J Mater Sci (2006) 41:8047–8058
DOI 10.1007/s10853-006-0647-x

Investigation of the electrophoretic deposition behaviour of non-aqueous ceramic suspensions

Kirsten Moritz · Eberhard Müller

Received: 14 January 2006 / Accepted: 6 July 2006 / Published online: 7 November 2006

Abstract The topic of the investigations was the electrophoretic shaping of AlN, SiC and Al_2O_3, respectively, using ethanolic suspensions of the powders. Suitable organic additives were chosen for achieving an effective suspension stabilisation and a sufficiently high electrophoretic mobility of the particles, which are the basic requirements for a successful electrophoretic deposition. Most of the EPD experiments were carried out in the direction of the gravitational force. Either the voltage or the current was kept constant during the deposition. In the case of the EPD of AlN, the dependence of the deposit mass on the experimental parameters has been investigated in detail and explained on the basis of changes in the effective electric field strength. Several factors influencing the effective field strength are discussed in this paper. By EPD from the different suspensions, green bodies with monomodal pore size distributions reflecting a high homogeneity of the particle packing were produced. It was shown that by the simultaneous deposition of non-oxide powders and sintering additives from suspensions with high solid contents deposits with a homogeneous distribution of the sintering additive can be obtained, whereas in diluted suspensions different electrophoretic mobilities cause a separation of the components.

K. Moritz (✉) · E. Müller
Institute of Ceramic Materials, Technical University Bergakademie Freiberg, Gustav-Zeuner-Str. 3, D-09596 Freiberg, Saxony, Germany
e-mail: moritz@ikw.tu-freiberg.de

E. Müller
e-mail: mueller@ikw.tu-freiberg.de

Introduction

Electrophoretic deposition (EPD) of powder or sol particles is a promising method, which has been used for example

- as shaping technique for producing monolithic ceramics, laminated or graded materials or ceramic microstructures,
- for infiltrating porous structures or fibre mats, and
- as coating technique for a large variety of materials and applications [1–5].

One of the main advantages is the suitability of this method for highly dispersed powders. Because only from well-dispersed, stable suspensions a dense and homogeneous particle packing in the deposits can be reached, the preparation of a suspension which shows a high stability against particle agglomeration is a very important prerequisite for a successful EPD. Simultaneously, the electrophoretic mobility has to be sufficiently high. To comply with these requirements, a suitable pH value is adjusted and/or organic aids are added. The electrophoretic mobility is proportional to the dielectric constant of the liquid and to the zeta potential and inversely proportional to the viscosity of the dispersing medium [6].

According to the well-known equation formulated in its original form by Hamaker [7], the deposit mass obtained in EPD depends on several suspension and processing parameters: on the already mentioned electrophoretic mobility, on the solid content of the suspension, on the electric field strength, on the area of the deposition electrode, and on the deposition time. During the EPD process, changes in some of these parameters can occur.

At first, the EPD under constant–voltage conditions should be discussed. In this case, the voltage applied between the electrodes is maintained constant during the deposition, but the so-called effective field strength, which controls the movement of the charged particles in the suspension has to be considered as a function of time. For most of the suspensions the effective field strength decreases with deposition time in constant–voltage EPD. This effect can be caused by the electrical resistance of the growing deposit and/or polarisation effects [1, 3, 7]. One possible influence is to be seen in changes of the so-called concentration overvoltage. If during the electrophoretic deposition the transport of reactants for the electrode reaction is slower than their consumption, the concentration at the electrode will drop and the concentration overvoltage will increase resulting in decreasing effective field strength [3].

It should be noted that the electrode material can also affect the deposition rate [8]. For example, the protective oxide layers formed on the surface of some metals (e.g., aluminium) by anodic corrosion cause an increase of the potential drop at the electrode [3].

The decrease in effective field strength during the EPD can be avoided under constant–current conditions.

A further parameter which may change depending on deposition time is the solid content of the suspension. If the solid content is not kept constant for example by a continuous inflow and outflow of the suspension, the decreasing powder concentration with time results in a decreasing deposition rate. An exception is the EPD from concentrated suspensions in the direction of the gravitational force discussed in detail in the present paper.

Both, aqueous and non-aqueous suspensions can be used for the electrophoretic deposition. Aqueous suspensions are advantageous for environmental and economical reasons, and high electrophoretic mobilities can be reached due to the high value of the dielectric constant of H_2O, but a problem is the gas bubble formation at the electrodes due to the electrolysis of water above its decomposition voltage. Therefore, special methods are necessary to prevent macropores in the deposits originating from the gas bubbles such as the use of cathode materials which can store hydrogen within their structure (e.g., palladium) [9, 10] or the so-called membrane method described in [11–13]. Whereas the first-mentioned way is restricted to thin cathodic deposits, the membrane method enables also the deposition of thicker green bodies. In the case of this method, the EPD cell is subdivided into two compartments by an ion-permeable membrane. One compartment contains the suspension, the other one an electrolyte solution. The particles are deposited at the membrane positioned between the electrodes, not at the electrode. Compared to the direct deposition at the electrode, additional factors influencing the EPD kinetics and the formation of the deposit have to be kept in mind. The ratio of the electrical conductivities of the liquid in the electrolyte compartment and of the suspension plays an important role [13]. It has a strong effect on the osmotic and electro-osmotic flows and on the effective field strength.

Non-aqueous dispersing liquids are to prefer for powders reacting with water [2]. Since the problems arising from the electrolytic decomposition of water can be avoided, non-aqueous suspensions are used if the particles are to be deposited directly at the electrode. Furthermore, Joule heating is greatly reduced compared to aqueous slurries because of the smaller electrical conductivities [3].

Among the non-aqueous media, alcohols are similar to water regarding the mechanisms by which the particles can acquire a surface charge [3]. Relatively high electrophoretic mobilities can be achieved in alcoholic suspensions.

The topic of the present paper is the EPD from ethanolic suspensions for producing AlN, SiC and Al_2O_3 green bodies, respectively.

Experimental

The powders used for the experimental investigations and their main characteristics are listed in Table 1. The particle size distributions were measured by dynamic light scattering. Diluted ethanolic dispersions containing the same organic additives like the suspensions in the EPD experiments were prepared for this purpose.

The compositions of the suspensions used for the electrophoretic deposition are summarised in Table 2.

AlN and SiC were chosen as two non-oxide powders with different chemical properties of the particle surface which require for this reason different organic additives to obtain an optimum stabilisation of the suspensions.

Most of the EPD experiments were carried out using AlN suspensions. Aluminium nitride is very sensitive to hydrolysis. Therefore, non-aqueous dispersing media are to prefer for this material. For investigating the simultaneous deposition of AlN and the sintering additive Y_2O_3, suspensions of an AlN/Y_2O_3 powder

Table 1 Characteristics of the powders

Powder	Manufacturer	Specific surface area (BET)[a] (m^2/g)	$d_{50,\,3}$ value of the particle size distribution[b] (μm)	Oxygen content of the non-oxide powders[c] (wt.%)
AlN Grade C	H. C. Starck, Germany	4.7	0.8	1.65
Y_2O_3 Grade C, used as sintering additive for AlN	H. C. Starck, Germany	14.8	0.4	–
SiC UF 25	H. C. Starck, Germany	24.9	0.3	1.98
α-Al_2O_3 CT 3000 SG	Alcoa, Germany	6.6	0.4	–
α-Al_2O_3 Taimicron TM-DAR	Taimei Chemicals, Japan	13.8	0.25	–

[a] ASAP 2010, Micromeritics Instrument Corporation, GA/USA

[b] HPPS, Malvern Instruments, UK

[c] Neutron activation analysis

mixture were prepared. The same amount of organic aids related to the powder surface as used for stabilising the pure AlN suspensions was added. Therefore, in Table 2 the unit "mg additive/m^2 powder surface" instead of "wt.%" is used in the case of the AlN/Y_2O_3 suspension.

The SiC suspension was originally developed for infiltrating carbon fibre mats by means of electrophoresis [14]. A non-aqueous suspension was favoured for this application because a gas bubble formation at the fibre fabric serving as deposition electrode had to be prevented.

Furthermore, suspensions of two alumina powders have been investigated for comparative studies. As will be shown in Results and discussion, these two Al_2O_3 powders are an example for the fact that also powders of the same chemical composition can differ in the electrokinetic properties of the suspensions due to differences in the surface chemistry.

For preparing the suspensions, the powders were dispersed in absolute ethanol (99.8% purity) containing the organic additives. The suspensions were ultrasonically treated for 3 min by means of an ultrasonic horn (Sonopuls HD 2200, Bandelin, Germany) using a cooling bath to avoid uncontrolled heating of the suspension. In the case of the powder Al_2O_3 CT 3000 SG, an aqueous slurry which had the same composition regarding to the solid content (in vol.%) and the organic additive like the corresponding ethanolic suspension was prepared in addition.

Because of the above-mentioned low resistance of AlN powders to hydrolysis, special attention was paid to the water content of the ethanol in this case. The absolute ethanol was additionally dried by means of a

Table 2 Suspensions used for the EPD experiments

Powder	Dispersing medium	Solid content	Organic additives[a]
AlN Grade C	Ethanol	60 wt.% (26.6 vol.%)	0.3 wt.% (0.65 mg/m^2) PAA + 0.7 wt.% (1.5 mg/m^2) triethylamine
97 wt.% AlN, 3 wt.% Y_2O_3	Ethanol	6.9 wt.% (1.75 vol.%) and 60 wt.% (26.5 vol.%)	0.65 mg PAA/m^2 powder surface + 1.5 mg triethylamine/m^2 powder surface
SiC	Ethanol	60 wt.% (27.0 vol.%)	2 wt.% polyethylene imine + 2 wt.% H_2O
Al_2O_3 CT 3000 SG	Ethanol	60 wt.% (22.9 vol.%)	0.75 wt.% PAA
	Deionised water	54.2 wt.% (22.9 vol.%)	
Al_2O_3 TM-DAR	Ethanol	60 wt.% (22.9 vol.%)	1.5 wt.% polyethylene imine

Polyacrylic acid (PAA): average molecular weight 2,000, Sigma-Aldrich, Germany; polyethylene imine: average molecular weight 25,000, Sigma-Aldrich, Germany; triethylamine: J. T. Baker, Netherlands

[a] Additive amount in wt.% related to the solid content

molecular sieve to ensure that the water content was negligible. The oxygen contents of the initial AlN powder and of the powder after 24 h contact with ethanol (additive-free and with organic additives) were measured by neutron activation analysis. Ethanol containing a small amount of water (96% ethanol) was used in comparison to the dried ethanol in these investigations. Suspensions of 20 wt.% solids loading were prepared and stirred for 24 h. After this time, the AlN was separated from the liquid by vacuum filtration, dried at 110 °C, and the oxygen content was analysed.

The water contents of the different grades of ethanol analysed by Karl–Fischer titration are listed in Table 3.

The organic aids (Table 2) were chosen according to their ability to stabilise the suspensions effectively and to provide sufficiently high electrophoretic mobility.

By measurements of the Electrokinetic Sonic Amplitude (ESA) as a measure of the zeta potential, the electrokinetic behaviour of the suspensions was characterised (ESA 8000, Matec Instruments, MA/USA).

The stability of the suspensions was examined by sedimentation tests and rheological measurements in preliminary investigations, which will not be discussed in this publication.

For measurements of the specific electrical conductivities, the suspensions were centrifuged and the conductivities of the suspension and of the centrifugate at a temperature of 25 °C were compared (conductometer LF 92, wtw, Germany).

Planar circular green bodies (40 mm in diameter) were produced by EPD. Platinum was used as electrode material. The voltage or the current were maintained constant during the deposition.

In the case of the ethanolic suspensions, the particles were deposited directly at the electrode. The electrode distance was usually adjusted to 20 mm. A glass ring whose inner diameter equalled the diameter of the green bodies to be fabricated was used as a "mould" to obtain deposits with sharp edges. The electrophoretic deposition was carried out in the direction of the gravitational force, in some comparative investigations also in the opposite direction.

Table 3 Water content of the ethanol analysed by Karl–Fischer titration

	H_2O content (wt.%)
96% ethanol	5.50
99.8% ethanol	0.13
99.8% ethanol, additionally dried by means of a molecular sieve	0.09

In contrast to the EPD from suspensions containing only one powder, the deposition of the AlN/Y_2O_3 powder mixture was continued up to a nearly complete deposition of the whole solid content to make separation effects better visible. The powder particles were deposited at the lower electrode, but the electrode distance was 30 mm in this case. By means of ICP-OES analyses, the yttria content of samples taken from the upper and the lower side of the deposits was determined.

For the electrophoretic deposition from the aqueous Al_2O_3 suspension, the membrane method was used. As mentioned above, the EPD cell consists of a suspension chamber and an electrolyte compartment in this method. Between the chambers the membrane was positioned. In the used cell, the electrode distance was 60 mm with a distance of 40 mm between electrode and membrane in the suspension compartment.

The electrophoretic deposition from the used well-dispersed, stable suspensions led to a high packing density of the particles. Thus, the deposits could be cleanly separated from the electrode without problems. Subsequently, they were dried at ambient temperature.

In all cases the thickness of the green bodies was nearly constant over the whole sample area. The surface of the deposits was smooth.

The organic additives were removed at 600 °C in air (Al_2O_3, AlN) or at 650 °C in argon atmosphere (SiC). Preliminary experiments showed that the increase in the oxygen content of the AlN was negligible under the used conditions. In the case of the SiC green bodies, Ar atmosphere was chosen with respect to the sintering mechanism using carbon black and B_4C as sintering additives. The main role of the carbon black is to reduce the oxide layer on the SiC particles [15]. Therefore, a possible increase in oxygen content should be avoided.

After the burn-out/pyrolysis step, the green densities and pore sizes of the deposits were measured. Green bodies prepared in the same way were sintered to dense ceramics, but investigations concerning the sintering behaviour are not the subject of this paper.

For calculating the green densities, the volume was determined from the geometrical dimensions and by means of a mercury volumenometer, respectively. The density values obtained by both methods agreed very well. The pore size distributions were measured by mercury intrusion (Autoscan 33, Quantachrome Instruments, FL/USA) using samples taken from the centre of the green bodies.

Table 4 Influence of the organic additives on the ESA of the ethanolic suspensions

	Additive-free suspensions	Suspensions with organic additives	
AlN Grade C	Positive ESA	PAA + triethylamine	→ negative ESA [16]
SiC UF 25	Slightly positive ESA	polyethylene imine	→ significantly enhanced positive ESA [14, 17]
Al_2O_3 CT 3000 SG	Slightly negative ESA	PAA	→ significantly enhanced negative ESA
Al_2O_3 TM-DAR	Positive ESA	polyethylene imine	→ slightly enhanced positive ESA

Results and discussion

Influence of the organic additives on the electrokinetic behaviour

In Table 4 the influence of the organic additives on the electrokinetic behaviour of the ethanolic suspensions is shown.

The surface of the aluminium nitride particles was positively charged in pure ethanol without organic additives. By adding a combination of polyacrylic acid (PAA) and triethylamine, an effective stabilisation of the AlN suspension could be obtained which was necessary for realising a high packing density in the electrophoretically deposited green bodies. The adsorption of the negatively charged acid molecules on the particle surface led to a negative ESA signal whose value was further enhanced by the basic amine because the amine enabled an increased ionisation of the PAA.

Furthermore, the adsorption of the PAA resulted in an improved resistance of the AlN powder to hydrolysis (Table 5). In the case of additive-free ethanolic suspensions, the oxygen content of the powder remained constant after a contact time of 24 h if dried ethanol was used, whereas the small water content in 96% ethanol caused an enhancement of the oxygen content due to the hydrolytic reaction. This increase in oxygen content was prevented by adding the combination of PAA and triethylamine or PAA alone. By contrast, the only addition of triethylamine promoted the hydrolysis of AlN in 96% ethanol, which can be explained by a catalytic action of the amine. The catalytic effect of bases on the hydrolysis of aluminium nitride is described in [18].

As discussed more detailed in [16], the additive combination PAA/triethylamine offers the possibility to use dried *or* 96% ethanol for preparing stable AlN suspensions suitable for the EPD. For the investigations described in the present paper, however, only AlN suspensions prepared with dried ethanol as dispersing medium were used.

Based on experiences known from the literature [19], polyethylene imine was chosen as an additive for stabilising the SiC suspension. According to [19], small amounts of water in a weight ratio of polyethylene imine to H_2O = 1:1 were also added to the suspension to promote the dissociation of the polymer. Whereas the additive-free suspension showed a very small, slightly positive ESA signal, a significant enhancement of this signal was reached by the adsorption of the added polymer which exhibits a basic character due to pairs of non-bonded electrons at the nitrogen atoms within its chains and is positively charged in the dispersing liquid (Table 4).

The two alumina powders differ largely in their surface chemical properties. In the case of the powder CT 3000 SG, a small negative ESA signal was measured in the additive-free ethanolic suspension. The value of the negative signal increased significantly if PAA was added. Simultaneously, an electrostatic stabilisation of the suspension was achieved. In contrast to the AlN, no further enhancement of the value of the negative ESA signal was obtained by adding triethylamine to the PAA containing suspension.

The additive-free suspension of Al_2O_3 TM-DAR showed a relatively high positive ESA signal which was increased to a minor extent by polyethylene imine. The suspension stability, however, could be markedly improved by the organic additive. Whereas the corresponding additive-free suspension was highly viscous and unsuitable for EPD, the stabilised suspen-

Table 5 Oxygen content of the AlN powder after 24 h contact with ethanol

Organic additive	Oxygen content (wt.%)	
	Dried ethanol	96% ethanol
Additive-free suspension	1.57	4.25
0.3 wt.% PAA, 0.7 wt.% triethylamine	1.65	1.63
0.3 wt.% PAA	Not measured	1.69
0.7 wt.% triethylamine	Not measured	9.17

Oxygen content of the initial powder: 1.65 wt.%

Relative error of the measurement: 5%

sion showed a low viscosity and enabled the deposition of dense green bodies.

Electrokinetic measurements using aqueous suspensions confirmed the different surface chemical properties of the Al_2O_3 powders. The ESA signal was determined as a function of the pH value. The initial pH values, i.e. the pH of the pure aqueous suspensions without any additives, and the isoelectric points are listed in Table 6. The ESA signal at the initial pH value was slightly negative in the suspension of Al_2O_3 CT 3000 SG and positive in the case of the TM-DAR powder. These results correspond with the electrokinetic behaviour of the ethanolic suspensions.

Table 6 Initial pH values and isoelectrical points of aqueous suspensions of the powder Al_2O_3 CT 3000 SG and Al_2O_3 TM-DAR, respectively (solid content of the suspensions: 2 vol.%)

	Initial pH value	Isoelectric point (pH_{iep})
Al_2O_3 CT 3000 SG	9.2	8.3
Al_2O_3 TM-DAR	5.5	9.6

Zone formation during the EPD in the direction of the gravitational force

During the electrophoretic deposition in the direction of the gravitational force using the 60 wt.% ethanolic AlN, SiC, and Al_2O_3 suspensions, respectively, a zone formation similar to the zone sedimentation which is typical for concentrated suspensions was visible. Figure 1 illustrates this zone formation.

Immediately after applying the electric DC field, the particles move to the oppositely charged deposition electrode. Simultaneously, a supernatant which is poor of solid is formed at the surface of the suspension. At the lower electrode the particles are deposited. The thicknesses of the deposit and of the supernatant increase with time whereas that of the suspension zone decreases until this zone is used up at the time t_{end}. In practice, however, the EPD is usually stopped according to the desired thickness of the deposit at a former point in time than t_{end}.

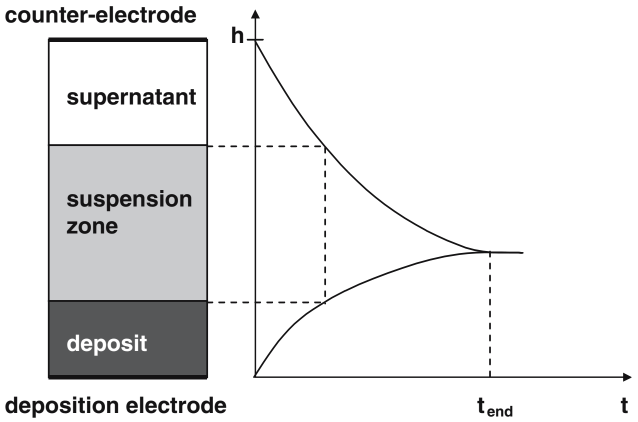


Fig. 1 Zone formation during the EPD in the direction of the gravitational force

Conductivity measurements

For investigating the contributions of the ionic species and of the charged particles to the conductivity of the suspension, the specific electrical conductivities of the suspensions and their centrifugates were compared. Besides the ethanolic suspensions, the aqueous suspension of the powder CT 3000 SG was investigated in this regard. As shown in Figs. 2 and 3, the conductivities of the centrifugates were higher than that of the suspensions. It can be concluded that during the EPD the current in the suspension is mainly carried by the free ionic species due to their higher mobility in comparison with the charged particles. The lower conductivities of the suspensions can be explained by the fact that in concentrated suspensions the ionic species are hindered in their movement by the particles. This effect predominates over the own contribution of the charged particles to the conductivity.

Electrophoretic deposition of AlN

In the following text the electrophoretic deposition from the ethanolic AlN suspension stabilised by PAA/triethylamine will be discussed more detailed. The particles were deposited at the anode in this case.

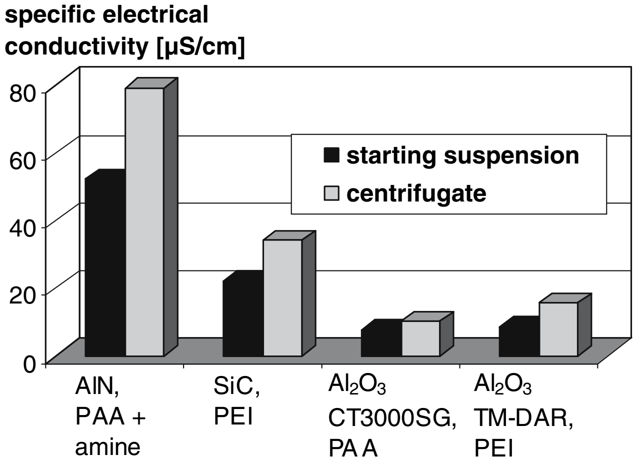


Fig. 2 Specific electrical conductivities of the ethanolic suspensions and of their centrifugates (solid content of the suspensions: 60 wt.%)

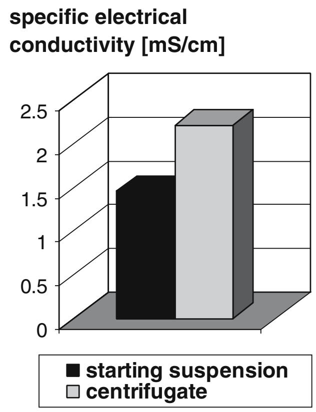


Fig. 3 Specific electrical conductivities of the aqueous Al_2O_3 CT 3000 SG suspension and its centrifugate

Table 7 contains the conductivities of the suspension zone and of the supernatant as well as the solid content of the suspension zone after different deposition times at an applied voltage of 30 and 50 V, respectively. The conductivity was measured in samples taken from these zones immediately after the EPD by means of a syringe. By drying the suspension samples, their solid content was determined. It has to be mentioned that possible gradients of the conductivity and/or the solid content within the single zones cannot be detected in this way.

As the values in Table 7 indicate, the solid content of the suspension zone remained nearly constant during the deposition. By contrast, the conductivity of this zone decreased slightly with time because of the migration of free ionic species to the electrodes resulting in a reduced concentration of these species in the suspension.

The conductivity of the supernatant was significantly lower compared to the suspension zone. On the basis of the above-mentioned investigation of the conductivities of the suspensions and the centrifugates it can be assumed that the low conductivity is mainly caused by a decreased concentration of ionic species, not by the very low particle concentration in the supernatant. Obviously, the transport of positively charged ionised amine molecules to the upper electrode (cathode) is slower than their consumption by the electrode reaction.

If the applied voltage between the electrodes was kept constant during the electrophoretic deposition, the current decreased with time. Several factors can contribute to this behaviour: the electrical resistance of the growing deposit and supernatant, the decreasing conductivity of the suspension zone, and an enhanced concentration overvoltage at the electrode/liquid interface due to a diminishing concentration of reactants for the electrode reactions. As described in [3], an increased cathodic concentration overvoltage can cause a significant increase in total electrical resistance due to the higher potential drop at the cathode even in the case of anodic deposition. Excepting the diminishing conductivity of the suspension zone, these factors

Table 7 Electrophoretic deposition of AlN: specific electrical conductivities of the suspension zone and of the supernatant, respectively, and solid content of the suspension zone depending on the deposition time

Starting suspension AlN Grade C, ethanol, PAA + triethylamine				
Specific electrical conductivity at 25 °C: 52.3 μS/cm			Solid content: 60 wt.%	
Electrophoretic deposition				
Applied voltage (V)	Deposition time (min)	Specific electrical conductivity at the end of the deposition time (μS/cm)		Solid content of the suspension zone (wt.%)
		Suspension zone	Supernatant	
30	5	49.2	*	59.8
	10	48.7	15.0	59.5
	15	48.3	14.9	59.7
	20	46.5	15.2	59.9
	25	*	14.1	*
	30	**	14.5	**
	35	**	11.0	**
50	5	47.6	14.8	59.1
	10	44.4	14.7	59.7
	15	**	14.2	**
	20	**	13.7	**
	25	**	14.0	**

* Not determined because of a low thickness of the zone

** Suspension zone was used up

lead simultaneously to a decrease in effective electric field strength during constant–voltage EPD.

As shown in Fig. 4a, the decreasing effective field strength resulted in a degressive curve of the deposit weight per unit of area vs. time. After a certain time depending on the applied voltage the suspension zone was used up, and no further increase in weight was obtained.

Considering the suspension zone to be an Ohmic resistance, the effective field strength can be described by Eq. 1.

$$\vec{E}_{\mathrm{eff},t} = \frac{\vec{j_t}}{\kappa_{\mathrm{sz},t}} \tag{1}$$

$\vec{E}_{\mathrm{eff},t}$ effective electric field strength
$\vec{j}_t$ current density
$\kappa_{\mathrm{sz},t}$ specific electrical conductivity of the suspension zone
t time

Assuming a homogeneous electrical field, it is possible to use scalar variables for the electric field strength (E) and the current density (j):

$$E_{\mathrm{eff},t} = \frac{j}{\kappa_{\mathrm{sz},t}} = \frac{I_t}{\kappa_{\mathrm{sz},t} \cdot A} \tag{2}$$

I_t current
A cross-sectional area perpendicular to the field lines

It has to be kept in mind that in Eq. 2 local differences in electrical conductivity, in solid content, and in field strength are neglected. Despite of simplifying assumptions, a simple experimental way for describing changes in effective field strength can be derived from Eq. 2.

Four measured values are required for this purpose:

- the electrical conductivity of the starting suspension ($\kappa_{s,0}$),
- the current measured immediately after the electric field was applied (I_0),
- the current at the end of the deposition time (I_t), and
- the final value of the conductivity of the suspension zone determined straight after the EPD experiment ($\kappa_{\mathrm{sz},t}$).

The relative change in effective field strength is expressed by:

$$\frac{E_{\mathrm{eff},t}}{E_{\mathrm{eff},0}} = \frac{I_t \cdot \kappa_{s,0}}{I_0 \cdot \kappa_{\mathrm{sz},t}} \tag{3}$$

$E_{\mathrm{eff},t}$ effective field strength at time t
$E_{\mathrm{eff},0}$ effective field strength at the beginning of EPD ($E_{\mathrm{eff},0}$ equals the applied field strength which is given by the applied voltage divided by the electrode distance.)

The decrease in $E_{\mathrm{eff},t}/E_{\mathrm{eff},0}$ with time shown in Fig. 4b reflects the decreasing effective field strength during the EPD under constant–voltage conditions.

The slope of the deposit weight per unit of area as a function of the applied voltage at fixed deposition times became lower with higher applied voltages (Fig. 5a). As also can be seen in Fig. 5a, no deposit was formed without an electric field, i.e. only by sedimentation, in the times relevant for the EPD. The degressive curve of the deposit weight versus voltage can also be explained by the decreasing effective field strength during the deposition. If higher voltages are applied, the effective field strength is more reduced in the same time than at low voltages. The dependence of $E_{\mathrm{eff},t}/E_{\mathrm{eff},0}$ on the applied voltage drawn in Fig. 5b confirms this explanation.

It is well-known that the decrease in effective field strength can be avoided if the current is maintained constant during the EPD. The increasing electrical resistance with deposition time causes an enhancement of the voltage in this case. However, the deposit weight did not show an exactly linear increase with time in constant–current EPD using the ethanolic AlN suspension stabilised by PAA/triethylamine (Fig. 6a). The slightly progressive curve is caused by the diminishing conductivity of the suspension zone, which led to an

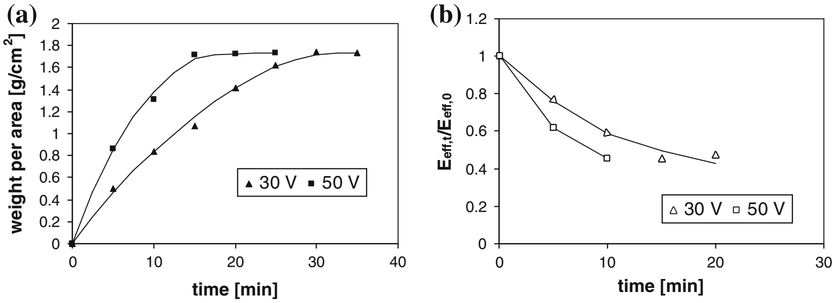


Fig. 4 Electrophoretic deposition of AlN under constant–voltage conditions: Deposit weight per unit of area (**a**) and $E_{\mathrm{eff},t}/E_{\mathrm{eff},0}$ (**b**) depending on time (starting suspension: 60 wt.% AlN, 40 wt.% ethanol, PAA + triethylamine; EPD in the direction of the gravitational force)

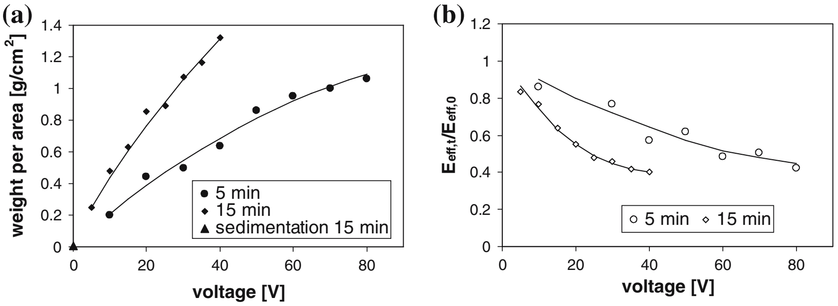


Fig. 5 Electrophoretic deposition of AlN under constant–voltage conditions: Deposit weight per unit of area (**a**) and $E_{\mathrm{eff},t}/E_{\mathrm{eff},0}$ at the end of the deposition (**b**) depending on voltage (starting suspension: 60 wt.% AlN, 40 wt.% ethanol, PAA + triethylamine; EPD in the direction of the gravitational force)

increase in effective field strength with time. The sharp bend in the curves shows the point at which the suspension zone was used up. Figure 6b showing $E_{\mathrm{eff},t}/E_{\mathrm{eff},0}$ depending on time illustrates the slight enhancement of the effective field strength during the electrophoretic deposition.

The progressive curves of the deposit weight per unit of area as a function of current (Fig. 7a) result also from the slight increase in effective field strength, which was in a given time larger at higher than at lower currents (Fig. 7b).

Comparison of the suspensions regarding the EPD results

The deposition experiments using the ethanolic suspensions of SiC and of the two different Al_2O_3 powders, respectively, confirmed that the solid content of the suspension zone decreased only to a minor extent during the EPD in the direction of the gravitational force. In contrast to the AlN suspension, the electrical conductivity of the suspension zone remained nearly constant. A further difference to the AlN suspension was the fact that the supernatant similar to the centrifugate showed a higher conductivity than the suspension. (The behaviour of the AlN suspension regarding the conductivity of the suspension zone and of the supernatant mainly arises from the migration of the ionised amine molecules to the counter-electrode and their electrochemical reaction at this electrode.)

The results of these investigations are summarised in Table 8.

As indicated by the values of $E_{\mathrm{eff},t}/E_{\mathrm{eff},0}$ compared to the deposit thicknesses (Table 8), the extent of the decrease in effective field strength during constant–voltage EPD was different for the four suspensions. Besides the electrophoretic mobility, differences in the change of effective field strength can be seen as a further factor that depends on the suspension composition and influences the deposition rate.

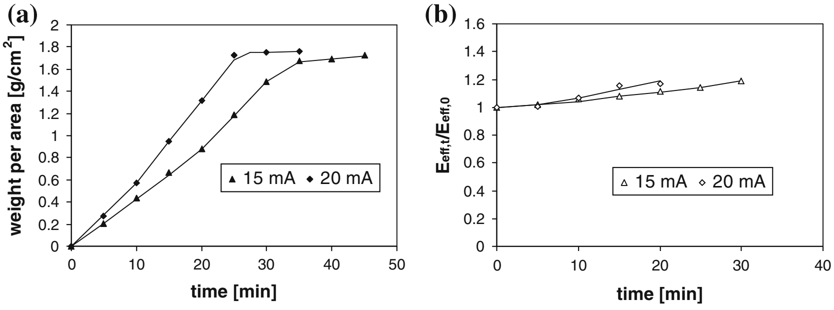
Furthermore, Table 8 contains the values of the relative green densities of the deposits.

In the case of aluminium nitride, the influence of the solid content of the suspension on the green density was investigated in additional experiments. The density of the green bodies increased with increasing solid content. At a solid content of 70 wt.%, green densities of approximately 60...61% TD were obtained.

In the case of all suspensions monomodal pore size distributions of the deposited green bodies reflecting a homogeneous particle packing were achieved (Figs. 8 and 9). The differences in the pore radii results from the different particle sizes of the powders.

Using the powder Al_2O_3 CT 3000 SG, the EPD from the ethanolic suspension at the upper and the lower

Fig. 6 Electrophoretic deposition of AlN under constant–current conditions: Deposit weight per unit of area (**a**) and $E_{\mathrm{eff},t}/E_{\mathrm{eff},0}$ (**b**) depending on time (starting suspension: 60 wt.% AlN, 40 wt.% ethanol, PAA + triethylamine; EPD in the direction of the gravitational force)



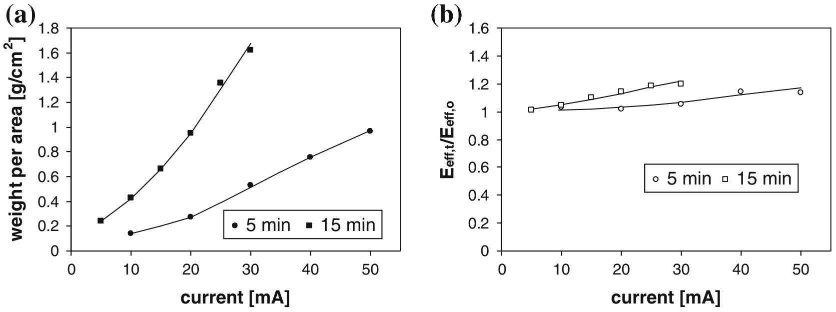


Fig. 7 Electrophoretic deposition of AlN under constant–current conditions: Deposit weight per unit of area (**a**) and $E_{\mathrm{eff},t}/E_{\mathrm{eff},0}$ at the end of the deposition (**b**) depending on current (starting suspension: 60 wt.% AlN, 40 wt.% ethanol, PAA + triethylamine; EPD in the direction of the gravitational force)

electrode as well as the EPD from the corresponding aqueous suspension were compared regarding the quality of the deposits. The pore size distributions of the last-mentioned green bodies show only minor differences (Fig. 9).

The green density obtained by the electrophoretic deposition of the Al_2O_3 powder against the gravitational force was 61.3% TD. The properties of the deposits at the upper and the lower electrode differed only slightly because no significant fractionation occurred in the case of the used concentrated suspension. By contrast, at low solid contents the interaction of the gravitational and the electric field can be used for producing green bodies with gradients in particle size or for a selective deposition of the nanosized fraction of a conventional powder [20]. Besides the solid content, the particle size distribution and the electric field strength are main parameters influencing the degree of fractionation.

By the electrophoretic deposition from the aqueous Al_2O_3 suspension using the membrane method (applied voltage: 80 V, deposition time: 5 min), a green density of 61.9% TD was achieved. A direct comparison with the EPD from the ethanolic suspension is not possible because of the different experimental conditions, but the results show that similar packing densities of the particles can be obtained by both methods.

Simultaneous electrophoretic deposition of non-oxide powders and sintering additives

In the case of the non-oxide powders, sintering additives are necessary to obtain dense ceramics by pressureless sintering. Yttria is a suitable sintering aid for AlN. Figure 10 shows the Y_2O_3 content at the electrode side and the suspension side of green bodies produced by electrophoretic deposition of an AlN/Y_2O_3 powder mixture.

If a diluted suspension was used for the EPD, the yttria content was found to be higher at the upper side than at the lower side of the deposit. By contrast, a homogeneous distribution of the sintering additive in the green body was reached using a suspension with a solid content of 60 wt.% = 26.5 vol.%.

Whereas differences in the value of the electrophoretic mobility cause a separation of the components

Table 8 Comparison of the different ethanolic suspensions regarding the results of the EPD in the direction of the gravitational force (solid content of the suspensions: 60 wt.%, applied voltage: 50 V, deposition time: 10 min)

		AlN, PAA + triethylamine	SiC, polyethylene imine	Al_2O_3 CT 3000 SG, PAA	Al_2O_3 TM-DAR, polyethylene imine
Specific electrical conductivity (μS/cm)	Starting suspension	52.3	22.1	7.6	8.4
	Suspension zone[a]	44.4	22.7	7.8	8.8
	Supernatant[a]	14.7	[b]	10.2	11.9
Solid content of the suspension zone (wt.%)[a]		59.7	59.8	59.0	59.1
$E_{\mathrm{eff},t}/E_{\mathrm{eff},0}$[a]		0.59	0.25	0.44	0.64
Deposit thickness (mm)		7.05	2.30	4.20	5.29
Relative green density (% TD)[c]		57.1	55.4	60.5	59.6

[a] t = 10 min; [b] low thickness of the supernatant; [c]TD: theoretical density; TD_{AlN}: 3.26 g/cm^3, TD_{SiC}: 3.21 g/cm^3, TD_{Al2O3}: 3.99 g/cm^3

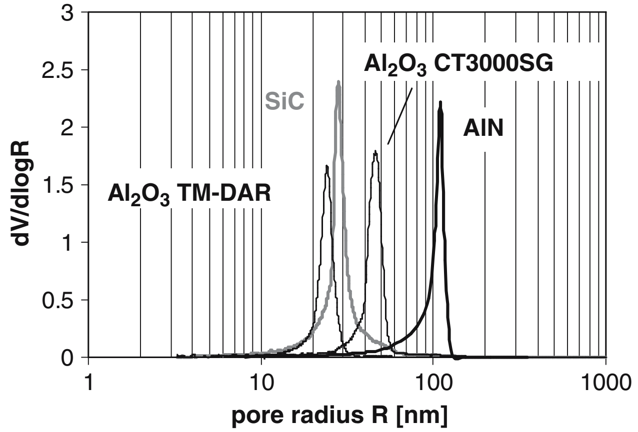


Fig. 8 Pore size distributions of the green bodies produced by EPD from ethanolic suspensions

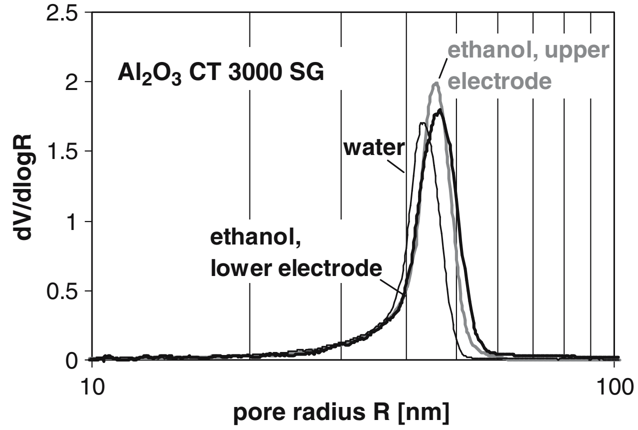


Fig. 9 Pore size distributions of green bodies produced by EPD from the ethanolic Al_2O_3 CT 3000 SG suspension and from the corresponding aqueous suspension

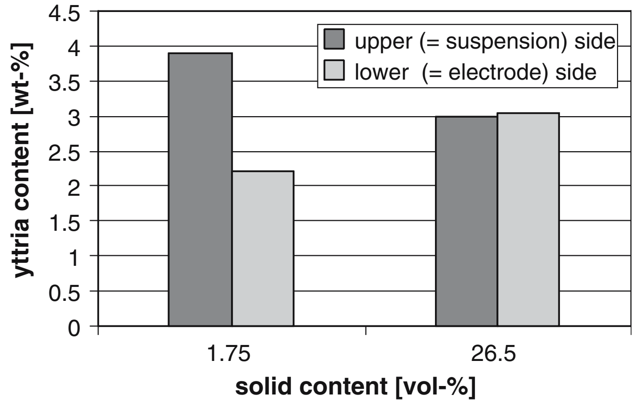


Fig. 10 Y_2O_3 content at the upper and at the lower side of green bodies produced by EPD from suspensions of an AlN/Y_2O_3 powder mixture (The EPD was continued up to a nearly complete deposition of the whole solid content.)

in diluted suspensions, a collective motion of the particles dominates at the higher solid contents usually used for EPD as described more detailed in a previous paper [21].

The AlN green bodies containing Y_2O_3 were pressureless sintered at 1850 °C (2 h holding time) in nitrogen atmosphere. Sintered bodies of nearly theoretical density were obtained.

Green bodies of homogeneous composition could also be produced by the simultaneous EPD of SiC and the sintering aids B_4C and C [17].

Figure 11 shows a photograph of electrophoretically deposited AlN green bodies. Besides the samples with a diameter of 4 cm, also plates of 14 cm in diameter were produced using larger electrodes made of stainless steel. The deposit thickness was usually in the range of a few millimetres (up to 10 mm), but green bodies with a thickness of 15 mm were deposited, too.

Summary

Stable ethanolic suspensions of AlN, SiC and Al_2O_3, respectively, were prepared by adding suitable organic dispersants. Planar circular green bodies showing monomodal pore size distributions were produced by electrophoretic deposition from these suspensions.

In the particular case of the EPD in the direction of the gravitational force described in this paper, the formation of three zones could be observed: the deposit, the suspension zone and the supernatant. The supernatant has to be considered as an additional factor influencing the effective electric field strength in constant–voltage EPD. Changes of the conductivity in the suspension zone can also influence the effective

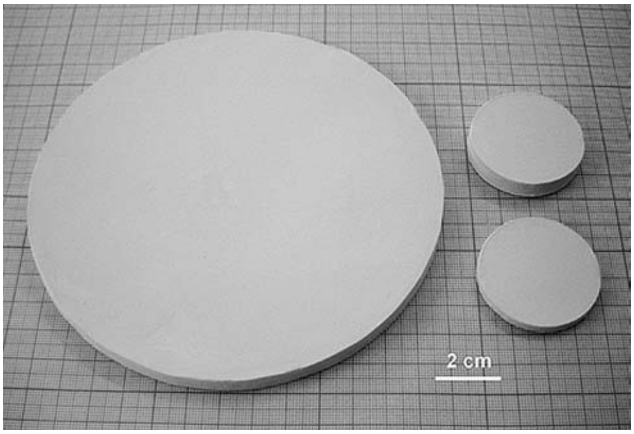


Fig. 11 Electrophoretically deposited AlN green bodies

field strength. The behaviour of the suspensions regarding this effects depends on its composition.

Measurements of the electrical conductivity of the suspensions and of their centrifugates confirmed that the current in the suspension is mainly carried by the free ionic species.

Investigations concerning the EPD of an AlN/Y_2O_3 powder mixture showed that in concentrated suspensions a collective motion of the particles dominates which enables the deposition of green bodies with a homogeneous distribution of the sintering additive despite of differences in the electrophoretic mobilities of the two powders.

Acknowledgement Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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