Growth of sapphire and oxide eutectic fibers by the EFG technique

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Abstract. Single-crystal sapphire and oxide binary (Al$_2$O$_3$-Y$_3$Al$_5$O$_{12}$, Al$_2$O$_3$-Er$_3$Al$_5$O$_{12}$, Al$_2$O$_3$-GdAlO$_3$) and ternary (Al$_2$O$_3$-ZrO$_2$(Y$_2$O$_3$)) eutectic fibers of 150-300 µm in diameters were grown by the edge-defined film-fed growth (EFG) technique. Microstructure and some properties of fibers were investigated.

1. Introduction
Single-crystal sapphire fibers have many physical properties that make them ideal candidates for infrared transmission as high as ~3.5 µm. Sapphire has an intrinsic loss of 0.13 dB/m at the Er:YAG laser wavelength of 2.94 mm; it is chemically inert; and it has the potential of delivering very high laser energies (>1 J/pulse) [1]. Furthermore, sapphire fibers are extremely durable and have a distinct advantage in medical applications because they can be safely inserted directly into the body. Very high optical transmission of sapphire fibers over a broad spectrum of wavelengths make them well suited for certain sensors. The resistance of sapphire can be employed in spectrometric and pyrometric measurements in harsh environments, e.g., inside chemical reactors, furnaces, combustion engines and in other extreme conditions.

The use of single crystal sapphire fibers as a reinforcement for metal and ceramic matrix composites promises a way to obtain materials to serve in structural elements at temperatures in excess of 1200°C in oxidizing conditions. Among oxides, sapphire is one of the best candidates for fiber material because of its combination of mechanical, thermal, and chemical properties.

The oxide-oxide eutectics (in situ composites with a fine microstructure on the µm scale) have been also investigated lately as materials with excellent flexural strength and creep resistance at high temperature [2]. Some binary and ternary eutectics are being developed for very high temperature structural applications such as turbine blades in future aeronautical turbines or thermal power generation systems [3].

Also in recent years, the self-organized eutectic micro- and nanostructures has been identified as materials which could act as photonic crystals [4] and also as metamaterials [5].

2. Fabrication and microstructure of sapphire and eutectic fibers
Sapphire and some eutectic fibers were grown by the edge-defined film-fed growth (EFG) technique [6]. In the EFG technique, fibers are grown from a melt film formed on the top of a capillary die, figure 1. The melt rises to the crystallization front within the capillary channel. The cross-section shape of fibers is mainly controlled by the die design, and its cross-sectional dimensions can vary only within
very narrow limits restricted by the meniscus-existence zone, with the melt meniscus catching on the
die free edge.

The experiments at 22 kHz induction heated graphite susceptor/molybdenum crucible set up were
conducted. An argon atmosphere under a pressure of 1.1-1.2 atm was used as ambient. The pulling
rates are between 1-70 mm/min. The raw material was crushed Verneuil boules for sapphire fibers
growth. Experimental runs used c-axis (<0001>) seeds to initiate growth for sapphire fibers. Sapphire
exhibits very high yield stress and creep resistance at high temperatures if it is oriented so that shear
stresses on the basal slip system are zero, as is the case when the tensile axis is parallel to the c-axis
[7]. The creep resistance of eutectic fibers is independent of crystallographic orientation of the
constituent phases and seems to be determined by the deceleration of dislocations at interfaces.

An automated control system for the growth of sapphire and eutectic fibers with use of the weight
sensor also requires the use of the program observation expression. The data of this expression at each
period of time are being compared with real signal of the weight sensor. Deviation of the real signal
from its program one forms then a control signal of the PID (proportional-integral-differential)
regulator. Oscillations of this deviation may have different characters. It can be relatively strong
(under overcooling) and relatively small (under overheating) [8,9]. In the case of the growth of the
fibers it is necessary to maintain the amplitude of these oscillation in a preset sufficiently narrow
range. The maintenance of this narrow range of these oscillation amplitude requires the use of the
second control loop which tunes the first PID-loop by the appropriate changing the program radii of
the fibers.

Figure 1. Schematic illustration of sapphire and eutectic fiber growth by the EFG technique. 1 - fiber; 2
- seed; 3 - melt; 4 - die.

Figure 2. Sapphire fibers grown by multi–run crystal growth process (at the left). SEM image of
sapphire fiber (at the right).
The process allows for the growth of multiple fiber strands from a single machine; in structural fiber production, 100 strands have been grown simultaneously. Sapphire fibers of 150-300 μm in diameter grown by multi-ran process are shown in figure 2.

Polarized-light images demonstrate the EFG sapphire fibers are single-crystal throughout their length, independent of the solidification rate. To reduce the optical transmission losses special system was developed for growth of fibers with smooth surface, figure 2.

Several eutectic oxide systems have been studied. This includes the Al₂O₃-Y₃Al₅O₁₂ and Al₂O₃-Er₃Al₅O₁₂ garnet system, extensively studied because of its exceptional creep resistance [10], Al₂O₃-GdAlO₃ perovskite and the Al₂O₃-ZrO₂ system. Figure 3 shows the cross-sectional images of an Al₂O₃-Y₃Al₅O₁₂ with a Chinese script eutectic microstructure, Al₂O₃-GdAlO₃ with rod-like microstructure (single-crystal GdAlO₃ rods of 0.3-2 μm in diameter in single-crystal sapphire matrix), and Al₂O₃-ZrO₂(Y₂O₃) with colony microstructure which corresponds to a cellular crystallization front. The addition of Y₂O₃ to Al₂O₃-ZrO₂ led to the pseudo-binary Al₂O₃-ZrO₂(Y₂O₃) eutectic in which different zirconia polymorphs (monoclinic, tetragonal or cubic zirconia) could be obtained just by changing the yttria content [11]. The presence of the zirconia polymorphs gave rise to a rich variety of microstructural morphologies and residual stress states, which controlled the mechanical properties [12].

![Figure 3. SEM micrographs of the transverse sections of Al₂O₃-Y₃Al₅O₁₂ (at the left), Al₂O₃-GdAlO₃ (at the middle) and Al₂O₃-ZrO₂(Y₂O₃) (at the right) eutectics grown by the EFG technique](image1)

![Figure 4. SEM micrographs showing the microstructure of an Al₂O₃-Er₃Al₅O₁₂ eutectic fiber grown by the EFG at different growth rates: 30 mm/h (at the left), 100 mm/h (at the middle) and 300 mm/h (at the right).](image2)
Microstructure of various oxide eutectics depending on growth rates were investigated. In general specific dimensions of phases corresponded to Hunt-Jackson [13] law at growth rates from 30 to 300 mm/h, figure 4.

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