Ordering nanostructure and properties of \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) eutectic ceramic composites prepared by combustion synthesis under low pressure

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Abstract: \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) eutectic ceramics were prepared by combustion synthesis using Al and Zr(NO\textsubscript{3})\textsubscript{4} as raw materials. \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) eutectic structure showed that randomly-oriented rod-like ZrO\textsubscript{2} phases were embedded in \( \text{Al}_2\text{O}_3 \) matrix with a spacing of about 280 nm. The bending strength and fracture toughness of the product reached 1060MPa and 11.2MPa-m\textsuperscript{1/2}, respectively, which were attributed to nanostructure eutectic, bridge and pull-out effects of the rod-like ZrO\textsubscript{2}.

Keywords: \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) eutectic ceramics; microstructure; mechanical properties; combustion synthesis

1. Introduction

Recently, \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) eutectic ceramics are attracting considerable interest because of their combination of high strength and toughness at elevated temperatures due to the special fiber or lamellar structure [1-3]. At present, several advanced techniques are employed to prepare \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) eutectic, including Bridgman, laser heated floating zone (LHFZ), edge-defined film-fed growth (EFG) and micro-pulling down (\( \mu \)-PD) method [4]. However, large bulk \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) eutectic in centimeter scale with fine interphase spacing (<1\( \mu \)m) is difficult to fabricate by employing the above mentioned methods. Combustion synthesis, which is a novel preparation and processing technique for high-temperature ceramic and compound, has the advantages of high reaction temperature (3000-4000K) and large thermal gradient (10\textsuperscript{3}-10\textsuperscript{6} K/cm) to prepare the large bulk eutectic ceramic [5,6]. Zhao et al reported the \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) eutectic with 30 cm diameter was fabricated by simultaneous thermit-combustion and gravity separation using CrO\textsubscript{3}, Al, ZrO\textsubscript{2}, Y\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} as raw materials [7], and Mei et al conducted a similar way to prepare \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) eutectic and studied the effect of gravity field on the microstructure of the products [8].

In our previous work, the microstructure of \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) eutectic coating prepared by combustion-assisted thermal explosion spraying was studied. The \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) coating can be divided into three regions according to the crystal structure along the growth direction. First region in contact with the Cu substrate was amorphous structure, and then was cellular crystal region, in which \( \text{Al}_2\text{O}_3 \) shows cystiform shape, and last dendrite \( \text{Al}_2\text{O}_3 \) crystal, the later-two of which was embedded in \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) eutectic matrix [9]. Moreover the \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) eutectic ceramic composites were obtained by explosion synthesis [10], but it had the disadvantages that the pressure was higher than 30MPa and the size of products was smaller than \( \Phi 20 \times 40\)mm. In this paper, \( \text{Al}_2\text{O}_3/\text{ZrO}_2 \) eutectic ceramics were fabricated by combustion synthesis under low pressure using Al and Zr(NO\textsubscript{3})\textsubscript{4} as raw materials. It had the advantages that the pressure was lower than 10MPa so that the safety of production could be ensured and large bulk products, which could reach \( \Phi 60 \times 50\)mm, could be obtained.

2. Experimental procedure

Al powders (99% purity, 5 \( \mu \)m) and Zr(NO\textsubscript{3})\textsubscript{4} (99% purity) were used as reactant. The reaction
was expected to take place as follow:

$$32\text{Al} + 3\text{Zr(NO}_3\text{)}_4 \rightarrow 10\text{Al}_2\text{O}_3 + 3\text{ZrO}_2 + 12\text{AlN} \quad (1)$$

Through adding appropriate amount of $\text{Al}_2\text{O}_3$ and $\text{ZrO}_2$ into reactant, the $\text{Al}_2\text{O}_3$/ZrO$_2$ eutectic ceramic could be obtained. In addition, the reaction temperature and $\text{Al}_2\text{O}_3$/ZrO$_2$ ratio in products could be adjusted to study the reaction mechanism and eutectic microstructure. The reactant components with adiabatic temperature of 2800, 3000, 3200 and 3400K, which were marked as AT1, AT2, AT3 and AT4, respectively, were selected to study the effect of reactant content on reaction temperature.

The microstructure of eutectic ceramic was observed by scanning electron microscopy (SEM, JSM-6390, Japan). The phase compositions were determined by X-ray Diffraction (XRD, D/MAX-RB, Rigaku, Japan). The flexural strength was measured by a three-point bending method with a cross-head speed of 0.5 mm/min and a span of 30 mm and sample dimension of 3 mm $\times$ 4 mm $\times$ 36 mm on a universal testing machine (Instron-1186, USA). The fracture toughness was measured by single edge-notched beam method with a cross-head speed 0.05 mm/min. A notch with a depth of 2 mm and a width of 0.4 mm was machined into test bars of 2 mm $\times$ 4 mm $\times$ 22 mm.

### 3. Results and discussion

It could be found from Fig.1 that the products consisted of $\text{Al}_2\text{O}_3$, ZrO$_2$ and ZrN. The existence of ZrN instead of AlN indicated that the reaction designed as equation (1) was unrealistic because of the unstability of AlN at high temperature. The product constitution as shown in Fig.1 indicated that the real reaction route should correspond to equation (2).

$$4\text{AlN} + 3\text{ZrO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{ZrN} + 0.5\text{N}_2 \quad (2)$$

The relationship between adiabatic temperature and Gibbs Free Energy in reaction (2) was calculated, as shown in Fig.2. It indicated that the Gibbs Free Energy of this reaction would fall below zero when the temperature rose above 1399 K. Since all combustion temperatures were above 2800K, in this study, the AlN was transformed into ZrN at last.
excess Al was added into the reactant on the basis of the reaction equation (3) in further investigation.

\[
8\text{Al}+3\text{N}_2+6\text{ZrO}_2 \rightarrow 4\text{Al}_2\text{O}_3+6\text{ZrN}
\]

(3)

The adiabatic temperature was calculated through thermodynamic analysis, as shown in Fig. 4. The measured reaction temperatures were marked in Fig. 4. It was found that the measured temperature was about 200K lower than the theoretical temperature. The adiabatic temperature of this combustion reaction could easily reach 4000K, which was much higher than the eutectic transformation temperature of Al\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2} system (2135 K) based on the Al\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2} equilibrium phase diagram [11], indicating the method employed in this paper had the distinct advantage to prepare Al\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2} eutectic ceramic. The reaction temperature curve measured by W/Re thermocouples was shown in Fig. 5. The temperature curve had a sharp rise once the reactant mixture was ignited, which was corresponding to adiabatic hypothesis. In addition, the cooling rate of reaction product was obviously fast, as shown in Fig. 5, which was favorable to obtain fine microstructure of Al\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2} eutectic ceramic.

![Fig. 3 The relationship between pressure and T\(_{ad}\) of the combustion synthesis for Al\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2} eutectic ceramic](image1)

![Fig. 4 The relationship between T\(_{ad}\) and reactant content of the combustion synthesis for Al\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2} eutectic ceramic](image2)

![Fig. 5 Temperature profile of the combustion synthesis for Al\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2} eutectic ceramic (T\(_{ad}\)=2673K)](image3)
of ZrO\(_2\) was less than 28\%, and thus ZrO\(_2\) exhibited the tendency to grow in the rod structure than lamellas.

Figure 7 showed the fracture morphology of Al\(_2\)O\(_3\)/ZrO\(_2\) eutectic composite. The fractography showed that pull-out of the ZrO\(_2\) rod and crack deflection were the main fracture modes in Al\(_2\)O\(_3\)/ZrO\(_2\) eutectic. Because the eutectic structure is in-situ formed in molten state during combustion synthesis process, nano-micron ZrO\(_2\) rods are entirely embedded in the Al\(_2\)O\(_3\) matrix, thus the prepared eutectic composite exhibits excellent mechanical properties. The maximum bending strength and fracture toughness of composites were 1060MPa and 11.2MPa-m\(^{1/2}\), respectively.

4. Conclusions

Al\(_2\)O\(_3\)/ZrO\(_2\) eutectic ceramics were fabricated by combustion synthesis under low pressure using Al and Zr(NO\(_3\))\(_4\) as raw materials. The eutectic microstructure showed that rod-like ZrO\(_2\) embedded in Al\(_2\)O\(_3\) matrix with a spacing of 280 nm. Due to nanostructured eutectic, pull-out and bridge effects of rod-like ZrO\(_2\), the bending strength and fracture toughness of the eutectic ceramic composites reached 1060MPa and 11.2MPa-m\(^{1/2}\), respectively.

References