

# On the advanced microstructural characterisation of additively manufactured alumina-zirconia based eutectic ceramics: Overview and outlook

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## **Abstract**

Recently, there have been a number of reports on the fabrication of Alumina-Zirconia ( $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  (AZ))-based eutectic ceramics using laser additive manufacturing (AM) techniques owing to the exceptional creep and oxidation resistance coupled with excellent microstructural stability in these materials. Moreover, a number of interesting microstructural features (in these materials) have been reported to be formed by the variation of process parameters (especially, laser scanning speed) associated with the aforementioned AM techniques. The present review provides an overview of the present state of research in the area of laser AM AZ-based eutectic ceramics and highlights the challenges and future outlooks in this avenue of research. In addition, the requirement of employing correlative microstructural characterisation in these materials has been highlighted in the outlooks section.

**Keywords:**  $\text{Al}_2\text{O}_3$ -based eutectic ceramics, Additive Manufacturing

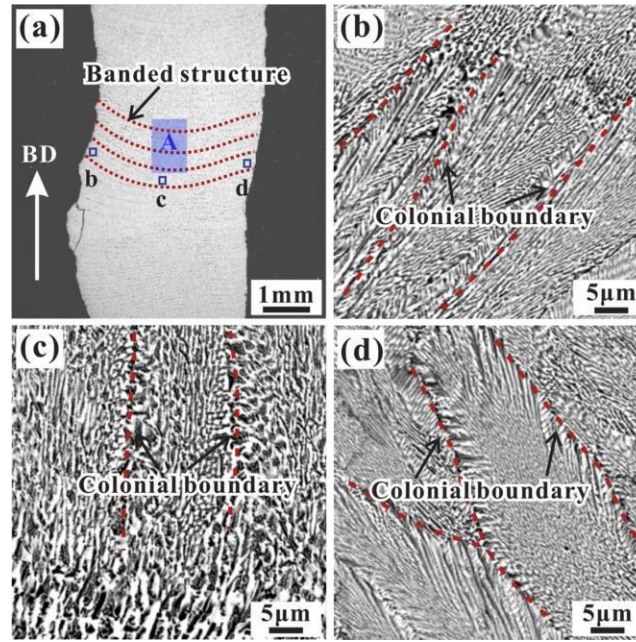
## **Introduction**

Alumina ( $\text{Al}_2\text{O}_3$ )-based ceramics find extensive industrial applications owing to a number of desirable properties which mainly include low density, high compressive strength, wear resistance, and electrical and thermal insulation properties [1]. A combination of good compressive properties of high-purity  $\text{Al}_2\text{O}_3$  along with biocompatibility makes  $\text{Al}_2\text{O}_3$  ceramic a potential candidate for dental and orthopaedic applications [2]. On the other hand, laser additive manufacturing (AM) techniques (especially laser AM techniques) are based on a layer by layer deposition of materials, which leads to a large-scale microstructural heterogeneity and formation of cracks (due to thermal stresses) in the deposited layers [3]–[5]. However, for the aforementioned AM techniques, the material (to be deposited) needs to possess a good fracture toughness so that it does not fracture due to the formation of cracks during the layerwise deposition [3], [6]–[9]. The main limitation of  $\text{Al}_2\text{O}_3$  ceramics is the low fracture toughness which restricts the application of laser-based AM techniques in these ceramics [1].

Adding Zirconia ( $\text{ZrO}_2$ ) to  $\text{Al}_2\text{O}_3$  ceramics has been reported to be an effective way of improving fracture toughness (in AM-based samples) through crack bridging and deflection mechanisms. Pappas et al. [1] have reported the influence of  $\text{ZrO}_2$  addition to AM-based  $\text{Al}_2\text{O}_3$  using laser direct deposition technique. Li and Zhang [10] have investigated the microstructure of  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  (AZ) ceramics fabricated using laser direct deposition technique with  $\text{ZrO}_2$  content  $>35$  wt.%. Wilkes et al. [11] have reported that preheating of every layer (using a  $\text{CO}_2$  laser beam) may be successfully employed to eliminate micro-cracking in AZ ceramics. Homeny and Nick [12] have investigated the structure-property correlation in AZ- $\text{Y}_2\text{O}_3$  eutectic ceramic. Moreno and Yoshimura [13] have investigated the stabilisation of  $\text{ZrO}_2$  lamella in rapidly solidified AZ eutectic ceramic. Trnovcova et al. [14] have investigated the microstructure and physical properties of directionally solidified AZ eutectic ceramic. The present review is aimed at providing an overview of the present state of research in the field of laser AM AZ-based eutectic ceramics by highlighting three recent investigations in the particular avenue. In addition, a future outlook in this avenue has also been briefly highlighted towards the end of the review.

### **1. Characterisation of colonial boundaries in AZ-GdAlO<sub>3</sub> eutectic ceramic fabricated using laser directed energy deposition**

Liu et al. [15] have investigated the microstructure of AZ-GdAlO<sub>3</sub> eutectic ceramic fabricated using laser directed energy deposition (LDED) technique. The formation of periodic banded structures was reported along the building direction (BD) and its formation was attributed to the abnormal growth of nanoscale features adjacent to the melt pool [15]. Within a eutectic colony, a “Chinese-script” eutectic structure with an entanglement of bright (GdAlO<sub>3</sub>) and dark phases ( $\text{Al}_2\text{O}_3$ ) was observed [15]. In addition, it was observed that colonies along the longitudinal section show a columnar morphology and are elongated perpendicular to the BD [15]. The aforementioned morphology of the colonies (along the longitudinal section) was mainly attributed to the heat conduction behaviour in the melt pool due to which the microstructural growth occurs against heat flow direction leading to an elongation of eutectic colonies (along the longitudinal section) perpendicular to the melt pool [15]. Moreover, the eutectic spacing was reported to decrease from  $\sim 0.63 \pm 0.11 \mu\text{m}$  at the sample surface to  $\sim 0.99 \pm 0.08 \mu\text{m}$  at the centre of the sample [15]. This has been attributed to a higher cooling rate at the surface as compared to that of the sample interior [15]. **Fig. 1(a)** shows concave bands along BD. **Figs. 1(b-d)** show the Scanning Electron Microscopy (SEM)-based microstructures in the different layers of the cladding layer with colonial boundaries clearly visible.



**Fig. 1** SEM micrographs (of the longitudinal section) of the AZ-GdAlO<sub>3</sub> eutectic ceramic: (a) periodic banded structure, (b) Left side of a deposited layer, (c) Centre of a deposited layer, and (d) Right side of a deposited layer [15].

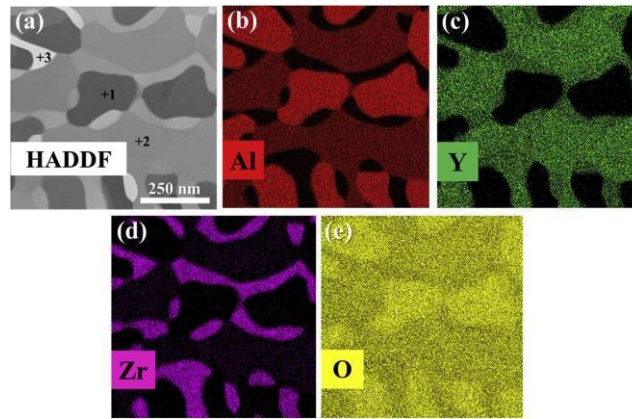
### 3. Microstructure obtained during solidification of selective laser melted AZ-GdAlO<sub>3</sub> eutectic ceramic

Liu et al. [16] have investigated the influence of laser scanning speed on the solidification of AZ-GdAlO<sub>3</sub> eutectic ceramic during selective laser melting (SLM) technique. The relative density of the solidified samples was reported to decrease from 98.7% to 95.7% with increasing laser scanning speed to ~48 mm/min [16]. In addition, it was observed that the primary heat transfer mechanism associated with the solidification phenomenon is thermal conduction due to which there was a decrease in both melting width and depth with increase in scanning speed [16]. Interestingly, it was also observed that the eutectic spacing in the top zone of the melt pool initially decreases with increasing laser scanning speed from 6 mm/min till 12 mm/min and then increases with increasing scanning speed from 12 mm/min till 48 mm/min [16]. The aforementioned trend in the eutectic spacing with scanning speed was attributed to a change in solidification rate controlling factor from laser scanning speed to the angle between the scanning direction and the growth direction of the microstructure [9], [16]. Quenching induced micro-cracks and increased surface roughness (due to bailing effect and presence of microstructural pores) were reported for scanning speeds of <12 mm/min [16]. Moreover, solidification defects were reported to be minimised for laser scanning speed of ~12 mm/min [16].

### 4. Nanostructured AZ-YAG fabricated using laser engineered net shaping technique

Fan et al. [17] have reported the fabrication of highly dense ( $\geq 98\%$ ) thin-walled Al<sub>2</sub>O<sub>3</sub>-YAG-ZrO<sub>2</sub> (AYZ) eutectic ceramic using LENS technique. The as-synthesized state of the material shows a cellular microstructure with the interpenetration of three phases (namely,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,

YAG and ZrO<sub>2</sub>) [17]. In addition, a morphological transition from planar to cellular eutectic microstructure (along BD) was reported for every deposited layer [17]. **Fig. 2(a)** shows a scanning transmission electron microscopy (STEM)-high-angle annular dark field (HAADF) image of AYZ ceramic in as-fabricated condition [17]. **Figs. 2(b-e)** shows the corresponding STEM-Energy Dispersive Spectroscopy (EDS) maps for different elements: Al, Y, Zr and O. The dark, grey and bright phases in STEM-HAADF image (**Fig. 2(a)**) correspond to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, YAG and cubic ZrO<sub>2</sub> phases respectively, as is also evident from **Figs. 2(b-e)** and **Table. 1** [17]. Besides, from **Figs. 2(c-e)** and **Table. 1**, it may be observed that ~18 mol.% Y<sub>2</sub>O<sub>3</sub> is dissolved in ZrO<sub>2</sub> in as-fabricated condition indicating that cubic ZrO<sub>2</sub> is stabilised by Y<sup>3+</sup> during cooling and solidification (during LENS) [17].



**Fig. 2** AYZ: (a) STEM-HAADF image, and corresponding STEM-EDS maps of (b) Al, (c) Y, (d) Zr, and (e) O [17]. Points 1, 2 and 3 marked in part (a) represent the regions where point EDS mapping has been performed. Results of point EDS mapping at points 1, 2 and 3 have been shown in **Table. 1**

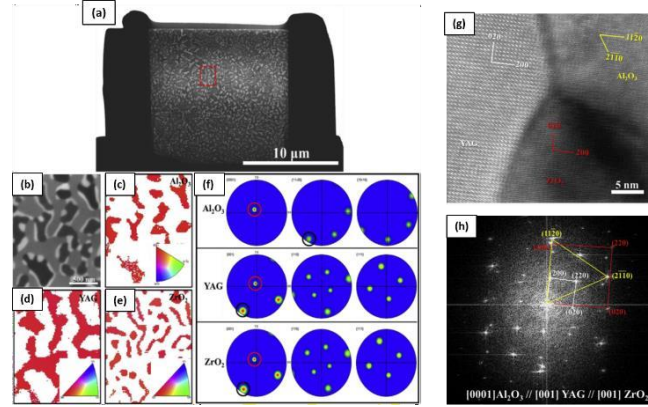
**Table. 1** Composition (in at.%) at points 1, 2 and 3 obtained using point STEM-EDS analysis [17]

Elements	1	2	3
Al	35	22.5	1.3
Y	0	8.4	7.9
Zr	0	0.6	17.1
O	65	68.5	73.7

An irregular interpenetration of fibrous eutectic structure was also reported to occur along the boundary region of the fabricated specimens [17]. This was attributed to a much higher rate of solidification at the boundary region as compared to that within the sample interior [17]. In addition, the orientation relation between the three phases at the interior of LENSEd samples was obtained as  $\langle 0001 \rangle_{\text{Al}_2\text{O}_3} // \langle 001 \rangle_{\text{YAG}} // \langle 001 \rangle_{\text{ZrO}_2}$  (with a slight deviation of  $\sim 3.5^\circ$  between  $\{001\}_{\text{YAG}}$  with  $\{11\cdot 20\}_{\text{Al}_2\text{O}_3}$  and  $\{001\}_{\text{ZrO}_2}$  obtained using Transmission Kikuchi Diffraction (TKD) technique and verified with High-resolution Transmission Electron

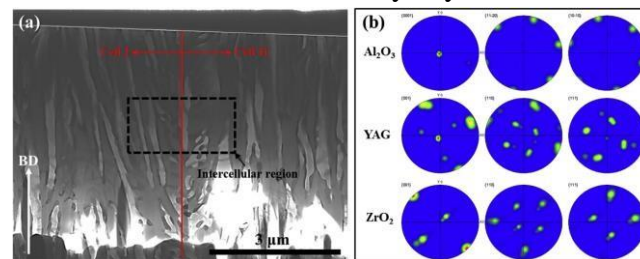


Microscopy (HRTEM) imaging of a triple junction formed between  $\text{Al}_2\text{O}_3$ , YAG and  $\text{ZrO}_2$  phases (**Fig. 3**) [17]. The aforementioned deviation may be attributed to a competitive effect between interfacial energy and growth kinetics [17]. For instance, the lower interfacial energy of  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  interface ( $\sim 0.74 \text{ J/m}^2$ ) as compared to that for  $\text{Al}_2\text{O}_3/\text{YAG}$  interface with an interfacial energy  $\sim 3.23 \text{ J/m}^2$  [17] may be attributed to a better parallel nature of  $\{11\text{-}20\}_{\text{Al}_2\text{O}_3} // \{001\}_{\text{ZrO}_2}$  when compared with that for  $\{11\text{-}20\}_{\text{Al}_2\text{O}_3} // \{001\}_{\text{YAG}}$  [9], [17].



**Fig. 3** AYZ: (a) SEM image of the electron transparent lamella of the transverse section of the LENSed specimen prepared using Focussed ion beam (FIB)-based liftout technique, (b) SEM image of region of interest for TKD mapping inside the cellular eutectic, (c), (d), and (e) TKD-based inverse pole figure (IPF) maps of  $\text{Al}_2\text{O}_3$ , YAG and  $\text{ZrO}_2$  respectively, (f) Pole figures for the three constituent phases:  $\text{Al}_2\text{O}_3$ , YAG and  $\text{ZrO}_2$  corresponding to (c), (d) and (e) respectively, (g) High-resolution Transmission Electron Microscope (HRTEM) micrograph of the transverse section showing a triple junction between  $\text{Al}_2\text{O}_3$ , YAG and  $\text{ZrO}_2$  phases, and (h) Fast Fourier Transformation (FFT) diffraction pattern corresponding to part (a) with zone axis:  $[0001]_{\text{Al}_2\text{O}_3} // [001]_{\text{YAG}} // [001]_{\text{ZrO}_2}$  [17]. A magnified view of the region highlighted using a red-dotted rectangle in part (a) has been shown in part (b).

**Fig. 4** shows an SEM image of the longitudinal section of LENSed AYZ specimen subjected to TKD analysis along BD [17]. The growth direction of the cellular eutectics remains the same as that for the transverse section of AYZ samples i.e.  $\langle 0001 \rangle_{\text{Al}_2\text{O}_3} // \langle 001 \rangle_{\text{YAG}} // \langle 001 \rangle_{\text{ZrO}_2}$  [17]. However, unlike the transverse section, the longitudinal section also shows YAG crystals with minor growth direction as  $\langle 111 \rangle$  [17]. This may be attributed to the deviation of these crystals (present mainly near cellular boundaries as shown in **Fig. 4**) from their habit planes and subsequent heading towards cellular boundary instead of remaining parallel with the cell growth direction. A similar observation has been reported for  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  cellular eutectic by Sayir and Farmer [18] and for Ni-Al-V eutectic alloys by Milenkovic et al. [19].



**Fig. 4** AYZ: **(a)** SEM image of the electron transparent lamella of the longitudinal section of the LENSEd specimen prepared using Focussed ion beam (FIB)-based liftout technique, TKD-based **(b)** pole figures of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, YAG and ZrO<sub>2</sub> [17]. Pole figures in part **(b)** have been obtained from the inter-cellular region enclosed with a block-dotted rectangular box in part **(a)**. In part **(a)**, BD abbreviates for building direction.

## 5. Summary and outlook

In the present review, the present state of research in the field of laser AM-based AZ ceramics has been briefly highlighted. The present focus (in this avenue) is to engineer the microstructure (based on optimising a number of process parameters associated with AM-based fabrication techniques) to render these ceramics superior in terms of mechanical properties compared to those fabricated using conventional techniques. However, in the context of eutectic ceramics (including AZ ceramics), characterisation of the different interfaces (mostly, the eutectic boundaries, in the present context) has not been addressed till date. For instance, in the context of laser AM-based AZ ceramics, the case study discussed in **section 4** is the only work (till date) which has been successfully able to use FIB-based liftout technique for obtaining electron transparent lamella from both transverse and longitudinal sections in AYZ ceramic in order to determine the orientation relationship between the individual phases ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, YAG and ZrO<sub>2</sub>) using TKD technique.

In the last four decades, grain boundary engineering (GBE) of both metallic materials and ceramics has evolved as a methodology to optimise the different properties of these materials based on replacing high-energy random high-angle GBs (HAGBs) with low-energy GBs [20], [21]. Particularly, in the context of metallic materials with mostly cubic crystal structures, GBE has been defined as a methodology to replace HAGBs with special HAGBs (with low-energy) also known as Coincidence Site Lattice (CSL) boundaries [22]–[25]. The entire methodology of GBE is based on reducing the overall GB energy in a microstructure so as to make the 2D interfaces (GBs and IBs) resistant to corrosion, oxidation, abnormal grain growth and intergranular fracture. Moreover, the most common method to obtain GBE microstructures in most metallic materials is thermo-mechanical processing (TMP) [26]. In the context of ceramics with more complex crystal structures, CSL theory fails and hence, the existence of low-energy CSL boundaries is hard to visualise [27]–[29]. Furthermore, the techniques used (especially TMP) to obtain GBE microstructures in metallic materials cannot be used in ceramics owing to their low deformability both at room and elevated temperatures. Hence, there lies a huge challenge in obtaining GBE microstructures in AZ ceramics. This also paves a new avenue of research in the context of AZ ceramics. In addition, one of the most recently evolved methodologies towards correlating the structure of GBs and interphase boundaries (IBs) with their local atomic-scale composition (in polycrystalline materials) is Correlative Microscopy [30], [31]. Particularly, in the context of metallic materials, this methodology has been extensively used to study both the structure and composition of GBs and also to address the five macroscopic and three microscopic degrees of freedom (DOFs) (of GBs and IBs). However, in the context of AZ ceramics, there is hardly any correlative microstructural investigation till date. This may be attributed to the complexity associated with crystal structures and sample preparation. Moreover, as mentioned in **section 1**, laser AM-based techniques are based on layer-by-layer deposition of materials. This adds up to the complexity (in terms of obtaining GBE microstructures) by inducing large-scale microstructural

heterogeneities (with high defect concentration) [32-41], resulting in non-equilibrium microstructures. Hence, obtaining GBE microstructures in AM-based AZ ceramics provides an immense potential towards future investigations in field of AZ ceramics.

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