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Al_2O_3–$Y_3Al_5O_{12}$(YAG)–ZrO_2 ternary composite rapidly solidified from the eutectic melt

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Abstract

In situ fabrication of new ceramic eutectic composites by rapid solidification of eutectic drops is a cheap and quick method compared to fabrication of directional solidification or multi-step fabrication methods of fiber reinforced/layered composites for high temperature use. This study reports the fabrication of ceramic composites during rapid solification of eutectics melts in the ternary oxide alumina–yttria–zirconia system. Layered ternary eutectics are obtained in the alumina–YAG–zirconia subsystem. The microstructure of Al_2O_3–$Y_3Al_5O_{12}$–ZrO_2 composites rapidly solidified from melts is presented.

Keywords: Al_2O_3; Composite; Microstructure-final; Structural application; Ternary eutectic; ZrO_2

1. Introduction

The periodic structure of the multi-oxide eutectic ceramics forms naturally during solidification from the eutectic melt.[1] The phase spacing (or eutectic lamella) and eutectic pattern formed are kinetically controlled during the solidification. The interphase spacing for each eutectic system is dependent mainly on the solidification rate, while the eutectic arquitecture of the composites depends on the volume fraction of each phase, the formation of faceted or non-faceted interphases, the movement of the liquid–solid front, the nucleation of multiple eutectic colonies, etc.

The studied composition corresponds to the ternary eutectic inside the Al_2O_3–$Y_3Al_5O_{12}$–ZrO_2 region of the Al_2O_3–Y_2O_3–ZrO_2 ternary oxide diagram.[2,3] Composites showing homogeneous structure and phase distribution could be obtained in spite of the high thermal residual stresses generated upon cooling. Due to the rapid growth during quenching, the multi-oxide composites obtained by melt quenching have thinner interphase spacings,[4,5] thus yielding lamella sizes well into the sub-micron range. The typical lamella sizes also corresponds to the size of inhomogeneities and defects not intrinsic of the eutectic pattern, which are inevitally formed during processing and critically control the mechanical properties of the composites, such as the fracture toughness. Therefore, there is a strong interest in determining the effects of rapid solidification routes in both the eutectic microstructure and the mechanical properties.

This study aims to present the novel eutectic arquitecture in rapidly solidified Al_2O_3–$Y_3Al_5O_{12}$(YAG)–ZrO_2 ternary eutectic composites obtained during rapid solidification of ternary eutectic melts in the alumina–yttria–zirconia system.[6] The fracture toughness of the as-solidified composites was determined by indentation methods.

2. Experimental

Starting materials were prepared from high purity (>99.9%) ZrO_2, Y_2O_3 and Al_2O_3 powders by dry and wet mixing in methanol using an alumina mortar. Pellets of the

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mixed powders were placed on a copper plate cooled by water and melted in air by the radiation of a Xe lamp. The spherical arc-melted specimen was quenched by rapidly moving the copper plate from the focal point. The cooling rate using the described method is estimated to be higher than 10^3 K s^{-1} [6] and solidification rates higher than 1 mm/s. Arc-melted materials were white spheres with diameters up to 1 cm.

The microstructure of the composites and component phases was determined by scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD) and micro-Raman techniques. Powder XRD patterns were obtained after grinding in ethanol using an agate mortar, using Cu Kα radiation in a curved graphite-beam monochromator.

The solidified pellets were cut with a diamond saw and the cross-sections were sequentially polished up to 1 μm. Surfaces of melted samples were prepared by diamond polishing and Pt–Pd coated before observation.

The crystalline phases present and the cation substitution in each phase (variable in the ternary system, due the extended mutual solubility in the different solid solution phases) were determined by XRD and Raman spectroscopy techniques. Hardness and fracture toughness were determined by Vickers indentations techniques on the polished surfaces, using applied loads from 9.8 to 98 N. The length of the radial cracks emanating from the indenter was measured in SEM micrographs of the cracks. At least 12 cracks were measured for the fracture toughness measurement in each sample.

3. Results and discussion

3.1. X-ray diffraction (XRD)

The XRD spectra of a composite after rapid solidification of the Al_2O_3–$Y_3Al_5O_{12}$(YAG)–ZrO_2 ternary eutectic is shown in Fig. 1. Identified crystalline phases are corundum (α-Al_2O_3), ytrium aluminium garnet ($Y_3Al_5O_{12}$, YAG) and zirconia–yttria solid solution with fluorite-type structure cubic zirconia. No other phase was found. The observed phases are those predicted by the solid phase regions of the subsolidus diagram in the ternary oxide system, determined in a previous study.[3]

The mutual solubility between the different oxides is very different, alumina shows very little solubility of either zirconia or yttria, while YAG exhibit a noticeable shifting of the peaks in the X-ray diffraction spectra, due to the presence of Zr cations substituting Y, while the highest solid solubility is found in the cubic zirconia phase, which is in fact a solid solution with ∼33 mol% Y_2O_3 and about as many cations of each Zr and Y, as has been confirmed by Raman spectroscopy.[3,7]

3.2. Eutectic microstructure after rapid solidification

The composite presents a fine structure, with typical phase spacings in the sub-micron range. Fig. 2 shows a polished cross-section. Rapid solidification results in a layered eutectic with zirconia placed as intermediate phase between parallel layers of alumina and yttrium aluminium garnet. The pattern can be described as an ordered/aligned eutectic, similar to alumina–zirconia eutectics, instead of an 'entangled' eutectic, typical of alumina–YAG eutectic composites.

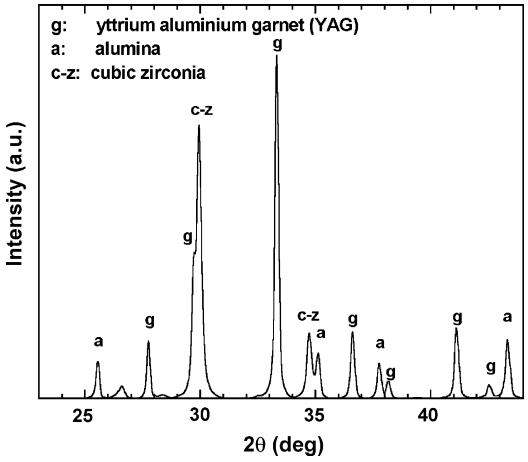

Fig. 1. XRD spectra of a composite after rapid solidification of the Al_2O_3–$Y_3Al_5O_{12}$(YAG)–ZrO_2 ternary eutectic. Identified crystalline phases are corundum (α-Al_2O_3), ytrium aluminium garnet ($Y_3Al_5O_{12}$, YAG) and zirconia–yttria solid solution with fluorite-type structure, cubic zirconia. The observed phases are those predicted by the solid phase regions of the subsolidus diagram in the ternary oxide system, determined in a previous study.[16]

3.2.1. Ternary microstructure

The microstructure of the ternary composite is shown in Fig. 3. In the SEM micrograph the different phases can be distiguished by their contrast: the black phase is alumina, grey is YAG and the white interphases correspond to zirconia. The zirconia phase is placed either as rods, which tend to be surrounded by alumina, or as a planar interphase between the alternating layers of alumina and YAG, which are aligned in each eutectic colony.

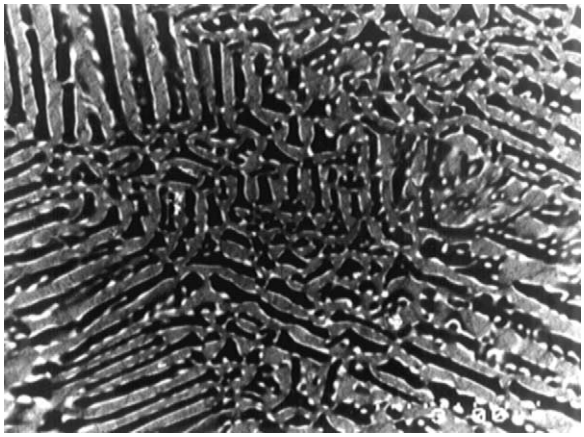

Fig. 2. SEM micrograph showing the polished cross-section of a pellet rapidly solidified from melt.

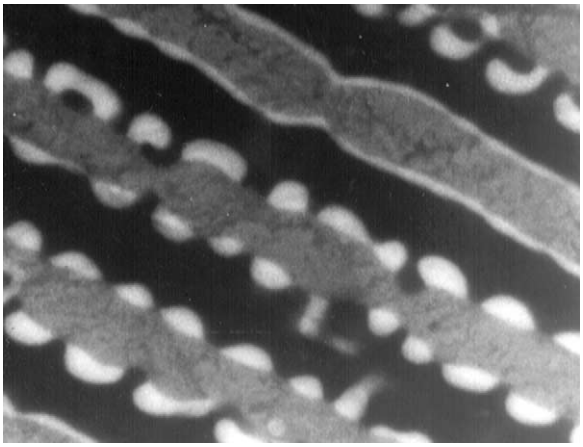

Fig. 3. SEM micrograph showing the Al_2O_3–$Y_3Al_5O_{12}$(YAG)–ZrO_2 ternary eutectic microstructure. The alumina layers (black), run in parallel with the garnet layers (with grey contrast) and the thinner white interphases in between, displaying rod or lamella patterns, correspond to the cubic yttria stabilized zirconia phase.

Zirconia acts as the intermediate phase typical of a layered ternary eutectic arquitecture,[8] present at each interphase (···–zirconia–alumina–zirconia–YAG–zirconia–···). The addition of zirconia and the preparation route at rapid solidification rates, therefore, alters the typical entangled arquitecture of alumina–YAG eutectic bicrystals promoting a more ordered eutectic pattern.

The fine lamella structure is due to the rapid solidification method used. Compared to directional solidification methods, i.e. Bridgman,[9–11] laser floating zone (LFZ)[12,13] or fiber pulling,[14] with solidification velocities ranging from 0.1 to less than 100 cm/h, the solidification velocities (and growth rate) in our composites are at least one order of magnitude higher than in the pulling down method and two orders of magnitude higher than in directional solidification. It is interesting to compare the microstructure reported here with reported directionally solidified composites in the ternary system. Bulk samples of several centimeters have been grown by Bridgman modified methods,[11] but the interphase spacings are at least one order of magnitude higher than in this composites. Laser floating zone method allows to obtain cylindrical geometries of up to several millimeters in diameter.[12] Eutectic fibers with an interphase spacing near the micron range have been grown recently grown by the 'μ-pulling down method',[13] an inverse-Stepanov technique suitable for the growth of fibers with submilimeter diameters. However, micro-fibers or bulk eutectics with a cylindrical geometry have limited applications, specially if a large surface of material is required, such as in coatings, or complex shapes are needed, and more economic preparation routes must be developed first. The present results indicate that rapid solidification can result in homogeneous bulk microstructure by using fast heat transfer conditions during cooling, therefore, the ternary eutectic seems to offer potential to explore in situ shaping during solidification, i.e. by melt casting.

There is not a unique eutectic microstructure, as the solidification of the eutectic melt will be strongly dependent of the heat transfer conditions. During rapid solidification there is a strong tendency to form well-aligned structures not only at the eutectic composition but relatively far from it, in a wide compositional range of quasi-eutectics.[14]

3.3. Indentation results

Values of the indentation fracture toughness were obtained using the Eq. (1)

$$K_{\mathrm{Ic}} = k\left(\frac{E}{H}\right)^{2/5}\left(\frac{P}{al}\right)^{1/2}, \quad (1)$$

where E is the Young's Modulus of the material; H, hardness; P, indentation load; a, half diagonal of the indent; l, crack length measured from the tip and k, dimensionless constant determined experimentally. The experimental details are described in.[15] Obtained values of the fracture toughness were $K_{\mathrm{Ic}} = 9.0 \pm 2.0\ \mathrm{MPa\,m^{1/2}}$.

Other fracture toughness values reported for different eutectic composites in the system are: between 2 and 4 $\mathrm{MPa\,m^{1/2}}$ for the Al_2O_3–YAG binary eutectic and up to ∼10 for yttria stabilized zirconia–alumina eutectics with layered structure.[16] In solidified eutectics, the indentation cracks appear often arrested, associated with the appearance of one or several parallel cracks with the same crack growth direction.[17] Crack branching and deflection and the elastic unbroken ligaments left in the crack wake behind the crack tip contribute to the toughness of solidified eutectics, compared to the monolithic phases. The reduction in phase spacings by one order of magnitude, compared to directionally solidified eutectics, causes the more rapid accumulation of interactions between the eutectic interphases and the crack during crack growth and in the crack wake.

The fracture toughness at high temperature may be significantly different that the measured room temperature fracture toughness reported here because of the contribution due to the residual stresses between the eutectic lamella,[18] due to the differences in thermal expansion coefficient.

4. Summary

An Al_2O_3–YAG–ZrO_2 ternary eutectic composite with an ordered ternary structure of successive alternating lamella: zirconia–alumina–zirconia–YAG···, has been obtained by the coupled growth of the three phases during rapid solidification from the ternary eutectic melt. The ternary microstructure obtained is presented. Both laminar and rod-type zirconia eutectics are observed, but not the entangled microstructure typical of unidirectionally solidified alumina–YAG eutectics.

The preparation of ternary composites by other preparation methods and experimental conditions will help to under-

stand and control the microstructure development in multi-eutectic ceramic composites, which is mainly kinetically controlled, rather than dictated by the thermodynamic equilibrium.

The fracture toughness measured by indentation methods, $K_{Ic} = 9.0\,MPa\,m^{1/2}$. The microstructural changes related to the size effect and the interaction mechanisms between the crack and the eutectic interphases need to be further investigated.

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