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Microstructure and mechanical properties of $Al_2O_3/Y_3Al_5O_{12}/ZrO_2$ ternary eutectic materials

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Abstract

Directionally solidified fibers and rods have been grown from the ternary $Al_2O_3/Y_3Al_5O_{12}/ZrO_2$ system using micro-pulling-down method. Fiber diameter could be varied 0.3 mm–2 mm at pull-rates ranging 6–900 mm/h and 500 mm in length. The ternary eutectic fibers had homogeneous colony patterned eutectic microstructures. The interlamellar spacing λ exhibited an inverse-square-root dependence on the growth speed v according to $\lambda = 8 \times v^{-1/2}$, where λ has the dimension of μm and v is in μm/s. The tensile strength was recorded 1730 MPa at 25 °C and 1100 MPa at 1200 °C for a fiber crystals grown at a growth speed of 900 mm/h. Eutectic rods having 5 mm of diameter and up to 80 mm in length were also successfully grown by the micro-pulling-down method. The eutectic rods showed 1400 MPa of mechanical strength by compressive mode at 1500 °C with homogeneous colony microstructures.

Keywords: Microstructures; Strength; Structural application; Ternary eutectic

1. Introduction

Since early 1960s, systematic investigations of oxide eutectics began and considerable research has been devoted to the structure and properties of these eutectics. However, real attention focused on these directionally solidified oxide eutectics from 1990s when their high structural stability up to nearly the melting temperature was reported.[1]

Late 1990s, promising results were reported for the Al_2O_3-based binary eutectic systems such as $Al_2O_3/GdAlO_3$,[1] $Al_2O_3/Y_3Al_5O_{12}$ (below abbreviated as YAG)[2–5] and Al_2O_3/ZrO_2.[6–10] Among them, Al_2O_3/YAG eutectic crystal showed a homogeneous 'Chinese Script' lamellar pattern. Eutectic fiber crystals grown by the micro-pulling-down (μ-PD) method yielded an great improvement in the mechanical properties.[5] The eutectic microstructures depended on the growth speed and their interlamellar spacing had an inverse-square-root relation to the growth speed.[11]

Since the beginning of new century, researches on the eutectic materials shifted from Al_2O_3-based binary to ternary system. Lee et al.[12–14] investigated microstructural changes and preliminary mechanical properties of Al_2O_3/ZrO_2 binary and $Al_2O_3/YAG/ZrO_2$ ternary eutectic crystal fibers as a function of solidification rate using μ-PD method. All the eutectic crystal fibers grown by μ-PD method showed much greater mechanical strength than bulk crystal grown by the conventional method.

μ-PD method demonstrated its excellent feasibility in not only eutectic fiber crystals growth but also the other various single crystal fibers, and it has also good potential for bulk crystal growth. In this study, therefore, bulk growth of $Al_2O_3/YAG/ZrO_2$ ternary eutectic crystal has been tried by μ-PD via simple modification of the crucible. Microstructural and preliminary mechanical characterizations were carried out for the grown bulk crystals.

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2. Experimental procedure

The μ-PD apparatus used in this study consisted of an iridium crucible coupled with an RF induction heating module, a cylindrical iridium after-heater, and appropriate thermal insulation, as described in Fig. 1. The crucible has a thin orifice hole on its bottom (end-tip).

In this μ-PD method, crystal is grown to the down direction from the bottom of the crucible, and the shape of grown crystal is decided by the shape of end-tip of the crucible. The end-tip, therefore, has a role of shaper for growing crystal. For that reason, we modified the shape of the end-tip of crucibles so that bulk crystals having over 3 mm of diameter can be grown. The modifications of the crucible were performed by twice to improve the diameter and the quality of grown crystals. Fig. 2 shows the illustration of the crucibles. In Fig. 2, crucible (a) is for the rod crystal having 3 mm in diameter, and crucible (b) for 5 mm in diameter. Each crucible has a central capillary hole about 0.3–0.4 mm in diameter and 1 mm in length.

Al_2O_3/YAG/ZrO_2 eutectic fiber crystal was used as a seed. The meniscus and growing crystal were observed by CCD

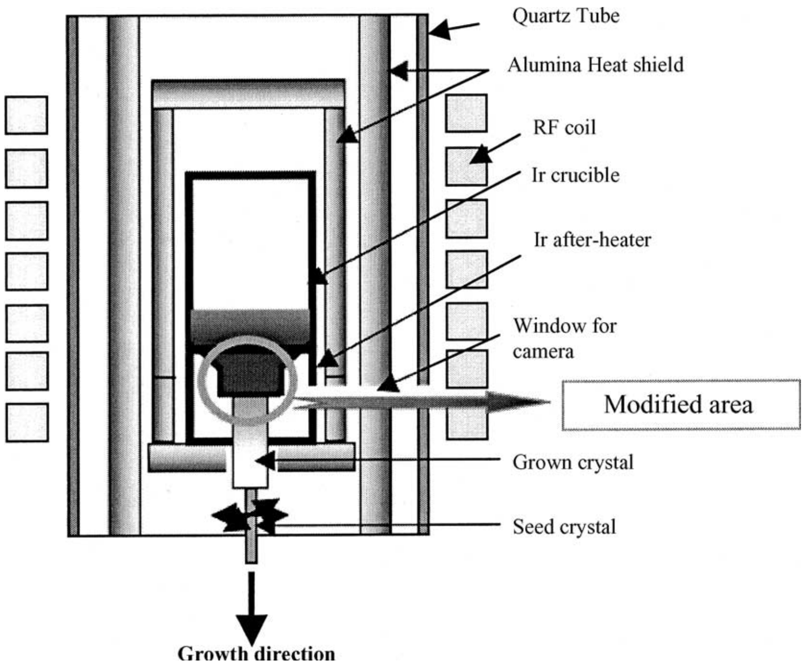

Fig. 1. Schematics of micro-pulling-down apparatus.

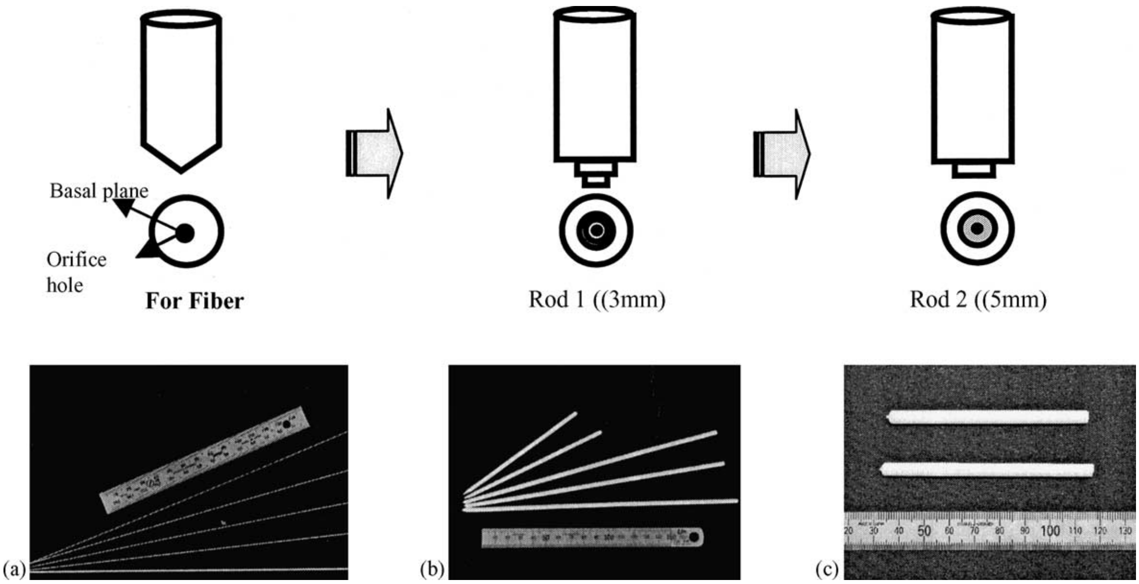

Fig. 2. Illustration of modification of the crucibles and as-grown Al_2O_3/YAG/ZrO_2 ternary eutectic crystals.

camera and monitor. The growth was performed under flowing Ar gas atmosphere. The growth process was controlled by manual adjustment of RF power and pulling rate.

5-N-purity Al_2O_3 (High-Purity Chemical Co.), 4-N purity ZrO_2 (Rare Metallic Co.) and 4-N purity Y_2O_3 (Nippon Yttrium Co.) were used for the starting materials. There are several ternary eutectic compositions in the system Al_2O_3 (alumina), Y_2O_3 (yttria) and ZrO_2 (zirconia). But only one point is for the alumina, YAG and zirconia ternary system, which is placed on the 65 mol% Al_2O_3, 19 mol% ZrO_2 and 16 mol% Y_2O_3, and its melting temperature is 1715 °C.[15] Hence, starting materials were mixed to ternary eutectic composition of alumina, YAG and zirconia.

Al_2O_3/YAG/ZrO_2 eutectic fibers of 0.3–1.0 mm in diameter and up to 500 mm in length tried to grow over the range of growth speed of 6–900 mm/h with cornical crucible. And also rod-shaped bulk crystals having 3–5 mm in diameter tried to grow with modified crucibles as depicted in Fig. 2.

The grown ternary eutectic crystals were characterized by XRD, SEM, energy dispersive spectroscopy (EDS), electron backscatter pattern (EBSP). Microstructure images were obtained from perpendicular polished cross-sections using the back-scattered emission (BE) and secondary electron (SE) modes of SEM. The intercellular spacings were evaluated on the chosen line on the perpendicular cross section to the growth direction.

To investigate the mechanical properties of the grown eutectic crystals, we examined the tensile strength for the fiber crystals using a universal testing machine (UTM) with crosshead speed of 0.5 mm/min at room temperature in air and high temperatures of 800, 1200 and 1500 °C in Ar atmosphere. Specimen length was approximately 200 mm. For the bulk crystals, compressive strength tests were performed at high temperature region from 1400 to 1600 °C in Ar atmosphere. Specimen dimension for the compressive strength test was 2 mm × 2 mm × 5 mm.

3. Results and discussion

The real melting temperature of Al_2O_3/YAG/ZrO_2 ternary eutectics measured in this experiment was 1720 ± 30 °C. As-grown Al_2O_3/YAG/ZrO_2 ternary eutectic fibers and some bulk crystals had an almost white color as shown in Fig. 2.

In the fiber growing, stable growth was obtained in the range of 6–900 mm/h with the comical crucible. It was possible to control the fiber diameter from approximately 0.3 to 2 mm within 5% of diameter stability. The maximum length was about 500 mm, limited by the apparatus.

In the bulk growing with the crucibles for rod crystal, stable growth was obtained in the growth speed below 120 mm/h. The crystals up to 3 mm in diameter and over 200 mm in length could be grown by the crucible (b) in Fig. 2. Using the crucible (c) in Fig. 2, the crystal having 5 mm in diameter and 80 mm in length could be grown successfully. The grown crystals by these modified crucibles showed diameter stability within 5%. Fig. 2 shows also some of as-grown crystals.

Back scattered electron images (BEI) of the microstructures observed from Al_2O_3/YAG/ZrO_2 ternary eutectic fiber crystals in perpendicular cross-section are shown in Fig. 3.

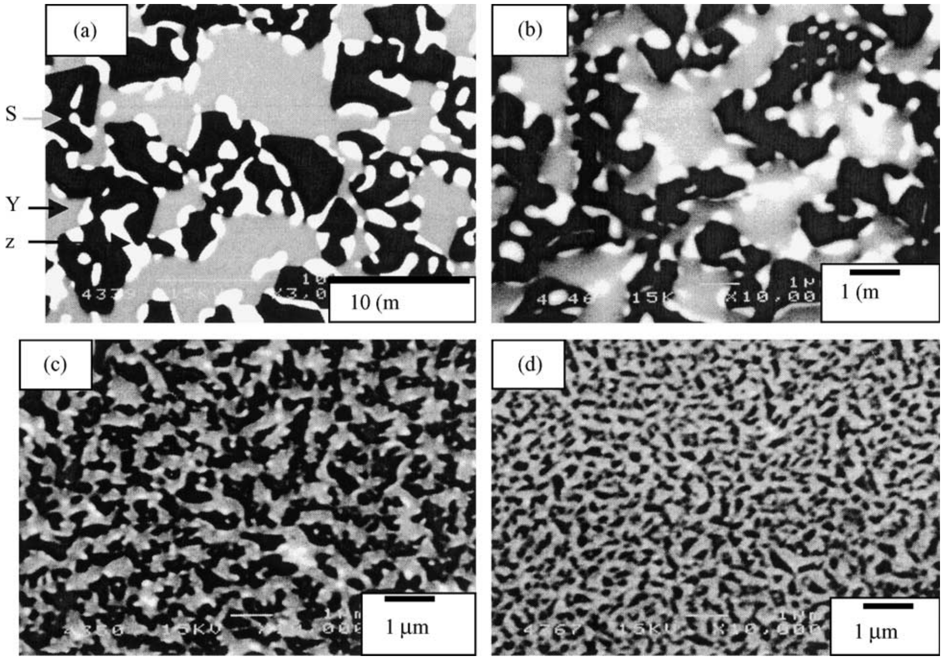

Fig. 3. Back scattered images of perpendicular cross-section of ternary eutectic fibers grown at various growth speed: (a) 6 mm/h, (b) 60 mm/h, (c) 300 mm/h and (d) 600 mm/h.

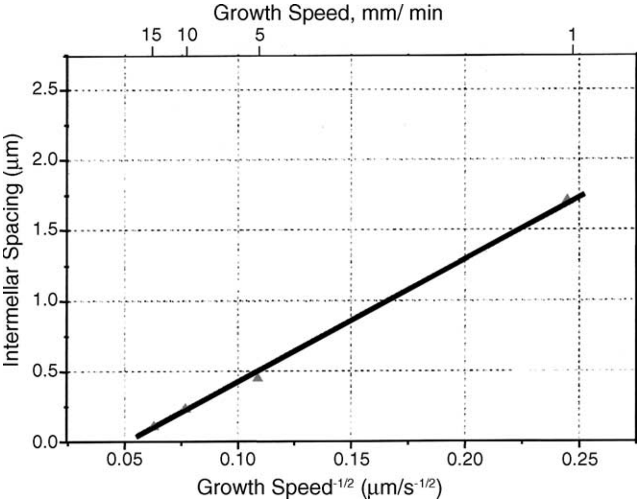

Fig. 4. Change of Interlamellar spacing of Al_2O_3/YAG/ZrO_2 ternary eutectic crystals as the function of growth speed.

Fig. 3(a) shows the typical phase distribution of Al_2O_3/YAG/ZrO_2 ternary eutectics grown at 6 mm/h of growth speed. The eutectic microstructure was composed of three phases distinguished by their different shapes and colors. By EDS analysis, the black matrix was shown to be Al_2O_3, and the gray colored second phase was YAG. ZrO_2 regions were distributed on the periphery of the YAG phase as relatively small particles that appear white in the micrograph.

Both YAG and ZrO_2 phases in the ternary eutectics showed different morphology than in their respective Al_2O_3-based binary eutectic systems.[11–13] Especially the particle-shaped ZrO_2 grains had a very different shape from their lamellar or cellular pattern in Al_2O_3/ZrO_2 eutectic fibers.[12,13] It could be observed that neighboring YAG grains were connected to each other, but the ZrO_2 particles were scattered.

The eutectic microstructure changed its size with growth speed, but not its shape, which was different from observations in Al_2O_3/ZrO_2 binary eutectics.[13,16] At lower growth speed, below 30 mm/h, the YAG phase showed an irregular shape with varying size, as shown in Fig. 3, but at growth speed over 60 mm/h, the interconnection between YAG grains got thick and the microstructure changed to ‘Chinese Script’ pattern with regular shape and size. The script size of the YAG phase was found to be uniform for each cross-section investigated.

The interlamellar spacing, i.e. script size decreased from 1.7 to approximately 200 nm as the growth speed increased from 60 to 900 mm/h in Fig. 4. The general relation $\lambda \sim v^{-1/2}$, where λ is the interlamellar spacing, and v is the solidification rate (growth speed), could also be applied to the script size of Al_2O_3/YAG/ZrO_2 ternary eutectics.

The proportionality constant is close to 8, if λ is in μm and v is in μm/s. This value is intermediate between 10 for Al_2O_3/YAG[11] and 1 for Al_2O_3/ZrO_2 binary eutectics.[12]

Fig. 5 shows the SEM microstructures of perpendicular cross-section of Al_2O_3/YAG/ZrO_2 ternary eutectic bulk crystal having 5 mm in diameter and grown at 30 mm/h of growth speed. Homogeneous ‘Chinese Script’ patterns could be seen on the whole cross-section observed from edge to core part. Microstructural homogeneity however, became worse with increasing the growth speed. At the growth speed of 60 mm/h, although major part of cross-section showed ‘Chinese Script’ pattern, some of part revealed not ‘Chinese Script’ pattern but ‘Geometric’ pattern as like Fig. 6.

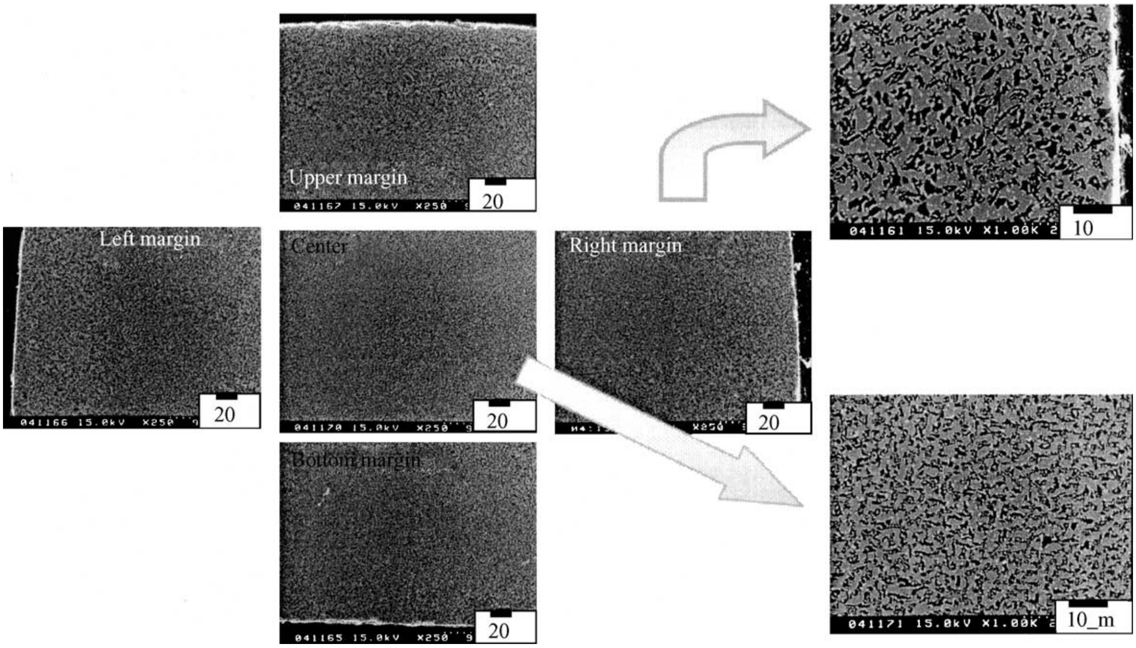

Fig. 5. SEM microstructure of perpendicular cross-section eutectic bulk crystals grown at 30 mm/h of growth speed.

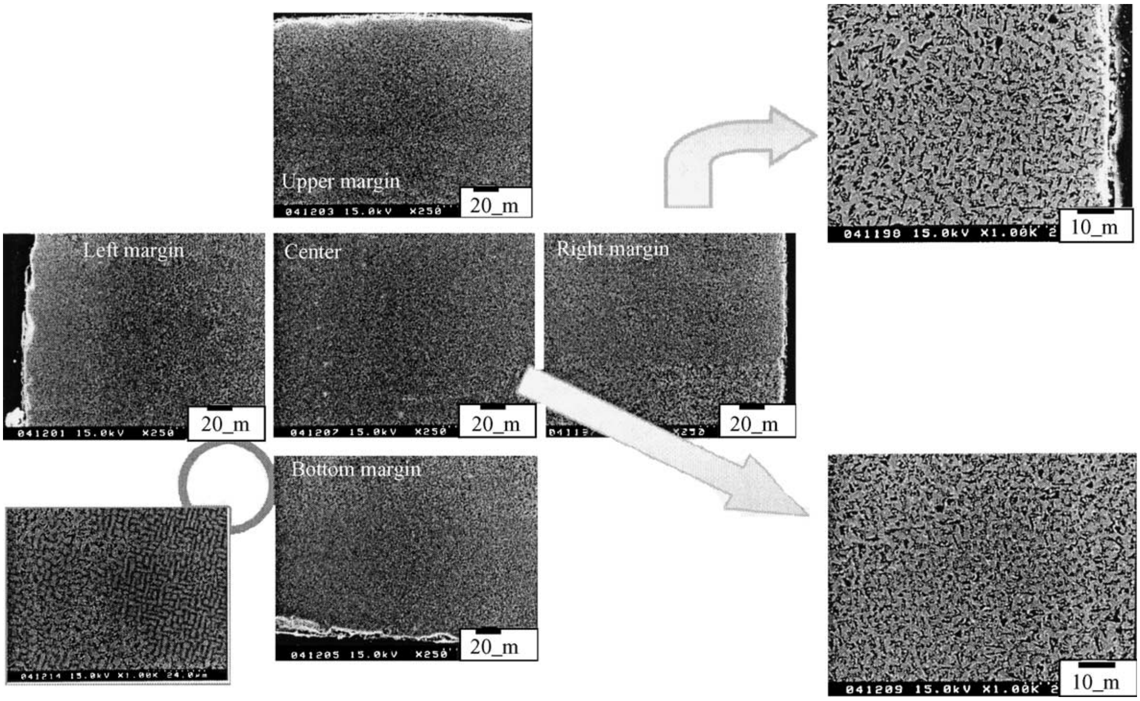

Fig. 6. SEM microstructure of perpendicular cross-section of Al_2O_3/YAG/ZlO_2 ternary eutectic bulk crystals grown at 60 mm/h of growth speed.

As the growth speed increased to 120 mm/h, microstructural disorder went from bad to worse. 'Geometric' pattern was prevailed to almost half of the cross-sectional area, and at some of edge part, the traces of microstructural collapse were observed as like Fig. 7.

To examine the orientational properties, both 'Chinese Script' and 'Geometric' patterned part were tested by electron back scatter pattern (EBSP) and pole figure for the perpendicular cross section to the growth direction. Fig. 8 showed EBSP and pole figure for the 'Chinese Script' patterned part. From this result, we could understand that matrix phase of sapphire oriented to ⟨30–30⟩ direction, and zirconia phase oriented to ⟨0 0 1⟩ direction, but YAG phase showed two kind of direction of ⟨8 0 0⟩ and ⟨1 1 1⟩. The reason why only YAG

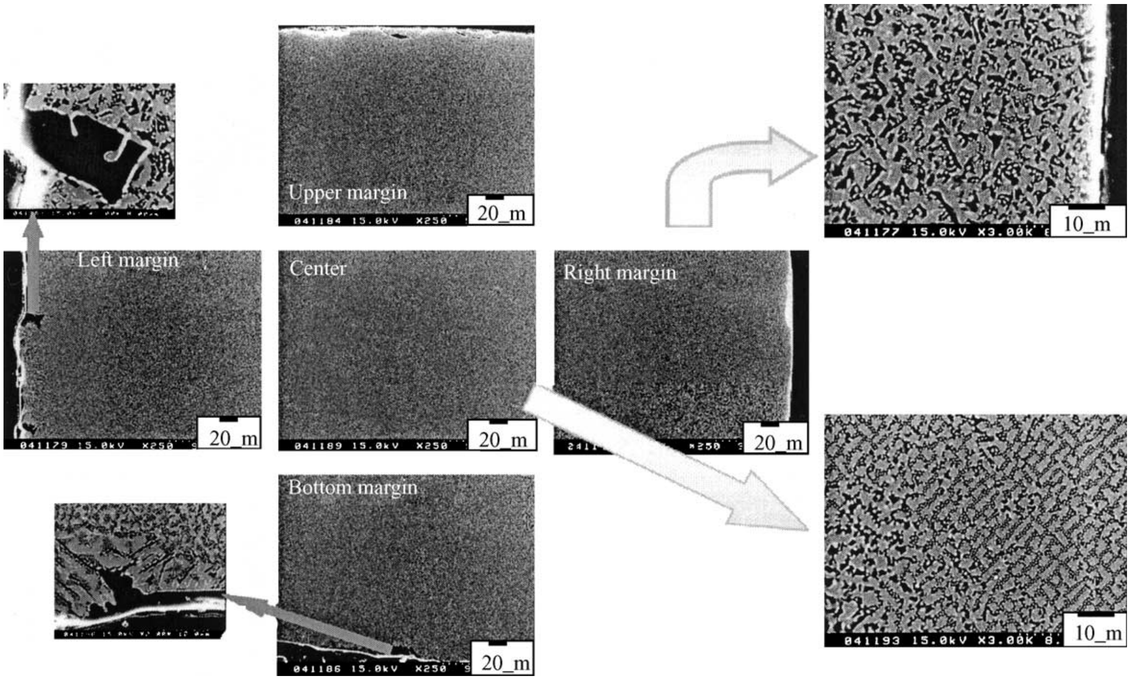

Fig. 7. SEM microstructure of perpendicular cross-section of Al_2O_3/YAG/ZrO_2 ternary eutectic bulk crystals grown at 120 mm/h of growth speed.

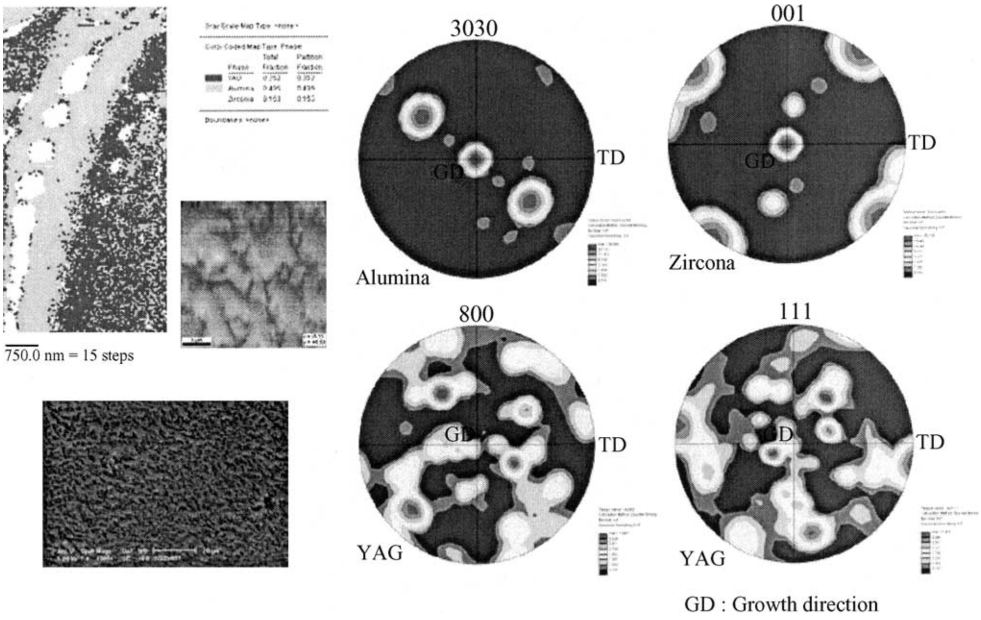

Fig. 8. EBSP and pole figures of ‘Chinese Script’ patterned area.

phase showed two kinds of orientations is not clear yet, and further investigation is going on.

EBSP and pole figure for ‘Geometric’ patterned area showed all three components oriented two kinds of orientation; ⟨30–30⟩ and ⟨0 0 0 1⟩ for sapphire, ⟨0 0 1⟩ and ⟨2 2 0⟩ for zirconia, and ⟨8 0 0⟩ and ⟨1 1 1⟩ for YAG as shown in Fig. 9.

In order to examine the mechanical properties of the grown Al_2O_3/YAG/ZrO_2 eutectic crystals, tensile strength tests were carried out for the fiber crystals, and compressive strength tests were performed for the bulk crystals. Tensile strength tests were performed for the eutectic fibers grown at the growth speed of 900 mm/h at various temperatures from room temperature to 1500 °C.

As shown in Fig. 10, the highest strength was 1730 MPa at room temperature; the strength diminished only slightly with temperature until it decreased drastically to 350 MPa at 1500 °C, due to the proximity of its melting temperature. The measured strength of Al_2O_3/YAG/ZrO_2 ternary eutectic fibers are much higher than the Al_2O_3/YAG and Al_2O_3/ZrO_2

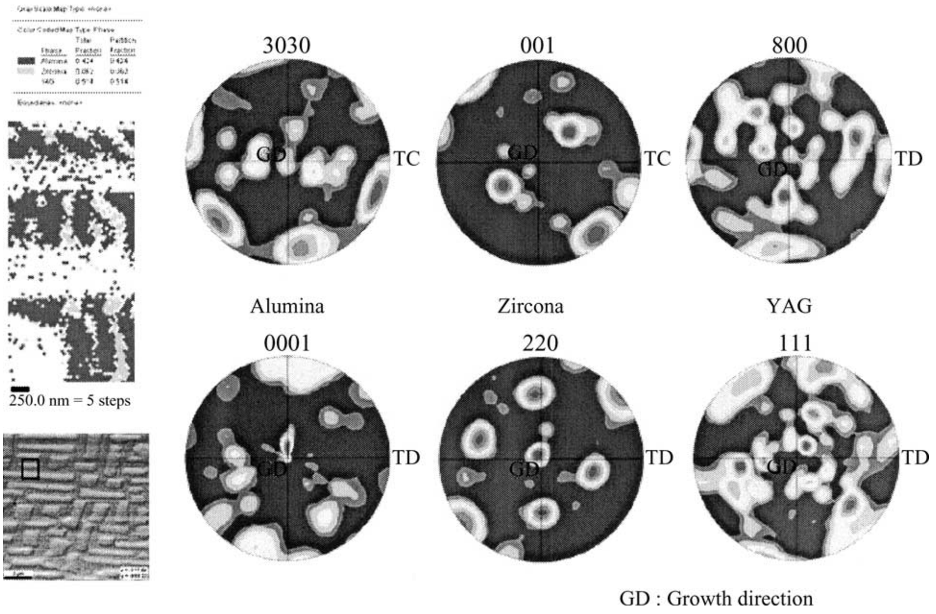

Fig. 9. EBSP and pole figures of ‘Geometric’ patterned area.

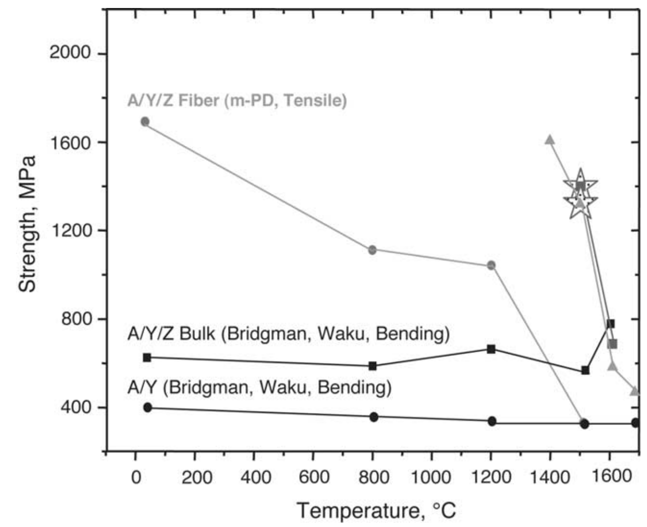

Fig. 10. Mechanical strengths of Al_2O_3/YAG/ZrO_2 ternary eutectic crystals at the various temperatures.

binary one[11,12] over the whole range of tested temperature except for 1500 °C. It is assumed that higher strength of the ternary eutectic fibers over Al_2O_3/YAG resulted from both the strengthening effect of ZrO_2 and the smaller script size.

Strength tests for the bulk crystals were examined at 1400–1600 °C. 1400 MPa of excellent compressive strength were recorded at 1500 °C and then decreased drastically to700 MPa at 1600 °C.

4. Conclusions

Al_2O_3/YAG/ZrO_2 ternary eutectic fiber and bulk crystals have been grown successfully by the micro-pulling-down method, and their microstructural and some mechanical properties were investigated. Fiber diameter could be varied 0.3–2 mm at pull-rates ranging 6–900 mm/h and 500 mm in length. The ternary eutectic fibers had homogeneous colony patterned eutectic microstructures. The interlamellar spacing, λ fitted well the inverse-square-root dependence on the pulling rate, v according to $\lambda = 8v^{-1/2}$, where λ is in μm and v is in μm/s.

The optimum growth speed for bulk growth of eutectic crystals having 5 mm diameter by the micro-pulling-down method was estimated about 30 mm/h at the state-of-the art hot zone configuration. The grown bulk crystals showed homogeneous colony patterned microstructure as like fiber crystal. The grown bulk crystals recorded 1400 MPa of compressive strength at 1500 °C.

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