# Electrophoretic deposition from aqueous suspensions for near-shape manufacturing of advanced ceramics and glasses—applications

J. TABELLION, R. CLASEN Department of Powder Technology, Saarland University, Bd. 43, D-66123 Saarbrucken, Germany E-mail: j.tabellion@matsci.uni.sb.de

Due to high deposition rates and the avoidance of inflammable, often hazardous organic solvents EPD from aqueous suspensions is a fast and low-cost shaping technique for ceramics and glasses. Since the deposition rate is independent of particle size EPD has an outstanding ability for the shaping of nano-particles. In this paper the shaping of complex silica glass and zirconia components, like tubes or structured parts by means of the membrane method is shown. Three-dimensional shaped porous polymer moulds were used as ion-permeable deposition surface. To enable near-shape manufacturing, mixtures of nanosized and microsized particles were electrophoretically deposited. No size-dependent separation was observed. Due to the very high green density of these green bodies (up to 84% of the theoretical value) shrinkage could be reduced to 4.7%. Not only oxide ceramics but also silicon carbide was deposited from aqueous suspensions. Apart from bulk SiC, protective coatings with a thickness of app. 60  $\mu$ m were applied on top of CFC substrates by EPD. Good adhesion was observed and no cracking occurred. Furthermore, electrophoretic impregnation was used for the modification of porous green bodies. Thus silica glasses with graded density and pore size as well as functionally graded composites were prepared. © 2004 Kluwer Academic Publishers

### 1. Introduction

Electrophoretic deposition (EPD) is a process known for decades [1], where charged particles move under the influence of a direct electric field towards an oppositely charged electrode and coagulate there to form a stable deposit. Although EPD has been applied on an industrial scale for years as enamelling and lacquering technique (cataphoresis) [2, 3], it is not yet established as a shaping process for functional ceramics and glasses. Among the ceramic coatings applied by EPD are e.g., phosphors [4], coatings for SOFCs [5], photovoltaic applications [6] or insulating layers [7]. In some cases even manufacturing on an industrial scale has become likely [8].

But in case of bulk ceramic or glass components no industrial manufacturing process has proved successful so far. Nevertheless, several ceramic systems were investigated on a laboratory scale, including alumina [9], zirconia [10], SiC [11, 12] and PZT [13]. Comprehensive reviews about EPD as shaping technique for ceramics are given in [14, 15]. In all of these cases organic solvents were used as dispersant, which seems to be one of the problems why EPD has never established yet for large-scale production of ceramics. First of all, the deposition rates are significantly lower in comparison with aqueous suspensions because of the much lower permittivity, thus very high electric field strengths have to be applied to achieve acceptable shaping times. Furthermore, severe safety precautions have to be met, if organic, often inflammable dispersants are used, especially in case of high voltages and/or high current densities. As a consequence the process cost increases. Finally, disposal of hazardous organic waste and treatment of the suspensions for recovery of the dispersant as well as the absorption of volatile cracking products during heat treatment can prevent the introduction of an EPD facility into an existing production line.

As an alternative aqueous suspensions can be used for the EPD of ceramics. Since only water is used as dispersant, no sophisticated safety precautions are necessary and treatment of the suspensions after EPD is easy. Most important, very high deposition rates can be reached for comparably low applied electric field strengths [16]. Thus process times can be reduced to several seconds to minutes depending on the material used. Clay components with a thickness of 10 mm could be shaped from aqueous sanitary slips within 15 s [17]. But the only industrial attempt to produce tiles by EPD from aqueous suspensions [18] failed.

The main problem associated with the use of aqueous suspensions for EPD, is the electrolysis-induced decomposition of water above a DC voltage of about 1.4 V. The electrolysis results in a movement of ions towards the oppositely charged electrode, where recombination

of the ions results in generation of gases. If the deposition takes place at one of the electrodes, these gases can be incorporated into the deposit, resulting in large and irregularly distributed faults. Several approaches have been made to avoid the formation of gas bubbles at the deposition surface.

First, the applied voltage can be kept lower than the decomposition voltage of water, which proved successful for the production of alumina microstructures [19]. But due to the low deposition rate only small wall thickness can be achieved. Another possibility is to use sacrificial electrodes. In [18] a process is described where zinc rollers are used as deposition electrodes. But the problem is that the deposition rate is limited due to electrode reactions and zinc ions are dissolved because of the electrolysis reaction. These contaminations prevent the application for pure materials.

Using cathode materials that can store hydrogen within their structure, like palladium, enables EPD from aqueous suspensions at the cathode. A process for shaping alumina ferrules is described in [20]. One severe disadvantage is the small amount of hydrogen that can be incorporated into the structure of these materials, which limits this process to components with low wall thickness. Furthermore, a positive  $\zeta$ -potential of the particles is a necessary demand.

A much more promising way is the membranemethod [21]. In this case the electrophoresis chamber is subdivided by a porous, ion-permeable membrane into two chambers that contain the suspension and another fluid, respectively. Deposition occurs at the membrane whereas the ions can pass the pores of the membrane so that recombination of the ions and generation of gas bubbles occurs at the electrodes. No gas bubbles can be incorporated into the deposit. This process was used for different materials like e.g., zirconia [22, 23] and silica glass [24]. Green density and pore size distribution of silica green bodies could be tailored [25]. After optimization the silica green bodies could be sintered to full density at 1320°C, which is about 100°C lower than for gel-cast green bodies of the same powder [26].

A further improvement in the manufacturing of silica glasses was achieved by using mixtures of nanosized and microsized silica particles. By means of EPD very homogeneous green bodies with very high green densities of up to 84%TD could be shaped. Shrinkage was reduced to 4 to 7% (linear) [27].

A modification of the EPD process is the electrophoretic impregnation (EPI), where nanosized particles are deposited within the pores or voids of a green body or fibre fabric. The principles of EPI are summarized in [28]. Investigations were made, to characterize the influence of several process parameters, like viscosity, solids content, surface charge of both particles and porous structure and ratio of pore to particles size, on the efficiency of the EPI process [29]. Applications of the EPI are the manufacturing of fibre-reinforced composites [30, 31] and the incorporation of functional secondary phases into glasses [32].

In this paper several applications of EPD by means of the membrane method as shaping technique for silica glass and advanced ceramics are shown. The aim of this work was to demonstrate that near-shape manufacturing of complex structures and large components is possible by EPD from aqueous suspensions.

#### 2. Experimental

#### 2.1. Materials and suspensions

Aqueous suspensions of nanosized fumed silica particles (Degussa Aerosil OX50, mean particle size 40 nm) were prepared by dispersing the particles in bidistilled water containing tetramethylammoniumhydroxide (TMAH) by means of a dissolver (LDV1, PC Laborsysteme). Vacuum was applied to avoid incorporation of air bubbles. TMAH was used to adjust the pH and thus the  $\zeta$ -potential of the silica particles as well as the viscosity of the suspension, both of which are very important factors for the EPD. A detailed description of the influence of pH on  $\zeta$ -potential, rheological properties, suspension structure and homogeneity can be found in [33]. The suspensions had a solids content of 30 wt%. In case of electrophoretic impregnation aqueous suspensions of OX50 or alumina (Al<sub>2</sub>O<sub>3</sub>-C, Degussa) with 5 wt% were used. Similarly, suspensions (solid loading 75 wt%) containing a mixture of fumed (OX50) and fused silica ( $D_{50} = 15 \ \mu m$ ) were prepared. The ratio of nanosized to microsized (fused) silica was 10:90 (per weight) In the same manner, aqueous suspensions of nanosized zirconia (Degussa Zirconia-3YSZ) and mixtures of nano- and microsized  $ZrO_2$  ( $D_{50} =$ 3  $\mu$ m, doped with 15.5 mol% ceria) were prepared.

In case of silicon carbide, aqueous suspensions with 45 wt% solids content were prepared as described above. The silicon carbide powder used was SiC SM15 from ESK with a  $D_{50}$  value of 0.77  $\mu$ m. To enable solid state sintering boron carbide and carbon black were added to the suspension as sintering additives. The mean particle size of the B<sub>4</sub>C used (Tetrabor F1500 from ESK) was 1.5  $\mu$ m, that of the carbon black powder (Degussa, FW200) 13 nm. A small amount of dispersing aid (0.2 wt% correlated to the amount of carbon black) was added to allow dispersion of the carbon black particles in water. To achieve a co-deposition of SiC and the sintering additives B<sub>4</sub>C and carbon black two different approaches were made. First of all, EPD was carried out from suspensions with a pH value of 11, where all particles have a  $\zeta$ -potential of the same sign. Alternatively, suspensions with pH 7 were used for EPD, where the carbides have a highly negative  $\zeta$ -potential whereas the carbon black particles have positive surface charge (cp. Fig. 6). pH was adjusted by adding different amounts of TMAH to the bidistilled water prior to dispersing the particles.

#### 2.2. Electrophoretic deposition/ electrophoretic impregnation

Electrophoretic deposition was carried out under constant applied voltage by the membrane method. A simple experimental set-up for the EPD of plates is shown in Fig. 1. An electrophoresis cell, with a cross section of  $40 \times 40$  mm<sup>2</sup>, was subdivided by an ion-permeable, porous polymer mould, so that deposition of particles (onto the porous mould) and recombination of ions (at



Figure 1 Experimental set-up for the electrophoretic deposition/impregnation process from aqueous suspensions.

the electrodes) were separated. Thus no gas bubbles were found within the deposit. One chamber was filled with the suspension, the other with bidistilled water containing different amounts of TMAH. The width of the different chambers was optimized after measuring the effective electric field strength within the electrophoresis cell [34]. This set-up was used to determine deposition rate, green density and pore size. For more complex shaped components the set-up had to be readjusted concerning the shape of the porous mould and the electrodes. The applied voltage was varied between 1 and 15 V/cm. Deposition time was 3 min in case of silica and zirconia and 30 s in case of the SiC coatings.

In case of electrophoretic impregnation, the same experimental set-up was used, but instead of the porous polymer mould a cast silica green body with open pores (26% porosity, mean pore size 1.8  $\mu$ m) was used. The electric field strength was varied between 1.5 and 6 V/cm and deposition time was 30 and 60 s, respectively.

After shaping, the green bodies and coated substrates were dried in air under ambient humidity. No cracking occurred for the green bodies and no cracking was observed for the SiC coatings for a thickness of up to 200  $\mu$ m. Sintering of the compacts was carried out either in vacuum (SiO<sub>2</sub> powder mixtures, 1500–1600°C), argon atmosphere (SiC, 1700–2100°C), air (zirconia, 1300–1700°C) or in a zone-sintering furnace (OX50, 1320°C).

#### 2.3. Characterization

Density and pore size distribution of green and sintered samples were measured by Archimedes method and mercury porosimetry (Porotec Pascal P140, P440), respectively. Microstructural homogeneity was investigated on basis of SEM and high resolution SEM (HR-SEM) images. Densification due to EPI was determined on basis of SEM images by means of image analysis software (ImageC). For this purpose, SEM pictures of not impregnated silica green bodies were taken as reference first. The densification of the impregnated green bodies was determined on the basis of SEM pictures with the same magnification, that were taken equidistantly (300  $\mu$ m) from the surface in contact with the suspension during EPI towards the bulk. A densification of 0% means that the same porosity is visible as for the not impregnated references. A densification of 100% means, that at the given magnification no porosity is visible. These values were correlated finally to absolute values of the density and pore size, achieved from Archimedes method and mercury porosimetry. Furthermore, Raman microscopy was used for a positionsensitive characterization of graded composites.

#### 3. Results and discussion

The deposition rate for the electrophoretic deposition of the different powders used was determined first, because only an exact control of this parameter can guarantee a reproducible manufacturing of components with given specifications concerning wall thickness and tolerances. The deposition rate for an aqueous suspension containing 30 wt% of nanosized fumed silica (OX50) is shown in Fig. 2 (dark line, circles) as function of the applied electric field strength for a deposition time of 3 min. A linear dependency was observed. The green density of the corresponding silica green bodies was not influenced by the electric field strength and was determined by Archimedes method to be 39.4%TD. This means that e.g., a green body with a thickness of 12 mm was deposited within 3 min for a field strength of 10 V/cm.

For nanosized zirconia a similar dependency of the deposition rate from the electric field strength was observed, but the absolute values are lower than for silica.



*Figure 2* Deposition rate as function of externally applied electric field strength for different materials and different particle size (deposition time: 3 min).

This is related to the lower value of the  $\zeta$ -potential of the zirconia particles. For an electric field strength of 10 V/cm a green body with a green density of 32%TD and a thickness of 4 mm was achieved was deposited within 3 min.

Furthermore, mixtures of nanosized silica (OX50) and fused silica were deposited (Fig. 2, dotted line). No significant difference was observed compared to pure OX50. The slightly lower values can be explained by the higher viscosity (240 mPa  $\cdot$  s at a shear rate of  $300 \text{ s}^{-1}$  compared to 60 mPa  $\cdot$  s in case of 30 wt% OX50). But what is most important, no influence of particle size on deposition rate was found. A green body with a green density of 74% TD and a thickness of 7 mm was achieved after 3 min deposition with a field strength of 10 V/cm. Finally, the deposition rate for the co-deposition of SiC, B<sub>4</sub>C and carbon black at pH 7 (Fig. 2, light line) was investigated. Again a linear dependency of the deposition rate from field strength was found. But the values are much lower than for silica or zirconia. This is obviously related to the much higher viscosity (460 mPa  $\cdot$  s at 300 s<sup>-1</sup>) and to the fact that the net-charge of the agglomerated SiC/carbon black and B<sub>4</sub>C/carbon black particles at pH 7 (cp. Fig. 6) is lower than for the pure carbides. A green body with a

green density of 49% TD and a thickness of 3 mm was achieved after 3 min EPD with 10 V/cm.

These results show that electrophoretic deposition from aqueous suspensions is a very fast shaping technique, even though the deposition rate strongly depends on the material, the solids content, viscosity and the  $\zeta$ -potential of the particles. Especially in the case of nano-particles and powder mixtures with bi- or multimodal particle size distribution, fast and homogeneous shaping is possible by means of EPD. Furthermore, these results show that wall or coating thickness can be controlled accurately and reproducibly in case of EPD by adjusting the applied electric field strength.

To compare EPD with competing shaping techniques, silica green bodies (plates) were shaped from an aqueous suspension with 30 wt% OX50 by means of EPD, slip casting and pressure casting, respectively. After drying, porosity was measured and microstructure was investigated.

Fig. 3 shows the specific cumulative pore volume of the silica green bodies measured by mercury porosimetry, which corresponds directly to the open porosity of the samples. On the right hand side of Fig. 3 two HR-SEM images are shown. The upper one shows a fracture surface of the silica green body shaped by pressure casting, the lower image shows the electrophoretically deposited green body. Both, mercury porosimetry and HR-SEM pictures show that the highest density and the best microstructural homogeneity is achieved if EPD is used as shaping technique, at least for nano-particles.

Electrophoretically deposited silica glass tubes (green state, left-hand side) of different diameter and with different wall thickness are shown in Fig. 4. These tubes were electrophoretically deposited from an aqueous suspension of nanosized fumed silica (OX50). A tubular polymer membrane was used as an ionpermeable deposition surface. As can be seen (Fig. 4, right-hand side) a fully dense and fully transparent silica glass tube was achieved after sintering at 1320°C. No gas bubbles were found. This shows that by means of electrophoretic deposition from aqueous suspensions



*Figure 3* Comparison of different shaping techniques by means of mercury porosimetry and HR-SEM images of fracture surfaces: Porosity and homogeneity of silica green bodies prepared from aqueous suspension of nanosized fumed silica (OX50) by EPD, slip casting and pressure casting, respectively.



40 mm

*Figure 4* Silica tubes (green state) shaped by EPD from an aqueous suspension of nanosized fumed silica (OX50) and silica glass tube after sintering (1320°C).

complex components can be shaped fast and with outstanding quality.

#### 3.1. Near shape manufacturing of complex-shaped glasses and ceramics by EPD of powder mixtures

Due to the high surface area of nano-particles the solids content of suspensions is limited (about 60 wt% in case of OX50) and so is the green density (up to 50%TD) [25]. The low green density results in a high shrinkage during drying and sintering of about 15 to 30% (OX50). Thus sophisticated process control is necessary for larger and more complex-shaped components. This makes near-shape manufacturing very complicated. One possible solution is to increase green density significantly. This can be achieved by combining powders with distinctly different particle size distribution, like mixtures of nanosized and microsized particles. It is most important that no size dependent separation of the particles occurs during shaping because this can result in inhomogeneous sintering behaviour and distortion of the component. Therefore, EPD seems to be a promising shaping technique for such powder mixtures, because deposition rate is independent from particle size (cp. Fig. 2). The process was successfully used for shaping of silica glass components [27] and within the scope of this work adapted to ceramic materials. As shown in Fig. 2 nanosized zirconia can be deposited very fast by EPD. But again only low green densities (<35%TD) can be reached due to the high surface area of the nanoparticles. This low green density results in a very high shrinkage during sintering ( $\approx 30\%$ ) and leads to the formation of micro cracks. Thus the maximum density reached is app. 96%TD at 1400°C [23]. By combining nanosized powders with micrometer powders green density could be increased significantly and shrinkage could be minimized (<12%). No particle separation due to the different sizes was observed within the deposit. Fig. 5 shows a porous polymer mould that was



Figure 5 Porous polymer mould and sintered zirconia component shaped by EPD (membrane method) from an aqueous suspension of nano- and microsized zirconia.

used as ion-permeable deposition surface for the EPD (left-hand side) and a sintered zirconia green body, electrophoretically deposited from an aqueous suspension of a mixture of nanosized (ZrO<sub>2</sub>-VP) and microsized zirconia. First of all, it can be seen, that complex-shaped porous membranes can be used for EPD from aqueous suspensions and as a result complex glass or ceramic components can be manufactured. Furthermore, only low shrinkage (10% linear) was observed because of the bimodal powder mixture used.

## 3.2. Electrophoretic deposition of silicon carbide from aqueous suspensions

Another application is the shaping of silicon carbide bulk components and coatings by EPD from aqueous suspensions. As described above deposition was carried out at pH 11, where SiC as well as the sintering additives, B<sub>4</sub>C and carbon black, had the same sign of the  $\zeta$ -potential, and at pH 7 where the carbides show a negative  $\zeta$ -potential while the carbon black has a positive surface charge (see Fig. 6, left-hand side). The deposition rate for pH 7 is shown in Fig. 2. For pH 11 a slightly higher deposition rate was observed, because of the lower viscosity. On the right-hand side of Fig. 6 green and sintered density of SiC green bodies are shown, electrophoretically deposited at pH 11 and pH 7, respectively. A significantly higher green density was observed for pH 11. Again, this can be explained by the lower viscosity. Nevertheless, a higher density was found for the sample deposited at pH 7 after sintering. First of all, this shows that co-deposition of SiC and the sintering additives  $B_4C$  and carbon black from an aqueous suspension is possible at both pH values because no sintering could have occurred if no sintering additives were deposited. Furthermore, the distribution of carbon black seems to be more homogeneous for the deposition at pH 7, which results in a better sintering behaviour. This corroborates the theory that a collective motion of carbide particles, coated with nanosized carbon black particles, occurs, if an electric field is applied for EPD. A quantitative analysis of the distribution of  $B_4C$  and carbon black within the green bodies has yet to be made.

Fig. 7 shows one further application of EPD of silicon carbide from aqueous suspensions apart from bulk components. A protective SiC coating was deposited onto the surface of a CFC substrate to fulfil oxidation protection at elevated temperatures. SiC was chosen because of its thermal expansion coefficient, which fits comparably well to CFC and lies between the thermal expansion coefficient of carbon fibres parallel and perpendicular to the fibre axis. A good adhesion of the SiC coating to the substrate was found after sintering at 1950°C. The coating showed no cracks and had a thickness of app. 60  $\mu$ m. To achieve better oxidation protection first experiments were carried out to apply a graded coating system with gradual change of



*Figure 6*  $\zeta$ -potential of SiC, B<sub>4</sub>C and carbon black as function of pH value (left-hand side) and density of electrophoretically deposited (ph 7, pH 11) SiC samples before and after sintering (right-hand side).



*Figure 7* CFC substrate with protective silicon carbide coating applied by electrophoretic co-deposition of SiC, B<sub>4</sub>C and carbon black from an aqueous suspension (SEM, fracture surface) after sintering.

the chemical composition from SiC at the substrate interface to mullite on top.

#### 3.3. Modification of porous green bodies by electrophoretic impregnation

Fig. 8 shows the fracture surface of a silica green body (SEM) after electrophoretic impregnation with nanosized fumed silica particles (OX50). The surface on the right-hand side was in contact with the suspension during EPI (suspension surface). As can be seen a graded densification was achieved with an impregnation depth of about 1 mm. Prior to EPI the silica green body showed a narrow monomodal pore size distribution with a mean pore radius of 1.8  $\mu$ m, investigated by mercury porosimetry. The density of the green bodies was determined by Archimedes method to be 74%TD. SEM pictures of not impregnated silica green bodies were taken and the porosity was determined by image analysis as reference. After EPI the pore channels at and near the suspension surface were completely filled with nanosized particles and the density was increased from 74 to 86% TD. As a consequence thereof the mean pore size was diminished from 1.8  $\mu$ m to 30 nm. With increasing distance from the impregnation surface a gradual decrease in densification and increase in pore size could be found (see Fig. 8, lower left-hand corner). At a distance of 0.8 mm from impregnation surface no nanosized particles could be found.

The influence of process parameters on depth and degree of densification was investigated by image analysis on basis of SEM pictures as described above. Fig. 9 shows the relative densification of silica green bodies as function of distance from the suspension surface for different applied electric field strengths. A relative densification of e.g., 70% means that 70% of the open porosity of the not impregnated silica green body, visible on the SEM images with a constant magnification, was densified with nanosized particles. A relative densification of 100% corresponds to a density of the silica green body of 86%TD.

As can be seen the EPI process is sensitive to small variations of the process parameters but can be controlled reproducibly. The highest relative densification at the suspension surface was found for an electric field strength of 3.0 V/cm, whereas for 1.5 and 6.0 V/cm significantly lower densifications were observed. A similar result was found for the depth of impregnation, which is much higher for 3.0 V/cm ( $\approx$ 8 mm) compared to 1.5 and 6.0 V/cm (1 and 4 mm, respectively). On the righthand side of Fig. 9 the three corresponding sintered silica glass samples are shown. Sintering temperature was 1525°C. At this temperature the electrophoretically impregnated parts are already transparent whereas the not densified parts are white because full density was not reached there. This can be explained by the higher density of the impregnated parts and the higher sintering activity of the nanosized silica particles incorporated by EPI.

Finally, not only a densification can be achieved by means of EPI but also graded composites can be manufactured. In this case a second material is deposited within the pore channels of a green body. An example is shown in Fig. 10, where a silica green body was electrophoretically impregnated with nanosized alumina particles.

The alumina particles act as crystallization nuclei during sintering and stimulate the formation of cristobalite. After sintering (1600°C) the polished cross section of the sample was characterized by means of Raman-microscopy. A Raman spectrum was measured every 300  $\mu$ m from surface towards the bulk of the composite. At the surface (P1) the characteristic spectrum for cristobalite was found, whereas at a distance



*Figure 8* Silica green body with graded density and pore size distribution (SEM, fracture surface) after electrophoretic impregnation (surface on the right-hand side in contact with suspension) with nanosized silica particles (OX50).



*Figure 9* Densification of silica green bodies as function of distance from impregnation surface for different electric field strength during EPI and silica glass samples with graded density after sintering (vacuum, 1525°C).



Figure 10 Silica glass/cristobalite composite with gradual decrease of cristobalite content from surface to bulk: Position sensitive characterization by Raman microscopy.

of 3 mm from the surface (P5) only the silica glass spectrum was found. At points P2 to P4 a superposition of both spectra was found with decreasing intensity of the cristobalite peaks with increasing distance from surface. This shows that a graded impregnation was achieved, although this measurement was only a semi-quantitative one.

#### 4. Conclusions

Electrophoretic deposition from aqueous suspensions by the membrane method is a fast, low-cost and flexible shaping technique for glasses and ceramics. High deposition rates are reached that allow shaping of large components with thick walls within several seconds to minutes even for nano-particles. Thus a silica green body with a thickness of 12 mm was deposited within 3 min (E = 10 V/cm). Silica tubes of different diameter and wall thickness were shaped of nanosized fumed silica and subsequently sintered to fully dense and transparent silica glass tubes.

Using three-dimensional shaped porous polymer moulds as ion-permeable deposition surface complex ceramic and glass components can be produced. But due to the high specific surface area the density of green bodies shaped of nano-particles is comparably low and high shrinkage (up to 30%) occurs during drying and sintering. To enable near-shape manufacturing shrinkage had to be reduced. This was achieved by EPD of mixtures of nanosized and microsized particles.

Furthermore, SiC was electrophoretically codeposited with B<sub>4</sub>C and carbon black, as sintering additives. Co-deposition was successfully carried out at pH 11, where all particles have a  $\zeta$ -potential of the same sign, and at a pH of 7, where the carbides show a negative surface charge whereas the carbon black particles have a positive  $\zeta$ -potential. In both cases solid state sintering was observed, with a better sintering behaviour

for the green bodies deposited at pH 7. Apart from bulk ceramics, protective SiC coatings were applied by means of EPD on top of CFC substrates.

A modification of porous green bodies could be achieved by electrophoretic impregnation, where nanosized particles were deposited within the pore channels of meso-porous green bodies. Thus, a homogeneous or graded densification can be achieved and composites with graded composition can be produced. The gradient can be tailored by adjusting the process parameters.

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#### References

- 1. H. C. HAMAKER and E. J. W. VERWEY, *Trans. Faraday* Soc. 36 (1940).
- 2. M. BENJAMIN and A. B. OSBORN, ibid. 36 (1940).
- 3. H. HOFFMANN, *Ceram. Bull.* **57** (1978) 6.
- 4. M. J. SHANE, J. B. TALBOT, B. G. KINNEY, E.SLUZKY and K. R. HESSE, *J. Coll. Interf. Sci.* **165** (1994).
- 5. I. ZHITOMIRSKY and A. PETRIC, *J. Europ. Ceram. Soc.* **20** (2000) 12.
- 6. D. MATTHEWS, A. KAY and M. GRÄTZEL, *Aust. J. Chem.* **47** (1994).
- 7. T. NARISAWA, T. ARATO, N. KOGANEZAWA, M. SHIBATA and Y. NONAKA, J. Ceram. Soc. Jpn. 103 (1995) 1.
- 8. G. J. VERHOECKX and N. J. M. V. LETH, *Electrochem.* Soc. Proc., 2002–21 (2002).
- 9. C.-Y. CHEN, S.-Y. CHEN and D.-M. LIU, *Acta Mater.* **47** (1999) 9.
- 10. F. HARBACH and H. NIENBURG, J. Europ. Ceram. Soc. 18 (1998).
- 11. F. BOUYER and A. FOISSY, J. Amer. Ceram. Soc. 82 (1999) 8.
- L. VANDEPERRE, O. V. D. BIEST, F. BOUYER, J. PERSELLO and A. FOISSY, J. Europ. Ceram Soc. 17 (1997).
- J. LAUBERSHEIMER, H.-J. RITZHAUPT-KLEISSL, J. HAUBELT and G. EMIG, *ibid.* 18 (1998).
- 14. P. SARKAR and P. S. NICHOLSON, J. Amer. Ceram. Soc. 79 (1996) 8.

- 15. M. S. J. GANI, Indust. Ceram. 14 (1994) 4.
- 16. R. CLASEN, S. JANES, C. OSWALD and D. RANKER, Ceram. Trans. 51 (1995).
- 17. I. HECTOR and R. CLASEN, *Ceram. Eng. Sci. Proc.* **18** (1997) 2.
- 18. M. S. CHRONBERG and F. HÄNDLE, *Interceram* **27** (1978) 1.
- H. V. BOTH and J. HAUßELT, *Electrochem. Soc. Proc.* 2002– 21 (2002).
- 20. A. V. KERKAR, R. W. RICE and R. M. SPOTNITZ, US Patient no. 5,194,129 (1993).
- R. CLASEN, in Proceedings of the 2nd Int. Conf. on Powder Processing Science, Berchtesgaden, 12–14. 10. 1988, edited by H. Hausner, G. L. Messing and S. Hirano (Deutsche Keramische Gesellschaft, Köln,1988) p. 633.
- 22. K. MORITZ, R. THAUER and E. MÜLLER, *cfi/Ber. DKG* 77 (2000) 8.
- 23. I. M. AKIMOVICH, Inorg. Mater. (Russia) 12 (1971) 7.
- R. Clasen, in "Science, Technology and Applications of Colloidal Suspensions" (Amer. Ceram. Soc., USA, 1995) p. 169.
- J. TABELLION and R. CLASEN, in "Innovative Processing and Synthesis of Ceramics, Glasses and Composites IV" (Amer. Ceram. Soc., USA, 2000) p. 185.
- 26. J. TABELLION and R. CLASEN, in Proceedings of the 26th Annual Conference on Composites, Advanced Ceramics, Materials and Structures, Cocoa Beach, Florida, USA, 2002, edited by H.-T. Lin and M. Singh (Amer. Ceram. Soc., USA, 2002) p. 617.
- J. TABELLION and R. CLASEN, to be published in Proceedings of the 27th Annual Conference on Composites, Advanced Ceramics, Materials and Structures, Cocoa Beach, USA, 2003.
- 28. S. HABER, J. Coll. Inter. Sci. 179 (1996) 2.
- 29. J. TABELLION, C. OETZEL and R. CLASEN, *Electrochem.* Soc. Proc. 2002-21 (2002).
- A. R. BOCCACCINI, C. KAYA and H.-G. KRÜGER, *Chem.-Ing. Tech.* 73 (2001) 5.
- 31. K. MORITZ and E. MÜLLER, *Key Engin. Mater.* **206–213** (2002).
- K. SMEETS, J. TABELLION and R. CLASEN, *ibid.* 206– 213 (2002).
- 33. K. SMEETS, J. TABELLION and R. CLASEN, *ibid.* 206– 213 (2002).
- 34. J. TABELLION and R. CLASEN, Innovative Processing and Synthesis of Ceramics, Glasses and Composites IV (Amer. Ceram. Soc., USA, 2000) p. 197.

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