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Slurry deposition by airbrush for selective laser sintering of ceramic components

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Abstract

To obtain ceramic components of high density by means of laser sintering, a high density of the green-compact is necessary. This is a problematic aspect when using ceramic granulates. We present a new procedure based on an airbrush spraying technique using slurries of high solid content. Alumina as well as zirconia slurries were developed and optimized for the process. After the layer-wise airbrush deposition of slurry, the microstructure of green, sintered and laser sintered samples were analyzed using SEM. On the basis of the high density of the green-compact achieved the described technique could be used for individual production of laser sintered structural ceramic components.

Keywords: Airbrush; Laser sintering; Suspensions; Al_2O_3; ZrO_2

1. Introduction

Individually contoured ceramic components are of decisive importance for functional, structural and biomedical applications. In a CAD/CAM controlled grinding process material is removed consecutively to form the part-specific shape. The procedure allows the use of material blocks of high bulk density thus achieving final parts of high strength. However, by using CAD/CAM the pieces have to be produced one by one. Components generated by Rapid Prototyping processes result from addition of material, generally in layers.[1] Through this so-called solid freeform fabrication it is possible to generate components of complex 3D-shape as well as to manufacture differently contoured parts in one process cycle.[2–5] Thus the advantages of Rapid Prototyping are combined with the individual production of ceramic products in terms of mass customization. Solid freeform fabrication describes a number of tool free manufacturing processes. Among these techniques are stereolithography,[3,6] laminated object manufacturing,[7,8] direct ink writing techniques[9] such as three dimensional printing[10,11] or direct inkjet printing[12–16] and selective laser sintering (sls).[17–20]

In previously published studies on selective laser sintering, two main strategies have been pursued concerning the condition of the material added. Preceding the laser sintering process the individual layers are deposited using either ceramic powder or a ceramic suspension. Various materials have been utilized. Laser sintering has been applied in the fusion of ceramic and a glassy raw material.[19] In this case, feldspar was used as a glass phase-forming component and a resolution of 40 μm was achieved.[19] For metallic powders an overall structural resolution of 30 μm was reported.[21,22] Simple bulk PZT was obtained by using the selective laser sintering process for a stoichiometric mixture of PbO, ZrO_2, and TiO_2 powders.[23] Implants made of hydroxyapatite composites were manufactured using the same method.[24] The selective laser melting technique has been used to generate bone substitute implants made of β-tricalcium phosphate cement and soluble alkaline borosilicate glass. The glass phase of the composite granulate material acted as a binder when molten by laser energy. The compressive strength of small specimens (6 mm width, 6 mm depth, 5.4–5.8 mm height) was 0.8 ± 0.05 MPa. The resulting pore structure of the specimens created was suitable for vascularisation.[25] Silicon carbide has also been used in laser sintering. Here the resulting porous specimens were subsequently infiltrated by silicon.[20] Surface sintering of SiO_2 green bodies by CO_2-laser has been reported as well.[26]

Layer-wise slurry deposition with subsequent laser sintering has been described in further studies,[17,27] in which laser

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sintering of porcelain and SiO_2[17] as well as compounds in the alumina–silica system[27] were reported. The slurry-based deposition of single layers was achieved by a doctor blade.

To achieve coatings or deposits of ceramic slurries, a paint technology as an alternative method to the use of a doctor blade is described in other studies. This versatile method of airbrush spraying was adapted for suspensions of ceramic powder, additives and a volatile carrier. Layers of 20–200 μm were achieved.[28–31]

This article focuses on the strategy of a layer-wise slurry application for the subsequent laser sintering process. Slurries with high amount of solid content provide a high density of the manufactured green body. Airbrush spraying was applied instead of spreading a suspension with a wiper to achieve homogeneous thin layers. The hypothesis is proved to be true that this can be achieved by combining the airbrush technique with a linear bearing guide. Therefore, adequate suspensions of alumina and zirconia were developed. The viscosity of the slurry as well as the drying process was considered when adapting the slurries to this technology. To achieve densely sintered components by laser sintering, a green body with an initial high density is necessary. Therefore, a high density of single layers resulting in green bodies of high density is an essential point for laser sintering.

2. Experimental procedure

2.1. Substrates for alumina and zirconia

As substrate materials for alumina, cordierite ($Mg_2Al_4Si_5O_{18}$, H-Th7/7 R 12B, type C410, Quarzsandwerke, Weissenbrunn, Germany) and aluminium titanate (Al_2TiO_5 RS, Sintertechnik, Pretzfeld, Germany) were used. Cordierite has a lower coefficient of thermal expansion than alumina. As cordierite decomposes to alumina, silica and magnesia at high temperatures, i.e. during laser sintering, the decomposition products are compatible with alumina. Al_2TiO_5 has a lower coefficient of thermal expansion than alumina as well. As Al_2TiO_5 decomposes to Al_2O_3 and TiO_2, the coefficient of thermal expansion is adjusted at the interface with alumina. Therefore, it is possible to use it as a substrate as well. Substrates for zirconia slurry were composed of magnesia-partially stabilised zirconia (3.5 Mg-PSZ, Sintertechnik, Pretzfeld, Germany). The substrates were uniaxially pressed in a cylindrical form (50 mm diameter) with $p = 100$ kN. The substrates were sintered at 1150 °C for 2 h (cordierite), 1550 °C for 3 h (Al_2TiO_5) and 1640 °C for 2 h (Mg-PSZ), respectively. All substrates were ground on a precision grinding machine (MPS 2 R 300 with diamond grinding wheel 6A2-175-5-4-76, BZ with metallic bond (bronze) G&N, Erlangen, Germany) to obtain coplanar, uniform surfaces.

2.2. Slurry preparation

The alumina and zirconia-based slurries were produced from powder and additives as follows. For these water-based slurries Al_2O_3 P172 SB (Alcan, Gardanne Cedex, France) was used as well as α-Al_2O_3 Baikalox SM8 (Baikowski Chemie, Annecy, France). For the zirconia slurries TZ-3Y-E (Tosoh, Tokyo, Japan) was utilized. A high amount of solid content (60–76 wt.% for alumina, 50–73 wt.% for zirconia) was applied. A 0.5–1 wt.% (weight percent relative to powder mass) of Dolapix CE 64 (Zschimmer & Schwarz, Lahnstein, Germany) as deflocculant and a 0–3.2 wt.% of Optapix PAF 35 (polyvinyl alcohol, Zschimmer & Schwarz, Lahnstein, Germany) as binder were used for the suspensions. Glycerine (Glycerol 85% Ph. Eur., Aug. Hedinger, Stuttgart, Germany) was utilized as an additive as well to ensure uniform drying. The slurries were attrition milled (alumina or steel pot, zirconia balls with 0.1 mm diameter) at 1000 rpm for 10 min. Details of the compositions are given in Table 1. The pH-value of the slurries was varied with nitric acid and ammonia, respectively. The solid content, the pH-value and the temperature of the substrates were varied to analyze the wetting behaviour of the alumina slurry on the substrate (Table 2).

2.3. Layer-wise slurry application

The layer-wise slurry application (suspensions II, III, V and VI) on the substrates was performed by an airbrush spray gun with internal mix. By its double-action trigger the addition of slurry and compressed air (3.25×10^5 Pa) was individually controlled. The nozzle had a diameter of 0.5 mm. A linear bearing guide moved the substrate (velocity 2.5–7 cm/s) through the area of sprayed suspension. The slurry layers were dried with an infrared (IR) heater (Fig. 1) at the end of each spray cycle. The specimens A and B were built up using slurry III, whereas slurry VI was used to obtain the 3D objects C, D, E and F.

2.4. Conventional sintering and laser sintering of samples

The alumina samples were sintered in an electric furnace, sample A at 1400 °C and sample B at 1500 °C for

Table 1
Composition of slurries, all specification of additives in weight percent (wt.%) relative to powder mass, except for pH-value

	I	II	III	IV	V	VI
SM 8	70	75	70	–	–	–
TZ-3Y-E	–	–	–	63	73	70
Dolapix CE 64	0.5	1.5	1	1	0.68	0.85
Optapix PAF 35	–	–	1.5	–	0–1.8	3.2
Glycerine	–	–	–	–	–	0, 1, 4 or 10
Tested pH-range	4.3–11.5			0–11.7		

Table 2
Prepared samples and their respective substrate and coating

	A	B	C	D	E	F
Substrate	$Mg_2Al_4Si_5O_{18}$ (cordierite)	$Mg_2Al_4Si_5O_{18}$ (cordierite)	3.5 Mg-PSZ (magnesia-partially stabilised zirconia)	3.5 Mg-PSZ (magnesia-partially stabilised zirconia)	3.5 Mg-PSZ (magnesia-partially stabilised zirconia)	3.5 Mg-PSZ (magnesia-partially stabilised zirconia)
Coating	Slurry III (Al_2O_3)	Slurry III (Al_2O_3)	Slurry VI (ZrO_2), 0 wt.% glycerine	Slurry VI (ZrO_2), 1 wt.% glycerine	Slurry VI (ZrO_2), 4 wt.% glycerine	Slurry VI (ZrO_2), 10 wt.% glycerine

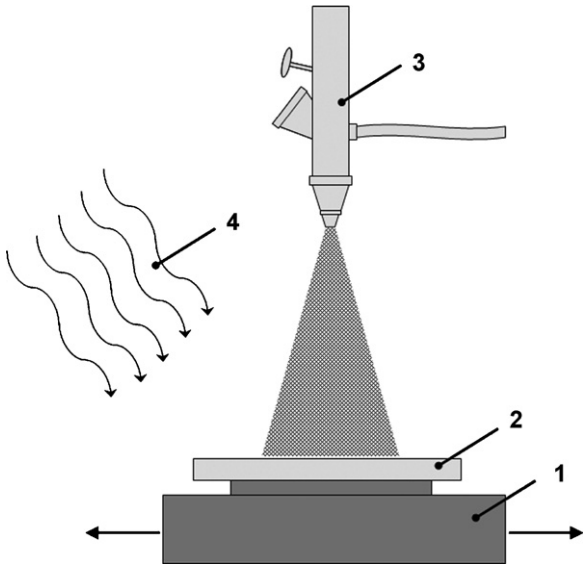

Fig. 1. Linear bearing guide (1) moves substrate (2) below the spray of the airbrush spray gun (3) in horizontal direction. The deposited slurry layers were dried by an infrared heater (4) drying each consecutive layer from above at the end of each spray cycle.

2 h. Fragments of the four specimens C–F of zirconia were sintered at 1450 °C for 2 h. To obtain laser sintered bodies (10 mm × 10 mm × 10 mm) the substrate with a dry green layer was exposed to CO_2-laser irradiation (EOSINT M 160, maximum 90 W power output). The laser scanning velocity was varied between 95 and 400 mm/s. Spacing between consecutive laser lines was 0.01–0.02 mm. The layer thickness of 0.1 mm was controlled by lowering the platform (in vertical direction). Subsequently another slurry layer was applied on the first layer using the airbrush method. By reiterating these steps, a ceramic body was generated on a substrate.

2.5. Analysis of microstructure

The green layers were analyzed using SEM (LEO 440i, Carl Zeiss SMT AG, Oberkochen), once detached from the Mg-PSZ or cordierite substrate. Both the conventionally sintered as well as the laser exposed specimens were prepared in cross-section and polished for analysis. The density of the conventionally sintered bodies was measured by Archimedes' principle.

3. Results

3.1. Slurry characterization

Photographs of slurry droplets on the substrates were taken and the contact angle was measured using an image manipulation programme. The wetting angle was reduced from 52° to 37° for zirconia (slurry IV) on Mg-PSZ substrate by increasing the pH-value from 9.4 to 11.7. For alumina slurry (slurry I) on cordierite substrate the wetting angle was reduced from 45° to 30° by increasing the pH-value from 9.4 to 10.5. The wetting angle of zirconia increased only slightly when the slurry was applied onto a first dry layer of slurry. For the alumina slurry, the difference

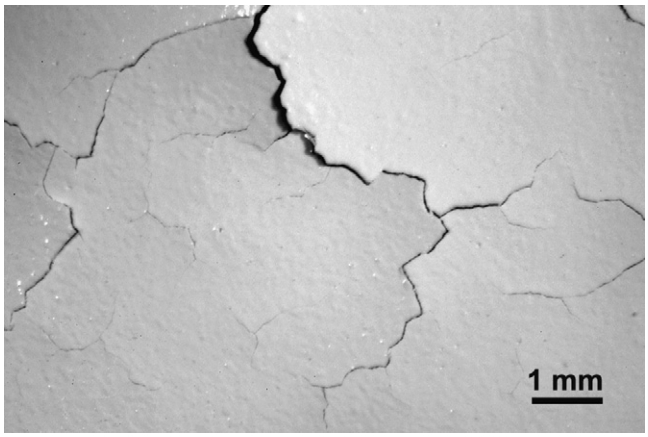

Fig. 2. Microscopic cracks at the surface of a dried sample (ZrO_2) after airbrush application on 3.5 Mg-PSZ substrate.

was more pronounced. The wetting angle was 69° when applied on a dry slurry layer.

3.2. Characterization of applied layers

The application of too much slurry resulted in overspray. Here no continuous plane and smooth surfaces were achieved. Moreover, as several layers of slurry spray were applied, areas of the surface chipped and cracked while drying (Fig. 2) whereas others appeared glazed. The surface of an insufficiently wetted layer showed a coarse grain, resembling a powdery structure. The fraction surface of a substrate with four layers of alumina slurry II (light grey) on a cordierite substrate (grey) appeared dense with a thickness <50 μm and in close contact to the substrate (Fig. 3). The specimen had a plane surface with fine and homogeneously distributed pores. During build-up possible defects were an insufficient wetting of the substrate. Thereby subsequently, the layers pealed off from the substrate during the succeeding build-up phases (Fig. 4). Whenever layers were insufficiently wetted by following layers, surface roughness as well as lateral cracks occurred. By optimizing the spraying-parameters, a green body was produced in 23 cycles with zirconia slurry containing 10 wt.% glycerine (Fig. 5). This green body F had an overall thickness of 1.46 mm (approximately 60 μm per layer).

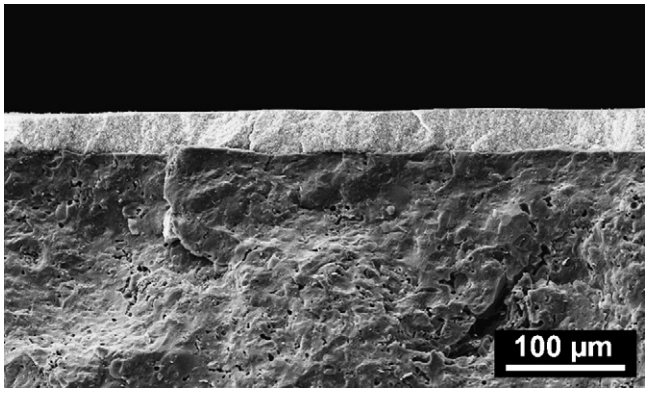

Fig. 3. Micrograph of fractured surface of four layers of dried alumina sample (slurry II) on a cordierite substrate.

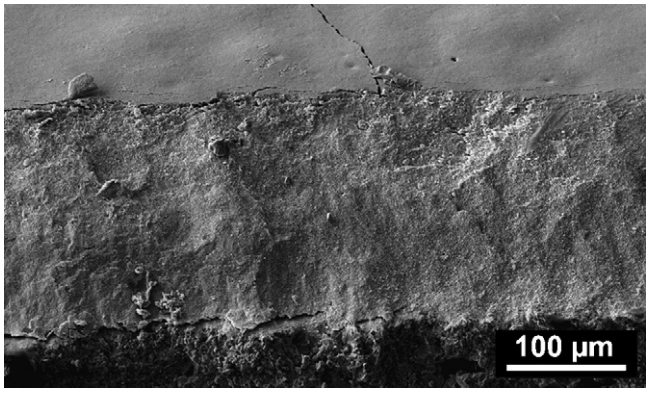

Fig. 4. Micrograph of a dried zirconia body, i.e. green, partly separated from the 3.5 Mg-PSZ substrate during build-up.

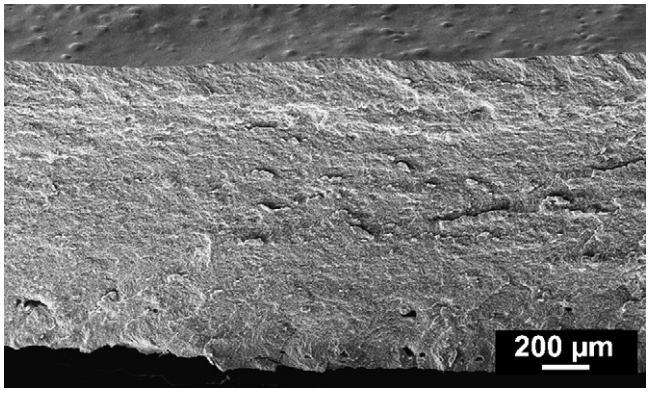

Fig. 5. Micrograph of fractured surface of dried airbrush built-up zirconia green body F (slurry VI with 10% glycerine content). It was detached from its 3.5 Mg-PSZ substrate for subsequent SEM analysis.

In the sample no cracks were detected. The adhesion between the layers appears to be satisfactory. The micrograph shows small irregularities on the surface (in the range of few microns) (Fig. 5). Comparable dense and high structures (10.9 mm) with up to 181 layers were built up with alumina.

The sintered alumina and zirconia samples both showed a homogeneous, dense microstructure with very small pores (size <1 μm) (Fig. 6). Concerning the zirconia, larger pores (approximately 50 μm) were found specifically in the area close to the layers that were previously connected to the substrate (bottom of specimen). Additionally, some single bigger pores are visible

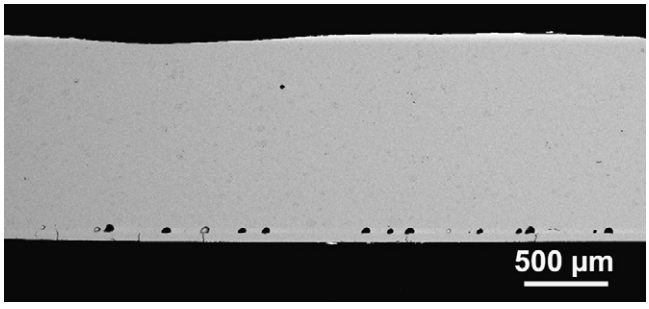

Fig. 6. Micrograph of a polished cross-section of the furnace sintered (1450 °C, 2 h) airbrush built-up green body F (slurry VI with 10% glycerine content). It was detached from its 3.5 Mg-PSZ substrate before sintering.

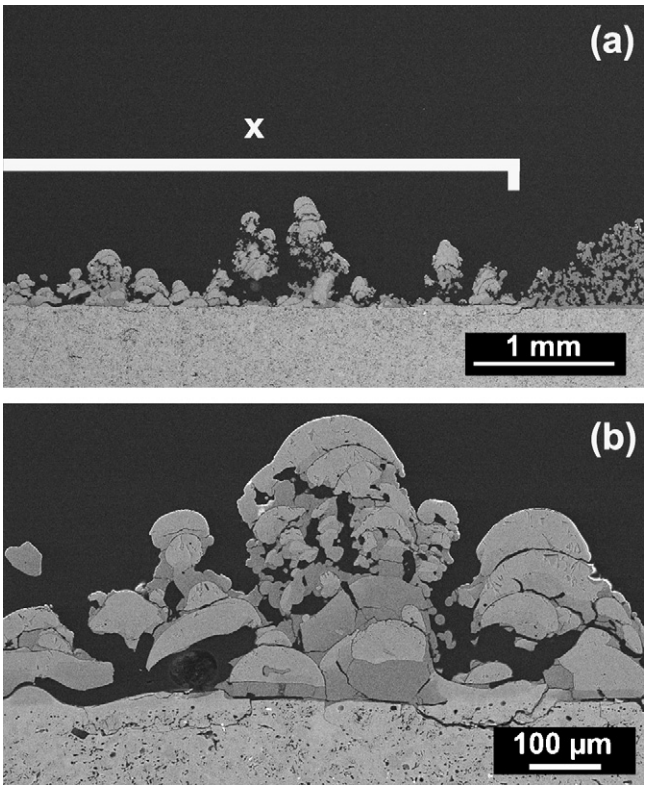

Fig. 7. Micrograph of a polished cross-section of an alumina specimen. Curved surfaces of several layers are displayed, each of which were sprayed and exposed to laser irradiation (laser power of 11 W), (a) general view, (b) detail, and (x) laser exposed area.

throughout the sintered body. The average density of the measured alumina specimens was 98.5% of the theoretical density and 98% for zirconia.

The sample shown in Fig. 7 was treated with a laser power of 11 W. The edges near the laser exposed area (right-hand side of the micrograph, Fig. 7a) show insufficient wetting by the following slurry layer. When irradiated with a power $\geq$7 W the substrate appeared to have a loss of material as well as cracks. Remains of layers of slurry deposition can be identified in Fig. 7b. Not all of these layer parts are sintered thoroughly. In this partially sintered structure micro cracks and removal of slurry are obvious as well. Though sintered areas (light grey) of layers are apparent, green areas (grey colour) (Fig. 7b) of the same layer still remain below.

4. Discussion

To achieve laser sintered ceramic components exhibiting high loading capacity a dense green body structure is an important prerequisite. As previous studies have shown this cannot be achieved using dry powder methods, which was the motivation to produce dense components by layer-wise slurry application. The focus concentrated on the adaptation and adjustment of the airbrush spraying technique for the laser sinter process.

Though a high amount of liquid in the slurry enhances the wetting behaviour, it contradicts the high density of green bodies required. Furthermore, in the case of high solid content of the slurry, an accelerated drying process was observed, which represents an undesired effect resulting in an enhanced risk of blocking the nozzle of the airbrush system. However, due to the subsequent laser treatment, no additives such as alcohol or alcanes could be used to enhance the wetting on the substrates or green parts of the manufactured constructions. The wetting angle depends on the pH-level and consequently on the viscosity of the slurry as well as the surface characteristics. The optimized wetting behaviour of the slurries allowed a homogeneous spray application in layers. The high solid content of the slurries had a positive effect on the drying process.

The reason for the partial delamination at the interface (Fig. 4) was the drying process. During the drying process, the built-up layer bent upwards at its perimeter. Since the adhesion of the single layers proved superior to the adhesion between the green body and the substrate, the green body was separated from the substrate.

For the zirconia slurry the addition of glycerine proved to be necessary to achieve a homogeneous crack-free drying of the applied layers. The best results were achieved with slurry VI containing 10% glycerine.

It is assumed that the small irregularities observed on the surface of the green body F (Fig. 5) occurred due to inhomogeneous distribution of glycerine in the slurry. An average layer thickness of less than 100 μm was achieved. This is of importance as the penetration depth of the laser beam in zirconia is less than 100 μm because of the low thermal conductivity of this material.

Concerning the samples of combined layer-wise airbrush application and laser sintering the laser power is a principal issue. Of importance was a low laser power. The only significant results were achieved on samples treated with a laser power of under 15% of maximum laser power (90 W), i.e. <13.5 W. A laser power below 2 W only resulted in drying of the samples. The edges close to a laser exposed area showed the same effect as an area irradiated with 2 W. Based on the microstructure analysis (Fig. 7) it can be concluded that those slurry layers were only dried and not sintered. In both cases, the wetting with a subsequent slurry layer was insufficient, resulting in a structure without adhesion between the layers. Henceforth, it was not possible to build-up dense bodies in these cases. The micro cracks and the removal of slurry in the sintered structures were a result of the laser treatment as well. The laser induced cracks and loss of material in the substrate. This could be a result of vaporization or superheating of the material.

In Fig. 7 curved surfaces of several layers are displayed, each of which were sprayed and exposed to laser irradiation. Though the surface of a lower layer is irregular, its topography is followed closely by the subsequent layer of slurry, as wetting on the sintered material was sufficient. The interface between two layers exhibits flaws where the layers did not adhere well. This effect was more pronounced in alumina than in zirconia.

Homogeneous structures were achieved as shown in cross-sections of green bodies as well as conventionally sintered specimens (Figs. 5 and 6). Despite this positive result, the final process of layer-wise laser sintered individual layers was unable to produce entirely dense structures. Especially using zirconia, no dense structures were achieved at sintering temperature due to

a lack of a glassy phase. A glassy phase melts and therefore acts as a binder for the zirconia particles. Furthermore, the sintering process by laser exposure is shortened to only few tenths of a second operating at very high temperature, whereas a conventional sintering process is longer, allowing diffusion processes to take place. However, areas were found that appeared to be sintered. This reveals that the laser beam should have generated localized temperatures above the melting point of zirconia. It is likely that a recrystallization process has subsequently occurred during the cooling down phase in those areas.

5. Conclusions

In this project, the high strength of the ceramic structure was of such importance that a glass phase was avoided. The project was initiated based on the assumption that the laser would melt the material layers which would then recrystallize while cooling down. Consequently, the uncontrolled growth of crystals would limit the strength achieved. The hypothesis of this work was proved to be true, i.e. that homogeneous thin layers suitable for the laser sintering process can be achieved using the airbrush technique. The results illustrate the difficulties of a material system without glassy phase. Yet, the analysis of the microstructure confirmed that sintering was possible in certain regions of the specimens. Thus further and more thorough investigations should focus on the basics and fundamentals of laser sintering of thin layers of ceramics. A glassy phase or a glass phase-forming component in the laser sintering process should be taken into consideration.

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References

1. Gebhardt, A., *Rapid Prototyping*. Hanser, München, 2000.
2. Tay, B. Y., Evans, L. R. G. and Edirisinghe, M. J., Solid freeform fabrication of ceramics. *Int. Mater. Rev.*, 2003, **48**, 341–370.
3. Doreau, F., Chaput, C. and Chartier, T., Stereolithography for manufacturing ceramic parts. *Adv. Eng. Mater.*, 2000, **2**, 493–496.
4. Uhland, S. A., Hohlman, R. K., Cima, M. J., Sachs, E. and Enokido, Y., New process and materials developments in 3-dimensional printing 3DP. *Mater. Res. Soc. Symp. Proc.*, 1999, **542**, 153–158.
5. Bourell, D., Wohlert, M., Harlan, N., Das, S. and Beaman, J., Powder densification maps in selective laser sintering. *Adv. Eng. Mater.*, 2002, **4**, 663–669.
6. Chartier, T., Chaput, C., Doreau, F. and Loiseau, M., Stereolithography of structural complex ceramic parts. *J. Mater. Sci.*, 2002, **37**, 3141–3147.
7. Schindler, K. and Roosen, A., Cold low pressure lamination of ceramic green tapes for the manufacture of 3D structures. *CFI*, 2006, **83**, 27–30.
8. Weisensel, H., Windsheimer, H., Travitzky, N. and Greil, P., Laminated object manufacturing (LOM) of SiSiC-composites. *CFI*, 2006, **83**, 31–35.
9. Lewis, J. A., Smay, J. E., Stuecker, J. and Cesarano III, J., Direct ink writing of three-dimensional ceramic structures. *J. Am. Ceram. Soc.*, 2006, **89**, 3599–3609.
10. Moon, J., Grau, J. E., Knezevic, V., Cima, M. J. and Sachs, E. M., Ink-jet printing of binders for ceramic components. *J. Am. Ceram. Soc.*, 2002, **85**, 755–762.
11. Kaufmann, U., Ritzhaupt-Kleissl, H. J., Harryson, U. and Johander, P., FASTFAB—a process for the free-form fabrication of 3D ceramic components. *CFI*, 2006, **83**, 13–17.
12. Ebert, J., Özkol, E., Telle, R., Fischer, H. and Uibel, K., Direct inkjet printing: a versatile method of complex shape manufacturing. In Heinrich, J.G. and Aneziris, C. (eds.), Proceedings of the 10th International Conference of the European Ceramic Society. Goeller Verlag, Baden-Baden, pp. 466–469, 2008.
13. Mott, M. and Evans, J. R. G., Zirconia/alumina functionally graded material made by ceramic ink jet printing. *Mater. Sci. Eng.*, 1999, **A271**, 344–352.
14. Oezkol, E., Ebert, J., Waetjen, A.M., Uibel, K. and Telle, R., Development of high solid content aqueous Y-TZP suspensions for direct inkjet printing using a thermal inkjet printer. J Eur Ceram Soc, 2008, **23**, accepted for publication.
15. Zhao, X., Evans, J. R. G., Edirisinghe, M. J. and Song, J. H., Direct ink-jet printing of vertical walls. *J. Am. Ceram. Soc.*, 2002, **85**, 2113–2115.
16. Noguera, R., Lejeune, M. and Chartier, T., 3D fine scale ceramic components formed by ink-jet prototyping process. *J. Eur. Ceram. Soc.*, 2005, **25**, 2055–2059.
17. Guenster, J., Gahler, A. and Heinrich, J. G., Rapid prototyping of ceramic components. *CFI*, 2006, **83**, 53–56.
18. Bourell, D. L., Marcus, H. L., Barlow, J. W. and Beaman, J. J., Selective laser sintering of metals and ceramics. *Int. J. Powder Metall.*, 1992, **28**, 369–381.
19. Exner, H., Hartwig, L., Streek, H., Horn, M., Kloetzer, S., Ebert, R. *et al.*, Laser micro sintering of ceramic materials. *CFI*, 2006, **83**, 44–52.
20. Lenk, R., Naagy, A., Richter, H.-J. and Techel, A., Material development for laser sintering of silicon carbide. *CFI*, 2006, **83**, 41–43.
21. Regenfuss, P., Hartwig, L., Kloetzer, S. and Ebert, R., Industrial freeform generation of microtools by laser micro sintering. *Rapid Prototyping J.*, 2005, **11**, 18–25.
22. Exner, H., Regenfuss, P., Hartwig, L., Kloetzer, S. and Ebert, R., Microsintering of miniature and precise components and tools. In Meyer, R. (ed.), Proceedings of the Euro-uRapid. IRB Verlag, Stuttgart, 2003.
23. Gureev, D., Ruzhechko, R. and Shishkovskii, I., Selective laser sintering of PZT ceramic powders. *Tech. Phys. Lett.*, 2000, **26**, 262–264.
24. Cruz, F., Simoes, J. F. A., Coole, T. J. and Bocking, C., Fabrication of customized bioceramic implants using selective laser sintering. *Natl. Conf. Rapid Prototyping Tooling Manuf.*, 2002, **3**, 63–70.
25. Fischer, H., Wilkes, J., Bergmann, C., Kuhl, I., Meiners, W., Wissenbach, K. *et al.*, Bone substitute implants made of TCP/glass composites using selective laser melting technique. *CFI*, 2006, **83**, 57–60.
26. Gahler, A., Heinrich, J. G., Kawanowa, H., Schwertfeger, F. and Guenster, J., Three-dimensional laser surface sintering of SiO_2 green bodies. *Int. J. Appl. Ceram. Technol.*, 2006, **3**, 331–335.
27. Gahler, A., Heinrich, J. G. and Guenster, J., Direct laser sintering of Al_2O_3–SiO_2 dental ceramic components by layer-wise slurry deposition. *J. Am. Ceram. Soc.*, 2006, **89**, 3076–3080.
28. Willoughby, C. E. P. and Evans, J. R. G., The preparation of laminated ceramic composites using paint technology. *J. Mater. Sci.*, 1996, **31**, 2333–2337.
29. Ruder, A., Buchkremer, H. P., Jansen, H., Malléner, W. and Stoever, D., Wet powder spraying—a process fort he production of coatings. *Surf. Coat. Technol.*, 1992, **53**, 71–74.
30. Polanco, R., Miranzo, P. and Osendi, M. I., Fabrication and microstructure of a ZrO_2-Ni functionally graded bonding interlayer using the airbrush spraying method. *Acta Materialica*, 2006, **54**, 2215–2222.
31. Schueller, E., Vassen, R. and Stoever, D., Production of thin ceramic layers for fuel cell electrolytes. Proceedings of Materials Week - International Congress on Advanced Materials, their Processes and Applications, Munich, Germany, September, 2000, 25–28.