In situ fabrication of highly-dense Al₂O₃/YAG nanoeutectic composite ceramics by a modified laser surface processing

Haijun Su a,b,*, Jun Zhang a, Weidan Ma a, Kaichen Wei a, Lin Liu a, Hengzhi Fu a, Shien-Ping Feng b, A.K. Soh c

a State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi’an 710072, PR China
b Department of Mechanical Engineering, The University of Hong Kong, Hong Kong
c School of Engineering, Monash University Sunway Campus, Malaysia

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Abstract

Alumina-matrix eutectic in situ composite ceramics present excellent high-temperature mechanical properties, which have been considered as promising next-generation ultra-high temperature structural materials. A modified laser surface processing is developed to in situ fabricate highly-dense Al₂O₃/YAG bulk nanoeutectic ceramics with large size and homogeneous three-dimensional network of nanoeutectic microstructure by introducing two-side remelting and high-temperature preheating. The crack and porosity are avoided, and the eutectic structure achieves a good continuous growth between two solidified layers. The eutectic phases show sharp interface bonding with a defined orientation relationship. The dislocations and crack deflection at high-density phase interfaces importantly contribute to the enhanced fracture toughness.

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1. Introduction

In order to meet the increase of inlet temperature of gas turbines and improve its thermal efficiency as well as reduce the pollution emissions such as CO₂ or NOₓ, the development and design of new ultra-high temperature structural materials with superior high-temperature performance and longevity above 1600 °C in oxidizing environment have been greatly focused on all over the world. 1–3 Directionally solidified oxide eutectic ceramic composite (DSOEC), a newly developed ultra-high-temperature structural material in recent few decades, has attracted extensive attention due to its excellent mechanical property at high temperatures. 4–7 Thus, it has been considered as one of the most potential alternatives to current traditional superalloys or sintered ceramics applied in the aerospace field.

In DSOEC, it is known that the eutectic phases can be simultaneously grown from melt, and the well-aligned growth arrays can be produced by controlling thermal flow direction. The directionally solidified eutectics not only combine the unique characteristic of each component material but also enhance the phase interface bonding, so that greatly improve the properties of the composite. 8,9 Of its numerous exciting properties, the one material property that stands out is DSOEC’s outstanding high temperature strength stability from room temperature up to high temperatures (near to its melting point). Especially, the DSOEC can availably serve in the aggressive oxidizing environments without coating as compared with other non-oxide materials. 10–13 Furthermore, highly homogenous and very fine microstructures based on eutectic structures having strongly bonded phases and high-density interphase areas can be obtained and tailored by rapid solidification or directional solidification technique with high temperature gradient, which can further improve the properties of materials. 14–18

However, up to date, it is still very little that directional solidification or rapid solidification is applied to produce DSOEC composites in the industrial practice. 3–16 One of the main reasons is that the conventional directional solidification technique,
such as Bridgman method, can prepare large eutectic ceramic rods, but the preparation procedure needs large crucibles (high purity Mo or Ir) and the crucibles can easily react with ceramic melt, leading to the melt pollution and high preparation cost due to non-reuse of crucibles.\(^{4,5,10,11}\) Moreover, the eutectic interphase spacing is large (10–20 \(\mu\)m) due to its low temperature gradient (<100 K/cm) and slow solidification rate, resulting in low production efficiency and reduced properties.\(^6\) Additionally, as noted, the laser floating zone remelting with high temperature gradient (>1000 K/cm) can produce eutectic ceramics with nanostructure and excellent properties, but it is only limited to small sample diameter (<1 cm).\(^{24,12}\) It is thus highly desirable to develop new preparation techniques for the oxide eutectic ceramic with large size, fine microstructure, high preparation efficiency and low cost to catch up its wide application.

Laser surface zone remelting is recently developed as a rapid solidification technique to prepare oxide eutectic ceramic composites with advantages of ultra-fine microstructure, free of crucible and high solidification rate. However, it is only focused on small eutectic plates with hundreds of microns in thickness so far.\(^{19–22}\) Herein, we report a modified laser surface (MLS) processing technique to prepare rapidly solidified \(\text{Al}_2\text{O}_3\)/YAG nanoeutectic ceramic rods having nearly full density and large size by introducing two-side remelting and high-temperature preheating. The homogenous microstructure and enhanced fracture toughness are obtained. The microstructure characteristic, interface structure, orientation relationship and toughening mechanism are investigated.

### 2. Experimental procedure

High purity (>4 N) \(\text{Al}_2\text{O}_3\) and \(\text{Y}_2\text{O}_3\) nano-powders were homogeneously mixed according to the eutectic composition (82 mol\% \(\text{Al}_2\text{O}_3\)/18 mol\% \(\text{Y}_2\text{O}_3\)) by wet ball milling. The mixed powders were die pressed to form rectangular precursor plates [65 mm \(\times\) (6–10) mm \(\times\) (3–5) mm] at room temperature and sintered at 1500 °C for 2 h to improve the handling strength. The modified laser surface processing of the precursor plate was performed in vacuum by using a laser surface atmosphere melting furnace.\(^{16,22}\) A high-purity \(\text{N}_2\) gas was filled into the chamber with a flow rate of 5–10 L/min in order to prevent from the formation of porosity. Two superimposed precursor plates were firstly located on the laser worktable with a 5-axis and 4-direction coupled motion, and then the back of the plates was preheated to 1200 °C by the furnace for 30 min. After that, an incident \(\text{CO}_2\) laser with beam diameter of 10 mm and power of 200–600 W from the laser window on the furnace up-surface started to scan and melt the upper surface of the superimposed precursor samples along the sample axis with different rates. When the upper surface of the samples was completely remelted, the samples were over-turned to restart the second remelting of the sample back surface, as schematically shown in Fig. 1. The laser scanning rate was 20–400 \(\mu\)m/s dependent on the sample thickness.

The density of MLS-processed specimens was measured by using Archimedes’s method. The microstructure was analysed using scanning electron microscopy (SEM, JSM-5800), energy dispersive spectroscopy (EDS, Link-Isis) and X-ray diffraction (XRD, Rigaku-MSG-158). The phase interface and orientation relationship were investigated by transmission electron microscopy (TEM, JEM-200CX) and high resolution transmission electron microscopy (HRTEM, JEM-2100F). The hardness and fracture toughness were determined by the Vickers indentation technique with load of 9.8 N for 15 s and an average value of 10 measurements was reported. The indentation size and crack length were measured by SEM. The hardness and fracture toughness were calculated according to the equation proposed by Antis\(^{23}\) as reported in previous literatures.\(^{24,25}\)

### 3. Results and discussion

Fig. 2 shows the macroscopic photograph of the rapidly solidified \(\text{Al}_2\text{O}_3\)/YAG bulk eutectic ceramic grown by the MLS-processing at the scanning rate of 20 \(\mu\)m/s. The obtained eutectic ceramic presents an approximate rod shape due to the melt surface tension with the diameter up to 8 mm and the length of 60 mm. The diameter and size are almost 2–4 times larger
than that of the eutectic ceramic rod availabley obtained by the melt growth method without using cubicle such as laser floating zone or laser surface remelting in the previous reports. 3,8,19 It indicates that the MLS-processing can remarkably enhance the thickness of solidified layer and achieve the rapid preparation of large bulk eutectic ceramics by introducing the laser two-side remelting. The sample diameter is dependent on the precursor shape and size as well as laser energy density and scanning rate. During the MLS-processing, the eliminations of cracks due to rapid cooling or residual stress as well as the inhibition of gas porosity introduced during melting process are the keys of influencing the ceramic melt preparation. In our case, the MLS-processed eutectic ceramic rod displays glossy surface with white color, and no crack or porosity is found on the surface and inside of the sample. It demonstrates that no impurity is introduced, and the growth defects such as porosity and crack have been well avoided, which is contributed by the high temperature preheating and second two-side laser remelting for effectively relaxing thermal stress and healing cracks. The surface finish increases with the increase of scanning rates, but tiny cracks sometimes still appear when the scanning rate is larger than 200 μm/s. The specimens exhibit a density of nearly 100% which is superior to the previously reported laser selective melted Al2O3/ZrO2 ceramic 26 and spark plasma sintered oxide eutectic ceramic. 27 There is an overall trend of decreasing density with increasing scanning rate. When the laser scanning rate is over 400 μm/s, the composite density tends to be below 99%.

Fig. 3 shows the typical cross-section microstructures of the MLS-processed Al2O3/YAG eutectic ceramics rod grown at the scanning rate of 40 μm/s. As shown in Fig. 3(a), the composite ceramic rods present dense and ultra-fine microstructure without cracks and defects. There is an obvious solidification interface layer between both the remelting layers. As seen, the microstructure from the outside to middle interface layer of the sample is very homogeneous, which is superior to the previously reported eutectic ceramics fabricated by the single side laser remelting method. 3,19,25 The homogenous microstructure from top/bottom to middle is mainly ascribed to the superheating treatment of second remelting and to no defect (pore or impurity) disturbance in the solidification interface front during the melt growth process. 18,28 The component phases, α-Al2O3 and YAG, are identified by XRD and EDS, and no other crystalline phases or amorphous phases are detected. The magnified microstructures of the top and bottom of the rod are depicted in Fig. 3(b) and (c). The two phases show well-coupled eutectic growth with an interpenetrating three-dimension network nanostructure aligned along the scanning direction (red arrow in Fig. 3b). As seen in the yellow arrow in Fig. 3(c), the morphology is completely different from the common regular eutectic structure in metal alloys such
as NiAl-Mo eutectic, indicating a complex irregular eutectic characteristic is mainly dominated by the branch growth of YAG phase due to its stronger faceted growth habit than Al₂O₃. The domain width of eutectic phases decreases with increasing the laser scanning rate, and it can be refined below 100nm when the rate is over 400 μm/s due to the high temperature gradient (~10⁴ K/cm) and large cooling rate (~400 K/s) for laser zone remelting. During eutectic solidification, the nucleation undercooling ΔT increases with cooling rate V, resulting in the decrease of eutectic spacing λ, namely, λ ∝ 1/V. The volume fractions of the eutectic phases determined by the SEM images are 44.6% and 55.4% for Al₂O₃ and YAG respectively, which is in agreement with the theoretical calculation from the eutectic phase diagram. It is also in accordance with the volume fraction range of theoretical prediction for the irregular lamellar eutectic classification based on Hunt–Jackson theory. Moreover, by careful examination, it is found that the eutectic microstructure of the second remelting layer (Fig. 3b) is slightly finer than that of the first remelting layer (Fig. 3c), which of similar phenomena was also found in the eutectic ceramic by laser direct forming. It demonstrates that the two-side laser second superheating can effectively refine the eutectic spacing. In the interfacial transition zone, a coarse coupled band eutectic structure (Fig. 3d) with the width of about 40 μm and strong faceted growth habit appears. The width of the band eutectic decreases with increasing the laser power and decreasing the laser scanning rate. Additionally, no sintered multicrystalline ceramic structure can be found in the interface zone, revealing that the two remelting layers successfully achieve the continuous eutectic growth by frequent branching (yellow arrows in Fig. 3d) of faceted Al₂O₃ and YAG phases which produce complex irregular eutectic structure.

During the growth of eutectic composites, the solidification process does not only affect the microstructure but also influences the preferred growth orientations. In directionally eutectics, the microstructures (lamellae or rods) usually are composed of single crystal phases preferentially growing along a defined crystallographic direction. Fig. 4 shows the phase interface TEM structure and electron diffraction pattern of selected area perpendicular to the rod axes of the MLS-processed Al₂O₃/YAG eutectic ceramic. It is clearly observed that the phase interface is clean and planar without intermediary phases detected, showing sharp morphology with well interface matching. According to Bragg diffraction law, the electron diffraction analysis at the phase interface center (Fig. 4b) determines that the MLS-processed Al₂O₃/YAG eutectic shows well-defined crystallographic direction and relationship: [1 0 1 0] Al₂O₃//[1 0 1] YAG and (0 0 0 1) Al₂O₃//(1 2 1) YAG, which are similar to that of Maze-rolles et al. by optical floating zone melting. Thus, the preferred crystallographic growth directions for Al₂O₃ and YAG phase during the MLS-processing are [1010] and [101], respectively. The minimum interfacial energy is produced aligned above directions and the configuration at the interface is also illustrated by the HRTEM image, as shown in Fig. 5. It is found that the arrays of atomic planes of both phases at interface are not corresponding but there is a crystal lattice misfit calculated to be 6.17% belonging to the half-coherent phase interface. The inverse Fourier transform at interface (inset of Fig. 5) further reveals that the accommodation between two phase structures is adjusted by the dislocations along the interface.

**Fig. 4.** TEM micrograph showing the eutectic phase interface of the MLS-processed Al₂O₃/YAG eutectic rod (a) and the selected area electron diffraction patterns at the Al₂O₃/YAG phase interface (b).

**Fig. 5.** The high-resolution transmission electron micrograph of the Al₂O₃/YAG phase interface. The inset is the inverse Fourier transform from the digitized image of the HRTEM interface.
Fig. 6(a) shows the variations of typical mechanical properties with the increase of laser scanning rates for the MLS-processed Al2O3/YAG eutectic ceramics. The interaction between the fine microstructure and cracks nucleated from the corners of Vickers indentations was analysed by SEM. At least ten valid tests were carried out on each sample. The results are comparable to the previously reported eutectic ceramics determined using the indentation method. The indentation cracks belong to Median cracks determined by the polished methods.\textsuperscript{17} It is indicated that the hardness increases rapidly with increasing laser scanning rate in the low rate range, but decreases when the rate is over 100 \(\mu\text{m/s}\), because the high scanning rate causes the reduced thickness of solidified eutectics and generates more defects such as micro-cracks or pores. Although the fracture toughness shows an increase with the scanning rate, it almost keeps constant when the rate is over 100 \(\mu\text{m/s}\). The maximum hardness and fracture toughness obtained by the optimized laser scanning rate of 100 \(\mu\text{m/s}\) are 18.7 GPa and 3.7 MPa m\textsuperscript{1/2}, respectively. The fracture toughness of eutectic is obviously higher than those of monocrystal Al2O3 (2.4 MPa m\textsuperscript{1/2}),\textsuperscript{33} YAG (3.0 MPa m\textsuperscript{1/2})\textsuperscript{33} and Al2O3/YAG binary eutectic (2.0 MPa m\textsuperscript{1/2}),\textsuperscript{24} and is close to that of Al2O3/ZrO2 binary eutectic (4.8 MPa m\textsuperscript{1/2})\textsuperscript{34} measured also by using the indentation method. The enhanced mechanical properties are primarily attributed to refined micro/nano-structured eutectic microstructures on the one hand.\textsuperscript{3,32} The ceramic fracture is a process of crack propagation and growth, in which the cracks inevitably produce interaction with the interphases. In previous reports for the Al2O3/YAG binary eutectic,\textsuperscript{6,24} the straight indentation crack normally propagates directly across the Al2O3 and YAG phases, leading to material fracture. As shown in the arrows in Fig. 6(b), for the MLS-processed Al2O3/YAG composite, the crack bridging and deflection at interface are clearly observed, indicating more fracture energy can be absorbed. The crack is finally stopped by the fine phase interface shown by red arrow in Fig. 7, and therefore the fracture toughness is effectively increased. The eutectic ceramic presents typical transgranular cracking propagation. Moreover, the considerable linear dislocations formed in the Al2O3 phase as compared with the YAG phase can also contribute to the toughness improvement,\textsuperscript{9} as shown in Fig. 7.

4. Conclusions

Rapidly solidified Al2O3/YAG nanoeutectic ceramic rods with large size (diameter \(>6\text{ mm}\)) and nearly full density are produced by a modified laser surface processing method. The laser two-side surface remelting and high temperature preheating effectively enhance the sample size, avoid crack generation and achieve continuous growth between two solidified layers. The composite presents a homogeneous three-dimensional network with the irregular eutectic structure consisting of micro/nano structured Al2O3 and YAG phases with a defined orientation relationship of [1 0 1] Al2O3/[1 0 1] YAG and (0 0 0 1) Al2O3/(1 2 1) YAG. The improvement of fracture
toughness is mainly ascribed to the microstructure refinement by rapid solidification, crack bridging and deflection induced at phase interfaces as well as the high density dislocations produced in the YAG phases.

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