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Nano-sized Al_2O_3-ZrO_2 eutectic ceramic structures prepared by ultrasonic-assisted laser engineered net shaping

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ABSTRACT

Nano-scale Al_2O_3-ZrO_2 eutectic ceramic structures with shapes of thin-wall and cylinder were prepared by ultrasonic-assisted laser engineered net shaping. In the preparation process, the power of ultrasonic was adjusted in real-time on the molten pool. The generation of refining grain by ultrasonic were discussed based on the principle of crystallography. Two methods to improve the fracture toughness were analyzed. The average eutectic spacing was 60–70 nm, and the fracture toughness was 7.67 MPa·$m^{1/2}$.

1. Introduction

Al_2O_3-ZrO_2 eutectic ceramic eliminates the interface amorphous phase of conventional ceramic. It improves the density of ceramic, increases the degree of structuring, and contributes to the uniformity of phase distribution. The combination at the two phase interfaces is firm and highly anisotropic. Even near the melting point, Al_2O_3-ZrO_2 eutectic ceramic still possesses high hardness, strength, and creep resistance [1–3]. Additionally, it presents excellent thermal stability and mechanical properties, which play important roles in increasing the temperature of the turbine in aero engine. More specifically, it improves the thrust ratio of the engine, reduces the burning consumption, improves the ballistic capability of main battle tank compound armor and enhances the anti-ablation and impact resistance of fast-fired weapon ceramic tubes [4–6]. Therefore, Al_2O_3-ZrO_2 eutectic ceramic becomes a hotspot of research.

Up to now, many methods were proposed to fabricate eutectic ceramic materials, such as micro-pulling-down method (μ-PD), Bridgman, Laser floating zone (LFZ), Edge-defined film-fed growth (EFG), and laser engineered net shaping (LENS). μ-PD can control the eutectic spacing within micron or even submicron scale [7], but it can be easily contaminated by crucible during fabrication process. Bridgman can prepare eutectic ceramic with complex shapes [8], but the low solidification rate, low temperature gradient, and large eutectic spacing greatly limit the preparation of eutectic ceramics with excellent performance. Compared with μ-PD, LFZ can avoid the pollution resulted from the influence of crucible, but the process range of μ-PD and LFZ are narrow, so the two methods are only suitable for the manufacturing of eutectic ceramics with small size [9]. LENS utilizes laser with ultra-high temperature to melt powder, so high solidification rate, high temperature gradient, and submicron-scale eutectic spacing can be achieved. The fabrication process of this method is simple, and it can shape directly without the need of prefabricated embryos, but the fracture toughness of the obtained parts is low and cracks easily generate on the samples [10]. The eutectic spacing of the ceramics prepared by μ-PD, Bridgman, LFZ, EFG, and LENS are all larger than 140 nm and the fracture toughness are always smaller than 5 MPa·$m^{1/2}$ [11–15]. Ultrasonic-assisted LENS takes advantage of ultrasonic crushing and super-cooled nucleation, which can decrease the eutectic spacing and improve the fracture toughness of eutectic ceramic significantly [16]. Therefore, ultrasonic-assisted LENS is preferable for manufacturing of eutectic ceramic with high quality.

2. Experimental procedure

In this paper, the experimental equipment is JK1002 type Nd:YAG continuous laser with 2 mm spot diameter and equipped with three DPSF-D3 tubes. Fig. 1(a) illustrates the working principle of

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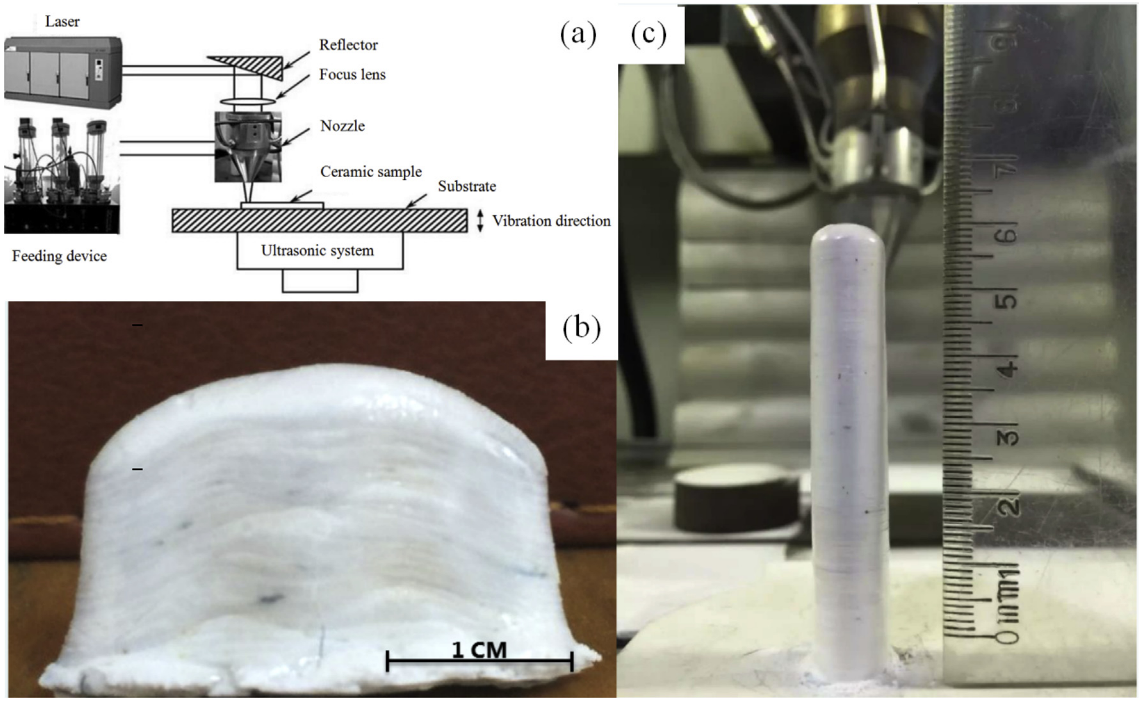

Fig. 1. Al_2O_3-ZrO_2 eutectic ceramic structures: (a) schematics of LENS; (b) thin-walled structure; (c) cylindrical structure.

LENS. The Al_2O_3 and ZrO_2 powder flowed through a coaxial nozzle and landed at the laser focal spot. During the process of forming, high purity argon was used as shielding and powder-carrying gas. In this paper, Ti-6Al-4V alloy (TC4) with size of $100 \times 100 \times 9$ mm^3 was used as substrate. The powder was made of 99.5% purity Al_2O_3 and 8 wt% of Y_2O_3 stable ZrO_2 spherical powders. The diameter of the powder was about 40–90 µm. Thin-walled structures were made for the basis of experimental research, these thin-walled structures were fabricated using continuous single channel and multilayer scanning path. After grinding and polishing of the sample, the Zeiss Supra55 SEM and EDS were used to observe the microstructures and composition of the ceramic. D/MAX-Ultima type X-ray diffraction (XRD) was used to characterize the ceramic sample and the initial powder. Micro-hardness was measured by WVC-1000B Vivtorinox hardness tester, and fracture toughness was calculated by indentation the crack length. Laser power, scanning speed, feeding rate, feeding proportion (ZrO_2 wt%), Z-increment were selected as 360 W, 380 mm/min, 1.6 g/min, 42.5%, and 0.22 mm respectively. The initial ultrasonic power was 120 W, and increased by 10 W when the height of the thin-wall structure increased by 1 mm. The thin wall (Fig. 1(b)) and cylinder (Fig. 1(c)) of Al_2O_3-ZrO_2 eutectics were built successfully.

3. Results and discussion

The microstructure of Al_2O_3-ZrO_2 eutectic ceramic with a fine three-dimensional network structure is formed, as shown in Fig. 2. According to EDS analysis results, the white phase is rich in ZrO_2 phase, while the black phase is rich in Al_2O_3 phase. The average eutectic spacing was measured to be 69.38 nm.

According to the classical nucleation theory, two conditions are required for the formation of solid crystal nuclei in super-cooled liquid phase. One is the largest size of the embryos r_{max} is larger than the critical nucleus size r_k in the fluctuation phase of under-cooled melt, the other is the energy fluctuations of the melt can provide enough energy needed for the formation of embryos. The expressions for the critical nucleus r_k and the critical nucleation energy ΔG_c are as follows: σ is Gibbs-Thomson effect, $f(\theta)$ is heterogeneous nucleation factor ($0 < f(\theta) < 1$) [17–19].

$$r_k = 2\sigma/\Delta G$$

$$\Delta G_c = 16\pi\sigma^3/3\Delta G^2 f(\theta)$$

$$\Delta G = G_S - G_L = \Delta H_S + T\Delta S_S + \Delta V_S \Delta P$$

As the pressure of the molten pool (ΔP) is increased by the action of ultrasonic, the change of free energy (ΔG) increases. Both the critical nucleus size r_k and the critical nucleation energy ΔG_c decrease. It is easy to form eutectic with smaller spacing. Fig. 3 shows the XRD patterns of Al_2O_3 powder, ZrO_2 powder and Al_2O_3-ZrO_2 eutectic ceramic,. The Al_2O_3 powder is mainly composed of α-Al_2O_3 phase, and the ZrO_2 powder mainly contains tetragonal solid solution (t-ZrO_2) phase. The eutectic ceramic show all the above-mentioned phases, demonstrating that the crystalline phases of the original powder were almost completely retained in the eutectic ceramic.

In Fig. 4 the average micro-hardness of the Al_2O_3-ZrO_2 eutectic ceramic is 16.22 GPa, which is calculated by hardness indentation diagonal length. The size of the four corner cracks in an indentation satisfies the discriminant of crack in Babbitt [20].

$$(K_{IC}\Phi/H_V a^{1/2})(H_V/E\Phi)^{2/5} = 0.035(l/a)^{-1/2}$$

K_{IC} is the fracture toughness of materials (MPa·m$^{1/2}$), Φ is Shape constraint factor ($\Phi \approx 3$), H_V is micro-hardness of materials (GPa), a is the half length of the indentation diagonal (µm), E is elastic modulus of materials (GPa), and l is the length of the crack (µm). The average fracture toughness of the Al_2O_3-ZrO_2 eutectic ceramic prepared by the ultrasonic-assisted LENS is 7.67 MPa·m$^{1/2}$. It can be concluded that the fracture toughness gets improved significantly. As shown in Fig. 2, refined grain, three-dimensional network structure and unobvious grain boundary between the two