MICROSTRUCTURE AND MECHANICAL PROPERTIES OF EUTECTIC COMPOSITE CERAMIC Al_2O_3/ZrO_2 BY EXPLOSION SYNTHESIS

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Abstract

Al_2O_3/ZrO_2 eutectic ceramics were prepared by explosion synthesis using Al and $Zr(NO_3)_4$ as raw materials. The Al_2O_3/ZrO_2 eutectic microstructure showed that the rod-like ZrO_2 phases with a diameter 200 nm were embedded orderly in Al_2O_3 matrix. With the increasing of the reaction temperature, the volume content of the Al_2O_3/ZrO_2 eutectic increased accordingly, and the diameter and phase spacing of rod-like ZrO_2 decreased, which was mainly attributed to the efficient diffusion and the large temperature gradient. Due to the fine structure of the Al_2O_3/ZrO_2 eutectic, the Vickers hardness and fracture toughness can reach 21GPa and 11.7 $MPa\cdot m^{1/2}$, respectively.

1. Introduction

Ceramic matrix composites offer improved toughness and strength compared with monolithic ceramics due to the dispersion of energy of cracks at the interface of the two phases [1]. Eutectic ceramics with a fine microstructure on micrometer or nanometer scale are a paradigm of in situ ceramic matrix composites [2], which have outstanding thermal stability and mechanical properties as compared with monolithic and conventional ceramic matrix composites [3]. The mechanical properties of two phase eutectic ceramics are better than that of either constituent alone, because of the strong constraining effects provided by the interlocking microstructure [4].

In the past, attention focused on metallic eutectics was more than eutectic ceramics, and most of the advances of eutectic growth and microstructure were achieved in metallic eutectics. This was because that the eutectic temperature of eutectic ceramics is higher than that of metallic eutectics and the preparation of eutectic ceramics was difficult. Most efforts of eutectic ceramics had been made on Al_2O_3-based eutectics [5-7], due to the outstanding creep resistance of sapphire along the c-axis. In the last two decades, as the development of processing of eutectic ceramics, there were several preparation techniques for eutectic ceramics, such as Bridgman method [8], laser heated floating zone method [9], micro pulling down method [10], explosion synthesis method and so on. Explosion synthesis method has some particular advantages compared with other methods. The preparation procedure of explosion synthesis is very simple. Also, it is an energy saving method because the materials can be heated by the energy released from the reaction without any other addition thermal resource. Furthermore explosion synthesis method can prepare bulk samples of large size.

In this paper, Al_2O_3/ZrO_2 eutectic ceramic was product by explosion synthesis method, and the relationship between the temperature and the microstructure was discussed.

2. Experimental procedure

The reactant powders were Al and $Zr(NO_3)_4$ powders. The explosion reaction for preparing eutectic ceramic was listed as follow:

$$Al + Zr(NO_3)_4 \rightarrow Al_2O_3 + ZrO_2 + N_2 \tag{1}$$

Through adding appropriate Al_2O_3 and ZrO_2 into reactant, the reaction temperature and Al_2O_3/ZrO_2 ratio in products can be adjusted. The raw materials were mixed by ball milling for 12 h using alumina milling-media.

In order to rapid solidification of melted Al_2O_3 and ZrO_2, the explosion synthesis took placed in a high pressure reactor with water cooling system, with an inside diameter of 25 mm. The gas pressure in the reactor ranges from 30 MPa to 100 MPa. The reaction temperature was measured by W/Re thermocouples (2100-2600 K).

The morphology of the cross-sections of the products was examined by scanning electron microscopy at 20 kV using a FEI Quanta 2000F. Energy dispersive X-ray spectroscopy (EDS) was used to elemental and microstructure analysis.

3. Results and discussion

Because the explosion synthesis of the Al_2O_3/ZrO_2 eutectic ceramic was completed instantly, the reaction can be regarded as an adiabatic procedure. The adiabatic temperature was calculated through thermodynamics analysis, as shown in Fig. 1. It indicated that the adiabatic temperature increased linearly with increasing Al content, and a temperature platform occurred at the Al_2O_3/ZrO_2 eutectic transformation temperature (2135 K). To obtain Al_2O_3/ZrO_2 eutectic ceramics, the reaction temperature of the explosion synthesis should be higher than the eutectic transformation temperature. The reactant components with adiabatic temperature of 2300, 2500, 2700 and 2900 K were selected to study the reaction temperature on the morphology and microstructure of the Al_2O_3/ZrO_2 eutectic.

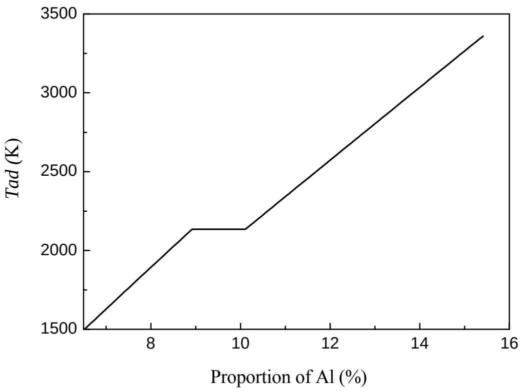

Fig. 1. Relationship between the T_{ad} and Al content.

In the sealed reactor, large content of nitrogen was released and produced high pressure during the explosion synthesis under high temperature in a short time, and the high pressure will increase the boiling point of Al_2O_3 and ZrO_2. Choosing proper reactant ratio of the Al to ZrO_2 can assure the appropriate reaction temperature to melt Al_2O_3/ZrO_2 eutectic. According the reaction (1), the pressure in the reactor produced by the released nitrogen gas and evaporation of Al_2O_3 and ZrO_2 was calculated theoretically based on Van der Waals equation. Fig. 2 shows the relationship between the reaction temperature and the pressure in the reactor. It can be found that the pressure in reactor increased with the increasing reaction temperature. A suddenly rising in pressure occurred at eutectic temperature of 2135 K because of the phase state change in reactant system. In addition, a more dramatic increasing occurred at the boiling point of Al_2O_3 and ZrO_2 (at temperature of about 4500 K). In this experiment, nitrogen pressure under 100 MPa was adopted to ensure the reactor safety and economical benefit.

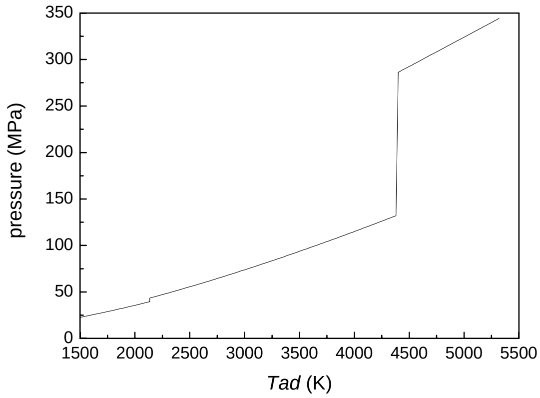

Fig. 2. The relationship between reaction temperature and pressure.

The reaction temperature was measured by W/Re thermocouples (2100-2600K), as shown in Fig. 3. As the figure indicated, explosive reaction has very quickly reaction velocity, and temperature rising and cooling of the samples were relative sharp, which is benefit for the formation of eutectics with fine structure. Due to the secondary exothermic of the hypereutectic, a slight temperature increasing was found during the cooling stage of the reaction. The formation enthalpy of $Zr(NO_3)_4$, which can not be inquired in thermodynamics manuals, was calculated by fitting method based on the measured reaction temperature (ΔH=2.9kJ/mol).

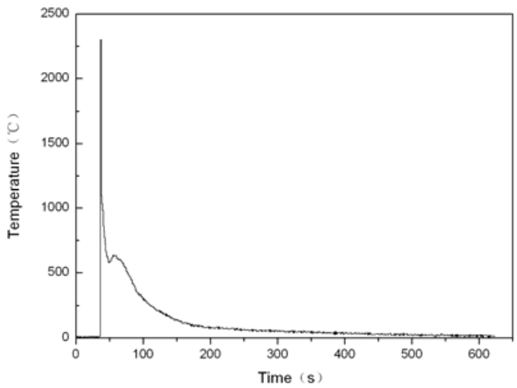

Fig. 3. Temperature profile of the explosion synthesis for Al_2O_3/ZrO_2 eutectic.

Fig. 4 shows the typical fractography of the Al_2O_3/ZrO_2 eutectic. The ZrO_2 phases embedded in Al_2O_3 matrix presented rod-like, and the diameter was about 200 nm. This fine structure was mainly attributed to the high cooling rate in the explosive reaction. Meantime, the fractography shows the pull-out of the ZrO_2 rods and the crack reflection, which can efficiently hinder the crack propagation and greatly improve the bending strength and fracture toughness. This is the reason that eutectics have relative high mechanical properties at room and elevated temperatures.

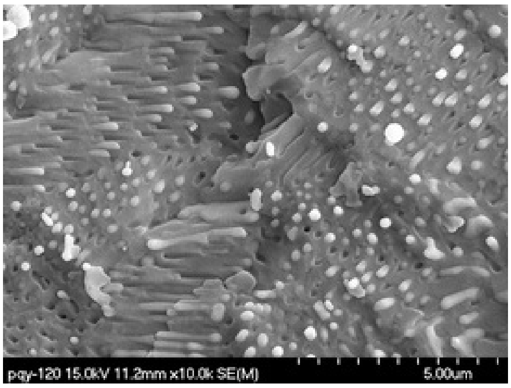

Fig. 4. SEM fractography of the fracture of Al_2O_3/ZrO_2 eutectic.

Fig. 5 shows the back scattered electron image of the Al_2O_3/ZrO_2 eutectic structure. As the figure showed, three directions of the ZrO_2 rods can be found. The Al_2O_3/ZrO_2 eutectic microstructure can be observed more clearly. In same eutectic crystal, rod-like ZrO_2 distributed uniformly with same diameter and interphase spacing.

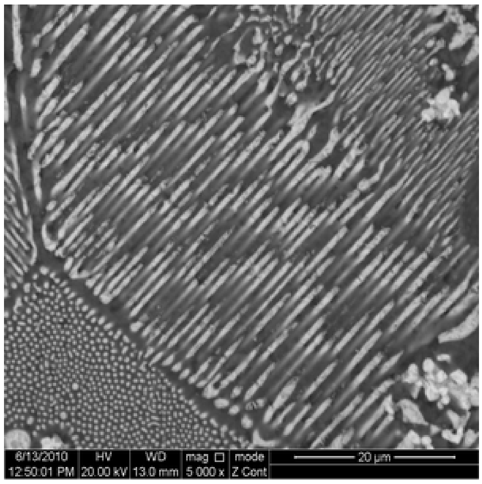

Fig. 5. Back scattered electron image of the Al_2O_3/ZrO_2 eutectic.

The formation of the eutectic ceramic was a complex physical and chemical procedure. Firstly, Al_2O_3 and ZrO_2 phases were melt under high reaction temperature, and then uniform liquid phase was formed by the diffusion between the liquid Al_2O_3 and ZrO_2. The uniform degree of the eutectic melt was determined by the reaction temperature and reaction time. At last, the eutectic ceramic was obtained during the cooling process.

Typical eutectic microstructure mainly presented three models: lamellas, rod and globule. The volume fraction of the two phases decided whether lamellas or rod eutectics structure formed. According to thermodynamics analysis, the morphology and distribution of the both eutectic phases should satisfy the minimum energy principle, namely, minimum interfacial area and energy. Based on the Ref [2], ZrO_2 rods in ZrO_2/Al_2O_3 eutectic are anticipated to form when the volume fraction is less than 28%, while the lamellas form when volume fraction is larger than 28%. To study the effect of reaction temperature on the morphology and distribution of the ZrO_2/Al_2O_3 eutectic, excess Al was added to the reactant, and this decreased the volume fraction of ZrO_2 phase, so ZrO_2 exhibited the trend to grow in the rod structure than lamellas.

Fig. 6 shows the morphology and distribution of Al_2O_3/ZrO_2 eutectic prepared under different reaction temperature. In general, the content of Al_2O_3/ZrO_2 eutectic in the products increased with the increasing reaction temperature, meantime, the diameter and phase spacing of the rod-like ZrO_2 decreased. Under reaction temperature 2500 K, the content of

Al_2O_3/ZrO_2 eutectic was small, and the diameter and phase spacing of the rod-like ZrO_2 was coarse. Many ZrO_2 particles, which have not transformed to eutectic, were found. The reason is that the mutual fusion of the Al_2O_3 and ZrO_2 was insufficient under the temperature of slightly higher than eutectic temperature in short time. With the reaction temperature increasing, the eutectic area was forming larger and the eutectic structure was changing finer, and at the same time the content and size of the ZrO_2 particles was decreasing. In summary, higher reaction temperature improve the mutual fusion of Al_2O_3 and ZrO_2, which was attributed to the formation of larger area of Al_2O_3/ZrO_2 eutectic, meantime, higher reaction temperature resulted in higher cooling rate and larger temperature gradient, and this also favor the with fine microstructure.

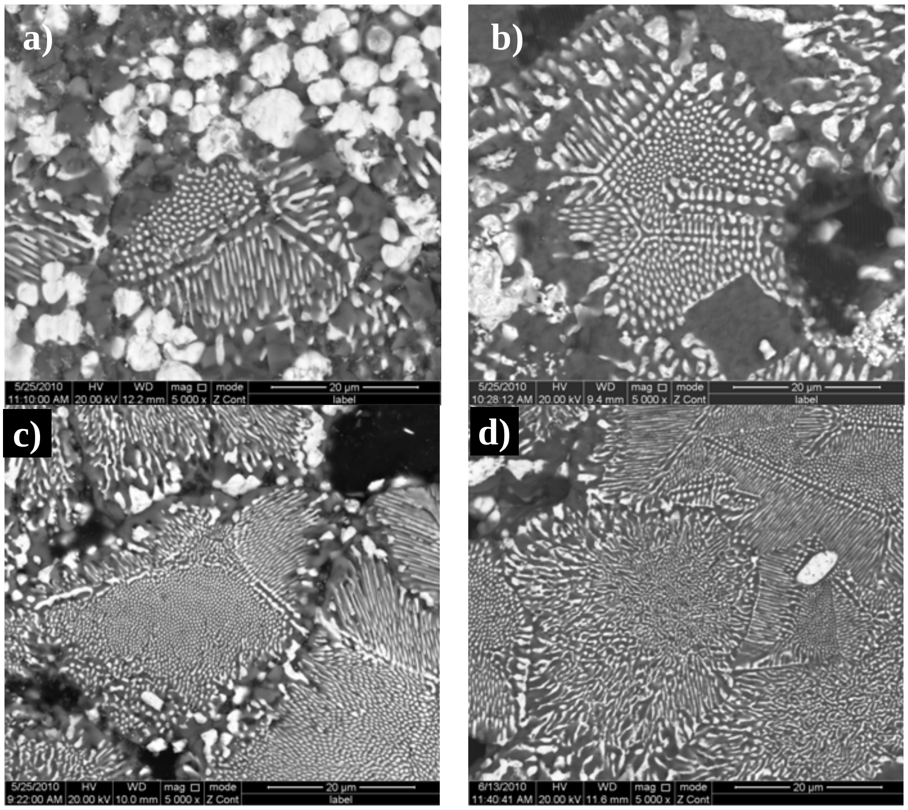

Fig. 6. Morphology and distribution of the Al_2O_3/ZrO_2 eutectic prepared under reaction temperature of a) 2300 K, b) 2500 K, c) 2700 K and d) 2900 K.

The key factor to improve the mechanical properties of the eutectics was to obtain fine eutectic microstructure. In this experiment, the high undercooling rate generated fine structure of Al_2O_3/ZrO_2 eutectic, which improved the mechanical properties effectively. The Vickers hardness and fracture toughness reached 21GPa and 11.7 $MPa{\cdot}m^{1/2}$, respectively.

4. Conclusions

Al_2O_3/ZrO_2 eutectic ceramics were fabricated by explosion synthesis. The microstructure of Al_2O_3/ZrO_2 eutectic showed rod-like ZrO_2 phase with a diameter smaller than 200 nm embedded orderly in Al_2O_3 matrix. With the increasing of the reaction temperature, the volume fraction of the Al_2O_3/ZrO_2 eutectic increased accordingly, and the diameter and phase spacing of rod-like ZrO_2 decreased, which was mainly attributed to the large temperature gradient. Due to the fine structure of the Al_2O_3/ZrO_2 eutectic, the Vickers hardness and fracture toughness can reach 21GPa and 11.7 $MPa{\cdot}m^{1/2}$, respectively.

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