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Thermogelation of Al_2O_3/Y-TZP films produced by electrophoretic co-deposition

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Abstract

There is a growing interest to develop reliable, economic and environmentally-friendly methods for manufacturing thin and thick coatings and layered systems. Electrophoretic deposition has demonstrated to be a suitable technique for manufacturing laminates and coatings. For thick films, the adhesion to the substrate and the shape retention become important problems that lead to low density, cracking, and heterogeneous surfaces. To overcome these problems, a new idea is proposed consisting in the formation of a thick deposit by EPD in water and its immediate consolidation by thermogelation of polysaccharides, which is introduced in the suspension and forms a gel structure on cooling during withdrawal of the substrate from the suspension bath. In this work the parameters involved in the electrophoretic codeposition of two phase suspensions (Al_2O_3/Y-TZP) containing carrageenan, on non-porous graphite substrates are studied. Dense self-supported films with thickness between 10 and 500 μm are obtained after a thermal treatment in which the graphite substrate burns out and the subsequent sintering cycle. The performance of gel-deposition is studied as a function of the concentration of carrageenan, the solids loading and the electrical conditions.

Keywords: Al_2O_3/ZrO_2; Composites; Electrophoretic deposition; Shaping; Suspensions; Thermogelation

1. Introduction

Much effort has been devoted recently to develop novel colloidal forming methods for increased reliability.[1] Among them, electrophoretic deposition (EPD) is very attractive for a variety of applications due to the simplicity of the process, the low cost equipment and the versatility for producing either bulk bodies, laminates or thin and thick coatings on complex shaped substrates. Electrophoresis involves the motion of charged particles towards an electrode as a consequence of an external dc field.

EPD has been widely studied for a great variety of particulate systems, including aqueous and non-aqueous suspensions.[2–4] Some works have focused on aqueous EPD because of the health, environmental and costs benefits of using water as suspending media.[5] However, it is well known that the use of water can lead to several problems, such as the faster kinetics, that difficults the control of the deposit thickness, and the hydrolysis of water, that promotes bubbling with a deleterious effect on the microstructure. Non-aqueous suspensions are superior in relation to the adherence of the deposit to the substrate and the thickness control. The adhesion between the deposit and the substrate in aqueous systems may be improved by using organic additives as polyeletrolytes, binders and surfactants.

Hence, the ceramic suspension becomes a complex system containing not only the particles and the suspending medium, but also the additives. Each component has an important role in the suspension formulation that can change the EPD behaviour and the adhesion to the substrate.

On the other hand, gelation of polysaccharides has received a great attention in recent years for manufacturing near-net-shaped self-supported pieces. The main advantages of gelling polysaccharides are that they are soluble in water, non toxic, and capable to produce firm gels at low concentrations. The consolidation of bulk bodies by gelation of polysaccharides on cooling (e.g. agar, agarose, carrageenan) has been reported elsewhere.[6–8]

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Previous work has demonstrated that ceramic–ceramic coatings can be obtained by simply dipping a green ceramic sheet into a well-dispersed ceramic suspension previously mixed at temperatures >60 °C with a solution of carrageenan. This gel-former improves wetting, so that a film is formed on withdrawal, which maintains adhered to the substrate and gelates on cooling.[9,10]

Preliminary EPD tests of carrageenan-containing suspensions on green ceramic substrates (with open porosity) had limited success[11] due to the lack of control of deposition kinetics of aqueous suspensions at low current densities, and the poor adhesion to the green tapes used as substrates.

In this work, the possibility to improve the thickness control and the adherence of composite films shaped by electrophoresis, based in the use of a gel-former as additive has been explored. The influence of the concentration of the gelling additive, the solid loading and the electrical parameters on the performance of gel-deposition, has also been studied.

2. Experimental

As starting powders an Al_2O_3 (Condea HPA05, USA), with mean particle size of 0.35 μm and specific surface area of 9.5 m^2/g, and a polycrystalline tetragonal zirconia with 3 mol% Y_2O_3, Y-TZP (TZ3YS, TOSOH, Japan), with mean particle size of 0.4 μm and surface area of 6.7 m^2/g, were used. Particle size distributions were measured with a laser analyzer (Mastersizer S, Malvern, UK). Surface area was measured by one point N_2 adsorption (Monosorb, Quantachrome, USA).

Stabilized aqueous suspensions of Al_2O_3/5 vol.% Y-TZP (AZ) were prepared to final solid concentrations of 20, 30 and 40 wt.% (i.e. 5.8, 9.5 and 14 vol.%, respectively), adding 0.8 wt.% (on a dry solids basis) of a polyacrylic acid polyelectrolyte (Duramax D3005, Rohm & Haas, USA). All the suspensions were ultrasonically homogenized using a 400 W sonication probe (IKA U400S, Germany) for 2 min.

A commercial carrageenan powder (Secogel TC, Hispanagar, Spain) was used as gelling agent. A 2 wt.% solution of carrageenan was prepared by heating at 90 °C up to dissolution and maintained at 60–65 °C. AZ suspensions were heated at 60–65 °C and mixed with the amount of carrageenan solution to reach final concentrations of 0.4, 0.8 and 1.2 wt.% with regard to the total water content.

The electrophoretic mobility of the suspensions without carrageenan was measured by microelectrophoresis (Zeta-meter, model 3.0, USA). The conductivity was measured with a microprocessor conductivity-meter (WTW, model LF320, Germany).

The thermogelling behaviour of carrageenan solutions was determined by measuring the evolution of the viscosity vs. temperature using a Rheometer RS50 (Haake, Germany). The sensor system consisted of a double-cone rotor and a stationary plate, protected with a solvent trap to reduce evaporation. Similar studies were carried out for all the prepared suspensions.

EPD experiments were performed in galvanostatic mode for deposition times of 5 min, using a power source AMEL, model 551 (UK). The configuration of the electrophoresis cell was adapted to coat foil-shaped substrates of semicondutive materials (graphite). The graphite electrodes were maintained at a separation distance of 2 cm from each other. The dipping area of the substrates was $\sim$12.5 cm^2. The equipment was provided with a lift in order to assure a constant withdrawal rate of 7.5 mm/s (that is, 45 cm/min, which is near the maximum provided by the lab device). This withdrawal rate was selected because it allowed to diminish the gelling time, assuring better uniformity and reliability, as it was demonstrated elsewhere.[9]

The mass contribution to the deposit was characterized by gravimetry after 24 h drying. Ceramic deposits and substrates were thermally treated at 800 °C for 1 h in air, to promote the graphite burning out, and sintered at 1550 °C for 2 h with heating and cooling rates of 5 °C/min. Microstructural observations were made by optical and scanning electron microscopy (SEM).

3. Results and discussion

The rheological behaviour of carrageenan aqueous solutions has been studied in previous work.[9] The main properties that control the gelling behaviour of the solutions of gel-former are summarised in Table 1. All properties, the gel strength (related to the gap of viscosity during the transition from sol to gel) the viscosity of the solution and the gelling temperature T_g increase with the carrageenan concentration.

The rheological behaviour of AZ suspensions with different solids loadings and carrageenan contents was studied by measuring the flow curves at 60 °C, where carrageenan is in the sol state, and the evolution of viscosity on cooling. The most significant properties of the AZ suspensions are shown in Table 2. The gelling temperature increases with the carrageenan content but is insensitive to variations in the solids loading for a constant concentration of carrageenan. For a concentration

Table 1
Gelling behaviour of the carrageenan solutions measured at 100 s^{-1}

Carrageenan concentration (wt.%)	T_g (°C)	η_{60} (mPa s)	η_{gel}/η_{sol}
0.6	27.9	13	>3
0.8	31.0	26	>3
1.0	33.5	33	>4
1.2	35.6	51	>5

Table 2
Rheological properties of AZ suspensions measured at 100 s^{-1}

Solids content (wt.%)	Carrageenan content (wt.%)	T_g (°C)	η_{60} (mPa s)	η_{gel}/η_{sol}	σ (mS/cm)
20	0.0	–	–	–	0.3
	0.4	24.8	12	>2	1.8
	0.8	31.9	56	>3	2.4
	1.2	36.4	81	>4	3.1
30	0.4	24.7	14	>2	1.5
	0.8	31.6	40	>3	2.4
	1.2	36.0	85	>3	3.2
40	0.4	24.9	18	>2	1.6
	0.8	–	–	–	2.6
	1.2	–	–	–	3.8

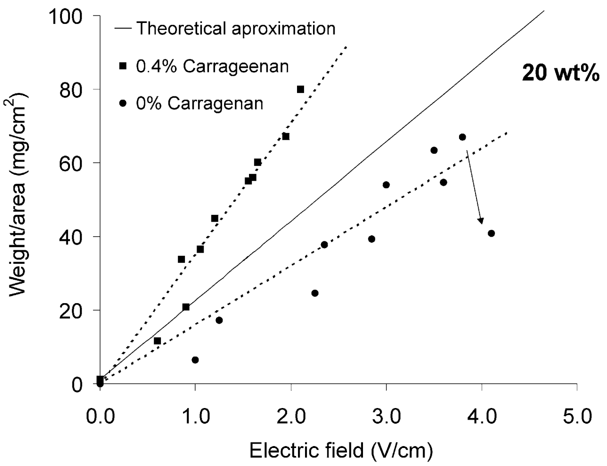

Fig. 1. Evolution of the deposited weight per unit area vs the applied electric field for 20 wt.% suspensions with 0 and 0.4 wt.% of carrageenan. The straight line determines the theoretical evolution of the deposited mass predicted by the Hamaker equation.

of 0.4 wt.% the T_g is near 25 °C, which can difficult gelation under room conditions.

Preliminary EPD tests were carried out for the 20 wt.% suspensions without carrageenan and with 0.4 wt.% carrageenan for comparison purposes. Fig. 1 shows the mass per unit area of deposits obtained from both suspensions at different current densities for 5 min tests. In order to allow a direct comparison of the results they were expressed in terms of electric field. Assuming that electrophoretic mobility was the same with and without carrageenan the deposit growth could be predicted in the light of Hamaker's equation:

$$m\ (E) = u_e\ ECt$$

where m is the deposited mass per unit area (kg/m^2), u_e is the mobility measured by microelectrophoresis (3.0×10^{-8} m^2/sV), E is the electric field measured from the voltage registered at the begining of the tests (V/m), C is the concentration of particles (235 kg/m^3) and t is the deposition time (300 s). The straight line in Fig. 1 represents the deposition growth predicted using the equation of Hamaker. It can be seen that deposition of aqueous AZ suspensions without carrageenan reaches a maximum after which the deposits fall down during the withdrawal, because of the poor adherence to the substrate. This suspension exhibits an irregular growth in which the deposited mass is lower than expected. This irregular growth reflects the heterogeneity of the obtained deposits. When introducing carrageenan, the deposition follows a regular trend and the deposited mass is larger than predicted. It must be taken into account that the suspension without carrageenan is deposited at room conditions. However, when carrageenan is added, the suspensions are manipulated and shaped at 60 °C, thus changing the conductivity from 0.3 mS/cm for the carrageenan-free suspension at 25 °C, to 1.8 mS/cm for the carrageenan-containing suspension at 60 °C. On the other hand, it was not possible to measure the zeta potential at these conditions with the available equipments. The difference between the conductivities of the suspensions with and without carrageenan had been corrected in the representation of the weight per unit area, in Fig. 1, since the electric fields represented are the value which was measured starting the test, and hence the suspension conductivity was just considered. So, the faster deposit growth of carrageenan-containing suspension could be related to higher values of electrophoretic mobility, but also to an active contribution of the carrageenan to the own shaping process.

Fig. 2 shows the evolution of mass per unit area vs. the electric field for suspensions with 0.4 wt.% carrageenan prepared to different solids loadings. All the films maintained adhered to the graphite substrate after drying, but there is a maximum weight above which the films cracked during drying. It is worthy to note that cracking appears when an electric field larger than a critical value of about 1.5 V/cm is applied, regardless the volume fraction of particles. The maximum mass per unit area without cracks are 55, 46, and 64 mg/cm^2 for solid loadings of 20, 30, and 40 wt.%, respectively (see Table 3).

It must be also noted that a coating layer develops on each face of the substrate during the EPD process. After sintering, the graphite sheet burns out and two isolated layers are obtained. The microstructural analysis performed by SEM on sintered samples revealed that these two layers had different thicknesses. In all cases, the mass deposited on the face in front of the counter-electrode represents roughly a 55% of the total deposited mass. The points at zero electric field in Fig. 2 correspond to dipping tests, where the mass per unit area is negligible in comparison to the mass deposited by EPD.

Fig. 3 shows the SEM microstructure of sintered films obtained from suspensions with 0.4 wt.% carrageenan and solids loadings of 20 wt.% (a), 30 wt.% (b), and 40 wt.% (c) by applying an electric field of 1.5 V/cm for 5 min. The pictures were made for layers obtained on the preferential deposition surface. The sintered films are always thicker than 150 μm. The deposit thickness clearly depends on the carrageenan content (Table 3), but there is not a clear dependency with the solids loading, although the apparent density seems to increase with the particles concentration. Comparable results have been observed for layers obtained by only dipping with similar suspensions.[10]

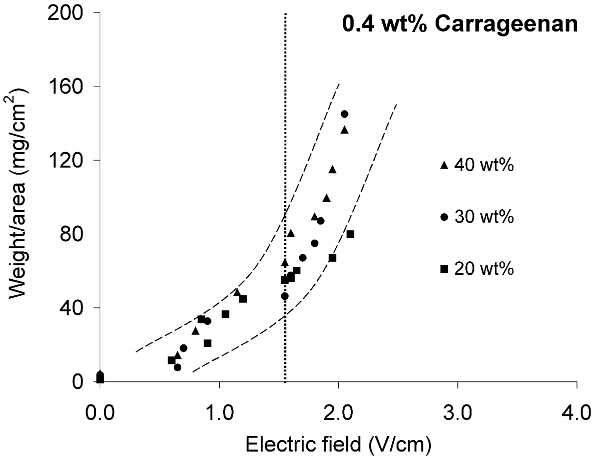

Fig. 2. Evolution of the deposited weight per unit area vs. the applied electric field for 20, 30 and 40 wt.% suspensions with 0.4 wt.% of carrageenan.

Fig. 4 shows the evolution of mass per unit area vs. the electric field for the suspensions with 0.8 wt.% carrageenan, which increases with the solids loading. The particles concentration has a critical role in the formation of a consistent gel structure, and suspensions with 20 wt.% solids cannot retain the shape and fall down during the withdrawal, thus the collected results have large errors with respect to the actual deposited mass. However, a higher carrageenan content makes it increase the gel strength of the deposited layer. Above a certain thickness the layer becomes very stiff and tends to release from the substrate on drying. The rigidity provided by the gel-former allows the released films to maintain homogeneous and free of cracks during drying and they shrink uniformly and without warpage. Again, films obtained under electric fields above 1.5 V/cm cracked during drying. The limiting mass per unit area to avoid either releasing or cracking are also shown in Table 3. Crack-free films as thick as 750 μm are obtained for 40 wt.% suspensions with 0.8 wt.% carrageenan.

Similarly, Fig. 5 shows the evolution of mass per unit area with the applied electric field for those suspensions containing 1.2 wt.% carrageenan. The evolution of the deposited mass follows the same trend than for suspensions with 0.8 wt.% carrageenan, with a power-law

Table 3
Characteristics of the EPD coatings

Carrageenan (wt.%)	Solids (wt.%)	Drying effects			
		Mass and thickness of films before releasing or cracking			
		Limit value for releasing		Limit value for cracking	
		Weight/area (mg/cm^2)	Sintered thickness (μm)	Weight/area (mg/cm^2)	Sintered thickness (μm)
0.4	20	None	–	55	270
	30	None	–	46	150
	40	None	–	64	265
0.8	20	Does not retain shape	Does not retain shape	–	–
	30	62	150	85	285
	40	14	85	141	750
1.2	20	Does not retain shape	Does not retain shape	–	–
	30	All	–	87	320
	40	All	–	143	530

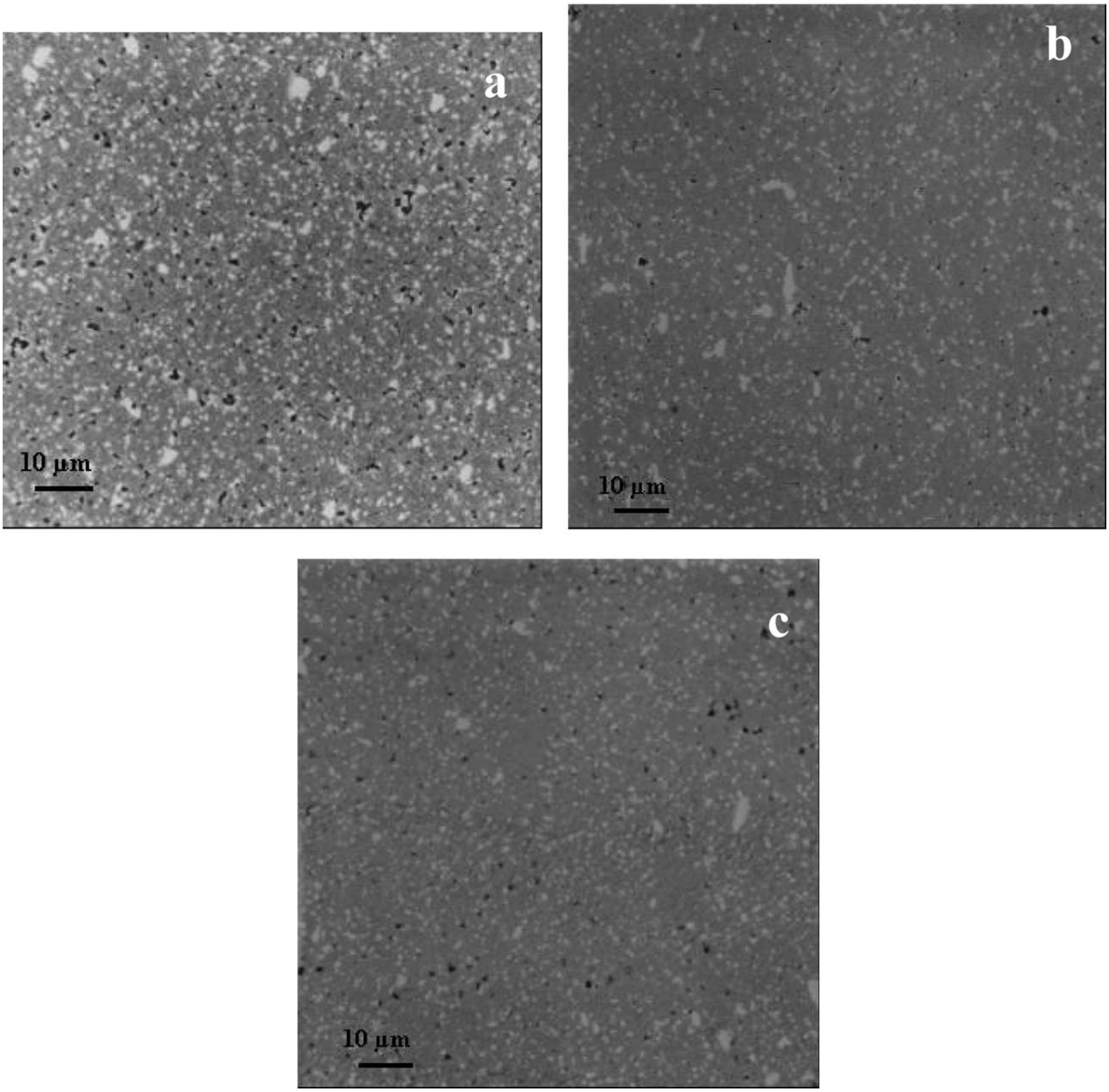

Fig. 3. SEM pictures of sintered films obtained by EPD from 20 wt.% (a) 30 wt.% (b) and 40 wt.% (c) AZ suspensions with 0.4 wt.% of carrageenan.

growth for 20 and 30 wt.% suspensions, and with slightly heavier deposits. For 40 wt.% suspensions, the deposit grows linearly and the deposited mass is the same as for 40 wt.% suspensions with 0.8 wt.% carrageenan.

The effect of increasing concentrations of carrageenan on the sintered microstructure can be seen in the SEM microphotographs of samples with 30 wt.% solids and carrageenan contents of 0.8 wt.% (a) and 1.2 wt.% (b), prepared under the same electrical conditions (1.5 V/cm, 5 min). Comparing with the microphotograph in Fig. 6b, a larger amount of gelling additive (⩾0.8 wt.%) leads to slightly higher residual porosity.

The effect of drying on the films obtained with the prepared suspensions are summarised in Table 3, also. It is important to note the effect of carrageenan concentration, so the films performed with 0.4 wt.% carrageenan suspensions did not release from the substrate after drying, since at this concentration, carrageenan cannot develop enough gel strength during cooling to overcome the adhesion of the deposit to the substrate. Contrarily, all deposits obtained from suspensions with 1.2 wt.% of carrageenan release without warpage during drying due to the too high gel strength developed in this case. A carrageenan content of 0.8 wt.% allows to obtain ceramic coatings that maintain adhered to the

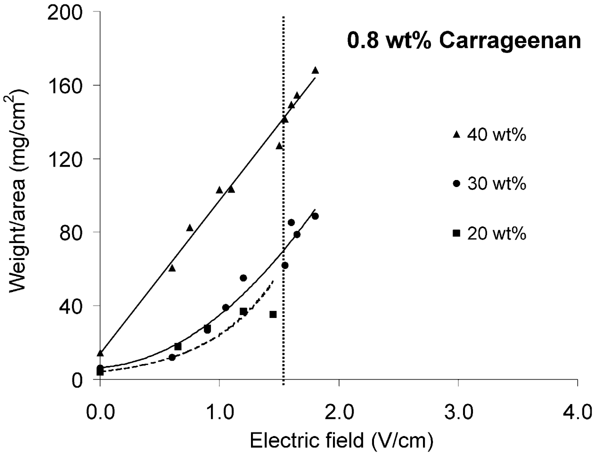

Fig. 4. Evolution of the deposited weight per unit area vs the applied electric field for 20, 30 and 40 wt.% suspensions with 0.8 wt.% of carrageenan.

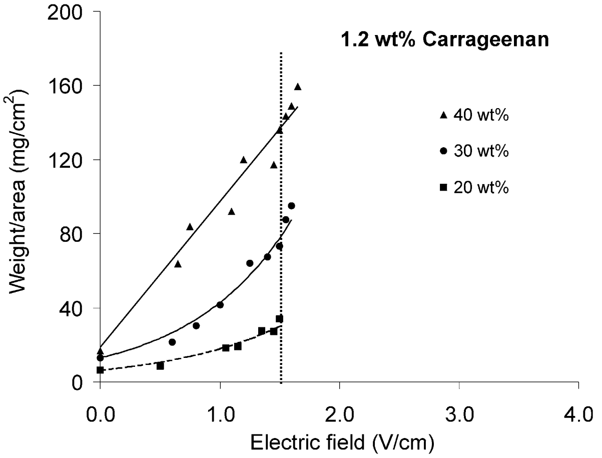

Fig. 5. Evolution of the deposited weight per unit area vs the applied electric field for 20, 30 and 40 wt.% suspensions with 1.2 wt.% of carrageenan.

substrate for mass/area values and thicknesses depending on the solid loading, up to 62 mg/cm^2 for 30 wt.% and 14 mg/cm^2 for 40 wt.% suspensions (sintered thickness of 150 and 85 μm, respectively).

Table 3 also shows that for all formulated suspensions, deposition has a limit over which films crack during drying. In fact whatever was the suspension, deposits prepared at electric fields $\geqslant$1.5 V/cm cracked, determining a first limit on the electrical conditions to be applied. MORL and SEM observations show the formation of large pores (Fig. 7) that correspond to bubbles originated from the H_2O electrolysis at the anode and trapped during the shaping process. Bubbles formation may be the responsible for cracking to occur. The presence of these large pores decreases with decreasing electric filed. If electrophoresis is performed applying electric fields $\leqslant$0.5 V/cm there is no risk of bubbles formation for any of the suspensions considered in this work.

Finally, the results of the described gel-electrophoresis process were compared with those reached by a similar coating technology, as the dipping process in the presence of carrageenan.[10] The maximum crack-free thickness attainable by dipping was ~30, and 90 μm for carrageenan contents of 0.8, and 1.2 wt.%, respectively, and 30 wt.% solid loading, which are thinner than those obtained by EPD.

Fig. 8 shows the microstructure of two films obtained with a 30 wt.% suspension with 0.8 wt.% of carrageenan by dipping (a) and by electrophoresis (b), applying an electric filed of 0.5 V/cm for 5 min. Films obtained by dipping show a small porosity homogeneously distributed as a consequence of the amount of carrageenan added to the suspension and its low solid loading. The

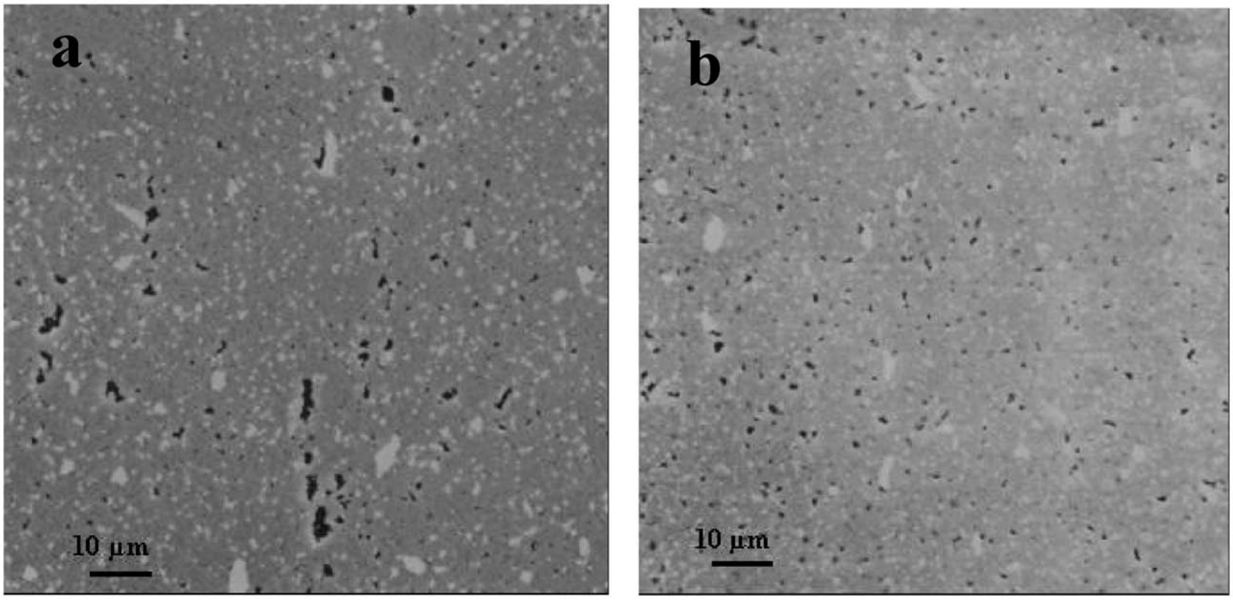

Fig. 6. SEM pictures of sintered films obtained by EPD from 30 wt.% AZ suspensions with 0.8 wt.% (a) and 1.2 wt.% (b) of carrageenan.

deposit obtained electrophoretically with the same suspension shows a higher density, verifying that the electrical strength developed during the EPD process promotes the particle reordering at the deposit, and hence improves the packing density. Summarising, under the optimised electrical conditions, EPD allows to obtain dense deposits with a wide range of thickness, while carrageenan increases the deposit adherence, thus improving the films formation.

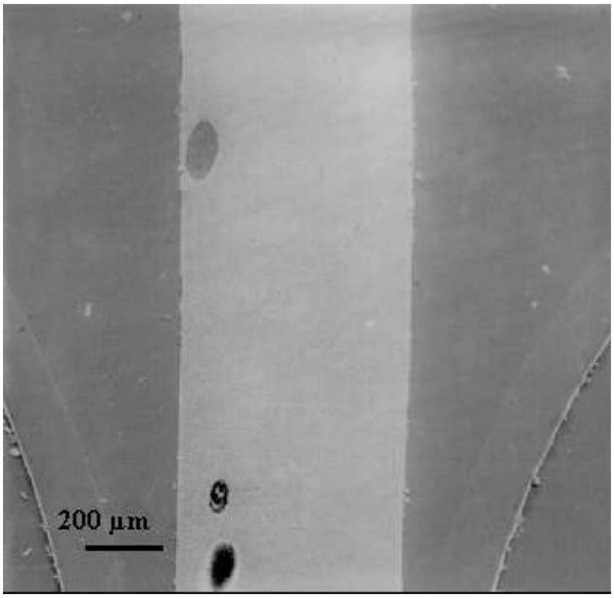

Fig. 7. SEM pictures of the sintered film obtained by EPD applying an electric field of 1.5 V/cm for 5 min to a 40 wt.% AZ suspension with 0.8 wt.% of carrageenan.

4. Conclusions

The electrophoretic codeposition of Al_2O_3/Y-TZP mixtures in water has been studied. A novel colloidal process has been described and optimised, which allows to shape dense thick films (> 10 µm). The process is based on the use of low concentrations of polysaccharides (e.g. carrageenan) that mixed at 60 °C with an aqueous suspension allows the formation of a film by electrophoretic deposition, and its subsequent gelation immediately after withdrawal.

Suspensions without carrageenan do not adhere to the substrate by dipping. Uniform coatings can be obtained by dipping using carrageenan, but some porosity remains due to the low solids loading of the suspensions. However, the additional force of the electric field in EPD allows a better rearrangement of the particles, thus leading to higher sintered densities.

The thickness, density and characteristics of films are depending on the concentration of the gelling additive, the solid loading of the slip and the electrical conditions. There is a deposit mass value, mainly depending on the carrageenan content, from which the films release from the substrate on drying. But homogeneous flat films can be obtained with maximum thickness of 150–750 µm, depending on the solid loading and the carrragenan content.

Above this limit cracking occurs. Cracks may be originated by the application of intense electric fields. In the systems studied in this work, it is recommended not to exceed an electric field of 0.5 V/cm in order to avoid the risk of bubbles formation.

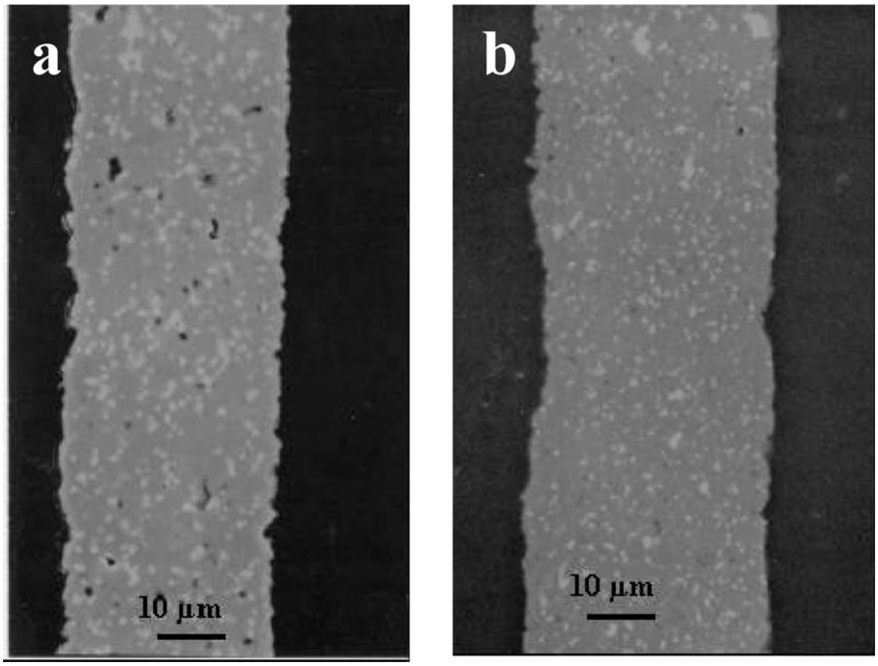

Fig. 8. SEM pictures of the sintered films obtained with a 30 wt.% suspension with 0.8 wt.% of carrageenan, by dipping (a) and by EPD applying an electric field of 0.5 V/cm for 5 min.

Acknowledgements

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