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Fabrication of alumina parts by electrophoretic deposition from ethanol and aqueous suspensions

Saša Novak *, Katja König

Jožef Stefan Institute, Department for Nanostructured Materials, Jamova 39, SI-1000 Ljubljana, Slovenia

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Abstract

This paper discusses the effect of the properties of alumina suspensions in ethanol and in water, on green and sintered ceramic parts formed by electrophoretic deposition. The results of the study demonstrate that a small amount of water present in ethanol suspensions as a hidden additive due to the hygroscopicity of alumina powder and ethanol can detrimentally affect the behaviour of the suspension, thus lowering the reliability of the process. Electrophoretic deposition from aqueous suspensions appears to be advantageous over ethanol, from a reliability standpoint, and due to higher achievable green and sintered densities of the deposits and higher deposition rates. Dolapix CE64 appears to be superior surfactant in water as it results in deposits with the lowest green and sintered porosities.

Keywords: A. Shaping; A. Suspensions; B. Porosity; D. Al_2O_3; Electrophoretic deposition

1. Introduction

Electrophoretic deposition (EPD) has attracted a great deal of attention in recent years due to its wide range of applications. It can be applied to any fine powder in a colloidal suspension, including oxides, carbides, nitrides, metals, and polymers. EPD can produce bulk freestanding parts with a complex shape, can form coatings, and can infiltrate 2D or 3D woven fibres [1–10]. With EPD, ceramic bodies are shaped directly from a stable colloidal suspension by a DC electric field, which causes the charged particles to move to and deposit on an oppositely charged electrode. The several basic requirements that must be fulfilled for a successful deposition are thoroughly described in many publications [11–17]. In practice, however, the success of the process and the quality of the deposits are not reliable and are often dependent on ‘‘hidden’’ parameters. Although EPD has been investigated for decades, the process is still not fully understood. A trial-and-error approach has been mostly used and often, non-optimal conditions are inadvertently selected for the deposition. Furthermore, this approach does not offer a lot of flexibility with different grades of powders. As a result, the low flexibility and lack of reproducibility yield in limited industrial applications.

Several papers have described the preparation of alumina deposits by EPD, preferably using non-aqueous suspensions of submicron powders and various dispersants [18–22]. These papers emphasise the importance of a high zeta-potential (ZP) and an appropriate conductivity. These studies focus on the deposition rate and yield as a function of the process parameters; however, less is known about how the process parameters and the suspension composition and properties relate to the behaviour of the deposit. It is well known that the packing density of ceramic green parts is of utmost importance in the production of advanced ceramics. For example, the particle packing density in green parts determines the sintering shrinkage, the density of the sintered ceramics, and the number of defects [23]. In order to fully exploit the advantages of the EPD process, these factors that affect the structure of the green parts need to be better understood.

In our work, we investigated the effect of the suspension's composition and the EPD process parameters on the properties of the deposits formed. Our goal was to determine the conditions for effective and reproducible fabrication of alumina parts, and hence to promote industrialisation of the process. We analysed the effect of media and surfactants in water and ethanolic suspensions, and we investigated the role of water as a hidden parameter in ethanolic alumina suspension.

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* Corresponding author. Tel.: +386 1 477 3271; fax: +386 1 477 3221.
E-mail address: sasa.novak@ijs.si (S. Novak).

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2. Experimental

Commercially available α-Al_2O_3 powder (Alcoa A16SG, with an average particle size of 0.7 μm), ethanol absolute (pro-analysis, Carlo Erba, Italy), and distilled water were used for the preparation of suspensions for the EPD. The powder was used in its original non-dried form (0.6 wt.% humidity), or it was dried at 150 °C for 3 h (to under 0.2% humidity). Dolapix CE64 (Zschimmer & Schwarz, Leinstein, Germany) and citric acid (Alfa Prod., Germany) were used as surfactants. The suspensions, which contained 50 wt.% of solids, were homogenised in an ultrasonic finger processor UP400S (Hielscher Ultrasonics, Germany).

The zeta-potential of the ethanol or aqueous suspensions for EPD was determined by measuring an electroacoustic signal in concentrated suspensions using a ZetaProbe device (Colloidal Dynamics, USA). The pH was adjusted by the addition of concentrated hydrochloric acid or sodium hydroxide, and it was evaluated with a 744 pH meter (Metrohm Ltd, Switzerland). For the ethanol suspensions, the pH is given as an operational pH (O.pH). Conductivity was measured by a conductometer (Knick Portamess, Germany).

The EPD was performed using freshly prepared suspensions at a constant voltage in the range 5–60 V. The distance between the square-shaped steel and zinc electrodes (20 mm × 20 mm) was 20 mm. The cell current was recorded during the deposition. After the deposition, the deposits were dried. The solids content in the deposit was determined on the basis of weight loss; this was used to evaluate the particle packing density in the fresh deposits in order to demonstrate an increase in solids content in the suspension during the EPD and hence the success of the EPD. The green density of the dry deposits was evaluated by measuring the porosity using a high-pressure mercury intrusion porosimeter Micromeritics AutoPore IV 9500 (Micromeritics, Australia).

The deposits were sintered at 1550 °C for 2 h. The microstructure of the sintered parts was observed at polished and thermally etched cross-sections using Field Emission SEM (Zeiss SUPRA 35VP). The average grain size and the porosity of the samples were evaluated by conventional stereological analysis of the microstructures.

3. Results and discussion

3.1. Preparation and characterisation of suspensions

The ZP of alumina powder in aqueous or ethanol suspensions as a function of operational pH (O.pH) was measured directly in the suspensions for deposition, i.e., in the non-diluted form. This gave us a reliable description of the suspensions; results with 50 wt.% solids are presented in Fig. 1. It is obvious that in acidic and alkaline regions, the measured ZP values are much higher for the aqueous suspensions than for the ethanol suspensions. The electrostatic stabilisation of powder by ionisation is much more effective in an aqueous medium, due to the higher dielectric constant of water. The isoelectric point (IEP) of powder in aqueous suspensions appears at approximately pH 8, while the IEPs in ethanol suspensions are quite higher, due to the stronger basic nature of the ethoxide ions in comparison to hydroxyl ions. In ethanol, the IEP is lower for the non-dried powder than for the dried powder (Fig. 1). This suggests that water that is unintentionally introduced by the hygroscopic alumina powder may contribute to variations in the electrokinetic properties of the non-aqueous suspensions, and consequently to the quality of the deposit, as will be shown below. Moreover, discrepancies in the reported values for the IEP of alumina in ethanol, frequently observed in the literature, may be partially due to the hygroscopicity of alumina powder and of ethanol.

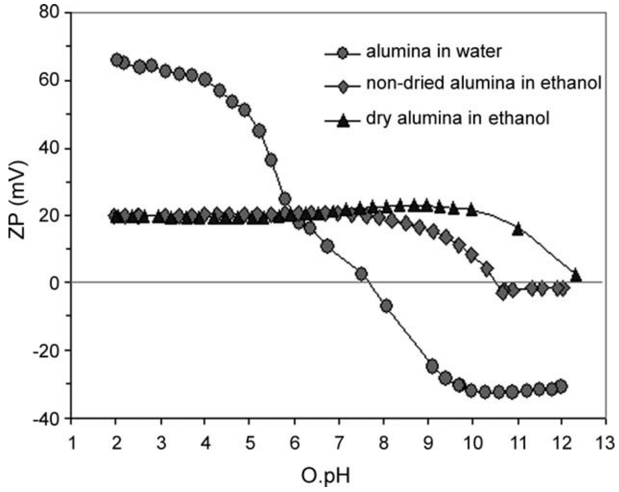

Fig. 1. Zeta-potential of alumina suspension in ethanol and in water as a function of operational pH (O.pH) (50 wt.% solids in suspensions).

The ZP can be significantly modified by the addition of surfactants. In this work we used citric acid (CA) and Dolapix CE64 (DC), and compared their effects on electrophoretic deposition from aqueous or ethanol suspensions. Zeta-potential as a function of the CA and DC concentration is presented in Fig. 2a and b, respectively. The addition of 0.3% citric acid increases the magnitude of the (negative) value of the ZP of the ethanol suspension of original alumina powder up to −62 mV; in water the maximum magnitude obtained was −48 mV. The addition of DC produced a similar effect in both ethanol and water (Fig. 2b), resulting in a value of −50 mV with the optimum addition. However, the effect of water presence in ethanol suspension is observed: for the suspension of non-dried powder, the highest magnitude value was obtained with 0.5 wt.% DC, while for dried powder, the highest magnitude was obtained with 1% addition, and the maximum ZP value was slightly lower than for the non-dried powder. This suggests that the behaviour of the ethanol suspension was tightly connected to a limited solubility of DC in ethanol, and hence was dependent on the amount of water present. In the case of the non-dried powder, the water present at the particle surfaces obviously enhanced the adsorption of DC. However, as is illustrated by the dashed curve in Fig. 2b, the addition of a small surplus of water (1%) had a detrimental effect on the suspension. The influence of CA and DC addition on O.pH change of suspensions is demonstrated in Fig. 2c; DC addition

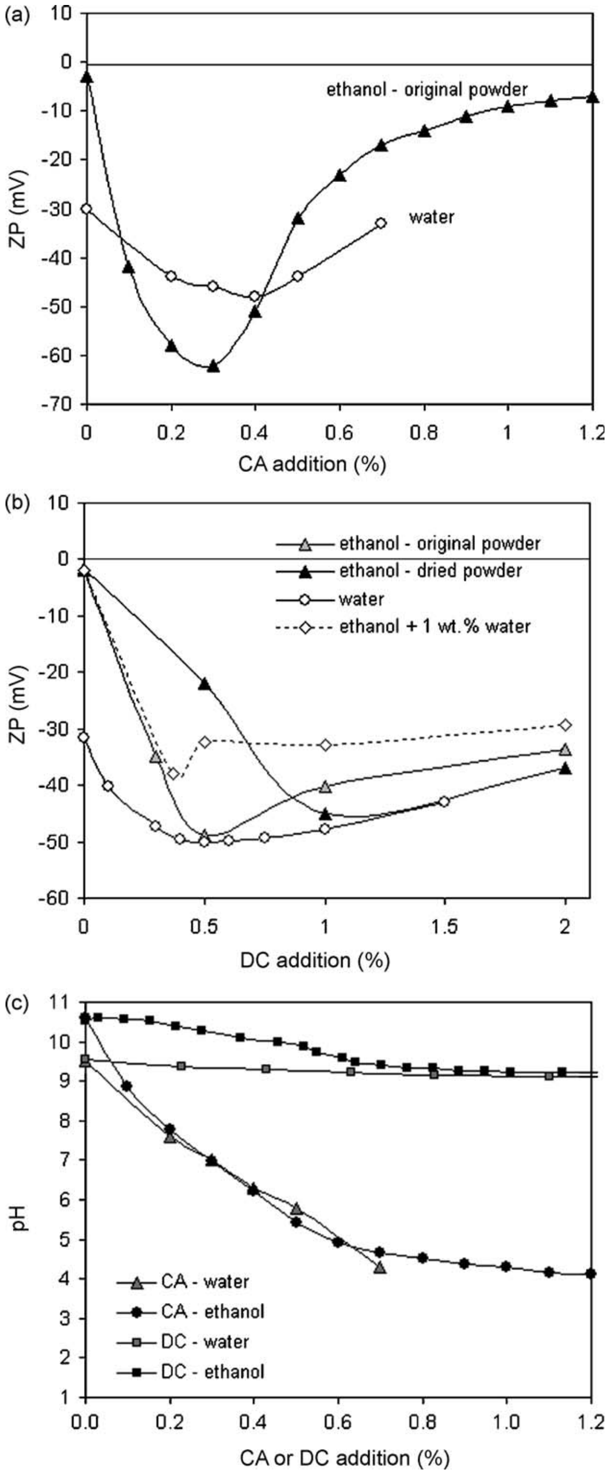

Fig. 2. The effect of (a) citric acid (CA), (b) Dolapix CE64 (DC) addition to aqueous and ethanol alumina suspensions on the zeta-potential and (c) the effect of CA and DC addition on O.pH change of aqueous and ethanol suspensions.

does not show considerable influence on initial O.pH change of suspensions, while CA-addition significantly decreases initial O.pH. The conductivity of the suspensions was strongly dependent on the liquid media used and on the composition and amount of the surfactants; thus, these factors also affected the ZP vs. conductivity ratio, which was suggested to be the key parameter for EPD [24]. The curves in Fig. 3a and b present the change of this ratio with increasing amount of CA or DC in the aqueous and ethanol suspensions, respectively. As in Fig. 2a and b, these curves exhibit maxima at the optimal amounts of the surfactants. Due to the lower dielectric constant of ethanol, the curves for the ethanol suspensions (Fig. 3b) appear at significantly higher values than those for the aqueous suspensions (Fig. 3a), as much as two (for DC) or three (for CA) orders of magnitude. It is also obvious that the ethanol suspension of dry alumina powder dispersed with DC exhibits a lower ZP vs. conductivity ratio than the suspension of non-dried powder. This implies that for the dry-powder suspension, less efficient EPD may be expected. However, the main observation is that water (humidity) presents a hidden detrimental parameter in EPD with ethanol suspensions; therefore, this may be the main reason for the frequently observed low reproducibility of the EPD process.

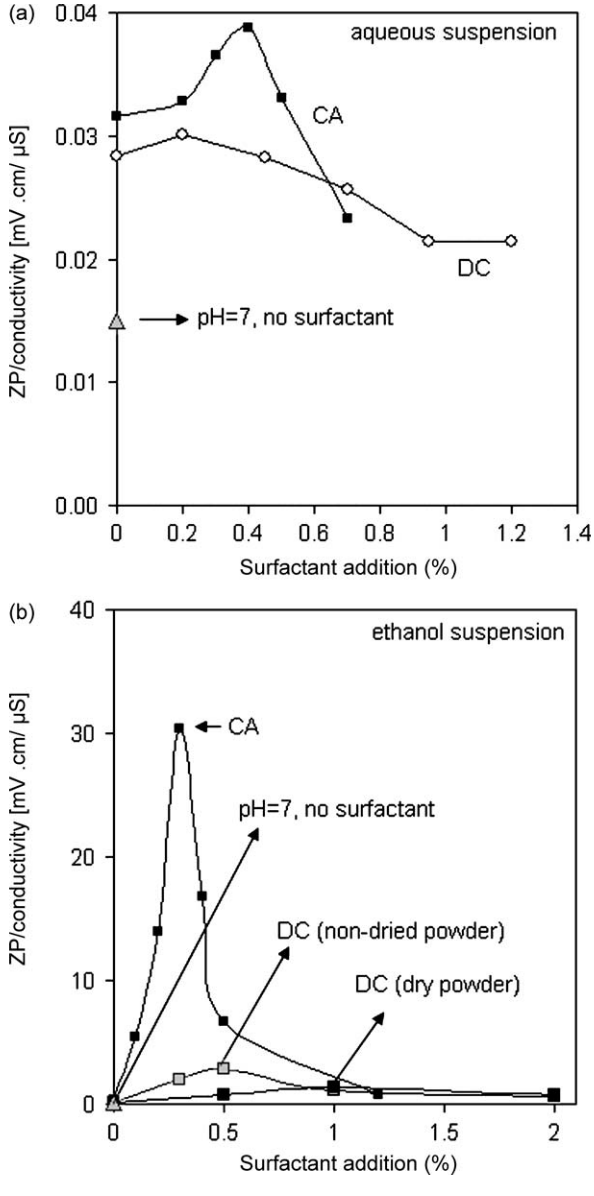

Fig. 3. ZP vs. conductivity ratio for (a) aqueous and (b) ethanol alumina suspensions as a function of a surfactant addition.

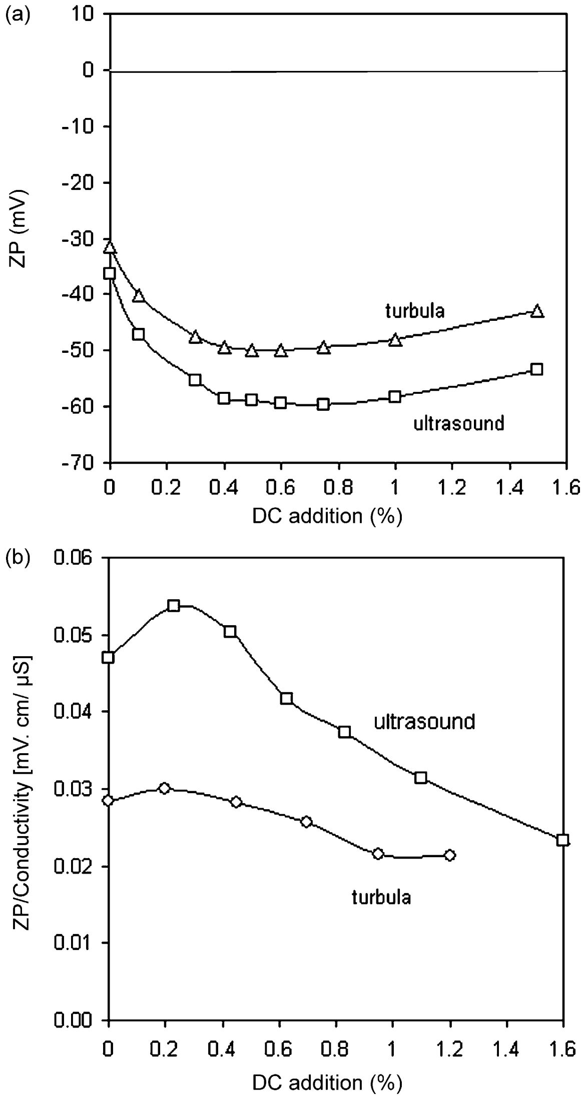

Fig. 4. Effect of homogenisation technique on (a) ZP and (b) ZP/conductivity ratio (aqueous suspension, 50 wt.% solids).

To further optimise the EPD process, we verified the effect of homogenisation by comparing the ZP and conductivity for suspensions mixed using two different methods: dispersion via multidirectional mixer (turbula) using grinding media for 2 h, and ultrasonic finger processor with an acoustic power density of 105 W/cm^2 for 5 min. The results illustrated in Fig. 4a and b show that the more intensive homogenisation created by a strong ultrasonic processor resulted in higher ZPs and lower conductivities, which was due to the better dispersant distribution on individual particles. This, however, did not significantly affect the pH change due to the CA and DC additions.

3.2. EPD experiments

The EPD experiments were performed with ultrasonically homogenised ethanol and aqueous suspensions containing 50 wt.% of the alumina powder and the optimal amount of the surfactants (see values in Table 1), in accordance with the results in Figs. 3 and 4. A zinc deposition electrode and semi-permeable paper was used to prevent bubble formation in the aqueous suspensions during the electrolysis. When we used ethanol and water suspensions with the pH adjusted to produce high ZP (without addition of surfactants), no deposit was formed at 10 V. This can be ascribed to a too low zeta-potential in the case of ethanol, and too high conductivity in the case of water. The resulting ZP vs. conductivity ratio is very low: 0.015 mV cm/µS for aqueous and 0.14 mV cm/µS for ethanol suspension (Fig. 3a and b) and as shown in Fig. 5a and b, for both suspensions with adjusted pH, the cell current during the deposition was much higher than during the deposition of the suspensions with the addition of DC or CA.

The results of the EPD experiments for suspensions containing CA or DC are provided in Fig. 6 as a function of the applied voltage. Fig. 6a shows the deposition rates, and Fig. 6b shows the corresponding particle packing density presented as the solids content in as-prepared (wet) deposits. This parameter was employed with the aim to demonstrate the success of the EPD process and also since it may be a good indication of the shrinkage during drying, which may also be connected to crack formation during drying.

As expected, the deposition rate in general increases with increasing voltage applied during the EPD (Fig. 6a). Despite much lower ZP vs. conductivity ratio, significantly higher rates are observed in the aqueous suspensions than in the ethanol. The highest deposition rate was observed for the CA-containing suspension, although the resulting solids content in the deposits was rather low (Fig. 6b). Conversely, the highest particle packing density achieved by EPD was in the DC-containing aqueous suspension. DC in ethanol resulted in much lower densities; also, low reproducibility was observed (the best achieved results are presented in Fig. 6b). As we discussed

Table 1
The properties of the deposits in relation to the starting suspensions (voltage, 10 V for aqueous and 60 V for ethanol suspension) and the properties of the resulting green and sintered parts.

	Suspensions				Fresh deposit		Green part		Sintered part	
	Surfactant		ZP	ZP/σ	Solids content		Average pore size	Porosity	Porosity	Average grain size
	(% m/m)		(mV)	(mV cm/µS)	(wt.%)	(vol.%)	(nm)	(% TD)	(%)	(µm)
Water	CA	0.4	−54	0.05	74	42	62	39	2.2	2.1
	DC	0.6	−62	0.03	86	61	58	36	2.2	2.3
Ethanol	CA	0.3	−62	30	85	53	72	41	3.5	1.6
	DC	0.5	−49	2.8	81	46	84	46	3.3	1.5

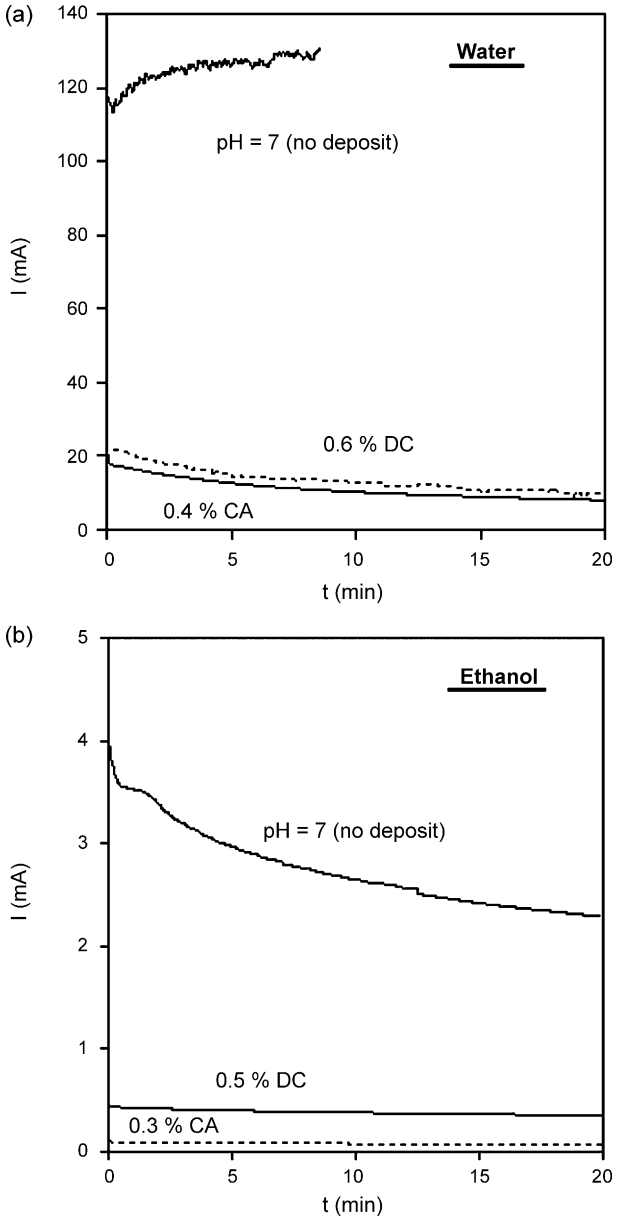

Fig. 5. Current change during the deposition of the (a) aqueous and (b) ethanol suspensions (voltage, 10 V and suspension solids content, 50 wt.%).

above, this is due to the variation of humidity in the surrounding environment.

Fig. 6b also shows that, except for the CA-containing aqueous suspension, nearly constant densities were obtained at voltages as low as 10–20 V. Higher voltages contributed only to a higher deposition rate.

The properties of the resulting characteristic deposits in relation to the starting suspensions, summarised in Table 1, revealed that a high zeta-potential can be achieved by using a proper amount of citric acid (CA) or DC CE64 in water and in ethanol. The highest deposit density, 64 vol.%, was obtained by the EPD of an aqueous DC-containing suspension. The porosity measurements of the green deposits confirmed that this sample contains the smallest pores, with the majority population around 50 nm in size (see Fig. 7). For the other deposits, the

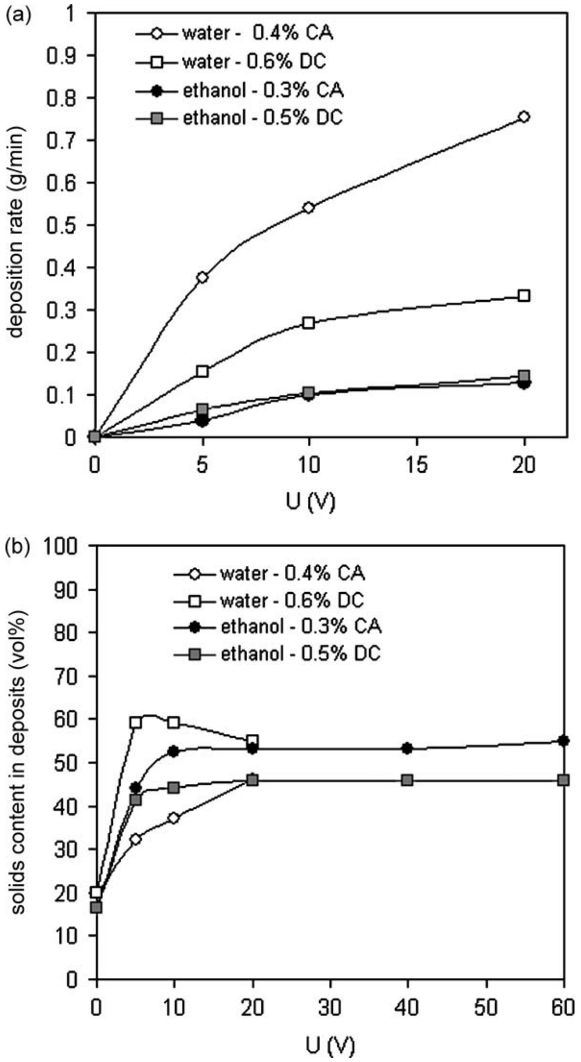

Fig. 6. Deposition rate and particle packing density (presented as solids content in wet deposit) as a function of applied voltage for aqueous and ethanol suspensions with optimal CA or DC addition (starting solid content, 50 wt.% and deposition time, 20 min).

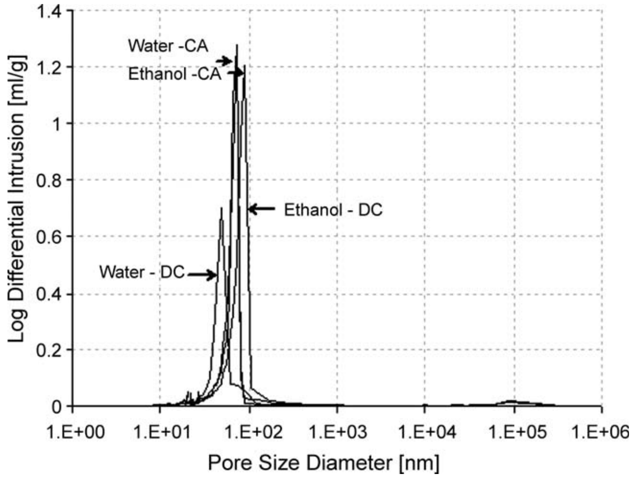

Fig. 7. Porosity distribution in the green parts.

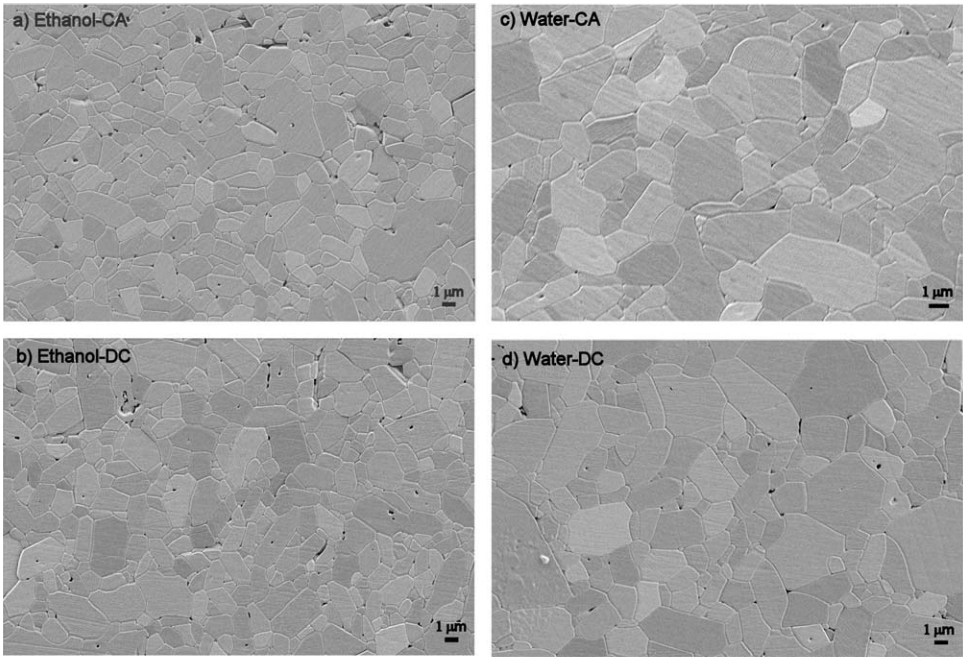

Fig. 8. SEM micrographs of alumina deposits prepared from ethanol (a and b) and aqueous suspensions (c and d), sintered at 1550 °C for 2 h.

average pore size is obviously slightly higher, which confirms that the starting suspensions were well dispersed. The slightly larger pores are reflected by the slightly increased volume porosity (Table 1).

The sintered, polished and thermally etched samples reveal microstructures (Fig. 8a–d) that correspond to the above observations for the green parts: the highest apparent density (porosity ~2%) was obtained by EPD of aqueous suspensions with CA and DC addition. Moreover, it may be observed that despite the same alumina powder was used and the samples were sintered simultaneously, the average grain size is noticeably larger in the samples from aqueous suspensions than that from the ethanol (see Table 1). The apparently higher sintering rate for the samples prepared from aqueous suspension could be tentatively ascribed to an effect of fine AlOOH formed.

4. Conclusions

In this work we studied and compared electrophoretic deposition of submicron alumina powder in ethanolic and in aqueous suspensions, stabilising the suspension using a pH change from either a citric acid or a DC addition. It is shown that the pH decrease was not sufficient for successful deposition, due to an insufficient surface charge in ethanol and too high conductivity in water. However, the addition of an optimal amount of anionic surfactant enables the production of stiff and dense deposits with a green density of dry deposits up to 64% in water and 59% in ethanol and high sintered densities.

The hygroscopic nature of alumina powder was shown to detrimentally affect the ZP and the conductivity of ethanol suspensions, consequently lowering the efficiency and the reproducibility of the EPD. Significant variations in the suspension's behaviour may appear due to hidden parameters such as unintentionally introduced water.

Thus, EPD from aqueous suspensions seems to be advantageous over ethanol, from a reliability standpoint, and due to higher achievable green and sintered densities of the deposits and higher deposition rates. Dolapix CE64 appears to be superior in water as it results in deposits with the highest densities. However, this does not hold for ethanolic suspensions, since its effect is influenced by the amount of water present.

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