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Preparation of an Alumina Aerogel with SiC Whisker Inclusion

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Abstract

Alumina aerogels containing silicon carbide (SiC) whiskers were prepared using supercritical drying methods, and their thermal properties were examined. The effects of the SiC whiskers on the alumina aerogel were evaluated. The composite aerogel prepared by the supercritical extraction showed a higher specific surface area than an alumina aerogel without whiskers. Many cracks were observed in the composite aerogel fired at 1200 and 1400°C for 5 h. This is due to the difference of thermal shrinkage between the alumina aerogel and the SiC whiskers. The specific surface area of the composite aerogel was 26·1 m^2/g, and that of the aerogel without whiskers 5·6 m^2/g. The same effect was observed in a composite aerogel prepared by a different supercritical drying method at a higher temperature and pressure.

Aluminiumoxyd-Aerogele, die Siliziumkarbid-Whisker (SiC) enthalten, wurden mittels superkritischer Trocknungsverfahren hergestellt und ihre thermischen Eigenschaften untersucht. Der Effekt der SiC-Whisker auf das Aluminiumoxyd-Aerogel wurde ermittelt. Das Verbund-Aerogel, hergestellt durch superkritische Extraktion, zeigte eine größere spezifische Oberfläche als das Aluminiumoxyd-Aerogel ohne Whisker. Im Verbund-Aerogel, das bei 1200 und 1400°C für 5 h gefeuert wurde, konnte eine Vielzahl von Rissen beobachtet werden. Dies wird durch die unterschiedliche Schrumpfung des Aluminiumoxyd-Aerogels und der SiC-Whisker hervorgerufen. Die spezifische Oberfläche des Verbund-Aerogels betrug 26·1 m^2/g, die des Aerogels ohne Whisker 5·6 m^2/g. Derselbe Effekt konnte an Verbund-Aerogel beobachtet werden, dessen Herstellung mittels einer anderen superkritischen Trocknungsmethode und bei höherer Temperatur und höherem Druck erfolgte.

Des aérogels d'alumine contenant des trichites de SiC ont été préparés par la méthode du séchage en condition supercritique et leurs propriétés thermiques ont été examinées. Les effets des trichites de SiC sur l'aérogel d'alumine ont été evalués. L'aérogel composite obtenu par extraction supercritique est caractérisé par une surface spécifique plus importante que celle de l'aérogel d'alumine sans trichites. De nombreuses fissures sont observées dans le cas de l'aérogel composite fritté à 1200 et 1400°C durant 5 h. Cela est dû à la différence de retrait thermique entre l'aérogel d'alumine et les trichites de SiC. La surface spécifique de l'aérogel composite vaut 26·1 m^2/g contre 5·6 m^2/g dans le cas de l'aérogel exempt de trichites. Le même effet est observé pour un aérogel composite obtenu par une autre technique de séchage supercritique à plus hautes températures et pression.

1 Introduction

Aerogels have a high porosity of more than 90%, high surface area and extremely low density. Therefore, they have been successfully applied as Cerenkov detectors, insulators and supports for catalysts.[1–4] The present authors have reported the preparation of alumina aerogels, their thermal properties and their application as methane combustion catalyst supports.[5] Maintaining the high surface area at temperatures of more than 1000°C is an important issue for combustion catalysts.[6,7] The alumina aerogels showed high specific surface areas at temperatures greater than 1000°C.[8] How-

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ever, they lost their specific surface areas with the formation of α-alumina phase from the transition alumina phases. Therefore, an alumina aerogel composite, formed with another material, has been synthesized to maintain a higher specific surface area than in the alumina aerogels alone. Silicon carbide (SiC) whiskers have been selected because of their high heat resistance, strength at high temperatures and wear resistance. Composites consisting of SiC whiskers dispersed in alumina aerogels have been prepared and their thermal properties tested.

2 Experimental

The preparation process of the SiC whiskers alumina aerogels is shown in Fig. 1. Aluminum *sec*-butoxide ($Al(OBu^{sec})_3$) and ethyl acetoacetate (etac) were mixed in the molar ratio 1 : 1 to produce an $Al(OBu^{sec})_2$–etac complex to control the speed of hydrolysis. Ethanol was added as the solvent. Water diluted with ethanol was gradually added to give a final ratio of $Al(OBu^{sec})_3$:H_2O = 1 : 3, and the $Al(OBu^{sec})_2$–etac complex was hydrolyzed to form an alumina sol at room temperature. The hydrolyzed alumina sol was maintained at 60°C for about 3 days. SiC whiskers (Standard type, Tokai Carbon Co. Ltd, Table 1) were mixed in the alumina sol. The SiC whiskers were dispersed well by stirring vigorously and by using ultrasonic waves. Figure 2 shows the zeta potentials of the hydrolyzed alumina sol and SiC whiskers in water. The zeta potential of the alumina sol is positive and that of the SiC whiskers is negative at pH 7. This pH is accordingly adequate

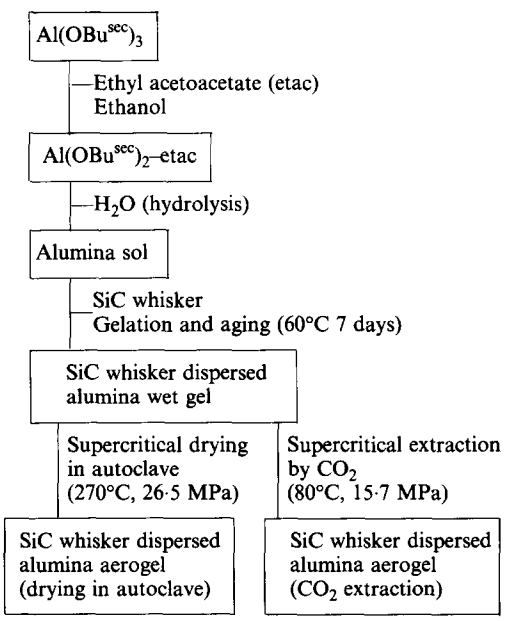

Fig. 1. Flow chart of the procedure to synthesize the composite aerogel and the alumina aerogel prepared in the CO_2 extractor.

Table 1. Data of SiC whiskers

Average specific surface area	1·6 m^2/g
Aspect ratio	10–40
Length	5–15 μm
Density	3·20 m^2/g
SiC	>99%
SiO_2	<0·5%
Al	<0·08%
Ca, Fe, Co	<0·05%

to avoid phase separation of the alumina and SiC whiskers in the solvent when the sol gelates.[10] The alumina sol containing dispersed SiC whiskers was maintained at 60°C to promote aging and gelation. The wet alumina gel with the SiC whiskers was then immersed in ethanol and dried by extraction with carbon dioxide under supercritical condition (mixture of carbon dioxide and ethanol using a CO_2 extractor at a temperature of 80°C and pressure of 15·7 MPa). The temperature and pressure were increased to 120°C and 19·6 MPa, respectively, to remove ethanol completely by the end of the extraction process. Thus, a monolithic alumina aerogel containing SiC whiskers uniformly dispersed was obtained.

In the other drying method, the wet alumina gel containing SiC whiskers was immersed in ethanol and placed in an autoclave. Temperature and pressure were increased to 270°C and 26·5 MPa, respectively, for 24 h. The ethanol in the supercritical state was then purged by dry nitrogen gas.

The specific surface areas of the aerogels were measured using the BET single-point method (Monosorb MS-15, Quantachrome). The microstructures of the aerogels were observed using scanning electron microscopy (SEM JSM-840A, JEOL). The crystalline phases were determined by X-ray powder diffraction (XRD) measurements using Cu-K_α radiation (RAD-IIC system, Rigaku Co.). The pore size distribution was measured using a mercury porosimeter (Poresizer, Parameritics).

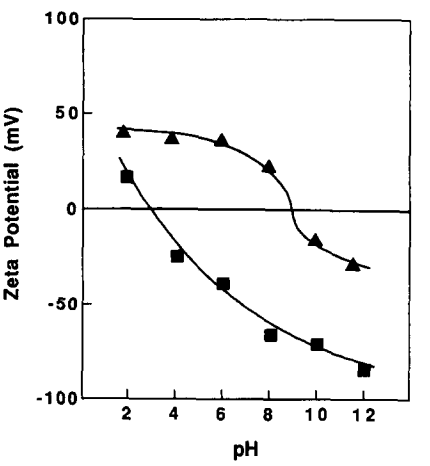

Fig. 2. Zeta potentials of (▲) the hydrolyzed alumina sol particles and (■) the SiC whiskers.

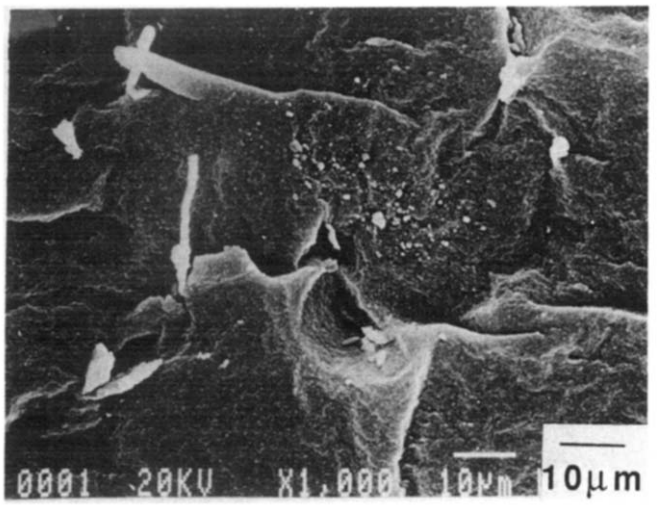

Fig. 3. SEM micrograph of the dried composite aerogel dried in the CO_2 extractor.

3 Results and Discussion

Figure 3 shows a SEM micrograph of the dried alumina aerogel with SiC whiskers (5 wt%) (abbreviated as 'composite aerogel') dried in the CO_2 extractor. The specific surface area of the dried composite aerogel was 568·4 m^2/g. SiC whiskers are observed in the alumina matrix. Some cracks are observed at the SiC whiskers. The cracks were probably made when the aerogel was broken into small pieces for sample preparation for the SEM.

Figure 4 displays the specific surface areas of the composite aerogel and of an alumina aerogel without whiskers, both dried in CO_2 extractor and fired at various temperatures for 5 h. The composite aerogel maintained higher specific surface areas than the alumina aerogel alone.

Figure 5 shows XRD patterns of the alumina aerogel and composite aerogel fired at 1100°C for 5 h. The α-alumina phase peaks are observed in addition to the θ-alumina phase ones for the

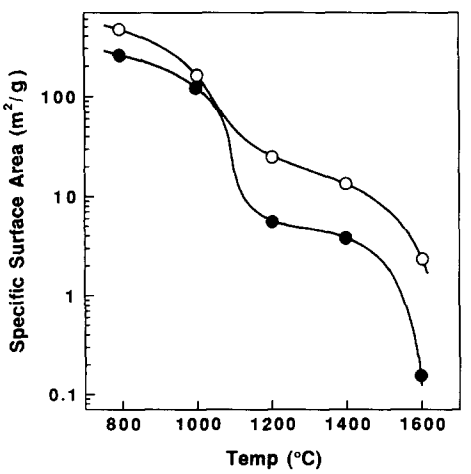

Fig. 4. Specific surface areas of (○) the composite aerogel and (●) the alumina aerogel prepared in the CO_2 extractor fired at 800, 1000, 1200, 1400 and 1600°C for 5 h.

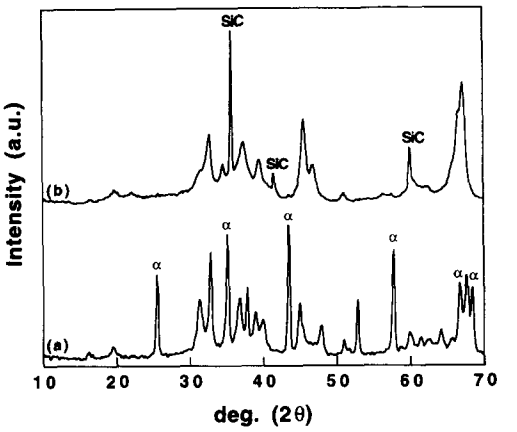

Fig. 5. XRD patterns of (a) the alumina aerogel and (b) the composite aerogel fired at 1100°C for 5 h.

alumina aerogel (Fig. 5 (a)). The phase transformation started from θ- to α-alumina. The θ-alumina phase peaks and SiC whisker peaks are observed for the composite aerogel (Fig. 5(b)). This data implies that addition of SiC whisker inhibits the α-alumina transformation compared to the alumina-only aerogel.

Figure 6 displays pore size distributions of the aerogels fired at 1200°C for 5 h. The composite aerogel has larger pores than the alumina aerogel. Figure 7 shows a SEM micrograph of the composite aerogel fired at 1200°C for 5 h. There are many cracks in the alumina matrix due to its shrinkage. The SiC whiskers prevent sintering of the alumina aerogel and cause the cracks. The larger pore size distribution of the composite aerogel is due to the inhibition of α-alumina transformation and prevention of sintering by SiC whiskers. The specific surface area of the composite aerogel fired at 1200°C for 5 h is 26·1 m^2/g, and that of the alumina aerogel 5·6 m^2/g (see Fig. 4). This higher specific surface area of the composite aerogel is also attributed to the same causes.

Figure 8 shows SEM micrographs of the composite aerogel and of the alumina aerogel fired at 1400°C for 5 h. The crystalline phase of both

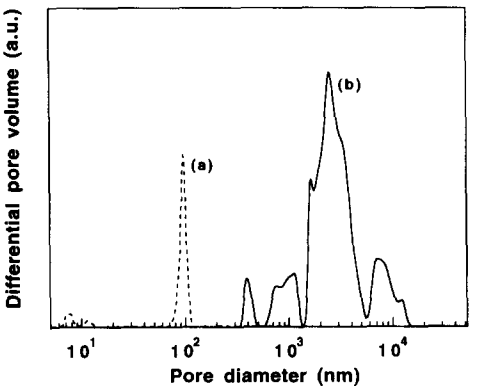

Fig. 6. Pore size distributions of (a) the alumina aerogel and (b) the composite aerogel fired at 1200°C for 5 h.

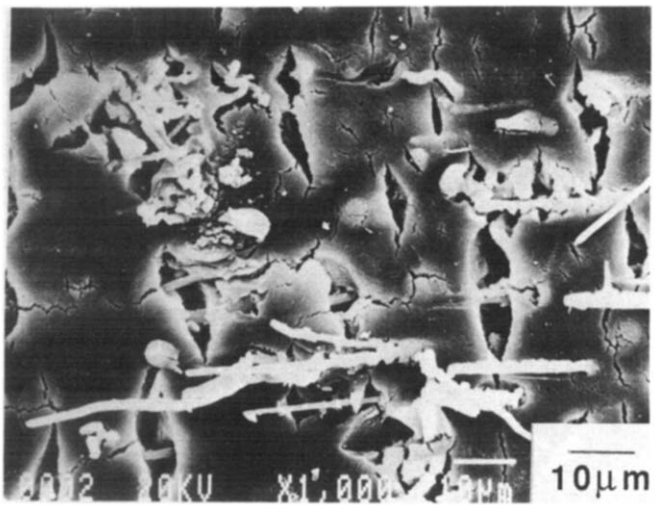

Fig. 7. SEM micrograph of the composite aerogel dried in the CO_2 extractor fired at 1200°C for 5 h.

aerogels is α-alumina phase under this firing condition. The morphology of the composite aerogel is similar to that fired at 1200°C for 5 h; the sintering had not progressed. In contrast, the alumina aerogel sintered and the microcracks observed in the composite aerogel do not exist.

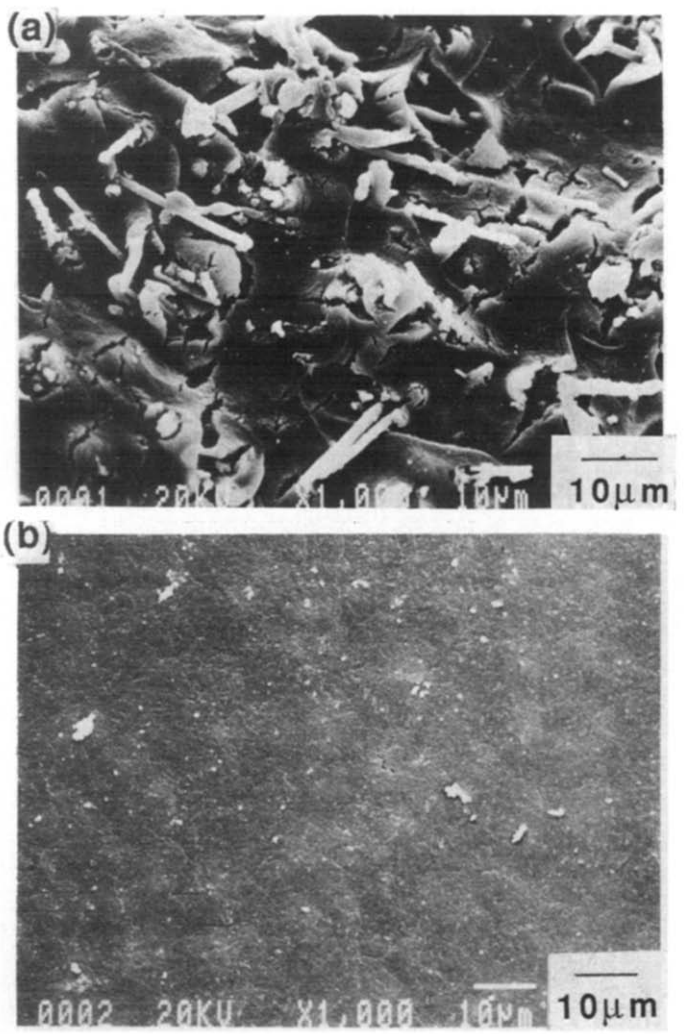

Fig. 8. SEM micrographs of (a) the composite aerogel and (b) the alumina aerogel prepared in the CO_2 extractor fired at 1400°C for 5 h.

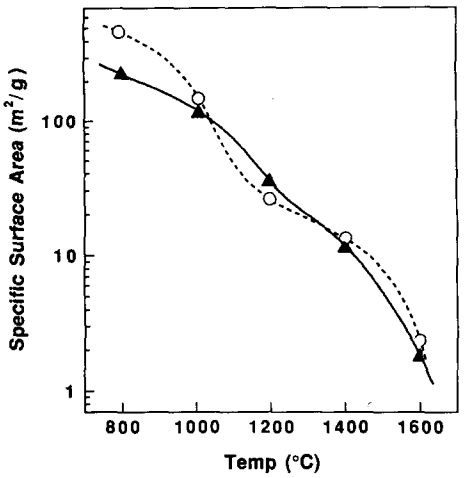

Fig. 9. Specific surface areas of the composite aerogels prepared in (○) the CO_2 extractor and (▲) the autoclave, fired at 800, 1000, 1200, 1400 and 1600°C for 5 h.

The alumina aerogels prepared in the autoclave at 270°C and 26·5 MPa (Fig. 1) showed higher specific surface area than those prepared in the CO_2 extractor.[8] Accordingly, an alumina aerogel containing SiC whiskers was prepared in the autoclave. Figure 9 the shows specific surface areas of the alumina aerogels with SiC whiskers prepared in the different supercritical drying methods fired at various temperatures for 5 h. The amount of SiC whiskers added was 5 wt% in the alumina aerogel prepared in the CO_2 extractor. In contrast, 20 wt% of SiC whiskers was added to the alumina aerogel prepared in the autoclave on the assumption that greater additions would be more effective in maintaining a high specific surface area. The composite aerogel prepared in the autoclave shows lower specific surface areas than that prepared in the CO_2 extractor at 800 and 1000°C. It is due to the addition of the larger amounts of SiC whiskers of higher density than the aerogels, the higher temperature and pressure in the supercritical drying process (see Fig. 1).[8] The composite aerogel prepared in the autoclave shows a higher specific surface area than that dried in the CO_2 extractor at 1200°C. This result can be attributed to a relative inhibition of the transformation into the α-alumina phase.[8] However, the specific surface areas of the composite aerogel prepared in the autoclave are slightly lower again than those of the aerogel prepared in the CO_2 extractor at 1400 and 1600°C, despite anticipation of an improvement of the specific surface area.

Table 2 lists the measured specific surface areas of the composite aerogel and the alumina aerogel alone prepared in the autoclave. The specific surface areas are shown for samples fired at 1200°C for 100 h, 1400°C and 1600°C for 5 h. The alumina aerogel transform into the α-alumina phase completely under these firing conditions.

Table 2. Specific surface areas (m^2/g) of the composite aerogel and the alumina aerogel prepared in the autoclave and fired at various temperatures and for various times 1200°C for 100 h, and 1400 and 1600°C for 5 h

	1200°C for 100 h	*1400°C for 5 h*	*1600°C for 5 h*
Composite aerogel	55·6	11·6	1·9
Alumina aerogel	12·9	9·5	1·8

Mullite and SiO_2 phases are detected for the composite aerogel. The composite aerogel shows higher specific surface area than the alumina aerogel fired at the temperature of 1200°C for 100 h, and slightly higher at 1400°C and 1600°C for 5 h.

4 Conclusions

Alumina aerogels containing SiC whiskers have been prepared in the CO_2 extractor and autoclave. SiC whiskers are uniformly dispersed in alumina aerogel. The composite aerogel prepared in the CO_2 extractor shows a higher specific surface area than that of the alumina aerogel alone. This is attributed to the ability of the SiC whiskers to prevent sintering of the alumina aerogel. This effect is also observed in the composite aerogels prepared in the autoclave.

Acknowledgement

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