Microstructure refinement–homogenization and flexural strength improvement of Al₂O₃ ceramics fabricated by DLP-stereolithography integrated with chemical precipitation coating process

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Abstract: In this study, the chemical precipitation coating (CP) process was creatively integrated with DLP-stereolithography based 3D printing for refining and homogenizing the microstructure of 3D printed Al₂O₃ ceramic. Based on this novel approach, Al₂O₃ powder was coated with a homogeneous layer of amorphous Y₂O₃, with the coated Al₂O₃ powder found to make the microstructure of 3D printed Al₂O₃ ceramic more uniform and refined, as compared with the conventional mechanical mixing (MM) of Al₂O₃ and Y₂O₃ powders. The grain size of Al₂O₃ in Sample CP is 64.44% and 51.43% lower than those in the monolithic Al₂O₃ ceramic and Sample MM, respectively. Sample CP has the highest flexural strength of 455.37±32.17 MPa, which is 14.85% and 25.45% higher than those of Samples MM and AL, respectively; also Sample CP has the highest Weibull modulus of 16.88 among the three kinds of samples. Moreover, the fine grained Sample CP has a close thermal conductivity to the coarse grained Sample MM because of the changes in morphology of Y₃Al₅O₁₂ phase from semi-connected (Sample MM) to isolated (Sample CP). Finally, specially designed fin-type Al₂O₃ ceramic heat sinks were successfully fabricated via the novel integrated process, which has been proven to be an effective method for fabricating complex-shaped Al₂O₃ ceramic components with enhanced flexural strength and reliability.

Keywords: Al₂O₃ ceramic; stereolithography; flexural strength; reliability; thermal conductivity; microstructure

1 Introduction

Alumina (Al₂O₃) ceramic has been widely used in thermal management applications, such as substrates, heat sinks, and packaging materials for integrated

circuits and LEDs, due to its high mechanical strength, excellent electrical insulation, high thermal conductivity as well as acceptable cost [1–3]. The power density in modern electronic systems is now increasing at an unprecedented speed, and thus it is urgent to fabricate the fin-type Al₂O₃ ceramic heat sinks and micro-channel substrates with complex shapes, in order to dissipate heat quickly and protect valuable electronic components effectively. However, the high hardness

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and low toughness of structural ceramics make it difficult to shape and machine complex-shaped ceramic parts [4]. The conventional ceramic-shaping methods, such as dry pressing, isostatic pressing, gel casting, injection molding, etc. [5–7], require the use of molds, leading to increased manufacturing cost [8], and cannot be used to fabricate Al_2O_3 ceramic parts with highly complex geometries and interconnected channels [9], thereby limiting the wide application of Al_2O_3 components. So there has been strong demand to develop a more effective approach to sidestep the aforementioned limitations and fabricate complex-shaped Al_2O_3 ceramic parts.

Additive manufacturing, also referred to as 3D printing and rapid prototyping, is a series of advanced manufacturing technologies to construct complicated prototypes from 3D CAD models [10]. The introduction of 3D printing technologies into the fabrication of advanced ceramics can address the issues such as mold dependence and difficulties in shaping complex-shaped ceramic parts [8]. Due to the excellent technical advantages of stereolithography such as high dimensional accuracy and good surface finish, efforts on applying stereolithography to ceramic fabrication have been made [11]. The stereolithography based additive manufacturing, including stereolithography apparatus (SLA) and digital light processing (DLP), is based on the controlled light-induced layer-by-layer photopolymerization of a liquid photosensitive resin mixed with ceramic powder [8,12]. For the DLP-stereolithography, a digital micromirror device (DMD) is used to dynamically project the mask image of sliced layers onto the surface of photosensitive resin, and the shape of a whole thin layer can be solidified simultaneously; hence it has a higher building speed compared with the SLA-stereolithography and is advantageous for the fabrication of ceramic components with a very good feature resolution [13,14].

To date, numerous studies have confirmed the viability and effectiveness of the stereolithography to fabricate Al_2O_3 ceramic parts. For instance, the Al_2O_3 ceramic windowpanes with fully dense microstructure were fabricated by Griffith and Halloran [15], who were the first to adopt stereolithography for ceramic freeform fabrication in 1996. The drying and debinding processes of SLA-stereolithography were optimized by Zhou *et al.* [16], and a defect-free Al_2O_3 cutting tool with a relative density of 99.3% was obtained. The DLP-stereolithography was used to prepare Al_2O_3 ceramic

parts with good surface quality and a relative density of 93.2%, which demonstrated the effectiveness of DLP-stereolithography [11]. Works by Santoliquido *et al.* [17] and Shuai *et al.* [18] have detailed the use of DLP-stereolithography for the fabrication of Al_2O_3 architectures with fine and complex lattice structures. However, it is worth noting that the presence of photosensitive resin in printed green parts and its removal during the debinding process can result in a large porosity in the debound parts [19], which can lengthen the pathways for substance migration at high temperatures and be an obstacle for the sintering densification [20,21]. For this reason, an increased sintering temperature is required for the debound samples to form dense ceramic parts. The exorbitant high sintering temperature (1550–1750 °C) of stereolithography-based 3D printed Al_2O_3 ceramics [15,16,22–27] is expected to cause the abnormal grain growth and heterogeneous microstructure of Al_2O_3 ceramics. For instance, as presented in Refs. [20,24], the grain sizes of the Al_2O_3 ceramics fabricated by stereolithography were 24 and 12 times larger than the average particle sizes of the feedstock Al_2O_3 powders, respectively; in addition, a satisfactory microstructure uniformity of the Al_2O_3 ceramics prepared by SLA-stereolithography can hardly be obtained even if the Al_2O_3 samples were sintered at a relative low temperature (1550 °C) [27]. The abnormal grain growth and non-uniform microstructure can result in lower flexural strength and reliability of ceramics [28,29], which will further shorten service lifetime of ceramic substrates and heat sinks [30] and thus restrict their application in electronics. Therefore, it is urgent to refine and homogenize the microstructure of Al_2O_3 ceramics prepared by stereolithography-based 3D printing, in order to improve the flexural strength and reliability of Al_2O_3 ceramics.

Yttria (Y_2O_3) is commonly used as the sintering additive in preparation of Al_2O_3 ceramics [31–36]. The addition of Y_2O_3 , which strongly segregates or precipitates in the form of yttrium aluminates at Al_2O_3 grain boundaries due to its limited solubility (< 10 ppm) in Al_2O_3 crystal lattice [31,32], is known to inhibit grain growth of Al_2O_3 and represent an effective way for microstructure refinement, through changing the activation energy of grain boundary diffusion and motion [33,34]. As a result, the mechanical strength of Al_2O_3 or Al_2O_3 -based ceramic can be noticeably enhanced [35,36]. This enhancement can be significantly improved

by the uniformly dispersed Y_2O_3 or yttrium aluminate second phases in Al_2O_3 matrix [37]. However, Y_2O_3 is conventionally doped by the mechanical mixing (MM) process [35], and it is difficult to obtain a homogeneous microstructure, especially a uniform distribution of yttrium aluminates [38]. In order to obtain the evenly distributed Y_2O_3 in Al_2O_3 matrix, the co-precipitation method was used to prepare Al_2O_3 –yttrium aluminum garnet (YAG) composite ceramics [39,40]; but great amounts of alumina and yttria precursors (nitrates) were used, and thus the yield of the composite powder is low and its preparation cost is high. Compared with the conventional MM process, the chemical precipitation coating (CP) process, which has been employed in the preparation of YAG, SiC, and translucent Al_2O_3 ceramics [41–43], shows more homogeneous mixing performance and can improve the microscopic uniformity of ceramics. Besides, only a small amount of Y-precursor was used in the CP process, which can make the yield of the composite powder to be higher than that prepared via the co-precipitation method. It is a remarkable fact that the dispersive performance of additives (Y_2O_3) in Al_2O_3 matrix is expected to lead to the morphology change of second phases (yttrium aluminates), and the thermal conductivity of ceramics can be highly affected by the grain growth and the morphology of second phases, as commonly seen in AlN ceramic [44,45]. Nevertheless, this CP process has never been used for the preparation of stereolithography-based 3D printed Al_2O_3 ceramics. To the best of our knowledge, few researches have evaluated the thermal conductivity of stereolithography-based 3D printed Al_2O_3 ceramics, which is significantly essential for thermal management applications of Al_2O_3 ceramics. So far, little attention has been devoted to the effect of the way of introducing additives on the thermal conductivity of Al_2O_3 ceramics.

In this study, a CP process was used to fabricate an amorphous Y_2O_3 coating on the surface of Al_2O_3 powder, in order to improve the dispersive homogeneity of Y_2O_3 in Al_2O_3 matrix. The coating effectiveness and integrity were examined in detail by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) measurements. In addition, to demonstrate the advantage of the CP process, the phase transformation, microstructure, and thermal and mechanical property comparisons were made between the CP and conventional MM processed Al_2O_3 samples. The current study shows that, as compared with the

conventional MM process, the CP process can effectively refine and homogenize the microstructure of the DLP-stereolithography based 3D printed Y_2O_3 – Al_2O_3 ceramics, thus enhancing their flexural strength and reliability without decreasing thermal conductivity.

2 Experimental

2.1 Preparation of Y_2O_3 – Al_2O_3 composite powders

Commercially available α - Al_2O_3 powder with an average particle size (D_{50}) of 200 nm (TM-DAR, Taimei Chemicals Co., Ltd., Japan) was used as starting material. Y_2O_3 additives were used to refine microstructure and enhance mechanical strength of Al_2O_3 ceramics [33,35,38]. Two batches of Y_2O_3 – Al_2O_3 composite powders were prepared by the CP and MM process, and both of them had the same content of Y_2O_3 . For the conventional MM route, 95 wt% of Al_2O_3 and 5 wt% of Y_2O_3 ($D_{50} = 500$ nm, Shanghai Macklin Biochemical Co., Ltd., China) powders were ball milled in ethanol for 6 h employing a planetary ball mill (QM-QX4, Nanjing NanDa Instrument Plant, China), with the milling speed set to 250 r/min. The MM system consisted of powders/ethanol/zirconia ball at a weight ratio of 1:3:2 in a Teflon container. After ball-milling, the powders were dried in a rotary evaporator and granulated through a 150 μ m sieve. For the CP route, the non-aqueous precursor and precipitant solutions were used for avoiding hard agglomeration of Y_2O_3 -coated Al_2O_3 composite powder during drying, and the whole CP process is shown in Fig. 1. The particle agglomeration is controlled by the network of self-equilibrated forces resulted by the tensile action of capillary bonds bridging the gaps between the constituting particles, and the capillary force (F_{cap}) calculated by integrating the Laplace–Young equation is proportional to the surface tension of liquid medium [46]; the surface tension of ethanol (22.3 mN/m) is much less than that of water (72.8 mN/m) [47], and thus the ethanol was used as the solvent for the precursor and precipitant in this work; moreover, this similar treatment approach can also be found in Refs. [48,49] for decreasing agglomeration degree of synthesized powders. Firstly, $Y(NO_3)_3 \cdot 6H_2O$ (99.99% purity, Shanghai Aladdin Bio-Chem Technology Co., Ltd., China) was dissolved in ethanol to prepare the precursor solution, where the concentration of Y^{3+} was accurately controlled to

Fig. 1 Schematic illustration of the chemical precipitation coating process.

0.05 mol/L. Secondly, the Al_2O_3 powder was slowly added in the prepared precursor solution, and mixed with 1.5 wt% of dispersants of polyethylene glycol (PEG 2000). The weight ratio of the Y_2O_3 (calculated based on the transformation of $\text{Y}(\text{NO}_3)_3$ to Y_2O_3) to Al_2O_3 was set to 5:95. Thirdly, the above suspension was dispersed in a bath under ultrasound for 60 min, and then vigorously stirred for 120 min to prevent the sedimentation of ceramic particles. Fourthly, the mixed solution (pH = 12.66) of ethylenediamine (EDA) and ethanol with the weight ratio of 1:2 was prepared as the precipitant solution, and was slowly dropped into the ceramic suspension under strong mechanical stirring to tailor the pH value of the suspension in the range of 9.3–9.5. During the dripping process of the precipitant solution, the precipitations of yttrium-amine complex were formed and simultaneously deposited on the Al_2O_3 powder surface, which can act as the preferential heterogeneous nucleation sites [50]. After the above precipitation coating process, the resultant suspension was continuously stirred for 120 min. Then, the as-prepared composite ceramic powders (Al_2O_3 coated with the yttrium-amine complexes) were washed with ethanol and air-dried at 60 °C for 10 h. Finally, the dried products were calcined at 450 °C for 2 h to decompose yttrium-amine complexes into Y_2O_3 , and the calcined powder was granulated through a 150 μm sieve.

2.2 Preparation of UV-curable ceramic suspension

Before the preparation of UV-curable ceramic suspensions, the pure Al_2O_3 , MM, and CP processed Y_2O_3 – Al_2O_3 powders were separately surface modified with oleic acid (OA, Shanghai Aladdin Bio-Chem Technology Co., Ltd., China). Firstly, the ceramic powder was dispersed in ethanol, and 1.0 wt% of OA

with respect to the mass of ceramic powder was used as a surface modifier. The suspension was ball-milled for 2 h employing a planetary ball mill to facilitate physical adsorption of OA on powder surface. Then the suspension was dried at 50 °C for 12 h to remove ethanol and the remaining powder was thermally treated at 80 °C for 6 h to promote chemical adsorption [27,51]. Finally, the treated ceramic powder was de-agglomerated by passing them through a 150 μm sieve.

The UV-curable ceramic suspension was prepared by adding 79 wt% of above modified ceramic powder into the photosensitive resin, which was fabricated by mixing ethoxylated pentaerythritol tetraacrylate (PPTA, Royal DSM, the Netherlands), 1,6-hexanediol diacrylate (HDDA, Royal DSM, the Netherlands), di-functional aliphatic polyurethane acrylate (U600, Royal DSM, the Netherlands), octanol (Shanghai Aladdin Bio-Chem Technology Co., Ltd., China), and polyethylene glycol (Shanghai Aladdin Bio-Chem Technology Co., Ltd., China) with commercial dispersant (BYK9077, BYK Additives & Instruments, Germany). The above ceramic suspension was ball-milled for 6 h at 350 r/min using a planetary ball mill. After the ball-milling process, the photoinitiator (Irgacure819, BASF, Germany), with an effective absorption peak range well matched with the wavelength of the UV light used for DLP processing in this work, was mixed into the homogeneous suspension to produce a UV-curable ceramic suspension.

2.3 DLP-stereolithography based 3D printing

3D printing was performed at room temperature by using a DLP-stereolithography based apparatus. The UV light source of the DLP printer is below the vat and has a wavelength of 405 nm with a light intensity of 10.5 mW/cm². A 3D model was first created using the

UG software and output to a STL file, and then the STL file was imported into the stereolithography machine and sliced into 2D images. The Al_2O_3 green bodies were obtained by DLP-stereolithography using the above-mentioned ceramic suspensions. During the DLP-stereolithography process, the UV light selectively cured the photosensitive resin in ceramic suspension based on the 2D images and created cross-linked polymer networks to bond ceramic particles together. The photopolymerisation process was generally proceeded in a layer-by-layer pattern. The layer thickness was set to 20 μm , and the cure depth was $83.00 \pm 2.51 \mu\text{m}$ by adjusting the exposure time to 3.0 s, giving a high vertical resolution and an adequate integration between layers. Once a single layer was cured, the vat was tilted down to detach the cured layer and the building platform was lifted to allow recoating the suspension layer at the bottom of the vat. Then the new layer was cured subsequently in exactly the same fashion. These steps were repeated until the whole green body was eventually fabricated.

2.4 Debinding and sintering

For printed Al_2O_3 green bodies, the post-processing steps including debinding and sintering were carried out to obtain Al_2O_3 ceramic parts. A two-step debinding process was adopted in this work, in which green bodies were firstly debound under vacuum to decelerate pyrolysis rate of resins and then debound in air to completely remove the residual carbon [16]. The debound samples were subsequently sintered in a muffle furnace (HTK 16/18, Thermconcept, Germany) at 10 $^\circ\text{C}/\text{min}$ from room temperature to 800 $^\circ\text{C}$, then at 5 $^\circ\text{C}/\text{min}$ up to 1650 $^\circ\text{C}$, with a final plateau of 2 h. Finally the furnace was cooled at 5 $^\circ\text{C}/\text{min}$ to 800 $^\circ\text{C}$, and then naturally cooled to room temperature. The sintered specimens were machined and polished to evaluate their thermal and mechanical properties. The 3D printed Al_2O_3 ceramics fabricated using the MM and CP processed (i.e., ball-milled and coated) $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ composite powders are referred to as Sample MM and Sample CP, respectively. In addition, the monolithic Al_2O_3 reference samples prepared by pure Al_2O_3 powder are referred to as Sample AL.

2.5 Characterization

The microstructure and element analysis of the coated Al_2O_3 powder were investigated by a transmission

electron microscope (TEM, Talos F200S, Thermo Fisher Scientific Inc., USA) coupled with an energy dispersive spectroscopy (EDS). The TEM sample (coated Al_2O_3 powder) was dispersed in ethanol with ultrasonic treatment and then dropped onto a holey-carbon-coated copper grid. An X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher Scientific Inc., USA) was used to study the surface chemistry of the MM and CP processed $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ powders. The contents of Y and Al in the MM and CP processed $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ powders were determined by an X-ray fluorescence spectrometer (XRF-1800, Shimadzu Co., Ltd., Japan), in order to identify whether both composite powders have the same chemical compositions.

The viscosities of the ceramic suspensions were tested using a rotational rheometer (MCR 301, Anton Paar, Austria). To study the decomposition profile of the 3D printed green body, TG–DSC analyses were conducted by a simultaneous thermal analyzer (STA449F3, Netzsch, Germany) at a heating rate of 10 $^\circ\text{C}/\text{min}$ over the temperature range from room temperature to 600 $^\circ\text{C}$. The relative density of the sintered Al_2O_3 ceramic samples was measured by Archimedes method using an analytical balance with an accuracy of 0.0001 g. The bending strength of samples with a size of 1.5 mm $\times$ 2.0 mm $\times$ 25 mm was evaluated by three-point bending tests [52]. Finish grinding of four long faces was performed using a 600 grit diamond wheel, and the four long edges were rounded with a radius of 0.15 mm. The two faces with the size of 2.0 mm $\times$ 25 mm were gently polished to 1 μm by applying diamond paste. The loading experiments were performed using a universal mechanical testing machine (Inspekt Table Blue 05, Hegewald & Peschke, Germany), with the crosshead speed set to 0.5 mm/min and the supporting span of 20 mm. A laser thermal conductivity instrument (LFA 447, Netzsch Instruments Co., Ltd., Germany) was used to determine the thermal diffusivity (α) of the sintered Al_2O_3 samples with a size of 10 mm $\times$ 10 mm $\times$ 2 mm at room temperature. The blocks were spray-deposited with a thin layer of colloidal carbon to enhance the absorption of the laser pulse. The value of the thermal conductivity (λ) for samples was calculated by

$$\lambda = \alpha \cdot \rho \cdot C \quad (1)$$

where ρ is the density and C is the specific heat capacity of the prepared samples [53]. In the present work, the thermal conductivity of Sample AL was

determined by taking the specific heat capacity value of the high purity Al_2O_3 ceramics ($0.755 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ at room temperature) [54]. Y_2O_3 doping can result in the formation of a second phase (yttrium aluminum garnet, YAG) in Al_2O_3 ceramic [38], and the specific heat capacities of the Y_2O_3 – Al_2O_3 system (Samples MM and CP) were calculated by using the Neumann–Kopp rule [55]:

$$C = \sum_{i=1}^n \omega_i C_i \quad (2)$$

where ω_i is the mass fraction of each phase which can be determined by XRD analysis, and C_i is the corresponding specific heat capacity for the constituents (Al_2O_3 and YAG). A documented value of $0.60 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ is used for the specific heat capacity of YAG [56,57].

The phase composition of the sintered samples was determined by X-ray diffraction (XRD, D8 Advance, Bruker Corporation, Germany). A scanning range of 2θ from 10° to 80° was applied. The mass percentage of the phases in the sintered sample was also semi-quantitatively estimated by analyzing the reference intensity ratio (RIR) value taken from the X-ray pattern [58]. The weight fraction of phase 1 in the sintered ceramics can be calculated by

$$X_1 = \frac{I_1}{\text{RIR}_1} \cdot \frac{1}{\sum_{i=1}^{n_{\text{phase}}} (I_i / \text{RIR}_i)} \quad (3)$$

where X_1 is the weight fraction of phase 1, I_i is the integrated intensity of the highest peak of the i -th phase in the analyzed ceramic, RIR_i is the reference intensity ratio of the i -th phase (taken from the powder diffraction database), and n_{phase} is the number of phases in the prepared ceramics.

To identify the fracture surface features and global distribution profile of Y element throughout the 3D printed samples, the images of fracture surface and the corresponding X-ray mapping analysis of Y element were studied by a scanning electron microscope (SEM, LYRA 3 XMU, Tescan, Czech) coupled with an energy-dispersive spectroscope (Inca X-Max50, Oxford Instruments, UK). Moreover, the prepared samples were polished with diamond paste and then thermally etched at 1550°C for 30 min. The microstructures of the polished and fracture surface of the sintered ceramics were characterized by the SEM. The average grain size was determined by the Nanomeasure

software, and at least 600 grain sizes were statistically analyzed for each sample. The Christiansen uniformity coefficient (CU) was used to quantitatively determine the distribution uniformity of the grain size in the sintered ceramics, which can be calculated using the following equations [59]:

$$CU = 1 - \sum_{i=1}^{n_{\text{grain}}} \frac{|x_i - \bar{x}|}{n_{\text{grain}} \bar{x}} \quad (4)$$

where $\bar{x}$ is the average grain size, which can be

calculated by $\bar{x} = \frac{1}{n_{\text{grain}}} \sum_{i=1}^{n_{\text{grain}}} x_i$, x_i is the size of the i -th

grain, n_{grain} is the total number of grains, and the larger CU value indicates the more uniform microstructure of sintered ceramic.

3 Results and discussion

3.1 Characterization of CP processed Al_2O_3 powder

The weight percent of Y/(Y+Al) of the MM and CP processed Y_2O_3 – Al_2O_3 composite powders were measured to be 7.12 and 7.40 wt%, respectively, by an XRF spectrometer, indicating that the composite powders prepared by MM and CP processes have nearly the same Y_2O_3 content. The microstructure of the CP processed composite powder was analyzed. TEM results of the CP processed Y_2O_3 – Al_2O_3 powder are presented in Fig. 2. The morphology of the CP processed Y_2O_3 – Al_2O_3 powder is shown in Fig. 2(a), which displays that an evident shell layer was closely, uniformly attached to the Al_2O_3 particle surface. From a high resolution image as shown in Fig. 2(b), the CP processed Y_2O_3 – Al_2O_3 powder has a typical core–shell structure with a relatively smooth surface layer, which is about $\sim 2.31 \text{ nm}$ thick. According to a further fast Fourier transform (FFT) pattern analysis, the dispersive diffraction halo in Fig. 2(c) shows that the shell is amorphous, and Fig. 2(d) presents the lattice fringes of Al_2O_3 (2–13) and (–114) planes with interplanar spacing of about 0.201 and 0.259 nm, respectively, indicating that the core is Al_2O_3 crystalline. This result verifies that a uniform amorphous deposition was formed on the surface of the Al_2O_3 particle. To check the element compositions of the amorphous layer, the EDS analyses were conducted on both amorphous layer (shell) and the bulk of the Al_2O_3 particle (core), shown in Figs. 2(e) and 2(f), respectively. The major

elements in the shell are Al, Y, and O with minor C and Cu. Obvious Al, O, C, and Cu peaks can be detected in the core, meanwhile detecting weak Y peak at about 1.93 keV. The C and Cu elements come from the holey-carbon-coated copper grid used in the TEM sample preparation. The spectral peak for Y in the shell is much higher than that in the core, suggesting the shell contains more Y than in the core. This EDS result indicates that the chemical composition of the shell is Y–O compound. The TEM and EDS results suggest that the Al_2O_3 particle is encapsulated by the amorphous

layer of Y–O compound.

The XRD patterns for the MM and CP processed Y_2O_3 – Al_2O_3 composite powders are shown in Fig. 3. The diffraction peaks of the MM processed composite powder can be identified as phases of α - Al_2O_3 and cubic Y_2O_3 , indicating that the MM processed powder is a mixture of α - Al_2O_3 and Y_2O_3 powders. However, the XRD pattern of the CP processed composite powder only shows sharp diffraction peaks assigned to α - Al_2O_3 , and a very broad peak of Y_2O_3 is present at 29.15° (which is the diffraction angle of the strongest

Fig. 2 (a) Representative TEM image of the CP processed Y_2O_3 – Al_2O_3 ceramic powder, (b) high magnification TEM image representing the surface of the CP processed powder, (c, d) the corresponding fast Fourier transform patterns of the shell and core, and (e, f) respective EDS spectra recorded from the shell and core.

Fig. 3 XRD patterns for the MM and CP processed Y_2O_3 – Al_2O_3 composite powders. The right image is the local enlargement of left image marked by green box.

diffraction peak of Y_2O_3), implying that the Y_2O_3 in the CP processed composite powder is amorphous. This result is consistent with the TEM observation and corresponding FFT pattern of the amorphous shell of the coated Al_2O_3 powder (Figs. 2(b) and 2(c)).

To examine the elements present and their chemical states on the ceramic powder surface, the XPS measurements of the MM and CP processed $Y_2O_3-Al_2O_3$ composite powders were carried out. The XPS survey scan and narrow scans of Y_{3d} are shown in Fig. 4, and the binding energies of the obtained peaks are referenced to the C_{1s} signal for C–H. Both the spectra of the MM and CP processed $Y_2O_3-Al_2O_3$ powders reveal the peaks for O_{1s} , Y_{3d} , and Al_{2p} , which indicate the presence of O, Y and Al, as shown in Fig. 4(a). Figures 4(b) and 4(c) show the narrow scan for Y_{3d} core level, and the raw data was fitted using the Thermo Advantage V5.52 software. The high-resolution Y_{3d} spectra (Figs. 4(b) and 4(c)) can be decomposed into couple of doublets related to the spin-orbit splitting of $Y_{3d} 5/2$ and $Y_{3d} 3/2$. The $Y_{3d} 5/2$ peaks locate at 157.96 and 157.55 eV for the CP and MM processed $Y_2O_3-Al_2O_3$ powders, respectively. These $Y_{3d} 5/2$ binding energies are in accordance with the documented values (158.1 and 157.4 eV) for $Y_{3d} 5/2$ of Y_2O_3 [60,61], so the $Y_{3d} 5/2$ in the CP processed $Y_2O_3-Al_2O_3$ powders can be assigned to Y^{3+} in Y_2O_3 . The quantitative calculations from the narrow scan results of Al_{2p} , O_{1s} , C_{1s} and Y_{3d} were performed to determine the chemical compositions of the MM and CP processed $Y_2O_3-Al_2O_3$ powders, as shown in Table 1. The Y/Al atomic ratio of the CP processed $Y_2O_3-Al_2O_3$ powder is calculated to be 0.2081, which is much greater than the Y/Al atomic ratio of the MM processed $Y_2O_3-Al_2O_3$ powder (0.0023) and stoichio-

metric mixture (95 wt% Al_2O_3 + 5 wt% Y_2O_3) (0.0238). The much higher value of the Y/Al atomic ratio in the CP processed $Y_2O_3-Al_2O_3$ powder can evidence that the surface of the CP processed Al_2O_3 powder is enriched with Y, i.e., Y is localized in the surface layer of the CP processed Al_2O_3 powder [62]. It can be concluded from the TEM, XRD, and XPS results that the surface of the Al_2O_3 ceramic powder is covered with an amorphous Y_2O_3 layer prepared by the CP process.

3.2 Characterization of the ceramic suspensions and printed green bodies

It is important to maintain a good flowability and a low viscosity for the ceramic suspension, because the photocurable suspension should be spread and recoated by the blade [63]. To understand the effect of Y_2O_3 addition on the rheological property of Al_2O_3 suspension, the comparative viscosities of the 20 vol% Al_2O_3 and $Y_2O_3-Al_2O_3$ ceramic suspensions were evaluated, as shown in Fig. 5. All the ceramic suspensions show shear thinning behavior, where their viscosities dropped with increasing shear rate and reached a steady state finally. The difference among the viscosities of the three suspensions is small at low shear rate (below 20 s^{-1}), e.g., the viscosities are $2.07\text{ Pa}\cdot\text{s}$ (Al_2O_3), $2.48\text{ Pa}\cdot\text{s}$ (MM processed $Y_2O_3-Al_2O_3$), and $1.97\text{ Pa}\cdot\text{s}$ (CP processed $Y_2O_3-Al_2O_3$) at 13 s^{-1} , respectively, and the small difference stems from the test error. As the shear rate increasing, the viscosities of the three suspensions are almost the same. This result indicates that the impact of the addition of Y_2O_3 on the rheological property of Al_2O_3 suspension can be neglected, whether Y_2O_3 is introduced via the MM or CP process.

Fig. 4 (a) XPS survey scan of the MM and CP processed $Y_2O_3-Al_2O_3$ powders; (b, c) respective XPS core level spectra of Y_{3d} in the MM and CP processed $Y_2O_3-Al_2O_3$ powders.

Table 1 Chemical compositions (at%) of the MM and CP processed Y_2O_3 – Al_2O_3 powders

Sample	C _{1s}	O _{1s}	Al _{2p}	Y _{3d}
MM processed Y_2O_3 – Al_2O_3 powder	24.88	44.76	30.29	0.07
CP processed Y_2O_3 – Al_2O_3 powder	36.62	39.52	19.75	4.11

Fig. 5 Viscosities of 20 vol% Al_2O_3 and Y_2O_3 – Al_2O_3 ceramic suspensions.

To get a dense ceramic part, the organic components in the printed green body must be removed by a debinding step. A two-step debinding process, consisting of a vacuum debinding step followed by an air debinding step, was adopted in this work [16]. The lower solid loading of ceramic suspension implies the higher organic components in the printed green body, which can amplify the signal intensity of TG–DSC test and improve its accuracy to analyze the thermal decomposition of the green ceramic body. So the green compact manufactured by the Al_2O_3 suspension with low solid loading (69 wt%) was used for the TG–DSC test, and the test results are shown in Fig. 6. Due to the fact that the TG–DSC analysis cannot be conducted in vacuum, the N_2 was used to simulate the oxygen-free environment for determining the thermal degradation behavior of printed green body in vacuum debinding step, and the test result is shown in Fig. 6(a). It can be seen that the thermal degradation of the organic components in the green body takes place over a broad temperature range between 150 and 500 °C, accompanied by weight loss and endothermic reactions. This ensures a continuous formation of thermal degradation products without temporary accumulation which can affect the structural integrity of the parts [23,64]. However, there exists a domain where the degradation rate is increased at the temperature range of 300–425 °C, as can be seen from the peak of DTG

Fig. 6 (a) TG–DSC curves for the printed green body tested in N_2 and (b) the vacuum-debound body tested in air.

curve, manifesting the majority of photopolymer is degraded at this temperature regime. The DSC curve depicted in Fig. 6(a) features three endothermic peaks at 232, 373, and 415 °C, with the peak observed at 373 °C being the most prominent. Therefore, a slow heating rate (1 °C/min) was used in the whole vacuum debinding process and hold points were introduced at the onsets of the endothermic peaks.

Afterwards, the air debinding step was required to remove the residual carbon in the black vacuum-debound body, thus preventing the generation of cracks in the sintered body [16]. The TG–DSC result for the vacuum-debound body tested in air is shown in Fig. 6(b). Unlike the thermal degradation behavior of green body in the absence of oxygen, an exothermic peak at 396 °C and a domain where the decomposition rate is increased at the temperature range of 346–446 °C are present in Fig. 6(b), due to the oxidative decomposition of the residual carbon, and its weight loss and decomposition rate are much lower than those of the green body degraded in oxygen-free environment. In addition, the green Al_2O_3 bulk sample was manufactured by the ceramic suspension with the 79 wt% solid loading, and its weight losses in the vacuum and air debinding processes were measured to

be $21.32\% \pm 0.15\%$ and $2.12\% \pm 0.04\%$, respectively, indicating the weight loss in the second air debinding process is much lower than that in the first vacuum debinding process. This is conducive to avoiding formation of defects (such as cracking, delamination, blistering, and bloating) in the debound body. Thus, the heating rate of the air debinding was reduced in the domain, and a hold point was introduced at the onset of the decomposition peak at 346°C .

An assessment of the distribution of Y_2O_3 in the printed green bodies was conducted via the elemental mapping analyses using SEM and EDS, as shown in Fig. 7. A significant difference in Y_2O_3 dispersion is observed in the MM and CP processed green compacts. The MM processed compact has large Y-patches distributed heterogeneously. The size of these Y-patches varies from 0.72 to $3.84\ \mu\text{m}$, and the average value is about $1.92 \pm 0.86\ \mu\text{m}$, which is much higher than the average particle size ($500\ \text{nm}$) of Y_2O_3 powder, manifesting the apparent agglomeration of Y_2O_3 particles during the MM process. On the other hand, the CP processed compact shows no apparent aggregate patches, and Y_2O_3 is uniformly distributed in the Al_2O_3 matrix. This finding indicates that the CP process can lead to an obvious enhanced homogeneous distribution of the sintering additives (Y_2O_3) in Al_2O_3 matrix as compared with the conventional MM process. This change in Y_2O_3 distribution is expected to tailor the microstructure of Al_2O_3 ceramic and morphology of second phase, which are essential to the mechanical and thermal properties of Al_2O_3 ceramic.

3.3 Phase analysis and microstructure of sintered Al_2O_3 ceramics

The XRD patterns of the 3D printed Al_2O_3 ceramic samples are shown in Fig. 8, and the peak intensities are normalized relative to the Al_2O_3 (211). Diffraction peaks of $\alpha\text{-Al}_2\text{O}_3$, as the only phase for Sample AL, are exhibited in Fig. 8(a). The XRD patterns of Samples MM and CP show $\alpha\text{-Al}_2\text{O}_3$ and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) as the primary and minor phase, respectively. With the addition of Y_2O_3 into Al_2O_3 , the YAG phase is generated by a series of reactions as follows [65,66]:

Combining the above reaction equations, a simplified expression can be obtained.

Based on Eq. (8), 5 wt% of Y_2O_3 can react with 3.76 wt% Al_2O_3 to form $\text{Y}_3\text{Al}_5\text{O}_{12}$ in the 5 wt% Y_2O_3 –95 wt% Al_2O_3 system, and thus the theoretical mass percentages of $\text{Y}_3\text{Al}_5\text{O}_{12}$ and Al_2O_3 in the sintered ceramic are calculated to be 8.76 and 91.24 wt%, respectively. The content of each phase in the prepared ceramic samples was estimated by the RIR analysis from the X-ray diffraction data and the result is listed in Table 2. It can be seen that the contents of $\text{Y}_3\text{Al}_5\text{O}_{12}$ in Samples MM and CP are 8.16 and 8.74 wt%, respectively, which are basically coincident with the theoretical calculation value. This result indicates that the Y_2O_3 had been completely reacted with Al_2O_3 in

Fig. 7 SEM images of the printed green surfaces of Samples: (a) MM and (b) CP and corresponding EDS mapping results for Al, O, and Y.

Fig. 8 XRD patterns for the prepared Al_2O_3 ceramic samples.

Samples MM and CP by high temperature sintering. Moreover, the calculated mass fraction of each phase can be used to determine the specific heat capacities of Samples MM and CP via Eq. (2).

Table 2 Phase content in the prepared Al_2O_3 ceramics estimated by the semi-quantitative method

Sample	Semi-quantitative phase content in ceramics (wt%)		Semi-quantitative phase content in ceramics (vol%)	
	Al_2O_3	$\text{Y}_3\text{Al}_5\text{O}_{12}$	Al_2O_3	$\text{Y}_3\text{Al}_5\text{O}_{12}$
AL	100.00	0	100.00	0
MM	91.84	8.16	92.79	7.21
CP	91.26	8.74	92.27	7.73

Figure 9 demonstrates the SEM observation on the microstructures of different sintered Al_2O_3 samples and their grain size distributions. In Fig. 9, the white zone at grain boundary areas corresponds to the $\text{Y}_3\text{Al}_5\text{O}_{12}$ second phase (Fig. 8), while the gray and black sections are Al_2O_3 grains and pores, respectively. Compared with Sample AL (Fig. 9(a)), Samples MM and CP (Figs. 9(b) and 9(c)) possess higher porosities, corresponding to the relatively higher density of Samples AL as shown in Fig. 10. It suggests that the densification of

Fig. 9 Microstructures and grain size statistics of (a) Sample AL, (b) Sample MM, and (c) Sample CP.

Fig. 10 Physical properties of the 3D printed Al_2O_3 ceramics.

Al_2O_3 matrix was slightly inhibited by the addition of 5 wt% of Y_2O_3 . On one hand, the yttrium segregation at $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ interfaces can block the diffusion of ions along grain boundaries, leading to a reduced grain boundary diffusivity and hence a decreased densification rate [33,34,67]. On the other hand, once above the Y_2O_3 solubility-limit in Al_2O_3 , the extra Y_2O_3 would react with Al_2O_3 matrix and then form $\text{Y}_3\text{Al}_5\text{O}_{12}$ precipitations via the solid state reactions (Eqs. (5)–(7)). The $\text{Y}_3\text{Al}_5\text{O}_{12}$ precipitations, present at grain boundaries and multigrain junctions in Al_2O_3 matrix, can result in Zener pinning action on grain boundary mobility and finally retarding the densification of Al_2O_3 matrix [37,68].

As shown in Fig. 9(a), the 3D printed monolithic Al_2O_3 ceramic possesses an obvious coarsening and inhomogeneous microstructure (grain size up to $4.78\text{ }\mu\text{m}$, with a low CU of 0.50), and Sample AL contains a few of elongated alumina grains with the evidence of abnormal grain growth. The introduction of Y_2O_3 enables the Al_2O_3 matrix grain size to be refined, due to the pinning effect of $\text{Y}_3\text{Al}_5\text{O}_{12}$ precipitations [33,37]. The mean grain sizes of Samples MM and CP are smaller than that in Sample AL by 26.78% and 64.44%, respectively. Furthermore, the grain size of Sample CP ($\sim 1.70\text{ }\mu\text{m}$) is 51.43% smaller than that of Sample MM ($\sim 3.50\text{ }\mu\text{m}$). It suggests that the different introducing ways of Y_2O_3 would result in different growth trends for the Al_2O_3 grains. Compared to Sample MM, Sample CP shows much refined $\text{Y}_3\text{Al}_5\text{O}_{12}$ precipitations and an increased degree of $\text{Y}_3\text{Al}_5\text{O}_{12}$ distribution range at grain boundary areas in the matrix. This precipitation feature displayed in Sample CP can lead to more areas of Zener pinning on grain boundary migration, and hence enable a much refined and homogenous Al_2O_3 matrix microstructure. In addition, in both Ref. [24] and

the present work, the same Al_2O_3 powder was used; although the sintering temperature ($1600\text{ }^\circ\text{C}$) in Ref. [24] is lower than that ($1650\text{ }^\circ\text{C}$) in the present work, the grain size of Sample CP is much less than the value reported in Ref. [24] ($2.6\text{ }\mu\text{m}$). The microstructure refinement is often expected to fabricate Al_2O_3 ceramic with higher strength according to the Hall–Petch relationship [69]. Furthermore, Sample CP has the narrowest grain size distribution, with a CU of 0.70, which is 12.90% and 40.00% higher than those of Samples MM and AL, respectively. This finding demonstrates that the CP process can make the microstructure of Al_2O_3 ceramic more uniform, which can play a crucial role in improving the reliability of Al_2O_3 ceramics.

3.4 Properties of 3D printed Al_2O_3 ceramics

The physical properties of the 3D printed Al_2O_3 ceramics are shown in Fig. 10. The relative density of pure Al_2O_3 ceramic (Sample AL) is higher than those of $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ system (Samples MM and CP), demonstrating that the addition of 5 wt% of Y_2O_3 is detrimental for the densification of Al_2O_3 ceramic. In addition, Sample CP has a higher relative density than Sample MM, which is consistent with the denser microstructure of Sample CP (Fig. 9(c)) compared to that of Sample MM (Fig. 9(b)), illustrating that the CP process can improve the relative density of the $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ system compared with the conventional MM process.

As displayed in Fig. 10, Sample AL has the lowest flexural strength, which is 8.45% and 20.29% lower than those of Samples MM and CP, respectively, i.e., the addition of Y_2O_3 is favorable to the improvement of flexural strength of the 3D printed Al_2O_3 ceramic. The improved flexural strength of the $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ system is resulted from the fine grain strengthening and dispersion strengthening of the $\text{Y}_3\text{Al}_5\text{O}_{12}$ particles [70,71]. The flexural strength of Sample CP is 14.85% higher than that of Sample MM, owing to the finer Al_2O_3 grain and more homogeneous microstructure of Sample CP (Fig. 9(c)); also the relative density improvement can lead to an increase in flexural strength of Sample CP, according to the empirical suggestion for the strength of ceramics [1]. Fracture surface SEM micrographs of the 3D printed ceramic samples are shown in Fig. 11. Fractures predominantly occurred in an intergranular mode for Samples AL and MM (Figs. 11(a) and 11(b)). On the other hand, a large

Fig. 11 SEM micrographs of the fracture surfaces of (a) Sample AL, (b) Sample MM, and (c) Sample CP. The transgranular fractures are marked with yellow circles.

proportion of Al_2O_3 grains fractured transgranularly in Sample CP (Fig. 11(c)). This indicates that the Al_2O_3 grain boundaries in Sample CP should be much stronger than those in Samples AL and MM, leading to the increased flexural strength for Sample CP.

Furthermore, reliability analysis was conducted by estimating the Weibull modulus of the flexural strength distribution using at least 16 samples [72]. The two-parameter Weibull distribution was calculated by the equation:

$$\ln \ln \left(\frac{1}{1 - P_f} \right) = m \ln \sigma_n - m \ln \sigma_0 \quad (9)$$

where $P_f = (n - 0.5)/N$ is an estimator of the fracture probability of the n -th ranked sample, n is the rank of the bending strength data, N is the total number of samples tested ($N = 16$ in the present work), m is the Weibull modulus, σ_n is the measured bending strength, and σ_0 is the Weibull material scale parameter [72]. A higher m value means a better uniformity of flexural strength and a higher reliability of ceramic. The flexural strength distribution of Samples AL, MM, and CP is shown in Fig. 12. The Weibull modulus for Sample MM is 35.33% lower than that for Sample AL, illustrating that the introduction of Y_2O_3 into Al_2O_3 via the conventional MM process can decrease the reliability of Al_2O_3 ceramic. The agglomeration of $\text{Y}_3\text{Al}_5\text{O}_{12}$ second (Fig. 9(b)) can make the homogeneity of Sample MM deterioration, thus leading the reduction of Weibull modulus. Compared to the Weibull modulus for Sample MM, a very drastic increase from 9.59 to 16.88 in the Weibull modulus for Sample CP was obtained, indicating a much higher reliability and repeatability. These above findings illustrate that the CP process is beneficial to simultaneously enhance the flexural strength and reliability of the 3D printed Al_2O_3 ceramic.

Fig. 12 Weibull plots for the flexural strength of Samples AL, MM, and CP.

It can be seen from Fig. 10 that the thermal conductivity of pure Al_2O_3 ceramic (Sample AL) is 14.54% and 15.37% higher than those of Samples MM and CP (Y_2O_3 – Al_2O_3 system), respectively. The addition of 5 wt% of Y_2O_3 causes a fall in thermal conductivity compared with that of pure Al_2O_3 and this is accompanied by the decreased relative density and formation of the second phase ($\text{Y}_3\text{Al}_5\text{O}_{12}$). The pores and second phases can enhance phonon scattering and decrease the effective conductive mean free path, therefore reducing the thermal conductivity according to the kinetic theory of phonons in solids [73,74]. Based on the Maxwell model, the thermal conductivity of ceramic sample with isolated pores dispersed in a ceramic matrix is written as [75]

$$\lambda = \lambda_0 \cdot \frac{2(1 - \phi)}{2 + \phi} \quad (10)$$

where λ is the apparent thermal conductivity of ceramic with pores, ϕ is the porosity of ceramic and $\phi = 1 - \text{RD}\%$ (relative density), and λ_0 is the thermal conductivity of completely dense ceramic without pore ($\phi = 0$). By substituting the measured thermal

conductivity and relative density of Sample AL into Eq. (10), the thermal conductivity of the dense Al_2O_3 ceramic is calculated to be $34.32 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is in accordance with the documental values ($33\pm 2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), for pure dense Al_2O_3 at ambient temperature [54]. From the mathematical analysis by Eq. (10), the increase of porosity can result in a drop in thermal conductivity. Thus the $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ system with lower relative density has a thermal conductivity inferior to the denser pure Al_2O_3 ceramic.

The component and structure of composite material has a significant effect on the thermal conductivity [76]. For $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ composite system (Al_2O_3 ceramic with a small amount of $\text{Y}_3\text{Al}_5\text{O}_{12}$ second phase), the Maxwell–Eucken (ME) model can be used to predict the thermal conductivity via the following equation [77–79]:

$$\lambda_c = \lambda_s \cdot \frac{2\lambda_s + \lambda_p + 2V_p(\lambda_p - \lambda_s)}{2\lambda_s + \lambda_p - V_p(\lambda_p - \lambda_s)} \quad (11)$$

where λ_c , λ_s , and λ_p are the thermal conductivities of the composite ceramic, Al_2O_3 , and $\text{Y}_3\text{Al}_5\text{O}_{12}$ phase, respectively, and V_p is the volume fraction of $\text{Y}_3\text{Al}_5\text{O}_{12}$ phase. In the present work, a value of $\lambda_p = 10.7 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ was used for the thermal conductivity of pure $\text{Y}_3\text{Al}_5\text{O}_{12}$ phase [80], which is much lower than the thermal conductivity of dense Al_2O_3 ceramic ($34.32 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). If the morphology of second phase is not completely isolated, the effect of the connectivity of second phase on the thermal conductivity of composite system cannot be ignored. An appropriate model is given by the effective medium theory (EMT), and the thermal conductivity of composite system is given by [77,81]

$$\lambda_c = \frac{1}{4} \left\{ \lambda_p (3V_p - 1) + \lambda_s (2 - 3V_p) + \left[(3\lambda_p V_p - \lambda_p + 2\lambda_s - 3\lambda_s V_p)^2 + 8\lambda_p \lambda_s \right]^{\frac{1}{2}} \right\} \quad (12)$$

The calculated thermal conductivities derived from Eqs. (10)–(12) are shown in Table 3. The formation of

$\text{Y}_3\text{Al}_5\text{O}_{12}$ precipitations with a low thermal conductivity can result in a drop in thermal conductivity of $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ system based on the ME and EMT model analyses. However, the thermal conductivities of $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ system estimated by the ME and EMT models are higher than the measured values of thermal conductivities of Samples MM and CP since the phonon scattering caused by the pores, and the second phase precipitations and grain boundaries can decrease the phonon mean free path and further lead to the reduction of thermal conductivity [74,77]. Thus, the addition of Y_2O_3 into Al_2O_3 is expected to reduce the thermal conductivity of 3D printed Al_2O_3 ceramic.

The grain boundaries can act as the scattering sites for phonons and reduce the thermal conductivity of ceramic [77]. This reduction can be enhanced by decreasing the grain size, which is attributed to the increased number of grain boundaries per unit length of heat path. However, compared to the coarse grained Sample MM, the fine grained Sample CP has a similar value of thermal conductivity, rather than a lower value, as shown in Fig. 10, because the thermal conductivity of ceramic is also highly affected by second phase morphology [45]. The SEM image and corresponding EDS mapping for Y on the fracture surfaces of Sample MM sintered at 1650°C are shown in Figs. 13(a1) and 13(a2). Sample MM has large Y patches distributed heterogeneously (Fig. 13(a2)), and these patches are on the average size of $2.85\pm 1.24 \mu\text{m}$, which is comparable to the grain size of Sample MM ($3.50\pm 1.68 \mu\text{m}$), manifesting an apparent agglomeration of $\text{Y}_3\text{Al}_5\text{O}_{12}$ phase during sintering. A presence of semi-connected $\text{Y}_3\text{Al}_5\text{O}_{12}$ aggregates can be observed in Fig. 13(a3), and the $\text{Y}_3\text{Al}_5\text{O}_{12}$ aggregates distributes continuously along Al_2O_3 grain boundaries in Sample MM. The second phased distribution of Sample CP sintered at 1650°C is shown in Figs. 13(b1)–13(b3). Sample CP has small Y patches distributed homogeneously (Fig. 13(b2)), and these patches are on the average size of $0.71\pm 0.26 \mu\text{m}$, which is much lower than the grain size of Sample CP ($1.70\pm 0.63 \mu\text{m}$). Combined with the results obtained from SEM micrograph of Sample CP

Table 3 A comparison between the calculated and measured thermal conductivities of $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ system

Calculation model	Sample	λ_s	λ_p	λ_{c0}	φ	$\lambda_{c\text{-calculated}}$	$\lambda_{c\text{-measured}}$
ME	MM	34.32	10.70	32.16	2.69%	30.88	29.16
	CP	34.32	10.70	32.00	2.47%	30.83	28.95
EMT	MM	34.32	10.70	32.13	2.69%	30.85	29.16
	CP	34.32	10.70	31.97	2.47%	30.80	28.95

λ_{c0} is the theoretical thermal conductivity of the $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ system without pores ($\varphi = 0$). $\lambda_{c\text{-calculated}}$ and $\lambda_{c\text{-measured}}$ are the calculated and measured thermal conductivities of $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ system, respectively.

Fig. 13 SEM images and corresponding EDS mappings for Y on the fracture surfaces of (a1, a2) Sample MM and (b1, b2) Sample CP; SEM micrographs of the polished and etched surfaces of (a3) Sample MM and (b3) Sample CP. The semi-connected second phases are marked with yellow circles.

(Fig. 9(c)), the small-sized $Y_3Al_5O_{12}$ particles tend to be concentrated at multigrain junctions without continuous distribution along Al_2O_3 grain boundaries. The morphologic change of the second phase from semi-connected (Sample MM) to isolated (Sample CP) can contribute to an improvement of the thermal conductivity of Al_2O_3 ceramics, according to the comparison between EMT model (Eq. (12)) for the interconnected second phase and ME model (Eq. (11)) for the isolated second phase [45,76]. In addition, compared to Sample MM, the higher relative density of Sample CP can lead to an increase in thermal conductivity. From all the above analysis, Sample CP has a close thermal conductivity to Sample MM due to the combined contribution of grain size, the second phase morphology, and relative density.

According to the above research results, the CP process is an effective method to enhance the flexural

strength and reliability of 3D printed Al_2O_3 ceramic. Typical Al_2O_3 ceramic components with complex shapes can be fabricated by a novel approach integrating DLP-stereolithography and CP process, and the images of the 3D-printed green and sintered bodies with different fin configurations are shown in Fig. 14. The surface smoothness of the green and sintered parts appears to be fine. In addition, the thermal debinding shrinkages of the components in the length, width, and height were measured to be 2.23%, 2.49%, and 1.89%, respectively. It should be noted that these shrinkage ratios are very small (lower than 3%), indicating that the thermal debinding has no apparent effect on the dimensions of the 3D-printed parts [20]. This is important for constructing parts with precise sizes and geometries. The average sintering shrinkages in the length, width, and height reached 20.90%, 21.33%, and 23.34% from their initial dimensions, respectively. The

Fig. 14 Optical image of (a) 3D-printed green and (b) sintered fin-type Al_2O_3 ceramic heat sinks fabricated by a novel approach integrating DLP-stereolithography and CP process.

height shrinkage is larger than those in other directions, and this is caused by the layer-by-layer forming characteristic derived from stereolithography-based 3D printing technology [82]. On the whole, the sintering shrinkages of the parts are uniform without obvious geometry deformation. The successful manufacturing of the pin-type heat sinks as shown in Fig. 14 can show potential application in thermal management in electronics and automotive industries [83]. Therefore, the fundamental study of this work can offer an alternative approach to fabricate ceramic heat sinks with complex shapes and excellent mechanical performance.

4 Conclusions

In this study, a special Al_2O_3 ceramic with complex shape, high strength, and fine grained and homogeneous microstructure was successfully fabricated by a novel approach integrating DLP-stereolithography and CP process. The CP process was used to synthesize Y_2O_3 -coated Al_2O_3 composite powder, which was then used to print complex-shaped Al_2O_3 bodies via DLP-stereolithography. It was found that:

1) The microstructure, phase, and surface element present analyses for the CP processed Al_2O_3 powder clearly demonstrate that an amorphous Y_2O_3 layer can be fully wrapped on the surface of Al_2O_3 powder, which will be favorable for improving the dispersive homogeneity of Y_2O_3 in Al_2O_3 .

2) The phase and microstructure comparisons among the 3D printed Al_2O_3 samples prepared via the pure Al_2O_3 powder, CP, and MM processed Y_2O_3 - Al_2O_3 powders show: i) The introduction of Y_2O_3 into Al_2O_3 can result in the generation of $\text{Y}_3\text{Al}_5\text{O}_{12}$ phase precipitations, which can reduce the grain size of Al_2O_3 due to the precipitation pinning; ii) the CP process can make the microstructure of the 3D printed Y_2O_3 - Al_2O_3 system denser, more uniform and refined, compared to the conventional MM process.

3) Sample CP has a flexural strength of 455.37 ± 32.17 MPa and a Weibull modulus of 16.88, which are 15.10% and 76.02% higher than those obtained for Sample MM, and are 25.45% and 13.82% higher than those of Sample AL, respectively, due to the grain refinement and microstructure uniformity enhancement in Sample CP. This result indicates that the CP process is conducive to simultaneously improving the flexural strength and reliability of the 3D printed Al_2O_3

ceramic.

4) The CP process can refine the microstructure of Y_2O_3 - Al_2O_3 system at no expense of the thermal conductivity. The fine grained Sample CP has a close thermal conductivity ($28.95 \pm 0.28 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) to the coarse grained Sample MM ($29.16 \pm 0.55 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), because the CP process can facilitate the formation of $\text{Y}_3\text{Al}_5\text{O}_{12}$ phase as isolated pockets at corners of Al_2O_3 grains, which can benefit the decrease of phonon scattering caused by the second phase.

5) Some fin-type Al_2O_3 ceramic heat sinks were successfully fabricated without obvious geometry deformation via the CP process followed by DLP-stereolithography, which may offer a new opportunity for thermal management applications of Al_2O_3 ceramic.

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