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

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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.

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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 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_2O) was evolved. H_2O 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].

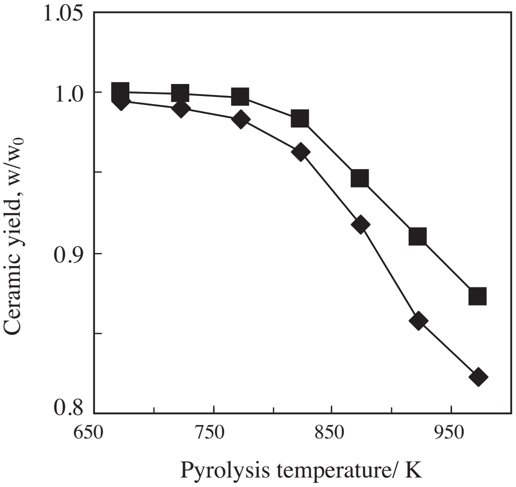

Fig. 1. Ceramic yield of radiation- and thermally cured PCS powders pyrolyzed in argon. Ceramic yield is the weight ratio of pyrolyzed powder to non-pyrolyzed powder. At 673 K, ceramic yield of 1 is plotted for non-pyrolyzed powder. (■) radiation-cured powder, (◆) thermally cured powder.

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