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Microstructural stability at elevated temperatures of directionally solidified $Al_2O_3/Er_3Al_5O_{12}$ eutectic ceramics

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ABSTRACT

The thermal microstructural stability of Al_2O_3–$Er_3Al_5O_{12}$ eutectic rods has been studied as a function of the solidification rate. The rods were directionally solidified by the Laser-Heated Floating Zone method, also known as Laser-Heated Pedestal growth technique. Their microstructures consisted of an interpenetrated network of both eutectic phases, whose size were controlled by the growth rate. The eutectics rods were heat-treated in air atmosphere at temperatures ranging from 1350 °C to 1650 °C up to 100 h. The coarsening kinetics was investigated from the evolution of the microstructure with the temperature and the time. The eutectics grown at 25 mm/h presented high thermal microstructural stability, with their microstructure remaining substantially unchanged even for the highest annealing temperature and the longest time. Eutectics grown at 350 mm/h experienced coarsening after 25 h at 1550 °C and those grown at 750 mm/h after 25 h at 1500 °C. Heterogeneous coarsening was found for heat treatments at 1650 °C.

1. Introduction

Directionally solidified eutectics (DSE) are composite materials processed in situ whose microstructure, and therefore their properties, can be controlled by the processing parameters, such as the solidification rate. Al_2O_3-based DSE ceramics in particular are very promising materials due to their interesting properties. These eutectics have a high melting point, microstructural stability up to temperatures very close to the melting point, excellent chemical stability and elevated creep resistance [1]. Moreover, the use of high solidification rates produces nanostructures and therefore, high-strength materials [2]. The combination of these properties allows outstanding mechanical behaviour at temperatures as high as 1900 K [3]. As a consequence, these eutectics are good candidates for high temperature structural applications. In addition to the above-mentioned properties, if rare earth oxides are included in the eutectic composition interesting optical properties appear. For instance, some rare earth ions, like Er^{3+}, present narrow emission bands coinciding with some photoconverters' sensitive regions. So, the use of these eutectics can be extended to functional applications such as selective emitters in thermophotovoltaic devices [4].

Due to the high temperature at which the Al_2O_3-based DSE ceramics can operate, the study of the thermal microstructural stability is of great interest, as microstructure coarsening can produce degradation in the material performance. Few studies of the thermal microstructural stability of Al_2O_3-based DSE ceramics can be found in the literature. The microstructural stability of Al_2O_3–$Er_3Al_5O_{12}$, Al_2O_3–$Y_3Al_5O_{12}$ and Al_2O_3–$GdAlO_3$ eutectics processed by the Bridgman technique at 5 mm/h was reported [5,6]. A high thermal stability was obtained in this case up to temperatures near melting point. However, studies in eutectics solidified at high growth rates and therefore, more likely to coarsen, are practically all limited to the case of Al_2O_3–$Y_3Al_5O_{12}$ processed by the Edge defined Film Growth method at 1218 mm/h and 762 mm/h [7,8]. In this eutectic significant coarsening at 1500 °C was observed.

In this work, Al_2O_3–$Er_3Al_5O_{12}$ eutectic ceramics have been prepared and their thermal microstructural stability in a wide range of temperatures has been determined. The eutectics were directionally solidified by the Laser-Heat Floating Zone method (LHFZ), also known as Laser-Heated Pedestal growth technique, varying the growth rate in order to achieve microstructures with different characteristic phase sizes. The coarsening kinetics of the eutectic rods was studied as a function of the growth rate up to 1650 °C.

2. Experimental details

Eutectic rods of Al_2O_3–$Er_3Al_5O_{12}$ were directionally solidified by the LHFZ method. Ceramics were prepared with a mixture of commercial powders of Er_2O_3 (Aldrich, 99.99%) and Al_2O_3 (Sigma-Aldrich, 99.99%) in the binary eutectic composition (81 mol%

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Al_2O_3, 19 mol% Er_2O_3). Precursor rods were prepared by cold isostatic pressing of the powder for 3 min at 200 MPa. The obtained rods were sintered in a furnace at 1500 °C for 12 h. The final precursor rods had a typical diameter of 2.5 mm.

Eutectic rods were obtained by directional solidification with the LHFZ method using a continuous wave CO_2 laser and different growth rates, 25 mm/h, 350 mm/h and 750 mm/h. First, to eliminate the precursor porosity, different densification stages were applied at low growth rate (100–250 mm/h). Final directional solidification growth was always performed with the grown crystal travelling downwards and without rotation of the crystal or the precursor. To eliminate the voids included in the solidified rod produced by the oxygen dissolved in the liquid phase, eutectic growth was performed in nitrogen atmosphere with a slight overpressure of 0.1–0.25 bar respect to ambient pressure [9]. The final processed rods had typical diameter values of 1–1.5 mm. From now on, the different processed rods will be referred to using the acronym AEx where x is the solidification rate.

For the thermal stability study, the annealings were performed in air atmosphere at different temperatures ranging from 1350 °C to 1600 °C in steps of 50 °C, for fixed periods of 25 h, 50 h and 100 h. The heating and cooling rates were 3 °C/min and 5 °C/min, respectively. The annealing at 1650 °C was performed only up to 50 h due to experimental limitations.

Microstructural characterisation was performed in transverse and longitudinal polished cross-sections of the as-grown and heat-treated rods by means of back-scattered electron images obtained in a Scanning Electron Microscopy (SEM) (model 6400, Jeol, Tokyo, Japan).

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the transverse cross-sections of the as-grown eutectic rods processed at (a) 25 mm/h, (b) 350 mm/h and (c) 750 mm/h. For the three solidification rates, an homogeneous and free of voids microstructure, was observed. It consisted of a three-dimensional interpenetrated network of two phases, also usually known as chinese script. The eutectic phases were identified by energy dispersive spectrometry (EDS) as Al_2O_3 (black phase) and $Er_3Al_5O_{12}$ (grey phase). Both phases were slightly elongated along the growth direction. The use of pulling rates higher than 750 mm/h led to microstructures in which both chinese script and fibrous pattern were present [10]. Due to this in homogeneity the microstructure stability study was uniquely performed in samples grown up to 750 mm/h. Fig. 2 shows the interspacing as a function of the growth rate for the samples investigated in this paper. The reduction of the phase size when the growth rate increases follows the Hunt–Jackson law predictions, $\lambda^2 \times \nu = C$ (where λ is the interspacing and ν is the growth rate) with a constant in this case of $C = 135\ \mu m^3/s$ [10].

After the heat-treatments, the microstructure of the eutectic rods was studied using SEM. The transverse and the longitudinal cross-sections of each sample were observed after each annealing treatment. Fig. 1 (d), (e) and (f) show the transverse cross-sections of AE25, AE350 and AE750, respectively, after 100 h at 1600 °C.

In the eutectic with the largest phase size, AE25, a high microstructural stability was found: the microstructure was invariable even after the annealing at 1650 °C. Similar behaviour was reported for the different binary eutectics processed at 5 mm/h [5,11].

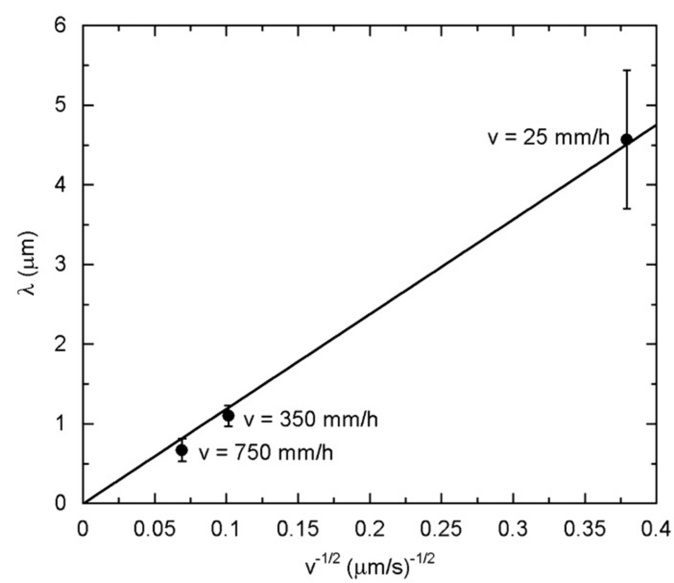

Fig. 2. Interspacing, λ, as a function of the growth rate ν.

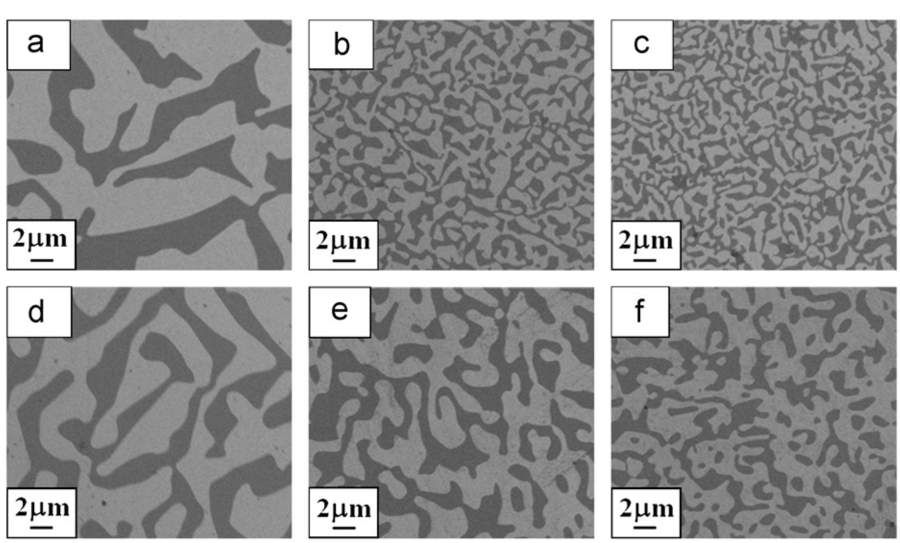

Fig. 1. Back-scattered electron micrographs of the transverse cross-section of (a) AE25, (b) AE350 and (c) AE750 as-grown, and (d) AE25, (e) AE350, (f) AE750 after annealing at 1600 °C, 100 h in air.