

Free Forming of Porous Ceramic Parts by Rapid Freeze Gelation (RFG)

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Abstract

A novel manufacturing route is presented called rapid freeze gelation (RFG) for the fabrication of silica-sol-based ceramic bodies via freeze consolidation without geometric restrictions. The layer-by-layer shaping method permits a constant freeze velocity over the entire consolidation process. Thus, ceramic parts with homogeneous microstructures can be produced and pore structures can be adjusted as intended. The final pore structure is templated by means of ice crystallization, which is controlled by the freezing conditions and the effect of freezing modifiers such as e.g. glycerol. Ceramic lattice structures are generated with a wide range of porosities up to highly porous networks. A crucial criterion for the quality of the freezing green bodies is the interfacial connection of layers. It is shown that slow freezing rates at temperatures slightly below the crystallization temperature of the suspension are favourable to ensure a strong interconnection between adjacent layers.

Keywords: Freeze gelation, rapid prototyping, porous ceramic

1. Introduction

Freeze casting of ceramic suspensions has been developed as a direct consolidation method to produce porous ceramic parts with adjustable porosity characteristics. These ceramics show high potential for applications in the field of catalytic processes and filtration. In particular, freeze gelation offers advantageous process features owing to the irreversible consolidation of aqueous colloidal suspensions filled with ceramic powder particles. Conventional drying is then applicable in the case of freeze gelation and involves the remelting of the ice phase without losing the shape of the consolidated parts. High green strength is reached, which allows easy handling of the parts, and near-net-shape processing is applicable with low sintering shrinkage. The current achievements of this highly flexible processing technique are described in a recent excellent review.¹

When the freezing front passes through the aqueous colloidal suspension, the local distribution of the inorganic particles and the water phase changes and remarkable movement and rearrangements of the components take place. As the water phase freezes, the inorganic particles are rejected from the growing ice crystals, leading to some phase separation. Purified ice crystals are then found next to residual suspension volumes with increased particle concentration from where the water phase has been partly removed. Thus, the repulsive forces of the silica colloids are overcome and the gelation process is initiated. The generated gel network is irreversibly consolidated and the water can be removed from the system without impairing the structural stability of the body.

The freeze sensitivity of colloidal sols has been investigated since the beginning of the last century.² The major challenge in current research studies is the control of ice crystal growth since this process determines the microstructure of the consolidated body and therefore defines important properties of the ceramic part. The ice crystal growth is influenced by many factors, and several research groups have been engaged in the identification of the decisive mechanisms. For colloidal systems implying high particle mobility, Peppin *et al.* pointed out different pore structures depending on particle concentration and freeze conditions and formulated a mathematical approach to predict the evolving microstructure. Perpendicular and parallel lamellar structures as well as polygonal solid patterns were achieved under defined conditions. How to control the evolution of the microstructure throughout the whole freezing process was demonstrated in a most recent study applying strictly controlled freezing conditions.⁵ As this work is particularly related to the lamellae spacing, the interconnectivity of the emerging pore channels has been the subject of ongoing research⁶, with dendritic patterns and entanglements of pore channels as favourable features for intended applications of these porous ceramics.

The microstructural parameters of the consolidated structure depend strongly on the freezing rate, and Stratham *et al.*⁷ have classified the results of the final structure in dependence of the cooling rate. Generally, low freezing velocities are favourable for dendritic structures, while moderate velocities lead to cellular ice structures and high velocities provide more equiaxed structures. Due to the fact that the freeze-sensitive suspensions are often cooled unidirectionally, the freeze velocity varies during

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the consolidation process corresponding to the growing distance of the freezing front to the cooling medium.⁸ Gradient pore structures are then observed changing from equiaxed structures within a few millimetres near the supercooled surface to perpendicular-orientated lamellae pore structures with increasing spacing at further distance from the surface. The crystallization starts next to the supercooled surface with a high number of crystallization nuclei preventing large ice crystal growth. The lamellar pore structures are the result of crystallization approaching the state of thermal equilibrium, thus a lower rate of nucleation is given and slow growth of large ice crystal is favoured. Gradient pore structures can be prevented with multiaxial freeze conditions. Waschkes *et al.*⁵ obtained lamellae pores with nearly identical diameters over the entire test specimen owing to constant freeze velocities in a double-sided cooling setup with independently temperature-controlled cooling plates arranged opposite each other.

In the present work porous ceramic parts are prepared without any gradients and heterogeneities in porosity as are inevitable in the conventional bulk freezing process owing to thermal gradients during cooling. This restriction in the selection of pore distribution and shaping is overcome with a new shaping method called Rapid Freeze Gelation (RFG). A nearly constant freeze velocity is realized over the entire body, which favours the adjustment of homogeneous pore distribution independent of the pore content and the size and shape of the body. The shaping method is based on established rapid prototyping (RP) processes that, in their conventional versions, use polymers and waxes to enable the manufacturing of complex structures directly from computer-aided design (CAD) files. The assembly is based on the principle of slicing the CAD model and the layer-wise build-up of the desired green part by incremental deposition of the material.

Many different consolidation solutions of RP systems for ceramic materials are under development, but only few of them are available in the commercial sector. An overview is given by Tay *et al.*⁹ Mainly three basic strategies are pursued: printing systems based on aqueous suspensions with low solid contents, extrusion systems with higher solid loadings^{10–12} and direct laser sintering systems which consolidate powders or tape-cast suspensions with local thermal treatment.^{13,14} Every system has its own advantages as well as restrictions. Printing systems work mainly with solid contents less than 15 wt% and are applied for parts with low heights. Systems with high solid loadings often require additives to adapt the rheological properties and to bind the ceramic particles before the subsequent sintering step. This route has been tested by several suppliers of established polymeric-based rapid prototyping machines implementing ceramic filling materials in their systems. The required binders have to meet the conditions of optimal flowability and cause additional porosity that can hardly be avoided or intentionally adjusted. The high content of polymeric components ultimately results in high sintering shrinkage and risk of material distortion. The third route of ceramic processing in RP is direct

laser sintering, which requires high-price laser technology and the precise control of high local temperature loading.

In contrast, RFG using freeze-sensitive silica-based suspensions opens new processing opportunities thanks to the easy handling of simple systems combined with the advantages of consolidation without thermal treatment and the call for homogeneous structure formation. Organic components are not necessary for the process of extrusion and are solely used for the adjustment of pores if a definite level of porosity is required. Based on these benefits, the RFG process offers a powerful method to establish microstructures with parameters that can be adjusted in line with the intended properties and applications of the free-formed ceramic parts.

Since it can control these product characteristics, Rapid Freeze Gelation is an interesting technology to produce individual and complex structures for several applications. In the field of filtration and catalysis, chemical- and thermal-resistant structures can be produced with predetermined bimodal pore size distributions. Optimal conditions for high fluid permeability and catalytic activity are then provided by the adjusted interspaces between adjacent strings, the micropores as residues of the ice templates and interparticle voids, respectively. Further applications are projected in the fields of barrier systems for gas cleaning and scaffolds for bone replacement and tissue engineering.

II. Experimental Procedure

(1) Preparation of colloidal suspensions

For all suspensions, commercially available silica sol (Köstrosol 3550) with a total solid content of 50 wt% was used as the basic component. The colloidal particles with a median size of 35 nm are stabilized with sodium hydroxide. The adjusted pH 9.5 ensures long-term stability. With the addition of mullite powder (Symulox M72MC) with a median particle size of 4 µm, a solid content of approximately 88 wt% was obtained for the standard mixed suspension termed M88. The suspension was prepared in a laboratory mixer by adding the powder to the sol and homogenized with a further 5 min of stirring. To destroy agglomerates, the suspension was put in a jar mill for 12 h. An additional stabilization procedure for the filling particles was not necessary, since sedimentation was not observed for the relevant rapid freeze gelation processing period of maximum 1 h. After preparation, the suspension showed shear-thinning behaviour typical of high solid loads. This pseudo-plasticity supports the shape stability of bodies after deposition. In combination with the spontaneous freezing effect, it is then not necessary to ensure a pronounced yield stress of the slurry to avoid mass flow after deposition. The solid loading capacity of the system can then be optimally exploited without being impaired by rheological restrictions.

Besides the standard composition M88, several modifications of the suspension were composed to obtain different final microstructures, including lamellar and more equiaxed pore structures as well as open pore networks. The freezing conditions were kept constant for all suspensions and the ice crystal growth was not intentional-

ly changed as is often the case with the more conventional method of freeze velocity variation. A more effective control of the ice crystal growth is then effected by suspension modification.

(2) Addition of glycerol

One opportunity to prevent ice crystal growth, favouring a more uniform microstructure, is the application of glycerol as previously investigated by other groups^{15,16}. Glycerol is soluble in water and lowers slightly the freezing point of aqueous suspensions. The trihydric alcohol attaches itself to the water molecules and affects the arrangement of the hydrogen bonding network. The course of crystallization and the size of ice crystals are directly linked to the amount of alcohol. A further benefit is the reduced volumetric expansion of the water/glycerol mixture, which lowers the risk of crack formation during freezing. The amount of glycerol added also has a distinct influence on the final green body stability observed for freeze-cast parts being dried by subsequent sublimation. Whereas glycerol contents < 20 wt% do not affect the shape or surface structure, higher amounts up to 30 wt% lead to moist and tacky parts. Additionally, the use of glycerol must be critically evaluated in the presence of dispersants which may result in the formation of micelle structures.

For the RFG process, 13 wt% of glycerol (Acros Organics, Belgium) was added to the freeze gelation suspensions termed M88G. With this small amount, crystallization is not completely suppressed; the crystal size is, however, clearly affected by the glycerol.

(3) Preparation of freeze-sensitive emulsions

To realize high open porosities, a new process route was adapted from the preparation of cellular ceramics based on direct foaming of high-alkane-phase emulsified suspensions (HAPES). Emulsions are defined as systems with more than one fluid immiscible with each other. Barg *et al.*¹⁷ prepared and emulsified aqueous alumina suspensions using sodium lauryl sulphate as anionic surfactant and decane as dispersed phase. Air bubbles, which would influence the foaming procedure and final porosity, were eliminated by de-aeration under reduced pressure. The emerging cellular ceramic structures were prepared by slip casting, autonomous foaming and drying over several days. The sintered alumina foams had open cell sizes in the range of 3 to 9 μm which were interconnected by dense struts. As a new approach, this process was linked with the freeze gelation process with the effect that the consolidation is strongly accelerated and the pore size is solely related to the decane droplet size. A fundamental study of freeze gelation of emulsions is in progress and will be published with more details of microstructural analysis.

For the RFG process, 0.6 wt% surfactant (Lutensid AS 2230, BASF) and 22.8 wt% decane ($\text{C}_{10}\text{H}_{22}$, Fluka) were added to the silica/mullite suspension. The suspension with total solid load of 65.3 wt% was emulsified in a laboratory mixer at a mixing velocity of 2500 rpm for 2 min under reduced pressure of 100 mbar. These samples are termed E65.

(4) Experimental setup and RFG process

The RFG setup is shown in Fig. 1. The building platform was positioned in a cooled soak bath composed of silica oil with hydrophobic behaviour. This arrangement offered the possibility to extrude and deposit the ceramic suspension into the cooled medium, avoiding interferences of the freezing process by the atmosphere, e.g. thermal turbulences and binding of water from atmospheric humidity on layer surfaces. The cooling temperature was controlled by a separate cooling circuit, avoiding turbulences in the liquid medium enclosing the extruded ceramic. Fast freezing was effected with fixed temperatures of the cooling medium slightly below the crystallization point of the applied suspensions at -4°C and -10°C . The ceramic suspensions were extruded with an extrusion velocity of 74 mm/s by the extrusion unit, which consisted of a piston, cylinder and an orifice with an aperture cross-section measuring 0.3 mm.

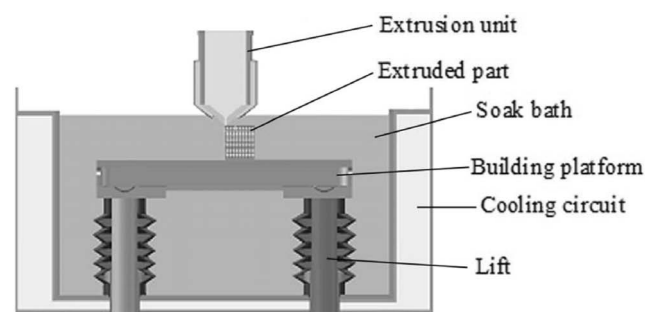


Fig. 1: Sketch of the extrusion assembly for the RFG process.

To build up the CAD-designed parts and structures, the extruder was moved in a horizontal plane according to the required position. After completing the extrusion process for each individual layer the building platform was lowered analogous to the thickness of the preceding layer.

A lattice structure with the size of 20 x 20 x 10 mm was chosen as the test geometry (Fig. 2). The spatial separation of the strings in the horizontal planes allowed conclusions to be drawn with regard to the effect of the extrusion parameters on geometric reproducibility and bonding behaviour at intersection points. The bonding of the strings in vertical direction was of particular interest. Whereas in conventional freeze casting procedures the bulk freezes continuously, in the RFG process the ceramic body is consolidated discontinuously layer by layer. The bonding of the newly deposited suspension to the formerly deposited and already frozen layer therefore demanded particular attention. The interconnection of freezing suspensions by successive bonding has not been described in the literature so far and should be examined as a joining method of components in different conditions, i.e. liquid and solid.

The extruded bodies were reheated to room temperature, during which the ice phase remelted. As the wet bodies keep their shape and stability owing to the colloidal network formation during freezing, the parts could be dried at ambient atmosphere and subsequently sintered at temperatures up to 1550°C . The geometrical fidelity, bonding qualities, and microstructure of the lattices were analyzed on polished and fractured surfaces using scanning electron

microscopy SEM (CamScan; USA). The pore size distributions were determined by means of mercury intrusion (Pascal 140 – 440; ThermoElectron Corp., Milan, Italy).

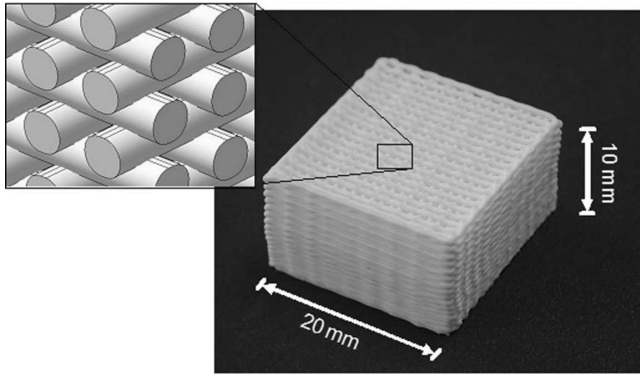


Fig. 2: Photo of extruded lattice structure and enlarged schematic view of the alignment of the extruded strings.

III. Results and Discussion

In order to evaluate the specific advantages and peculiarities of the RFG process, the study has been focussed on (1) the formation of lattice structures, (2) the bonding processes between two adjacent strings and (3) the microstructural characteristics to be realized during deposition, freezing, drying, and sintering. During the time interval between the deposition events of two adjacent strings, the freezing process is proceeding in the previously deposited strut (A) while the succeeding string (B) is going to be deposited in its viscous state owing to its higher temperature. Some partial and transient remelting may then take place in the contact region of string (A), which could help ensure efficient bonding between the two strings. Since the evolution of the microstructure is controlled to a large degree by crystallization and crystal growth of the ice phase, the thermal gradients and transients are of great importance for the final microstructure.

(1) Lattice formation

The broad variability of lattice structures to be formed with the RFG process is demonstrated in Fig. 3. The effects of the deposition variables on the emerging types of lattice structure are illustrated under fixed conditions for slurry composition and viscosity; the temperature of the cooling medium is also unchanged. Lattice structures are deposited layer by layer, with each layer consisting of parallel extruded strings and the orientation of the strings changing from one layer to the next by 90°. Crossing of the strings from adjacent layers therefore appears as shown schematically in Fig. 3. Depending on the extrusion parameters, the emerging lattice structures can reach a fairly high density, which is enabled by the rather large deformation of the strings before their consolidation by freezing. On the other hand, a lighter lattice with reduced contact areas between adjacent struts can also be obtained. This is illustrated in Fig. 4, which shows micrographs of polished sections of the crossing area for both cases.

The process parameters governing the evolution of the lattice structure are the volumetric mass flow $\dot{v}_s$, the travelling velocity of the extrusion nozzle v_A and the displace-

ment of the nozzle h being lifted to the position of the next layer after completion of the previous layer. The effects of these deposition parameters define a building factor BF according to equation (1).

$$BF = \frac{\dot{v}_s}{v_A} (h^{-2}) \quad (1)$$

The factor BF corresponds to the slope of the lines in Fig. 3 and BF values between 1.06 and 3.2 were realized in the extrusion test series. With presetting of the parameters as shown in Fig. 3, the RFG process leads to the intended lattice structures with different densities. The effect of different ratios of the volumetric mass flow $\dot{v}_s$ on the travelling velocity v_A as a function of the nozzle displacement h is manifested by the two limit cases when the mass flow is too fast or too slow. If the mass flow is below the lower limit, the space between the nozzle and the previously deposited string cannot be properly filled and the new string is extruded without any noticeable back pressure. The string then freezes before touching the formerly deposited layer and the cylindrical string geometry allows only line contact between adjacent strings. This constellation leads to insufficient strength to withstand the thermal stresses during drying and sintering. A mass flow $\dot{v}_s$ beyond the upper limit leads to complete filling of the space between the nozzle and the formerly deposited layer and, as a result of the high back pressure, to extensive squashing of the strings. Owing to their extreme deformation, the strings overlap and the high fidelity of structure formation is lost. An adequate ratio of the relevant parameters is then needed as described by the BF factor, ensuring sufficient space filling and contact area between adjacent strings without losing the shape precision of the deposited parts.

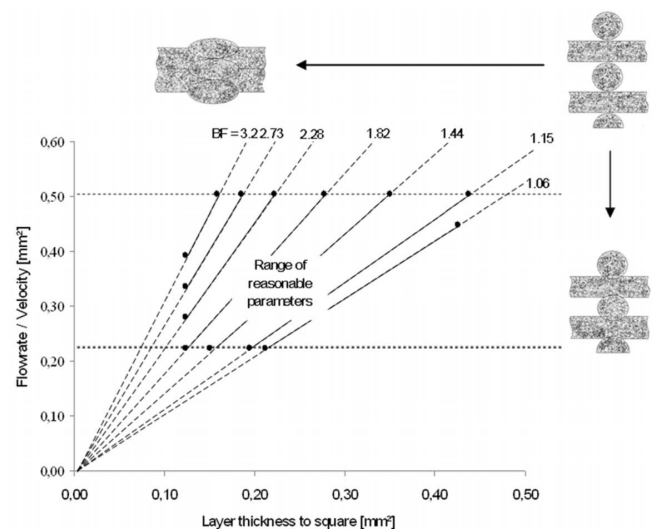


Fig. 3: Shape of strings and density of lattice structure depending on the BF factor. A range of RFG parameters leading to consolidated lattice structures is marked in the figure.

(2) Layer bonding

As revealed by the microsections in Fig. 4, bonding between adjacent strings is not acceptable in these cases. The distinct border between two strings deposited one after

the other is clearly visible. The disturbed transition between adjacent regions within a monolithic part is a common problem in moulding processes (injection moulding, slip casting, etc.) if the generation of the part does not proceed continuously and the moulding process is interrupted.

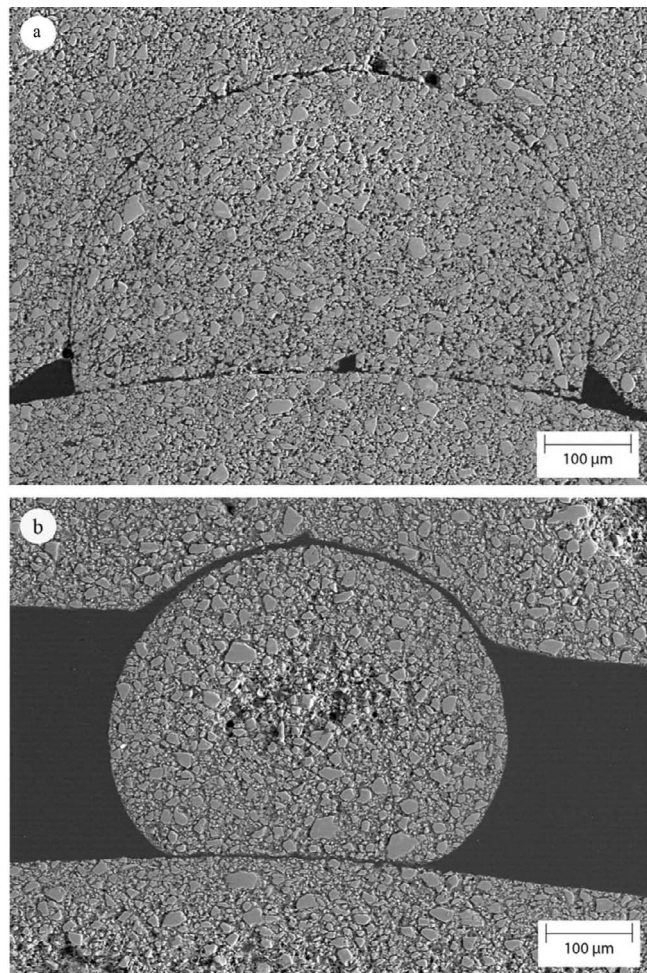


Fig. 4: Polished sections of the contact area of adjacent strings as prepared with different process parameters: (a) BF = 3.2; (b) BF = 1.06.

This feature is even more pronounced in case of the RFG process, since extrusion and deposition of the struts is accompanied by phase transformation, i.e. freezing of the water phase. The typical situation of string deposition can then be envisaged as bringing two strings in close contact where the previously deposited string is solid because it is frozen while the succeeding string is deposited in its viscous state. Thus, both strings differ in their surface state to some degree owing to the phase transformation and separation processes. Although this microstructural discontinuity describes a principal feature of the RFG process, it is the purpose of the RFG development work to minimize the effects of these discontinuities in the lattice structure. One of the most effective means for this purpose is to effect a partial remelting in the string contact region caused by heat transfer from the new viscous string to the previously deposited frozen string. This effect can be achieved most simply with the appropriate choice of the temperature of the cooling medium. The best compro-

mise can be achieved with this choice when remelting is ensured without impairing the stability of the lattice structure. In case of the samples with discontinuous transitions between adjacent strings as shown in Fig. 4 (a) and (b), the temperature of the cooling medium was fixed at -10°C . This temperature is too low to allow sufficient remelting to avoid any disruption between adjacent strings. In contrast to this “deep freezing” case, a cooling temperature slightly below the crystallization temperature favours the continuous formation of the lattice structure even with this layer-by-layer process. As demonstrated in Fig. 5, this result is achieved at the higher cooling temperature of -4°C .

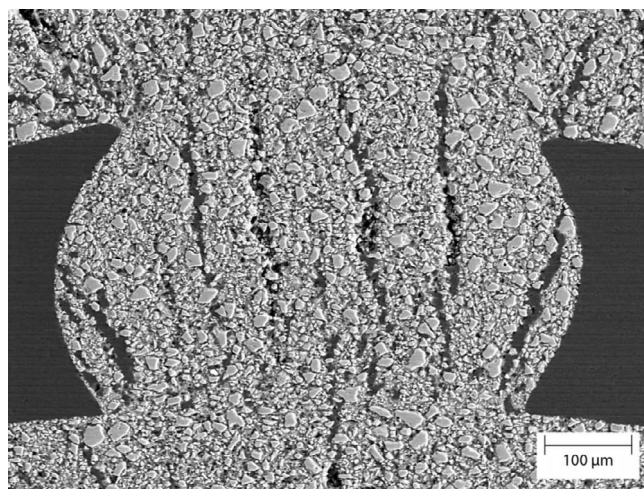


Fig. 5: High bonding quality and continuous lattice formation in the green M88 sample for moderate cooling rates near the crystallization temperature of -4°C .

Owing to the minor undercooling, the subsequently deposited strings have sufficient thermal energy to remelt the near-surface region of the formerly deposited string. Thus, the consolidation proceeds as a continuous process across the original border line between the two strings and no gap appears between them (Fig. 5).

The structural stability of a frozen colloidal suspension is retained even after remelting of the ice phase, which is an effect of the irreversible sol-gel transition caused by the freezing process.⁸ The growing ice crystals repress the solid particles of the suspension and lead to increasing particles densities between the ice crystals. Besides the principal tendency of colloidal systems to gelation, an additional physical effect can be observed which is based on the forced closer contact of the colloids owing to their increased concentration. For the particular suspension in this study, which consists of μm -mullite particles (filler) and nm-silica colloids, this effect is visualized in Fig. 6. The high concentration of silica colloids leads to their assembly and dense packing in the interface of the filler particles. The interstitial volumes between the filler particles are then occupied by these colloidal assemblies, ensuring irreversible bonding and forming a kind of cemented mullite network. This process is very effective in providing a robust green microstructure providing the lattice structure is not disturbed by gap formation between adjacent strings owing to overhasty freezing.

(3) Microstructures from the RFG process

If an aqueous colloidal suspension containing larger filler particles is extruded in the RFG process with moderate freezing velocities, a lattice structure can be reproducibly formed without delamination, as is demonstrated in Fig. 7.

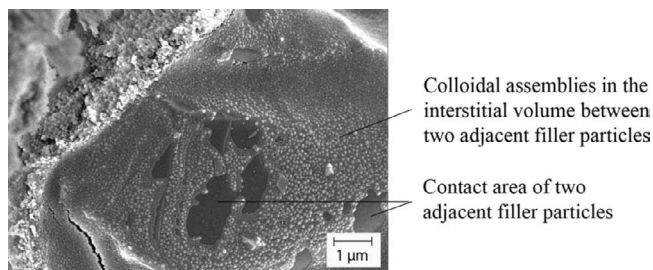


Fig. 6: Colloidal silica particles form a nearly dense interface between the larger filler particles and glue them together in the green part.

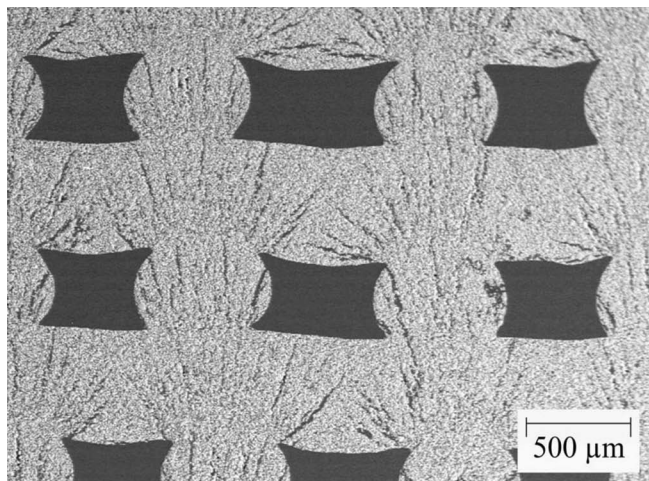


Fig. 7: Cross-section of lattice structure prepared with the standard suspension M88. Lamellae pore channels crossing the microstructure.

After freezing, reheating and drying, these parts retain considerable strength in their green state, which allows their further handling without any problems. The green strength is caused by the irreversible sol-gel transition and network formation which is not interrupted by delamination of two adjacent strings. In addition, the large pores templated by the former ice crystals are integrated in the microstructure without impairing the lattice stability. These elongated pores prove the fact that the consolidation proceeds continuously from the earlier deposited string to the succeeding string. The originally distinctive border line between both strings is replaced by a region owned by both strings, where freezing and gel network formation proceed, leaving no trace of the original border. This is manifest in the polished section of a sample after sintering at 1550 °C for 2 h as shown in Fig. 8(a).

The pore size distribution reveals a bimodal character as shown in Fig. 9(a). The large interstitials of the lattice structure are not detected by the Hg porosimetry used in this study. The two main frequencies around 15 and 1000 nm are related to the interstitials of the colloidal network and the ice-templated pores, respectively.

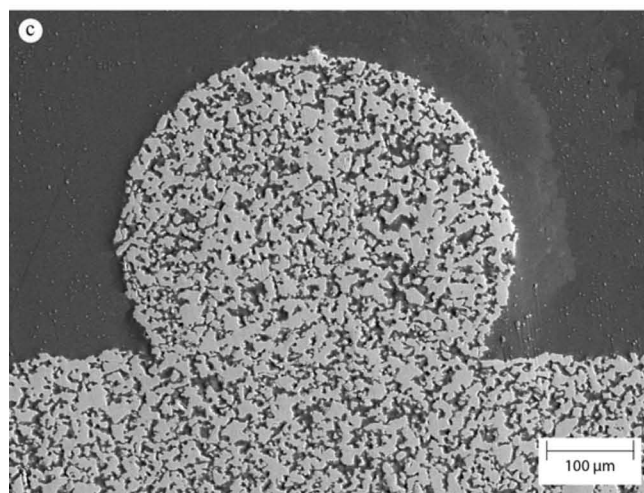
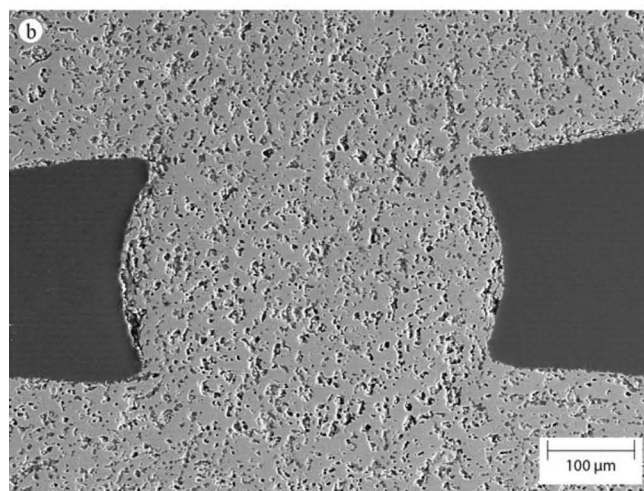
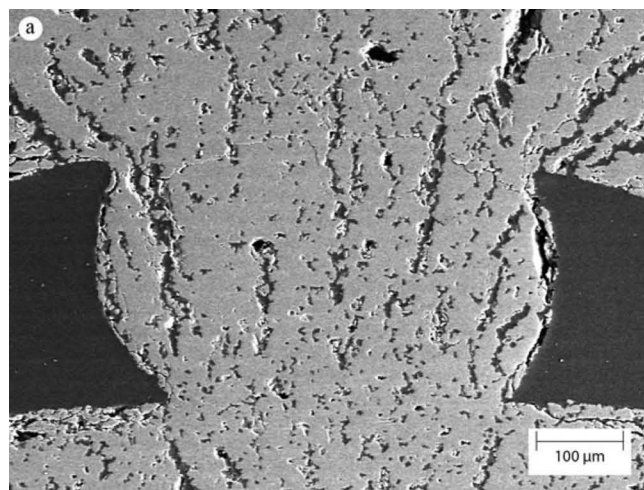


Fig. 8: Pore structure of sintered bodies depending on slurry composition, sintered at 1550 °C: (a) Channel-like pore structure for suspension M88, (b) Large fraction of closed pores for suspension M88G with glycerol, (c) Highly open porous structure for emulsion E65.

The freezing behaviour and the resulting microstructure can be effectively modified with the addition of glycerol to the aqueous suspension. The growth of ice crystals can be suppressed and the freezing temperature be lowered. The freezing conditions then have to be adapted to the changed solidification temperature and -7 °C has been determined as appropriate temperature of the cooling medium in the case of the glycerol-containing sample M88G. Although

the bimodality of the pore size distribution is retained, both peaks are approaching each other and the main frequencies are found at around 30 and 350 nm as shown in Fig. 9(b). The homogeneous microstructure of M88G is documented in Fig. 8(b), revealing both the absence of any delamination processes and elongated pores from former ice crystals. Both microstructures in Fig. 8(a) and (b) are compared in Fig. 8(c) with the sintered sample formed by the RFG process with the emulsified suspension E65. This microstructure is again to be characterized by its homogeneous delamination-free lattice structure and a high porosity that is known to reach values around 95 % in bulk systems.¹⁷

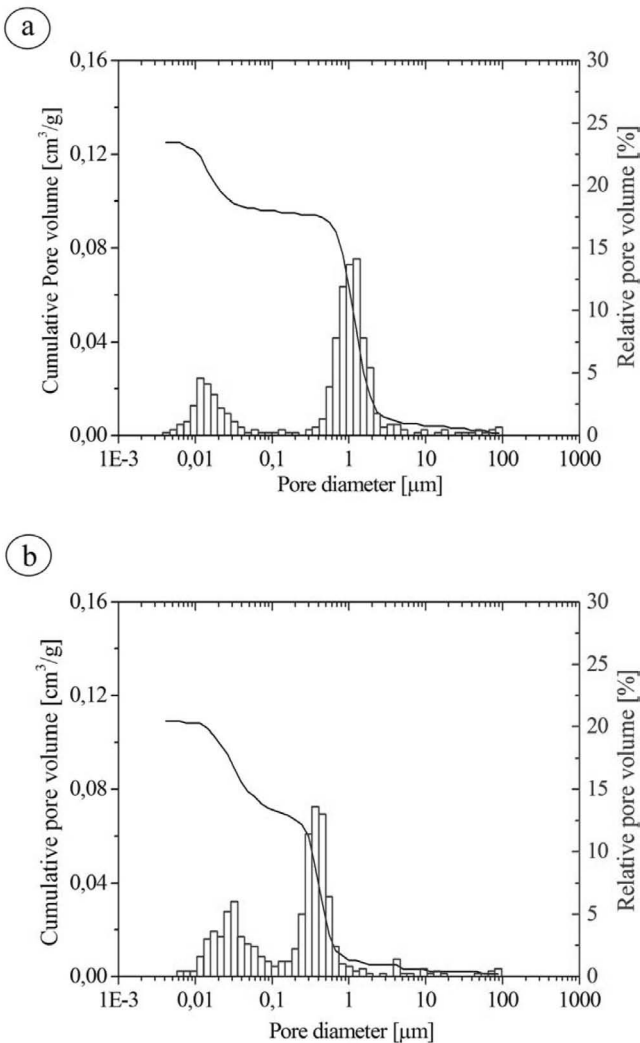


Fig. 9: Pore size distribution of green bodies depending on cooling temperature and suspension composition: suspension M88 at -4°C (a), suspension M88G with glycerol extruded at -7°C (b).

During sintering, the different pore types reveal their varying potentials to shrink and to be eliminated by sintering mechanisms. As presented in Fig. 10, the sintering process leads to characteristic differences between the various samples. The small pores from the interstitial voids between the colloidal particles are eliminated in all sintered samples. The foam-like microstructure of the E65 suspension is characterized by a high porosity of 30 vol% with uniform pores measuring $5\text{ }\mu\text{m}$ in diameter while slightly smaller pore sizes are detected by means of Hg porosime-

try in the more densified microstructures of the samples M88 and M88G.

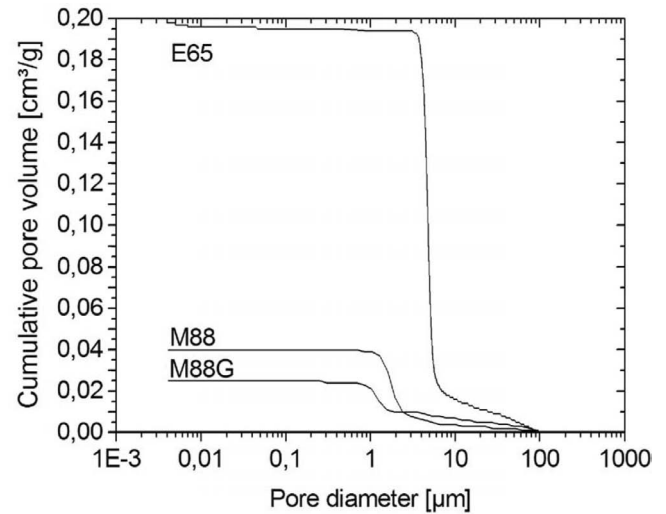


Fig. 10: Cumulative pore volumes in sintered (1550°C) samples depending on suspension modification and composition.

IV. Conclusions

The novel RFG process allows the processing of silica-sol-based ceramic powder suspensions via a rapid prototyping route. This layer-by-layer generation of ceramic components is characterized by the high degree of shaping variability of the deposited parts. The particular advantage of this method relates to the constant freezing rate which is easily fixed through the entire production process, leading to homogeneous microstructures. In contrast, the more conventional bulk freeze casting techniques are subjected to larger thermal gradients with the consequence of rising tendencies towards anisotropic features of the microstructure and the properties of the fabricated parts.

The risk of delamination processes taking place between adjacent layers is excluded in the RFG process by adapting moderate freezing temperatures and freezing rates. These adjusted parameters lead to gapless joints between adjacent layers owing to local remelting and fusing of their contact regions. Suitable deposition parameters are then defined and noted as the building factor BF, resulting in strong, crack-free structures of the parts with adjustable densities and lattice features.

The assembly of colloidal particles in the interface of adjacent ceramic filler particles is a constitutive element of the freeze-induced gelation process. The increased concentration of colloids in the interface is a consequence of the freezing process with its ongoing ice formation, repulsion of foreign particles by the growing ice crystals and phase separation processes. Improved bonding and network formation of the colloids and filler particles is initiated in these volumes of high particle densities.

Compressive stress fields originated by the lowered ice density in comparison to liquid water provide an additional mechanical effect favouring these bonding processes. As a consequence, sol-gel transformation proceeds as an irreversible process allowing conventional drying of the reheated wet parts without cracking. The capillary forces operating inside the parts during drying do not

overcome the induced bonding strength. Easy handling of the strong green parts and their storage or application as filters, carriers and substrates in aqueous environments are then possible without dissolution and fracture processes.

The pore size as well as their shape and the porosity level can be adjusted as required by individual applications of the deposited parts. For these purposes, the RFG process has been proven to allow extrusion and deposition of modified suspensions that have been emulsified with the addition of alkane phase or freezing modifiers, e.g. glycerol.

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