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], A. Yoshikawa[a], S. Durbin[a], B. Epelbaum[a], T. Fukuda[a] and Y. Waku[b]

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

[b]Japan Ultra-high Temperature Materials Research Center, Ube, 755-0001, Japan

Abstract

Fiber growth of Al_2O_3/ 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.

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KEYWORDS : eutectic, fiber crystal growth, micro pulling down method, microstructure

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* Corresponding author. E-mail address : hase@lexus.imr.tohoku.ac.jp

1. Introduction

Structural materials which have a tensile strength of at least 1000MPa 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/$GdAlO_3$ 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 Al_2O_3 (5N purity), Y_2O_3 (4N), and Gd_2O_3 (3N) produced by 'High-Purity Chemicals Co.', and Dy_2O_3 (4N), Ho_2O_3 (4N), and Er_2O_3 (4N) 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.

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 μmϕ 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 vacuum 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 200μm, and lengths are about 500mm. 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 $\sigma_s=\sigma_o+kd^{-1/2}$, 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/$GdAlO_3$ eutectic. But sapphire/$GdAlO_3$ 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 25h and 75h. Sapphire/$Y_3Al_5O_{12}$ showed fine thermal stability, but, with sapphire/$Dy_3Al_5O_{12}$, grain growth was observed. This means that sapphire/$Dy_3Al_5O_{12}$ 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

Figure 7 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/$Dy_3Al_5O_{12}$ was the strongest among the eutectic fibers grown at a given pulling rate. Other materials cannot be used above 1500°C. Figure 8 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 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/$Dy_3Al_5O_{12}$ eutectic fiber showed the smallest microstructure and the strongest mechanical property.

Acknowledgment

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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.

Figure captions

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

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

Fig. 3. Powder XRD pattern of eutectic fibers.

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.

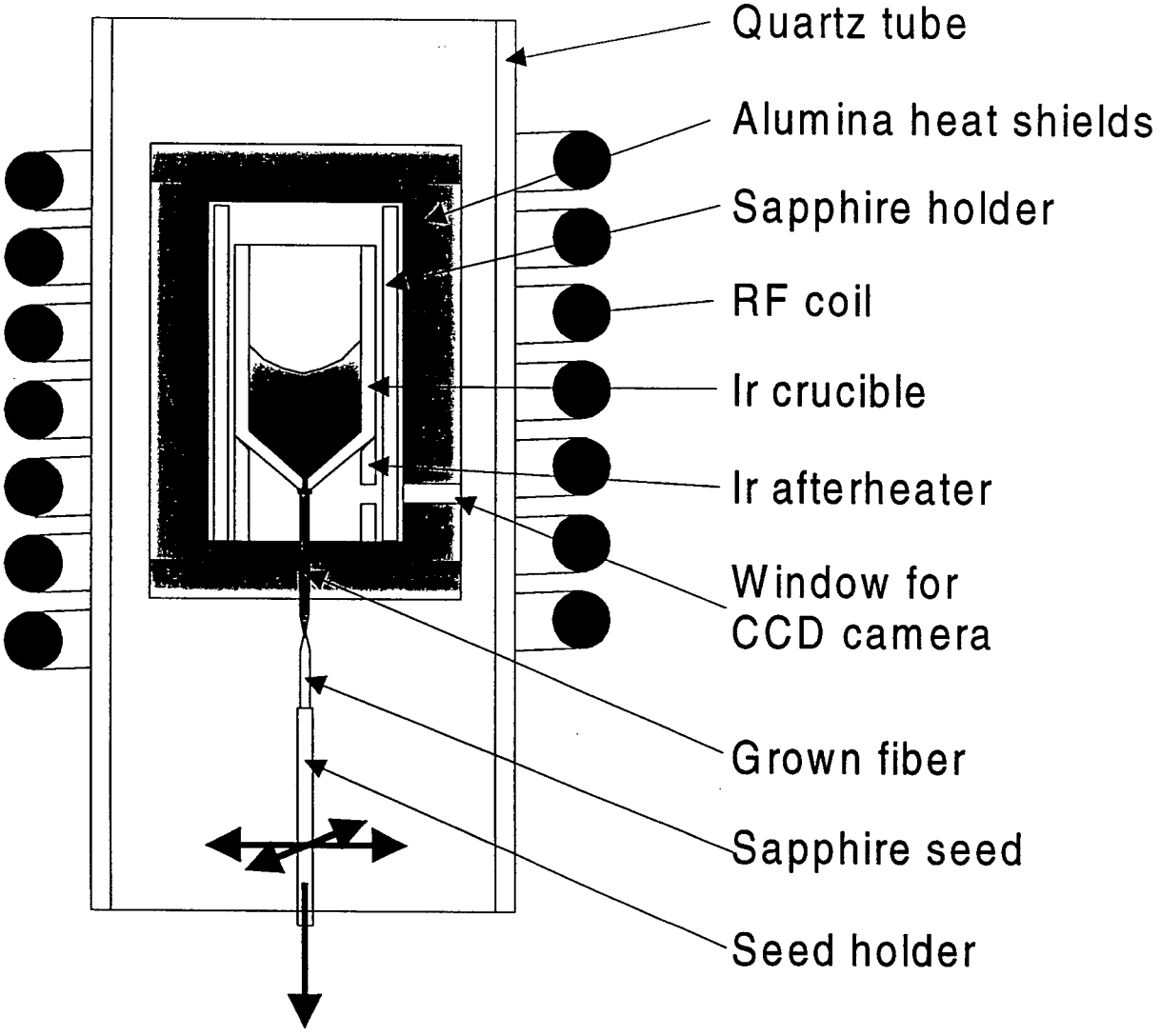
Fig. 6. Backscattered electron images (BEI) before and after heat treatment of eutectic fiber samples at 1500 °C in air. (Dark region : sapphire, bright region : R-Al-O).

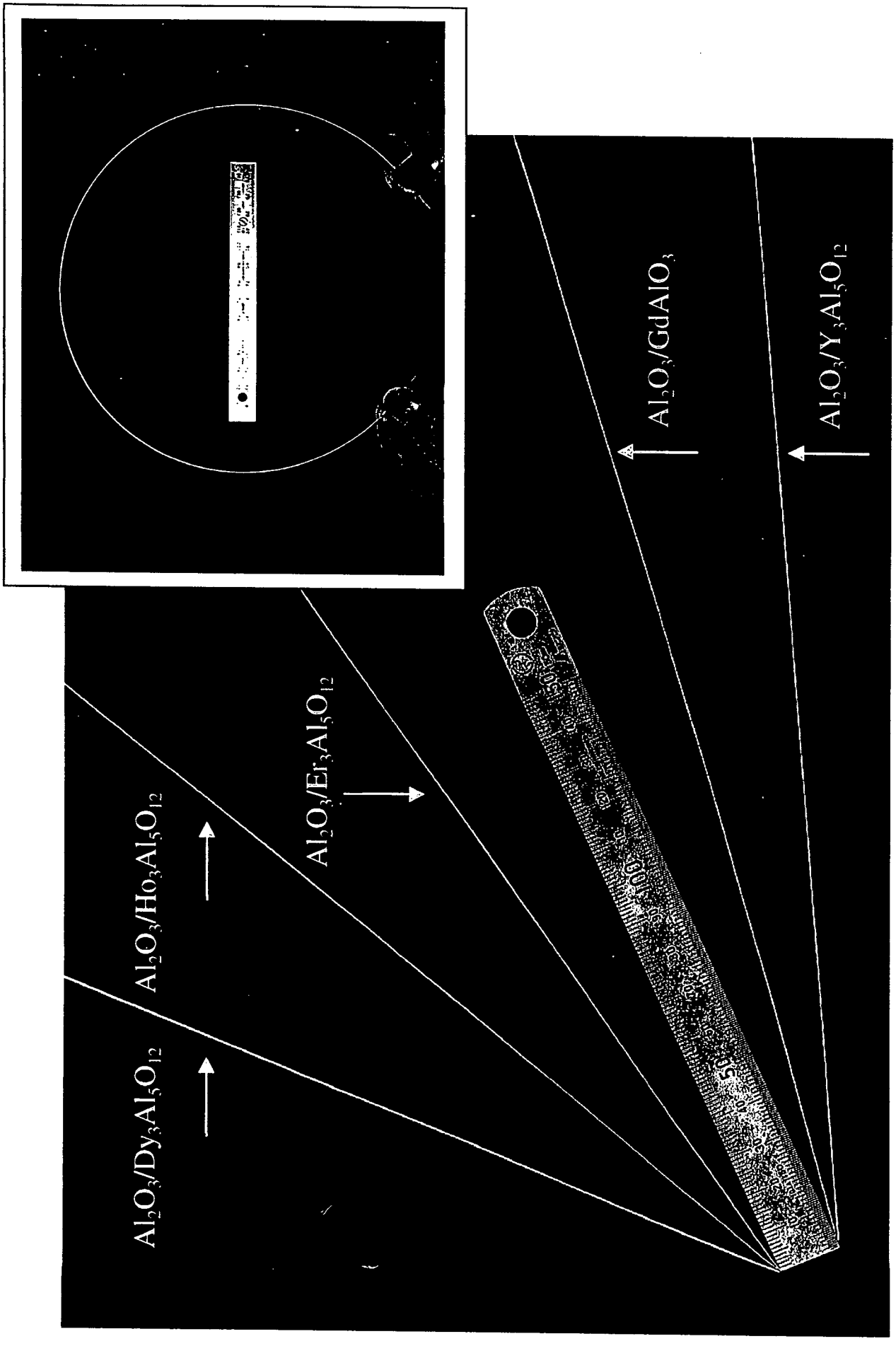
Fig. 7. Tensile strength of eutectic fibers and reference materials.

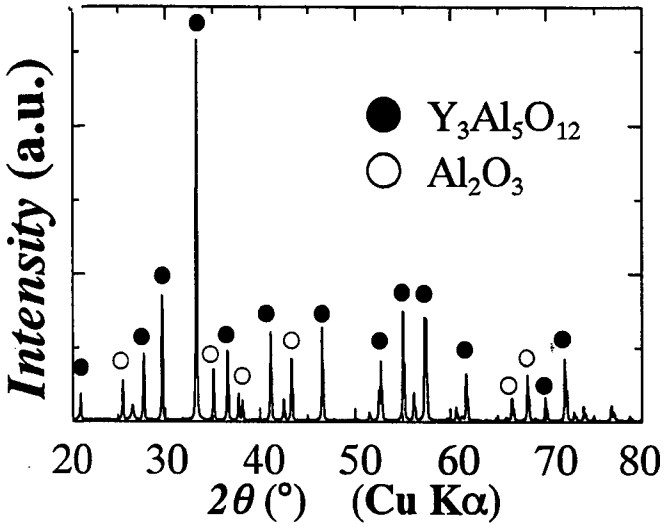
Fig. 8. Mechanism of the high tensile strength.

Table caption

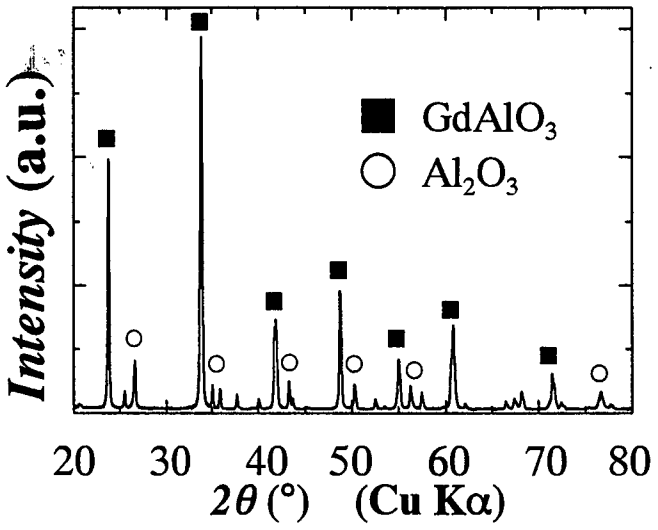
Table 1. Eutectic compositions


Quartz tube
Alumina heat shields
Sapphire holder
RF coil
Ir crucible
Ir afterheater
Window for CCD camera
Grown fiber
Sapphire seed
Seed holder

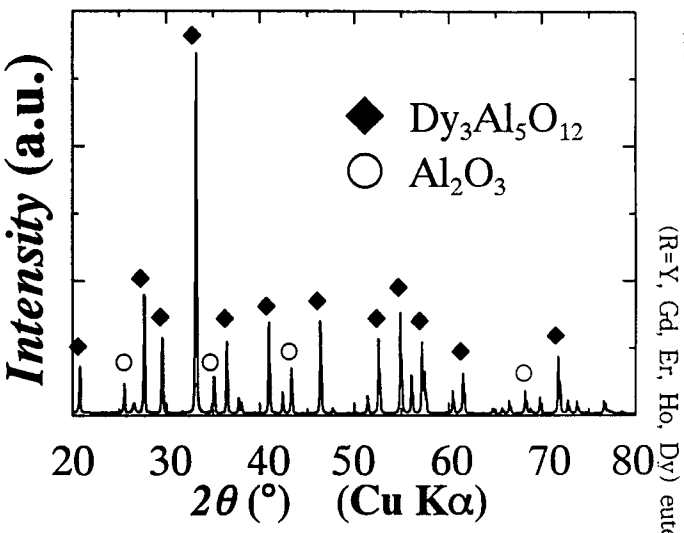

$Al_2O_3/Dy_3Al_5O_{12}$
$Al_2O_3/Ho_3Al_5O_{12}$
$Al_2O_3/Er_3Al_5O_{12}$
$Al_2O_3/GdAlO_3$
$Al_2O_3/Y_3Al_5O_{12}$



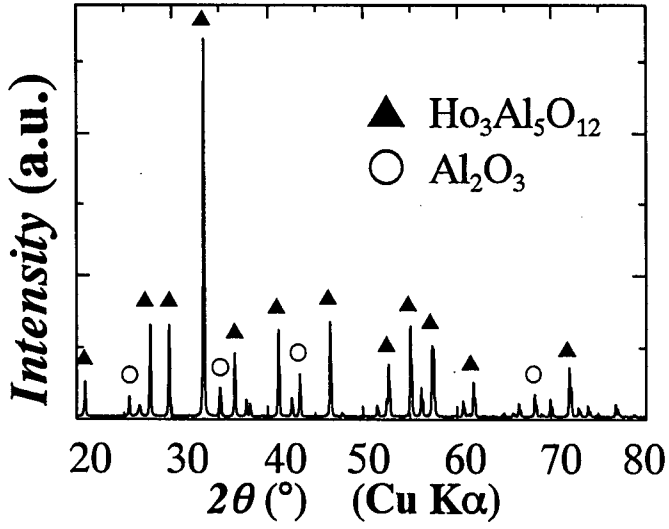
Sapphire/$Y_3Al_5O_{12}$



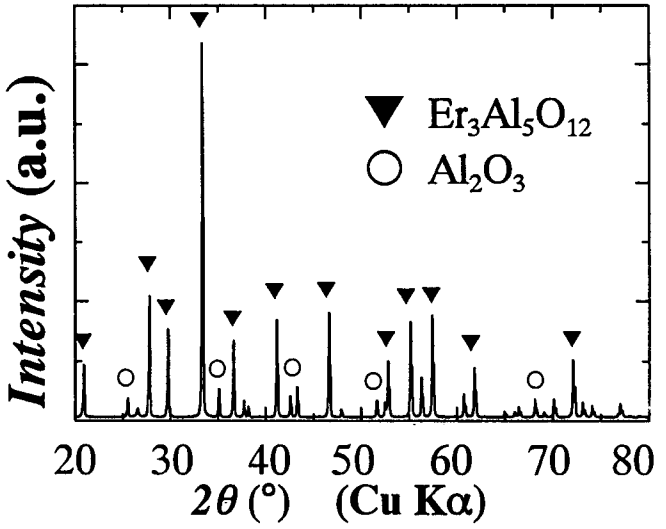
Sapphire/$GdAlO_3$



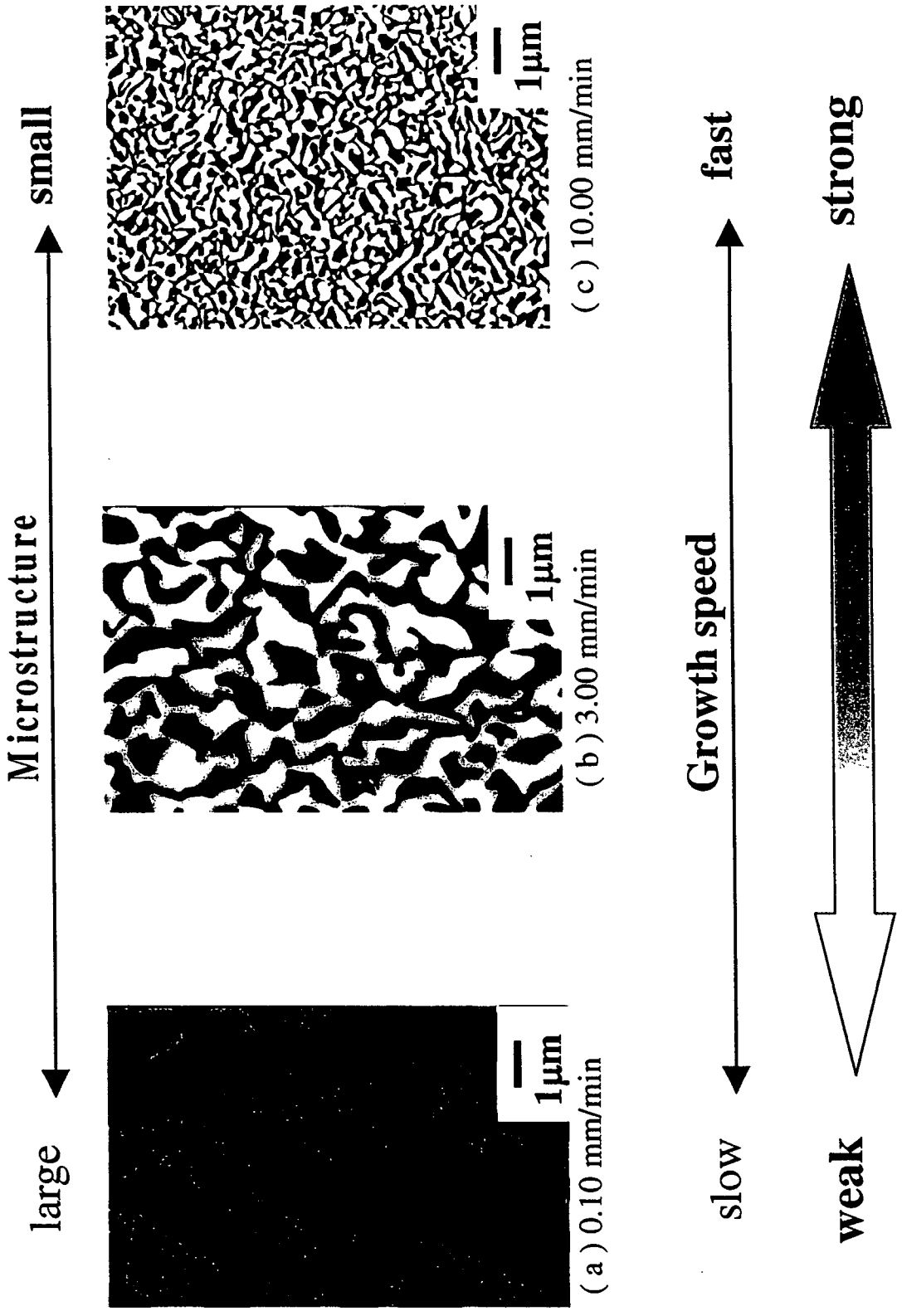
Sapphire/$Dy_3Al_5O_{12}$

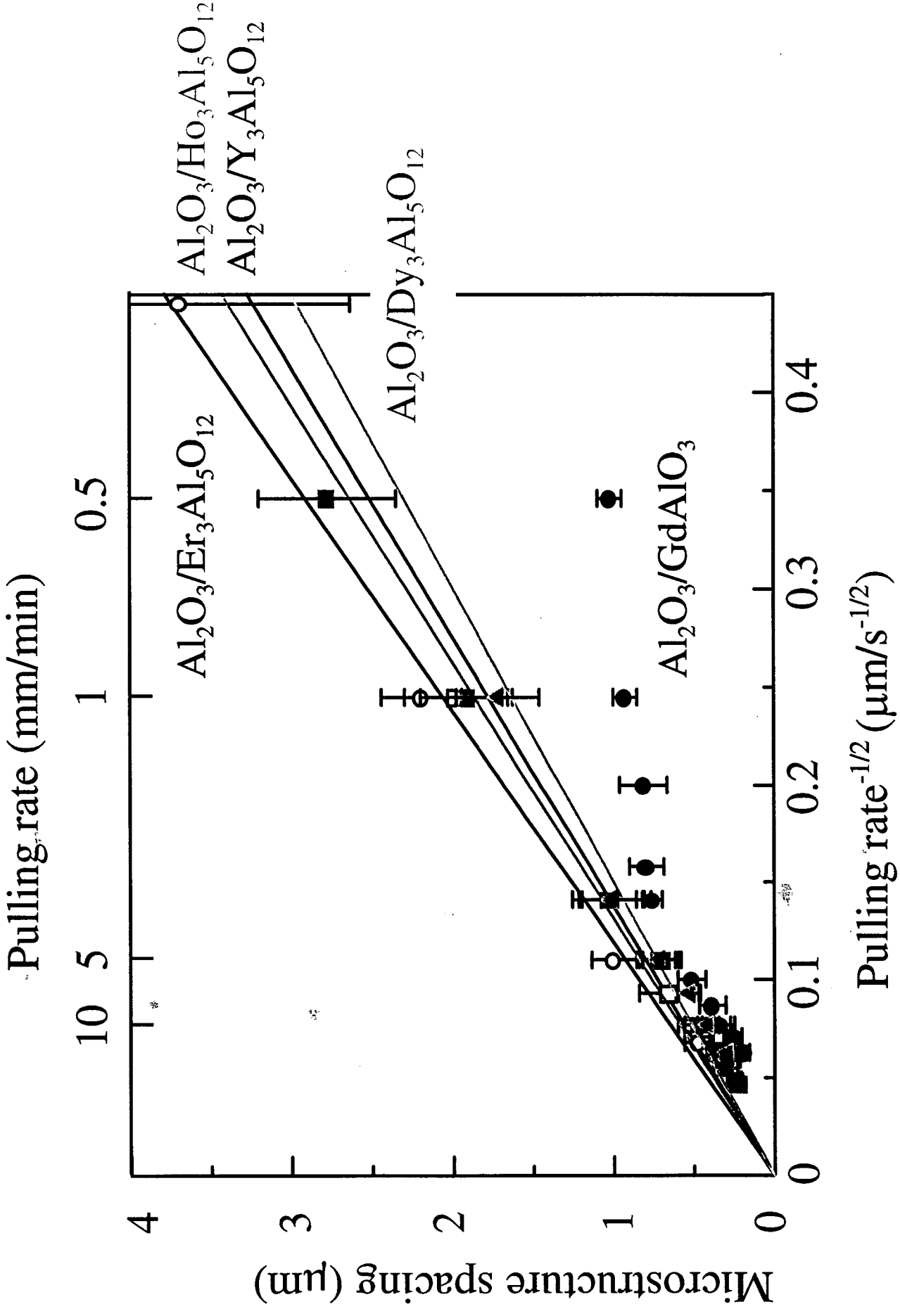


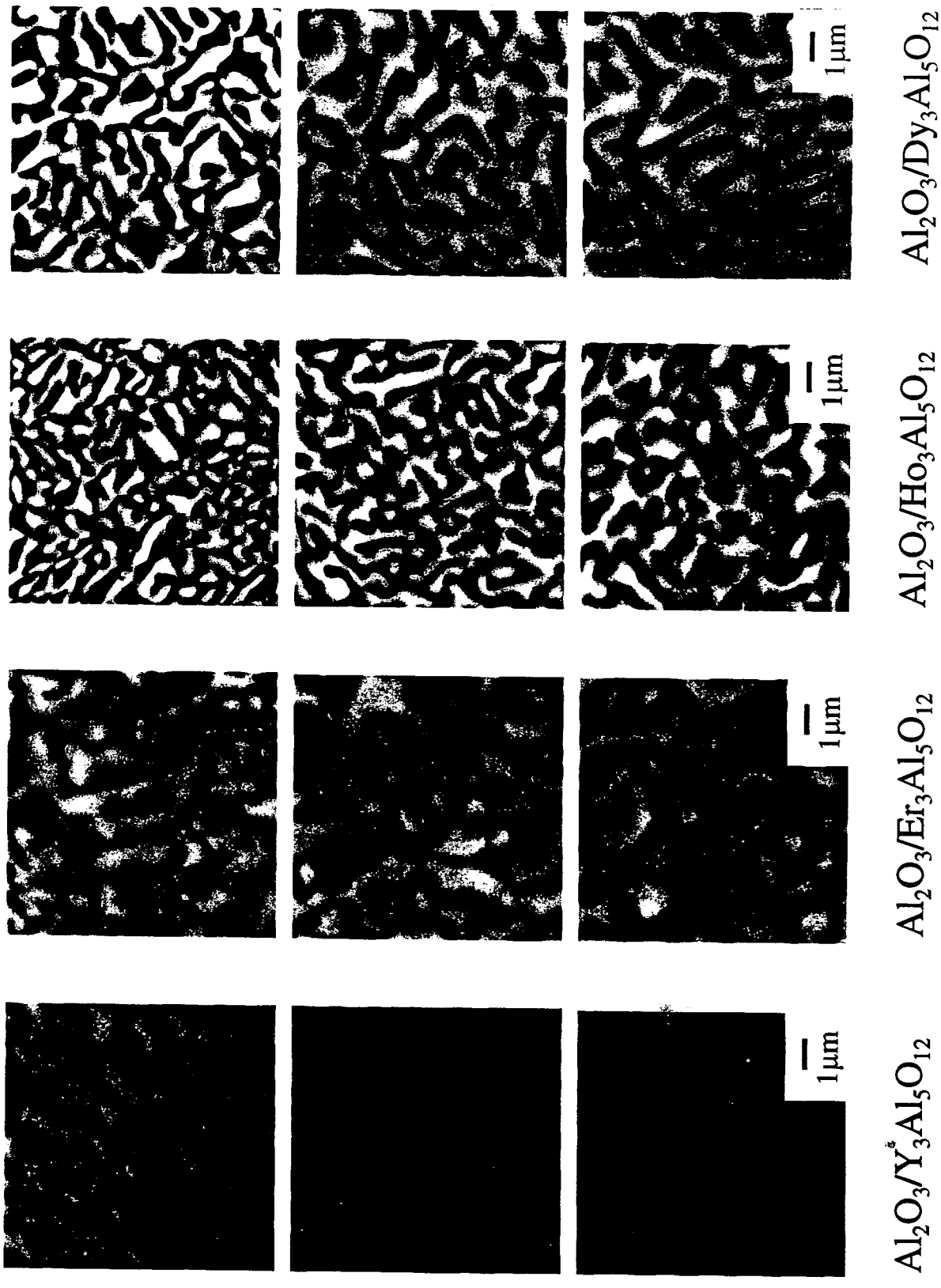
Sapphire/$Ho_3Al_5O_{12}$



Sapphire/$Er_3Al_5O_{12}$

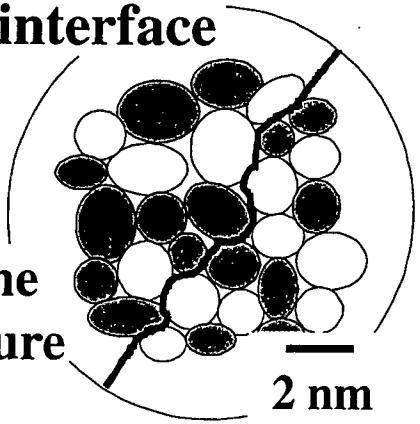

Microstructure
large
small
Growth speed
slow
fast
strength
weak
strong
1μm
(a) 0.10 mm/min
1μm
(b) 3.00 mm/min
1μm
(c) 10.00 mm/min


Microstructure spacing (μm)
Pulling rate (mm/min)
Pulling rate$^{-1/2}$ (μm/s$^{-1/2}$)
$Al_2O_3/Ho_3Al_5O_{12}$
$Al_2O_3/Y_3Al_5O_{12}$
$Al_2O_3/Dy_3Al_5O_{12}$
$Al_2O_3/Er_3Al_5O_{12}$
$Al_2O_3/GdAlO_3$
0
1
2
3
4
0
0.1
0.2
0.3
0.4
10
5
1
0.5


as grown
after 25 h heat treatment
after 75 h heat treatment
1μm
$Al_2O_3/Y_3Al_5O_{12}$
$Al_2O_3/Er_3Al_5O_{12}$
$Al_2O_3/Ho_3Al_5O_{12}$
$Al_2O_3/Dy_3Al_5O_{12}$

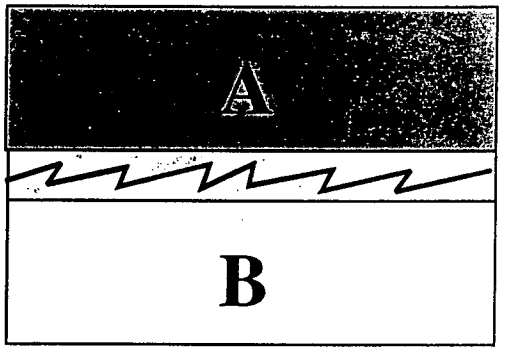
composition	growth velocity	temperature °C	tensile strength MPa (R.T.)
$Al_2O_3/Y_3Al_5O_{12}$ fiber	20mm/min	1500	576.5 (927.3)
$Al_2O_3/Dy_3Al_5O_{12}$ fiber	15mm/min	1500	563.9 (926.3)
$Al_2O_3/Y_3Al_5O_{12}$ fiber	15mm/min	1500	552.1 (910.5)
$Al_2O_3/Ho_3Al_5O_{12}$ fiber	15mm/min	1500	551.2 (910.7)
$Al_2O_3/Er_3Al_5O_{12}$ fiber	15mm/min	1500	541.2 (883.7)
$Al_2O_3/Y_3Al_5O_{12}$ bulk (Bridgman)	5mm/hour	1500	150 (200)
Si_3N_4 bulk		1350	200
Hi-Nicalon SiC/SiC composite		1350	50 - 150
Porous Nextel 720 Mullite/Mullite composite		1200	200

Break at the interface



Easy to break at the elevated temperature

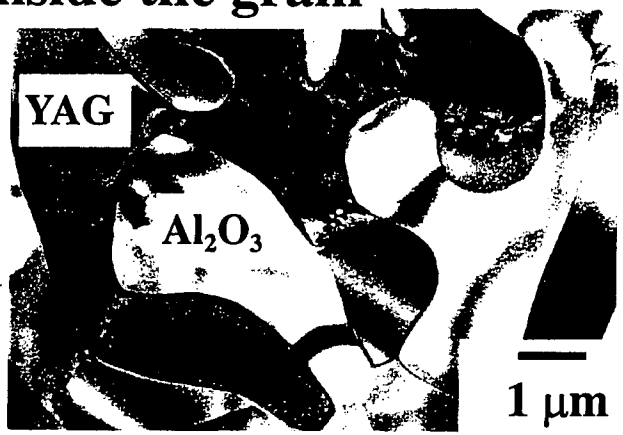
sintered composite



crack

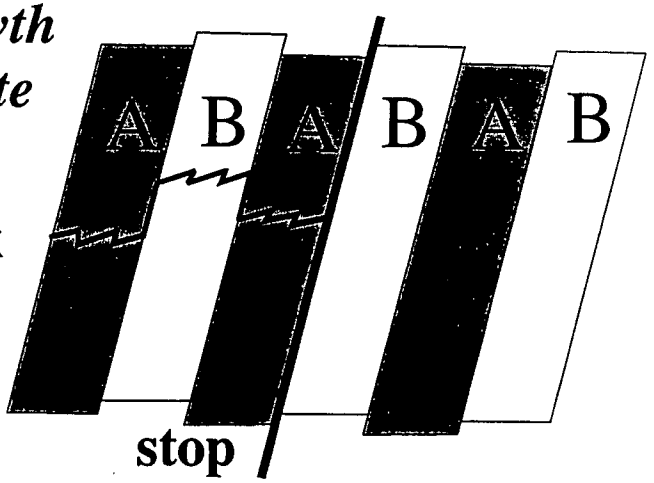
Easy to break

Break inside the grain



Hard to break even at elevated temperature

melt growth composite



crack

Hard to break

sapphire/$Y_3Al_5O_{12}$	81.3 mol % Al_2O_3 and 18.7 mol % Y_2O_3
sapphire/$GdAlO_3$	77 mol % Al_2O_3 and 23 mol % Gd_2O_3
sapphire/$Dy_3Al_5O_{12}$	81 mol % Al_2O_3 and 18 mol % Dy_2O_3
sapphire/$Ho_3Al_5O_{12}$	81 mol % Al_2O_3 and 18 mol % Ho_2O_3
sapphire/$Er_3Al_5O_{12}$	81 mol % Al_2O_3 and 18 mol % Er_2O_3