Nanofibrilar Al_2O_3-ZrO_2-$Er_3Al_5O_{12}$ eutectics processed by the laser floating zone method

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Ceramic composites are attracting increasing attention because of the broader diversity and improvement in the properties that can provide as compared with those of the conventional ceramics. Directional solidification of ceramic oxide eutectics allows in-situ composites to be produced. Full density materials are obtained when eutectics are grown from the melt. Moreover, the eutectic growth allows a homogeneous mixing of the phases and a control of the phase size with the solidification rate, following the Hunt-Jackson law: $\lambda \propto v^{-1/2}$, with λ the interphase spacing and v the growth rate. Reduction of the microstructure characteristic size can lead to unusual structural and functional properties.

In the field of structural materials, directionally solidified eutectics based in Al_2O_3 appear as candidates for thermo-mechanical applications at high temperature due to their good creep resistance and microstructure stability [1]. Recently, a strong dependence of the flexural strength of Al_2O_3-$Y_3Al_5O_{12}$ eutectic rods with the phase size was reported [2], outstanding mechanical properties being achieved in nanostructured Al_2O_3-$Y_3Al_5O_{12}$-ZrO_2 eutectics [3].

The application field of these materials can be extended with the addition to the eutectic composition of rare earth oxides as Er_2O_3. Rare earth ions in crystals emit radiation in narrow bands, allowing their use as selective emitters even at high temperature. In particular, the spectral matching of the Er^{3+} emission band with the sensitive region of the GaSb photoconverter makes the Al_2O_3-$Er_3Al_5O_{12}$ eutectic selective emitter an adequate material for thermophotovoltaic systems [4]. The efficiency of the rare earth oxide emitters can be increased by reducing the emitter characteristic dimension [5].

Both structural and functional application involves the microstructure fineness. Increasing the number of components to the melt and the use of high solidification rates can result in a highly reduced phase-sized material. Among the different directional solidification procedures to grow ceramic eutectics, the techniques based on floating zone appear as excellent methods as no crucible is needed, the thermal gradients at the liquid/solid interface are very large ($\approx$ 6000ºC/cm) and, consequently, high growth rates can be used. Hence, the control of the crystal microstructure is possible in a wide variety of growth parameters; in particular, very fine microstructure (λ~100 nm) can be achieved with high growth rates in these systems.

In this work, eutectic Al_2O_3-$Er_3Al_5O_{12}$-ZrO_2 rods were processed by directional solidification using the laser floating zone method at growth rates ranging from 25mm/h to 1200 mm/h. Homogeneous and defect-free microstructures were observed for all the solidification rates. The microstructure was examined by Scanning and Transmission Electronic Microscopy and presented three different phases that were identified by electron and X-ray diffraction as α-Al_2O_3, $Er_3Al_5O_{12}$ (EAG), and cubic Er-stabilized ZrO_2. The Er_2O_3 solubility in ZrO_2 was determined by Electron Dispersive Spectroscopy. At rates below 1000 mm/h, the eutectic microstructure consisted of a homogeneous interpenetrating network of the three eutectic phases. However, when higher solidification rates were used, the microstructure adopted a fibrous pattern. The phase-size was strongly dependent on the solidification rate, decreasing at the nanometre range for the samples grown at the highest rate. Figures 1a and 1b show TEM and SEM images of the transverse and longitudinal sections of an $Al_2O_3/Er_2O_3/ZrO_2$ ternary eutectic rod processed at growth rates of 1200 mm/h. The microstructure consists of bundles of single crystal $Er_3Al_5O_{12}$ and Al_2O_3 whiskers (~200 nm in width) with smaller ZrO_2 whiskers (<50 nm in width) between them. Al_2O_3 crystals were c-oriented and presented the typical triangular shape.

The thermal expansion mismatch between the three constituent phases of the eutectic led to residual stresses in the material. The hydrostatic component of the stress tensor of the Al_2O_3 crystals was measured with the technique of piezospectroscopy using the fluorescence from trace Cr^{3+} impurities. The residual stress in alumina was found to be compressive, varying from -270 MPa to -100 MPa at room temperature, depending on the growth rate.

The mechanical properties were investigated as a function of the growth rate at room temperature. Hardness and fracture toughness were measured from the microhardness Vickers test and mean values of 15.7 GPa and 4.2 $MPam^{1/2}$ were obtained, respectively. Both properties were not dependent on the phase size. Flexural strength was measured from three-point flexural tests. The mechanical strength showed a large dependence on the growth rate, raising from 1.2 GPa for rods grown at 25 mm/h up to 3.4 GPa for samples solidified at 1200 mm/h. The high flexural strength obtained for this material was explained in terms of it microstructure as the nanometric size of the phases reduces the critical crack length and, as a result, a large strengthening of the material is obtained.

References:

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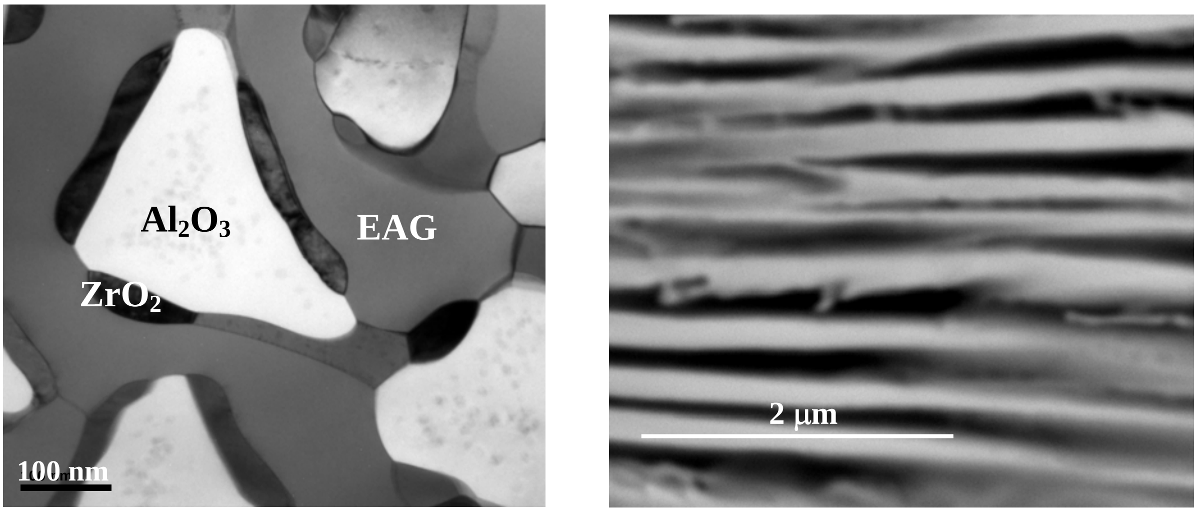
Figure 1: (a) TEM micrograph of the transverse cross-section of the Al_2O_3-EAG-ZrO_2 nanofibrilar eutectic. b) SEM micrograph of the longitudinal cross-section in the same material.



(a) **(b)**