Effect of a Catalyst on the Formation of SiC Whiskers from Polycarbosilane. Nickel Ferrite as a Catalyst

Shinji Otoishi* **and Yoshihiro Tange**

Research Laboratory, Okura Industrial Co., Ltd., 1515, Nakatsu-cho, Marugame, Kagawa 763-8508

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The effect of a catalyst, nickel ferrite, on the formation of SiC whiskers from porous bodies containing polycarbosilane and milled carbon fibers was studied. SiC whiskers were deposited at above 1373 K from porous bodies having a catalyst, while noodle-like SiC products were obtained at above 1473 K from porous bodies having no catalyst. A scanning electron-microscopic analysis and an energy-dispersive X-ray analysis revealed that SiC whiskers were formed via a vapor–liquid–solid process. An X-ray diffraction measurement revealed that the whiskers consisted of β-SiC, and that their crystallinity was significantly high in spite of the heating temperature (1373 to 1623 K). Based on changes in the infrared absorption spectra and gas-evolution curves during the heating process, it was presumed that the pyrolyzing process of polycarbosilane in the two kinds of porous bodies, one with a catalyst, and the other without a catalyst, remarkably resembled each other. SiC whiskers were proved to grow remarkably with decreasing the Si–O bondings by infrared spectroscopy and a chemical analysis. It could therefore be presumed that the formation mechanism of the SiC whiskers was analogous to that of silica–carbothermal reduction.

SiC whiskers have been attracting attention as a reinforcing material for use in plastics, metals and ceramics,[1—3] because they are fine and have a mechanical strength close to the theoretical level. Therefore, many studies on the formation of SiC whiskers have been performed.

On the other hand, since an investigation by Yajima[4] of a precursor for SiC fibers, numerous new organometallic polymers have been developed as precursors for many kinds of non-oxide ceramics: SiC, Si_3N_4, TiN, AlN, BN etc. Especially, polycarbosilane (PCS) as a precursor for SiC ceramics has been widely studied by many researchers.[5—7] For example, Hasegawa and Okamura[8] studied the pyrolysis of PCS for SiC fibers and the structure of SiC fibers. In their papers they described that the decomposition of Si–H and C–H in $SiCH_3$ and Si–CH_2–Si bonds, such as dehydrogenation and demethanation, converts PCS into an inorganic structure with a network and a three-dimensional structure. In other words, the pyrolysis of PCS into SiC fibers followed a typical solid-state reaction process.

We previously reported[9] that SiC whiskers were formed by heating in Ar gas of a porous body produced by polymerization and drying a polymerizable W/O-type emulsion containing PCS and milled carbon fibers. Furthermore, from a SEM observation, in which a spherical part was observed on the whiskers' edge, it was revealed that SiC whiskers were formed via the vapor–liquid–solid (VLS) process. Thus, SiC whiskers prepared from PCS were formed by a mechanism basically different from that for the pyrolysis generally adopted for the syntheses of SiC fibers from PCS. The difference was that the former mechanism involved a vapor-phase reaction.

Several authors have studied the VLS growth process of SiC whiskers. Milewski et al.[10] studied the SiO–CH_4–H_2 system with stainless-steel particles used as a catalyst and Bootsma et al.[11] studied the SiO_2–C–H_2 system with iron used as a catalyst. Thus, it is well known that the preparation of SiC whiskers via the VLS process needs a catalyst which acts as a liquid (L). Consequently, it was assumed that in our previous system[9] there was a metal contaminant which acted as a catalyst for the formation of SiC whiskers via the VLS process.

The objectives of this study were to specify the metal contaminant and to clarify the difference in the pyrolysis process of PCS and the formation process of SiC in both the presence and absence of a catalyst.

Experimental

Materials. Commercial polycarbosilane (PCS, Nippon Carbon Co., Ltd.) was used. The milled carbon fibers (MCF, Pitch-based, Nippon Sheet Glass Co., Ltd.) were approximately 13 μm in diameter and 200 μm long. The styrene (St), trimethylolpropane trimetacrylate (TMPT, Shin-Nakamura Chemical Co., Ltd.) and sorbitan sesquiolate (SSO, Kao Corporation) used in this study were of industrial grade. The ammonium peroxosulfate (APS, Wako Pure Chemical Industries, Ltd.) was a special reagent grade. The diiron nickel tetraoxide ($NiFe_2O_4$, Nickel ferrite, Soekawa Chemicals) had a purity > 99.9%.

Preparation of Porous Bodies. MCF was treated with a 2 mol dm^{-3} HCl solution in order to remove any metal contaminant. $NiFe_2O_4$ (0.05×10^{-3} kg) was mixed with HCl-treated MCF (10×10^{-3} kg) in an alumina mortar. A mixture of St (6.4×10^{-3} kg),

TMPT (1.6×10^{-3} kg) and SSO (2.0×10^{-3} kg), as the emulsifier, was stirred uniformly in a 200 ml polyethylene beaker equipped with a motor-driven propeller stirrer (50 mm in diameter). PCS (2.0×10^{-3} kg) was dissolved in the above mentioned solution with additional stirring. A mixture of HCl-treated MCF and $NiFe_2O_4$ was added while the solution was being stirred, and a paste was formed. APS (0.08×10^{-3} kg), as a polymerization initiator, dissolved in water (20.0×10^{-3} kg), was slowly added to the paste with vigorous stirring in order to prepare a W/O type emulsion.

The W/O type emulsion was sealed in a glass test tube (15.6 mm in diameter and 180 mm long) with a silicone rubber plug, and heated at 333 K for 43.2 ks for polymerization. After being taken out of the test tube, the polymer was further heated and dried at 333 K for 86.4 ks in order to prepare a porous body by evaporating the water formed as a dispersed phase.

Heating of Porous Bodies. The porous body was first pre-heated at 823 K for 18.0 ks in a box furnace with a retort (Koyo Lindberg Co., Ltd., Model 51442) in a flow of nitrogen gas at a rate of 1.67×10^{-5} $m^3\,s^{-1}$ in order to remove any organic components produced from St, TMPT, and SSO. The pre-heated product was further heated after having been transferred to an atmospheric furnace (Fuji Denpa Kogyo Co., Ltd., FVS-R-80/60 FRET-10), at a various temperatures for 18.0 ks in a flow of argon gas at a rate of 0.83×10^{-5} $m^3\,s^{-1}$.

Measurement. Chemical analyses of the metal contaminant were carried out using inductively coupled plasma (ICP) emission spectroscopy (SPS 7000 Plasma Spectrometer, Seiko Instrument). A thermogravimetric analysis (TGA; SSC/5200 TG/DTA220, Seiko Instrument) was performed on the MCF. The product was observed using a scanning electron microscope (SEM; JSM-5410LV, JEOL). An energy-dispersive X-ray (EDX) analysis (JED-2110, JEOL) was carried out on the spherical part of the whiskers. An infrared spectra measurement (IR; 1720-X, Perkin Elmer) and an X-ray diffraction (XRD) analysis (TW-1700, Philips, Cu $K\alpha$, 40 kV, 40 mA, 10—80° of 2θ at 0.05° s^{-1}) were performed on the products. A step scanning method (57—63° of 2θ, step size 0.01° of 2θ, counting time 5 s $step^{-1}$) was used to estimate the full width at half maximum and the intensity of the (220) diffraction line of β-SiC. The gases released from the porous bodies under heat were determined using a Pirani vacuum gauge, where the porous bodies were heated in a vacuum to follow the system pressure. The silicon and oxygen in the products were analyzed using alkali fusion/ICP emission spectroscopy and combustion/infrared absorptiometry, respectively.

Results and Discussion

Chemical Analysis of MCF. By ICP emission spectroscopy and TGA it was proved that the MCF was contaminated with ca. 1800 ppm of iron and ca. 490 ppm of nickel, and that the ash content of the MCF was ca. 3400 ppm. It was considered that iron and nickel were mixed in the MCF while manufacturing them. Thus, we examined the effect of iron, di-iron trioxide, nickel, nickel monooxide, and their mixtures on the formation of SiC whiskers from PCS. However, we could not find any sufficiently effective material as a catalyst. Next, we examined the effect of the ash of MCF on the formation of SiC whiskers from PCS. As a result, it was proved that the ash of MCF is a very effective material as a catalyst. Figure 1 shows the XRD pattern of the ash of MCF. From Fig. 1 the ash of MCF can be seen to comporise $NiFe_2O_4$ (travorite) and Fe_2O_3 (hematite). From these

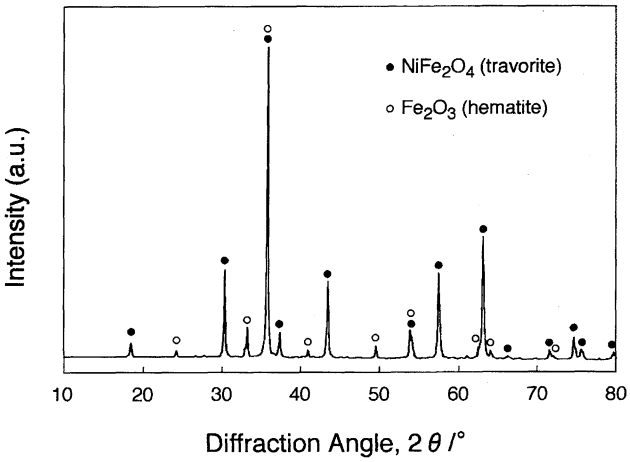

Fig. 1. XRD pattern of the ash of MCF.

results, we adopted $NiFe_2O_4$ as a catalyst (0.5 wt% to MCF) for the formation of SiC whiskers.

SEM Observation and EDX Analysis of Products. The heating of a porous body containing PCS, HCl-treated MCF, and $NiFe_2O_4$ (porous body A) in Ar at 1473 K for 1 h resulted in the formation of SiC whiskers having a spherical part on their edge. Figure 2 shows a SEM photograph of a whisker (Fig. 2(a)) and the EDX spectrum of the spherical part of the whisker (Fig. 2(b)). These observations revealed that the spherical part on whisker' s edge comprised nickel and iron derived from $NiFe_2O_4$.This means that the formation of SiC whiskers from porous body A proceeds via the VLS process.

Figure 3 shows SEM photographs of heated porous body A and a heated porous body containing PCS and HCl-treated MCF (porous body B) at 1373 to 1573 K for 5 h. In the case of porous body A, whiskers were deposited at 1373 K and grew significantly with increasing the heating temperature.

On the other hand, in the case of porous body B, no whiskers were deposited at 1373 K. At 1473 and 1573 K, however noodle-like products were obtained.

It was concluded from these observations that the requirement of certain impurities, for example $NiFe_2O_4$, for whiskers' growth and the absence of whiskers' growth without impurities, were of great significance in our PCS–MCF–Ar system.

IR Spectra Measurement. Figure 4 shows the IR spectra of heated porous body A. At 873 K, the characteristic absorption bands of PCS[12] at 2950 and 2900 cm^{-1} (C–H stretching), 2100 cm^{-1} (Si–H stretching), 1410 cm^{-1} (C–H deformation of $Si–CH_3$), 1355 cm^{-1} (CH_2 deformation of $Si–CH_2–Si$), and 1260 cm^{-1} ($Si–CH_3$ deformation) were scarcely observed, while bands at 3340, 1045, 820, and 460 cm^{-1} were observed. The 820 cm^{-1} band corresponds to the Si–C stretching vibration. The 460 cm^{-1} band corresponds to the deformation vibration of O–Si–O,[13] which suggests the presence of a Si–O bond in the product, either as cross-linked oxygen or as free SiO_2. The absorption band at 1045 cm^{-1} is considered to result from the peak related to the Si–O stretching vibration (1080 cm^{-1}),[13] caused by the formation of a Si–O bond in the product, which overlaps the peak

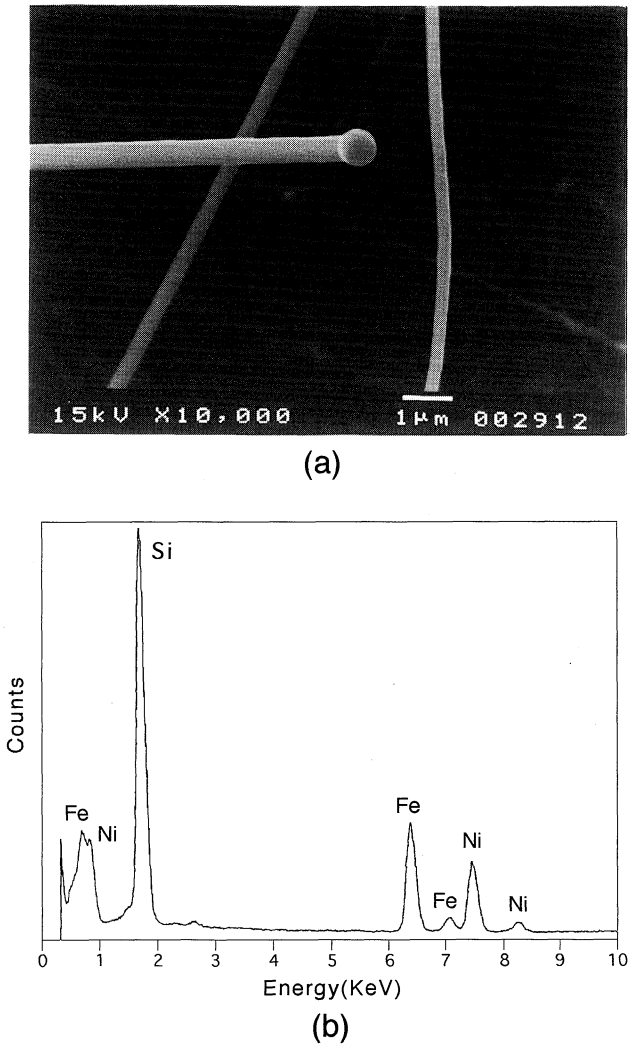

Fig. 2. SEM photograph of SiC whisker obtained by the heating at 1473 K for 1 h (a) and EDX spectrum of the spherical part of the whisker (b).

at 1020 cm^{-1} (CH_2 wagging of Si–CH_2–Si). The broad band around 3440 cm^{-1} resulted from a superposition of the vibration bands of the hydroxyl group of Si–OH and stretching vibrations of the adsorbed water molecules.

Up to 1373 K, the absorption spectra changed with a slight decrease in the ratio of the absorbance at 1045 cm^{-1} to that at 820 cm^{-1}. The absorption bands at 1045 and 460 cm^{-1} were not observed at all at 1473 K, or at higher temperatures, at which the whiskers grew noticeably.

The changes in these IR spectra were very similar to those of a heated PCS+MCF porous body (porous body C),[9] which involves nickel and iron as metal contaminants.

Figure 5 shows the IR spectra of heated porous body B. The changes in these IR spectra are very similar not only to those of the heated porous bodied C, but also to those of heated porous body A.

From these results, it is presumed that the pyrolyzing processes of PCS in these three porous bodies remarkably resemble each other.

XRD Measurement. Figure 6 shows the XRD patterns of porous body A heated at 1273 to 1623 K for 5 h. The broad diffraction peaks at $2\theta = 23.8$ and 43.6° [14] are due to MCF in the heated porous body. At 1373 K, three diffraction peaks at $2\theta = 35.7$, 60.1, and 71.9° are slightly observed besides the broad peaks due to MCF. These are the (111), (220), and (311) diffraction lines of β-SiC. At 1473 K, these three peaks are apparently observed and two new peaks at $2\theta = 33.7$ and 41.3° are observed. The former arises from stacking faults of β-SiC,[15] and the latter is the (200) diffraction line of β-SiC. The peak heights of these four peaks at $2\theta = 35.7$, 41.3, 60.1, and 71.9° increased with increasing the heating temperature above 1473 K, and a new peak at $2\theta = 75.6°$, which is the (222) diffraction line of β-SiC, was observed above 1573 K.

Figure 7 shows the XRD patterns of porous body B heated at 1273 to 1623 K for 5 h. No peaks due to SiC were observed at 1373 K, at which the (111), (220), and (311) diffraction lines of β-SiC were slightly observed on porous body A (Fig. 6(b)). However, three diffraction peaks at $2\theta = 35.7$, 60.1, and 71.9° were apparently observed at 1473 K. These were the (111), (220), and (311) diffraction lines of β-SiC. As shown in Fig. 3(a), whisker deposition, which resulted from the pyrolysis of PCS, was apparently observed above 1373 K. On the other hand, as shown in Figs. 3(d) and 3(e), only a few trace of nodules were observed at 1373 K, and nodule deposition was apparently observed above 1473 K. The above results of the XRD patterns of porous body B (Fig. 7) support these SEM observations. In addition, no whiskers, but nodules, were formed from porous body B (Fig. 3). It is thought that these nodules, resulted from the pyrolysis of PCS, were formed via the vapor–solid process, in which the liquid (L) was not concerned, because there was no catalyst in this body. Wagner and Doherty[16] have shown that VLS crystals can grow at supersaturations much smaller than those required for vapor–solid growth. Consequently, it is thought that the concentration of the gases containing Si and C, thought to be SiO and CO, was not enough to form nodules, but is enough to form whiskers at 1373 K. The peak heights of these three peaks due to a β-SiC increase with increasing the heating temperature above 1473 K. Furthermore, a new peak at $2\theta = 41.4°$, which is the (200) diffraction line of β-SiC, was observed at 1623 K.

Figure 8 shows the relationship between the heating temperature and the full width at half maximum (FWHM) of the (220) diffraction line of β-SiC for heated porous body A and heated porous body B. The FWHM of heated porous body A scarcely depends on the heating temperature, being ca. 0.4°. This result suggests that the whisker crystallinity is significantly high in spite of the heating temperature (1373 to 1623 K). On the other hand, the FWHM of heated porous body B decreased with increasing the heating temperature from 0.93 to 0.44°. This result suggests that the crystallinity of β-SiC increases with increasing the heating temperature.

Figure 9 shows the relationship between the heating temperature and the area of the (220) diffraction line of β-SiC for heated porous body A and heated porous body B. There exists a quantitative relation between the area of the (220) diffraction line of β-SiC and the amount of produced β-SiC.

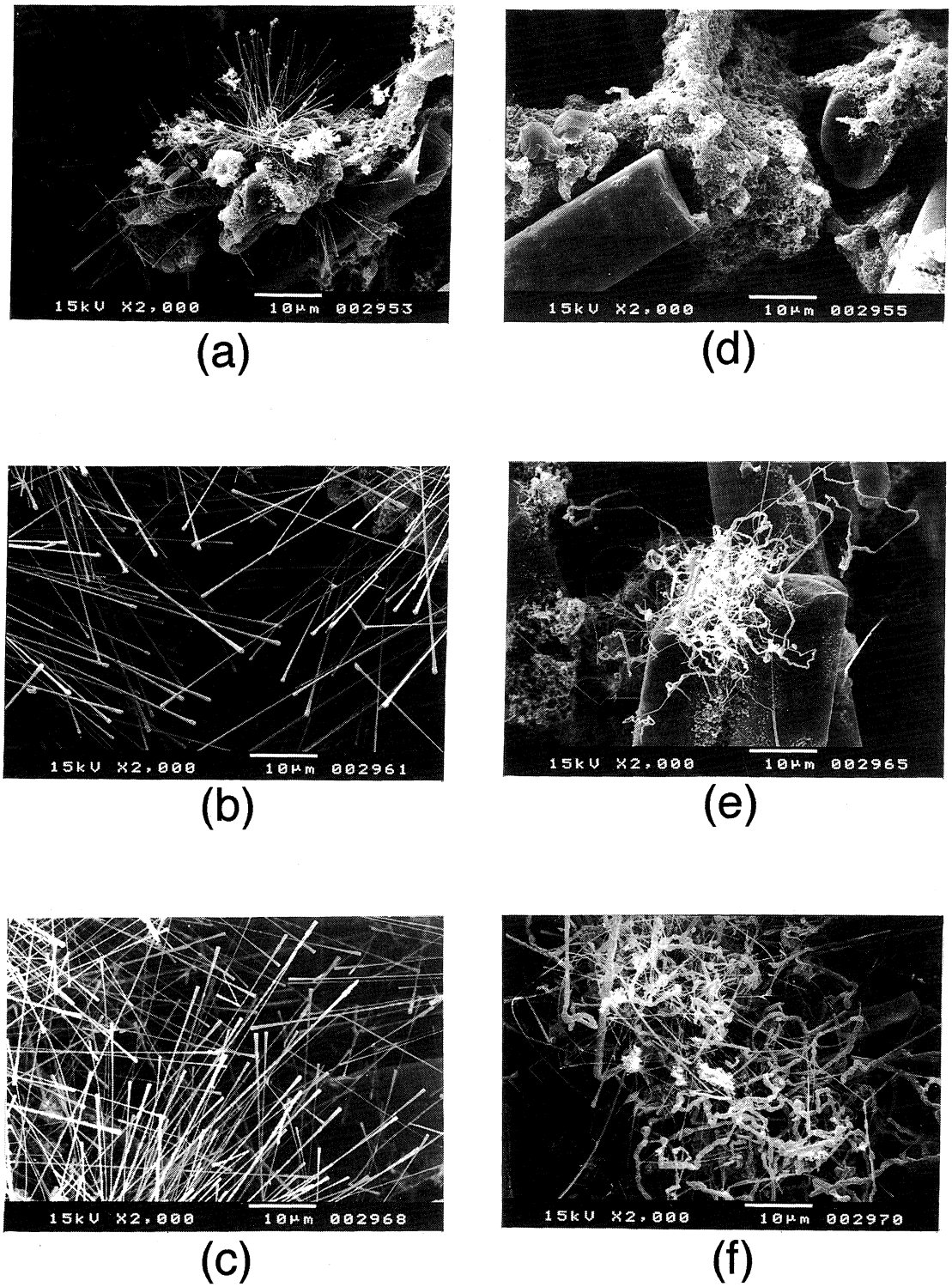

Fig. 3. SEM photographs of the heated porous body A at 1373 K (a), 1473 K (b), and 1573 K (c), and the heated porous body B at 1373 K (d), 1473 K (e), and 1573 K (f).

The area of the (220) diffraction line of β-SiC for heated porous body A at 1623 K was expressed as 100 a.u.. The area of the (220) diffraction line of β-SiC for heated porous body A increased approximately linearly with increasing the heating temperature. The area of the (220) diffraction line of β-SiC for heated porous body B at 1473 K is almost the same as that for heated porous body A. However, it becomes smaller than that for heated porous body A with increasing the heating temperature. This means that the amount of the product, namely β-SiC, for porous body B is smaller than that for porous body A. It is understood that, in the case of porous body A, the gases containing Si and C thought to be SiO and CO are efficiently consumed during the formation of β-SiC whiskers via the VLS process; however, in the case

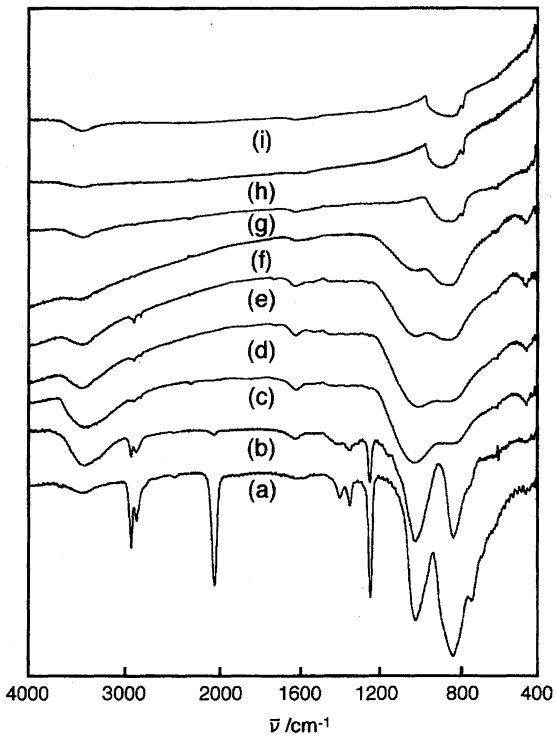

Fig. 4. IR spectra of PCS powder (a), porous body A preheated at 823 K for 5 h in N_2 (b), and porous body A heated at 873 K (c), 1073 K (d), 1273 K (e), 1373 K (f), 1473 K (g), 1573 K (h), and 1623 K (i) for 5 h in Ar.

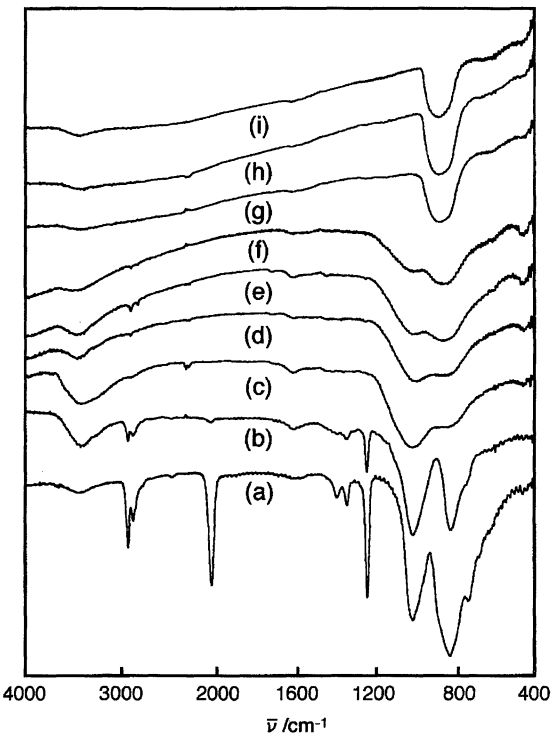

Fig. 5. IR spectra of PCS powder (a), porous body B preheated at 823 K for 5 h in N_2 (b), and porous body B heated at 873 K (c), 1073 K (d), 1273 K (e), 1373 K (f), 1473 K (g), 1573 K (h), and 1623 K (i) for 5 h in Ar.

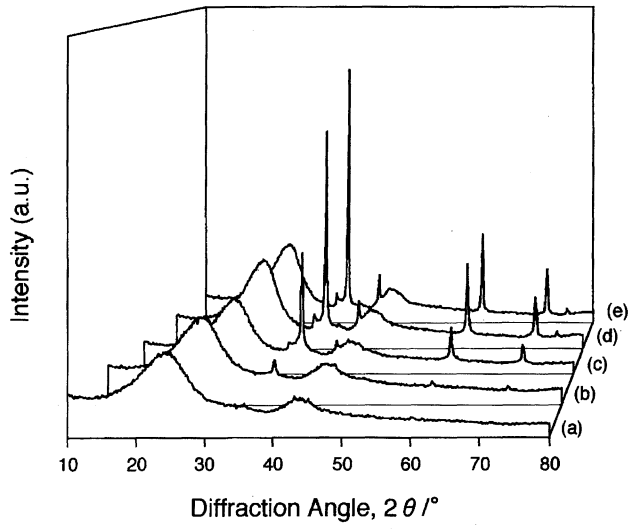

Fig. 6. XRD patterns of porous body A heated at 1273 K (a), 1373 K (b), 1473 K (c), 1573 K (d), and 1623 K (e) for 5 h in Ar.

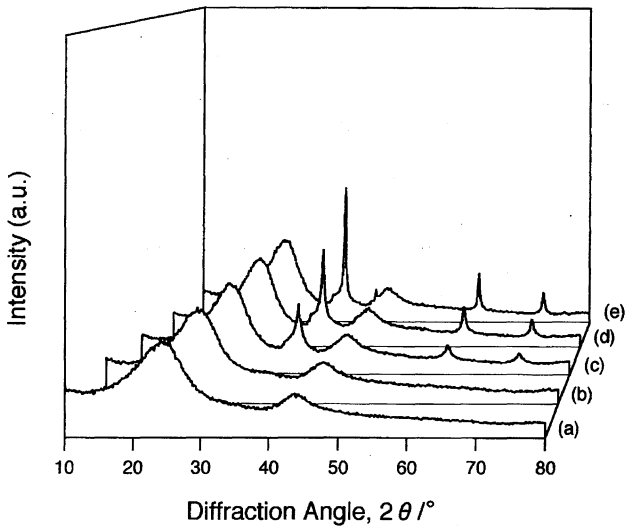

Fig. 7. XRD patterns of porous body B heated at 1273 K (a), 1373 K (b), 1473 K (c), 1573 K (d), and 1623 K (e) for 5 h in Ar.

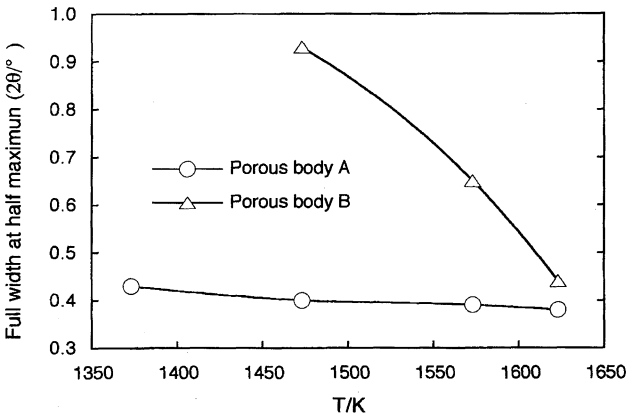

Fig. 8. Relationship between the heating temperature and the full width at half maximum of the (220) diffraction line of β-SiC for the heated porous body A and the heated porous body B.

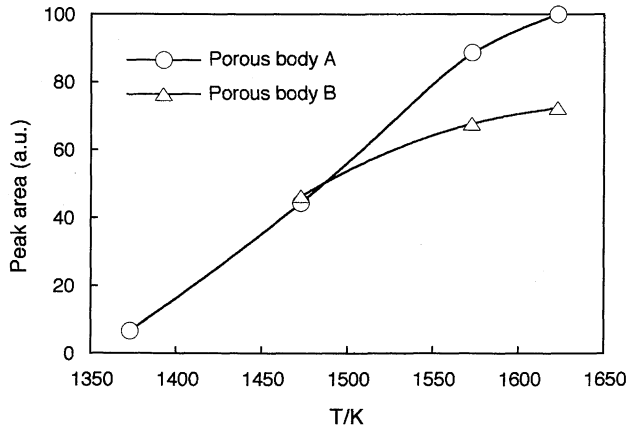

Fig. 9. Relationship between the heating temperature and the area of the (220) diffraction line of β-SiC for the heated porous body A and the heated porous body B.

of porous body B, the gases are exhausted from the furnace chamber, to some extent.

Evolution of Gas during Heating Process. Figure 10 shows gas-evolution curves of porous body A and porous body B at 1023 to 1673 K. The former shows a curve having the main peak at 1373 K with a shoulder at the lower temperature side of the main peak. The temperature of this main peak is in good agreement with that at which whiskers begin to be deposited. Consequently, it is thought that this main peak is caused by the evolution of gases containing Si and C thought to be SiO and CO. Porous body B also showed a curve having a peak at 1373 K. We previously reported[9] that porous body C showed a gas-evolution curve having a main peak at ca. 1373 K. As mentioned above, based on the changes in the IR spectra, it is presumed that the pyrolyzing process of PCS in these three kinds of porous bodies remarkably resemble each other. These results regarding gas evolution are considered to strongly support this presumption.

Silicon and Oxygen Contents of Products. Figure 11 shows the molar ratios of oxygen to silicon (SiO_x) of unheated PCS powder[9] and heated porous body A and heated porous body B at 823 to 1573 K. The value of the (SiO_x)

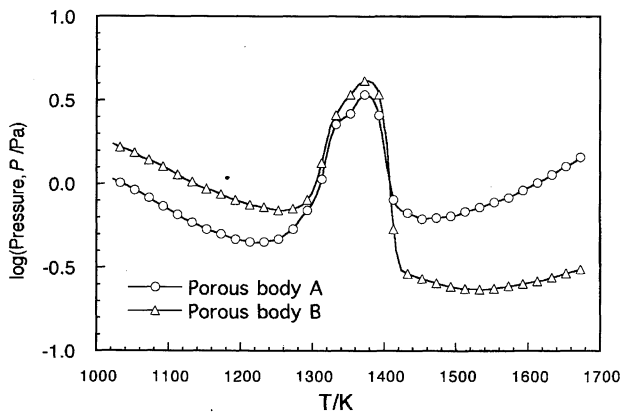

Fig. 10. Gas evolution curves of the porous body A and the porous body B in the heating at 1023 to 1673 K.

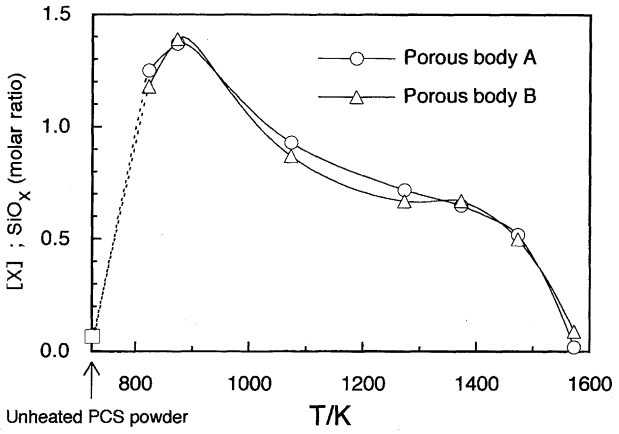

Fig. 11. Molar ratios (SiO_x) of PCS powder, porous body A pre-heated at 823 K for 5 h in N_2 and heated at 873 to 1573 K for 5 h in Ar and porous body B pre-heated at 823 K for 5 h in N_2 and heated at 873 to 1573 K for 5 h in Ar.

ratio at each heating temperature in these two porous bodies was almost the same as each other.

First, the changes in the (SiO_x) ratio up to 873 K are discussed. Both porous bodies, pre-heated at 823 K in N_2 and heated at 873 K in Ar, have a (SiO_x) ratio roughly represented by $SiO_{1.2}$ and $SiO_{1.4}$, respectively. This suggests a remarkable oxidation of PCS in both porous bodies. The oxygen atoms in both porous bodies are derived not only from small quantities of oxygen present in the furnace, but also from TMPT and SSO, organic components in the porous bodies.[9] As shown in Figs. 4 and 5, at 823 K, the broad IR absorption band is observed at 3440 cm^{-1}, and the band at 2100 cm^{-1} (Si–H stretching vibration) has remarkably decreased, no band being observed at 460 cm^{-1}. From these results, it seems that the bond form of oxygen was ≡Si–O–H. However, at 873 K, an absorption band at 460 cm^{-1} corresponding to O–Si–O deformation vibration was observed. Therefore, it is inferred that PCS is cross-linked by oxygen atoms by the following reactions:

$$\equiv Si\text{–}O\text{–}H + CH_3\text{–}Si\equiv \longrightarrow \equiv Si\text{–}O\text{–}Si\equiv + CH_4 \quad (1)$$

$$2\equiv Si\text{–}O\text{–}H \longrightarrow \equiv Si\text{–}O\text{–}Si\equiv + H_2O \quad (2)$$

Okamura et al.[17] reported on the formation of silicon nitride fibers and silicon oxynitride fibers from PCS fibers cured by electron irradiation and by oxidation, respectively. In their literature, the chemical structure of PCS by oxidation curing was illustrated. Figure 12 shows a chemical-structure model of PCS in both porous bodies pre-heated at 823 K and heated at 873 K with reference to the model proposed by them.

Next, the changes in the (SiO_x) ratio above 873 K are discussed. The (SiO_x) ratio gradually decreased with increasing the heating temperature up to 1373 K, while it drastically decreased above 1473 K. This agrees with the IR spectra changes; no band was observed at 460 cm^{-1} corresponding to O–Si–O deformation vibration above 1473 K. Moreover, as shown in Figs. 3, 6, and 7, whiskers or noodle-like products were drastically deposited and XRD peaks due to β-

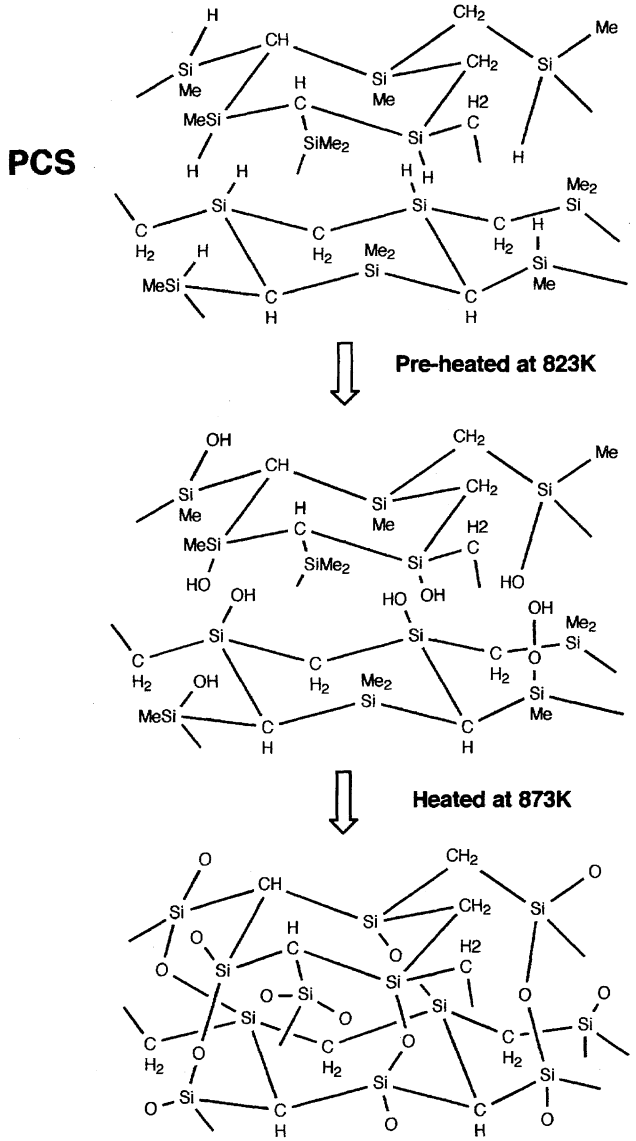

Fig. 12. Chemical structure model of PCS in porous bodies pre-heated at 823 K and heated at 873 K.

SiC were apparently observed above 1473 K. From these results, it seems that the formation of whiskers or noodle-like products is analogous to a silica-carbothermal reduction. However, it is not known at this stage whether the C in the silica–carbothermal reduction was derived from the PCS or from the MCF.

Conclusions

The SiC whisker-formation process from PCS with $NiFe_2O_4$ as a catalyst was investigated, and the following results were obtained:

(1) β-SiC whiskers were obtained with $NiFe_2O_4$ as a catalyst, while noodle-like SiC was obtained without $NiFe_2O_4$.

(2) The formation of the SiC whiskers with $NiFe_2O_4$ as a catalyst proceeded via the VLS process.

(3) The pyrolyizing process of PCS for the formation of SiC whiskers with $NiFe_2O_4$ as a catalyst was much the same as that of noodle-like SiC without a catalyst.

(4) SiC whiskers grew with a high degree of crystallinity at the beginning of their formation, while the crystallinity of noodle-like SiC increased with increasing the heating temperature.

(5) The formation of SiC whiskers with $NiFe_2O_4$ as a catalyst was analogous to a silica-carbothermal reduction, because Si–O bonds in the porous body were depleted as the SiC whiskers grew.

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