ELECTROPHORETIC DEPOSITION OF ALUMINA FROM NON-AQUEOUS DISPERSIONS

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ABSTRACT

Alumina has been deposited from an ethanolic suspension of commercial alumina powder stabilized with polyacrylic acid. The process has been studied by systematical variation of the deposition conditions and the properties of the suspensions. The microstructure of the deposited green plates is homogeneous except a thin porous layer (200 μm) at the electrode facing side. After sintering this porous layer is still present and causes a lower fracture strength of the electrode facing side in comparison to the solvent facing side of the compact. Methods for optimizing the microstructure are discussed.

INTRODUCTION

The production of ceramic components with good mechanical properties and reliability requires a fine and homogenous microstructure without critical defects in the sintered compact. This property can be improved by use of fine and ultrafine powders and for this reason submicron powders are of increasing interest. Since the processing of fine powders by conventional forming techniques is difficult, it is necessary to adapt the forming technique to the special properties of the powders. One technique is the electrophoretic deposition of ceramic powders from suspensions which is known for a long time /1-4/. But until now no attempts have been made to study this method with regard to the improvement of homogeneity and reliablity of ceramic compacts. In the present paper we will report about some fundamental correlations of the parameters which determine the electrophoretic deposition of alumina from non-aqueous suspensions and the resulting microstructure of the green compact as well as the strength of the sintered bodies. Non-aqueous suspensions were used to avoid the formation of gas bubbles by electrolysis of water.

EXPERIMENTAL

The suspensions were prepared by ultrasonic agitation /5/
from commercial alumina powder (Alcoa A16SG) in a mixture
of ethanol, water and polyacrylic acid (PAA) as the sus-
pending agent. The alumina content was varied between 10
and 60 wt.-% and the concentration of PAA ranged from 1.2
to 2.0 wt.-% referring to the Alumina content.

Deposition experiments were performed in a cylindrical
cell with 50 mm diameter and variable electrode distance
up to 100 mm. The applied voltage was changed between 10
and 300 V and the deposition time was varied between 2 and
25 minutes. The direction of deposition was parallel to
the field of gravity. The green plates (3 mm thickness)
were dried at 50 °C and a standard procedure was used for
sintering (1640 °C, 10 min). The particle size distribu-
tion in the suspension was determined by sedimentation and
after a sedimentation time of 16 hours particles larger
than 1 μm were separated. All suspensions studied in this
paper were treated in this way before using them for
deposition experiments. The zeta-potential was determined
by measuring the movement of the boundary surface in a
U-tube in an electric field.

RESULTS AND DISCUSSION

Electrophoresis:

Electrophoresis is based on the movement of charged parti-
cles in a liquid caused by an electric field. The surface
charge of the alumina particles in the suspension is ob-
tained by polyacrylic acid which is stucked on the parti-
cle surface. In addition to this, the PAA serves as a
binder for the deposited particles. In a first approxima-
tion the deposited mass can be described by equation (1)
which is a simplification of the more complicated descrip-
tion given by /6/.

$$m(t) = A \cdot c \cdot t \cdot U \cdot \epsilon \cdot Z / (n \cdot d) \qquad (1)$$

A: electrode area   U: applied voltage
c: powder concentration   Z: zeta-potential
t: time of deposition   n: viscosity
ϵ: permittivity   d: electrode distance

This equation shows that the deposited mass depends on two
different sets of parameters. The first is directly corre-
lated to the suspension properties as the solid content,
the zeta-potential, the permittivity and the viscosity.
The second one belongs only to the deposition conditions
as electrode area and distance, time of deposition and the
applied voltage. The parameters which describe the deposi-
tion (see eq. 1) were investigated.

Suspension properties:

The electrophoretic deposition of green compacts requires
stable suspension as well as high deposition rates for an
economical processing. For these reasons the suspension
stability was optimized including high desposition rates.
According to eq. 1 the following parameters were opti-
mized: solid content (a high content was desired), zeta-
potential, PAA concentration, permittivity and viscosity.
Since these parameters are not independent of each other,
the influence of the PAA concentration and the solid con-
tent was investigated at first. It was found that the
zeta-potential is very sensitive to the PAA-concentration
and the solid content. The highest values (-38 to -44 mV)
are obtained at 1.3 to 1.5 wt.-% PAA for alumina content
of 40 wt.-%. The variation of the alumina concentration
between 20 and 40 wt.-% at constant PAA concentration
(1.4 wt.-%) caused a zeta-potential change between -44 to
-48 mV. The permittivity does not depend on the PAA con-
tent and decreases from 27.2 to 22.1 with the alumina
content increasing from 10 to 60 wt.-%. The viscosity de-
pends only on the alumina content and increases from 1.3
to 4.4 mPa·s (10 to 60 wt.-% alumina).

Deposition rates:

The deposition rate has been studied as a function of the
applied voltage and the alumina content. The suggested
(eq. 1) linear relationship between deposited mass on the
one and voltage and time on the other side could be
proved, as shown in fig. 1 and 2. With increasing alumina
content the deposited mass for constant time or voltage
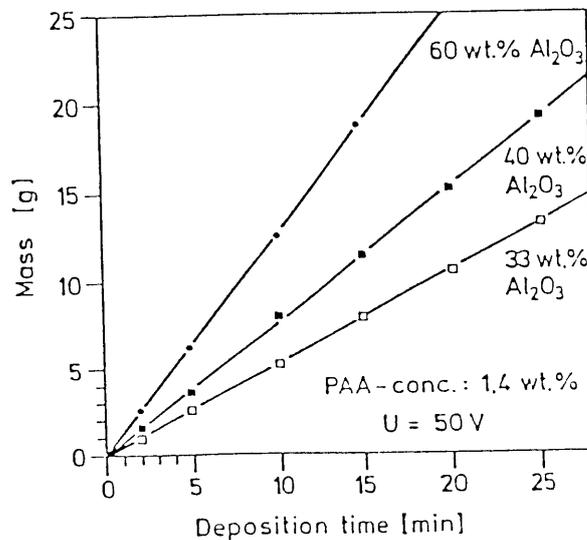increases.

Fig. 1   Deposited mass as function of the deposition
         time for different alumina contents
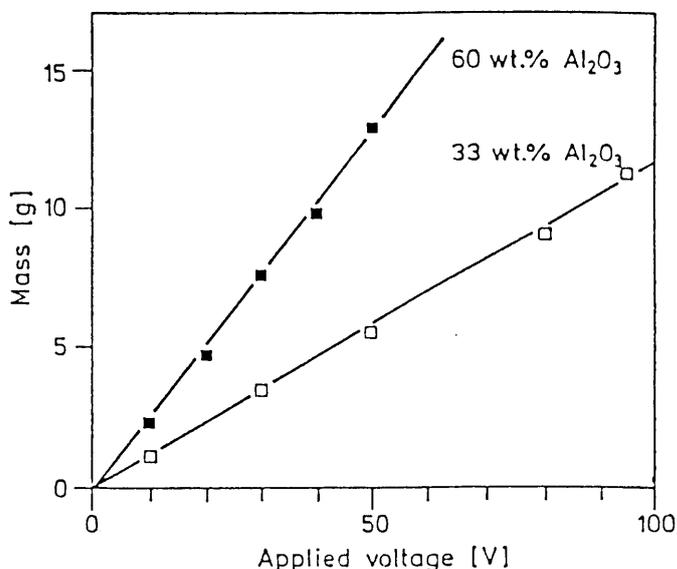   PAA-conc.: 1.4 wt.-%, applied voltage: 50 V

Fig. 2   Deposited mass as a function of the applied
         voltage for different alumina concentrations
         PAA-conc.: 1.4 wt-%, deposition time: 10 min

Characterization of the green plates:

The microstructure of the green plates was investigated by
scanning electron microscopy (SEM). The solvent facing
side of the green plate (fig. 3 a) exhibits a homogenous
microstructure with dense packed particles. In contrast
the microstructure of the electrode facing side (fig. 3 b)
is more heterogenous caused by agglomerates and large
pores. This unexpected behavior was studied by further
experiments and it could be shown that this type of sur-
face microstructure is not primarily caused by the removal
of the green plate from the electrode. Furthermore the
surface is not affected by the suspension parameters and
is not caused by a possible electrolysis of water leading
to the formation of gas bubbles. From the present state of
our knowledge the porous microstructure of the electrode
side is directly connected to the deposition mechanisms,
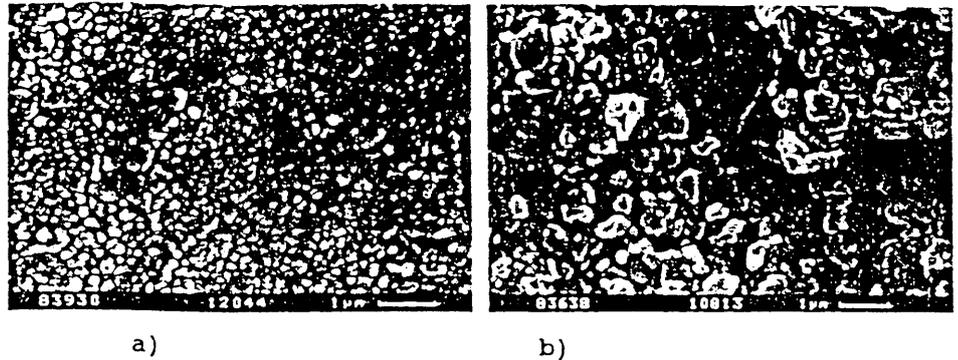as it will be shown later.

a)   b)

Fig. 3   SEM-microgaphes of green plate
         a: solvent facing side, b: electrode facing side

In order to determine the depth profile of the porous
layer of the electrode facing side several layers with
varying thicknesses were deposited, starting with 0.2 mm
and increasing the layer thickness up to 1.5 mm. The
porosity of the different layers was measured by the
Hg-penetration method. After calculating the average plate
density as a function of the thickness, the differential
density can be calculated according to eq. (2):

$$P_d \cdot d = \Sigma \; p_i \cdot d_i \quad i=1 \text{ to } n \qquad\qquad (2)$$

P_d : density of the deposited layer
d : thickness of the deposited layer
p_i : differential density
d_i : differential thickness

The average values of the differential densities p_i as
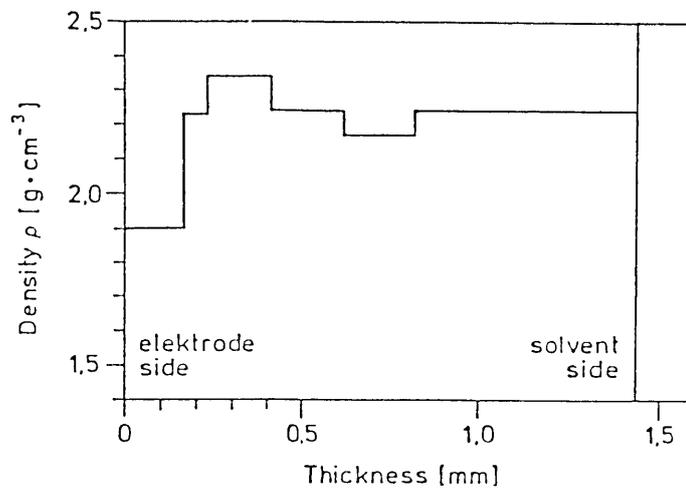a function of the plate thickness are shown in fig. 4.

Fig. 4   Differential density as a function of the plate
         thickness

It is obvious that the first layer (200 μm) is signifi-
cantly less dense than the overall density of the plate.
The pore size distribution (determined by Hg-porosimetry)
of the first layer showed a higher number of pores greater
than 10 μm too, which is in agreement with the SEM-micro-
graphs. The density of the porous layer is 1.9 g/cm^3 and
density of a green compact is 2.25 g/cm^3. The formation of
a porous layer was observed for different suspensions and
deposition parameters. To reduce the porous layer thick-
ness the influence of the deposition voltage was studied
for a standard suspension (1.4 wt-% PAA, 33 wt-% alumina)
and a constant electrode distance (30 mm). The results are
shown in fig. 5. The density of the first deposited layer
increases from 10 to 100 V and decreases slowly up to
300 V. The maximum density (2.05 g/cm^3) is achieved at
100 V. The influence of the applied voltage on the density
of the thicker layers is not so distinct. The reasons for
the formation of porous layers with a distinct thickness
may be attributed to the mechanism of the deposition pro-
cess and the discharge of the particles. However, this
assumption has to be proved by further experiments.

Fracture strength of sintered plates:

The fracture strength was determined by a double ring test
to get information about the microstructural defects of
the sintered plates. Therefore both sides of the plates
were tested under tension stress. The results are repre-
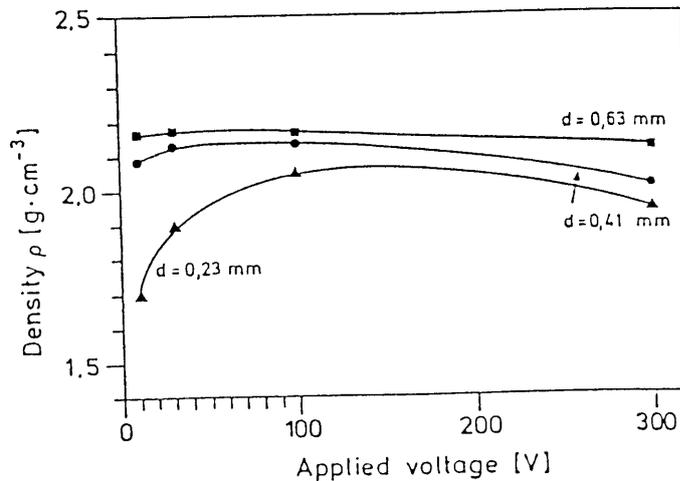sented in a Weibull-plot in fig. 6.

Fig. 5   Density as a function of the applied voltage for
different green layer thicknesses

The average of the fracture strength of the solvent side
is 442 MPa, in comparison with 344 MPa of the electrode
side. The lower strength of the electrode side is due to
its surface defects formed in the green state, which are
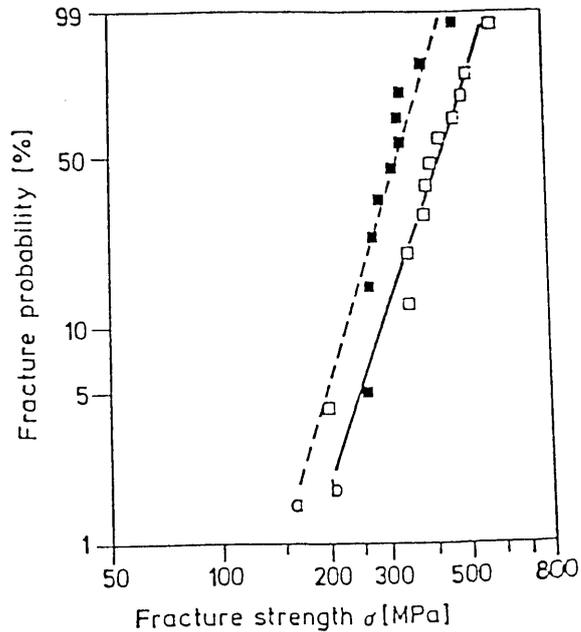also responsible for the low Weibull modulus of about 5.

Fig. 6 Weibull-plot of fracture strength of sintered
plates a: electrode side, b: solvent side
(PAA-conc.: 1.3 wt.-%, alumina cont.: 40 wt.-%,
voltage: 50 V, sintering temp.: 1640 °C, 10 min.)

CONCLUSIONS

The electrophoretic deposition of alumina from a non-
aqueous suspension was studied in the present paper. It
could be proved, that electrophoresis is a suitable method
for an agglomerate-free processing of submicron powders,
because agglomerates can be separated directly from the
suspension by sedimentation or centrifugation without
additional processing steps. Furthermore the forming
technique leads to a very homogeneous microstructure in
the green compacts and offers the possibility to reduce
the size of critical defects and improve the reliability
of ceramic products. Further efforts will be done to
optimize the deposition process and the properties of
sintered product.

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