

## Study of directionally solidified eutectic $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (3% $\text{Y}_2\text{O}_3$ ) doped with $\text{TiO}_2$

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An study of directionally grown samples of the eutectic composition in the  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  (3 mol%  $\text{Y}_2\text{O}_3$ ) system, with small  $\text{TiO}_2$  additions (1 wt%), is presented. The microstructural changes induced by this addition are analysed using SEM (EDX) techniques. The mechanical changes, when  $\text{TiO}_2$  is added, are studied by measuring the flexural strength by three point bending. Also, the toughness is determined by Vickers indentation method. When slow growth rates (10 mm/h) are used, interpenetrated and homogeneous microstructure is obtained, independently of the  $\text{TiO}_2$  doping. When growth rates are higher (300 and 1000 mm/h) the structure changes and the phases are organized in form of colonies or cells, which have smaller size when  $\text{TiO}_2$  is present. This size reduction is accompanied with an increase of the toughness.

*Keywords:*  $\text{Al}_2\text{O}_3\text{-ZrO}_2$ , eutectic, directional solidification,  $\text{TiO}_2$  doping

### Estudio del eutéctico $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (3% $\text{Y}_2\text{O}_3$ ) dopado con $\text{TiO}_2$ obtenido por solidificación direccional

Este trabajo presenta un estudio de muestras crecidas direccionalmente del sistema  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  (3 mol%  $\text{Y}_2\text{O}_3$ ) en su composición eutéctica con pequeñas adiciones de óxido de titanio (1% de  $\text{TiO}_2$  en peso). Se analizan los cambios microestructurales inducidos por esta adición mediante SEM (EDX) y se estudian los cambios en su comportamiento mecánico medido por flexión en tres puntos, así como la tenacidad de fractura mediante indentación Vickers. Con velocidades lentas de solidificación (10 mm/h) se obtiene en ambos casos una microestructura homogénea e interpenetrada, mientras que a velocidades mayores, 300 y 1000 mm/h, se forma una estructura en las que las fases se organizan en forma de colonias o células, siendo éstas de menor tamaño en las muestras dopadas. Esta disminución en el tamaño viene acompañada de un aumento de la tenacidad de fractura medida por indentación.

*Palabras clave:*  $\text{Al}_2\text{O}_3\text{-ZrO}_2$ , eutéctico, solidificación direccional,  $\text{TiO}_2$

## 1. INTRODUCTION

The  $\text{Al}_2\text{O}_3$ -based eutectic systems, when they are grown from the melt through a controlled system, show interesting mechanical properties (1, 2, 3), both to high and room temperature. Also, they show good toughness and chemical stability that make them a promising materials for structural applications (4, 5).

In a previous report,  $\text{Al}_2\text{O}_3\text{-ZrO}_2(\text{Y}_2\text{O}_3)$  has been directionally solidified by a laser floating zone (LFZ) technique (6). Relationships between growth parameters and  $\text{Y}_2\text{O}_3$  amount have been deduced, and it has been demonstrated that care must be carried out to avoid the presence of defects. The most common defects are pores and bands (7, 8), which lead to poor mechanical characteristics. From the mechanical point of view, the optimal  $\text{Y}_2\text{O}_3$  amount has been established in 3 mol % with respect to  $\text{ZrO}_2$ , while the optimal growth velocity has been established in  $v < 50$  mm/h. In this conditions, very fine and homogeneous interpenetrated microstructure is obtained, which lead to flexural strength around 1.2 GPa (7, 9).

Some previous works (10, 11) have studied the  $\text{TiO}_2$  addition on the  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  system by a solid state reaction method. In this work, the effect of 1 wt%  $\text{TiO}_2$  addition in the  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  (3 mol %  $\text{Y}_2\text{O}_3$ ) eutectic system is studied in samples which are totally melted in LFZ process. The effect on the microstructure and mechanical properties is established when different growth rates are used.

## 2. EXPERIMENTAL

Starting powders,  $\text{Al}_2\text{O}_3$  (99.99%, Aldrich),  $\text{ZrO}_2$  (99+%, Alfa) and  $\text{Y}_2\text{O}_3$  (99.99%, Aldrich), were mixed in the eutectic proportion (12): 62 mol%  $\text{Al}_2\text{O}_3$ , 36.86 mol%  $\text{ZrO}_2$  and 1.14 mol%  $\text{Y}_2\text{O}_3$ . In the doped samples 1 wt%  $\text{TiO}_2$  (99.9+%, Aldrich) was added to the previous composition. They were mixed and milled in a zirconia ball mill to avoid contamination, using acetone media and dried and fired in air at 1000°C.

These powders were mixed with polyvinylalcohol, and used to prepare cylindrical precursors, 120 mm long and 3 mm diameter, by cold isostatic pressing with an applied pressure of 200MPa. The obtained cylinders were then sintered for 12 h at 1500°C in air. Afterwards, the sintered cylinders were used as feed in a LFZ melting installation, where a continuous CO<sub>2</sub> laser ( $\lambda = 10.6 \mu\text{m}$ ) focalised in form of a ring was used to melt a small volume of the sample. This melt is travelling all along the precursor at different growth rates to obtain directionally solidified samples. The chosen growth rates have been established at 10, 300 and 1000 mm/h. In all the cases no relative rotation between feed and seed has been applied. In this process a diameter reduction is performed in order to obtain a final diameter of around 1 mm.

Mechanical characterisation was performed on small pieces (15 mm long) of the obtained bars. Flexural strength measurements were made by the three-point bending test, in an Instron 5565 machine, with a 10 mm loading span fixture and a punch displacement speed of 30  $\mu\text{m}/\text{min}$ . Toughness has been determined using a Vickers indentation method (Matsuzawa MXT50) on polished sections of the samples, with an applied load of 9.8 N. The obtained cracks are Palmqvist type, and the Niihara et al. expression (13) for these type of cracks has been used to make the calculations.

Microstructure of the broken and polished samples was determined using a JEOL 6000 SEM microscope provided with an energy dispersive spectroscopy (EDX) device. Raman measurements were performed at room temperature in a backscattering geometry using an optical spectrometer (model XY, DILOR) with a diode array multichannel detector.

### 3. RESULTS AND DISCUSSION

The microstructure of the samples is shown in Figure 1. As previously reported, two typical eutectic microstructures are obtained (6), one corresponding to the samples grown at 10 mm/h (Figures 1a and 1b), and the other obtained at higher growth speeds (Figures 1c to 1f). At low rates, a typical coupled eutectic microstructure is obtained, indicating that the growth process is produced from a planar solidification front. This microstructure is formed by an intergrowth of ZrO<sub>2</sub> lamellae (white contrast) in a continuous Al<sub>2</sub>O<sub>3</sub> matrix (black contrast). The TiO<sub>2</sub> addition leads to a reduction of the ZrO<sub>2</sub> lamellae size (from 1.6 to 1.5  $\mu\text{m}$ ), as can be expected from its known application as grain-refining agent. EDX analysis has shown that Ti cations are only located in the ZrO<sub>2</sub> rich zones, in agreement with the binary phase equilibrium diagram (14, 15). One major induced effect by TiO<sub>2</sub> addition on the cellular structure is the reduction of the colony grain size, from 37.4 to 30.2  $\mu\text{m}$  at 300 mm/h and from 12.2 to 10.4 at 1000 mm/h, as it was described for the coupled microstructure.

On the other hand, a different effect is caused by TiO<sub>2</sub> addition on this microstructure, which is the coarsening of the intercellular interface. Similar behaviour has been observed when bigger amounts of Y<sub>2</sub>O<sub>3</sub> have been added to the eutectic Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> system (16). EDX analyses have shown that Ti cations are located preferentially at the colonies interfaces, showing concentrations approximately three times higher than inside the colony grains, as a consequence of their low solubility at low temperature in the ZrO<sub>2</sub>. Furthermore, new phases are identified in these zones: TiO<sub>2</sub>, ZrTiO<sub>4</sub> and Al<sub>2</sub>TiO<sub>7</sub>, according with the ternary phase diagram equilibrium (17).

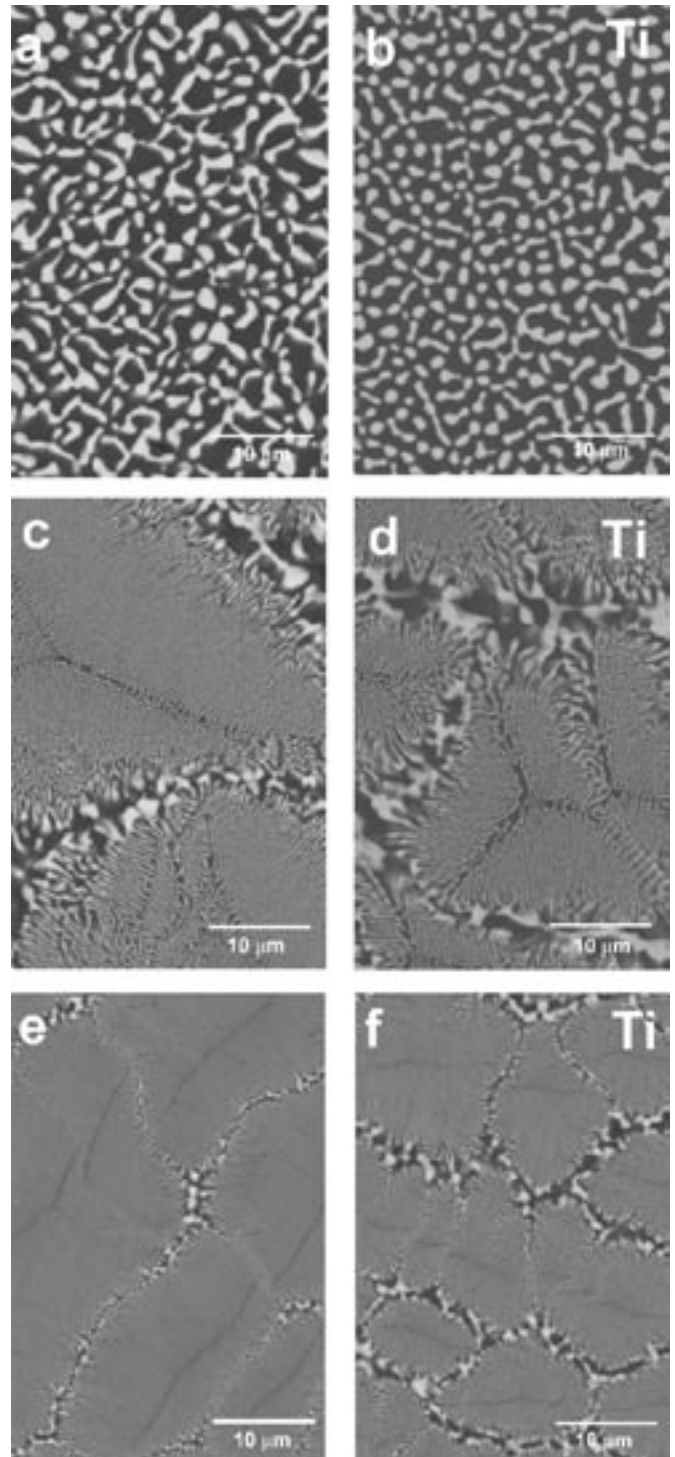


Fig. 1-Transversal microstructures of Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>(3 mol% Y<sub>2</sub>O<sub>3</sub>) eutectic rods grown at different rates. Samples a and b at 10 mm/h; c and d, at 300 mm/h; and e and f at 1000 mm/h. Dark contrast corresponds to Al<sub>2</sub>O<sub>3</sub> rich phase; white contrast ZrO<sub>2</sub> rich zones.

Another interesting result derived from these analyses, is the radial segregation of Y<sub>2</sub>O<sub>3</sub>, which can reach concentrations of about two times higher in the centre than in the border of the rods, and it is independent of TiO<sub>2</sub> doping. The knowledge of the Y<sub>2</sub>O<sub>3</sub> distribution is necessary in order to know the ZrO<sub>2</sub> phase stabilization. In this work, no monoclinic ZrO<sub>2</sub> phase has been detected through the sample volume, but

this  $\text{Y}_2\text{O}_3$  segregation can be very important for other  $\text{Y}_2\text{O}_3$  compositions.

In Table I the mechanical results for flexural strength and toughness measurements for all the samples are shown. Only toughness data for transversal sections are displayed, because no cracks were observed on longitudinal sections, even when using the maximum load (9.8N) of the microhardness apparatus. As it can be clearly seen,  $K_{Ic}$  is improved with  $\text{TiO}_2$  addition. For undoped samples  $K_{Ic}$  values are decreasing as growth rates increase. This behaviour is more pronounced when growth speed increases from 300 to 1000 mm/h (around 30%), than from 10 to 300 mm/h (only 6%). When  $\text{TiO}_2$  is added, an increase on  $K_{Ic}$  is observed in all the cases, with respect to the undoped samples. This increase is really notorious, ranging from 20% for samples grown at 10 mm/h to around 45% for samples grown at higher rates. From this point of view is clear that the best results are obtained when using high growth speeds, combined with the presence of  $\text{TiO}_2$ . Furthermore, contrarily to the undoped samples, an increase is detected when growth speed changes from 10 to 300 mm/h (around 10%).

TABLE I. AVERAGE VALUES OF FLEXURAL STRENGTH AND TOUGHNESS FOR THE DIFFERENT SAMPLES AND GROWTH CONDITIONS.

	10 mm/h 0% $\text{TiO}_2$	10 mm/h 1% $\text{TiO}_2$	300 mm/h 0% $\text{TiO}_2$	300 mm/h 1% $\text{TiO}_2$	1000 mm/h 0% $\text{TiO}_2$	1000 mm/h 1% $\text{TiO}_2$
$\sigma_{\text{max}}$ (GPa)	1.26±0.37	0.90±0.15	1.34±0.38	1.17±0.22	1.15±0.40	1.79±0.14
$K_{Ic}$ (MPam <sup>1/2</sup> )	5.68±0.76	6.89±1.97	5.34±0.73	7.59±2.25	3.72±0.61	5.43±2.38

When observing the mechanical strength values (see Table I), some aspects must be remarked. First of all, an increase is detected when growth rate changes from 10 to 300 mm/h, in all the samples (doped and undoped). This change is more important with  $\text{TiO}_2$  doping, going from around 6% for undoped samples to 30% for the doped ones. When growth speed is increased to 1000 mm/h the behaviour is different, depending on the presence of  $\text{TiO}_2$ . For undoped samples, the minimum strength value is obtained, but contrarily, for doped samples is the highest. In this case (1000 mm/h doped sample) a spectacular increase of nearly 100% with respect to

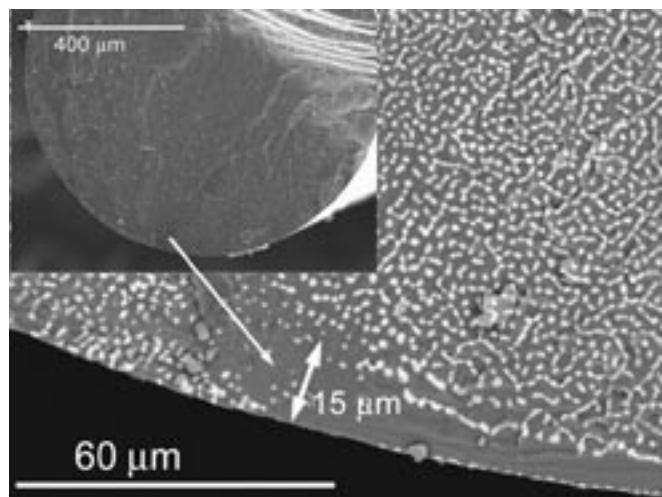


Fig. 2-Fractography of a doped sample grown at 10 mm/h showing a typical superficial inhomogeneity ( $\text{Al}_2\text{O}_3$ -rich region), controlling the strength of this rod.

10 mm/h, and about 50% when compared with 300 mm/h is found. Furthermore, the measured value for these conditions is the highest value obtained for all the samples in all the conditions. It is an excellent result, exceeding about 50% the highest values reported in the literature (7, 9).

Strength behaviour in these materials is mainly depending on the defects generated in the growth process (18). Bending tests are specially affected by surface defects (banding, segregations, flaws, etc). On the fractured samples, it has been found the presence of microstructure inhomogeneities (see figure 2) that explain the obtained strength values. For this reason, it is not possible to find a relationship between the different typical microstructures and the bending behaviour.

The high toughness of  $\text{Al}_2\text{O}_3\text{-ZrO}_2(\text{Y}_2\text{O}_3)$ , which has been attributed to the presence of thermoelastic residual stresses (18), is improved in this work by the presence of new Ti-rich phases. The improvement of the toughness, produced by the Ti-addition, is found for all the growth conditions.

#### 4. CONCLUSIONS

Long rods of the eutectic  $\text{Al}_2\text{O}_3\text{-ZrO}_2(3\text{ mol}\% \text{Y}_2\text{O}_3)$  system, with and without  $\text{TiO}_2(1\text{ wt}\%)$  addition have been directionally grown by a laser floating zone method at different growth rates. It has been established that the resulting microstructure is a function of the growth rate, obtaining interpenetrated microstructure at low rates (10 mm/h) and a cellular growth at higher rates (300 and 1000 mm/h). The effect of  $\text{TiO}_2$  doping on the microstructure is the grain size-refinement, the intercolonies coarsening and the segregation of new Ti rich phases ( $\text{ZrTiO}_4$ ,  $\text{Al}_2\text{TiO}_5$  and  $\text{TiO}_2$ ) in these zones.

It has also been demonstrated that  $\text{TiO}_2$  addition improves the mechanical properties, reaching strength values exceeding 50% the highest values reported in the literature. Even, if under certain conditions, it seems to be unfavourable the  $\text{TiO}_2$  on maximum strength (10 and 300 mm/h), this is explained by the presence of superficial inhomogeneities.

More work must be performed in order to avoid growth microstructural defects, which affect negatively the mechanical properties of the bulk material. One possible way to solve this problem can be the change on growth conditions through rotation between feed and seed.

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