

Electrophoretic Deposition of Aqueous Alumina Slips

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(Received 14 March 1996; revised version received 3 June 1996; accepted 11 June 1996)

Abstract

Electrophoretic deposition (EPD) of aqueous alumina slips on a graphite electrode is studied. The suspension is characterized in terms of viscosity, zeta potential and conductivity. The conductivity has proved to be a determining parameter for obtaining deposits. Well-dispersed slips having an adequate value of conductivity are used for constant current density experiments. Current densities of 1.6 to 12.8 mA cm⁻² are applied for 10 min. After defining the optimal slip properties for the deposition, both the process development and the final properties of the materials obtained depend on the current/time relationship. Alumina deposits obtained at different current densities are characterized. The best conditions for obtaining uniform and dense coatings are 6.4 mA cm⁻² for up to 10 min. The applied current allows not only to modify the properties and microstructure of the deposit, but also to increase the margin of slip conductivity assuring the success of the EPD process, that is, the working conditions. © 1997 Elsevier Science Limited. All rights reserved.

1 Introduction

Electrophoretic deposition (EPD) is a powerful method for the production of coatings and both thin and thick films.^{1–4} Conventional coating techniques such as dip-coating or spin-coating are useful to obtain thin films, but are limited to a few micrometers.^{5,6} The EPD process allows production of thick and dense coatings over a conducting material with a good thickness control and complex shape. This process has been used to produce superconductors and microlaminate composites.^{7–10}

In EPD, charged particles migrate to an electrode of opposite charge under the influence of a dc electrical field. The suspension must have a high stability which can be achieved electrostatically or by adding charged polymers or surfactants.¹¹ After the motion of particles by

electrophoresis, a second process, the deposition, takes place.¹² According to this, the EPD process requires the control of the suspension properties as well as the selection of the electrical parameters involved during forming.

Regarding the suspension properties, different parameters must be considered. In casting processes the main controlling parameter is the viscosity. In EPD the solid loading is very low and the viscosity cannot be used to evaluate the dispersion state. Thus the suspension must be studied in terms of zeta potential and conductivity. It has been pointed out that if the suspension is too conductive, particle motion is very low and if the suspension is too resistive, the particles charge electronically and stability is lost.^{13,14} That is, the deposition rate depends on the zeta potential but the ionic flow crossing a surface increases when the charge by unit of weight decreases. This makes it a necessary to arrive at a compromise in such a way that the deflocculant concentration must be as low as possible to minimize the ionic charge, but assuring that the suspension is stable enough to avoid sedimentation.¹⁵

In any application of electrophoresis the composition of the suspension is of great importance. Most of the work on EPD has been done in non-aqueous medium.^{1–9,12,13,16,17} The desired properties in the suspension vehicle are low viscosity, high dielectric constant and low conductivity. Organic liquids have been preferred due to their higher density, good chemical stability and low conductivity. The major problems associated with the use of organics are that higher voltages are required and their toxic nature and health hazards may require special handling. The use of water has the advantage of a high dielectric constant and avoids environmental problems.^{10,15,18,19} Several works consider the influence of some slip properties, such as the type and concentration of deflocculant, the zeta potential, the use of binders and plasticizers and the rheological behaviour, etc.^{10,12,14,16,19–22}

The aim of this work was to study the parameters affecting the EPD of aqueous Al_2O_3 suspensions onto a graphite electrode, which has been selected to allow the easy separation and characterization of the deposited material. The suspension properties (rheology, zeta potential and conductivity) have been studied and correlated with the imposed electrical conditions, which strongly depend on them. The suspension requirements for obtaining a deposit, as well as the selection of electrical conditions to enhance the properties of the deposited materials have been studied and interrelated.

2 Experimental

An $\alpha\text{-Al}_2\text{O}_3$ powder (Alcoa A16SG, USA) with a mean particle size of $0.5\ \mu\text{m}$ and a specific surface area of $8\ \text{m}^2/\text{g}$ has been used as ceramic material for deposition. Aqueous slips were prepared with a solids content of 5 wt% using a high-shear mixer (Silverson L2R, UK) for 3 min. The stability of the slip was studied by adding different concentrations of a commercial deflocculant, Dolapix CE-64 (Zschimmer-Schwarz, Germany), which is a carbonic acid based polyelectrolyte.

The slip properties as well as the processing parameters for EPD were studied. The properties considered for the slips are the following: colloidal stability, rheology and conductivity. Colloidal stability was studied by measuring the zeta potential of slips containing different concentrations of the selected deflocculant. For this measurement a mass transport analyzer was used. In this technique, the electrophoretic mobility is calculated from the difference in weight of a cell, in which a Pt electrode is located, before and after applying a certain current intensity for a fixed time. Although the slip is deflocculated with a polyelectrolyte which can adsorb onto the particle surface, the measurement of the zeta potential can give some qualitative idea about the best dispersing conditions. The rheological behaviour is usually studied to fix these conditions. A concentric cylinder viscosimeter (Haake, Rotovisco RV20, Germany) was used. Slips with 70 wt% solids and containing different deflocculant concentrations were also prepared for viscosity measurements to locate the optimum dispersing conditions, because the slips used for EPD have a very low solid loading and the viscosity is too low to see any differences. The relationship conductivity/temperature of all prepared slips was measured using a WTW conductimeter.

The EPD experiments were performed using a power supplier (Labconco, mod. 433-3250, USA)

which can operate at both constant voltage and constant current density. In this work all the experiments were performed maintaining constant current density.

The electrolytic cell is a glass beaker containing the electrodes suspended in the slip. The counter-electrode consists of a square foil of Pt and the working electrode is graphite with the same geometry. Both electrodes had a specific surface of $6.25\ \text{cm}^2$. The electrodes are assembled to a metric screw and maintained at a constant distance of 2 cm. This device assures the geometry and, hence, the reproducibility of the process.

The slips were stirred with a magnetic stirrer at low speed to avoid turbulence during the deposition process.

Three kinds of experiments were performed, all of them at constant current density conditions. First, in order to study the slip conditions that ensure deposition, a constant current density of $6.4\ \text{mA cm}^{-2}$ was applied using slips prepared with different conductivity values. EPD experiments were performed at three fixed temperatures (24° , 31° and 38°C). Once an adequate slip conductivity range was selected, another set of EPD experiments was carried out applying different current densities (from 1.6 to $12.8\ \text{mA cm}^{-2}$) for 10 min.

The thickness of the deposits obtained in the green state was determined with a Digimatic Indicator (Mitutoyo, accuracy $\pm 5\ \mu\text{m}$). The deposits were dried in air and subsequently separated from the electrode. The green densities were measured by Hg immersion, but a high dispersion was obtained due to the low weight of the deposits. The deposits processed at different current conditions were sintered in an electric furnace at $1550^\circ\text{C}/2\ \text{h}$. The sintered density was measured by water immersion. The sintered compacts obtained were observed by scanning electron microscopy on polished and thermally etched surfaces. The mean grain size was determined by the intercept line method.

3 Results and Discussion

3.1 Slip properties

Slip forming processes are based on the preparation of a stable and uniform suspension with relatively high concentration of solids in which the deflocculation curves are a key parameter that allows fixing the processing conditions in terms of viscosity. When plotting the viscosity as a function of a slip characteristic, such as pH, deflocculant concentration, etc, a minimum value is obtained corresponding to the best dispersing

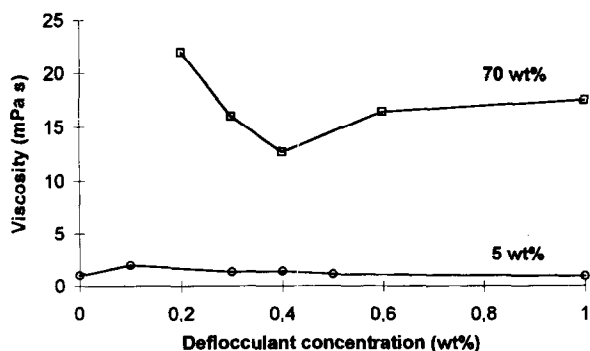


Fig. 1. Variation of the slip viscosity with deflocculant concentrations at two solid loadings (5 wt% and 70 wt%), for a shear rate of 500 s^{-1} .

conditions. However, when a low-concentration slip is prepared, the viscosity values are too low to locate a minimum value in the deflocculation curve.

Figure 1 shows the variation of the apparent viscosity versus deflocculant content at a shear rate of 500 s^{-1} , for Al_2O_3 slips prepared at two different solid loadings. For concentrated slips (70 wt%) a clear viscosity minimum is obtained for a deflocculant concentration of 0.4 wt%. On the other hand, the deflocculation curve for a low-concentration slurry (such as those required for EPD experiments, with 5 wt% solids) has no clear differences, because the viscosity for all prepared slips is very low. Thus the viscosity measurements cannot be used as a controlling parameter as in the concentrated slip used for casting processes.

Although the rheological behaviour cannot define the slip preparation conditions, the colloidal stability can be determined by means of zeta potential measurements. The dispersant employed in this work is a polyelectrolyte which provides an electrosteric stabilization to the slip. The zeta potential only gives information about the double layer interactions and does not consider the steric hinderance. However, the zeta potential variation with the dispersant concentration may be used qualitatively for comparison purposes. Figure 2 shows the zeta potential as a function of the deflocculant concentration. The

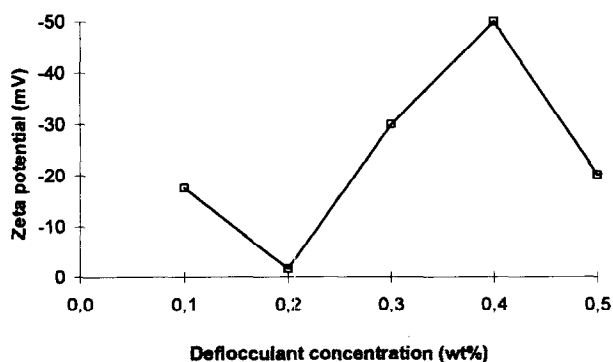


Fig. 2. Zeta potential variation with deflocculant concentration.

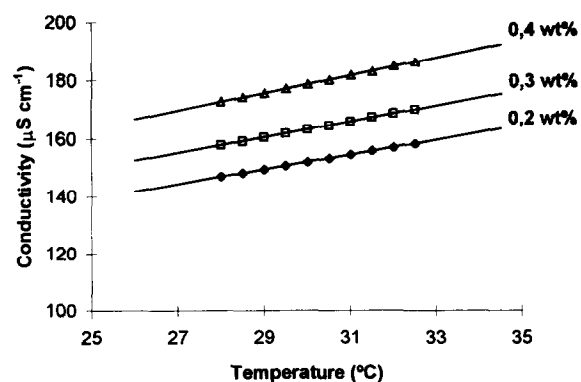


Fig. 3. Variation of the slip conductivity with temperature at different deflocculant concentrations (0.2, 0.3 and 0.4 wt%).

maximum value is obtained for a concentration of 0.4 wt%, but the concentration from 0.3 wt% is high enough to assure a good stability. According to the zeta potential values, concentrations of deflocculant of 0.3–0.4 wt% were selected as the most suitable for EPD experiments.

Another important slip parameter to be considered is the electrical conductivity as proposed in previous work.²³ The conductivity/temperature ratio of Al_2O_3 slips containing different deflocculant concentrations, prepared in the same conditions as those prepared for the rheological measurements, has been determined. The resulting values are plotted in Fig. 3. The conductivity increases linearly with temperature for any deflocculant concentration and increases also for increasing concentrations for a constant temperature. The measurement of the conductivity is very precise, having a very small error margin. The possible errors during weighing produce a significant deviation in the conductivity and, hence, the conductivity measurement can be used to control more precisely the concentration of deflocculant added than the weight of the deflocculant content.

It is well known that in constant current density experiments, when the ceramic deposit is forming, the voltage must increase to assure that a constant current is passing through. The final voltage defines the development of the deposit. Hence, considering the three slip parameters studied, EPD experiments have been conducted on slips containing different concentrations of deflocculant, that is, with different conductivities. Figure 4 represents the final voltage measured after the deposition experiments obtained applying the same current density (6.4 mA cm^{-2}) at three experimental temperatures (24° , 31° and 38°C).

As observed in this figure, for a temperature of 31°C the final voltage changes with the slip conductivity according to a gaussian curve. In all cases a minimum voltage of $\sim 100 \text{ V}$ is measured when a deposit is obtained. Taking this value as a border

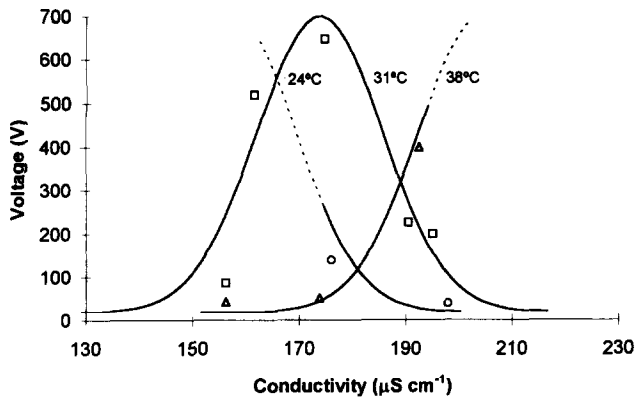


Fig. 4. Final voltage obtained in EPD experiments with slips having different conductivities, applying a current intensity of 6.4 mA cm^{-2} for 10 min at different tested temperatures (24, 31 and 38°C).

condition to obtain deposits, there is a relatively narrow margin of slip conductivity in which the process proceeds. For a lower temperature there is a similar behaviour in which a lower conductivity must be required to get the maximum, as observed in the tail plotted in Fig. 4 for 24°C . For a higher temperature the curve shifts up. The first part of the curve for a temperature of 38°C is also plotted in the figure.

3.2 Electrical conditions

Different slips have been prepared and subjected to EPD experiments at different current densities for 10 min deposition time. In Fig. 5 the conductivity of well-dispersed slips (with 0.4 wt% deflocculant) is plotted versus temperature. The conductivity conditions of the slips after their preparation are adequate for these EPD experimental conditions as demonstrated by the fact that all of them produce a deposit. This suggests that once the best dispersing conditions are reached the formation of the deposit must be possible for any applied current density (in the Al_2O_3 graphite system and the margins considered here). The deposit growth can be followed by the voltage increase during the deposition, as plotted in Fig. 6

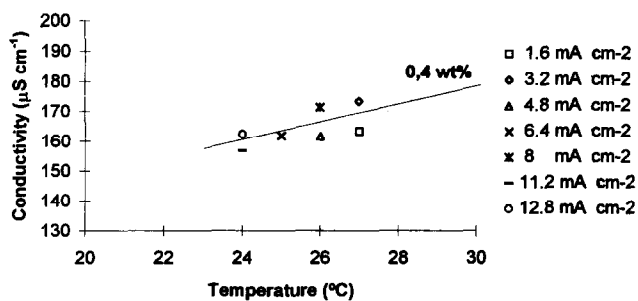


Fig. 5. Conductivity values related to the experimental temperature of deflocculated slips with 0.4 wt% of Dolapix CE-64 and tested at different current densities (from 1.6 to 12.8 mA cm^{-2}).

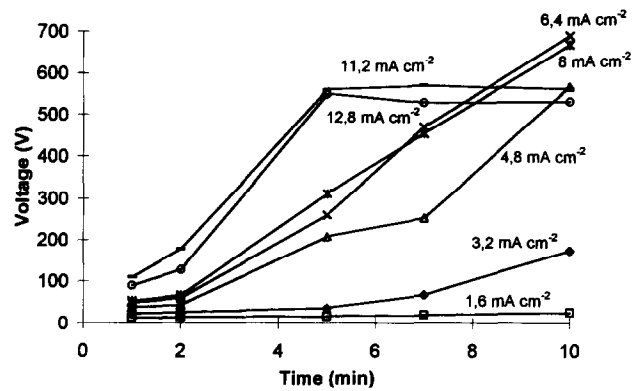


Fig. 6. Voltage evolution vs deposition time for different current densities (from 1.6 to 12.8 mA cm^{-2}).

for different current densities. The increase in the voltage directly depends on the applied current. Different behaviours can be seen in the figure. For low current densities (e.g. 1.6 mA cm^{-2}) the voltage does not increase and no deposit is obtained after 10 min. Probably some deposit could be obtained by increasing the deposition time. For applied currents of 3.2 to 8 mA cm^{-2} an important voltage increase is observed after 2 min deposition. The slope increases, after 2 min deposition, with the applied current. The curve has an exponential form for intensities up to 6.4 mA cm^{-2} and becomes linear at 8 mA cm^{-2} , that is, the formation rate is constant up to the end of the experiment. For higher intensities (9.6 – 12.8 mA cm^{-2}) a very fast increase in the voltage in the first minutes is observed. After 5 min deposition no variation in the voltage is recorded, thus suggesting that the deposit growth does not progress further.

At this point it is expected that the different growing kinetics could affect the characteristics of the deposited material. The green density of the dry samples obtained at intensities ranging from 3.2 to 12.8 mA cm^{-2} vary from 52.9 to 53.8%, increasing directly with the measured voltage. However, these measurements are not reliable because the samples are very thin and brittle, and

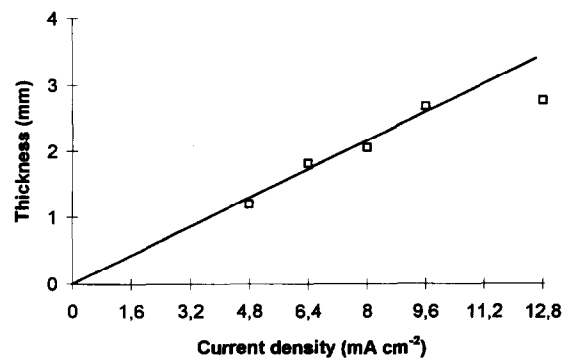


Fig. 7. Thickness of green deposits obtained at different current densities.

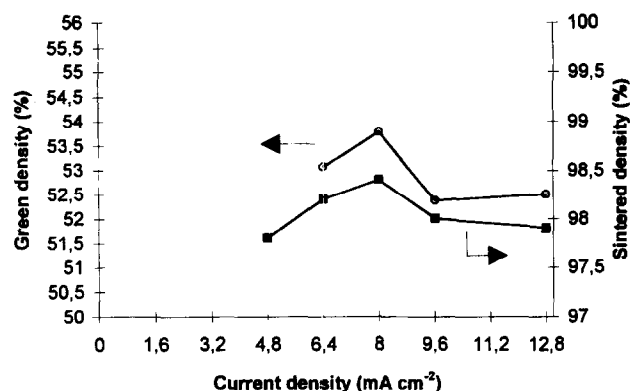


Fig. 8. Relative density of deposits obtained at different current densities in the green state and sintered at 1550°C/2 h.

they break easily. Figure 7 shows the thickness of the deposit versus current density for deposition times of 10 min. The general trend of this plot may be adjusted to a linear evolution of thickness with intensity up to 9.6 mA cm⁻²; from this value a deviation from the linearity is observed. This irregular behaviour may be compared with those plotted in Fig. 6 and could indicate that for high intensities (>9.6 mA cm⁻²) the growth kinetics cannot be controlled. There are certain electrical conditions which must be satisfied in order to assure a reproducible thickness formation.

The relative density of the deposits formed at different current densities and sintered at 1550°C/2 h is plotted in Fig. 8. Although no big differences in density are obtained (from 97.7 to 98.5%, ± 0.5), a clear tendency can be seen to increase with the current density up to 8 mA cm⁻². A small decrease in density is measured again for deposits obtained at 9.6 mA cm⁻² or more, confirming the behaviour shown in Figs 6 and 7 for these values. The same behaviour is observed in the green densities, also plotted in Fig. 8, thus confirming the observed tendency.

All three figures suggest that both the deposit thickness and the relative density increase with the applied intensity. However, there is a limit at 9.6 mA cm⁻², after which the process cannot be controlled adequately. These results are not in accordance with those corresponding to other related forming processes, such as slip or pressure casting, in which the green density decreases when the wall thickness formation rate increases. In the case of EPD, when the current density increases, both the deposit thickness and its relative density tend to increase. That is, a thicker and more densely packed coating can be produced with a proper control of the imposed electrical conditions.

Figure 9 shows the microstructure of sintered deposits obtained at three different current densities (3.2, 6.4 and 12.8 mA cm⁻²). From the micrographs no significant differences are observed.

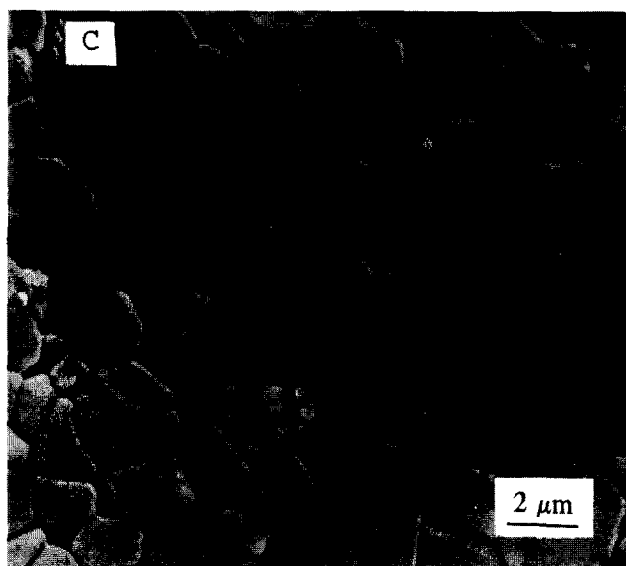
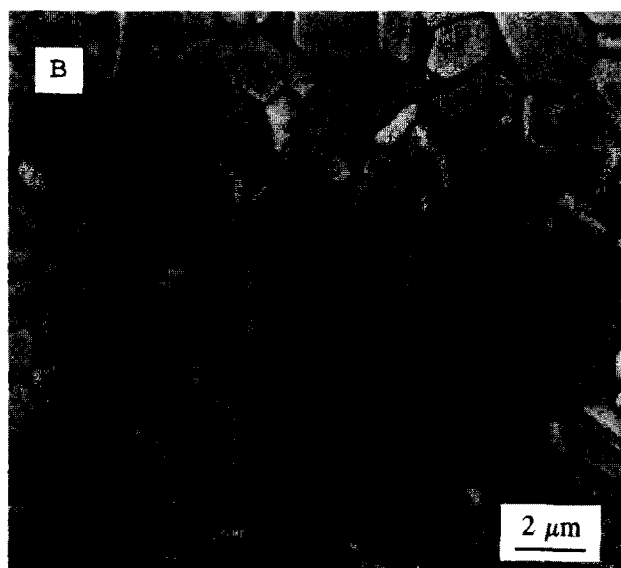
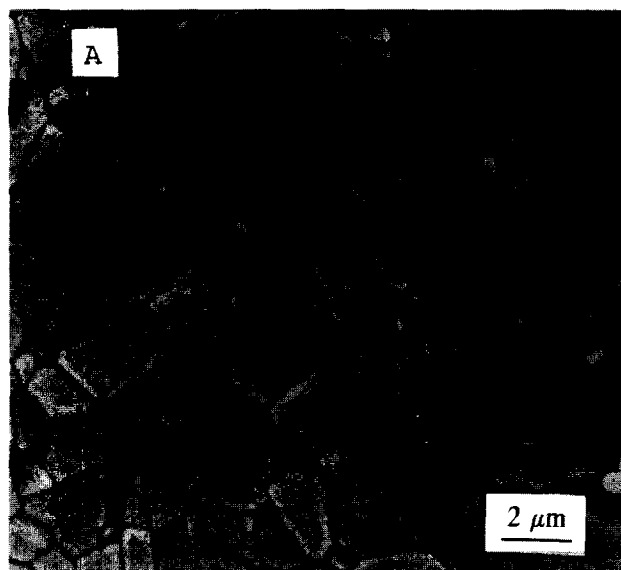


Fig. 9. Micrographs (SEM) of deposits obtained applying current densities of 3.2 (A), 6.4 (B) and 12.8 mA cm⁻² (C), for 10 min.

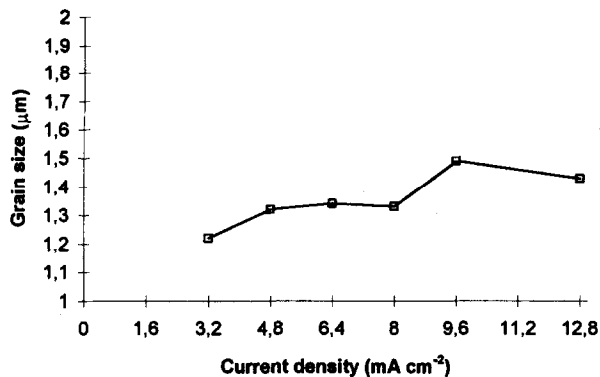


Fig. 10. Calculated mean grain size of sintered deposits obtained at different current density values (from 3.2 to 12.8 mA cm⁻²).

The sintered density is high, although a small porosity still remains in the compacts, mainly at the triple points and within the grains. The measurement of the mean grain size by the intercept line method reveals a small increase for increasing current densities, especially for the higher values, as observed in Fig. 10.

Turning again to Fig. 6, the results described above seem to indicate that the best deposits (in terms of thickness and density) are obtained when the evolution of the measured voltage with the deposition time is linear, as plotted in the figure.

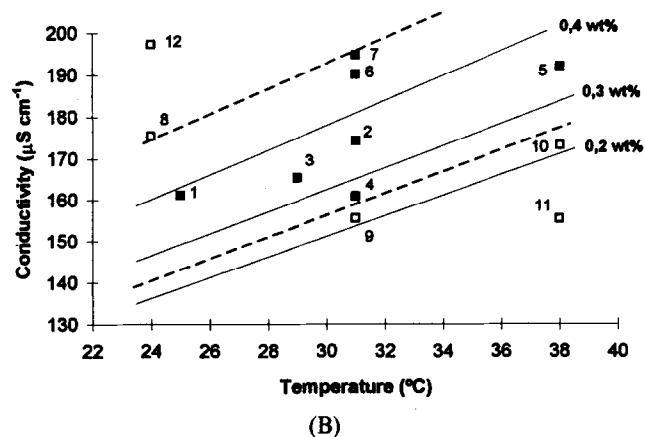
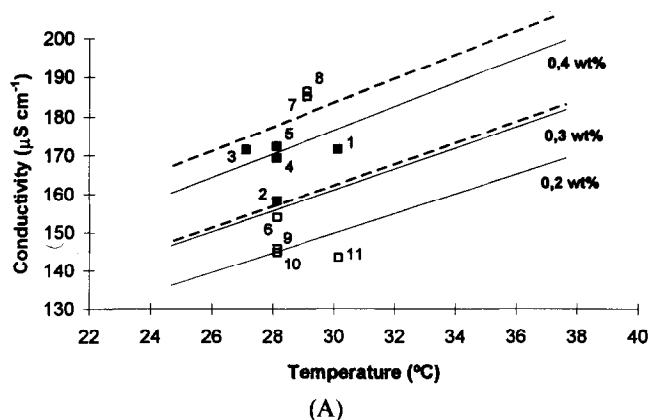


Fig. 11. Conductivity values related to the experimental temperature of tested slips at applied current densities of 3.2 (A) and 6.4 mA cm⁻² (B).

Deviations from this linearity decrease the reliability of the process and produce less homogeneous coatings.

3.3 Relationship between slip properties and electrical conditions

Figures 11 A and B plot the conductivity value of slips subjected to EPD experiments at 3.2 mA cm⁻² and 6.4 mA cm⁻² for 10 min. In these figures the full squares represent the experiments in which a deposit is obtained. These points allow us to define linear limits for the deposition as a function of conductivity and temperature. Outside these margins no deposit is obtained. These limits depend obviously on the characteristics of the slip and can change with the deflocculating conditions, the components of the system, etc.

Figure 12 shows the evolution of voltage with deposition time (up to 10 min) for the EPD experiments performed for the same slips whose conductivity and temperature values are plotted in Figs 11 A and B. When a deposit is formed, a resulting voltage higher than 100 V is measured. Comparing the curves obtained for both current densities it can be observed that the final voltages after 10 min EPD are lower for current densities of 3.2 mA cm⁻² indicating that the deposit is thinner

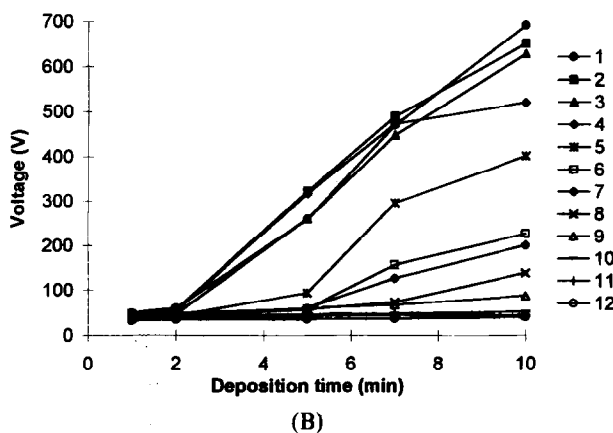
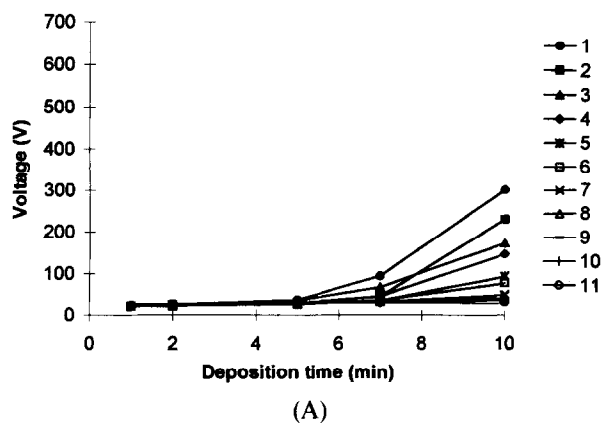


Fig. 12. Voltage evolution vs deposition time for applied current densities of 3.2 (A) and 6.4 mA cm⁻² (B).

and/or less dense. It can be also observed that for 3.2 mA cm^{-2} a minimum time of 5 min is required to obtain a deposit. For higher current densities (i.e. 6.4 mA cm^{-2}) the deposit can be obtained after 2 min and the measured voltages are higher and increase linearly with the deposition time. These conditions will be preferred when thick coatings are needed. Summarizing, the most important results are referred to the fact that these useful conductivity limits also depend on the applied intensity. For current densities of 6.4 mA cm^{-2} the working zone of the slip conductivity values is wider than that corresponding to 3.2 mA cm^{-2} , thus enhancing the processing conditions. That is, the conductivity of the slip is not only a determining factor for the success of EPD, but is strongly related to the electrical parameters imposed on the system. Optimizing the current density it is possible to enhance the deposit properties and microstructure, and to increase the working limiting conditions.

4 Conclusions

A broad study of Al_2O_3 /graphite system for EPD process has been made. The most interesting conclusions are described below.

The EPD process depends on both the characteristics of the slip and the imposed electrical conditions. The slip conductivity has been stabilized as a key parameter to define the processing conditions. To ensure the success of the process, specific requirements of conductivity must be satisfied. This can replace the rheological control used in casting processes as a powerful slip characterization parameter.

Experiments performed at different constant current densities reveal that the deposit thickness and the relative density increase with the applied current up to 8 mA cm^{-2} , for a deposition time of 10 min. The best conditions correspond to a linear behaviour of voltage increase, that is, a constant growing rate of the deposit. Current densities higher than 8 mA cm^{-2} produce deviations of the linear behaviour and the control of the process is lost. In other words, too high current densities produce fast deposit formation and hence heterogeneity and poor packing density.

The study of the last group of the experimental results suggests that there is a strong dependence between the slip properties and the applied intensity. The first determine whether deposit can be formed or not, whereas the last allows to modify the range of the working conditions and to change the deposit-growing kinetics and hence, its final properties.

Acknowledgements

The authors thanks to Dra. Alicia Durán for helpful discussions. This work has been supported by CICYT (Spain), under contract MAT94-0741.

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