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Ceramization process of polyvinylsilane as a precursor for SiC-based material

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A SiC-based material was synthesized from polyvinylsilane (PVS) by pyrolysis at 1400 K in Ar gas atmosphere. In the ceramization process of PVS, several kinds of gases such as hydrogen, silanes, and hydrocarbons were evolved in the temperature range from 500 to 800 K. The total ceramic yield from PVS was about 36%. PVS was heat-treated using several temperature programmes by reflux heat treatment with a view to increase the ceramic yield. The total ceramic yield increased to 59% by the reflux heat treatment at 600 K. The apparent SiC crystallite size and the atomic ratio of carbon to silicon (C/Si) of the SiC-based material obtained by pyrolysis at 1400 K were almost the same for the PVS reflux-treated and the PVS not heat-treated; an apparent SiC crystallite size of about 2.4 nm, and C/Si of about 1.5. © *2003 Kluwer Academic Publishers*

1. Introduction

Silicon carbide (SiC), which has high strength and good thermal resistance, is one of the most promising candidates as a high temperature structural material in the fields of aerospace and fusion reactor. However, it is too difficult to mold parts with complex shape, because the SiC is non-sinterable ceramics.

Yajima *et al.* developed a pioneering technique for Si—C fiber synthesis, that is, the Si—C fiber was synthesized from polycarbosilane (PCS) [1]. Adopting an organosilicon polymer as a starting material, mold parts with desirable shape can be achieved easily. Starting with Yajima's proposal, many researchers have studied about synthesis of novel polymers for SiC-based material and their ceramization processes, and about synthesis of fibers, films, and so on [2–8].

In the synthesis process of SiC-based material from organosilicon polymers, the ceramic yield and volume shrinkage are very important parameters for material designing. In order to synthesize SiC-based material in high yield, it is necessary to promote crosslinking of polymers in the pyrolysis process. Therefore, introduction of reactive double bond or Si—H bond is examined in the polymer synthesis [9–11].

Polyvinylsilane (PVS) was synthesized by Itoh *et al.* [12]. The backbone of PVS is constituted by Si—C bonds. The PVS does not contain double bond in the structure, but contains rich Si—H bond. This polymer is liquid at ambient temperature and has high formability, so that it is a very attractive polymer as a precursor for SiC-based material. PVS has already been studied as a precursor for a matrix material of ceramic matrix composite (CMC) [13]. On the other hand, we have studied synthesis of Si—C fibers from a polymer blend of PVS and PCS, and a very fine Si—C fiber with average diameter of 6 μm has been obtained [14, 15]. As mentioned above, PVS is a very useful polymer to synthesize a high performance SiC-based material. However, the ceramization process of the PVS has not been investigated. In this paper, the ceramization process of the PVS was investigated by thermogravimetric analysis, gas chromatography, and so on.

By the way, Iseki *et al.* have reported that the ceramic yield from polymethylsilane was increased by reflux heat treatment [16, 17]. The reflux heat treatment is a method where volatile components generated during heat treatment under an inert gas atmosphere are forced to return into the system and to react with the polymer again by reflux. In this paper, reflux heat treatment of the PVS was also examined with a view to increase the ceramic yield.

2. Experimental procedure

2.1. Material

Polyvinylsilane (PVS), supplied by Mitsui Chemicals, Inc., is synthesized by radical polymerization of

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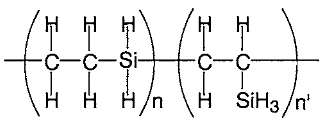


$$-\!\left(CH_2-CH_2-SiH_2\right)_n\!-\!\left(CH_2-CH(SiH_3)\right)_{n'}\!-$$

Figure 1 Chemical formula of polyvinylsilane.

vinylsilane ($CH_2{=}CHSiH_3$) in an autoclave using azobis(isobutyronitrile). It is a viscous liquid polymer with a weight average molecular weight (M_w) of 2.8×10^3, a number average molecular weight (M_n) of 9.6×10^2, and polydispersity (M_w/M_n) of 2.90 [12]. The chemical formula of PVS is shown in Fig. 1. The unit ratio of n/n' is almost 1.

2.2. Heat treatment of PVS

PVS was heat-treated in the temperature range 500–700 K for 2 h under Ar gas atmosphere. The heat treatment was conducted in two ways. One is the heat treatment in open system, and the other the reflux heat treatment. In the case of the reflux heat treatment, the volatile components are cooled and returned into the system by a condenser set at low temperature range of the furnace. The details about reflux heat treatment have been described by Iseki *et al.* [17]. The PVS heat-treated was pyrolyzed at 1400 K for 2 h in Ar to obtain SiC-based material.

2.3. Measurements and analyses

Thermogravimetric analysis (TGA) of PVS was conducted. PVS was heated to 1400 K at a heating rate of 60 K/h in Ar gas atmosphere, and change of mass during heating was measured using an electronic balance (FM-MARK II, A&D).

PVS was heated from room temperature to 500 K at a heating rate of 60 K/h under vacuum, and held at 500 K for 2 h. The gases evolved during heat treatment were analyzed by gas chromatography (G-5000, Hitachi). After analysis, the specimen was heated again to the temperature of 600 K, 100 K higher than the previous temperature (500 K) with a heating rate of 60 K/h under vacuum, and held for 2 h. The gases evolved during heat treatment were analyzed again. This process was repeated up to the temperature of 1400 K.

The evolved gases were identified by gas chromatography/mass spectrography (GC/MS). In this case, PVS was heated to 800 K with a heating rate of 60 K/h under vacuum, and held at 800 K for 2 h. Evolved gases were analyzed by GCMS-Q5050 (Shimadzu).

Fourier-transform infrared (FT-IR) spectra of the PVS after heat treatments were recorded by KBr method (FT-IR1650, Perkin Elmer).

The crystallized phases existing in the PVS pyrolyzed at 1400 K were identified with an X-ray diffractometer (RINT1100, Rigaku). Then, the apparent SiC crystallite size, d_{111}, was calculated from the width at half peak height of the (111) peak of β-SiC by employing the Scherrer formula.

The contents of silicon and carbon in the PVS pyrolyzed at 1400 K were measured by elemental analysis.

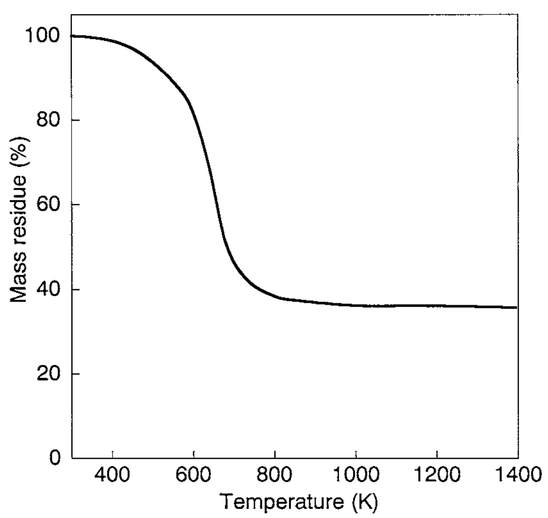


Figure 2 TGA curve of as-received PVS under Ar gas atmosphere.

3. Results and discussion

3.1. Ceramization process of PVS

Fig. 2 shows the TGA curve of as-received PVS from room temperature to 1400 K in Ar. The mass decreases by about 60% in the temperature range from 500 to 800 K. Above 800 K, mass decrease becomes slight, and the mass residue at 1400 K is about 36% of the starting value. The large mass loss in the temperature range from 500 to 800 K is caused by gas evolution, so the evolved gases from PVS by heat treatment were analyzed.

Fig. 3a shows the gas evolution of hydrogen (H_2), silanes, and hydrocarbons from the as-received PVS. The H_2 evolves above 500 K, having a peak at 700 K, and is detected even at 1400 K. The H_2 gas evolution can be divided into three regions, shown as broken lines. In the lowest temperature range (500–800 K), H_2 evolves mainly due to the scission of Si—H bonds because the covalent bond energy of Si—H (318.0 kJ/mol) is lower than that of C—H (410.5 kJ/mol) [18]. In the middle temperature range (800–1000 K), scission of C—H bonds occurs predominantly. In the higher temperature range (above 1000 K), Si—C bonds are formed, and steric hindrance occurs in the structure by formation of 3-dimensional network. The C—H bonds remaining in the structure are broken by heat treatment at high temperature, and then H_2 evolves. Such behavior of H_2 gas evolution has been reported for polycarbosilane which is a typical organosilicon polymer for SiC-based material [19]. The H_2 gas evolution in Fig. 3a indicates that the PVS is not converted into ceramics completely at the temperature of 1400 K.

So far, it has been difficult to identify the gaseous silanes by the gas chromatography, however, we had identified them by using GC/MS in this work. The gaseous silanes evolve in the temperature range from 500 to 900 K, and consisted of silane (SiH_4), methylsilane (CH_3SiH_3), dimethylsilane ($(CH_3)_2SiH_2$), ethylsilane ($C_2H_5SiH_3$), and $R1R2SiH_2$ ($R1 + R2 = C_4$) (Fig. 3b). This evolution of gaseous silanes causes the large mass loss in the temperature range from 500 to 800 K shown in Fig. 2. The gaseous hydrocarbons evolve in the temperature range from 500 to 1300 K

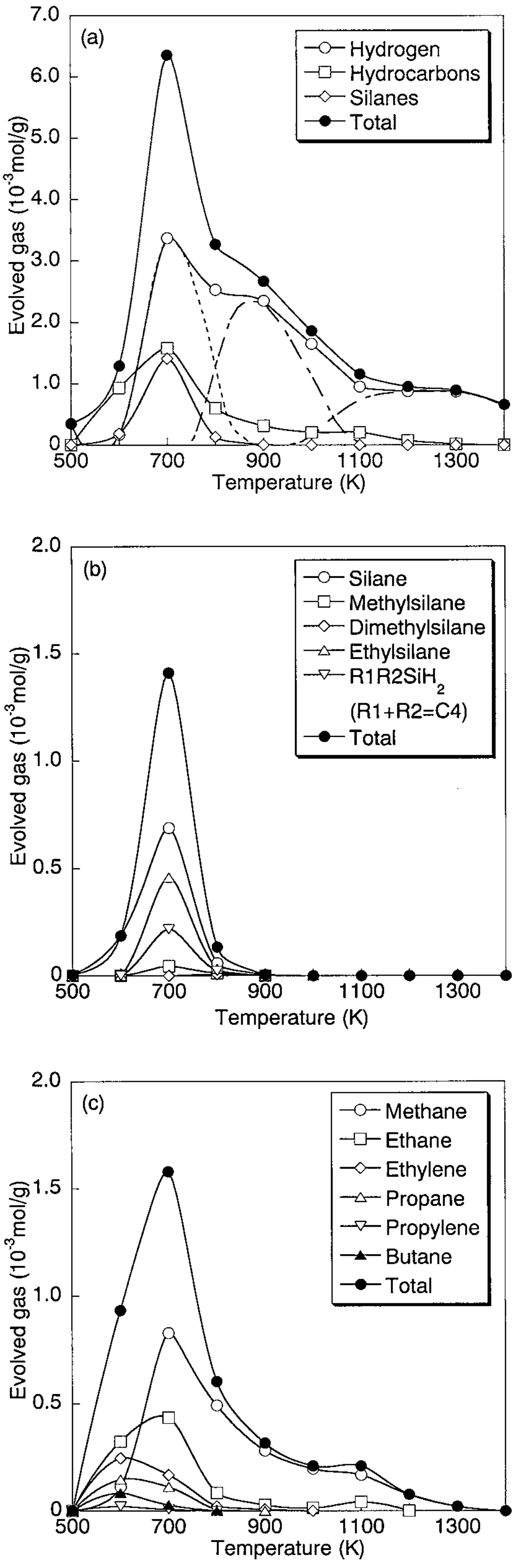


Figure 3 Gas evolution from as-received PVS during heat treatment: (a) hydrogen, total silanes, and total hydrocarbons, (b) silanes, and (c) hydrocarbons.

(Fig. 3c). The major gas is methane (CH_4), and minor gases are ethane (C_2H_6), ethylene (C_2H_4), propane (C_3H_8), propylene (C_3H_6), and butane (C_4H_{10}).

The mechanisms of gas evolution of silanes and hydrocarbons are considered as following reactions. The silyl radical ($\cdot SiH_3$) is produced by scission of $-SiH_3$ side group. The methyl radical ($\cdot CH_3$) is produced by scission of end group or decomposition of ethane. The ethyl radical ($\cdot C_2H_5$) is also produced by scission of end group same as the methyl radical.

$$\cdot SiH_3 + \cdot H \rightarrow SiH_4$$

$$\cdot SiH_3 + \cdot CH_3 \rightarrow CH_3SiH_3$$

$$\cdot SiH_3 + \cdot C_2H_5 \rightarrow C_2H_5SiH_3$$

$$\cdot C_1 + \cdot SiH_3 \rightarrow C_1SiH_3 + \cdot C_3 \rightarrow C_4SiH_2 + \cdot H$$

$$\cdot C_2 + \cdot SiH_3 \rightarrow C_2SiH_3 + \cdot C_2 \rightarrow C_4SiH_2 + \cdot H$$

$$\cdot CH_3 + \cdot H \rightarrow CH_4$$

$$\cdot C_2H_5 + \cdot H \rightarrow C_2H_6$$

$$:CH_2 + :CH_2 \rightarrow C_2H_4$$

$$C_2H_4 + :CH_2 \rightarrow C_3H_6$$

$$\cdot C_2H_5 + \cdot CH_3 \rightarrow C_3H_8$$

$$\cdot C_2H_5 + \cdot C_2H_5 \rightarrow C_4H_{10}$$

As mentioned above, the as-received PVS is converted into ceramics with a yield of about 36%, evolving gases of H_2, silanes, and hydrocarbons in the temperature range from 500 to 800 K.

3.2. Reflux heat treatment of PVS

PVS was reflux heat-treated before the pyrolysis with intension to increase the ceramic yield. Fig. 4a shows TGA curves of PVS reflux heat-treated at appointed temperatures. For comparison, TGA curves of PVS heat-treated in the open system are shown in Fig. 4b. For the reflux heat-treated PVS, the onset temperature of large mass loss shifts to higher temperature at the treatment temperature above 550 K, and the mass residue at 1400 K increases drastically. At the treatment temperature of 700 K, the mass residue at 1400 K increases to about 91%. On the other hand, in the case of the heat treatment in the open system, the mass residue increases drastically at the treatment temperature above 650 K. And the mass residue at 1400 K is about 84% at the treatment temperature of 700 K.

The TGA curves in Fig. 4 do not reflect the polymer recovery after the heat treatment. When the PVS is heat-treated above 500 K, the mass decreases due to the evolution of gases and volatile components as shown in Figs 2 and 3. Table I shows the polymer recovery after heat treatment and total ceramic yield after pyrolysis at 1400 K. The polymer recovery decreases on increasing the treatment temperature in both cases. However, in the case of the reflux heat treatment, the polymer recovery and the total ceramic yield are higher than that for heat treatment in the open system. The total ceramic yield from PVS reflux heat-treated above 550 K is more than 50%, and it reaches the maximum of 59% at the treatment temperature of 600 K. However, the total ceramic yield from PVS reflux heat-treated above 650 K becomes low. This is because the amount of the components which come out of the system is more than the amount of the components which return into the system in case of the reflux heat treatment above 650 K.

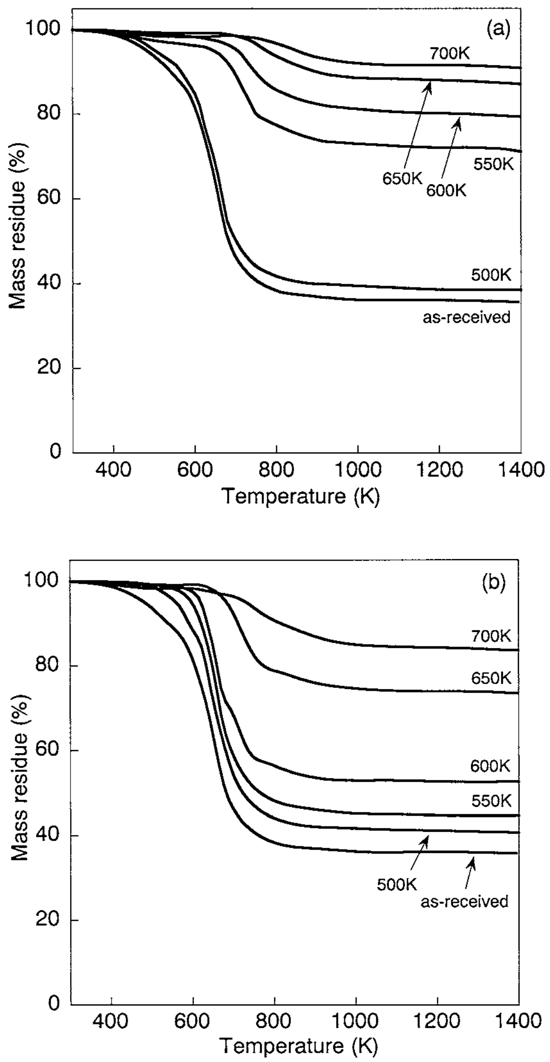


Figure 4 TGA curves of heat-treated PVS under Ar gas atmosphere: (a) reflux heat treatment and (b) heat treatment in the open system.

According to this result, it is clear that the most suitable temperature for the reflux heat treatment of PVS is 600 K.

As mentioned above, the reflux heat treatment leads to an increase in the ceramic yield. This is caused by the volatile components returned into the system which react with the PVS again, as discussed below.

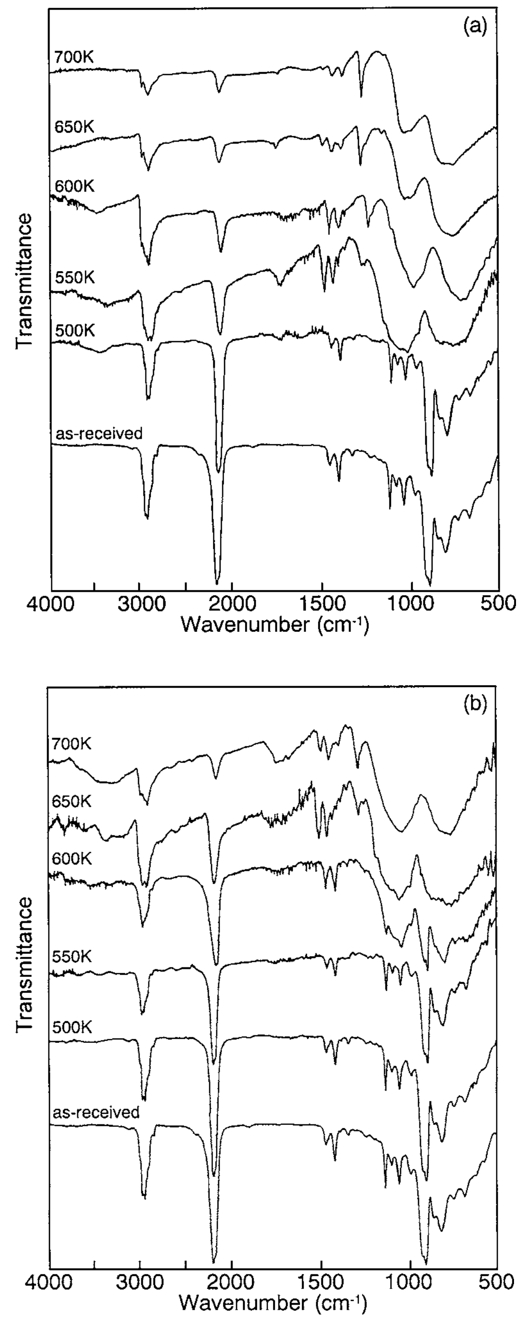


Figure 5 FT-IR spectra of PVS after heat treatment: (a) reflux heat treatment and (b) heat treatment in the open system.

Fig. 5 shows change of FT-IR spectra of PVS after reflux heat treatment and heat treatment in the open system. For the as-received PVS, peaks assigned to C—H stretching (2950, 2900 cm^{-1}), Si—H stretching (2100 cm^{-1}), Si—H stretching in Si—H_2 and/or Si—H_3 (2145 cm^{-1}), C—H deformation (1460, 1410 cm^{-1}), CH_2 deformation in Si—CH_2—CH_2—Si (1130 cm^{-1}), CH_2 deformation in Si—CH_2—Si (1020 cm^{-1}), Si—H deformation in Si—H_2 (940, 867 cm^{-1}), Si—H deformation in Si—H_3 (945, 837 cm^{-1}) are shown. In the case of the reflux heat treatment above 550 K, the

TABLE I Polymer recovery after heat treatment and total ceramic yield after pyrolysis at 1400 K

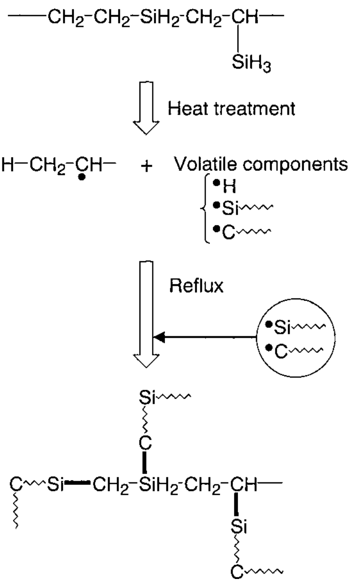
	Reflux heat treatment (%)			Heat treatment in the open system (%)		
Treatment temperature (K)	Polymer recovery	Mass residue from TGA	Total ceramic yield	Polymer recovery	Mass residue from TGA	Total ceramic yield
500	100	39	39	90	41	37
550	78	71	56	81	45	36
600	74	80	59	68	53	36
650	65	87	57	47	78	37
700	58	91	53	40	84	33

TABLE II Apparent crystallite size and chemical composition of PVS after pyrolysis at 1400 K

	Treatment temperature (K)	Crystallite size (nm)	Chemical composition (wt%)			C/Si (atomic ratio)
			C	Si	Other	
Reflux heat treatment	500	2.44	39.2	59.5	1.3	1.54
	550	2.48	38.0	58.0	4.0	1.53
	600	2.34	38.2	58.0	3.7	1.54
	650	2.43	37.9	57.7	4.4	1.54
	700	2.48	36.7	55.9	7.3	1.54
Heat treatment in the open system	500	2.43	36.9	59.0	4.1	1.46
	550	2.47	38.3	58.9	2.8	1.52
	600	2.46	38.8	60.2	0.9	1.51
	650	2.40	38.2	58.7	3.2	1.52
	700	2.36	38.1	57.1	4.8	1.56
Without heat treatment	–	2.42	37.4	59.5	3.2	1.47

peaks assigned to Si—H bond (2100, 945, 940, 867, and 837 cm^{-1}) decrease. And two broad peaks due to CH_2 deformation in Si—CH_2—CH_2—Si and Si—CH_2—Si (around 1100–1000 cm^{-1}) and due to Si—C stretching (around 800 cm^{-1}) become remarkable (Fig. 5a). Such broad peaks at around 1100–1000 cm^{-1} and 800 cm^{-1} indicate that the surroundings of —CH_2 and Si—C are complex.

When the PVS is heat-treated above 550 K, H radicals, Si radicals, and C radicals are produced as volatile components by scission of bonds, and gases such as H_2, silanes, and hydrocarbons evolve, as shown in Fig. 3. However, some parts of radicals which do not contribute to the gas evolution are forced to return into the system by reflux, and they are considered to react with the PVS to form the Si—C network (Scheme 1).



Scheme 1 Scheme of reflux heat treatment of PVS.

In the case of the heat treatment in the open system, two broad peaks due to formation of Si—C bonds at around 1100–1000 cm^{-1} and 800 cm^{-1}, become remarkable at the treatment temperature above 650 K (Fig. 5b). This suggests that the Si—C network is formed at lower temperature (above 550 K) by the reflux heat treatment than by heat treatment in the open system (above 650 K).

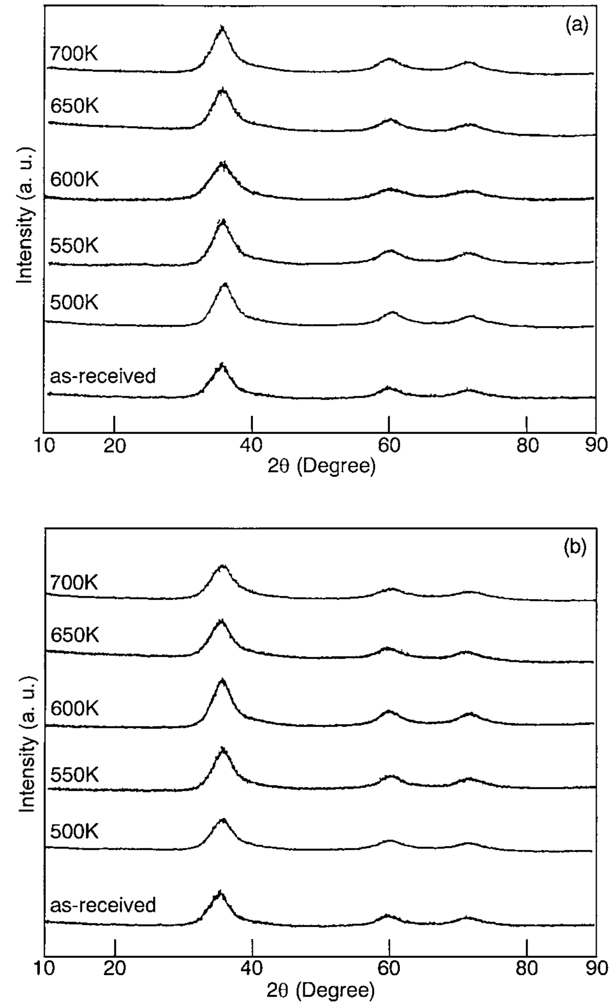


Figure 6 XRD patterns of PVS pyrolyzed at 1400 K in Ar: (a) reflux heat treatment and (b) heat treatment in the open system.

Fig. 6 shows XRD patterns of PVS pyrolyzed at 1400 K in Ar after reflux heat treatment and heat treatment in the open system. All XRD patterns show three broad peaks at 2θ = about 35.6, about 60.0, and about 71.8° assigned to (111), (220), and (311) of β-SiC, respectively [20]. The apparent SiC crystallite size of each specimen estimated by using Scherrer formula and the atomic ratio of carbon to silicon (C/Si) estimated by elemental analysis are summarized in Table II. Whatever the heat treatment, the apparent crystallite size and the C/Si ratio of the pyrolyzed PVS are almost the same as those for pyrolyzed PVS without heat treatment; the apparent SiC crystallite size is about 2.4 nm, and C/Si about 1.5. This result means that crystallite size and composition of the SiC-based material obtained from PVS do not depend on heat treatment mode.

4. Conclusions

In this paper, the ceramization process of polyvinylsilane (PVS) from polymer to ceramics was investigated and PVS was reflux heat-treated with a view intension to increase the ceramic yield. The following concluding remarks can be formulated.

(1) As-received PVS is converted into SiC-based material with a yield of about 36%, with an evolution of H_2, silanes, and hydrocarbons in the temperature range from 500 to 800 K. There is still the evolution of H_2 at 1400 K, which means the PVS need to be pyrolyzed at higher temperature to convert into ceramics completely.

(2) The reflux heat treatment promotes formation of Si—C network comparing with the heat treatment in the open system. The most suitable temperature for the reflux heat treatment of PVS is 600 K, the total ceramic yield increasing to a maximum of 59%.

(3) Whatever the heat treatment, the apparent SiC crystallite size and the C/Si atomic ratio of the pyrolyzed PVS are almost the same as those of pyrolyzed PVS without heat treatment; the apparent SiC crystallite size being of about 2.4 nm, and C/Si of about 1.5.

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