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Journal of the European Ceramic Society 25 (2005) 1369–1372

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Stabilization of zirconia lamellae in rapidly solidified alumina–zirconia eutectic composites

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Abstract

In-situ fabrication of ceramic eutectic composites by rapid solidification of eutectic drops is a cheap and quick method compared to directional solidification or to multi-step fabrication methods of fiber reinforced/layered materials for high temperature use. Binary eutectic composites with a homogeneous periodic microstructure have been obtained by directional solidification of eutectic melts for many years, but typical solidification velocities used in directional solidification are limited to the range of cm/hour or, more recently, up to 15 mm/min. The present study aims to determine the effects of faster solidification rates on the structure of the alumina–zirconia binary composites obtained at higher growth rates by rapid solidification from eutectic melts in air or vacuum. A binary composite with zirconia stabilized in the high-temperature tetragonal form is presented. The stabilization of the tetragonal phase has not been observed before in bulk crystalline pellets of binary Al_2O_3–ZrO_2 eutectic composites.

Keywords: Alumina (Al_2O_3)–zirconia (ZrO_2) nanocomposite

1. Introduction

Ceramic composites with a naturally assembled structure can be formed by solidification of eutectic melts and the phase interspacing reduced by decreasing the time available for diffusion of species in the transition from the compositionally homogeneous liquid to the different solid phases.[1] Due to the rapid growth during quenching, the composites have thinner interphase spacings.[2–4] The typical lamella sizes also corresponds to the size of inhomogeneities and defects not intrinsic of the eutectic pattern, which are inevitably formed during processing and critically control the mechanical properties of the composites. Therefore, there is a strong interest in determining the effects of rapid solidification routes in both the eutectic microstructure and the mechanical properties. However, the difficulty of obtaining bulk ceramic composites with homogeneous structure increases with solidification velocity. The fabrication of binary eutectics by rapid solidification techniques yielded moderate success in the past, producing partially amorphous or inhomogeneous samples, because it is difficult to maintain a homogeneous heat transfer at high cooling rates.[5–9] Therefore, rapid solidification methods were used to fabricate eutectic powders, but not layered eutectic crystals. More recently, Al_2O_3–ZrO_2 eutectics with submicron phase spacings have been obtained as fibers[10] (with diameters from 0.2 to 2 mm) and plates (with thicknesses up to 250 μm).[11]

This study presents the preparation of alumina–zirconia eutectic and quasi-eutectic composites with reduced lamella spacing, using rapid solidification. The effect of solidification velocities of several mm/s on the crystallization and the microstructure of eutectic is presented. Composites with homogeneous structure and phase distribution were obtained in spite of the high thermal residual stresses generated upon cooling.

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doi:10.1016/j.jeurceramsoc.2005.01.013

2. Experimental

Starting materials were prepared from high purity (>99.9%) ZrO_2 and Al_2O_3 powders by dry and wet mixing in methanol using an alumina mortar. Pellets of the mixed powders were melted in air by the radiation of a Xe lamp and rapidly quenched on a copper plate cooled by water.[3,4] The cooling rate using the described method is estimated to be higher than 10^3 K/s and solidification rates higher than 1 mm/s. Arc-melted materials were white spheres with diameters up to 1 cm.

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 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.

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.[12] Powder X-ray diffraction patterns were obtained using Cu Kα radiation in a curved graphite-beam monochromator. The proportion of tetragonal zirconia was evaluated from the experimental intensities using the ratio $I_T[1\,1\,1]/(I_M[1\,1\,1]+I_T[1\,1\,1]+I_M[1\,1\,1])$, where I_T and I_M are the intensities of the corresponding tetragonal and monoclinic peaks.

3. Results and discussion

3.1. X-ray diffraction (XRD)

The spectra of the raw powders matched the vibrational features of JCPDS Card Files No. 10-173 (α-Al_2O_3) and 36-420/37-1484 (monoclinic ZrO_2). The XRD analysis of rapidly solidified binary composites from non-eutectic melts with compositions in the alumina-rich region showed also additional features corresponding to tetragonal zirconia, with lower intensity than the monoclinic zirconia. The tetragonal content in rapidly solidified non eutectic composites was in the order of ∼5%.[13]

The XRD spectra of a composite after rapid solidification of the Al_2O_3–ZrO_2 binary eutectic is shown in Fig. 1. Identified crystalline phases are corundum (α-Al_2O_3) and tetragonal zirconia. The XRD spectra indicate that the solidification conditions promote the stabilization of the high-temperature tetragonal allotrope at room temperature. The causes of stabilization are the enhanced solid solubility of alumina into zirconia at higher temperatures, which can be retained during quenching, therefore causing the stabilization of the tetragonal phase;[14] the constraining effect of the alumina phase,[15] with lower thermal dilatation coefficient than zirconia; and a size effect, as zirconia domains have lower surface energy in the tetragonal form. For free nanoparticles, the typical size for transformation is ∼15 nm.[16]

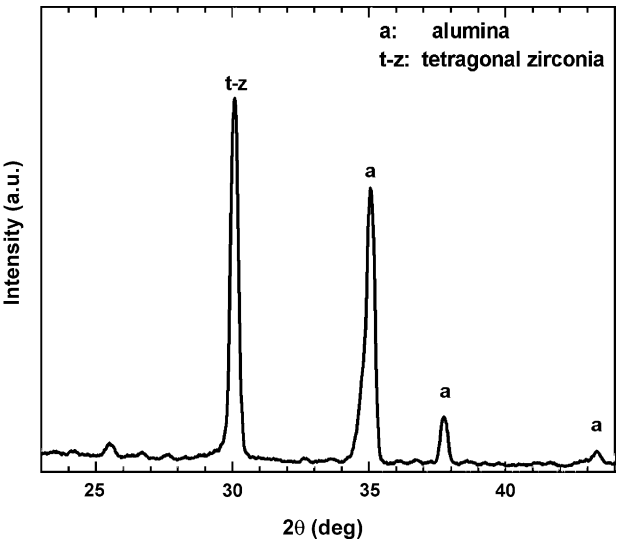

Fig. 1. XRD spectra of a composite after rapid solidification of the Al_2O_3–ZrO_2 binary eutectic. Identified crystalline phases are corundum (α-Al_2O_3), and tetragonal zirconia.

The mutual solubility between the different oxides is very different, alumina shows very little solubility of zirconia, while the significant high temperature solubility of alumina in zirconia can be maintained at room temperature because fast solidification prevents the sample attaining thermodynamical equilibrium at lower temperatures. Due to the sluggish cations movement below ∼1500 °C, the alumina substituted lattice can retain the high-temperature composition. In unconstrained, microsized zirconia domains, the martensitic transformation from tetragonal to monoclinic is triggered during cooling regardless of the diffusion velocities of cations if the alumina content in the lattice is not sufficient to stabilize the tetragonal form. Therefore, the presence of monoclinic zirconia in non-eutectic composites solidified using the same method mentioned above indicates that the stabilizing effect of alumina is not sufficient per se to retain the tetragonal form.

In non-eutectic composites the homogeneous reduction of zirconia phase spacing does not take place as it does for solidified eutectic, so the size reduction and the constraining effect of the alternating layers in the eutectic architecture are not effective.

The constraining effect of alumina can hinder the transformation of the tetragonal structure in the zirconia particles, because the needed volume expansion associated to the tetragonal-monoclinic transformation. The effect has been observed by many authors in sintered alumina–zirconia composites.[17] It is worth noting that the level of thermal residual stresses that eutectics phase boundaries can stand without opening is significantly higher than in sintered composites.[18]

Previous studies by Claussen et al.[6] and Mckittrick et al.[7,8] have showed the solidification of amorphous in the binary system and the precipitation/crystallization of tetragonal grains in the amorphous by thermal treatment. Due to its lower activation energy and lower surface energy, as the tetragonal phase is structurally closer to the amorphous state than monoclinic zirconia, it is possible to obtain even pure tetragonal zirconia at room temperature, without adding any stabilizing agent.[16] There is no amorphous in the crystalline composite obtained upon solidification of the eutectic melt in this study, therefore the low temperature retention of tetragonal zirconia observed here cannot be due to precipitation from glass. This is also evident from the eutectic microstructure, which is described later. While in the precipitation from amorphous the dominant zirconia phase formed is tetragonal, in the case of eutectic composites only the monoclinic allotrope is generally obtained in the solid composite. The microstructure is significantly different, of isolated and small nanoprecipitates in the former case and of continuous layered structures in eutectics solidified from melt, as it was shown by Claussen et al.[6] in rapidly solidified pellets, with diameter ~200 μm, containing both types of structures. The crystalline zirconia allotrope in eutectic fibers with diameter of up to 2 mm obtained by Lee et al.[10] at growth rates up to 15 mm/min and in laser-melted eutectic plates obtained by Larrea et al.[11] is also the monoclinic form. Zirconia lamella thicknesses reported were, respectively, 110 and 160 nm. Bourban[19] showed that it is possible to reduce further the lamella size locally by laser remelting of alumina–zirconia eutectics. The XRD results indicate that the eutectic composites studied here, with a tetragonal content of 100%, have smaller eutectic spacing.

3.2. Eutectic microstructure after rapid solidification

Fig. 2 shows a polished cross-section of the binary composite. The composites present a fine structure, where eutectic colonies or grains can be distinguished. Typical diameters of the colonies in the cross-section micrographs are ~20 μm.

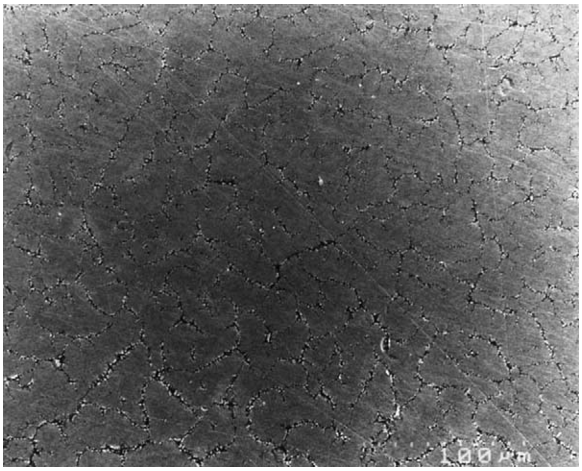

Fig. 2. SEM micrograph showing the structure of the rapidly solidified alumina–zirconia eutectic composite in a polished cross-section.

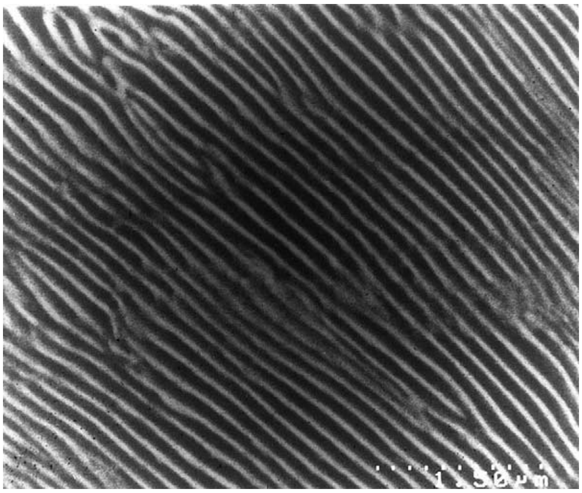

Fig. 3. SEM micrograph showing the Al_2O_3–ZrO_2 binary eutectic microstructure. The alumina layers (black), run in parallel with the zirconia layers (white) inside each eutectic colony.

The eutectic pattern inside a colony is shown in Fig. 3, the black phase in the scanning electron microscope (SEM) micrograph corresponds to alumina and the white phase to zirconia. Rapid solidification results in a layered eutectic with alternate alumina and zirconia layers. The pattern can be described as an ordered eutectic in each eutectic colony, with typical phase spacings below 100 nm for Al_2O_3 and below 50 nm (~30 nm) for ZrO_2 inside each eutectic colony.

The fine lamella structure is due to the rapid solidification method used. Although it is not the scope of this report to estimate the growth rate during melt quenching, compared to directional solidification methods (i.e. Bridgman,[20] laser floating zone (LFZ)[11,21,22] or fiber pulling,[10] 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 two orders of magnitude higher than in directional solidification and about one order of magnitude higher than in laser floating zone methods, as supported by the microstructural observations of the typical eutectic spacings. It is worth to note that micro-fibers or bulk eutectics with a cylindrical geometry obtained by modified-Stepanov techniques and laser floating zone methods have limited applications and are expensive to produce.

More economic preparation routes of high temperature ceramic eutectics must be developed, specially if a large surface of material is required, such as in coatings, or complex shapes are needed. The present results indicate that rapid solidification can result in homogeneous bulk microstructure by using fast heat transfer conditions during cooling, therefore rapid solidification of eutectic seems to offer potential to explore in-situ shaping during solidification, i.e. by melt casting and an inexpensive preparation route.

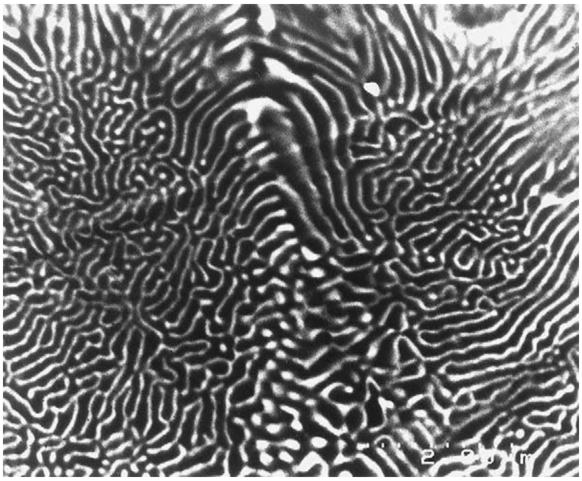

Fig. 4. SEM micrograph showing a boundary between eutectic colonies.

4. Summary

An Al_2O_3–ZrO_2 binary eutectic composite with zirconia stabilized in the tetragonal form throughout the bulk of the composite, due to the effect of rapid solidification, has been presented. The effects of rapid solidification to promote the stabilization of the tetragonal zirconia form have been discussed and the eutectic architecture of the rapidly solidified composite has been presented (Fig. 4).

Acknowledgements

Financial support from the Spanish Ministry of Science and Technology is gratefully acknowledged.

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