

Microstructure and high temperature mechanical properties of sapphire/R-Al-O (R = Y, Gd, Er, Ho, Dy) eutectic fibers grown by micro-pulling-down method

K. Hasegawa, A. Yoshikawa, S.D. Durbin, B.M. Epelbaum, T. Fukuda and Y. Waku*

Institute for Materials Research, Tohoku University, Katahira 2-1-1 Sendai 980-8577, Japan

**Japan Ultra-high Temperature Materials Research Center, Ube 755-0001, Japan*

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Abstract Fiber growth of Al₂O₃/R-Al-O (R = Y, Gd, Dy, Ho, Er) eutectic by the micro-pulling down method is described. The thermal stability and strength at elevated temperature of each material is evaluated in relation to the microstructure.

1. Introduction

Structural materials which have a tensile strength of at least 1000 MPa at temperatures above 1500°C, in air, are required for applications in such fields as aerospace and thermal power generation, but are not yet realized in practice. Carbon-based or Graphite-based materials are strong at room temperature, but cannot be used above 650°C in an oxidizing atmosphere. For most brittle materials, the strength decreases proportionally to the 2/3 power of T/T_{melt}. Recently, directionally solidified ceramic eutectics have been investigated for potential use as structural materials at elevated temperatures. In 1997 Waku *et al.* [1] reported that sapphire/YAG and sapphire/GdAlO₃ eutectic composites have high strength at elevated temperatures, as well as excellent thermal stability. In addition, Yoshikawa *et al.* [2], Epelbaum *et al.* [3] demonstrated fiber growth of these materials. In this paper, we report on our studies of these and related new fiber-form eutectics, which have improved mechanical properties and would be used in reinforced composites.

2. Experimental

2.1. Starting materials and compositions

The starting materials were Al₂O₃ (5 N purity), Y₂O₃ (4 N), and Gd₂O₃ (3 N) produced by 'High-Purity Chemicals Co.', and Dy₂O₃ (4 N), Ho₂O₃ (4 N), and Er₂O₃ (4 N) produced by 'Nippon Yttrium Co.'. These powders were dried, weighted in proper proportions and mixed directly in the crucible. The compositions used are listed in Table 1.

Table 1
Eutectic compositions

sapphire/Y ₃ Al ₅ O ₁₂	81.3 mol% Al ₂ O ₃ and 18.7 mol% Y ₂ O ₃
sapphire/GdAlO ₃	77 mol% Al ₂ O ₃ and 23 mol% Gd ₂ O ₃
sapphire/Dy ₃ Al ₅ O ₁₂	81 mol% Al ₂ O ₃ and 18 mol% Dy ₂ O ₃
sapphire/Ho ₃ Al ₅ O ₁₂	81 mol% Al ₂ O ₃ and 18 mol% Ho ₂ O ₃
sapphire/Er ₃ Al ₅ O ₁₂	81 mol% Al ₂ O ₃ and 18 mol% Er ₂ O ₃

2.2. Fiber growth assembly and procedure

Sapphire/R-Al-O (R = Y, Gd, Dy, Ho, Er) eutectic fibers were grown by the micro-pulling-down (μ -PD) method from an iridium crucible with a 275 μ m ϕ hole, as shown schematically in Fig. 1. Induction heating at a frequency of 5 kHz, specially designed for the fabrication of crystals and composites at high temperature (above 1800°C), was applied. The fibers were grown in Ar atmosphere (gas flow 2 l/min) to avoid oxidation of the crucible. This apparatus is described in greater detail in Yoshikawa *et al.* [2].

2.3. Evaluation techniques

Microstructures were investigated using a scanning electron microscope (SEM, Japan Electron) and a transmission electron microscope (TEM, Japan Electron), and a RAD-type X-ray diffractometer (XRD, Rigaku). The thermal phase stability of the microstructure was investigated by scanning electron microscope (SEM, Japan Electron).

Tensile stress-displacement tests were carried out such that the applied tension was parallel to the fiber axis (pulling direction). Tests were conducted at a strain rate of 10⁻⁴ Ns⁻¹, in air at room temperature and in vac-

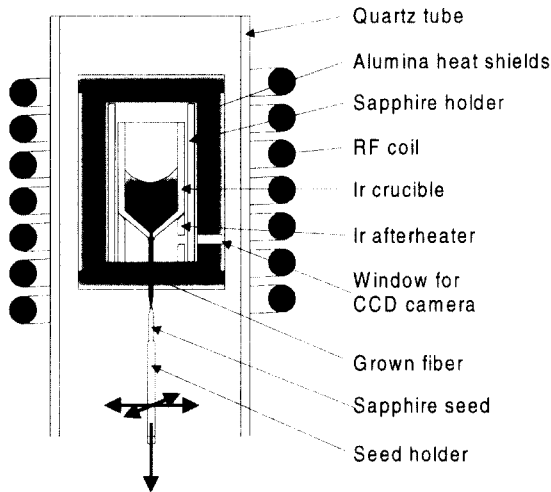


Fig. 1. Schematic of micro-pulling-down (μ -PD) method for high temperature.

uum at 1500°C. The tests were carried out using the high-temperature uniaxial tension-compression facility at Japan Ultra-high Temperature Materials Research Center.

3. Results and discussion

3.1. Microstructure

Figure 2 shows some of the fibers obtained. Typical diameters are around 200 μ m, and lengths are about 500 mm. We have achieved pulling rates up to 28 mm/min. The fibers show excellent flexibility. Figure 3 shows the powder X-ray diffraction patterns of each composition grown. Since all peaks are sharp and could be indexed, we conclude that these eutectic fibers have a crystalline microstructure and contain no significant impurities.

Figure 4 shows a backscattered electron image (BEI) of the fiber microstructure. We found that the microstructure, which forms a three-dimensional interpenetrating network, can be controlled via the growth rate; higher growth rate yields finer domains. According to Petch's relation $\sigma_c = \sigma_0 + kd^{-1/2}$, where σ is strength and d is microstructure size, finer microstructure, should give stronger fibers. But because of the relation between temperature gradient, growth velocity, and growth stability, there is a limit to the pulling speed. For further refinement, we must find new eutectic materials which have smaller microstructure at a given pulling speed. Figure 5 shows the relation between pulling rate and microstructure size for each material studied. We obtained the smallest microstructure with sapphire/GdAlO₃ eutectic. But sapphire/GdAlO₃

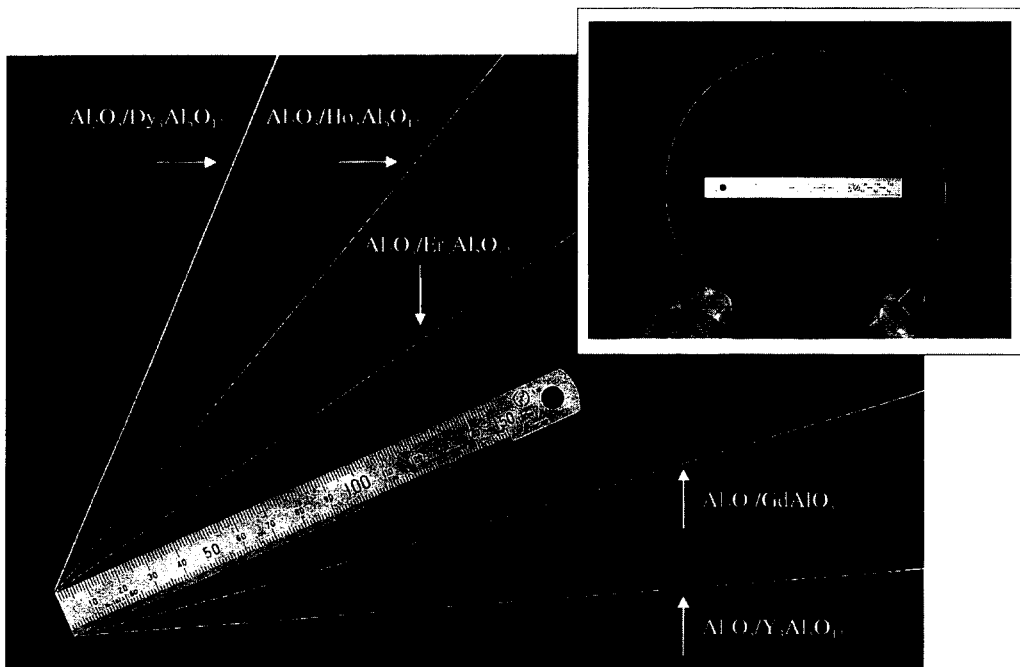


Fig. 2. Eutectic sapphire/R-Al-O (R = Y, Gd, Dy, Ho, Er) fibers.

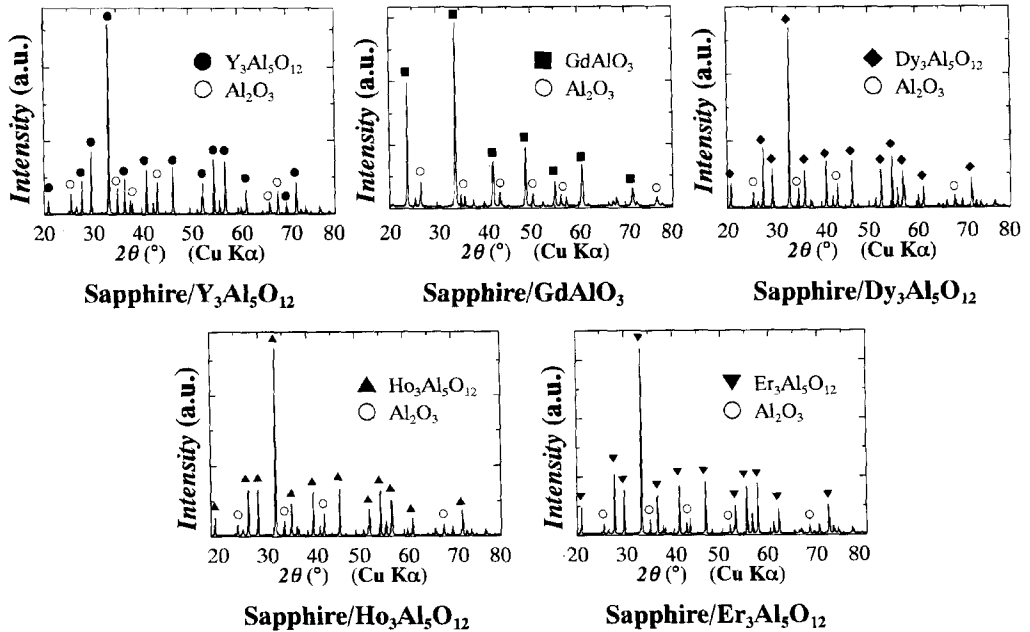


Fig. 3. Powder XRD pattern of eutectic fibers.

eutectic has some problems; it easily lost growth stability and is very sensitive to compositional inhomogeneity. Garnet materials are relatively easy to grow, and most of them showed nearly the same microstructure size.

3.2. Thermal stability of microstructure

Figure 6 shows BEI of the microstructure for fibers as-grown and after heat treatment at 1500°C in air atmosphere 25 h and 75 h. Sapphire/Y₃Al₅O₁₂ showed

fine thermal stability, but, with sapphire/Dy₃Al₅O₁₂, grain growth was observed. This means that sapphire/Dy₃Al₅O₁₂ may not maintain its strength for a long time at high temperature. We are now further studying this difference in thermal stability.

3.3. Strength

Table 2 shows tensile strength data for our eutectic fibers and several reference materials. The fibers were several times stronger than bulk material at both R.T. and 1500°C. Sapphire/Dy₃Al₅O₁₂ was the strongest

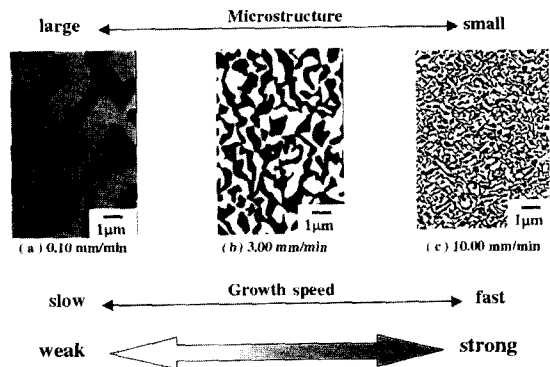


Fig. 4. Backscattered electron images (BEI) of cross sections of sapphire/YAG fibers grown at different rates. (Dark region: sapphire, bright region: YAG).

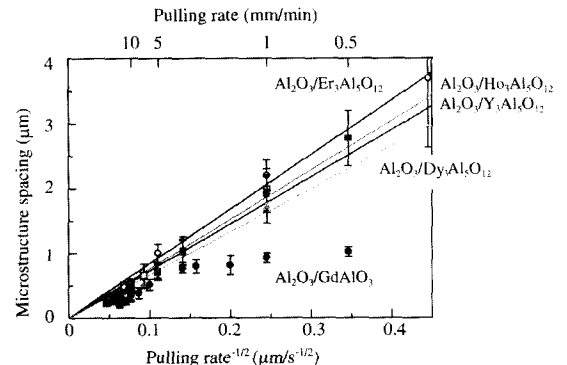


Fig. 5. Relation between microstructure spacing (average domain width) and pulling rate.

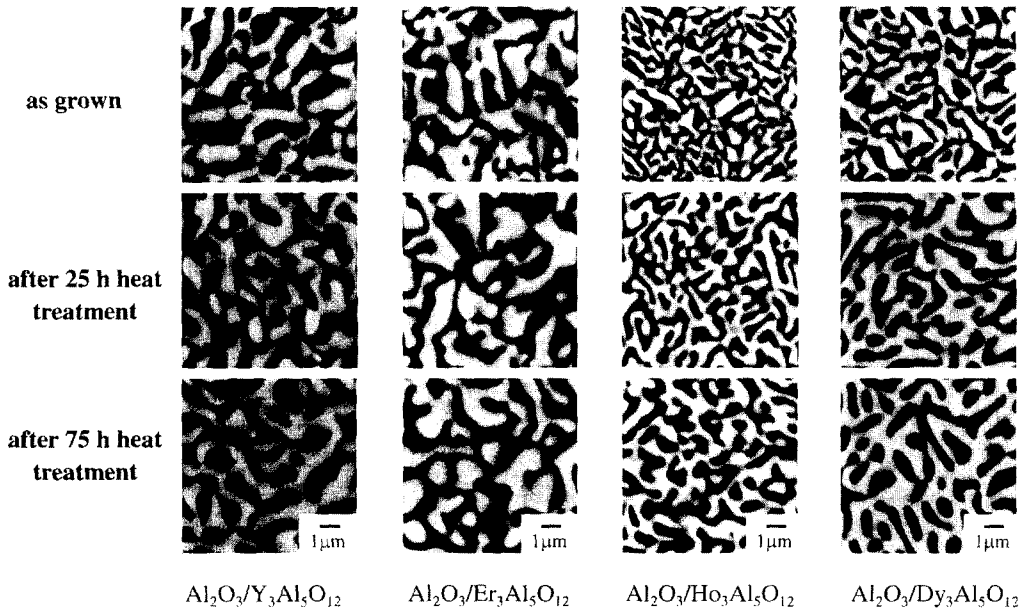


Fig. 6. Backscattered electron images (BEI) before and after heat treatment of eutectic fiber samples at 1500°C in air. (Dark region: sapphire, bright region: R-Al-O).

Table 2
Tensile strength of eutectic fibers and reference materials

composition	growth velocity	temperature °C	tensile strength MPa (R.T.)
Al ₂ O ₃ /Y ₃ Al ₅ O ₁₂ fiber	20 mm/min	1500	576.5 (927.3)
Al ₂ O ₃ /Dy ₃ Al ₅ O ₁₂ fiber	15 mm/min	1500	563.9 (926.3)
Al ₂ O ₃ /Y ₃ Al ₅ O ₁₂ fiber	15 mm/min	1500	552.1 (910.5)
Al ₂ O ₃ /Ho ₃ Al ₅ O ₁₂ fiber	15 mm/min	1500	551.2 (910.7)
Al ₂ O ₃ /Er ₃ Al ₅ O ₁₂ fiber	15 mm/min	1500	541.2 (883.7)
Al ₂ O ₃ /Y ₃ Al ₅ O ₁₂ bulk (Bridgman)	5 mm/hour	1500	150 (200)
Si ₃ N ₄ bulk		1350	200
Hi-Nicalon SiC/SiC composite		1350	50~150
Porous Nextel 720		1200	200
Mullite/Mullite composite			

among the eutectic fibers grown at a given pulling rate. Other materials cannot be used above 1500°C. Figure 7 suggest the mechanism of the high tensile strength of eutectics at elevated temperature, in comparison with sintered material. Since sintered composite don't melt completely in the manufacturing process, there seems to be amorphous material in the boundary area. At high temperature, grain growth will occur and the material cracks at this weak boundary area. But in the case of eutectic fibers grown by the μ-PD method, materials melt completely in the process, and grains do not grow easily. Such materials break through the grains. Consequently, the eutectic material has

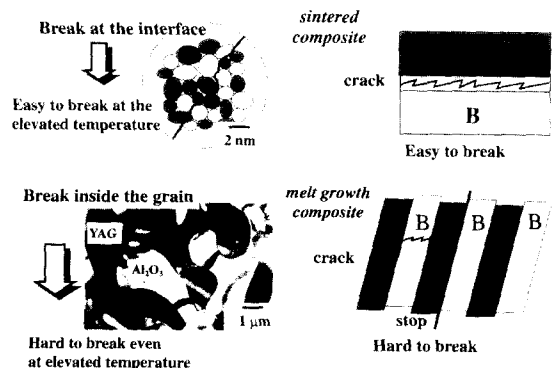


Fig. 7. Mechanism of the high tensile strength.

high strength at elevated temperature.

4. Conclusions

Eutectic fibers of sapphire/R-Al-O (R = Y, Gd, Dy, Ho, Er) have been grown by the micro-pulling-down method. Microstructure can be controlled by the pulling-down speed and by substitution of the rare earth element. Obtained fibers were several times stronger than that of bulk at both R.T. in air and 1500°C in vacuum. Among grown fibers, sapphire/Dy₃Al₅O₁₂ eutectic fiber showed the smallest microstructure and the strongest mechanical property.

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Reference

- [1] Y. Waku *et al.*, Nature 389 (1997) 49.
- [2] A. Yoshikawa *et al.*, Jpn. J. Appl. Phys. Vol. 38 (1999) L1623.
- [3] B.M. Epelbaum *et al.*, J. Cryst. Growth 198/199 (1999) 471.