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Green ceramic machining: A top-down approach for the rapid fabrication of complex-shaped ceramics

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Abstract

Green ceramic machining (GCM) has been investigated as an alternative method for the mould-free fabrication of complex-shaped ceramics, where ceramics in 'unsintered' green state are machined to complex-shaped via CAD/CAM technology. Recent advancement of CNC machining technology makes GCM a potential alternative for the rapid fabrication of ceramics, especially for some one-of-a-kind products. In this work, we investigated two processing routes to make ceramic green bodies which were suitable for green machining. The effects of processing methods on the green ceramic strength and toughness, machinability and surface finishing of the final ceramics were discussed. Examples of applications of the GCM in the fabrication of ceramic lattice scaffolds for bone tissue engineering and dental restorations have been demonstrated. The results show that gelformed ceramics have better mechanical properties and machinability than protein coagulation cast ceramics. But the debinding for gelformed thick wall components was found more difficult. It is therefore more suitable for the fabrication of ceramic microcomponent or thin sheet structures such as ceramic lattice scaffolds. Protein coagulation cast ceramics have good machinability and surface finishing for thick wall ceramic components. However, inhomogeneous and anisotropic shrinkage of complex-shaped ceramics were observed during sintering stage. Possible causes and solutions have been discussed.

Keywords: Milling; Shaping; Finishing; Rapid prototyping; Green ceramics

1. Introduction

Solid freeform fabrication (SFF) has been investigated extensively for the direct fabrication of complex-shaped ceramics without the use of mould since late 1980s.[1–3] The SFF technology is composed of a spectrum of techniques which include stereolithography,[4] 3D printing,[5] direct ink jet printing,[6] robocasting,[7] and fused modelling deposition.[8] The technology is based on a 'bottom-up' approach whereby a 3D CAD model is first decomposed or sliced into thin cross-sectional layer representations. Then, to build the sophisticated shape, each layer is selectively added or deposited and fused to the previous layers. It is extremely useful in some one-of-a-kind applications such as orthopaedic implants or dental restorations, where ceramics or bioceramics has been used for patient-specified prostheses. In such applications, mass production of complex-shaped ceramics from the current moulding or pressing techniques is inadequate and may not be cost-effective. Therefore, rapid and cost-effective fabrication techniques for customer-specified net-shaped ceramics are highly desirable.

So far SFF technology as applied to ceramics is far less successful as in the direct fabrication of polymers and metals due to the brittleness, hardness and refractory nature of ceramics. Most of the SFF technology has only been used to build up complex ceramics in green state, i.e. post-processes such as debinding and sintering have to be performed. Apart from the technical problems encountered in the SFF technology such as anisotropic shrinkage due to the residual stresses arisen from polymer binder drying in printing based methods or high shear field in extrusion based methods, an intrinsic disadvantage for the SFF is the surface quality which adversely affects inherent

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materials properties of the final products and, in turn, the fabrication rate. Current SFF technology can produce ceramic parts with complex shapes, but with poor surface finishing. The SFF processes generate 'stair-steps' on inclined surfaces from the layer-by-layer approach. Such stair-steps not only reduce the dimension accuracy, but also decrease the ceramic strength and toughness owing to the stress concentrations from the surface discontinuities where brittle ceramics are extremely notch sensitive. While any attempt to improve the surface quality by reducing the layer thickness or using nano-sized powders will inevitably increase the production time and compromise the cost-effectiveness.

On the contrary, rapid advent of computer numerical controlled (CNC) machining technology provides a 'top-down' approach in which a ceramic blank is machined down to a desired shape. In dentistry, chair-side CAD/CAM systems based on direct machining of sintered ceramics have been developed to fabricate ceramic dental crowns and bridges in clinics for many years.[9–12] The materials used include glass ceramics and porcelains,[13,14] as well as alumina and zirconia.[15,16] However, recent studies have strongly indicated that directly machined ceramic restoratives suffered from a persistent near surface damage during machining process due to the brittleness and low damage tolerance of ceramics.[17] Post-machining surface modifications, e.g. films and coatings, have been proposed to minimise the effects of machining-induced defects.[18] This will inevitably increase complexity and costs. An alternative solution is to machine the ceramics in a partially sintered state, where the machining forces are not as large as for fully sintered ceramics.[19] The secondary sintering process may also 'heal' some machining-induced damages. But the brittle nature of partially sintered ceramics is still difficult to control in order to achieve the accuracy and good surface finish. Another alternative—green machining, i.e. machining ceramics in their green (unsintered) state, has been proposed to possibly overcome the above problems, where ductile deformation makes cutting operation much easier to control in the machining of 'plastic' green ceramics. Though it has been proposed as a competing net shape manufacturing method for ceramics since early 1990s,[20] the advancement of the technology has been hindered by the weakness and fragility of ceramic green bodies formed using conventional ceramic forming techniques such as slip casting or die pressing, where the green strengths are normally <5 MPa. Gelcasting has first been used for green ceramic machining due to its improved green strength (ca. 10–30 MPa) than that from conventionally pressed or cast ceramic green bodies.[21] However, gelcasting has not been widely accepted by industry due to the toxic monomers used in the processing. Cold isostatic pressing (CIP) with the addition of polymer binders has also been reported to make strong green ceramics for green machining. In this work, we investigated two green ceramic forming processes, i.e. protein coagulation casting (PCC) and gelforming to fabricate 3D net shape ceramics via green machining and demonstrated their potential applications for the rapid fabrication of ceramics in some one-of-a-kind biomedical applications such as dental restoratives and patient-specified scaffolds or prostheses.

2. Experimental

2.1. Fabrication of green ceramics

The process for fabrication of alumina compacts via the PCC involved preparation of aqueous alumina slurries with mixed binder of egg white protein–sucrose system as reported previously.[22] Duramax D-3005 (ammonium salt of polyacrylic acid, Rohm and Haas, USA) was used as a dispersant. In the present study, 55 vol.% alumina (Alcoa CT 3000 SG, USA) loading was used with 8 vol.% of the egg white protein along with 3 wt.% sucrose on dry alumina powder weight basis. The function of sucrose was a rheology modulator as well as a plasticizer. The slurries were prepared by ball milling the above mix in the presence of spherical zirconia media in 600 ml polypropylene bottles with 200 ml of slurry and zirconia milling media (diameter of 3 mm and 1.4:1 of powder to media weight ratio). Following 24 h of milling, the slurry was filtered through a sieve to separate the zirconia milling media. The slurry was then de-aired by adding a defoamer (1-octanol) and rolling for an hour without the milling media. The de-aired slurries were cast into petroleum jelly-coated rectangular plastic moulds to make 50 mm × 30 mm × 20 mm bars for CNC machining. The moulds were placed in an oven preheated to 40 °C for 12 h. The green parts were then removed from the mould and dried at 80 °C overnight. In this way, coagulation and drying were carried out in a single step.

The process of alumina green ceramic tapes with a 55 vol.% solid loading via gelforming involved a twin-roll mixing of alumina powders with a high molecular weight polyvinyl butyral-polyvinyl alcohol copolymer (PVB–PVA) as a binder and cyclohexanone as a solvent. In order to facilitate the mixing process, relatively large amount (20 vol.%) of polymer binder was used. After degassing overnight under a contact pressure of ca. 1 MPa, the alumina dough was calendared to a 1 mm thick tape. The tape was then dried and gelled at 40 and 120 °C for 12 h, respectively.

2.2. CNC green machining of ceramics

A bench-top CNC milling machine (MDX 650, Roland DG Ltd., Japan) was used. It was a belt driven fully automated computer-controlled milling machine, which could be operated at variable rpm of 3000–12,000 with maximum *x*–*y*, and *z* speed of 14 mm/s. In the present study, the *x*–*y* and *z* direction speeds were optimised to obtain smooth samples at minimum machining time. Green machining was carried out using diamond-coated flat end milling tools with different tool size from 0.5 to 5 mm. Green ceramic samples were mounted on an aluminum plate using hot melt glue. The plate was then mechanically clamped on the base of the CNC machine. To fabricate complex-shaped ceramic objects, either CAD or scanned imaging files were transferred to standard STL files, which were then input to the CNC machine and a machining path simulation was performed before the machining operation. The ceramics were green machined through a roughening and finishing operation, respectively, to obtain good surface finishing.

2.3. Shrinkage analysis of green-machined ceramics

A high speed-scanning machine (Cyclone, Renishaw, UK) was used to acquire digital images using a contact scanning probe and the Tracecut digitising software. The software allowed for the data capture and manipulation, as well as the creation of a CNC program or CAD output. To demonstrate the feasibility of ceramic green machining as a alternative rapid prototyping method for net shape ceramics, a single molar tooth model was scanned and machined from green ceramic compacts produced using the PCC method. To ensure the accuracy, a 0.5 mm 'ball' style probe and a 90 mm stylus were used. Shrinkage analysis was also carried out using the scanning technique to measure the sintering shrinkage of green-machined ceramics in x, y, and z directions.

2.4. Characterisation of green and sintered ceramics

The green and sintered densities of the fully dried and sintered samples were measured using the Archimedes principle. The mechanical properties of dried and sintered samples were tested for flexural strength measurement in a three-point bending configuration. The size of the samples used for strength testing was 35 mm × 4 mm × 3 mm. The flexural strength was measured with a span of 25 mm, at a crosshead speed of 0.5 mm/min using a mechanical testing machine (Lloyd Instruments, UK). The fractured and as-machined surfaces were examined under the scanning electron microscope (JEOL, JSM-6060LV, UK). To investigate the machining effects on mechanical properties of sintered alumina ceramics produced via the PCC, three-point bending strengths of the as-machined and surface polished alumina ceramics were measured and compared. Statistic analysis using Weibull modulus was conducted for both ceramics as reported by Antón et al.[23] The surface roughness of the as-machined and sintered surfaces was examined using a Surf Test SV-2000 (Mitutoyo, Japan).

3. Results and discussion

Fig. 1 shows the stress–strain curves of the PCC and gelformed alumina compacts under three-point bending. It can be seen that the gelformed green ceramics have far better mechanical strength because a high content of polymer binder was used. The toughness was also much better compared to the PCC green ceramics as illustrated with lager displacement in the stress–strain curves. These characteristics reflected in different machining behaviours and the resultant surface finishing of the green ceramics. Our previous studies showed that the 'ductile' machining behaviour with ribbon-like swarfs was observed for the gelformed ceramics. Machined surface roughness was much lower than that of the PCC ones.[22] Due to the better mechanical properties, the edge retention of the machined green ceramics is also different (Fig. 2). Less chips and better edge retention are evident for the gelformed samples. The measured surface roughness of the sintered ceramics from gelforming is one order of magnitude smaller than that from the PCC (0.1 μm versus 2.1 μm). However, compared to most of the bottom-up SFF techniques, the surface finishing from green-machined ceramics are much better. A green-machined PCC ceramic part and its corresponding microstructure are shown in Fig. 3. Smooth and translucent alumina part is clearly evident for the PCC processed ceramics. The three-point bending strength results for both as-machined and polished alumina ceramics produced using the PCC show that their mechanical strengths are similar (as-machined: 317 MPa versus polished: 328 MPa), but the Weibull modulus is reduced from w.m. = 9.5 for the polished to w.m. = 5.9 for the as-machined (Fig. 4). This indicates that green machining has still generated some surface defects which contribute to the reduction of the Weibull modulus and hence the reliability of the ceramics, even though their

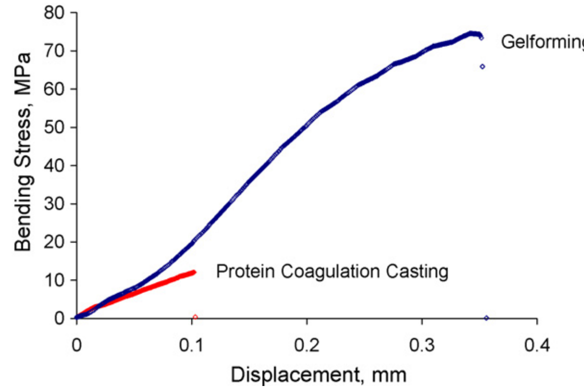

Fig. 1. Three-point bending stress–strain curves for green ceramics processed from gelforming and PCC.

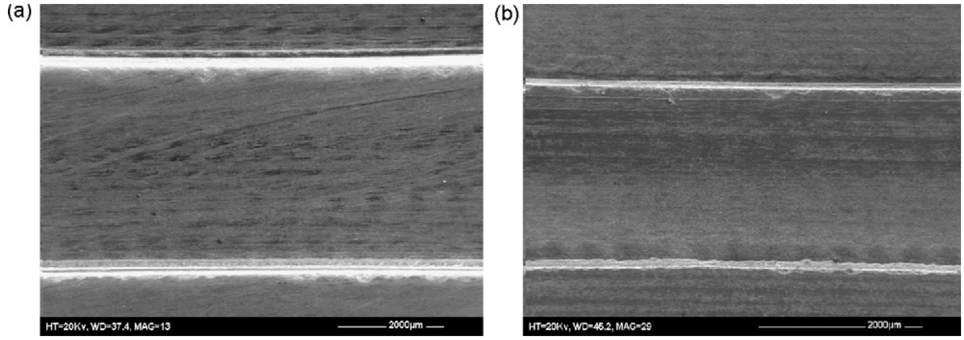

Fig. 2. SEM micrographs of green-machined steps for ceramics processed from (a) PCC; (b) gelforming, showing that gelformed ceramic has better edge retention and definition.

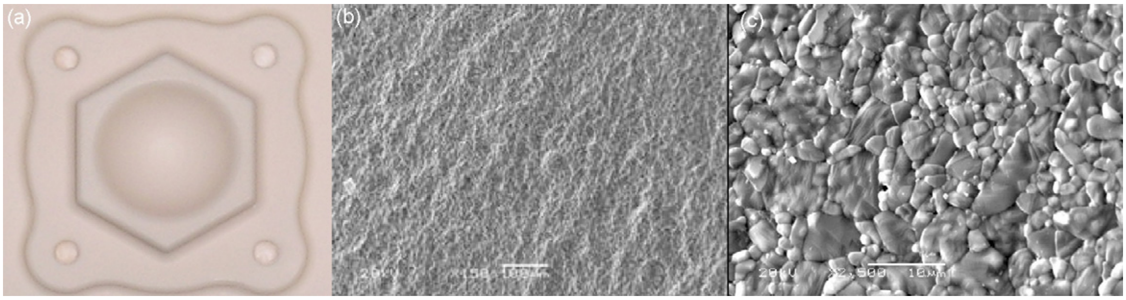

Fig. 3. Green-machined ceramics (a) from PCC processing; (b) fracture surface of green ceramics; (c) sintered surface, showing dense microstructures.

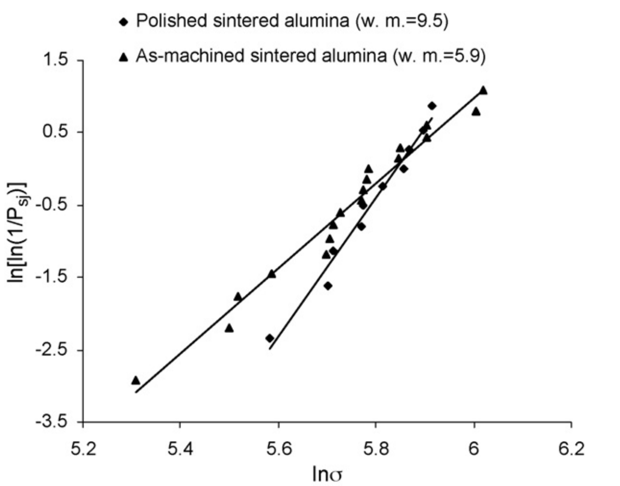

Fig. 4. Weibull modulus plot of sintered PCC alumina ceramics with polished and as-machined surfaces.

surface roughness was measured to be at the range from 0.1 to 2.5 μm.[22]

Nevertheless, though our experiments demonstrated excellent 'ductile' machining behaviour and surface finishing for the gelformed ceramics, it was also found that debinding for the gelformed ceramics was extremely difficult for thick cross-section samples because of the high volume fraction of binder content (ca. 18–20 vol.%) and high molecular weight of PVB–PVA. Extra long debinding time (>24 h) and slow heating rate (<0.5 °C/h) were need to avoid the 'bloating' of the gelformed ceramics. This would restrict its application for rapid prototyping of thick wall components using the GCM.

Possible applications for ultra-high strength green ceramics from gelforming were explored for the fabrication of ceramic thick films and microcomponents or microstructures, particularly those with high aspect ratios,[24–26] where binder removal would not possess severe problems because of the thin cross-section and the short diffusion distance of decomposed polymer binders to escape from ceramic components. Fig. 5 shows an example for gelformed ceramics to produce ceramic lattice structures via the GCM for potential applications such as bone tissue engineering scaffolds. Because of its excellent machinability and strength, gelformed ceramic sheets were easily machined with double-sided dual channels as shown in Fig. 5(a). The channel size was controlled by the milling tool size (minimum 0.1 mm), and the channel shape and spacing could be freely adjusted depending on the requirements of applications. The green-machined sheets were assembled and laminated under contact pressure using diluent binder/butanol solution as a binder. After sintering, 3D spatially defined ceramic lattice structures were fabricated.[27] This provides an alternative route other than the SFF to fabricate such lattice structures. One of the potential advantages of this route is better mechanical properties of the resultant lattices compared to the SFF deposited ceramic lattice structures. Fully dense ceramic lattices can be obtained (see Fig. 5c insert) because of the high solid loading and green density in gelforming processing.[28]

Another possible application for the GCM is the ceramics dental crowns or bridges used in restorative dentistry. Currently, most ceramic dental crowns and bridges have been fabricated using direct machining of either fully sintered or partially sintered ceramics.[10,19] Ceramic machining in the unsintered 'green' state could overcome a few problems encountered in the direct machining as discussed previously. Fig. 6 shows an

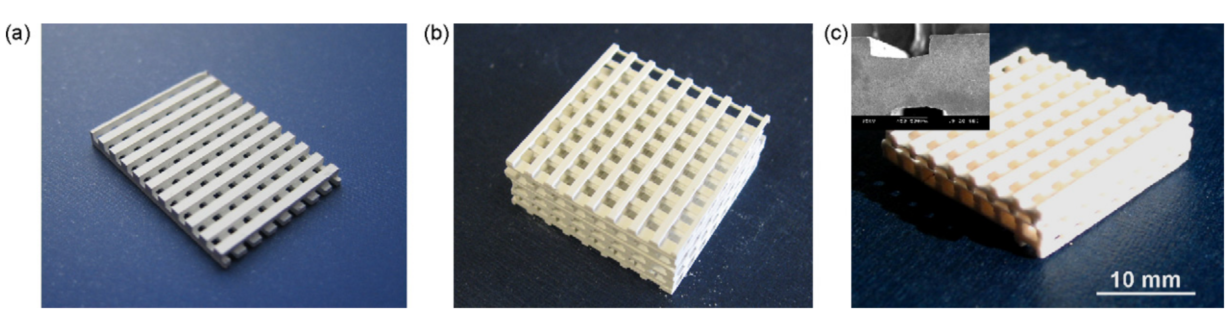

Fig. 5. (a) Green-machined ceramic sheet with double sided dual channels; (b) assembled and green bonded green ceramic lattices; (c) sintered ceramic lattices. The insert shows that no obvious interface between two bonded ceramic sheets after sintering.

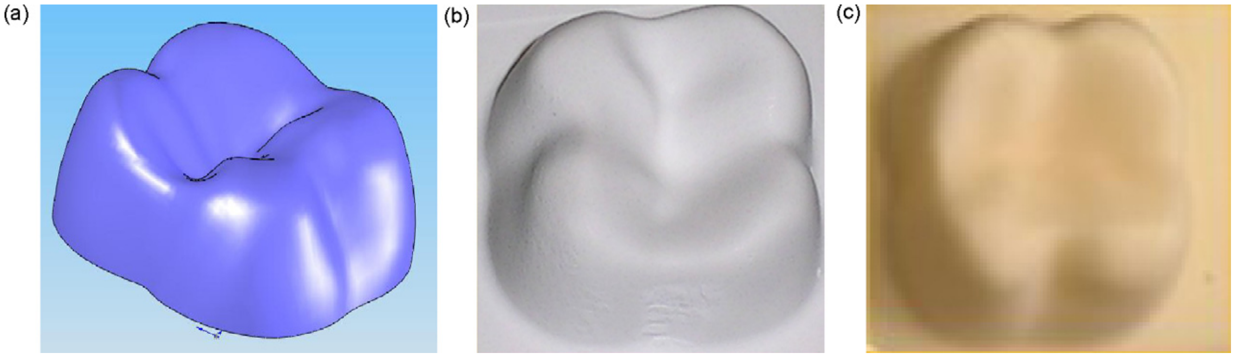

Fig. 6. (a) STL file from scanned tooth model; (b) CNC machined green ceramic; (c) sintered ceramic molar tooth model.

example of green-machined molar tooth from a PCC alumina ceramic block using a three-axis desk-top CNC machine. The STL file was generated from the scanning image of a molar tooth model (Fig. 6a). The PCC green compact was then machined to the desired shape using optimised parameters (Fig. 6b). After sintering at 1550 °C for 2 h, a smooth and dense alumina molar tooth was obtained (Fig. 6c).

Since dimensional shrinkage occurs inevitably during sintering process from the machined green compacts to the final sintered ceramics, characterisation of the sintering shrinkage in three-dimensions for complex-shaped ceramics will be useful to ensure the dimensional tolerance for the specific applications. In the dental restoration application, marginal fitting of the ceramic restoratives is vital for the prevention of secondary caries, accurate prediction and control are therefore very important to the final fitting.

Machined ceramic tooth model at both green and sintered state were digitised using the Cyclone. The point cloud acquired points every 0.1 mm at 0.5 mm step size. As many points as possible were obtained using the Tracecut software to obtain accurate scanning. However, too many points would freeze the surface construction. Appropriate data reduction was needed to clean up noisy points. To ensure the accuracy of scanned image, several treatments were carried out on the point data. First, the scanned tooth model was separated as four parts by curves. 'B-plane' treatment was used to generate curves by connecting

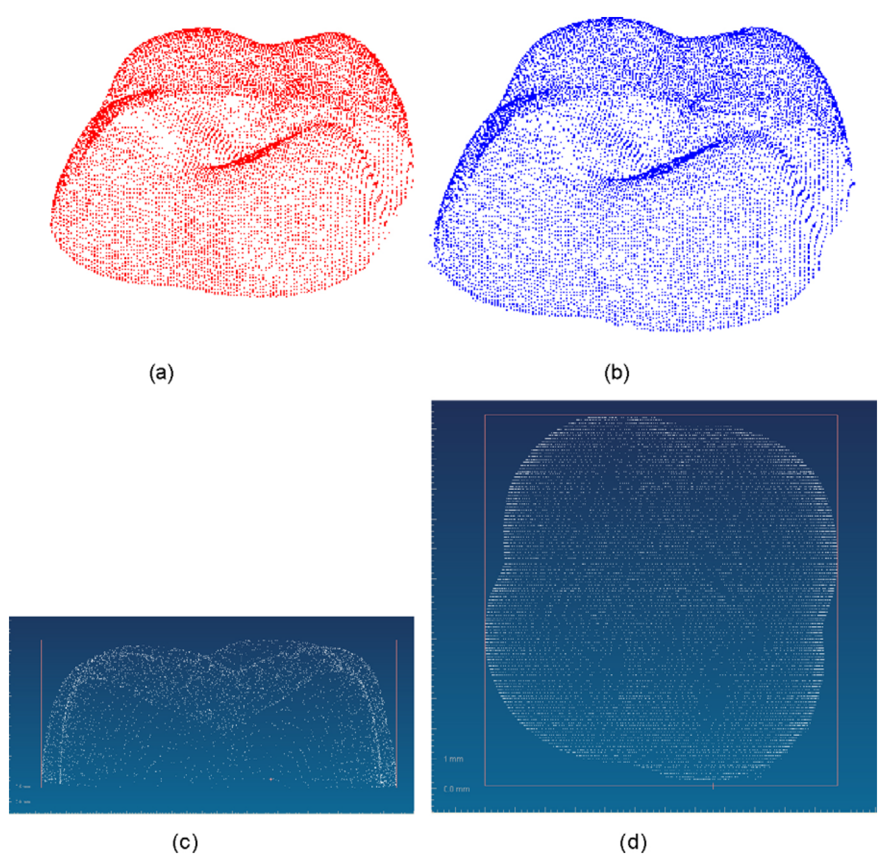

Fig. 7. Scanned data for (a) sintered ceramic tooth model; (b) green ceramic tooth model; (c) side view; (d) top view of image profiles. The shrinkage is calculated from the dimension changes from top view (x, y direction) and side view (z direction).

individual points. 'Curve continuity' and 'reparameterisation' were then applied to ensure the relevant curves were joined together with the same point data. Finally, surfaces were reconstructed by curve fitting with point clouds. After the merge of reconstructed surfaces with point clouds, the maximum difference was found to be 38 μm.

The reconstructed surfaces for green and sintered tooth model were compared. As shown in Fig. 7, the dimension change during the sintering stage in x, y and z direction was measured in top view and front view, respectively. The sintering shrinkage was calculated in different directions using the following equation:

$$\text{Sintering shrinkage}\,(\%) = \frac{H_{\text{green}} - H_{\text{sintered}}}{H_{\text{sintered}}} \times 100 \qquad (1)$$

where H_{green} and H_{sintered} are dimensions of green and sintered ceramics in each direction, respectively.

The sintering shrinkage calculated in x, y and z direction was found to be 12.0%, 15.1% and 21.4%, respectively. Ideally, homogeneous shrinkage is desirable for the accurate prediction and control of the dimensions of the final products. Careful observation and analysis of the sintering shrinkage data indicate that the actual shrinkage is dependent on the constraint imposed on the green samples during sintering. The shrinkage in the z direction was the largest because of the 'friction-free' state of the green ceramic during sintering. There was no any constraint to hinder the sintering shrinking. On the contrary, in the x–y direction, the frictional constraint between the green ceramics and porous setter may result in a mechanical interlocking effect and hinder the free shrinking and moving between the green ceramics and setter materials in the sintering stage. The static frictional forces will be directly related to the surface quality and dimensions of machined surfaces.[29] To confirm that the inhomogeneous shrinkage was not caused by the compositional inhomogeneity of the PCC processed green ceramics, we found a homogeneous shrinking occurred in x–y directions for PCC cube samples when set on a coarse alumina powder bed during sintering. Therefore, it seems that two approaches could be adapted to ensure the accurate prediction and control of the dimensional changes during the GCM by choosing either a 'shrinkage-free' (i.e. zero-shrinkage) ceramic such as reaction-bonded $ZrSiO_4$ ceramic.[30] or a 'friction-free' setter material. A recent study indicated that ceramic microspheres setting on polished setter materials could significantly reduce the friction forces since its coefficient of static friction was much lower than that without microspheres.[29]

4. Conclusions

Green ceramic machining (GCM) provides a possible alternative for the rapid fabrication of complex-shaped ceramics. It offers several distinct advantages compared to other technologies currently used for the fabrication of net shape ceramics in terms of the cost-effectiveness and surface finishing. The key to the successful application of the GCM includes the suitable ceramic processing for machinable green ceramics and the controllable sintering shrinkage. This study shows that both gelforming and PCC processes are viable processing methods for the fabrication of green ceramics which possess good mechinability and surface quality. This has been demonstrated in the GCM of ceramic lattice structures and molar tooth model. However, attention needs to be taken during the sintering stage to avoid inhomogeneous shrinkage resulted from the mechanical interlocking between the green ceramics and setter materials. Possible solutions have been discussed, which include the use of 'friction-free' setter materials or the design of 'shrinkage-free' ceramic systems.

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