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Change of Phase Transformation Temperature at Fabricated Membrane using Sol-gel Method

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ABSTRACT

The supported and unsupported boehmite (γ-AlOOH) membranes were prepared using a boehmite sol. The supported membrane was consisted of a porcelain support, two intermediate α-Al_2O_3 layers, and a top boehmite membrane. XRD patterns showed that the supported top membrane had a higher θ- to α-Al_2O_3 transformation temperature compared to the unsupported membrane. This result was also confirmed from microstructural study of the membrane. The shift in the phase transformation temperature should be explained by difference of a stress generated in the supported top membrane due to interaction between the support layers and the top membrane.

Key words : Phase transformation, Microstructure, Boehmite membrane, Sintering, Porcelain support

1. Introduction

In recent years, there has been growing interest in preparing ceramic membranes for separation purposes.[1-9] The use of ceramic membranes is more interesting than organic ones because the former provide numerous advantages such as high thermal and chemical stability, long life, pressure resistance, and catalytic properties in application.

In general, ceramic materials have several crystallographic modifications and transform by nucleation and growth with high activation energies. As stated by other researchers,[10] most of the activation energy of a transformation is utilized in the nucleation process. At high temperatures, grain growth followed by densification and consequent change in pore size and size distribution can additionally occur. On the other hand, boehmite (γ-AlOOH) exhibits the following transformation sequence upon heating:[11]

$$\text{boehmite} \rightarrow \gamma\text{-}Al_2O_3 \rightarrow \delta\text{-}Al_2O_3 \rightarrow \theta\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3$$

The dehydration of boehmite occurs at 450°C to form γ-Al_2O_3 having a well-defined pore structure.[12] An increase in the heat-treatment temperature generates transformations to the other transitional-phase aluminas such as δ- and θ-Al_2O_3 with changes in the pore structure to accommodate densification.[8] Finally, boehmite transforms to α-Al_2O_3 by a nucleation and growth process at approximately 1200°C.[13] Microstructure of the transformed α-Al_2O_3 is composed of pores, grains, and pore channels. It is important to note that these phase transformations accompany a microstructural change, because a first criterion in selectivity of membrane filtration processes, which are usually divided into filtration (pore diameters greater than 10^4 nm), microfiltration (from 10^2 to 10^4 nm), ultrafiltration (from 1 to 10^2 nm), and reverse osmosis (up to 1 nm), is a narrow pore size distribution.[9]

On the other hand, the transformations are usually accompanied by a volume change. In the case of supported membranes the volume change is expected to be prevented by the rigid support, which may influence the transformations and their microstructures and lead to cracking and/or peeling of the membrane from the support. Thus, understanding the relationship between the phase transformation and the accompanying microstructural change will give a significant indication for applications of the membrane. In this paper, we report the phase transformations and microstructural evolution of supported and unsupported boehmite membranes.

2. Experimental

The top membrane of 3 μm in thickness was made using a boehmite sol, which was prepared by dispersing boehmite powder (Condea Chemie GmbH, Germany) of 2.1 g in a distilled water of 100 ml and peptizing the solution with a 0.07 M HNO_3 solution. The remaining conditions were identical to those applied to the intermediate layers. An unsupported membrane was also prepared by drying the boehmite sol in petri dishes at room temperature. Thickness of the formed membrane was 10 m. The unsupported membrane was used for characterization as there was no interaction with the support and the intermediate layers. The top membrane and the unsupported membrane were heated in a tempera-

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ture range from 500 to 1400°C.

Microstructural evolution of the supported and unsupported membranes was observed by scanning electron microscopy (Model DS-130, Akashi, Tokyo, Japan). The membrane-constituting phases were analyzed by X-ray diffractometry (XRD, Model RINT/DMAY-2000, Rigaku, Tokyo, Japan) at the operating condition of 30 kV-100 mA, using Cu Kα radiation with a graphite monochromator. The phase constitution was investigated by thin-film geometry where the incident X-rays enter into the membrane with a small glancing angle fixed to 1.0°. For the XRD measurements, the samples had dimensions of 15 × 15 mm.

3. Results and Discussion

XRD patterns of the supported and unsupported membranes obtained at different temperatures showed their structural evolution (Figs. 1(a) and 1(b)). No difference was observed in the XRD patterns of the two types of samples to 900°C. There were difficulties in observing the transformation temperatures of the polytypes (γ-Al_2O_3, δ-Al_2O_3, and θ-Al_2O_3) due to similarity of their peak positions and the poor crystallinity. Thus, our attention was concentrated on the process whereby θ-Al_2O_3 transformed to α-Al_2O_3. We analyzed the transformation behavior with a peak around 65° 2θ, which is characteristic of α-Al_2O_3 phase, and a peak around 26° 2θ related to θ-Al_2O_3 phase.[14,15] The peaks appeared in the XRD patterns of the samples processed at 1000°C. The two phases competed with each other during the heat treatments. The θ-Al_2O_3 in the supported top membrane completely transformed into α-Al_2O_3 at 1300°C, whereas the complete transformation in the unsupported membrane occurred at 1200°C.

A more detailed observation on the transformation was carried out, particularly in a temperature range of 1200 to 1300°C. Fig. 2 shows the change of intensity of θ-Al_2O_3 peak around 65° 2θ and that of α-Al_2O_3 peak around 26° 2θ in the XRD patterns obtained from the membranes after calcination at different temperatures. As mentioned above, the characteristic peaks of θ- and α-Al_2O_3 phases appeared at 1000°C for the two types of the samples. The peak intensity of θ-Al_2O_3 phase increased to 1100°C for the unsupported membrane and 1200°C for the supported top membrane. Above the temperatures, the peak intensities abruptly decreased with an increase of the treatment temperature. In contrast, the peak intensity of α-Al_2O_3 phase gradually increased to 1150°C for the unsupported membrane and 1230°C for the supported top membrane. Above the temperatures, the peak intensity suddenly increased with an increase of the treatment temperature. The complete transformation of θ- to α-Al_2O_3 phase occurred at 1200°C for the

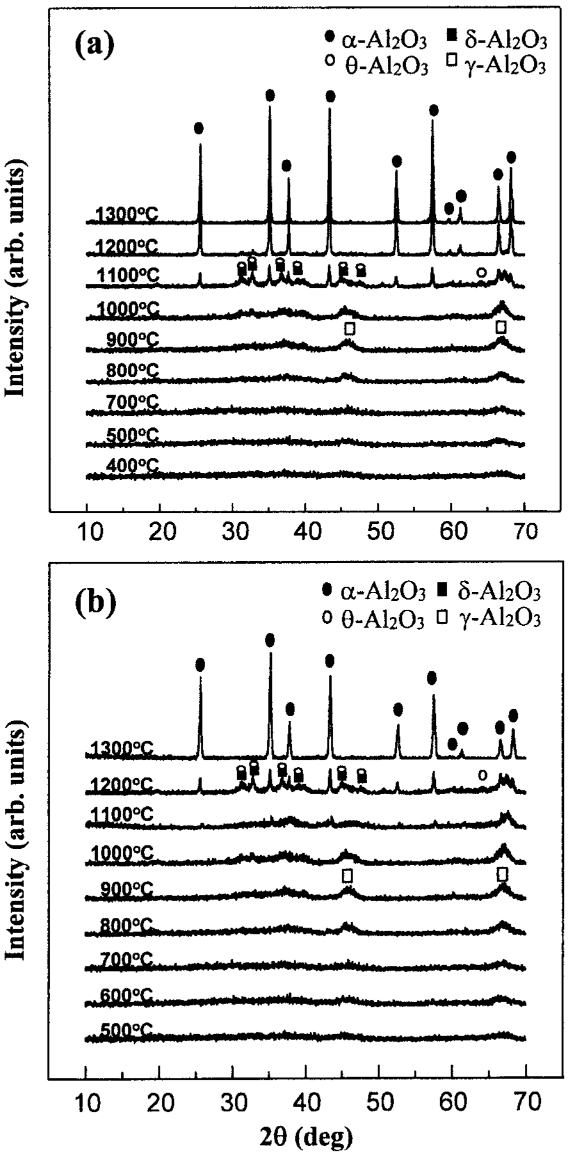

Fig. 1. XRD patterns of the membranes processed at various temperature: (a) unsupported membrane and (b) supported top membrane.

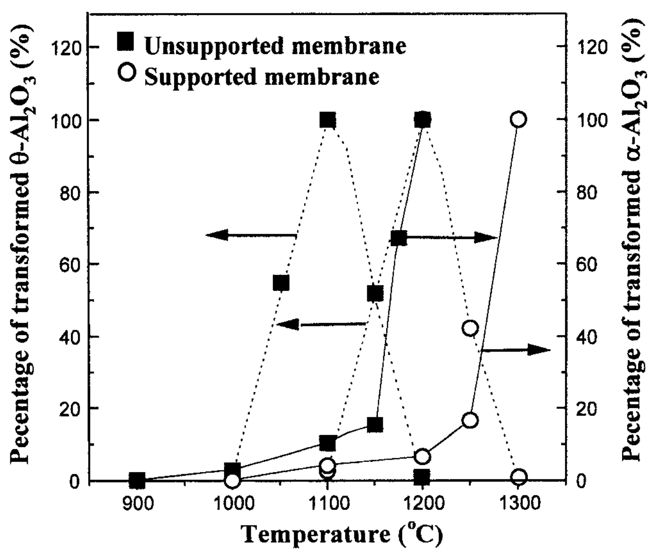

Fig. 2. Change of peak intensities of θ- and α-Al_2O_3 phases in the membranes vs calcination temperature.

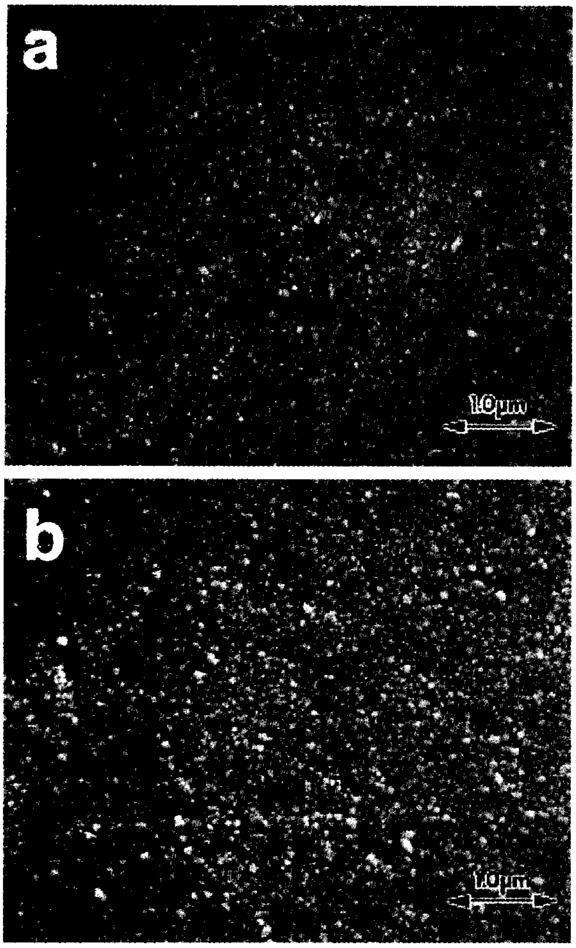

Fig. 3. Scanning electron micrographs of the membranes treated for 1 h at 900°C: (a) supported top membrane and (b) unsupported membrane.

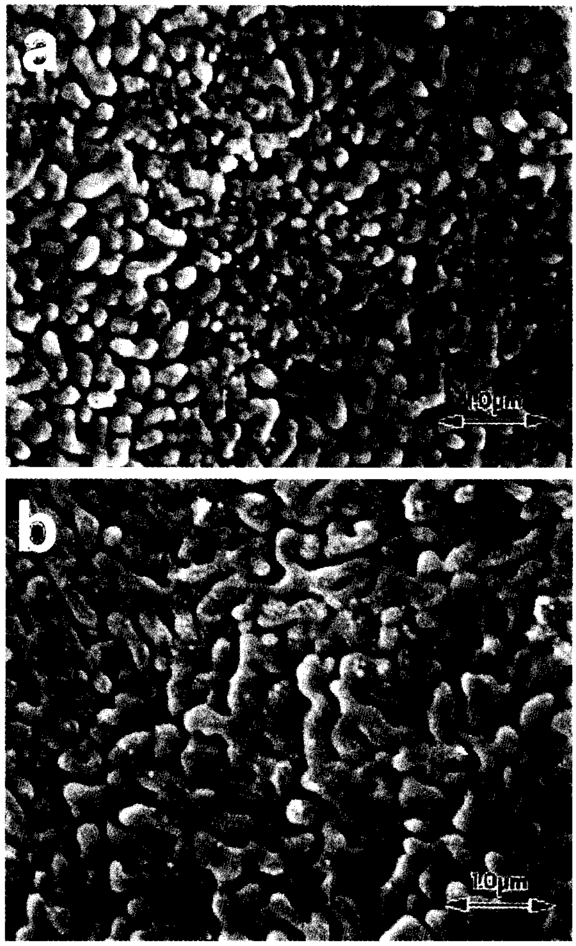

Fig. 4. Scanning electron micrographs of the membranes treated for 1 h at 1200°C: (a) supported top membrane and (b) unsupported membrane.

unsupported membrane, which is consistent with that reported previously.[11] In the case of the supported top membrane, the transformation completely occurred at 1300°C. Namely, the supported top membrane showed an 100°C higher transformation temperature than the unsupported membrane.

A similar effect has been observed for microstructures of the membranes. We examined microstructures of the membranes after heating at 900°C (Fig. 3). The microstructural difference between the supported and unsupported membranes was less significant, which is consistent with the X-ray results in the Fig. 1. The effect of the transformed structures on microstructural development was further examined after heating at 1200°C (Fig. 4). The supported top membrane was characterized by the bimodal grains consisting of two types of grains about 50 and 300 nm in size. In contrast, the unsupported membrane displayed interconnecting grains, which have often been observed in α-Al_2O_3 membrane. It is important to note that such a microstructure was not observed for the supported top membrane even after sintering at 1200°C for 1 h, as seen in Fig. 4(a). This suggests that interaction between the support and intermediate layers and the supported top membrane may generate the microstructural difference. After heating at 1300°C, the supported top membrane revealed a structure with some porosity surrounded by interconnecting grains (Fig. 5(a)). It is also interesting to note that the unsupported membrane consisted of larger grains than the supported top membrane (Fig. 5). This indicates that grain growth occurs faster in the unsupported membrane than in the supported top membrane at the same temperature.

Now, we try to explain the shift in the transformation temperature with a stress generated in the supported top membrane. A negative volume change of about 10.08% occurs during the θ- to α-Al_2O_3 phase transformation.[11] As mentioned earlier, in the case of a supported membrane the layer is restrained from shrinking in a direction parallel to the support, which will lead to a buildup of stress in the membrane. The formed stress may be responsible for the shift in the transformation temperature. It is significant to know how transformation temperatures and microstructures vary with thickness and porosity of the membrane, the intermediate layers, and the support. The stress for a supported membrane is expected to decrease with an

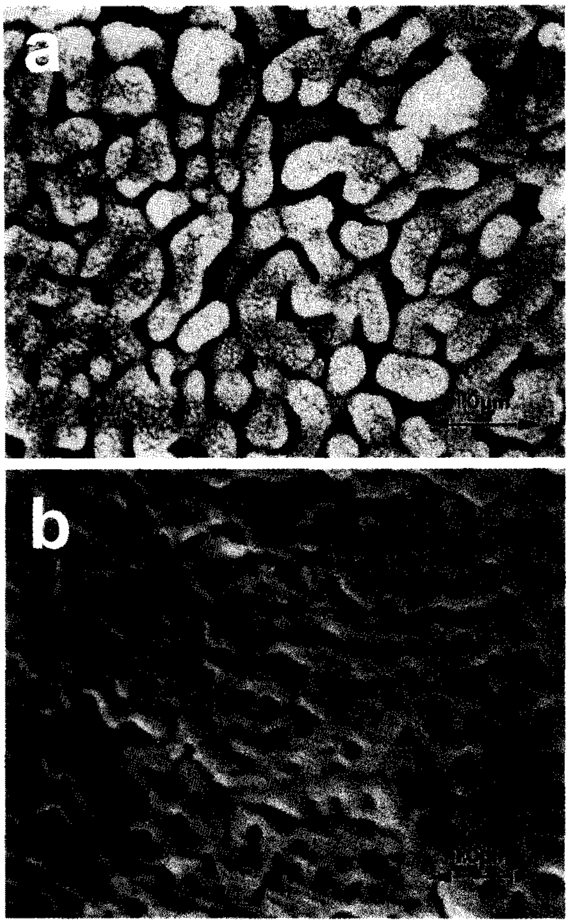

Fig. 5. Scanning electron micrographs of the membranes treated for 1 h at 1300°C: (a) supported top membrane and (b) unsupported membrane.

increase in thickness of the membrane. Voncken *et al.*[16] reported that the observed maximum level of the stress for an Al_2O_3 membrane with a thickness of 2 μm was about 180-200 MPa and 150 MPa for an Al_2O_3 membrane of a thickness of 3 μm. We should also consider Young's modulus among several parameters which influence the stress, because the Young's modulus in general decreases with an increase of porosity, which leads to a decrease of the stress. Such a systematic approach is necessary for a successful interpretation of the interaction between the support and intermediate layers and the supported top membrane. However, such an investigation has not yet been carried out, which will be further investigated in a forthcoming study.

4. Summary

Supported and unsupported boehmite membranes (γ-AlOOH) were prepared using a boehmite sol. The supported membrane system in this study consisted of a porcelain support, two intermediate α-Al_2O_3 layers, and a top boehmite membrane. XRD patterns showed that the complete transformation of θ- to α-Al_2O_3 phase occurred at 1200°C for the unsupported membrane and 1300°C for the supported top membrane. Namely, the supported top membrane showed an 100°C higher transformation temperature than the unsupported membrane.

A similar effect was observed for microstructures of the membranes. The unsupported membrane processed at 1200°C displayed interconnecting grains, which have often been observed in α-Al_2O_3 membranes. However, such a microstructure was not observed for the supported top membrane treated at the same temperature. After heating at 1300°C, the supported top membrane showed a structure with some porosity surrounded by interconnecting grains. We explained the shift in the transformation temperature with a stress generated in the supported top membrane due to interaction between the support and the intermediate layers and the top membrane.

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