Microstructure and Mechanical Properties of Al_2O_3/ZrO_2 Directionally Solidified Eutectic Ceramic Prepared by Laser 3D Printing

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Directionally solidified eutectic ceramics such as Al_2O_3/ZrO_2 are promising structural materials for applications in harsh environment with an ultrahigh temperature. In this work, through adopting assistant heating laser 3D printing, Al_2O_3/ZrO_2 eutectic samples were manufactured with suppressing the formation of cracks. The dependence of the average rod spacing (λ_{av}) on the scanning rate (V) follows a relation with $\lambda_{av}V^{0.5} = 1\ \mu m^{1.5}\ s^{-0.5}$. Typical eutectic microstructures, so-called complex regular, were analyzed with respect to its evolution with modulating the growth conditions. Formation mechanism of the solidification defect, shrinkage porosity, was discussed and the defect is found to be significantly suppressed by optimizing the solidification parameters. The maximum hardness and fracture toughness are measured to be 16.7 GPa and 4.5 MPa m$^{1/2}$, respectively. The interplay between the propagation of cracks and the Al_2O_3/ZrO_2 interface is discussed.

1. Introduction

Alumina based directionally solidified eutectic ceramic (DSEC), owing to its excellent high temperature mechanical properties, is recently considered to be a promising alternative to nickel based superalloy, for the fabrication of a new generation aero space engine turbine blade[1–4]. For instance, the flexure strength of Al_2O_3/$ZrO_2(Y_2O_3)$ eutectic is about 800 MPa at 1673 K[5] and the value of Al_2O_3/$Y_3Al_5O_{12}$(YAG)/ZrO_2 reaches up to 860 MPa at 1873 K, which is nearly 2 times larger than that of the a-axis sapphire (approximately 450 MPa)[6]. Additionally, Chen et al.[7] studied the effect of cooling rate on the microstructure and mechanical properties of Al_2O_3/YAG/ZrO_2 eutectic ceramic and the obtained fracture toughness was 4.13 ± 0.8 MPa m$^{1/2}$. Fu et al.[8] prepared the Al_2O_3/YAG/ZrO_2 eutectic with a refiner microstructure by the use of melt superheating. Unlike conventional ceramic, the sintering and the post heat-treatment are not needed in the preparation of DSEC. However, due to their high melting point (>2073 K), costly crucible has to be used in the directionally solidification apparatus during fabrication. Additionally, the adoption of traditional cold-working manufacturing of these materials for fabrication of a pre-designed device component is very difficult due to the intrinsic brittleness of the oxides. These disadvantages greatly impede the industrial application of DSEC.

Recently, laser three dimensional (3D) printing has been demonstrated with several intriguing characteristics, e.g. mold free, highly flexible, and low cost, and is proven to be a promising technique in aviation industry and medical science where sophisticated components are desired[9,10]. Developing the method for a precise and rapid fabrication of DSEC parts by the laser 3D printing is highly desired for the development and application of the advanced ceramics. For instance, Yves-Christian et al.[11] produced the net shaped samples with nano-sized microstructures and flexural strengths of above 500 MPa. Additionally, Mitteramskogler et al.[12] prepared several ceramic parts by using the laser 3D printing, and the relevant critical technologies were discussed. However, during the direct application of the 3D printing to the ceramics, a large solid temperature gradient, due to the local heat input by the focused laser beam, will be a critical problem as micro-cracks may occur in the samples due to the high local stresses. In principle, one straightforward method for diminishing and suppressing the formation of the cracks is preheating the sample to reduce the temperature gradient. For instance, Yves-Christian et al.[11] preheated the sample by a CO_2 laser, and the preheating area is about 30 mm × 40 mm and the net-shaped samples of almost 100% densities were obtained.

In this work, a preheating assisted laser 3D printing is designed for processing DSEC focusing on the precise fabrication technology, solidification behavior and the mechanical properties

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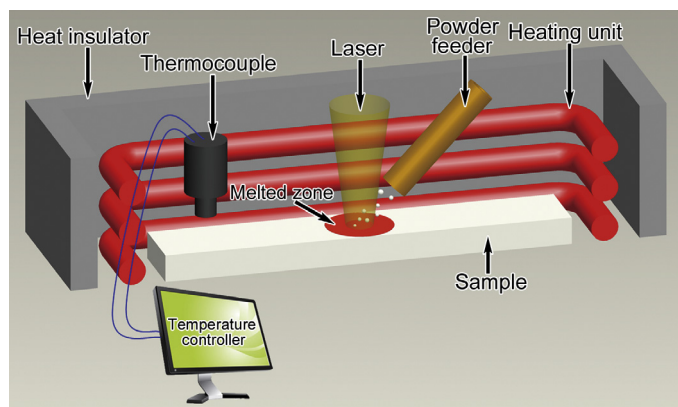 *E-mail address:* gaobo@fmmu.edu.cn (B. Gao).

Fig. 1. Schematic diagram of the equipment and the experimental process of the laser 3D printing.

of DSEC. Moreover, taking account of the high stress induced by laser processing, the target material was carefully chosen. Among the several well-investigated DESC systems, Al_2O_3/ZrO_2 eutectic possesses the highest fracture toughness at room temperature (7.8 MPa $m^{1/2}$)[13] compared with $Al_2O_3/Y_3Al_5O_{12}$ (2–2.4 MPa $m^{1/2}$)[14], $Al_2O_3/Er_3Al_5O_{12}$ (1.9 MPa $m^{1/2}$)[15], $Al_2O_3/GdAlO_3$ (5–6 MPa $m^{1/2}$)[1] and $Al_2O_3/Y_3Al_5O_{12}/ZrO_2$ (4.3 MPa $m^{1/2}$)[16] eutectic. Therefore, Al_2O_3/ZrO_2 eutectic is selected as the target material, which tends to bear the high stress during cyclic heating and cooling under the laser 3D printing. Furthermore, the microstructure evolution of Al_2O_3/ZrO_2 eutectic is investigated by examining the behavior of the complex regular eutectic microstructure. Additionally, the formation mechanism of the typical solidification defects is analyzed by considering the solidification sequence, and the solidification defects are found to be eliminated by optimizing the processing parameters. Finally, the relationship between the mechanical properties of Al_2O_3/ZrO_2 eutectic and the processing parameters is established. Finally, the toughening mechanism of ZrO_2 is discussed with consideration of the cracks propagation pattern.

2. Experimental

The setting of the equipment and the schematics of experimental process of the laser 3D printing are shown in Fig. 1, which consists of a PRC2000 continuous wave CO_2 laser, a four-axis numerical control working table, a powder feeder with a lateral nozzle and a preheating system close-loop controlled by the thermal couple and the temperature controller (Shimaden, SRS13A). The whole experimental process was carried out in a controlled atmosphere glove box. The laser was mounted on an overhead carriage, and the beam was directed into the glove box through a window on top of the chamber. The controlled atmosphere glove box was filled with argon gas, and argon gas was also used to deliver the oxide powders.

Commercial powders of 58.5 wt% Al_2O_3 and 41.5 wt% ZrO_2 compositions were used to prepare precursors. The ZrO_2 component includes 8 wt% Y_2O_3 for stabilization of the tetragonal phase of ZrO_2 at room temperature. The oxide powders were mechanically mixed by wet ball milling with an aqueous solution of polyvinyl alcohol to obtain a homogeneous slurry and then dried at 473 K in air for

1 h. Afterward, the 70 mm × 10 mm × 5 mm bar precursors were prepared by uniaxial die pressing at 25 MPa for 10 min, followed by pressureless sintering at 1673 K for 2 h to increase the density and provide handing strength. The powder of Al_2O_3/ZrO_2 eutectic with the size of ~150 μm and spherical shape produced by pelleting was laser deposited on the ceramic precursor.

The substrate was preheated to 1000 °C. The laser beam was directed to the substrate to create a molten pool into which the eutectic powders were injected through the powder feed nozzle. The oxide powders were melted and subsequently resolidified to form the clad layer. The laser 3D printing parameters are listed in Table 1. The crack free samples with the size of 20 mm × 8 mm × 8 mm can be obtained.

The solidified samples were treated by general metallographic analysis methods. The microstructure of the composite were determined by scanning electron microscopy (SEM, JSM-5800), energy dispersive spectroscopy (EDS, Link-Isis), and X-ray diffraction (XRD, Rigakumsg-158).

The rod spacing was evaluated by scanning the transverse sectional images along a chosen line being perpendicular to most of the phase domains traversed, and then calculating the number of identical pixels in successive segments along the line[17–20]. The average rod spacing (λ_{av}) is obtained by the arithmetic average of all of the measured values.

The hardness and fracture toughness are measured on the polished surface of the samples at room temperature by using the Vickers indentation technique following the ASTM C1327-99 standard. The indentations were made using 9.8 N loads for 15 s, and at least ten valid microindentations were conducted in each cross-section. The hardness and fracture toughness are calculated according to the following equations proposed by Niihara[21] for Palmqvist cracks:

$$H_v = 0.4636P/a^2 \tag{1}$$

$$K_{IC} = 0.035(E/H_v)^{2/5}(a/l)^{1/2}H_v a^{1/2} \Phi^{3/5} \tag{2}$$

where H_v is the Vickers hardness, K_{IC} is the fracture toughness, E is the Young's modulus of the material (we have taken the value of 343 ± 7 GPa measured by Pastor et al.[13]), P is the indentation load, a is half of the indentation diagonal, l is the crack length and $\Phi \approx 3$ is a constrain factor. This method is simple, convenient, nondestructive and low-cost to evaluate the hardness and fracture toughness of small and relatively brittle specimens. The sample size is large enough for the Vickers indentation test. Such technique has received great attention in recent years for measuring the mechanical properties of ceramic[22–25].

3. Results and Discussion

3.1. Microstructure evolution

The XRD analysis indicates that the microstructure is composed of Al_2O_3 and ZrO_2 phases (Fig. 2). Fig. 3 shows the typical transverse section microstructure (Fig. 3(a)) and EDS analysis of the phases with different colors (Fig. 3(b, c)). It indicates that the black zone is Al_2O_3 phase (Fig. 3(b)) and the white zone is the ZrO_2 phase (Fig. 3(c)).

Table 1
Processing parameters of laser 3D printing

Laser power (W)	Scanning velocity (μm/s)	Powder feeding rate (g/min)	Shielding gas flux (L/min)	Spot diameter (mm)	Overlap (%)	Increment of z (mm)
200–500	50–300	8–12	4–8	2.5	25	0.3