J. Am. Ceram. Soc., 92 [2] 549–552 (2009)
DOI: 10.1111/j.1551-2916.2008.02911.x


Journal

# Fabrication of an $Al_2O_3$/YAG/$ZrO_2$ Ternary Eutectic by Combustion Synthesis Melt Casting Under Ultra-High Gravity

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**This work presents a novel method for preparing an $Al_2O_3$/YAG/$ZrO_2$ ternary eutectic whereby combustion synthesis melt casting has been combined with the ultra-high gravity (UHG) technique. The fabricated product had a relative density of 99.3% of the theoretical one. Phase composition and microstructure analyses indicated that the application of UHG resulted in a metal-free ceramic microstructure with no porosity or microcracks. The microstructure comprises $ZrO_2$ rods dispersed in $Al_2O_3$. The product had 17.82 GPa Vickers hardness and 5.51 $MPa \cdot m^{1/2}$ fracture toughness.**

## I. Introduction

In 1997, Waku *et al.*[1] reported that a directionally solidified eutectic ($Al_2O_3$/YAG, where YAG is yttrium–aluminum garnet, $Y_3Al_5O_{12}$) with a continuous three-dimensional interpenetrating microstructure exhibited outstanding high-temperature mechanical properties (up to 2073 K), thermal and microstructural stability, and oxidation resistance as compared with conventional composites. The main factors influencing the properties of the eutectic solidified from the melt are the phase spacing (or eutectic lamella) and the eutectic pattern. The phase spacing for each eutectic system depends mainly on the solidification rate, while the eutectic pattern depends on the volume fraction of each phase, the formation of faceted or nonfaceted interphases, etc.

The methods of fabricating eutectic oxides from a melt can be classified into two groups: (a) unidirectional solidification in a container and (b) pulling of a solid from the melt meniscus.[2] The Bridgman method is one of the former methods, whereby thermal gradient is generally below $10^2$ K/cm and interphase spacing is usually larger than 10 μm. Higher thermal gradients ($10^3$–$10^4$ K/cm) and consequently a smaller interphase spacing (<1 μm) can be attained using the melt zone methods, which are suitable for preparing high-performance fibers with submillimeter diameters.

Highly exothermic combustion reactions are generally considered for generating sufficient heat to increase the temperature of a system much above the melting point of products consisting of both metals and ceramics, especially when the reactions are carried out under ultra-high gravity (UHG). Because the UHG field can enhance the transmission of heat and mass, consequently, the burning rate and the intensity of the thermite reaction are increased.[3] If such combustion reactions are conducted under a high centrifugal force, then the essential conditions of ultra-high temperature required for the eutectic ceramics to melt along with a rapid cooling rate for refining the interphase spacing during the subsequent solidification are fulfilled. In the present work, we have investigated a novel method of combustion synthesis (CS) melt casting under UHG for producing an $Al_2O_3$/YAG/$ZrO_2$ ternary eutectic with good characteristic in terms of phase composition, microstructure, and mechanical performance.

## II. Experimental Procedure

Powders of Al (purity 99.9%, 100 μm), $Fe_2O_3$ (purity 99.99%, 44 μm), $Y_2O_3$ (purity 99.999%, 6.9 μm), and $ZrO_2$ (purity 99.99%, 20 μm) were used as the starting materials. The reactant powders, which had an $Al_2O_3/Y_2O_3/ZrO_2$ molar ratio of 65.8/15.6/18.6, were well mixed by ball milling in ethanol media for 2 h. The reaction of the reduction of $Fe_2O_3$ was expected to take place according to the following equation[4]:

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe + 836\ \text{kJ} \qquad (1)$$

The homogenized reactant powder was cold pressed into a cylindrical graphite crucible with an inner diameter of 30 mm. Each sample was 200 g. The density of the powder compact was about 55% of the theoretical value. The crucible was mounted on a Ni-based super alloy rotor in an apparatus that was specially designed and constructed in our laboratory for carrying out the combustion synthesis meltcasting under ultra-high gravity (CSMC-UHG). The CSMC-UHG apparatus is schematically represented in Fig. 1. The experimental procedure was as follows: (a) the rotor started rotating to achieve an acceleration of about 600 *g* (where *g* is the gravity acceleration, 9.8 m/s$^2$) at the end edge of the sample; (b) ignition of the mixture; (c) evacuation of the chamber down to $10^{-5}$ MPa to remove reaction gases; (d) cooling of the sample.

The crystallographic phase analysis was performed using X-ray diffraction (XRD) (Model D/max-2500, Rigaku, Tokyo, Japan). The microstructure of the samples was observed by scanning electron microscopy (SEM) (Model S-4300, Hitachi, Tokyo, Japan). The density of the samples was determined by the Archimedes method by immersion in water. The hardness and the fracture toughness were measured with a Vickers indentation equipment using a load of 5 kg applied for 15 s, using the equations[5,6] $H_V = k_1P/d^2$ and $K_{IC} = k_2(E/H)^{1/2}(P/c^{3/2})$, where $H_V$ is the Vickers hardness, $K_{IC}$ is the fracture toughness,

J. Ferreira—contributing editor

Manuscript No. 25424. Received October 30, 2008; approved November 20, 2008.
This work was supported by the National Natural Science Foundation of China (Grant No. 50772116) and National High-Tech and New Materials Projects (Grant No. 2006AA03Z112).
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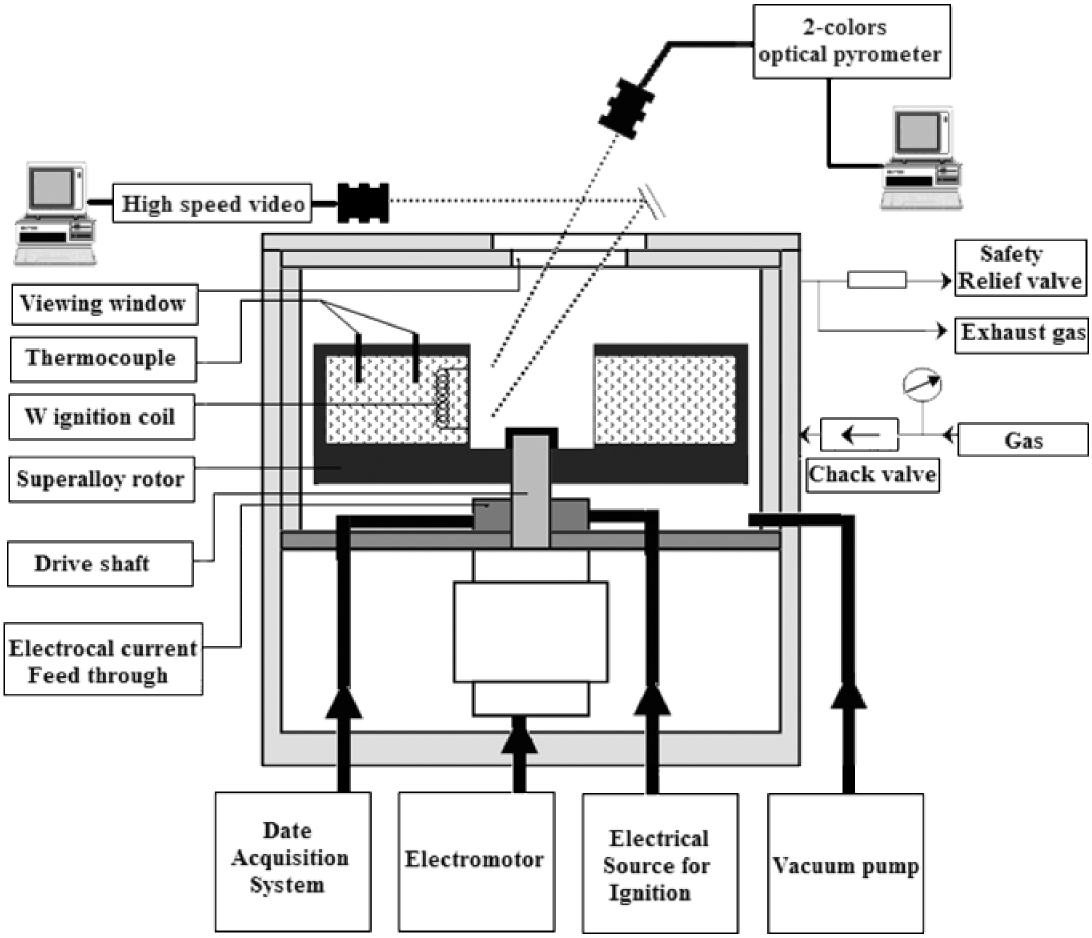


**Fig. 1.** Schematic diagram of the apparatus designed and constructed for carrying out combustion synthesis melt casting under ultra-high gravity.

$P$ is the indentation load, $d$ is the indentation diagonal, $E$ the Young's modulus of the material, attained from nanoindentation test, $c$ is the crack length, and $k_1$ and $k_2$ are the dimensionless constants determined experimentally. The mean values were obtained from five different independent measurements.

## III. Results and Discussion

The X-ray diffractogram of the product presented in Fig. 2 shows that the product of CSMC-UHG under gravity conditions of 600 $g$ consists of $Al_2O_3$, YAG, and $ZrO_2$ (YSZ, $Y_2O_3$-stabilized $ZrO_2$). This finding suggests that the molten Fe should have been completely separated from the molten ceramic before its solidification under the UHG field.

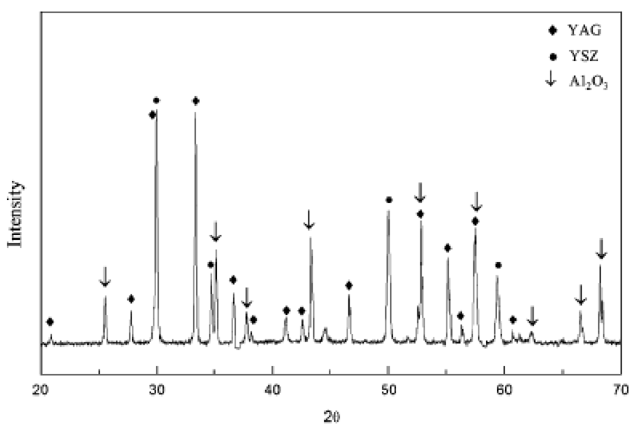


**Fig. 2.** X-ray diffractogram of an $Al_2O_3$/YAG/$ZrO_2$ ternary eutectic prepared under a UHG field. YAG, yttrium-aluminum garnet, $Y_3Al_5O_{12}$; YSZ; $Y_2O_3$-stabilized $ZrO_2$; UHG, ultra-high gravity.

From the density measurements, the relative density of the product was found to be 99.3% of the calculated theoretical value, indicating a highly dense material. This result agrees fairly well with the SEM observations of the microstructure of the products, shown in Fig. 3. The microstructure features an entangled network with no pores or cracks. At a higher magnification (Fig. 4), it is observed that the phase spacing is submicrometer, i.e., $\leq 500$ nm. Such a small scale is likely caused by a large thermal gradient. The pattern consisting of a parallel array shown in Fig. 4 distributes in the samples, which may have been caused by local special cooling condition, and this requires further study. According to the energy-dispersive spectroscopy (EDS) elemental analysis, whose spectra are shown in Fig. 5, the black zones are attributed to $Al_2O_3$, the gray zones to YAG, and the fine white zones to $ZrO_2$. The Al peak in the spectra of $ZrO_2$ may be caused by the signals received from the Al element in the neighboring areas, because the EDS beam spot is probably larger than the relatively small $ZrO_2$ area. The phases of YAG and $Al_2O_3$, with smaller areas of $ZrO_2$, penetrate into each other. The microstructure of the interface between the $Al_2O_3$ and the YAG phases is "faceted to faceted." The phase of $ZrO_2$ is largely dispersed in the form of rods in $Al_2O_3$, but it also seldom appears in the phase of YAG.

The obtained dense microstructure, featuring the characteristics of a composite material, resulted in good mechanical properties; specifically, the maximum Vickers hardness reached 17.82 GPa and the maximum fracture toughness reached 5.51 $MPa \cdot m^{1/2}$.

## IV. Discussion

At elevated temperatures of the combustion reaction, molten iron ($T_m = 1809$ K), molten ceramics phases in the form of ternary eutectics ($T_m = 1990$ K), and pores should coexist. Under

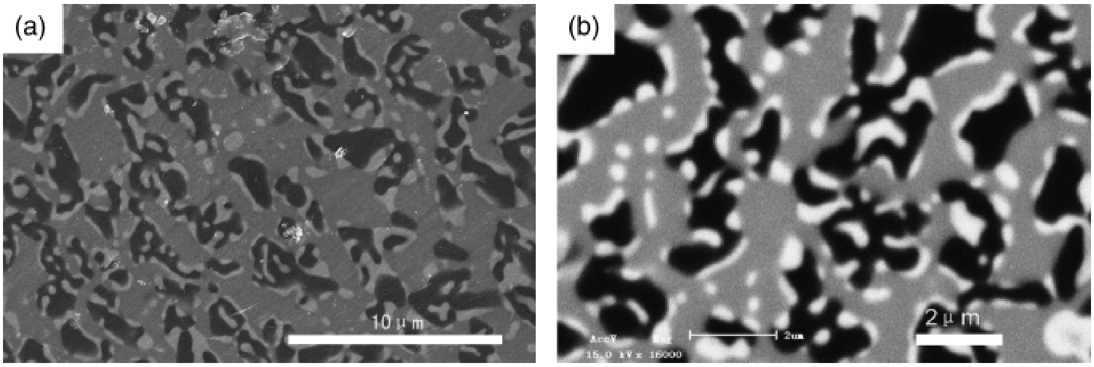


**Fig. 3.** Microstructure of the as-fabricated $Al_2O_3$/YAG/$ZrO_2$ ternary eutectic, observed by scanning electron microscopy: (a) secondary electron image; and (b) backscattered electron image.

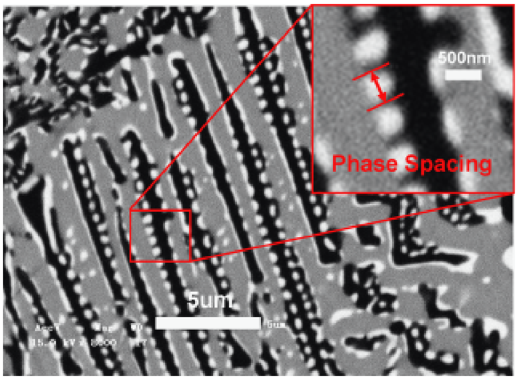


**Fig. 4.** Submicrometer scale phase spacing observed by backscattered electron.

the UHG field, the separation of these three phases should obey Stock's law. Accordingly, the velocity of each phase can be calculated by the following equation

$$V = \frac{2}{3}\frac{(\rho_1 - \rho_2)}{\eta} agr^2, \tag{2}$$

where $V$ is the moving rate of the dispersed phase, $r$ the diameter of the dispersed phase, $a$ the UHG magnitude, $\rho_1$ the density of the dispersed phase, $\rho_2$ the density of the consecutive medium, and $\eta$ the viscosity of the consecutive medium. According to Eq. (2), under a gravity of 600 $g$, a ceramic spherical droplet with a diameter of 10 μm needs $<1$ s to travel a distance of 20 mm through molten iron. For the case of a spherical pore under exactly the same aforementioned conditions, the calculated time is $<5$ s. Thus, complete separation of pores from molten $Al_2O_3$ is possible under such high gravity values. Therefore, the UHG field favors the fast elimination of pores from the molten ternary eutectic ceramics, resulting in a highly dense microstructure, which was observed in the experimental results.

The observed microstructure with the particular features of the distribution of three phases in the ternary eutectics apparently satisfies Jackson's criterion.[2] The Jackson interface roughness parameter is defined as $\alpha \approx \Delta S_f/R$, where $\Delta S_f$ is the entropy of fusion and $R$ is the gas constant. If $\alpha > 2$ for one of the phases, then the growth of that phase is limited by the nucleation rate and facets are easily produced. In the present work, the calculated order for developing facets is $\alpha_{YAG} > \alpha_{Al_2O_3} > 2 > \alpha_{ZrO_2}$. Hence, the microstructure of the interface between $Al_2O_3$ and YAG is anticipated to be "faceted to faceted" (planar sharp interfaces), while the interface between $Al_2O_3$ and YSZ should be "faceted to nonfaceted"

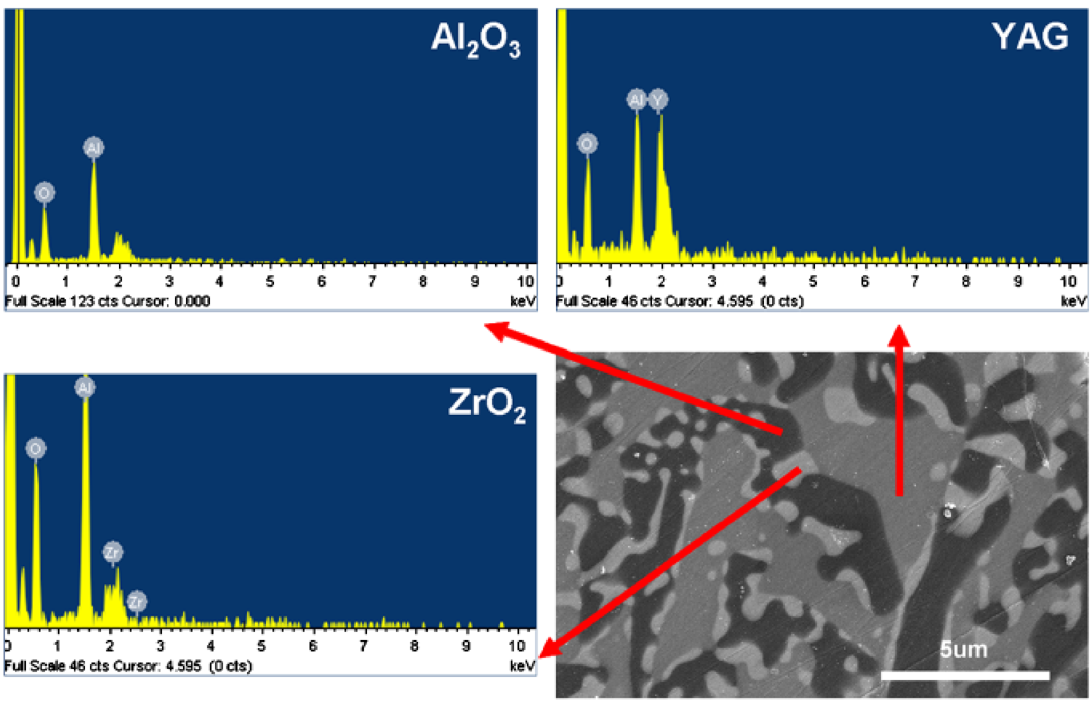


**Fig. 5.** Energy-dispersive spectroscopy elemental analysis of the component phases of the as-fabricated $Al_2O_3$/YAG/$ZrO_2$ ternary eutectic. YAG, yttrium–aluminum garnet, $Y_3Al_5O_{12}$.

(curved smooth interfaces).[2] Therefore, the $Al_2O_3$ and YAG phases showed a typically faceted morphology with triangular or tetragonal shapes, while $ZrO_2$ tends to grow in rods or lamellas instead of a faceted configuration. In the simplest case of isotropic surface energy, $ZrO_2$ rods are anticipated to form when the volume fraction of the minor phase is $<28\%$, while lamellas should form when it is above 28%. In the present study, the theoretically calculated volume fraction of $ZrO_2$ was 13.6%. Thus, $ZrO_2$ intrinsically exhibited the tendency to grow in the rod form than lamellas.

Although the different phases formed were separated from each other with well-defined interfaces, there were no cracks formed along or across these interfaces. This indicates both strong interfacial adhesion and small residual stresses (likely due to the mismatch of the thermal expansion coefficients or mechanical properties) along the interface. Accordingly, such microstructural composite prepared via this particular method is anticipated great vitality. Hence, it can be considered for further experimentation with regard to potential applications that involve mechanical and thermal fatigue conditions.

The above advantageous characteristics of the interfaces among the phases, along with the dense microstructure with features of composite material, resulted in a material with better mechanical properties than those obtained for $Al_2O_3$/YAG/$ZrO_2$ eutectics produced via other preparation methods. For instance, Pena *et al.*[7] have reported that the preparation of directionally solidified $Al_2O_3$/YAG/$ZrO_2$ ternary eutectic rods grown by a laser-heated floating-zone method resulted in a material with a maximum hardness of 14.8 GPa. Lee *et al.*[8] have reported a maximum hardness of 17.4 GPa for a similar product prepared using the μ-PD method. In general, the hardness of eutectic oxides is primarily affected by the hardness of the single crystalline oxides of the eutectic. The highest hardness values of $Al_2O_3$–YSZ have been reported as 18–20 GPa, while those of $Al_2O_3$–YAG eutectics are 13–16 GPa. In the present work, the measured hardness value of 17.82 GPa for the $Al_2O_3$/YAG/YSZ ternary eutectic lies between the values of $Al_2O_3$–YAG and $Al_2O_3$–YSZ.

## V. Conclusion

The ternary eutectic material of $Al_2O_3$/YAG/$ZrO_2$ was successfully fabricated via a novel method, which integrates combustion synthesis and ultra-high gravity (CSMC-UHG). The product obtained at UHG of 600 *g* had a fine and dense microstructure. No pores, cracks, or impurities of other phases were registered. The final product had a relative density of 99.3% of the theoretical one, Vickers hardness 17.82 GPa, and fracture toughness 5.51 $MPa \cdot m^{1/2}$.

The microstructure of the ternary eutectic consisted of an entangled network of three phases, penetrating into each other such that the interface between $Al_2O_3$ and YAG is "faceted to faceted," $ZrO_2$ rods are distributed in $Al_2O_3$, and the interphase spacing is at a submicrometer scale.

The experimental results indicate the $Al_2O_3$/YAG/$ZrO_2$ eutectic material produced via the proposed method for further consideration and experimentation in applications involving mechanical and thermal fatigue stresses. Moreover, further development and improvement of the UHG conditions, optimization of the mold shape design, and better control of cooling will likely make CSMC-UHG a promising method for producing large-scale bulk eutectic ceramics with submicrometer phase spacing.

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