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Fabrication of porous magnesium spinel (MgAl$_2$O$_4$) with cylindrical pores by unidirectional solidification

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Abstract. A porous magnesium spinel (MgAl$_2$O$_4$) with cylindrical pores was fabricated by unidirectional solidification in pressurized 1%H$_2$-99%Ar mixed gas. A small amount of Al$_2$O$_3$ phase was formed in porous MgAl$_2$O$_4$ bulk. Two different kinds of pores with large cylindrical and small facet shape were formed in the solidified samples. The former pores were dominant in the porous structure. The cylindrical pores were formed at solid-liquid interface due to hydrogen solubility gap. On the other hand, the small facet shape pores were formed by vaporization of MgO component on the cooling step in the solidification process. The pore length of the cylindrical pores decreased with increasing total pressure due to increasing the chance to nucleate pores during the solidification.

1. Introduction

Porous ceramics with excellent chemical stability at high temperatures is a promising for a filter in corrosive gas flow and in demand for integrated coal gasification combined cycle (IGCC) power generation system [1-3]. MgAl$_2$O$_4$ ceramic with high thermal and chemical resistances at high temperatures is a candidate for the gas filter in the system [3,4].

The pore size between 10 micron and several hundred microns is suitable for the gas filter application [1]. Several research groups have been proposed the fabrication process of the porous ceramics with open pores. Zhang et al. fabricated porous alumina with unidirectionally aligned continuous pores by sintering of cotton fiber with alumina coat [5]. Isobe et al. prepared porous alumina with oriented cylindrical pores by an extrusion method [6]. However, in these methods, it is difficult to control the porosity and pore size of the porous alumina. The authors have proposed a fabrication process of porous alumina with cylindrical pores by unidirectional solidification in pressurized hydrogen atmosphere [7]. In this method, the porosity and pore size can be controlled by hydrogen partial pressure and total pressure [7].

The present paper reports the fabrication of porous magnesium spinel with cylindrical pores by unidirectional solidification in pressurized 1%H$_2$-99%Ar mixed gas in order to elucidate the formation mechanism of the pores.

2. Experimental Procedure

For the preparation of MgAl$_2$O$_4$ feed rod, high purity alumina (99.99% purity, Sumitomo Chemical Co. Ltd.) and magnesia (99.9% purity, Konoshima Chemical Co. Ltd.) powders were used as starting
materials. The powders with the stoichiometric ratio were mixed with a binder in water and the slurry was poured into a mold. After drying in air, calcination was performed at 1200°C for 7.2 ks in air and then, the feed rod with 8 mm in diameter and 150 mm in length was prepared.

The solidification was carried out using optical floating zone apparatus in 1%H₂-99%Ar mixed gases in the range from 0.1 MPa to 0.7 MPa. Xenon lamp was used as a heating source. The xenon lamp and melting zone were placed on the focus in the elliptical mirror. The feed rod was hooked on upper shaft and another feed rod was fixed with lower shaft. This melting system was set up in a quartz tube. The environmental gas was introduced into the quartz tube. The transference velocity of the floating zone was fixed to 200 mm/h.

The cross-sections of the samples perpendicular and parallel to the solidification direction were observed by SEM (JEOL JSM-6360T). The porosity of the samples was calculated from the transversal cross-section images.

3. Result and Discussion

Figure 1 shows the transversal and longitudinal cross-sections of the samples fabricated in 1%H₂-99%Ar mixed gas of 0.1, 0.2, 0.4, 0.6 and 0.7 MPa. Cylindrical pores are aligned in the solidification direction. In addition to the cylindrical pores, a small amount of small facet shape pores are also formed in the bulk as indicated by arrows.

![Figure 1](image)

Fig.1 Transversal and longitudinal cross-sections of samples fabricated in 1%H₂-99%Ar mixed gas.

Figure 2 shows the powder X-ray diffraction pattern of the sample fabricated under total pressure of 0.2 MPa. A small amount of Al₂O₃ phase can be detected as secondary phase. This fact indicates that a small amount of MgO component vaporized during the solidification process.

Figure 3 shows the porosity change as a function of the total pressure. The porosity did not change with the total pressure. If the pores are formed at solid-liquid interface due to hydrogen solubility gap between solid and liquid phases, the pressure of inner pore depends on the total pressure according to the following equation (1) and the volume of pores decreases with increasing total pressure according to Boyle's law. Then, the porosity of the samples decreases with increasing total pressure.
\[ P = \frac{2\gamma}{R} + P_0 \]  

Where \( \gamma \), \( R \) and \( P_0 \) denote the surface tension of the liquid MgAl_2O_4 phase, the radius of the pore and the total pressure, respectively. However, the porosity does not change with total pressure. In the case of formation for porous alumina with cylindrical pores by unidirectional solidification, the porosity decreased with increasing total pressure and increased with increasing hydrogen partial pressure [7]. The pores are formed at solid-liquid interface due to hydrogen solubility gap between solid and liquid phases.

Figure 4 (a) and (b) show the porosity and average pore diameter changes as a function of the total pressure; the porosity and pore size are evaluated for large cylindrical pores excluding the spherical small pores. The porosity and pore size decrease with increasing total pressure and increase with increasing hydrogen partial pressure as shown in Fig.4. Hence, it is confirmed that the cylindrical pores in the samples are formed at solid-liquid interface due to hydrogen solubility gap between solid and liquid phases during the unidirectional solidification as in the case of porous alumina in reference [7].
Obviously, the pore length of the cylindrical pores decreases with increasing the total pressure as shown in Fig.1. When hydrogen solubility in the liquid MgAl₂O₄ phase obeys Sieverts’ law, hydrogen solubility increases with increasing the total pressure and then, the chance to make the pores increases with the total pressure during the solidification.

Since non-porous MgAl₂O₄ was obtained by the solidification under 100%Ar atmosphere, the formation of the small pores is closely related to the hydrogen solubility in the solid phase. It is expected that the hydrogen solubility in solid MgAl₂O₄ phase also increases with increasing hydrogen partial pressure according to Sievert’s law. Hence, it is considered that the evaporation rate of MgO component from the solid phase below melting point is accelerated by the dissolved hydrogen in the solid phase and then, many small pores are formed in the bulk. The evaporation of MgO component from MgAl₂O₄ was reported by Altman [8] and Sakamoto et al. [9]. The magnesium partial pressure according to equation (2) is hundred times larger than that of magnesium oxide due to equation (3) at high temperatures [8].

\[
\begin{align*}
MgO(s) &= Mg(g) + \frac{1}{2}O_2(g) \quad (2) \\
MgO(s) &= MgO(g) \quad (3)
\end{align*}
\]

It can be understood the reduction reaction of equation (2) is accelerated by the dissolved hydrogen in the solid MgAl₂O₄ and the porosity increases with increasing the amount of dissolved hydrogen atom, namely, hydrogen partial pressure.

4. Conclusion
A porous magnesium spinel with cylindrical pores and small facet shape pores can be fabricated by unidirectional solidification in pressurized Ar-H₂ mixed gas. The cylindrical pores are formed at solid-liquid interface due to hydrogen solubility gap between solid and liquid phase. On the other hand, small pores are formed by vaporization of MgO component from the solid MgAl₂O₄ on the cooling step after the solidification that is accelerated by dissolved hydrogen in solid MgAl₂O₄ phase. The pore length of the cylindrical pores decreases with increasing total pressure due to increasing the hydrogen solubility in the liquid phase.

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