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Fabrication and microstructural characterization of porous SiC membrane supports with Al_2O_3–Y_2O_3 additives

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ABSTRACT

Porous silicon carbide membrane supports were prepared using alumina and yttria additives (1–4 wt%) with various weight ratios of Al_2O_3/Y_2O_3 (23/77–60/40) and sintering at 1500–1800 °C. The relationships between the processing factors and the porosity, pore size and microstructure were examined. Variation of the sintering temperature, the amount of additive used and the ratio of Al_2O_3/Y_2O_3 were found to be effective for control of the pore size and microstructure. The pore size and grain size of membrane support with 1 wt% additive increased with the sintering temperature. For SiC membrane supports containing 4 wt% additive, pore size and grain size were dependent on the alumina ratio in additive. Smaller grains and fine pores around 200–300 nm were detected for specimens with higher Al_2O_3 content (60/40) in the additive. In contrast, for specimens with low Al_2O_3 content (23/77) in the additive, the grain and pore sizes were enlarged. This difference was attributed to the effect of Al_2O_3 content on the temperatures of liquid phase formation during sintering.

1. Introduction

Porous ceramics have attracted significant interest for use as catalyst supports, molten metal filters and gas separation membrane used at high temperature, because of their excellent thermal stability, mechanical properties and chemical resistance [1–3]. Recently, various ceramic membranes have been developed for hydrogen separation at high temperature [4–6]. α-Alumina has been mainly used as a membrane support for most of the research conducted, although alumina has a serious problem in that it has poor thermal shock resistance.

Silicon carbide (SiC) is a promising material for use at high temperature, and has been widely utilized for high temperature applications, such as diesel particulate filters (DPF) [7]. Compared to oxide ceramics such as alumina and silica, SiC has a lower self-diffusion coefficient and excellent thermal shock resistance, which strongly suggests that SiC may be useful as a high temperature membrane support. Some research regarding the preparation of a SiC support and investigation of its permeability have been reported. Suwanmethanond et al. [1] studied the effect of starting powders and the amount of doping agents on the porosity and pore size of SiC membrane supports. Lin and Tsai [2] reported that the properties of alumina-doped SiC supports were considerably affected by additive amount. We have also reported on the microstructure of porous SiC support using alumina as an additive, where the liquid phase formed influenced the porosity and pore size of the SiC obtained [3]. The previous studies have shown that the porosity, pore size and strength of porous SiC can be varied by the formation of liquid phase.

The liquid phase is formed at around the eutectic points of the additives, and penetrates into the space between the grains. Particle rearrangement then occurs, which can cause some shrinkage and densification. During the middle or final stage of densification, dissolution of raw powder into the liquid phase and reprecipitation proceed, which causes significant shrinkage and densification. These phenomena are known for dense materials, whereas the microstructural evolution of porous SiC membrane supports has seldom been studied with respect to liquid phase formation.

Of the previous reports on the fabrication of membrane supports using liquid phase formation, earlier studies on porous SiC have mostly focused on Al_2O_3 additives. The Al_2O_3–Y_2O_3 additive, which is another typical sintering aid for SiC with a lower eutectic temperature around 1400 °C (Al_2O_3–Y_2O_3–SiO_2) [8–10], has not been well utilized to produce porous SiC. The effects of the amount of additive and the mixing ratio of Al_2O_3/Y_2O_3 on the microstructure and pore characteristics have not been systematically investigated.

In the present study, Al_2O_3 and Y_2O_3 were used as sintering additive for SiC. One purpose was to investigate the porosity and pore size of porous SiC supports produced with Al_2O_3 and Y_2O_3 additives. Another more important purpose was to examine the microstructural evolution by varying the processing factors, such as the sintering temperature, amount of additive, and the ratio of

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Table 1
Compositions of starting mixtures.

Sample designation	Al_2O_3 in ($Al_2O_3+Y_2O_3$) (wt%)	Mixing ratio (wt%)	
		SiC	$Al_2O_3+Y_2O_3$
A23-1	23	99	1
A23-2		98	2
A23-4		96	4
A40-1	40	99	1
A40-2		98	2
A40-4		96	4
A60-1	60	99	1
A60-2		98	2
A60-4		96	4

Al_2O_3/Y_2O_3 in the additive to determine how the liquid phase can influence the microstructure and mechanical properties of porous SiC supports.

2. Experimental procedure

High purity β-SiC (Ibiden Co. Ltd., Japan) powder with an average particle size of 0.30 μm was used as a raw material. The additives used were high purity Al_2O_3 (Taimei Chemicals Co. Ltd., Japan) and Y_2O_3 (Shin-Etsu Chemical Co. Ltd., Japan). Mixtures with ($Al_2O_3+Y_2O_3$)/SiC weight ratios of 1/99, 2/98 and 4/96 were blended in ethanol for 1 h using a planetary mill with a SiC pot and SiC balls, where the weight ratio additive compositions of Al_2O_3–Y_2O_3 were 23/77, 40/60 and 60/40. Table 1 lists the mixing ratio and the specimen designation, according to the amount of Al_2O_3–Y_2O_3 additive and the Al_2O_3 content in the additive. After mixing, the slurries were dried using a rotary evaporator and an oven at 110 °C for more than 4 h, and then screened through a 110-mesh sieve. The green bodies (pressed compacts) were formed into disk shapes without any binder using a steel mold at 40 MPa and then treated by cold isostatic press (CIP) at 100 MPa. The resulting disk specimens were approximately Ø20 mm × 5 mm. The green bodies were placed in a capped graphite crucible and sintered at 1500, 1600, 1700 and 1800 °C for 2 h under Ar gas flow. The heating rate from room temperature to 1200 °C was 20 °C/min, and from 1200 °C to the set temperature was 15 °C/min.

The densities and porosities of the sintered specimens were measured by water displacement using the Archimedes method, according to Eqs. (1) and (2),

$$d = \frac{\rho W_a}{W_w - W_l} \tag{1}$$

$$P = 100 - 100 \times \frac{d}{\mathrm{TD}} \tag{2}$$

where W_l, W_w and W_a represent the weight in water, the wet weight and dry weight, respectively, ρ is the water density at the measurement temperature, P is total porosity, and TD is theoretical density. After measuring dry weight, the specimens were soaked in water and subjected to vacuum. When the Archimedes method is used for porous materials without sufficient vacuum, the buoyancy of the pores affects the weight of the specimen in water, resulting in an erroneous density measurement. After soaking in water, the sample was placed under vacuum until no bubbles were observed (ca. 1.5–2.0 h), and the weight in water (W_l) was then measured. After removal of surface excess water, the wet weight of the specimen (W_w) was measured [11].

$$P_o = \frac{W_w - W_a}{W_w - W_l} \tag{3}$$

$$P_c = 100 - P_o - 100 \times \frac{d}{\mathrm{TD}} \tag{4}$$

In addition, P_o (open porosity) and P_c (closed porosity) were also calculated by Eqs. (3) and (4). The densities of the green bodies (before sintering) were calculated according to their weights and dimensions.

Microstructures were observed using field emission-scanning electron microscopy (FE-SEM; Jeol-6330F, Japan) and transmission electron microscope (FE-TEM; HITACHI HF-2000, Japan) with EDS (Delta type; Kevex, USA). The pore size distributions were measured by mercury porosimetry (Yuasa Ionics Inc., PoreMaster-GT, Japan) in the range from approximately 10 nm to 200 μm. The weight of the specimens used for porosimetry measurements was around 1.0 g. The diametrical compressive strength was measured using a testing machine (MTS Systems Corporation, Sintech 10/GL, Minnesota, USA), and calculated using Eq. (5) [12,13]:

$$\sigma = \frac{2P}{\pi D t} \tag{5}$$

where σ, P, D and t are strength, breaking load, sample diameter and thickness, respectively. The load was applied on the side of the specimen surface at a cross-head speed of 0.5 mm/min. For every material composition, at least five specimens were tested.

3. Results and discussion

3.1. Variation of porosity, pore size and microstructure with sintering temperature and additive

Fig. 1 illustrates the linear shrinkage of the various samples as a function of sintering temperature. First, the supports with 1 wt% additive (A23-1, A40-1 and A60-1) exhibited little linear shrinkage, regardless of the sintering temperature. In contrast, the linear shrinkage of the other supports (with increased additive amount) increased with the sintering temperature. Secondly, shrinkage was found to be affected by alumina ratio in the additive. The specimen with larger alumina ratio in the additive exhibited the larger linear shrinkage. The shrinkage of the A60-4 support sintered at 1800 °C had a maximum value around 7%.

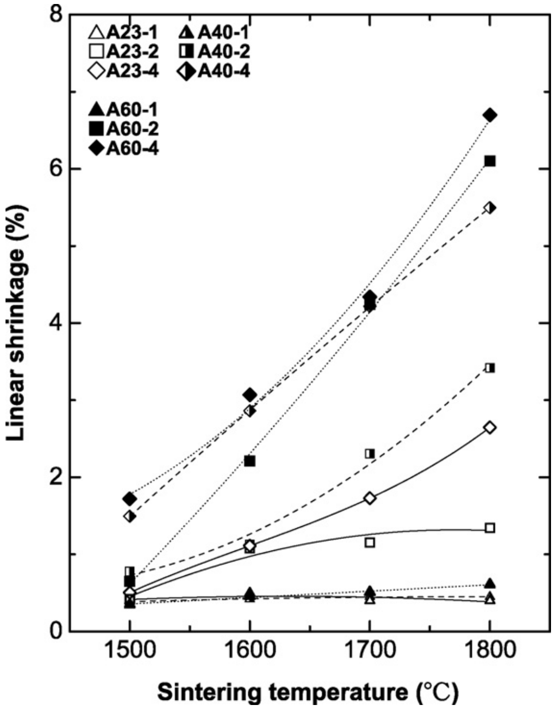

Fig. 1. Linear shrinkage versus sintering temperature.