Narrowing of Al_2O_3 , $\text{Y}_3\text{Al}_5\text{O}_{12}$ and ZrO_2 Eutectic Lamellae by Rapid Solidification in Al_2O_3 Based Eutectic Composites

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The fabrication of bulk ceramic composites with homogeneous structure in the nano-scale is a difficult challenge. Multi-step methods based on synthesis and sintering of ceramic nanopowders, or methods using deposition from gas phases are complex and require high energy input with very low energetic efficiency, so they are not practical. However, bulk ceramic composites with a naturally self-assembled structure may be formed by solidification from eutectic melts. Smaller eutectic spacing may be obtained by using rapid solidification. We report here the rapid solidification in an arc-image furnace of eutectic melts in the system alumina- $\text{Y}_3\text{Al}_5\text{O}_{12}$ -zirconia. Ceramic eutectic composites grown from melt have homogeneous bulk structure and lamella sizes in the submicron to the nanoscale range.

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1. Introduction

Oxides ceramics have intrinsic properties such as oxidation resistance, chemical and thermal stability. However, they also have poor resistance to thermal shock and in general to crack propagation and growth, which results in rapid material degradation and catastrophic fracture. One successful approach to improve the thermo-mechanical stability of ceramic oxide composites has been their fabrication by solidification from eutectic melts.¹⁾ Eutectic composites fabricated by unidirectional solidification have excellent strength and creep resistance at high temperature.²⁾ The strengthening of grain boundaries characteristic of eutectics is especially required for long-term service in high temperature applications.³⁾ The refining of the microstructure in eutectics composites with thinner lamella size will result in higher strength by reduction in flaw size, inhomogeneities and stress accumulation points.

However the fabrication of oxide eutectics by more rapid solidification techniques has yielded moderate success, producing partially amorphous or inhomogeneous samples, because it is difficult to maintain a homogeneous heat transfer at high cooling rates.⁴⁻⁹⁾ Therefore rapid solidification methods have been used to fabricate eutectic powders, but not layered eutectic crystals. The smaller lamella sizes in eutectic composites by unidirectional solidification are in the few microns range. The aim of this work is to obtain a eutectic composite with lamella size in the sub-micron range, by using rapid solidification in an arc-image furnace.

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 mixed powders with the eutectic composition¹⁰⁾ were placed on a copper plate cooled by water and melted in air in an arc-image lamp furnace by the radiation of a Xe lamp (Ushio UF-10001). The spherical arc-melted specimens were

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} .¹¹⁾ Arc-melted materials were white spheres with diameters of a few mms.

Powder X-ray diffraction patterns were obtained from arc-melted samples after grinding in ethanol using an agate mortar, using $\text{CuK}\alpha$ radiation in a curved graphite-beam monochromator (MXP3VA, MAC Science Company, Ltd, Tokyo, Japan). Surfaces of melted samples were prepared by diamond polishing and Pt-Pd coated before observation by scanning electron microscopy (SEM) in the back scattering mode.

Inter lamellar spacings were measured by a linear intercept method, counting the number of lamella intercepted by lines of known length perpendicular to the direction of the lamella. The relative lamella thickness ratios between alumina/ $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) and alumina/zirconia were calculated from magnified micrographs.

3. Results and Discussion

The as-solidified samples presented good homogeneity and were free of surface flaws, cracks and porosity. The XRD pattern in Fig. 1 corresponds to a ternary composite with alumina, YAG and cubic fluorite-type zirconia-yttria solid solution as the three crystalline phases. As-solidified surfaces show waves associated with periodic lamella entanglement of aligned eutectic colonies. The surface of an as-solidified pellet can be observed in Fig. 2.

The smooth surface corresponds to the as-solidified bulk ceramic composite, without any machining or polishing, with the interface shape theoretically predicted by Jackson and Hunt.¹²⁾ The curvature of the boundary offset the effect of the compositional changes across the interface in the liquid in front of the lamella, caused by lateral diffusion of the components during phase separation.

Lamella sizes are homogeneous throughout the solidified sample. The comparison with recent experimental data of characteristic interlayer spacing in directionally solidified binary eutectic composites in the system,^{1,13)} indicates that the

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Fig. 1 XRD pattern from the solid bulk sphere after quenching. The peak marks correspond to (x) alumina, (O) yttrium aluminium garnet and (+) zirconia.

Fig. 2 Surface of an as-quenched solidified pellet. The surface is smooth and free of cracks, showing a continuous lamellar eutectic. The darker eutectic lamella is alumina, YAG appears with a lighter color, and forms the thicker lamella. Bright dots correspond to zirconia.

Fig. 3 Comparison of the lamella sizes obtained with previous experimental results,¹³⁾ in a lamella vs. solidification rate plot.

observed lamella sizes corresponds to growth rates higher than 1 mm s^{-1} (Fig. 3). In spite of the rapidness of the process, the kinetics is homogeneous because the simplicity of the heat-transfer and the absence of thermal inertia by thermal image heating. We use the most simple heat transfer conditions. Heating in an arc imaging furnace with an ellipsoidal mirror offers the advantages of very low thermal inertia, direct heating without using container, uniform radial temperature distribution and good stability. The cooling method allows rapid heat transfer in the sample. In those conditions homogeneous unbroken lamellar structures are obtained, in spite of the high growth rate.

4. Conclusions

Lamella spacing in an alumina-YAG-zirconia eutectic composite have been narrowed down by using rapid solidification from melt in an arc-image lamp furnace. Estimated growth rates are above 1 mm s^{-1} . The finely structured material may find application as ultra-high temperature thermal barrier coating.

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