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Study of directionally solidified eutectic Al_2O_3-ZrO_2(3%Y_2O_3) doped with TiO_2

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An study of directionally grown samples of the eutectic composition in the Al_2O_3-ZrO_2 (3 mol% Y_2O_3) system, with small TiO_2 additions (1 wt%), is presented. The microstructural changes induced by this addition are analysed using SEM (EDX) techniques. The mechanical changes, when 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, interpenetratred and homogeneous microstructure is obtained, independently of the 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 TiO_2 is present. This size reduction is accompanied with an increase of the toughness.

Keywords: Al_2O_3-ZrO_2, eutectic, directional solidification, TiO_2 doping

Estudio del eutéctico Al_2O_3-ZrO_2 (3% Y_2O_3) dopado con TiO_2 obtenido por solidificación direccional

Este trabajo presenta un estudio de muestras crecidas direccionalmente del sistema Al_2O_3-ZrO_2 (3 mol% Y_2O_3) en su composición eutéctica con pequeñas adiciones de óxido de titanio (1% de 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: Al_2O_3-ZrO_2, eutéctico, solidificación direccional, TiO_2

1. INTRODUCTION

The Al_2O_3-based eutectic systems, when they are grown from the melt trough 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, Al_2O_3-ZrO_2(Y_2O_3) has been directionally solidified by a laser floating zone (LFZ) technique (6). Relationships between growth parameters and Y_2O_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 Y_2O_3 amount has been established in 3 mol % with respect to 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 TiO_2 addition on the Al_2O_3-ZrO_2 system by a solid state reaction method. In this work, the effect of 1 wt% TiO_2 addition in the Al_2O_3-ZrO_2 (3 mol % Y_2O_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, Al_2O_3 (99.99%, Aldrich), ZrO_2 (99+%, Alfa) and Y_2O_3 (99.99%, Aldrich), were mixed in the eutectic proportion (12): 62 mol% Al_2O_3, 36.86 mol% ZrO_2 and 1.14 mol% Y_2O_3. In the doped samples 1 wt% TiO_2 (99.9+%, Aldrich) was added to the previous composition. They were mixed and milled in a zircona ball mill to avoid contamination, using acetone media and dried and fired in air at 1000ºC.

These powders were mixed with polivinilalcohol, 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 where then sintered for 12 h at 1500ºC in air. Afterwards, the sintered cylinders were used as feed in a LFZ melting installation, where a continuous CO_2 laser (λ = 10.6 μm) 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 μm/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_2 lamellae (white contrast) in a continuous Al_2O_3 matrix (black contrast). The TiO_2 addition leads to a reduction of the ZrO_2 lamellae size (from 1.6 to 1.5 μm), 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_2 rich zones, in agreement with the binary phase equilibrium diagram (14, 15). One major induced effect by TiO_2 addition on the cellular structure is the reduction of the colony grain size, from 37.4 to 30.2 μm 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_2 addition on this microstructure, which is the coarsening of the intercellular interface. Similar behaviour has been observed when bigger amounts of Y_2O_3 have been added to the eutectic Al_2O_3-ZrO_2 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_2. Furthermore, new phases are identified in these zones: TiO_2, $ZrTiO_4$ and Al_2TiO_5, according with the ternary phase diagram equilibrium (17).

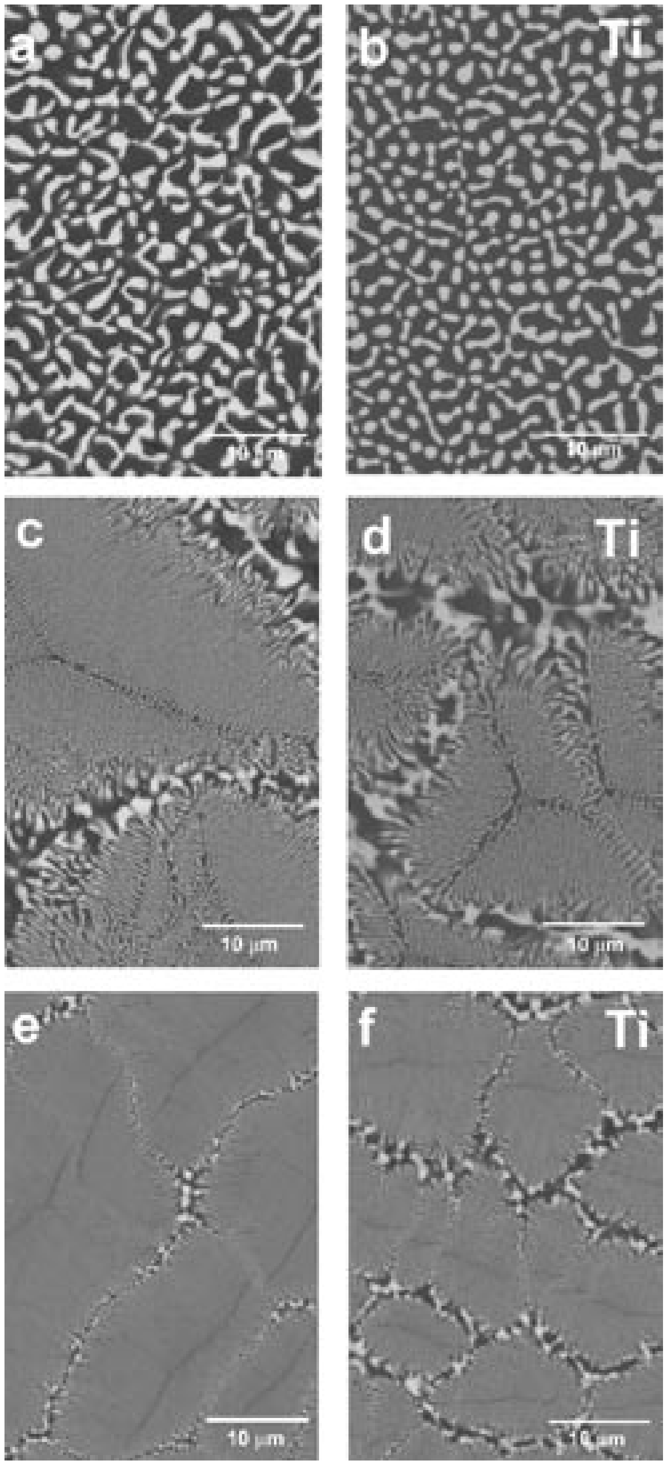

Fig. 1-Transversal microstructures of Al_2O_3-ZrO_2(3 mol% Y_2O_3) eutectic rods grown at different rates. Samples a and b at 10 mm/h; c and d, at 300 mm/h; and e and f at 1000 mm/h. Dark contrast corresponds to Al_2O_3 rich phase; white contrast ZrO_2 rich zones.

Another interesting result derived from these analyses, is the radial segregation of Y_2O_3, 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_2 doping. The knowledge of the Y_2O_3 distribution is necessary in order to know the ZrO_2 phase stabilization. In this work, no monoclinic ZrO_2 phase has been detected through the sample volume, but this Y_2O_3 segregation can be very important for other Y_2O_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 TiO_2 addition. For undoped samples K_{Ic} values are decreasing as grown 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 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 TiO_2. Furthermore, contrarily to the undoped samples, an increase is detected when growth speed changes from 10 to 300 mm/h (around 10%).

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 Al_2O_3-ZrO_2 (Y_2O_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.

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

	10 mm/h 0% TiO_2	10 mm/h 1% TiO_2	300 mm/h 0% TiO_2	300 mm/h 1% TiO_2	1000 mm/h 0% TiO_2	1000 mm/h 1% TiO_2
σ_{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}($MPam^{1/2}$)	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 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 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

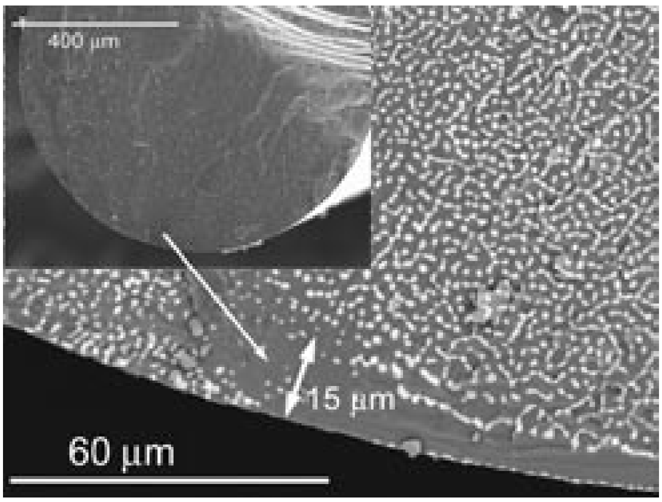

Fig. 2-Fractography of a doped sample grown at 10 mm/h showing a typical superficial inhomogeneity (Al_2O_3-rich region), controlling the strength of this rod.

4. CONCLUSIONS

Long rods of the eutectic Al_2O_3-ZrO_2 (3 mol% Y_2O_3) system, with and without TiO_2 (1 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 TiO_2 doping on the microstructure is the grain size-refinement, the intercolonies coarsening and the segregation of new Ti rich phases ($ZrTiO_4$, Al_2TiO_5 and TiO_2) in these zones.

It has also been demonstrated that 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 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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