

Micro-porous ceramics using directionally solidified $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic crystals

Jong Ho Lee[†]

Gwangju Research Center, Korea Institute of Industrial Technology, Gwangju 500-460, Korea

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Abstract Novel process was tried to obtain micro-porous ceramic body containing continuous pore channel. $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic fibers and rods have been grown successfully by the micro-pulling-down method, and the microstructures and optical characterizations of grown crystals were performed. $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic fibers of 0.3~1 mm in diameter and about 500 mm in length, and the rods having 5 mm in diameter with approximately 60 mm in length have been grown with the 6~120 mm/hr of growth speed. The eutectic fibers showed homogeneous microstructure in which MgO fiber aligned to the growth direction in the MgAl_2O_4 (spinel) matrix. The grown crystals looked semitransparency under naked eyes. Optical and orientational characterizations were performed. The second phase of MgO (periclase) was easily removed by selective etching with hydrochloric acid, and then porous bodies were obtained.

Key words $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic crystal, Rod, Micro-pulling-down method, Directional solidification, micro-porous body

1. Introduction

Directionally solidified eutectic crystals are attracting considerable interest for the various research fields due to their versatile properties. Eutectic systems make out the particular eutectic microstructure depending on the solidification behavior of their components.

It is thought that the versatile properties of the eutectic crystals result from their particular eutectic structures. The shape and size of eutectic structures are affected from the solidification speed also. Some of oxide eutectic systems make the structure that fiber/whisker like second phase aligned to the matrix. Numerous applications require thermally and chemically stable materials for micro-porous system fabrication. Various micro-porous systems require channel structures that form an array of parallel channel.

Directional solidification can provide an effective method to produce geometrical arrays that are conducive for micro-system fabrication. Considerable efforts have been devoted to controlling and improving the microstructures [1, 2]. Because these eutectic crystals showed unusual anisotropic properties, many of directionally solidified eutectic crystals have been studied for finding an application in structural materials, electronic and optical devices.

A lot of attention focused on these directionally solidi-

fied oxide eutectics from 1990s when their high structural stability up to nearly the melting temperature was reported [3]. Late 1990s, promising results were reported for the Al_2O_3 -based binary and ternary eutectic systems such as $\text{Al}_2\text{O}_3/\text{GdAlO}_3$ [3], $\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) [4, 5], $\text{Al}_2\text{O}_3/\text{ZrO}_2$ [6-9] and $\text{Al}_2\text{O}_3/\text{YAG}/\text{ZrO}_2$ [10].

These researches were aimed only to the high temperature structure application over 1500°C based on the structural stability. The target materials for this application are commonly showed ‘Chinese Script’ microstructure. On the other hand, there are various patterns of microstructure in eutectic systems such as fibrous aligned structure. $\text{MgAl}_2\text{O}_4/\text{MgO}$ [11, 12] and ZrO_2/MgO [13] eutectic crystals yield a fibrous aligned microstructure in which fiber/whisker like MgO (periclase) crystals regularly aligned in the MgAl_2O_4 matrix. If we make an appropriate treatment to the grown crystals, we may find further promising application with these fibrous aligned microstructures for example the photonics devices or catalysts.

In this work, we have grown $\text{MgAl}_2\text{O}_4/\text{MgO}$ crystal by the micro-pulling-down (μ -PD) method, and tried to prepare the porous body by selective etching the MgO (periclase) fibrous phase for novel application such as photonics and catalyst devices.

2. Experimental Procedure

Figure 1 illustrates the micro-pulling-down (μ -PD in

[†]Corresponding author
Tel: +82-62-600-6170
Fax: +82-62-600-6179
E-mail: jholee@kitech.re.kr

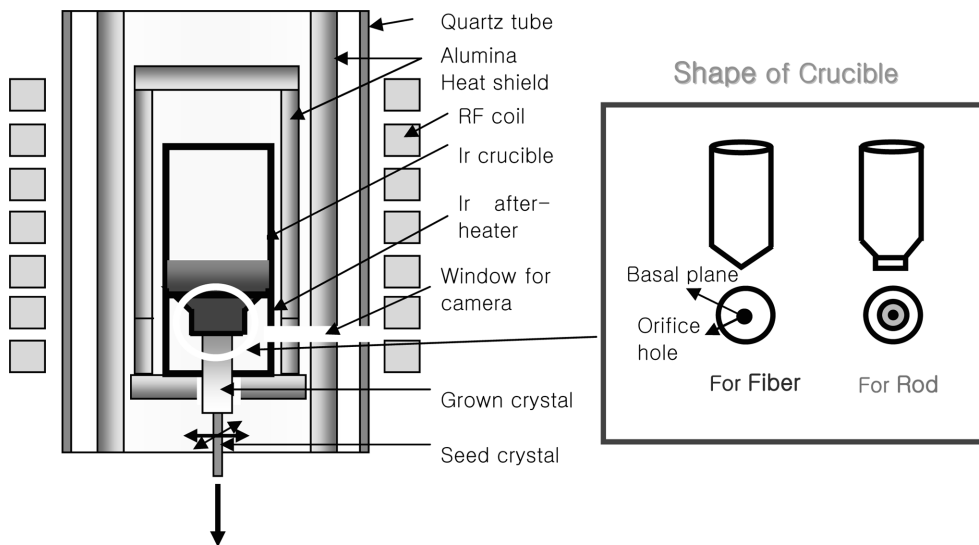


Fig. 1. Illustration of micro-pulling-down apparatus.

below) apparatus used in this study. The μ -PD apparatus consisted of an iridium crucible coupled with an RF induction heating module, a cylindrical iridium after-heater, and appropriate thermal insulation. The crucible has a thin orifice hole on its bottom.

In this μ -PD system, the crystal is grown to the down direction from the bottom hole of the crucible, and the shape of grown crystal is decided by the shape of end-tip of the crucible. On this ground, we used two kinds of crucibles to grow two kind of shape of crystal: one is for fiber below 1.5 mm in diameter, and the other is rod having approximately 5 mm in diameter. Figure 1 also shows the illustration of the crucibles. Each crucible has a small central orifice hole about 0.3~0.4 mm in diameter and 1 mm in length.

Al_2O_3 (5N-purity, High-Purity Chemical Co.) and MgO (4N purity, Rare Metallic Co.) were used as starting materials in this study. There is only one eutectic composition between Al_2O_3 and MgO two component system, which is at 55 wt% Al_2O_3 and 45 wt% MgO , and its melting temperature is around 1995°C [14]. Starting materials therefore, were mixed to eutectic composition in mortar with ethanol and then dried in oven.

Sapphire <0001> fiber was used as a seed crystal. The meniscus and growing crystal were observed by CCD camera and monitor. The growths were performed under flowing Ar with 2 % O_2 gas atmosphere. The growing process was controlled by manual adjustment of RF power and growth rate.

$\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic fibers of 0.3~1.5 mm in diameter and up to 500 mm in length tried to grow over the range of growth speed of 6~120 mm/hr with conical

crucible. And rods of 5 mm in diameter and 50 mm in length also tried to grow with crucibles for rod growth as depicted in Fig. 1.

The grown eutectic crystals were characterized by XRD (Rigaku Co.), SEM (JEOL Co.) and EDS (Oxford Co.). Microstructure images were obtained from perpendicular polished cross-sections using the back-scattered emission (BE) of SEM.

The diameter stability of grown fiber was checked by measuring the diameter with micrometer at an interval of 1 inch for the stable growth region of fiber.

In order to prepare the porous body by selective etching of only MgO phase, acid treatment was carried out with hot 4 N hydrochloric acid for about 2 hours for the slices of eutectic crystal. The etched slices were characterized under SEM.

3. Results and Discussion

Two kind of shape of $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic crystals could be grown as shown in Fig. 2: one is fiber crystals of 0.5~1.5 mm of diameter and up to 500 mm in length, and the other is rod crystals about 5 mm of diameter and 60 mm in length. Stable growth was obtained in the range of 6~120 mm/hr. In the fiber growth, it was possible to control the fiber diameter from approximately 0.3 mm to 1.5 mm within 10 % of diameter stability. The maximum length of grown fibers was about 500 mm, limited by the apparatus.

Rods also could be grown in the range of 6~120 mm/hr, and their diameter could be controlled within 5 % of

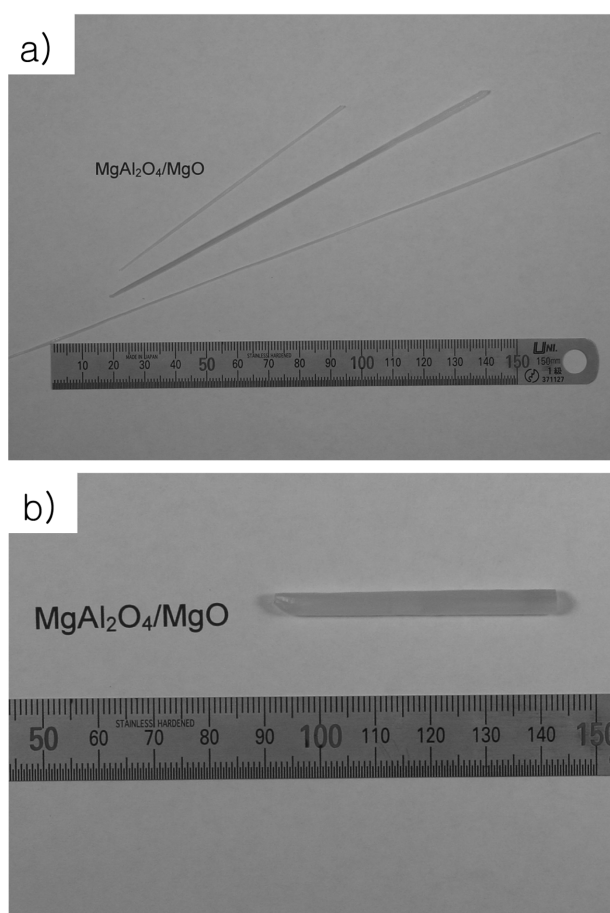


Fig. 2. As-grown $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic crystals: a) fibers, b) rod.

stability. The lengths of grown rods were about 60 mm depending on the charging amount of raw material.

As-grown $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic crystals were semi-transparent as observed visually and polishing the cross-sections increased the optical character closed to transparency. Figure 3 showed polished slice of 1 mm thick-



Fig. 3. Sliced and polished specimen of $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic.

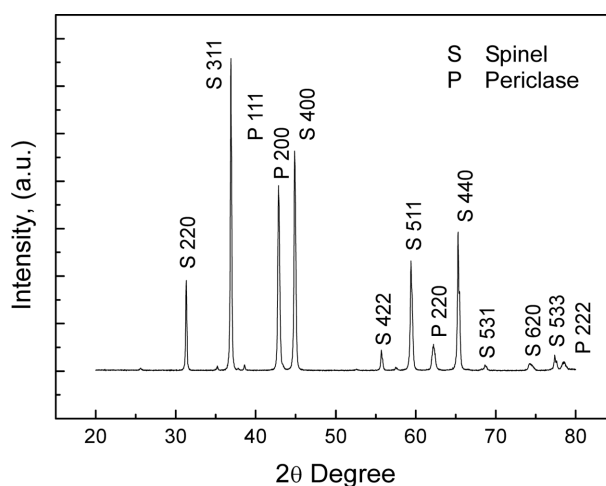


Fig. 4. XRD pattern of pulverized $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic.

ness of $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic rod crystal, which was cut to transverse cross-section to the growth direction and then polished. In general, eutectic crystals have not any transparency, because they have two or more phases having different refractive indices and complicate microstructures. From this point of view, $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic crystal showing semitransparency is a very unusual case and considered resulting from small deviation of refractive index and lattice misfit between two phases. Refractive index of these two materials is very similar (1.773 and 1.736 for MgO and MgAl_2O_4 respectively) [15]. 4 % of lattice misfit between two phases are also very small [16].

Figure 4 shows a powder XRD pattern of crushed $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic crystals. All phases were composed of crystalline MgAl_2O_4 (spinel) and MgO (periclase) and there was no any trace of other phases. To

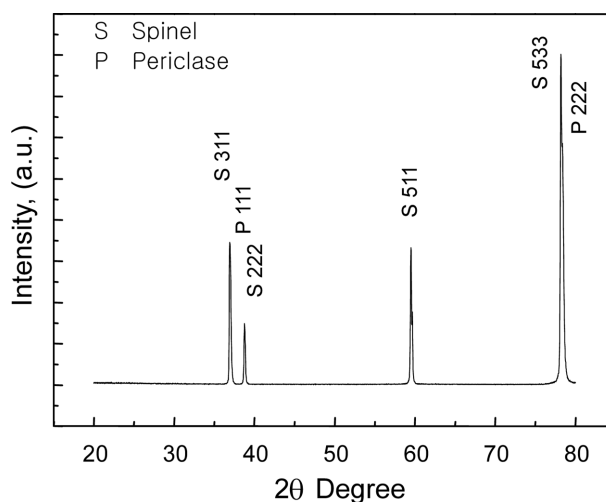


Fig. 5. XRD pattern of transverse cross-section of $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic rod.

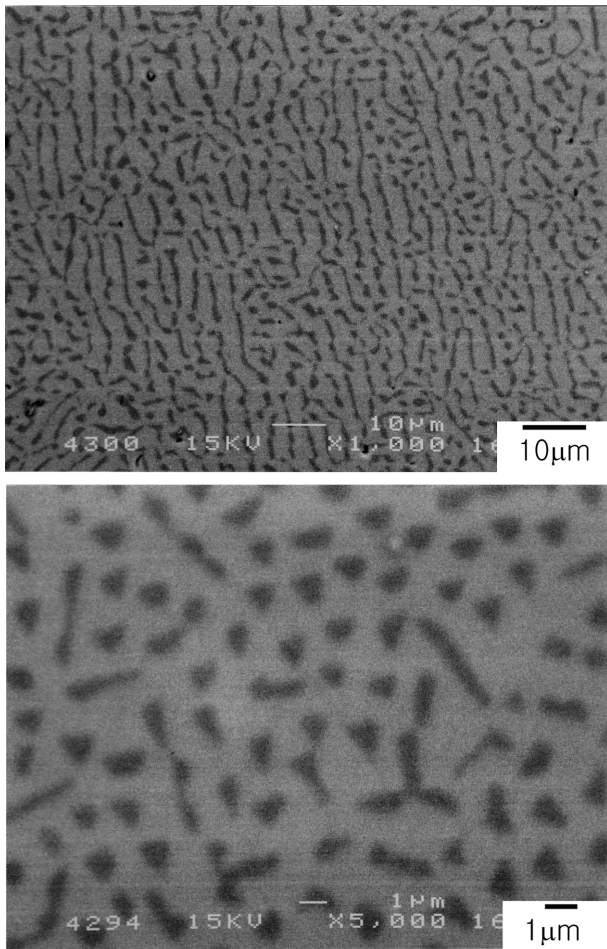


Fig. 6. SEM microstructure of transverse cross-section of $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic rod grown at 30 mm/hr of solidification speed.

determine the growth direction, XRD pattern was measured on the transverse section for the growth direction of rod crystal. The result plotted in Fig. 5 showed just only (111)-type reflections for both spinel and periclase, indicating that both phases grew in the respective [111] directions.

Typical microstructure and phase distribution of $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic crystals were as like Fig. 6. By EDS analysis, bright matrix was shown to MgAl_2O_4 and small and dark second phases were MgO in this micrographs. The eutectic microstructure was consisted of MgO fibers in a spinel matrix. The MgO fibers revealed roughly triangular shape in cross section although some of part they appeared elongated as like lamellar. Kennard *et al.* [11] reported that microstructure of $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic crystals changed from lamellar to colony pattern as the solidification rate was increased from 9 mm/hr to 89 mm/hr. In this work, triangular shape of MgO phase was obtained at the solidification speed of approxi-

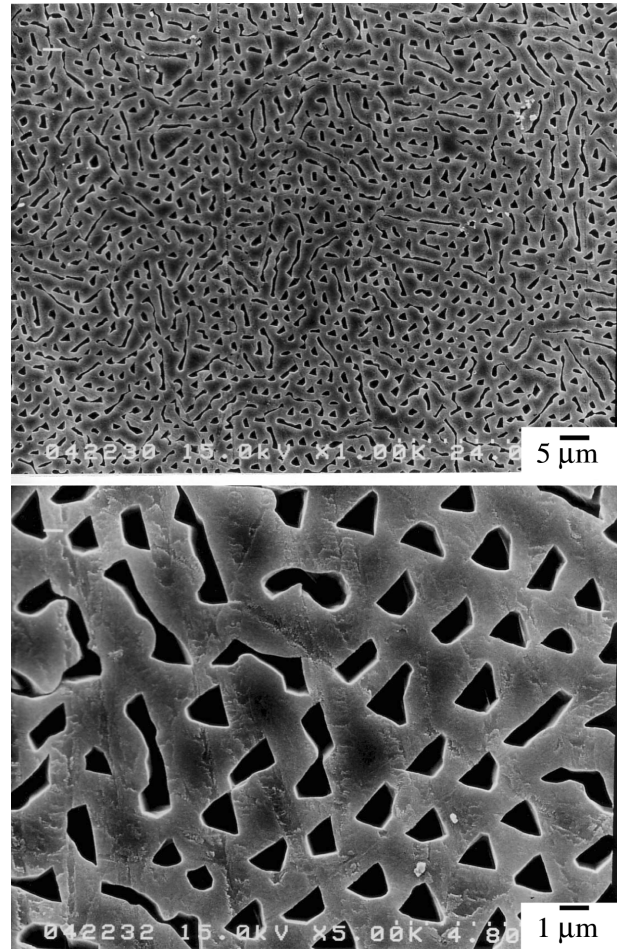


Fig. 7. SEM microstructure of sliced $\text{MgAl}_2\text{O}_4/\text{MgO}$ eutectic rod after selective etching.

mately 30 mm/hr.

The goal of this work is placed on the realization of porous crystal body which is having continuous pore channel with circular or close to circular shape. Hence, the rod crystal grown at 30 mm/hr of solidification rate was sliced and examined its etchability. The thickness of each slice was about 1 mm, and 4 N HCl was used as the etching agent. Etching was carried out for about 2 hrs under boiling.

Figure 7 showed the microstructure after etching. It was appeared that almost all MgO phases were removed by etching and it showed completely porous crystal body. It was supposed that this porous crystal body can be applied for new application such as catalyst or photonics devices after special treatment for open channel.

4. Conclusions

Novel process was tried to obtain micro-porous ceramic

body containing continuous pore channel. MgAl₂O₄/MgO eutectic crystals have been successfully grown by the micro-pulling-down method. The grown crystals showed semitransparency. Eutectic microstructure showed that periclase (MgO) fiber aligned in the spinel (MgAl₂O₄) matrix. The periclase fiber removed easily by 2 hrs etching with hot hydrochloric acid (HCl), and porous crystal bodies having continuous pore channel were obtained. It was supposed that this porous crystal body can be applied for new application such as catalyst or photonics devices after special treatment for open channel.

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