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# Fabrication of fibre reinforced green bodies by electrophoretic deposition of silicon powder from aqueous suspensions

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Fine silicon powders with a mean particle size of 0.5 $\mu$m were used to prepare aqueous suspensions for electrophoretic deposition (EPD). A cellulose film membrane was proved to be a cost-efficient alternative material to the dialysis hoses with excellent properties for the EPD-process. Several organic additives were tested to stabilise the suspension against sedimentation effects, to increase the electrophoretic mobility of particles and to optimise the mechanical properties of the dried green bodies. Mainly the electrokinetic sonic analysis (ESA) was used to characterise the influence of the additives and several parameters like solids content and ionic strength on the thickness of the electrical double layer. A computer-controlled and monitored EPD led to a dense and homogeneous packing of the powder and contributes to the understanding of deposition mechanisms. Even severe machining of the dried green bodies was possible. Using the planetary milled silicon powder the small spaces between the carbon (C-) or silicon carbide (SiC-) monofilaments of the fibre fabrics were infiltrated homogeneously by the silicon particles.

## 1. Introduction

EPD is a manufacturing process to handle sub-micron and micron particles and to get high package densities of the green bodies [1]. In this work silicon powder was selected to form a reaction-bonded $Si_3N_4$ (RBSN) matrix for CMCs because of the small dimensional changes during nitridation [2]. The relatively low temperature of less than 1400°C for reaction bonding leads to low reaction level of the fibres with the silicon powder and allows the use of C- as well as SiC-fibres with diameters of 7 to 10 $\mu$m, especially in the case of coated fibres [3]. For very fine milled silicon powders it was demonstrated, that the temperature for reaction bonding in nitrogen atmosphere can be lowered to 1250°C [4, 5]. Frequently, ceramic RBSN-matrix composites (CMCs) produced by common powder processing were hot pressed. In this case, the very thick SiC-fibres ($\sim$140 $\mu$m) of the type SCS-6 from Textron were used because of the lower sensitivity to degradation during heat treatment [6–8]. To avoid or reduce fibre damage during densification a high packing of the silicon particles should be achieved by EPD.

Although EPD has been frequently performed in organic solvents [9], in this investigation water was used due to reasons of industrial safety, a high deposition rate at low electric fields [10] and the environmental protection. The problem of gas bubble formation because of the electric field strength higher than $\sim$2 V/cm was solved by introducing a cellulose membrane film instead of the common dialysis hoses in front of the electrode as described by Clasen *et al.* [11, 12].

## 2. Experimental procedure

### 2.1. Materials

Commercially available silicon powder (Grade AX 05, H.C. Starck, Germany) was used for this study. To reduce the particle size the powder was ball milled in a planetary mill using a silicon nitride grinding medium for up to 30 h (typically 8 h) employing different organic solvents like ethanol or acetone. The ball-to-powder weight ratio ranged from 10:1 to 40:1, and the milling speed was $\sim$160 rpm. To measure the particle size range and specific surface area of the silicon powders the laser light scattering method (Model: Cilas 850 HR, Quantachrome, United States) and Brunauer-Emmett-Teller (BET) adsorption (Model GEMINI 2370, Micromeritics, United States) techniques were used.

As an alternative membrane a regenerated and uncoated cellulose film (325 P, Sylvaphane, Netherlands) normally utilised in the packaging industry was used. Sylvaphane produces some different uncoated regenerated cellulose films, which are suitable for EPD-processing. The advantages are availability in large dimensions, good mechanical characteristics primarily in aqueous media and insolubility in water based or organic solvents and the low price (Table I).

Different commercially available and self-synthesised organic additives were tested to allow an efficient electrophoretic deposition, to improve

TABLE I Data sheets of the regenerated cellulose film Sylvaphane *P* used in this paper

| Type | Thickness ($\mu$m) | Reel-width (mm) | Reel-length (m) |
|---|---|---|---|
| | | Dimensions | |
| 325 P | 22.6 | 50–1490 | 1600–6400 |
| | | Physical properties | |
| Density (g/cm$^3$) | | | 1.44 |
| Tensile strength (MPa) | | | 55–120 |
| Young's modulus (GPa) | | | 3–5 |
| Water vapour permeability (g/(m$^2$*d)) | | | 1500 |
| Used reel: 0.5 m × 50 m; Price ∼1 €/m$^2$ | | | |

TABLE II Organic additives used to improve the efficiency of electrophoretic deposition and the mechanical stability of the deposited silicon particles

| Type | Company | Substance |
|---|---|---|
| | a) Suitable dispersing agents | |
| SF11 | Self-synthesised | Acrylic acid/butyl acrylate copolymer |
| KD1 | Self-synthesised | Acrylic acid based |
| WK119 | Self-synthesised | Acrylic acid/maleic acid/ methacrylic acid copolymer |
| WK60 | Self-synthesised | Poly allyl alcohol |
| | b) Suitable binders | |
| Acronal S702 | BASF | Synthetic latex based |
| Styrofan D623 | BASF | Synthetic latex based |

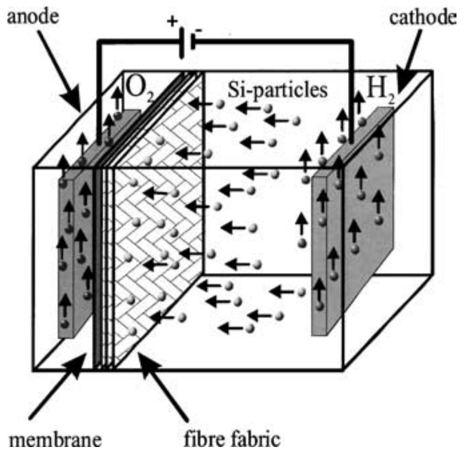

*Figure 1* Anodic deposition of the silicon powder on fibre fabrics from aqueous suspensions by the membrane technique.

the mechanical stability and to enable the handling of the resulting green bodies. In Table II only those organic additives, which were most suitable are listed. The self-synthesised dispersing agent named SF 11, a statistical copolymer of acrylic acid and butyl acrylate including 30 wt% active substance content, primarily was used in this work. For the binder, a commercially available copolymer of the type Acronal S702 (BASF, Germany) was utilised.

Two types of fibre fabrics were placed in front of the membrane to be impregnated by means of the electrophoresis of Si-particles (EPI). A carbon coated silicon carbide fibre fabric (Nicalon Nl-607 Harness Satin, Nippon Carbon, Japan) as well as a carbon fibre fabric (Sigratex KDL 5002/12, SGL Carbon Group, Germany) uncoated and coated with pyrolytic carbon (PyC) (Schunk Kohlenstofftechnik, Germany) were used (Table III).

## 2.2. EPD-Cell

The EPD (Fig. 1) was carried out in a self-designed polyvinyl chloride (PVC) cell, which allows both easy handling and a relatively large effective deposition area of (90 × 100) mm. The space between the stainless steel electrodes and the membrane was adjustable from 10 to 40 mm. The power supply (SM 300-10 D, Delta Elektronika, Netherlands) providing both constant voltage (CV) up to 300 V and constant current (CC) up to 10 A was connected to a computer for programming and monitoring. A software programmed in Lab-View$^{\text{TM}}$ (National Instruments, United States) was applied for online monitoring the current and voltage during deposition.

## 2.3. Silicon suspensions

The suspensions were obtained by introducing the silicon powder with different solids contents in water adding different organic additives like dispersing agents and binders under normal stirring at ∼500 rpm. To prevent the powder from sedimentation and to homogenise the suspension in a second step, high speed stirring (∼20000 rpm) and an ultrasonic mixing were applied. Suspension characteristics, such as electrophoretic mobility, conductivity and viscosity, were determined by ESA (Model MBS 8000, Matec, United States) and rheological measurements (RHEOLAB M 100, Physica Messtechnik, Germany) using the silicon powder AX 05 in the as-received condition.

## 3. Results and discussion

## 3.1. Silicon powder

The particle size distribution and the surface area of the silicon powder before and after milling are given in Table IV. Best results were achieved by milling for 8 h in ethanol with spheric grinding bodies and a ball to powder ratio of 1:40 by weight using the small balls leading to a mean particle size of $d_{50} = 0.5$ $\mu$m. The

TABLE III Characteristics of the fibre fabrics used

| Type | Fibre | Weave | C-Coating (nm) | Sizing | Fineness of yarn (tex) |
|---|---|---|---|---|---|
| Nicalon Nl-607 | SiC | Satin | ∼30 | PVA | 200 |
| Sigratex KDL 5002/12 | C | Plain | None | Epoxy | 200 |
| Sigratex KDL 5002/12 | C | Plain | ∼150 | None | 200 |

TABLE IV Characteristics of the silicon powder used before and after milling

| | Particle size ($\mu$m) | | | |
|---|---|---|---|---|
| Powder | $d_{10}$ | $d_{50}$ | $d_{90}$ | Surface area (m$^2$/g) |
| Grade AX 05 | 0.50 | 3.07 | 6.61 | 2.98 |
| 8 h milled in EtOH | 0.29 | 0.50 | 0.78 | 29.35 |

organic was needed to prevent the milled silicon from hydrolysis due to the increase of the surface area.

### 3.2. Membrane

The real pore-diameters of the membrane are difficult to measure (<100 nm, mercury porosimetry) especially in a wet and stretched condition during EPD, but they are so small that even organic molecules (e.g., $C_6H_{12}O_6$) or ions (e.g., $OH^-$ or $H_3O^+$) could not pass easily the membrane without an electric field. Therefore, the membrane material is suitable for sub-micron particles deposition, however, the conductivity of the suspensions has to be lower than that of the compensation fluids to avoid an osmotic flow against the EPD direction.

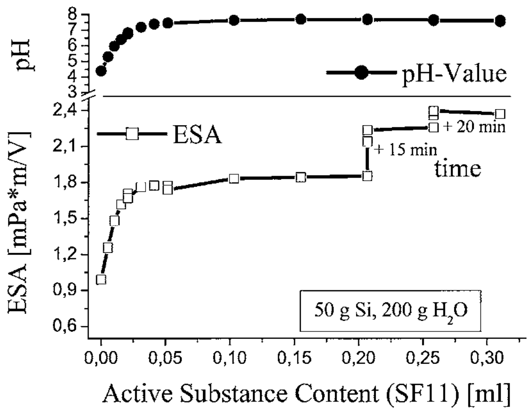

*Figure 3* Influence of dispersing agent SF11 and its active substance content on the ESA signal and the pH-value. After the first saturation it takes some time to achieve a further coating of the surface shown in the graph.

### 3.3. Suspension characteristics

ESA-measurements are very suitable for the characterisation of the suspensions because of the direct proportionality of the signal to the electrophoretic mobility of the particles even when they are not spherical (cp. $\zeta$-potential). Thus, the ESA-signal is an indication for the value of the surface charge. As already reported, silicon particles in aqueous suspensions have negative surface potential at pH-values above the isoelectric point of about 2 due to the acidic Si—OH groups as a result of surface hydrolysis reactions [13]. Therefore, there is an increase of the ESA-signal at higher pH-values, however, pH-values above 9 should be avoided due to intensive gas bubble formation by the surface reaction. A further increase of the surface charge and a steric repulsion of the silicon particles were achieved by adding an organic dispersing agent, and consequently, the sedimentation behaviour of the powder was improved. Fig. 2 shows the ESA-signal dependent on the silicon content for various self-synthesised and commercially available additives. These results demonstrate, that the addition of the self-synthesised copolymer SF11 leads to the highest ESA-values. Fig. 3 gives the ESA-signal and the pH-value dependent on the active substance content of the used dispersing agent as well as the time dependency of adsorption. The high surface activity and the high efficiency of the dispersing agent SF11 are demonstrated in this figure.

Well dispersed suspensions with reduced sedimentation lead to sufficient EPD-results (e.g., homogeneity, deposition rate, green density etc.) because of the higher binding energy coming from the strong repulsive forces which have to be overcome [14].

Different binders were introduced to allow a crack free drying under normal room conditions and to improve the mechanical stability of the green bodies showing high brittleness at the beginning of the investigation. ESA-signal and pH-value dependent on the addition of $NH_3$-solution and the influence of the binder is shown in Fig. 4. As a result, only the commercially available binder of the type Acronal S702 leads to an increased ESA-signal. This is an indication for an enhanced absorption on the silicon powder surface. Therefore, an improved surface charge was observed.

As often described, the lowest viscosity corresponds to the highest ESA-signal and highest stability of the suspension against sedimentation effects. In Fig. 5 it is demonstrated that the dependency of viscosity from the

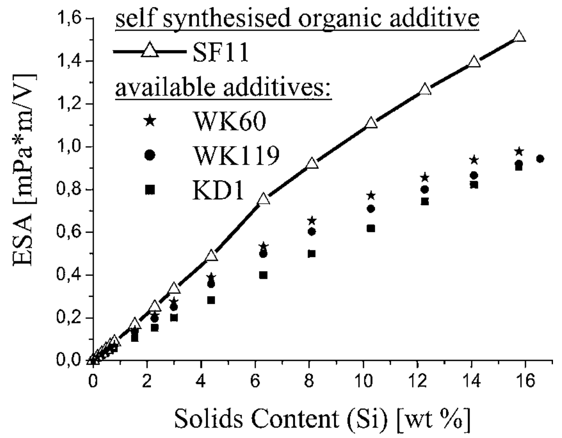

*Figure 2* Influence of the solids content on the ESA-signal. The highest ESA-signal achieved by adding the self synthesised dispersing agent SF11 and its dependency to the solids content of the suspension.

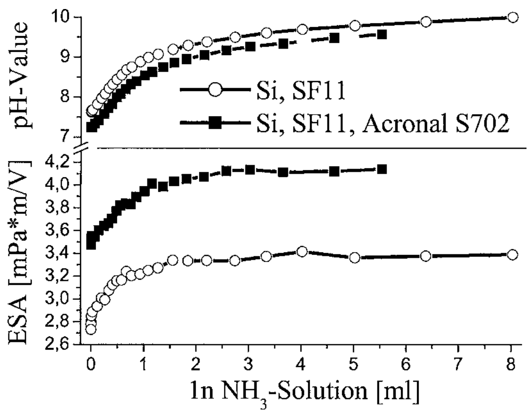

*Figure 4* ESA-signal and pH-value characteristics dependent on the addition of $NH_3$-solution before and after introducing the binder Acronal S702 to the suspension of silicon powder and the dispersing agent SF11.

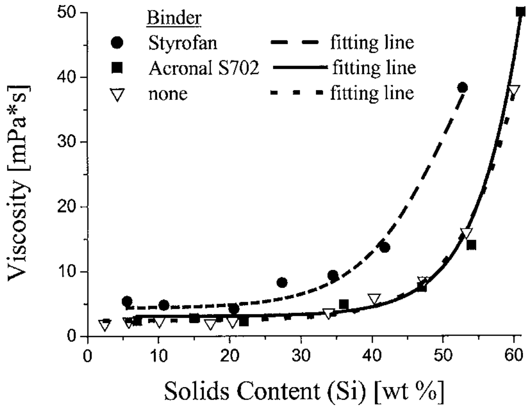

*Figure 5* Influence of different binders on the viscosity of the silicon suspensions containing the dispersing agent SF11. The increase of viscosity by addition of binders was minimised when using the binder Acronal S702 (BASF). The solid lines are fitted to the data by a sigmoidal function.

solids content can be fitted by a sigmoidal function:

$$\eta(x) = \frac{(A_1 - A_2)}{(1 + e^{((x-x_0)/B)})} + A_2$$

with $\eta$ viscosity; $x$ solids content and the fitting parameters $A_1 \eta(x \to 0)$; $A_2 \eta(x \to \infty)$; $x_0$ inflection point and $B$ the gradient of $\eta$ for $x = x_0$.

Introducing organic additives to the Si-suspensions, this behaviour was observed in all cases.

However, the main advantage of the binder was the improvement of mechanical behaviour of the green body characteristics allowing machining with common tools like sawing and drilling (Fig. 6). The binder leads to slightly flexural compounds with reduced brittleness as a prerequisite for scaling up green body dimensions by laminating techniques.

### 3.4. Computer controlled EPD

The anodic deposition of the particles enables the use of stainless steel electrodes. A small weight loss of the anode material was observed during EPD, but there was no permeability of the membrane for these ionic impurities and, therefore, no Fe-ions were detected in the suspension.

Instead of measuring the deposited weight, as frequently described [15], in this paper the EPD was performed by computer programming and monitoring the voltage and the current over deposition time. The data give some indications about the EPD-process:

– Sometimes an increase of the voltage for half a minute at the beginning was observed under constant current conditions. The differences in the conductivities of the suspension and compensation fluid might be responsible for this phenomenon caused by the osmotic flow of water through the membrane.

– The steady increase of the resistance due to strong sedimentation of the particles in the case of not optimised organic additives and suspension preparation was observed.

– Intensive gas bubble formation in front of the membrane in the deposit caused by decomposition of the water occurs, if the voltage exceeds a certain value, which depends on the parameters of the EPD-process. Therefore, strong signal fluctuations of the voltage were observed.

These negative mechanisms can be avoided by addition of suitable organic additives, by optimised processing of the suspensions and by using an adapted compensation fluid as well as by adjustment of the EPD-parameters. Because of the constant resistance of the cell in the case of optimised conditions (Fig. 7), no difference between deposition under constant current and constant voltage was observed.

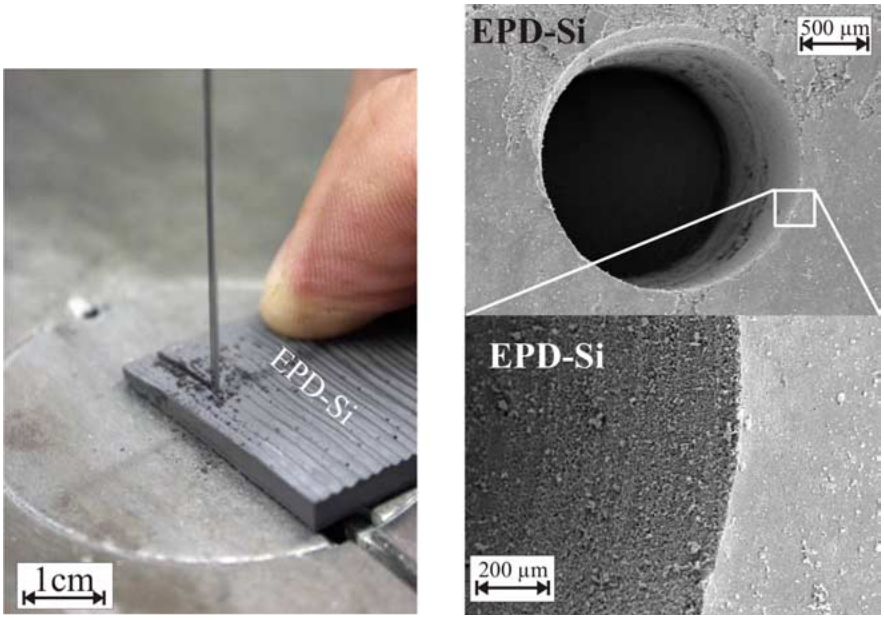

*Figure 6* Sawing of the electrophoretic deposited green body containing 3 wt% organic additives by a mechanical fret saw and SEM pictures of a drill hole in electrophoretic deposited silicon green body achieved by using a normal HSS-drill.

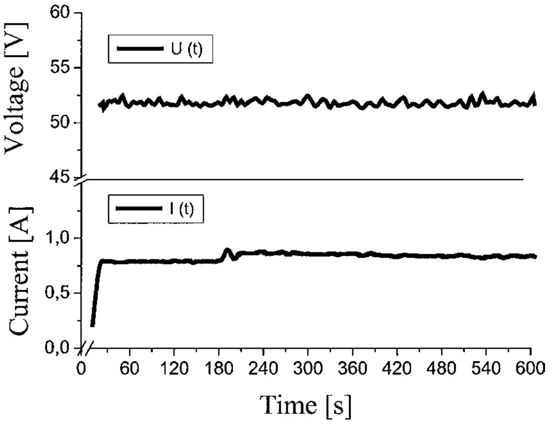

*Figure 7* Voltage and current over time during computer monitored EPD under optimised conditions.

Optimised EPD of silicon particles results in a high packing density of more than 60 vol% and sufficient mechanical properties for machining without any large pores with diameters greater than the particle size caused by decomposition of the water. The relatively large green bodies (90 × 100 × 8) mm without fibres were achieved in a few minutes, and crack free dried under normal room conditions. To produce fibre-reinforced composites, the fibre fabrics were introduced in the EPD-process in a first step as single layers (Fig. 8). To achieve bodies with higher thickness a multiple layer composite was formed by a serial laminating process of several fibre fabrics including stepwise EPD for each layer. In the case of milled Si-powder, a homogeneous infiltration of the whole fibre fabric can be achieved (Fig. 9).

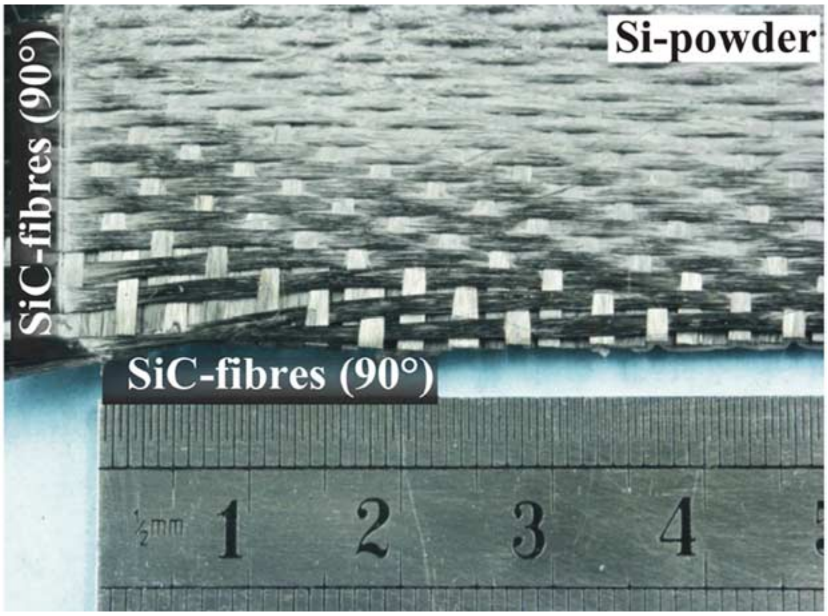

*Figure 8* Silicon infiltrated SiC-fibre fabric by EPD with a single 2D layer.

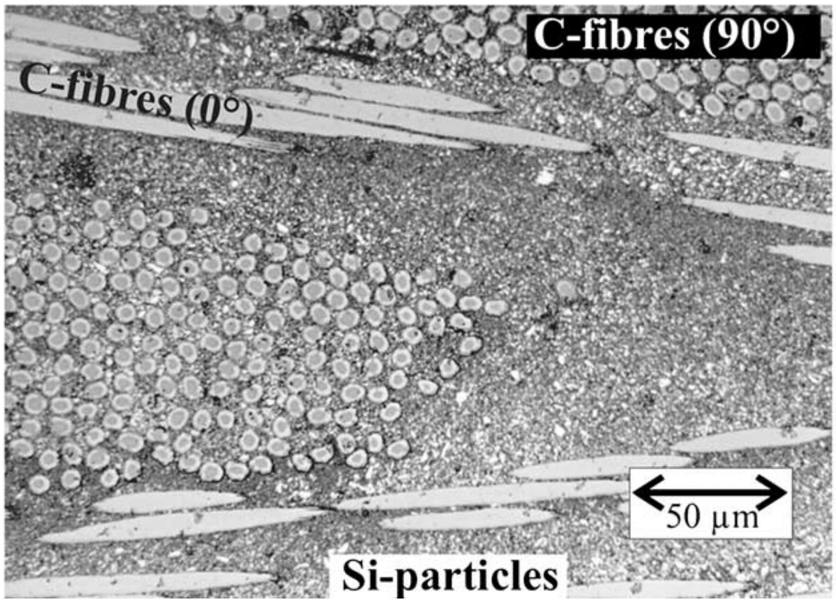

*Figure 9* Micrograph showing a polished section of a 2D-C-fibre fabric homogeneously infiltrated with milled silicon powder ($d_{50} = 0.5\,\mu$m) even between the fibre monofilaments.

## 4. Conclusions

Electrokinetic sonic analysis (ESA) is an advantageous method to characterise the suspensions for the EPD-process because of the direct correlation between the signal and the electrophoretic mobility. Therefore, an efficient and homogeneous deposit with a high packing density of the particles and a good stabilisation against sedimentation effects is due to a high ESA-signal of the suspension.

Especially, the use of efficient organic additives like the self-synthesised dispersing agent (SF11) is necessary to improve the surface charge. The introduction of an optimised binder is important to increase the green strength and to reduce the brittleness of the component. Thus, green machining and laminating techniques to scale up compact dimensions are possible. By the use of the computer-controlled EPD, gas bubble free deposits with a green density of higher than 60% theoretical density can be achieved. Excellent green machining can be obtained by only 3 wt% content of the optimised organic additives in the deposited green bodies. Therefore, the removal of the organic can be performed by heating up to 500°C in air without any damaging or cracking, even for a heating rate of 5 K/min. The EPD experiments with fibre fabrics prove that, in the case of milled Si-powder, a homogeneous infiltration even between the single monofilaments can be achieved.

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