Aqueous electrophoretic deposition of $\text{Al}_2\text{O}_3$/ZrO$_2$ layered ceramics

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Abstract
Layered ceramics are being prepared by different forming methods such as slip or tape casting, dip coating, etc. Microlaminate materials have been also prepared by electrophoretic deposition (EPD), but usually from non-aqueous suspensions. In this work, the preparation of Al$_2$O$_3$/ZrO$_2$ layered ceramics from aqueous suspensions is described. The growth of the deposit thickness can be controlled in order to design laminar ceramics either as coatings or as self-supported deposits, with a few thick layers, reducing warping effects, and avoiding environmental problems.

1. Introduction
Electrophoretic deposition (EPD) has gained interest in the production of coatings and films by different processing methods [1–4]. An important field of application of this technique deals with the production of laminar ceramic composites. Bissinger et al. [5] and Sarkar et al. [6] have studied the production and characteristics of different oxide microlaminate systems obtained from non-aqueous suspensions. However, the use of water presents important advantages such as the lower potentials required for the deposition, and more important, the environmental problems associated with the use of organics. In this sense, very few works have reported the formation of thick films by EPD in water [7–9].

On the basis of previous works in which the parameters involved in the production of Al$_2$O$_3$ thick films and bodies by EPD in water [10,11], the aim of this work is to establish the conditions for a reliable fabrication of Al$_2$O$_3$/Y-TZP layered composites in aqueous media. This work demonstrates the possibility of obtaining ceramic laminates with relatively thick layers, similar to those obtained by other traditional forming methods such as slip casting [12] or tape casting [13]. Composites containing up to 11 layers with a total thickness from 100 to $>300$ $\mu$m are obtained.

2. Experimental
The following starting powders were used: (1) Al$_2$O$_3$ Alcoa (A16SG, USA), with a mean particle size of 0.4 $\mu$m and a specific surface area of 8
m²/g, and (2) tetragonal zirconia polycrystals with 3% mol Y₂O₃, Y-TZP (TZ3YS, TOSOH, Japan), with a mean particle size of 0.4 μm and a specific surface area of 6.7 m²/g.

Aqueous slurries of both powders were prepared to a solid content of 5 wt.%. For stabilization, a commercial carbonic acid based polyelectrolyte (Dolapix CE-64, Zschimmer-Schwarz, Germany) was used. The slips were prepared using a high shear mixer (Silverson L2R, UK) for 3 min. The dispersing conditions were optimized by measuring the zeta potential and the conductivity of the slurries at different deflocculant concentrations. Zeta potentials were determined using a mass transport analyzer (Micromeritics, USA). The conductivity was measured using a WTW conductimeter.

EPD experiments were performed for stabilized slurries of each material by applying a constant current density of 2.8 mA cm⁻² for deposition times up to 10 min. A LABCONCO 433-3250 (USA) power source was used. The electrolytic cell is a glass beaker containing the counterelectrode Pt and the working Zn electrode. The distance between electrodes was 2 cm and the geometry of the cell was maintained constant. The voltage variation was registered during the experiment. The thickness was determined on the dry green deposits with a digital indicator.

Layered deposits were obtained by sequential deposition experiments alternatively changing both slurries to form deposits with different numbers of layers, up to 11. Each layer was formed after 1 min deposition.

Both the monolithic and the layered deposits were left in air 48 h for drying, and were subsequently sintered at 1550°C/2 h. Microstructural observations were made by optical microscopy on polished sintered surfaces.

3. Results and discussion

The zeta potential of Al₂O₃ slips containing 0.6 wt.% deflocculant is 20 mV. The corresponding value for Y-TZP is 45 mV, more than twice that of Al₂O₃.

The quantity of deposited mass (m) can be theoretically calculated from the Hamaker equation, as follows

\[ m = \frac{\varepsilon_0 \varepsilon_r E}{1.5 \eta c \zeta L t}, \]

thus depending on the electrical properties of the suspending liquid (dielectric constant) and its viscosity (η), the properties of the suspension (concentration, C, and zeta potential, ζ), the geometry of the system (distance between electrodes, L) and the imposed electrical conditions (applied field, E, which is inversely related to the conductivity, and deposition time, t).

According to the measured zeta potential values, it can be expected that the deposited mass will be higher for Y-TZP.

The important role of the slip conductivity in EPD has been described previously [10,11]. In this case, the conductivity for Y-TZP slurry is lower (130 μS cm⁻¹ at 26°C) than that corresponding to the Al₂O₃ slurry (195 μS cm⁻¹ at 26°C), thus altering their expected deposition behavior.

The voltage evolution along the 10 min EPD experiment for both slurries is plotted in Fig. 1. The voltage increases rapidly during the first minute of the deposition process and remains constant for longer deposition times. The measured voltage is always higher for the Y-TZP slurry because of its lower conductivity. Depots of both materials were prepared at different deposition times under similar

![Fig. 1. Voltage variation of Al₂O₃ and Y-TZP slips containing 0.6 wt.% deflocculant (A06 and Z06, respectively) during 10 min deposition experiments.](image)
conditions to evaluate the growth rates. The results can be seen in Fig. 2. As observed, a linear growth with time is obtained for both materials and the formation rate is rather similar. However, from Fig. 1 the voltage does not increase any more after the first minute of the deposition. This means that the resistance of the formed deposit is very low and the registered voltages must be related only to the electrical conductivity of the slips. The origin of this effect must be found in the nature of the electrode, consisting of an easily oxidizable substance, as Zn. During the EPD tests in aqueous media, Zn$^{2+}$ cations are formed in the substrate, which can easily move through the deposit by either diffusion or migration phenomena [14]. According to the values plotted in Fig. 2, homogeneous coatings or deposits as thick as 500 μm can be obtained for monolithic materials after 10 min continuous deposition.

Taking into account the rate of thickness evolution of each slurry with time, EPD experiments were designed to obtain layered deposits while maintaining the current density constant. Fig. 3 shows a general view of the microstructure of Al$_2$O$_3$/Y-TZP layered composites with 10 layers obtained by aqueous EPD. Under these conditions a very similar layer thickness is obtained for the different materials. This confirms the formation rate results for the monolithic deposits, but suggests that the zeta potential measurements are a little confusing probably due to the fact that this technique is not suitable when some adsorption of the additives onto the particles surface occurs.

On the other hand, the total thickness is lower than in the case of monolithics because in the case of layered materials, the deposition process is not continuous for 10 min, but the addition of sequential 1 min experiments and the first seconds of each one is consumed to achieve the maximum current density.

Despite the differences in the thermal expansion coefficients between unlike layers, no cracking occurs because it has not achieved a critical thickness, as reported by Ho et al. [15]. According to that work, the critical thickness for cracks originated due to biaxial compression in the alumina layer is around 400 μm for laminates with the same layer thickness,
as the one obtained here. The propagation of cracks in the layers with residual tensile stresses depends also on the thickness of the adjacent layer [16], which in this case, does not achieve the critical value.

Several microstructures can be designed with different numbers of layers. Deposit thicknesses higher than 150 \(\mu m\) (in the green state) produce self-supported multilayer materials whereas lower thicknesses are required to obtain microlayered coatings. Fig. 4 shows the microstructure of a layered deposit prepared in the same conditions, but with only four layers. This structure has a total thickness of 110 \(\mu m\) after sintering and was the thinnest one which could be removed from the electrode in this work. The main problem of these microlayered materials during sintering is related to the difference in the shrinkage behaviour between Al\(_2\)O\(_3\) and Y-TZP layers, which is high enough to promote warping of the layered structure because the total thickness is quite small. If the material was symmetric with a layer sequence of the type ABABA, this warping effect could decrease or even disappear.

It is possible to modify the layer thickness of each material by simply changing the deflocculant content of the slip. Layered composites were also prepared with the same Y-TZP slips and by changing the deflocculant concentration in the Al\(_2\)O\(_3\) slips to 0.4 wt.\% The microstructure of the resulting 10-layer material can be seen in Fig. 5. In this case, the Al\(_2\)O\(_3\) layers are significantly thinner than the Y-TZP ones, and the material warps. Fig. 6 shows the microstructure of a symmetric multilayer material containing 11 layers prepared in the same way to that of Fig. 5, wherein the total flatness of the resulting sample can be observed. Therefore, warping can be avoided when a symmetric material is prepared.

4. Conclusions

The electrophoretic deposition (EPD) technique was used to form layered Al\(_2\)O\(_3\)/Y-TZP materials with similar or different layer thicknesses from aqueous suspensions. The variation of the deflocculant content allows change in the relative thickness of the different layers without affecting the homogeneity and reliability of the process. The control of these slip parameters makes possible the design of a variety of microstructures with a significant decrease in the required number of layers, in a rapid, economic and non-contaminating way. Warping of these thin layered materials can be avoided by designing a symmetrical microstructure.

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References