0.2. The precursors pyrolyzed at 1273 K are probably composed of carbon, silica domain containing Si-O-Ti and anatase.

During the isothermal heat treatment process at 1873 K, the precursors pre-pyrolyzed at 1273 K show about 40% of mass losses. The monitored mass loss curves (Fig. 5) indicate that the addition of TTIP accelerated the carbothermic reduction process. The mass loss curves become stable about at a holding time of 0.5–1.5 ks. SEM micrographs of the obtained powders after the 4.5 ks holding reveal the aggregated grain sizes of 80–220, 160–350 and 270–540 nm for the undoped, 0.125Ti and 0.4Ti powders. The compositions of these powders, estimated by elemental analyses (high temperature combustion and EPMA), are summarized in Table 3.

Figure 6 shows the XRD patterns of the obtained powders. The TiC crystal structure is almost same as the SiC crystal structure. The TiC lines can not be separated out from the SiC line in the 0.125Ti powder. In the 0.4Ti powder, the TiC lines have been separated out from the SiC lines. Not only TiC but also the trace of Ti₃O₅ is observed. The peak at 41.4° is strengthened by the increase in the TiC content. This should be due to the (200) line of TiC, which is known to possess strong intensity as compared with the (200) line of SiC.

XRD pattern of undoped powder indicates relatively large peak at 33.6°C, which corresponds to the stacking faults in "β-SiC",^{6),7),34)–36)} while the 0.4Ti powder shows trace of the stacking faults in its XRD pattern. Less stacking faults in

Fig. 6. XRD patterns of the obtained powders.

Fig. 7. TEM micrographs of the obtained powders: (a) undoped powder, (b) 0.4Ti powder.

" β -SiC" crystallites in the 0.4Ti powder probably sharpen the SiC peaks to be separated out from the TiC peaks.

Figure 7 shows the TEM micrographs of the undoped powder and the 0.4Ti powder. Observed crystallite sizes are usually 50–100 nm. The grains observed in SEM are the aggregate of these crystallites. The TiC crystallites can not be distinguished from the SiC crystallites in the 0.4Ti powder. Perhaps, TiC crystallites in this powder possess not only a similar crystal structure but also similar size and morphology to those of the SiC crystallites. On the other hand, the TEM micrograph of the undoped powder indicates the existence of the elliptic SiC crystallites containing a lot of stacking faults, which have disappeared in the 0.4Ti powder.

Figure 8 shows ^{29}Si NMR spectra of the undoped powder and the 0.125Ti powder. The spectrum of the undoped powder consists of a large broad signal at -19 ppm with a small spike at -16 ppm and a shoulder at -25 ppm. The broad signal at -19 ppm is characteristic in not spherical " β -SiC" grains, in which one-dimensional disorder (stacking faults) of lamella patterns were observed.³⁷⁾ The broadness should reflect the fluctuation in chemical nature of silicon atoms in the disordered " β -SiC" structure. On the other hand, the spectrum of the 0.125Ti powder consists of three sharp signals at -16 , -20 and -26 ppm. Such sharp signal in NMR spectra of " β -SiC" has been explained on the basis of the thin layer of " α -phase" sandwiched with thick β -SiC zones

Fig. 8. ^{29}Si NMR spectra of the obtained powders: (a) undoped powder, (b) 0.125Ti powder.

on both sides. They are previously observed in near-spherical-shaped SiC grains.³⁷⁾ Even in the 0.125Ti powder, effect of the Ti doping on diminishing the stacking faults in

the SiC crystallites is suggested, although the SiC and TiC peaks are overlapping in its XRD pattern.

In order to explain the effect of Ti doping in this SiO₂-TiO₂-C system, liquid phase formation during the carbothermal reduction process at 1873 K is a considerable mechanism. It is known that SiO₂-TiO₂ system yields liquid phase at 1823 K with the TiO₂/SiO₂ molar ratio of 0.117.^{38),39)} Since some of the titanium in our system is trapped in the silica network, the SiO₂-TiO₂ liquid phase can be formed easily. The formed liquid phase should contribute the accelerated mass loss, the aggregated morphology of the formed SiC-TiC powders and the diminished stacking faults of the SiC crystallites.

4. Summary

IR and NMR spectra suggest the existences of the TiQ₃ (Si-O-Ti) in the prepared precursor. Quantitative estimation of the ²⁹Si NMR spectra reveals that TiQ₃ ratio in the silicon atom coordination is saturated at ca. 10 mol%. Beyond the Ti/Si ratio of 0.2, the formation of anatase is suggested. The addition of titanium in the system accelerates carbothermic reduction at 1873 K, which have been finished at 0.5–1.5 ks. The TEM micrographs of the powders indicate the aggregated grains consisting of the SiC and TiC crystallites (50–100 nm in crystallite diameters). The size and morphology of TiC crystallites are almost the same as those of SiC in appearance. In the 0.4Ti powder, however, number of elliptic SiC crystallites possessing the disordered lamella patterns decrease. Thus the XRD lines of SiC are sharpened and are separated out from those of TiC. The SiO₂-TiO₂ liquid phase formation during the heat treatment at 1873 K is suggested to play an important role in the carbothermic reduction process which yields the SiC-TiC powders.

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