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Microstructural stability and orientation relationships of directionally solidified Al_2O_3-$Er_3Al_5O_{12}$-ZrO_2 eutectic ceramics up to 1600 °C

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Abstract

Al_2O_3-$Er_3Al_5O_{12}$-ZrO_2 eutectic ceramic rods were directionally solidified using the laser floating zone method at different growth rates, 25, 350 and 1200 mm/h. The microstructure obtained, in terms of both morphology and phase size, was strongly dependent on the growth rate. However, electron backscatter diffraction experiments showed that the growth directions were the same for all the processing rates, $[0\,0\,0\,1]_{Al_2O_3}//[1\,0\,0]_{EAG}//[1\,0\,0]_{ZrO_2}$. The microstructural stability was investigated up to 1600 °C as a function of the growth rate. Ceramics with the largest phase size presented high stability, their microstructure remaining substantially unchanged at the highest annealing temperature for 100 h. Eutectics processed at higher growth rates and with a finer microstructure showed coarsening after heat treatments. The sample grown at 350 mm/h coarsened at 1450 °C whereas the eutectic solidified at 1200 mm/h thickened at 1400 °C. The growth directions remain unaffected for all growth rates. The mechanisms of microstructural coarsening were investigated.

Keywords: $Al_2O_3/Er_3Al_5O_{12}/ZrO_2$; Directionally solidified eutectic ceramics; Microstructural stability; Coarsening; Orientation relationships

1. Introduction

Directionally solidified eutectic ceramics (DSEC) are materials constituted by two or more eutectic phases whose microstructure can be controlled by the solidification conditions.[1] Most of the properties of the eutectics depend on the shape and size of the phases. The relationship between microstructure and properties allows the characteristics of DSEC to be controlled by the processing parameters.

Among DSEC, those based on Al_2O_3 have been the subject of a large number of studies because of their outstanding mechanical properties up to temperatures very close to the melting point, and an excellent microstructural and chemical stability,[2] which make them promising materials for structural applications at high temperatures.[2,3] Most of the studies found in the literature have focused on eutectics of the $Al_2O_3/Y_2O_3/ZrO_2$ system.[4–7] Mechanical properties have been reported to depend strongly on the microstructural size, showing a significant improvement when the size of the eutectic phase is reduced.[5] Outstanding flexural strength close to 5 GPa was obtained for the Al_2O_3-$Y_3Al_5O_{12}$-ZrO_2 ternary eutectic (AYZ), with nanometric phases due to the high rates used in processing.[8] In addition, high strength retentions up to 1900 K were found for the Al_2O_3-$Y_3Al_5O_{12}$ binary eutectic (AY).[5]

Recently, other Al_2O_3-based DSEC including rare earth oxides in their eutectic composition have been studied. The incorporation of rare earth ions allows the field of applications of these materials to be extended. In addition to structural applications at high temperatures, they can be used in functional applications such as selective thermal emitters in thermophotovoltaic devices.[9] We should note that both applications implicate high operating temperatures. When the materials are exposed to high temperatures for long periods of time, microstructural coarsening may appear, producing the degradation of the material performance. Martínez-Fernández et al. studied the high temperature creep deformation of directionally solidified $Al_2O_3/Er_3Al_5O_{12}$. They reported that the material presented a very high creep resistance, comparable to c-axis sapphire, concluding that creep deformation was diffusion controlled.[10] In fact, they limited the study of creep curves to temperatures below 1500 °C because of the microstructural evolution of the samples. Then, Mazerolles and co-workers studied the microstructure, interfaces and high temperature creep behaviour of Al_2O_3-Ln_2O_3 (Ln = Gd, Er, Y) DSEC.[11,12] They pointed out that the

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absence of intermediate phases at the interfaces, as well as the crystallographic orientation relationships between phases, give rise to a strong cohesion between components. They also confirmed that deformation climb process was controlled by bulk diffusion. The remarkable creep resistance of these materials would be related to the quality of these interfaces. Furthermore, they also extended their study to ternary eutectics with the addition of a toughening phase (ZrO_2) Despite the significant interest in the performance of these materials at elevated temperature, the thermal microstructural stability of Al_2O_3-based DSEC has been scarcely investigated. Very few microstructural stability studies of the binary Al_2O_3-$Y_3Al_5O_{12}$, Al_2O_3-$Er_3Al_5O_{12}$ and Al_2O_3-$GdAlO_3$ eutectics[13–17] can be found in the literature and, to our knowledge, none related to any ternary DSEC.

The aim of this paper is to study the microstructural stability of the Al_2O_3-$Er_3Al_5O_{12}$-ZrO_2 (AEZ) ternary eutectic at a wide range of temperatures, up to 1600 °C. Al_2O_3-$Er_3Al_5O_{12}$-ZrO_2 eutectic rods were grown using the laser-heated floating zone method (LHFZ) and at different growth rates in order to investigate the influence of the microstructure on thermal stability. For this purpose, the evolution of the eutectic interspacing and interfacial area as a function of the annealing treatment was analyzed using Field Emission Scanning Electron Microscopy (FESEM). Growth directions and orientation relationships of the different phases for both eutectics, as-grown and annealed at 1600 °C for 100 h, were determined by Electron Backscattering Diffraction (EBSD).

2. Materials and experimental details

Eutectic rods of Al_2O_3-$Er_3Al_5O_{12}$-ZrO_2 were directionally solidified by the LHFZ method. Ceramics were prepared with a mixture of commercial powders of Er_2O_3 (Aldrich, 99.99%), Al_2O_3 (Sigma–Aldrich, 99.99%) and ZrO_2 (Aldrich, 99%) in the ternary eutectic composition (65.9 mol% Al_2O_3, 15.5 mol% Er_2O_3, 18.6 mol% ZrO_2).[18] 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 at 25 mm/h, 350 mm/h and 1200 mm/h growth rates. To eliminate the precursor porosity, different densification stages were applied at a low growth rate (100–250 mm/h). The final directional solidification was always performed with the grown crystal travelling downwards and without rotation of the crystal or the precursor. Processing was performed in a nitrogen atmosphere with a slight overpressure of 0.1–0.25 bar respect to ambient pressure[19] in order to avoid the presence of voids in the solidified rods. 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 AEZ*x* where *x* is the solidification rate.

For the microstructural stability study, annealings were performed in air at 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.

Microstructural characterization was performed in polished transverse and longitudinal cross-sections of the as-grown and heat-treated rods by means of back-scattered electron images obtained in a Merlin Field Emission Scanning Electron Microscopy (FESEM) from Carl Zeiss (Germany). The energy of the incident electrons was 0.75 keV and we used an in-lens detector equipped with a filtering grid to reject electrons with energy lower than 0.72 keV in order to increase the contrast between the different phases. Specimens for this characterization were prepared using conventional metallographic methods. The eutectic interspacing, λ, and the amount of interfacial area per unit volume or surface density, S_v, in both as-grown and heat-treated rods, were measured using linear interception methods.[20] Due to the complex microstructure of these eutectics, formed by three different phases disposed in irregular arrays, the interspacing was defined as the length between two consecutive EAG crystals. It was calculated from transverse cross-section micrographs using a maximum of twenty randomly drawn lines containing at least four λ. The surface density was obtained from micrographs of the transverse and longitudinal cross-sections using the number of interphase intersections in a counting circle, in order to avoid texture effects.

In order to determine the growth directions and orientation relationships between phases, for the as-grown material and after the most extreme ageing treatment (100 h at 1600 °C), EBSD experiments were performed in transverse cross-sections using the FESEM equipment mentioned above. The accelerating voltage was of 10–15 kV with 1 nA probe current. The specimens were tilted at 70°, at distances of 14.5–17.5 mm from the pole piece and 178.5 mm from the EBSD detector (HKL, Oxford Instruments, UK), which consisted of a CCD camera set at resolution of 514 × 384 using 4 × 4 binning. Two Kikuchi patterns were acquired (90–100 ms of acquisition time) every 0.02–0.15 μm, averaged out and automatically indexed (7 bands out of 50 reflectors) to determine the crystal orientation at every point.[21] In order to avoid charge accumulation on the sample surface due to the AEZ being an electrical insulator, the specimen was not coated but instead an N_2 micro jet was pointed towards the surface of the sample during the experiments for charge compensation.[22]

The specimen preparation for EBSD experiments required a special method because the electron diffraction patterns are generated on a very thin surface layer (~40 nm thick) that has to be free of strains.[23] It consisted of polishing transverse cross-sections of the samples in progressive steps using Struers LaboPol-4 automated polisher, first with SiC paper (15 μm and 10 μm particle size with the polishing wheel rotating at 40 rpm and under a load of 2.5 N), subsequently with diamond paste (3 μm and 1 μm particle size, 120 rpm, 2.5 N) and finally with colloidal silica (0.04 μm particle size, 100 rpm, 2.5 N) for 15 min.

3. Results and discussion

3.1. Microstructural stability and coarsening kinetics

The FESEM micrograph analysis of samples with different heating treatments was used to study the evolution of the