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Study of the gas inclusions in $Al_2O_3/Y_3Al_5O_{12}$ and $Al_2O_3/Y_3Al_5O_{12}/ZrO_2$ eutectic fibers grown by laser floating zone

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Abstract

Gas bubbles appear in some metal oxides grown by directional solidification in air when high growth rates are used. The incorporation of bubbles in Al_2O_3–YAG (AY) and Al_2O_3–YAG–ZrO_2 (AYZ) eutectic crystals grown using the laser floating zone method was investigated. The effect of different growth experimental parameters was considered. Growth rate, rod diameter and growth atmosphere were found to be determinant in order to reduce the gas inclusions. The optimization of the growth parameters allowed to grow AY and AYZ eutectic crystals free of bubbles at very high growth rates at which interphase spacings smaller than 300 nm were obtained.

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1. Introduction

Directionally solidified eutectics (DSE) based in ceramic oxides are object of numerous studies because of their outstanding mechanical properties and their thermal and microstructural stability [1]. Al_2O_3-based DSE is one of the eutectic oxide systems, which has received more attention due to its excellent mechanical properties that are retained up to temperatures close to the melting point [2,3]. Studies on binary and ternary eutectics of the Al_2O_3–Y_2O_3–ZrO_2 system can be found in the literature [4–8]. The binary Al_2O_3–YAG (AY) and ternary Al_2O_3–YAG–ZrO_2 (AYZ) eutectic rods have been reported to show an excellent mechanical flexural strength [3,9,10]. They are expected to be a very interesting material in the field of aeronautics, aerospace and power generator technologies and their application to gas turbine systems has been investigated [11,12]. These eutectic composites have been researched and developed as bulk materials [13] as well as reinforcement fibers [9]. Recently, a procedure for preparing large surfaces of eutectic composites directionally solidified from the melt has been reported [14].

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 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 (~100 nm) can be achieved with high growth rates in these systems. Moreover, the floating zone method allows to grow eutectic oxide fibers as fine as 200 μm [15] to be used as reinforcing phase as well as rods larger than 2 mm of diameter [16], which allows the properties of the bulk material to be explored.

Recently, flexural strengths as high as 2 GPa at room temperature was observed in eutectic rods of AY and

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AYZ systems processed using the laser floating zone (LFZ) technique [16,17]. The mechanical flexural strength was found to increase with the growth rate as the microstructure becomes finer. In AY eutectic fibers, the room-temperature flexural strength of 0.6 GPa obtained for fibers grown at 25 mm/h, raised to 1.23 and 1.9 GPa when the growth rate increased to 350 and 750 mm/h, respectively. In addition, the strength retention of the AY eutectics at high temperature was remarkable, and the rods with the finest microstructure withstood 1.53 GPa at 1900 K [17].

However, growth at high rates increases the presence of voids in the solid with the consequent degradation of the mechanical properties. Many examples can be found in the literature of ceramic crystals grown using the floating zone method in which gas inclusions were present. In most of them, bubble-free crystals grown at high rates were not possible to obtain and the use of lower growth rates was obliged in order to reduce porosity [18–21]).

The mechanism of formation and behavior of these gas inclusions has been widely studied both in actual compounds and in theoretical models and the origin of the porosity has been proposed to be in gas impurities solved in the melt. During solidification, the concentration of the gas increases in the solid–liquid interface, since the solubility of a gas in a solid is generally smaller than that in a liquid. When the gas concentration raises enough, a gas bubble can nucleate. The bubble will grow and can be trapped by the solid, staying as a pore in the crystal. Different methods for avoiding bubble formation during solidification have been described in the literature. Growth parameters such as the crystal growth rate, crystal diameter or sintering conditions were found to have a large influence on bubble formation [22–24]. Wilcox and Kuo [24] derived a theory for bubble nucleation in solidified gas solutions, concluding that the tendency to form these bubbles increased with growth rate and ambient gas pressure and decreased with stirring and the height of liquid over crystals.

In this work, the influence of the growth rate, rod diameter, rotation and atmosphere in the processing of AY and AYZ eutectic rods using LFZ will be explored. As a conclusion of this study, pore-free samples grown at rates as high as 750–1200 mm/h showing a homogeneous nanosized microstructure can be obtained when melt is performed in an oxygen-free atmosphere.

2. Experimental procedure

Eutectic rods of AY and AYZ were prepared by the LFZ technique. Ceramics were prepared using a mixture of commercial powders of Y_2O_3 (Aldrich, 99%), Al_2O_3 (Aldrich, 99.99%) and 8% yttria-stabilized zirconia (Tosoh Corporation) in the binary (81.5 mol% Al_2O_3, 18.5 mol% Y_2O_3) and ternary (65 mol% Al_2O_3, 19 mol% ZrO_2, 16 mol% Y_2O_3) eutectic compositions. Al_2O_3 powders were milled using a vibratory mill (model MM20000, Restch, Haan, Germany) and fired in air at 1000° for 1 h. Precursor rods were prepared isostatically pressing the powder for 2 min at 200 MPa. The obtained rods were sintered in air in a furnace at 1500 °C during 12 h.

Eutectic rods were obtained by directional solidification with the LFZ method using a CO_2 laser and a variable growth rate between 300 and 1200 mm/h. The growths were performed at different atmospheres: in air (at ambient pressure), in vacuum (2.5×10^{-2} mbar), in argon and in nitrogen–air mixtures with nitrogen volume percentage ranging from 0% to 100%. In the case of argon and nitrogen–air mixtures, the growth chamber was kept at a slight overpressure of 0.1–0.25 bar in respect to ambient pressure. The rods were grown without rotation of the crystal and precursor, except when the effect of the rotation in the porosity was explored.

After different densification stages to avoid precursor porosity, rods with diameters varying between 0.5 and 1.6 mm were obtained. These densification stages consisted of several LFZ growths at low growth rate (100–250 mm/h) performed at the atmosphere used for the final crystal growth. Reductions in rod diameter were achieved when necessary by setting a lower speed to the precursor that to the grown rod. Last stage was always performed with the molten zone traveling upwards.

A molten zone of length of about 1.5 times the rod diameter was maintained by adjusting the laser power input. Longer molten zones were used at growth rates higher than 750 mm/h in order to make sure of the melting of the rod center, not exceeding in any case two times the rod diameter. The laser power was practically independent on the growth rate. However, a power laser reduction was necessary when reducing the rod diameter (60–70 W for rod diameters of 1.5 mm, 20–30 W for rod diameters of 0.8 mm)

Transverse and longitudinal cross sections of the grown rods were cut and polished for scanning electron microscopy (SEM). The microstructure was studied using a SEM (model 6400, Jeol, Tokyo, Japan).

From now on, the different specimens will be referred to using the acronym AYx, (binary eutectic rods) and AYZx (ternary eutectic rods) where x is the growth rate.

3. Results

SEM microphotographs showing the microstructure of the transverse section of the AY300, AY750, AYZ300, AYZ750 grown in air are presented in Fig. 1(a–d) respectively. In the case of AY samples, an interpenetrating network of Al_2O_3 (black) and YAG (white) was observed for all the growth rates. For the AYZ samples, the ternary eutectic microstructure consisted of Al_2O_3 (dark) and cubic Y_2O_3-stabilized ZrO_2 (YSZ) (white) phases dispersed and YAG (grey) domains interconnected. A finer microstructure was observed when growth rate was increased. Interlamellar space, λ, was estimated from the SEM microphotographs. When the growth rate was raised, the interlamellar space decreased as values as low as 0.55 μm for a growth rate of 1000 mm/h. For AYZ samples, the