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Growth of $MgAl_2O_4$/MgO eutectic crystals by the micro-pulling-down method and its characterization

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Abstract

$MgAl_2O_4$/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. $MgAl_2O_4$/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/h of growth speed. The eutectic fibers showed homogeneous microstructure in which MgO fiber/whisker aligned to the growth direction in the $MgAl_2O_4$ (spinel) matrix. The grown crystals looked semitransparence under naked eyes. Optical and orientational characterizations were performed. The second phase of MgO was easily removed by selective etching with hydrochloric acid, and then porous single crystalline bodies were obtained.

Keywords: Microstructure; $MgAl_2O_4$/MgO eutectic crystal; Electron microscopy; Optical properties; Functional applications

1. Introduction

Directionally solidified eutectic crystals yield fine oriented particular microstructures with strong coherent bonding between component phases. 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 solidified 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 $Al_2O_3/GdAlO_3$,[3] $Al_2O_3/Y_3Al_5O_{12}$ (below abbreviated as YAG),[4,5] Al_2O_3/ZrO_2[6–9] and Al_2O_3/YAG/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. $MgAl_2O_4$/MgO[11,12] and ZrO_2/MgO[13] eutectic crystals yield a fibrous aligned microstructure in which fiber/whisker like MgO 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 $MgAl_2O_4$/MgO crystal by the micro-pulling-down (μ-PD) method, and tried to prepare the porous crystal body by selective etching the MgO fibrous phase for novel application such as photonics and catalyst devices.

2. Experimental procedure

Fig. 1 illustrates the micro-pulling-down (abbreviated to μ-PD in 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,

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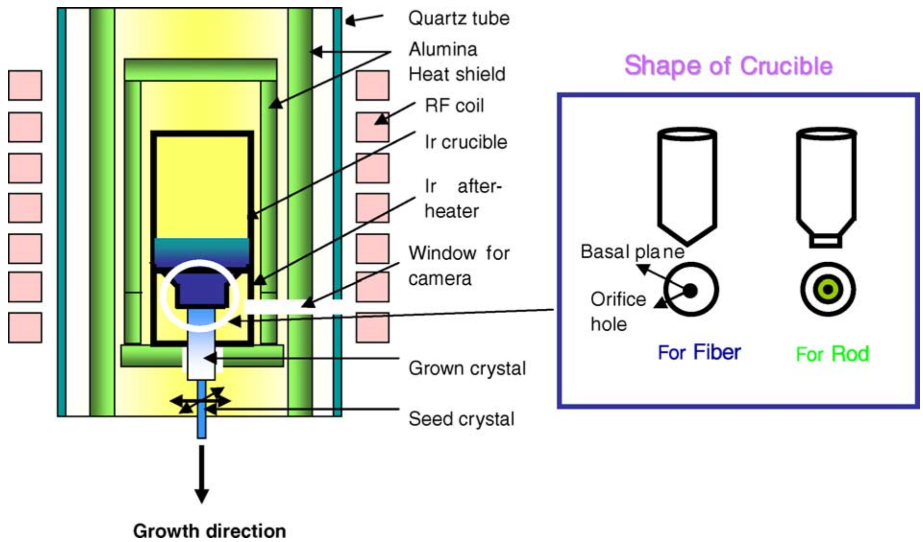

Fig. 1. Schematics of micro-pulling-down apparatus and the crucibles.

and appropriate thermal insulation. The crucible has a thin orifice hole on its bottom (end-tip).

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. Fig. 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 <0 0 0 1> 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.

$MgAl_2O_4$/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/h with cornical 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) and secondary electron (SE) modes of SEM.

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

In order to prepare the porous crystal body by selective etching of only MgO phase, acid treatment was carried out with 4N hydrochloric acid for about 2 h for the slices of eutectic crystal.

3. Results and discussion

Two kind of shape of $MgAl_2O_4$/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/h. 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/h, and their diameter could be controlled within 5% of stability. The lengths of grown rods were about 60 mm depending on the charging amount of raw material.

As-grown $MgAl_2O_4$/MgO eutectic crystals were semitransparent as observed visually and polishing the cross-sections increased the optical character closed to transparency. 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, $MgAl_2O_4$/MgO eutectic crystal showing semitransparency is a very unusual case. Fig. 3 showed polished slice of 1 mm thickness of $MgAl_2O_4$/MgO eutectic rod crystal, which was cut to transverse cross-section to the growth direction and then polished.

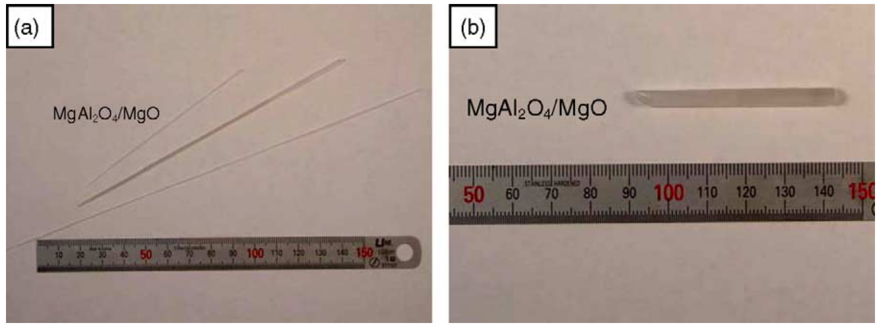

Fig. 2. As-grown $MgAl_2O_4$/MgO eutectic crystals: (a) fibers and (b) rod.

Fig. 3. Sliced $MgAl_2O_4$/MgO eutectic rod.

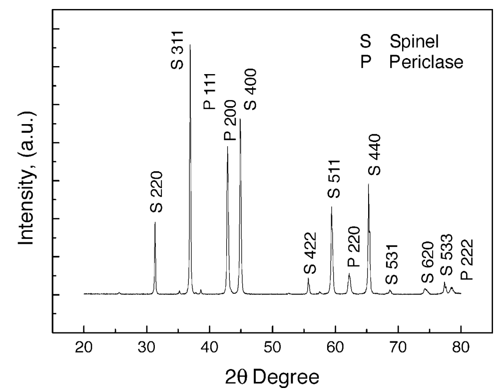

Fig. 4. XRD pattern of pulverized $MgAl_2O_4$/MgO eutectic crystal.

[Fig. 4](#) shows a powder XRD pattern of crushed $MgAl_2O_4$/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 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 (1 1 1)-type reflections for both spinel and periclase, indicating that both phases grew in the respective [1 1 1] directions.

Typical microstructure and phase distribution of $MgAl_2O_4$/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

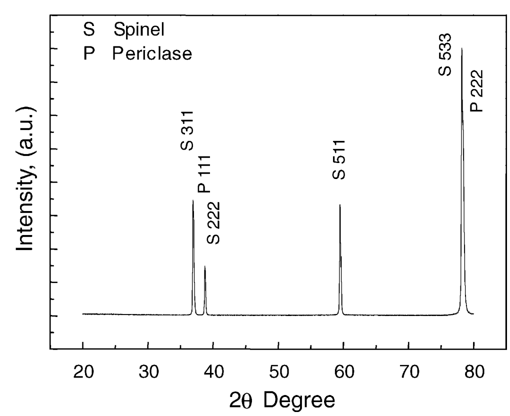

Fig. 5. XRD pattern of transverse cross-section of $MgAl_2O_4$/MgO eutectic rod.

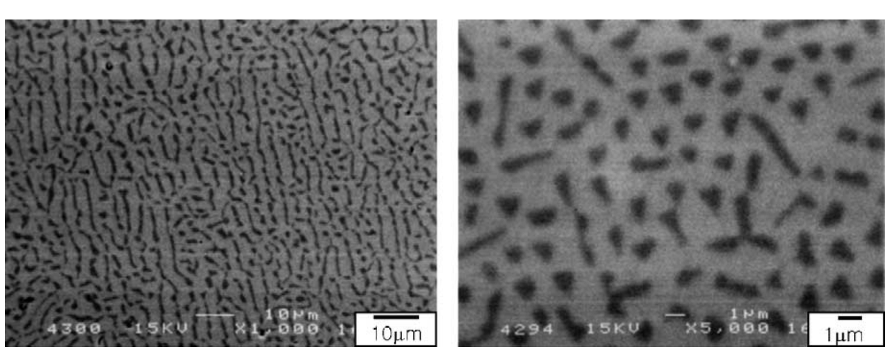

Fig. 6. SEM microstructure of transverse cross-section of $MgAl_2O_4$/MgO eutectic rod grown at 30 mm/h of solidification speed.

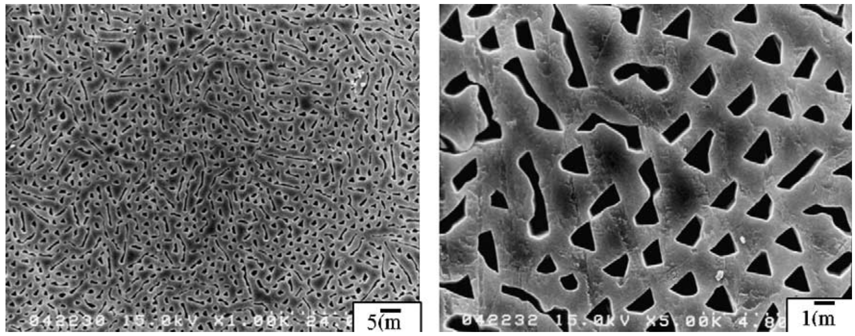

Fig. 7. SEM microstructure of sliced $MgAl_2O_4$/MgO eutectic rod after selective etching.

cross-section although some of part they appeared elongated as like lamellar. Kennard et al.[11] reported that microstructure of $MgAl_2O_4$/MgO eutectic crystals changed from lamellar to colony pattern as the solidification rate was increased from 9 mm/h to 89 mm/h. In this work, triangular shape of MgO phase was obtained at the solidification speed of approximately 30 mm/h.

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/h of solidification rate was sliced and examined its etchability. The thickness of each slice was about 1 mm, and 4N HCl was used as the etching agent. Etching was carried out for about 2 h under boiling.

Fig. 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

$MgAl_2O_4$/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 ($MgAl_2O_4$) matrix. The periclase fiber removed easily by 2 h etching with 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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References

1. Schmid, F. and Viechnicki, D., Oriented eutectic microstructures in the system Al_2O_3/ZrO_2. *J. Mater. Sci.*, 1970, **5**, 470–473.
2. Fischer, G. R., Manfredo, L. J., McNally, R. N. and Doman, R. C., The eutectic and liquidus in the Al_2O_3/ZrO_2 system. *J. Mater. Sci.*, 1981, **16**, 3447–3451.
3. Waku, Y., Nakagawa, N., Wakamoto, T., Ohtsubo, H., Shimizu, K. and Kohtoku, Y., A ductile ceramic eutectic composite with high strength at 1,873 K. *Nature*, 1997, **389**, 49–52.
4. Waku, Y., Nakagawa, N., Ohtsubo, H., Ohtsubo, H., Shimiz, K. and Kohtoku, Y., High-temperature strength and stability of a unidirectionally solidified Al_2O_3/YAG eutectic composite. *J. Mater. Sci.*, 1998, **33**, 1217–1225.
5. Yoshikawa, A., Epelbaum, B. M., Fukuda, T., Suzuki, K. and Waku, Y., Growth of $Al_2O_3/Y_3Al_5O_{12}$ eutectic fiber by micro-pulling-down method and its high-temperature strength ans thermal stability. *Jpn. J. Appl. Phys.*, 1999, **38**, L55–L58.
6. Ando, T. and Shiohara, Y., Metastable alumina structures in melt-extracted alumina–25 wt.% zirconia and alumina–42 wt.% zirconia ceramics. *J. Am. Ceram. Soc.*, 1991, **74**, 410–417.
7. Lee, J. H., Yoshikawa, A., Durbin, S. D., Yoon, D. H., Fukuda, T. and Waku, Y., Microstructure of Al_2O_3/ZrO_2 eutectic fibers grown by the micro-pulling-down method. *J. Cryst. Growth*, 2001, **222**, 791–796.
8. Lee, J. H., Yoshikawa, A., Kaiden, H., Fukuda, T., Yoon, D. H. and Waku, Y., Microstructure of Y_2O_3 doped Al_2O_3/ZrO_2 eutectic fibers by the micro-pulling-down method. *J. Cryst. Growth*, 2001, **231**, 179–185.
9. Sayir, A. and Farmer, S. C., The effect of the microstructure on mechanical properties of directionally solidified $Al_2O_3/ZrO_2(Y_2O_3)$ eutectic. *Acta Mater.*, 2000, **48**, 4691–4697.
10. Lee, J. H., Yoshikawa, A., Fukuda, T. and Waku, Y., Growth of Al_2O_3/YAG/ZrO_2 ternary eutectic fibers and microstructure. *J. Cryst. Growth*, 2001, **231**, 115–120.
11. Kennard, F. L., Bradt, R. C. and Stubican, V. S., Eutectic solidification of MgO–$MgAl_2O_4$. *J. Am. Ceram. Soc.*, 1973, **56**, 566–569.
12. Kennard, F. L., Bradt, R. C. and Stubican, V. S., Mechanical properties of the directionally solidified MgO–$MgAl_2O_4$ eutectic. *J. Am. Ceram. Soc.*, 1976, **59**, 160.
13. Kennard, F. L., Bradt, R. C. and Stubican, V. S., Directional solidification of the ZrO_2–MgO eutectic. *J. Am. Ceram. Soc.*, 1974, **57**, 428–431.
14. Alper, A. M., Mcnally, R. N., Ribbe, P. H. and Doman, R. C., The system MgO–$MgAl_2O_4$. *J. Am. Ceram. Soc.*, 1968, **45**(6), 263–268.