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Swelling of radiation-cured polymer precursor powder for silicon carbide by pyrolysis

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Akinori Takeyama *, Akira Idesaki, Masaki Sugimoto, Masahito Yoshikawa

Quantum Beam Science Directorate, Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma, 370-1292, Japan

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ABSTRACT

Ceramic yield, density, volume change and pore size distribution were measured for radiation- and thermally cured PCS powder when they were pyrolyzed in the temperature range of 673–973 K. Higher ceramic yield was obtained for radiation-cured powder due to smaller amount of evolved gas. Temperature dependence of volume change and the total pore volume show that the formation and disappearance of pores in the powders were determined by the volume shrinkage and evolution of decomposed gases. Volume shrinkage narrowed the pore size distribution for radiation-cured powder. For thermally cured powder, the narrowing of size distribution was disturbed by aggregated pores. Smaller amount of evolved gas from radiation-cured powder relative to thermally cured powder prevented the aggregation of pores and provided the narrow size distribution.

1. Introduction

High oxidation resistance and thermal stability of polymer derived silicon carbide (SiC) made it a promising material for hydrogen separation membranes used in high temperature conditions [1–7]. The conversion of polymer precursor, polycarbosilane (PCS), into SiC by pyrolysis is accompanied by evolution of decomposed gas and volume shrinkage/expansion of PCS. If one prepares SiC gas separation membrane from a PCS film, shrinkage of the film by the conversion should be suppressed as small as possible, since it easily caused formation of large pores in the film, called as pinholes. Pinholes induce undesirable diffusion of gases through the membrane, which lowered the selectivity. Numbers and diameter of pinholes formed in prepared SiC membrane are affected by preparation methods. The membrane prepared from PCS film cured by conventional thermal oxidation curing method includes somewhat larger pores than kinetic diameter of H_2 molecule (0.289 nm), which act as pinholes for diffusion of larger molecules, such as N_2 (0.36 nm), while using electron-beam curing method, pinholes formation was suppressed [6].

So far, the conversion of PCS to SiC was studied from the viewpoint of evolution behavior of decomposed gases [8], chemical structure [9,10], increase/decrease of density and evolution of pore volume or size distribution [11]. When the thermally cured PCS was converted into SiC, micropore volume of thermally cured PCS powder increased with increasing the pyrolysis temperature from 573 to 823 K. With further increasing the temperature from 823 to 923 K, micropore volume was decreased. Other researchers [12] also showed micropores formation in thermally cured PCS powder by the pyrolysis. The diameter of micropore formed in the powder after the pyrolysis was slightly larger than 0.6 nm. Uniform sized micropores were reported due to prevention of aggregation of micropores.

The pore formation behavior of PCS during the conversion closely related to gas permeation properties of SiC membrane; however, no study about the pore formation behavior of PCS cured by electron-beam irradiation is found. In this report, structural evolution and pore formation behavior were investigated for radiation- or thermally cured PCS powder when they were pyrolyzed. Comparing the former with the latter, the pore formation behavior is clarified.

2. Experimental

Polycarbosilane (PCS Type A, Nippon Carbon Co. Ltd) powder was a starting material. The size distribution was measured by analyzing the microscopic image of the powder using NIH Image-J.

* Corresponding author. Tel.: +81 27 346 9501; fax: +81 27 346 9687.
E-mail address: takeyama.akinori@jaea.go.jp (A. Takeyama).

The average diameter of the powder was 4 micrometer. For electron beam curing, the powder was put on a cupper plate cooled by water and irradiated by electron beam in helium. Helium was used to prevent oxidation of radicals formed in irradiated PCS [6,8]. Electron beam energy and total dose were 2 MeV and 12 MGy. Irradiated powder was annealed at 673 K to kill radicals formed in PCS for handling the powder in air, which were very reactive species and easily oxidized. Annealed powders were weighed, and subsequently placed in quartz tube for pyrolysis at several temperatures of 723, 773, 823, 873, 973 K for 30 min in argon. Prior to pyrolysis, quartz tube was evacuated and the pressure inside the tube reached below 0.5 Pa. Argon flow rate was approximately 1×10^{-4} m^3/min. Purity of Ar was more than 99.995%. Concentration of residual oxygen in the firing atmosphere was lower than detectable limit of gas chromatograph Shimadzu GC-8A, 10 ppm. To date, we successfully prepared numbers of SiC membranes with required gas permeation properties for hydrogen separation following this pyrolysis process [5,6]. It indicates that the feature of the pore size distribution of prepared membrane was not temporarily changed by the concentration of residual oxygen in the tube. Similarly, we think both the feature of the pore size distribution in cured PCS powder and pore formation behavior were not affected by residual oxygen.

For thermal curing, PCS powder was oxidized by annealing in air at 473 K for 1 h. Weighed thermally cured powder was pyrolyzed following the above procedure. Hereafter, the PCS powders cured by either electron beam irradiation or thermal oxidation were named as radiation- or thermally cured powder. After pyrolysis, radiation- and thermally cured powders were weighed again to calculate the weight change before/after the pyrolysis. Separately, the weight of raw PCS powder was measured to obtain weight change before/after curing.

Densities of those powders were measured by Archimedes method. We note that obtained density using Archimedes method often might be the apparent density. It allows us to calculate apparent volume change rather than real volume change of powders, which is obtained by picnometry. Apparent volume change reflects changes of total pore volume and pore size distribution in addition to real volume change. On the other hand, real volume change has little relation with changes of pore volume and size distribution. Hence, measurement of the apparent density rather than the real density was adopted for understanding the pore formation behavior.

Volume change (apparent volume change) defined as a ratio of pyrolyzed to non-pyrolyzed powder's volume was calculated from the weight change and density. Fourier transform infrared spectroscopy (FT-IR, Horiba FT-710) in attenuated total reflectance (ATR) mode was employed to observe crosslinking of PCS. Nitrogen adsorption isotherm was measured at 77 K to obtain total pore volume and micropore size distribution of these powders. Total pore volume means total volume of pores whose diameter is less than about 60 nm. Micropore size distribution was calculated from adsorption isotherm following t-plot method [13].

3. Results and discussion

Ceramic yield, the weight change of pyrolyzed PCS powder, is shown in Fig. 1. Note that ceramic yield of 1 corresponds with as-cured powders, so as to compare easily the weight change of powders. At 673 K, radiation-cured powder lost the weight of about 0.5% relative to raw PCS powder. While thermally cured powder gained the weight approximately 10% relative to the raw powder, as oxygen was incorporated into PCS polymer network by curing, for radiation-cured powder, the slope of the ceramic yield curve gently decreased until 823 K. Major decomposed gases of hydrogen (H$_2$) and methane (CH$_4$) were gradually evolved from PCS powder
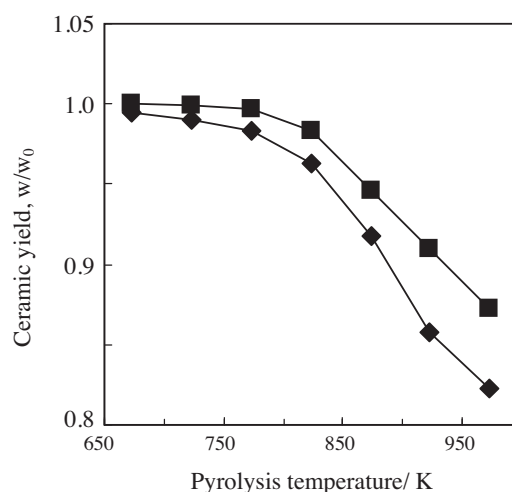

Fig. 1. Ceramic yield of radiation- and thermally cured PCS powders pyrolyzed in argon. Ceramic yield is the weight ratio of pyrolyzed powder to non-pyrolyzed powder. At 673 K, ceramic yield of 1 is plotted for non-pyrolyzed powder. (■) radiation-cured powder, (♦) thermally cured powder.

in this temperature range [8]. As the temperature was raised from 823 to 873 K, the slope became steep by increased amount of H$_2$ and CH$_4$. Nearly the same amount of H$_2$ as CH$_4$ was evolved in this range. For thermally cured powder, at 673 K, the ceramic yield was slightly lower than 1 as water (H$_2$O) was evolved. H$_2$O was evolved as a result of decomposition of hydroxyl groups formed by thermally curing. With increasing the temperature, the slope of the curve became steeper than that for the radiation-cured powder. H$_2$ and CH$_4$ were mainly evolved in the temperature range below 800 K. With increasing the temperature over 800 K, CH$_4$ was predominantly evolved. As shown in Fig. 1, larger amount of gases evolved from thermally cured powder caused lower ceramic yield. The fact that evolution of larger amount of gases from thermally cured powder coincides with gas evolution behavior [8].

Fig. 2 (a) and (b) shows the density and calculated volume change of pyrolyzed powders. Note that the volume change of 1 corresponds with that for raw PCS powder. In Fig. 2(a), the density of radiation-cured powder was decreased with increasing the temperature up to 723 K. It is worth noting that the powder did not continuously shrink by the pyrolysis, regardless of continuous decomposition as shown in Fig. 1. As the temperature increased over 723 K, the density increased. For thermally cured powder, after gradual decrease up to 823 K, the density suddenly increased. Over 823 K, the densities of both powders are comparable. Calculated volume change was shown in Fig. 2(b). Both radiation- and thermally cured powders swelled in the low temperature range and shrank with increasing the temperature. The volume for thermally cured powder was slightly larger than that for radiation-cured one over 823 K, although the density for the former was similar to that for the latter as shown in Fig. 2(a). It is derived from weight gain of thermally cured powder due to incorporation of oxygen in PCS polymer network by curing.

Fig. 3(a) was FT-IR spectra for radiation-cured powder pyrolyzed at 673, 723, 773, 823, 873 and 973 K. Absorption band around 800 and 1000 cm^{-1} is assigned to Si–CH$_3$ rocking and CH$_2$ deformation in Si–CH$_2$–Si. Small sharp peak at 1250 cm^{-1}, tiny broad peak at 2100 cm^{-1} and broad peak at 2950 cm^{-1} are assigned to Si–CH$_3$ deformation, Si–H stretching and C–H stretching, respectively [1,10]. Both Si–H and Si–CH$_3$ bonds appeared until 873 K; however, at 973 K, those have disappeared and a peak assigned to CH$_2$ deformation in Si–CH$_2$–Si was very weak. According to evolved gases analysis [8], cleavage of Si–H and Si–CH$_3$ bonds produced almost the same amount of H$_2$ and CH$_4$. It shows that
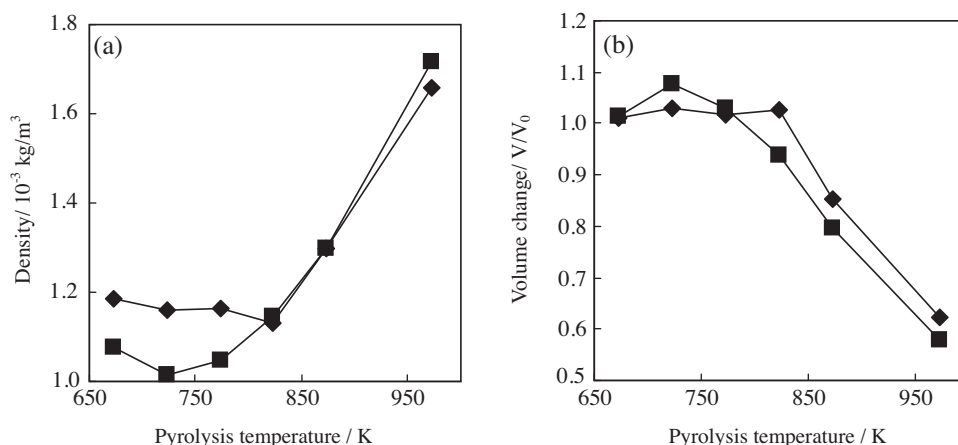
Fig. 2. Plots of (a) density and (b) volume change of pyrolyzed PCS powders. Volume change of 1 is plotted for raw PCS powder. (■) Radiation-cured powder, (♦) thermally cured powder.

the number of cleaved Si—H was comparable to that of Si—CH$_3$. Network structure was constructed in radiation-cured powder by cleavage of Si—H and Si—CH$_3$ and deformation of Si—CH$_2$—Si, as the temperature increased up to 973 K. Fig. 3(b) was FT-IR spectra for thermally cured powder. At 673 K, a broad peak shown at around 3680 cm^{-1} was assigned to free OH stretching [14]. OH was formed in the powder as a result of oxidation of Si—H when the powder was thermally cured. Absorbed H$_2$O on the surface also attributed to the peak. At 723 K, immediately OH band disappeared. This corresponds with evolution of water in low temperature region. For

higher temperature than 773 K, peaks assigned to Si—CH$_3$ and CH$_2$ deformation in Si—CH$_2$—Si were mainly responsible for crosslinking. Evolved gas analysis [8] showed that CH$_4$ was predominantly evolved in the temperature range higher than around 800 K. At 973 K, the peak for Si—CH$_3$ disappeared.

Total pore volume is shown in Fig. 4. For either radiation- or thermally cured powder, total pore volume increased with increasing the pyrolysis temperature from 673 to 823 K. It indicates that numbers of pores were formed by pyrolysis. With increasing the temperature, total pore volume for radiation-cured powder was not observed at 973 K. Pores formed in the powder were so small that nitrogen molecule could not access them, while for thermally cured powder, still some amount of pores were left at 973 K. Total pore volume for thermally cured powder was larger than that of radiation-cured one at every pyrolysis temperature. Larger amount of gas evolved from thermally cured powder attributed to larger total pore volume.

In Fig. 3, total pore volume of both powders increased with increasing the temperature and reached maximum at 823 K. In contrast, in Fig. 2, the volume increased up to 773 K for radiation-cured or 823 K for thermally cured powder. In Fig. 3, total pore volume decreased over 823 K. On the other hand, in Fig. 2, the volume was also decreased in the same temperature range. These results show that the formation and disappearance of pores were determined by the evolution behavior of gases and volume shrinkage.
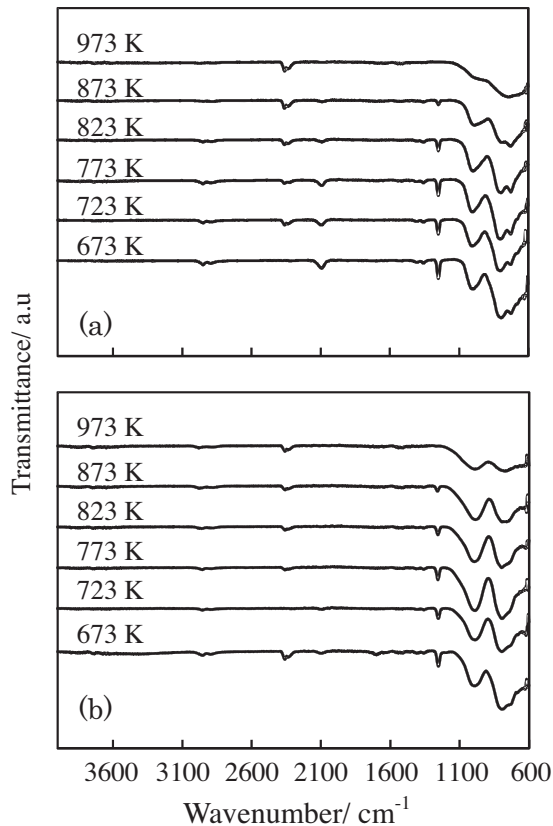

Fig. 3. FT-IR spectra of radiation- and thermally cured PCS powders. The pyrolysis temperatures were 673, 723, 773, 823, 873 and 973 K for 30 min in argon. (a) Radiation-cured power, (b) thermally cured powder.
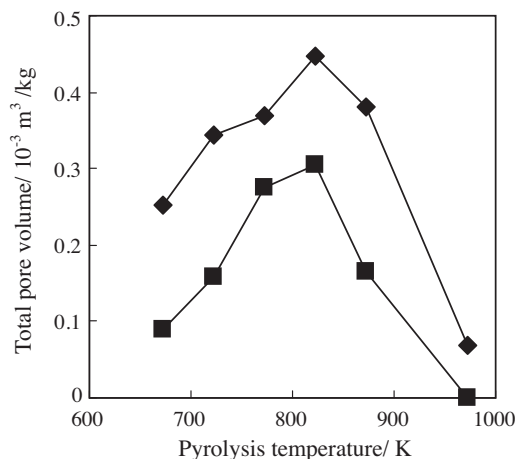

Fig. 4. Plots of total pore volume calculated from nitrogen isotherm vs. pyrolysis temperature. (■) Radiation-cured powder, (♦) thermally cured powder.
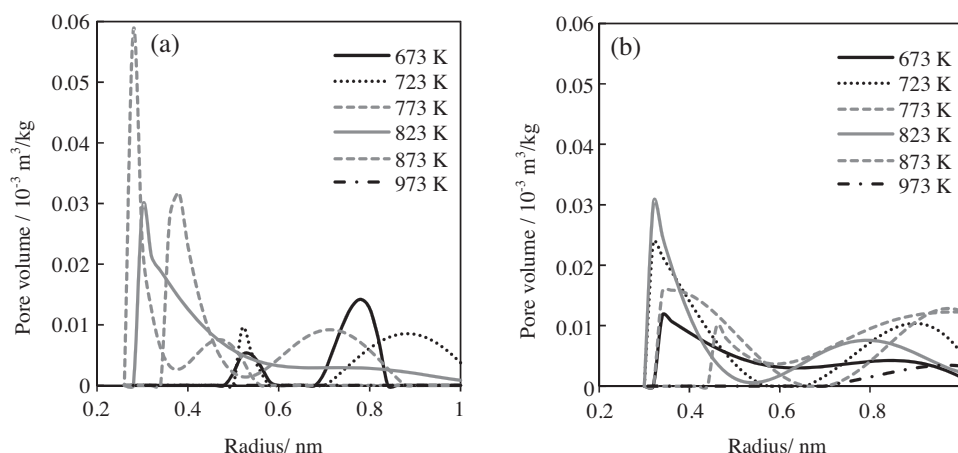
Fig. 5. Micropore size distribution of pyrolyzed (a) radiation- and (b) thermally cured PCS powders. (a) Radiation-cured power, (b) thermally cured powder.

Fig. 5(a) and (b) shows the size distributions of micropores for (a) radiation- and (b) thermally cured powder calculated from nitrogen isotherm curve. Micropore is defined as a pore with the widths not exceeding about 2 nm [15]. In Fig. 5(a), for radiation-curing, small peak around 0.5 nm and relatively large peak around 0.8 nm are shown at 673 K. At the pyrolysis temperature of 723 K, the peak position of the latter peak shifted to around 0.9 nm and the peak was broadened. Peak shift and broadening suggest aggregation of micropores. For the former peak around 0.5 nm, the peak height increased approximately twice as high as that of as-annealed powder, while peak width was somewhat narrowed. As pyrolysis temperature increased from 723 to 773 K, a broad peak at 0.7 nm besides a large peak at around 0.4 nm was observed. The radius of 0.4 nm for the larger peak is close to that of previously reported network space of PCS [12]. The size distribution shifted to smaller radius region than that observed for 723 K. This suggested that PCS powder started shrinking by crosslinking of polymer chains of PCS. At 823 K, a long tailed peak appeared at radius of about 0.35 nm. The tailed peak was formed by construction of polymer networks as a result of frequent crosslinking of mobile polymer chains as well as aggregation of micropores. At 873 K, a steep peak emerged at radius of around 0.3 nm. At this temperature, relatively large micropores disappeared and the distribution was narrowed by shrinkage. At 973 K, finally micropores disappeared and were not detectable by adsorption of nitrogen molecules.

For thermally cured powder shown in Fig. 5(b), distribution of micropore was broad at 673 K. Aggregation of micropores by evolution of H_2O gave rise to the broadening. At this temperature, large pores were not formed by aggregation because of low mobility of polymer chains. At 723 K, two peaks appeared, although the distribution did not shift to smaller or larger radius region. At 773 K, suddenly the distribution shifted to larger radius region and a large peak at radius of around 1 nm appeared. Aggregation of micropores shifted the size distribution to longer radius region. At 823 K, the distribution shifted to shorter radius region again. The powder started shrinking by crosslinking of polymer chains. At 873 K, the shift of the distribution was not observed. A large peak emerged at radius of around 0.9 nm by the aggregation. According to evolved gas analysis [8], evolved amount of H_2 and CH_4 reached maximum at approximately 900 K. In particular, immediately increased CH_4 attributed to the aggregation. At 973 K, decrease of evolved CH_4 as well as H_2 caused disappearance of micropores in the small radius region. In contrast, relatively large micropores still existed. This implies that small micropores disappeared by shrinkage; however, large micropores survived due to gas evolution or aggregation. In Fig. 5(b), apparent narrowing or disappearance of the peak was not observed at 873 and 973 K as observed for radiation-cured

powder in Fig. 5(a). Relatively small number of Si-H bonds in thermally cured PCS powder might somewhat disturb smooth crosslinking of polymer chains and shrinkage in high temperature range, although larger amount of evolved gases mainly caused the formation and aggregation of pores. Of cause, for thermally cured powder, the size distribution was narrowed to some extent by choosing carefully curing and pyrolysis conditions [12]. Such narrowing of the distribution was attained by large shrinkage to prevent the aggregation. However, the gas permeation property of SiC membrane prepared from thermally cured PCS showed that some amount of large pores (pinholes) were left in spite of the narrowing. It indicates that there was a limit of the narrowing by shrinkage, while we previously reported suppression of pinholes formation in SiC membrane prepared from radiation-cured film [6]. Due to smaller amount of evolved gas, narrow size distribution desirable for hydrogen separation was easily obtained.

4. Conclusion

Ceramic yield, density, volume change and pore size distribution were measured for radiation- and thermally cured PCS powder when they were pyrolyzed in the temperature range of 673 to 973 K. Higher ceramic yield was obtained for radiation-cured powder due to smaller amount of evolved gas. Temperature dependence of volume change and the total pore volume show that the formation and disappearance of pores in the powders were determined by the volume shrinkage and evolution of decomposed gases. Volume shrinkage narrowed the pore size distribution for radiation-cured powder. For thermally cured powder, the narrowing of size distribution was disturbed by aggregated pores. Smaller amount of evolved gas from radiation-cured powder relative to thermally cured powder prevented the aggregation of pores and provided the narrow size distribution.

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