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Ni-YSZ self-supported films by gel electrophoresis

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Abstract

The manufacturing of metal–ceramic self-supported films by a colloidal process for fuel cell applications is reported. Ni and Ni-YSZ (with 30 vol.% YSZ) self-supported films have been prepared by combining electrophoretic deposition in water suspensions with thermogelling properties of carrageenan. Deposition is carried out on graphite electrodes which are removed on heating. The effect of the suspension solids loading and the concentration of gelling binder on the suspension rheology and electrophoretic deposition (EPD) performance are studied, as well as the deposition kinetics to optimize the deposit formation. Formed deposits are treated in air at 800 °C for graphite burning out and further sintered in reducing N_2/10% H_2 atmosphere at temperatures ranging from 1100 to 1400 °C. Porous films with homogeneous distribution of phases are obtained.

Keywords: A. Shaping; A. Suspensions; A. Films

1. Introduction

Among suspension-based forming techniques, electrophoretic deposition (EPD) is one of the most versatile for designing complex shapes and microstructures. EPD offers the possibility to produce controlled coatings and self-supported films with a wide range of thicknesses, from 1 to 200 μm, and its simplicity makes it the process useful for large-scale production.

Electrophoretic deposition has become an attractive route for the deposition of thin particulate films on porous substrate electrodes, followed by co-firing, which constitutes a low cost alternative for shaping thin electrolyte layers (microns), as those used for the fabrication of solid oxide fuel cells (SOFC) [1,2]. Currently, most published works describe the electrophoretic deposition of either anode supported electrolytes [3–6], in which the anode consists of an YSZ-NiO composite or an YSZ-Ni cermet, or cathode supported electrolytes [7–9], where the substrate is usually made of lanthanum–strontium manganate (LSM). Both materials are compatible with the processing temperatures needed to densify the electrolyte (<1400 or <1350 °C, respectively), thus providing a significant flexibility to the process.

Open literature reports the fabrication of complete cells alternating different processes and intermediate thermal treatments [3,4,8]. Although EPD is mainly used for manufacturing the electrolytes, some authors have reported also the EPD of one of the cell electrodes [3,10,11].

In the most general case a dense thin film of YSZ is produced by EPD from an organic suspension using a porous substrate shaped before by other methods, such as pressing [5,7,8], tape casting [9] or sol–gel [4]. Recent trends in colloidal processing focus on the use of aqueous suspensions attending to environmentally friendly and low cost production, which has made it possible to build up complex structures by EPD. Composite films or coatings have been produced in aqueous medium by combining EPD and electrodeposition (ELD) [12] and by electrophoretic co-deposition of different powders [13].

In previous works, a methodology was reported for manufacturing laminates by combining EPD and/or dipping with the use of thermogelling polysaccharides that promote

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gelation of the deposited layers on withdrawal. This procedure allows the direct consolidation without intermediate thermal treatments of complex structures comparable to those existing in SOFC devices, such as sandwich layers or functionally graded coatings [14,15].

This work studies the possibility to obtain self-supported Ni-YSZ films with an appropriate anode microstructure as a first step to develop a complete SOFC system. The manufacture of self-supported films by combining physical deposition mechanisms involving suspensions (e.g., dipping and EPD) with the consolidation of the layer after withdrawal by thermogelation of carrageenan is applied to ceramic–metal composites.

2. Experimental

The following starting powders were used: Nickel T110 (INCO, Canada) and cubic ZrO_2 stabilized with 8 mol% Y_2O_3 (TZ-8YS, TOSOH, Japan). Powders have a mean particle size of 2.5 and 0.4 μm, a surface area of 1.0 and 4.7 $m^2 g^{-1}$, and a density of 8.7 and 6.0 $g cm^{-3}$, respectively. Particle size distributions were measured with a laser analyzer (Matersizer S, Malvern, UK). Surface area was measured by one point N_2 adsorption (Monosorb, Quantachrome, USA). Powder density was measured with a helium picnometer (Multipicnometer, Quantachrome, USA).

Aqueous suspensions of Nickel (100N) and Ni/ZrO_2 mixture with relative ratios 70/30 (v/v) (30Z) were prepared by ultrasonic mixing using a 400 W sonication probe (IKA U400S, Germany) for 3 min. According to previous work [16] suspensions were stabilized with 1 wt.% of a commercial polyacrylic acid based polyelectrolyte (Duramax D-3005, Rohm and Haas, USA) adding tetramethylammonium hydroxide (TMAH) up to pH 10.

As gelling agent, a commercial carrageenan powder (Secogel TC, Hispanagar, Spain was used). A 2 wt.% solution of carrageenan was prepared by heating at 90 °C until dissolution. The hot solution (60–65 °C) was added to the suspensions until concentrations of gelling agent of 0.6 and 0.8 wt.% with regard to the total water content were reached. The final solids contents were 5.5, 14 and 17 vol.% for the 100N suspensions (0.5, 1.2 and 1.5 $kg l^{-1}$, respectively) and 14 and 17 vol.% for 30Z suspensions (1.1 and 1.3 $kg l^{-1}$, respectively), after carrageenan addition.

Thermogelling behavior was determined by measuring the evolution of the suspension viscosity versus temperature using a rotational rheometer (Haake RS50, Germany). The sensor system consisted of a double-cone rotor and a stationary plate, protected with a solvent trap to reduce evaporation.

EPD experiments were performed in galvanostatic conditions using a power source AMEL (mod. 551, UK). Current densities ranging from 0.15 to 5.0 $mA cm^{-2}$ were applied for 5 min using 100N suspensions with different carrageenan contents. EPD kinetics was determined applying 0.2 $mA cm^{-2}$ and deposition times up to 15 min, for 100N suspensions with different solids contents and 14 vol% suspensions of mixture 30Z. Commercial graphite foils were used as work electrode or substrate, acting as molds to maintain the desired flat shape of the deposited material, and also as counterelectrode. Both electrodes were separated at a distance of 2 cm each other. The immersed area of the preform was 2 cm × 5 cm. EPD equipment was provided with a lift in order to assure a constant withdrawal rate of 7.5 $mm s^{-1}$. The temperature of the suspensions with carrageenan was maintained at 60 °C during the deposition tests in order to prevent the gelation of the additive. On withdrawal, the gel-coated substrates were left at room temperature for drying.

The mass of each deposit was characterized by gravimetry after 48 h drying. Samples were firstly treated at 800 °C for 1 h in air to burn out the graphite and immediately sintered in a N_2/10% H_2 atmosphere at 1100, 1200, 1300 and 1400 °C for 1 h with heating and cooling rates of 5 °C min^{-1}. Microstructural observations were made by scanning electron microscopy (SEM).

3. Results and discussion

Dense and porous nickel compacts were fabricated by thermogelling adjusting the amount of the gelling agent added to the suspension in order to avoid the excessive or differential shrinkage of the piece, and also demonstrating that manipulating the suspension conditions, the colloidal processing route in water does not involve a significant oxidation in the nickel powder and the green samples [17]. Necessarily, stability and gelling conditions must be now studied focused to the development of nickel thin self-supported films (up to 100 μm). Fig. 1 shows the evolution of viscosity on cooling (at a shear rate of 100 s^{-1}) for 5.5 and 14 vol.% 100N suspensions with 0.6 and 0.8 wt% of carrageenan. The viscosity at 60 °C of suspensions with the same solids loading increases with carrageenan content from 30 to 40 mPa s, demonstrating the thickening effect of polysaccharide solution. On the other hand, viscosity also increases with solids content for a constant carrageenan content (from 40 to 61 mPa s in suspensions with 0.8 wt.%

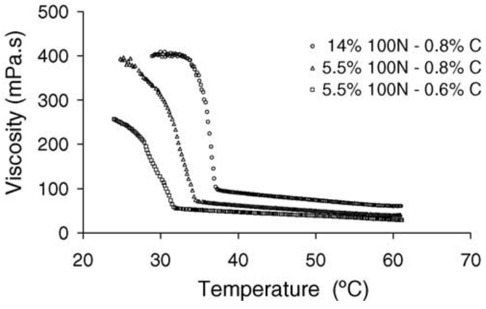

Fig. 1. Evolution of viscosity on cooling of 100N suspensions with different solids loadings and carrageenan contents (shear rate: 100 s^{-1}).

Table 1
Rheological properties of 100N and 30Z suspensions measured at 100 s^{-1}

Composition	Solids loading		Carrageenan content		T_g (°C)	η_{60} (mPa s)	η_{gel}/η_{sol}	σ (mS cm^{-1})
	vol.%	kg/l	wt.% liq.	wt.% sol.				
100N	5.5	0.5	0.6	1.18	31	30	>3.6	2.1
			0.8	1.59	35	40	>5.2	2.7
	14	1.2	0.8	0.57	37	61	>6.5	4.3
	17	1.5	0.8	0.45	–	–	–	4.6
30Z	14	1.1	0.8	0.62	33	44	>7.5	–
	17	1.3	0.8	0.49	–	–	–	–

of carrageenan). The rheological parameters characteristic of the gel formation, such as gelling temperature and gel strength (related to the gap of viscosity during the transition from sol to gel) also increase with solids loading and carrageenan content. This means that for suspensions with significant volume fraction of particles, the particles structure has an important role in the maintenance of the network structure developed on gelation, as stated in previous work [18]. The main properties of the gelling process and the conductivity of 100N and 30Z suspensions, related to the solids loadings (volumetric fraction and weight concentration) and the carrageenan concentration (with regard to the total water or the total powder), are summarized in Table 1. The suspension conductivity is controlled by charged specimens arising from the dissociation of the molecules of dispersants and ionic polysaccharide, which depend also on the solids loading.

When the volume of zirconia increases the viscosity decreases, but the gel strength seems to slightly increase. Although the volume fraction of powders in both the 100N and the 30Z suspensions is the same (14 vol.%), the last contains a higher amount of carrageenan (0.62 wt.%) than the former (0.57 wt.%), which can justify some differences in the gelling behavior.

Preliminary EPD tests were carried out for the 5.5 vol.% suspensions with 0.6 and with 0.8 wt.% carrageenan. Fig. 2 shows the mass per unit area of deposits obtained from both suspensions at different current densities for 5-min tests. Results are expressed in terms of electric field to allow a direct comparison of the results, as its calculation already considers the suspension conductivity.

It can be seen that deposition of aqueous Ni suspensions with 0.6 wt.% of carrageenan is almost negligible for electric fields lower than 1.6 V cm^{-1}, in opposition to the early deposit formation for the 0.8 wt.% suspension. The faster deposit growth is probably related to the higher values of electrophoretic mobility, but the content of carrageenan plays also a role, as suggested by the differences in the rheological measurements. Films heavier than 30 mg cm^{-2} cracked during drying, due to the accumulation of large bubbles at the anode during electrophoresis [15]. So, applied current intensities should be low enough to assure that electric field maintains below 1 V cm^{-1}.

EPD kinetics of 100N suspensions with 0.8 wt.% carrageenan was studied at a current density of 0.2 mA cm^2 (<1 V cm^{-1}). Fig. 3 plots the evolution of weight per unit area versus deposition time. The graphic shows that for time zero (i.e., dipping tests) the deposit weight largely increases for suspensions with a solids content of 17 vol.%, in good agreement with the significant thickening of the suspension (Table 1). This effect maintains in the deposits obtained by EPD and a deposition rate of ~10 mg cm^2 min^{-1} is reached. However, an excessive deposition rate and high thermogelling content promote poor particles packing, so that films heavier than 50 mg cm^{-2} deform during drying and crack. In the diluted 5.5 wt.% suspension kinetics shows a negligible deposition by electrophoresis up to 15 min. Although this suspension exhibits the lower gel strength (with a gap of viscosity of 3.6) the packing density is too low to overcome the shrinkage of the carrageenan gel during drying, and hence films shrink and deform on releasing from the graphite substrate. Suspensions with 14 vol.% solids have an

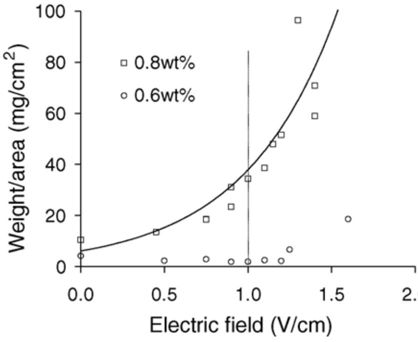

Fig. 2. Weight/area evolution vs. applied electric field of 5.5 vol.% 100N suspensions with 0.6 and 0.8 wt.% carrageenan contents.

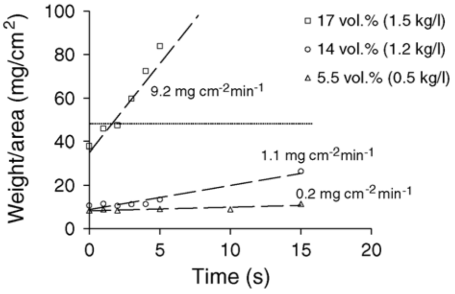

Fig. 3. Growing kinetics of deposits vs. solids loadings for 100N suspensions.

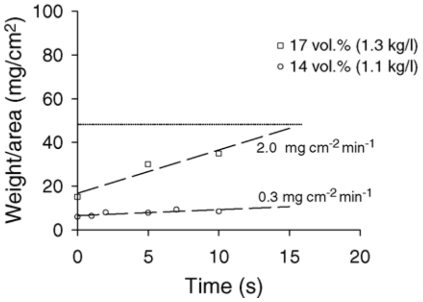

Fig. 4. Growing kinetics of deposits vs. solids loadings for 30Z suspensions.

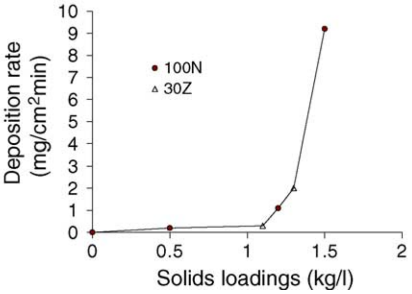

Fig. 5. Evolution of the electrophoretic deposition rate of the prepared suspensions with solids loading.

intermediate kinetics, which allows to obtain homogeneous and crack-free films adhered to the graphite substrate. These conditions were selected for preparing metal–ceramic suspensions.

Fig. 4 shows the deposition kinetics of 30Z suspensions with 0.8 wt.% of carrageenan and 14 and 17 vol.% solids loadings, developed under similar electric conditions. In this case all obtained deposits are homogeneous and maintain

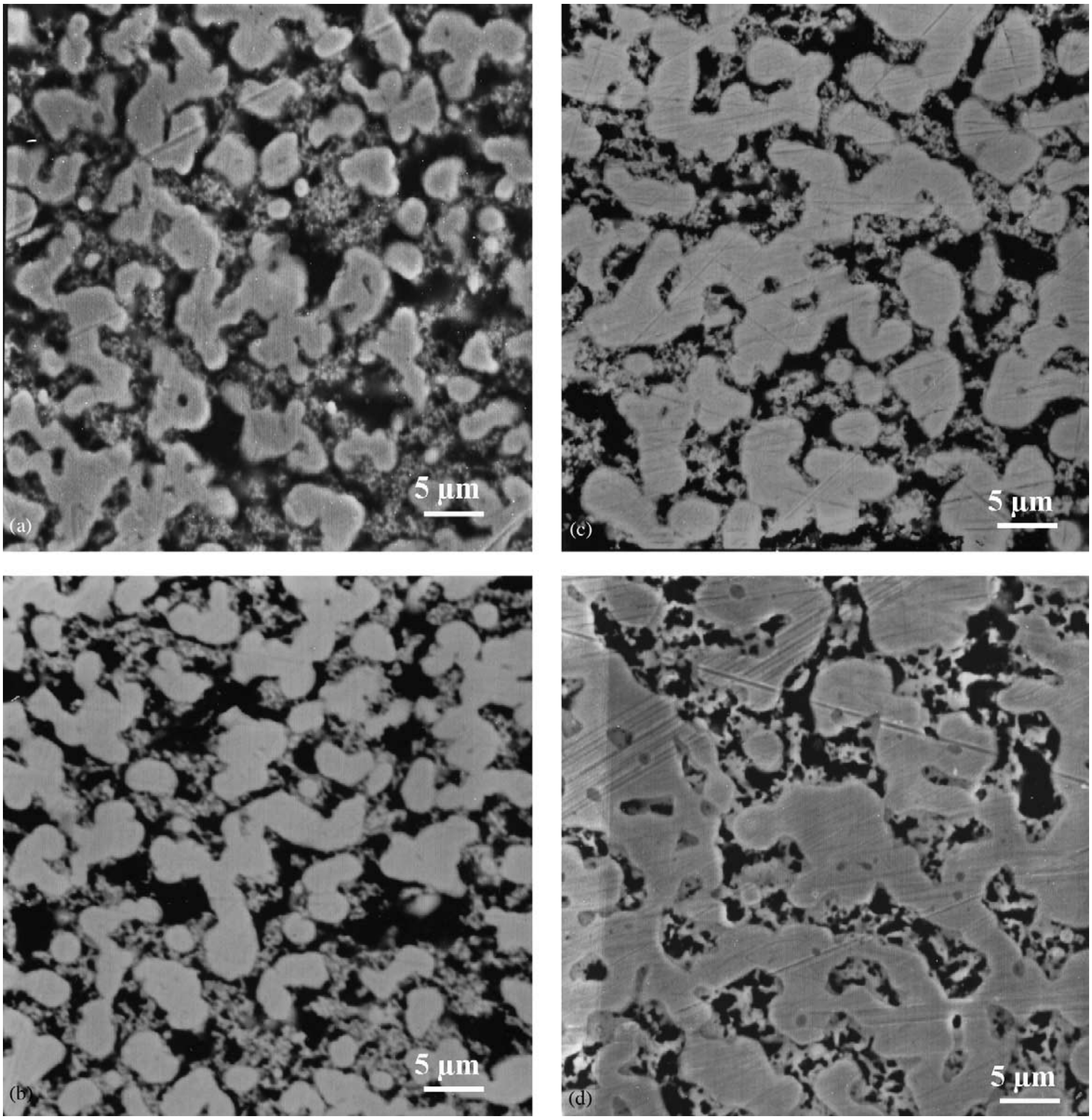

Fig. 6. SEM pictures of self-supported films obtained after thermal treatments at 1100 (a), 1200 (b), 1300 (c) and 1400 °C (d) for 1 h.

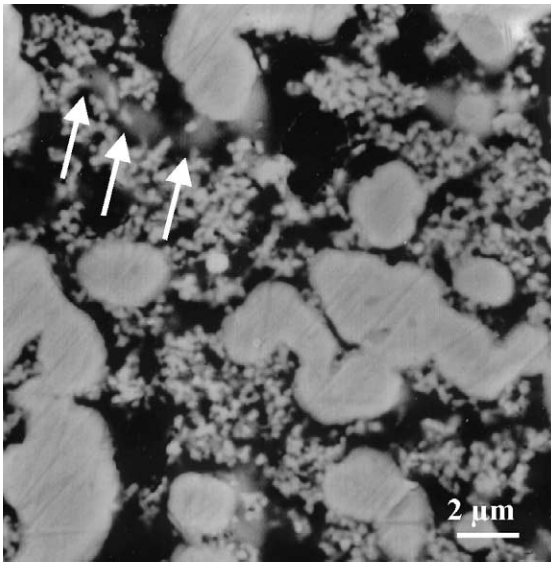

Fig. 7. Characteristic SEM microstructure of a Ni-YSZ composite developed after a thermal treatment of 1200 °C for 1 h.

adhered to the graphite substrate during drying. The 30Z suspension with 14 vol.% solids has a low kinetics (0.3 mg cm^{-2} min^{-1}), while with 17 vol.% solids has an intermediate kinetics, similar in order of magnitude than that of the 14 vol.% 100N suspension (deposition rates being from 2 to 1.1 mg cm^{-2} min^{-1}, respectively) as they have rather similar mass of powders.

Fig. 5 plots the deposition rates calculated from Figs. 3 and 4 for both 100N and 30Z suspensions as a function of the solids loading (kg/l). In agreement with conventional EPD models [19] this plot shows that studied suspensions follow an exponential function, demonstrating the important role of solids loading in the deposit growth. The sharp increase of deposition rate may be related to two different reasons: (1) the increasing viscosity of the suspensions with higher solids contents, which allows the formation of a thick deposit just by dipping, and (2) the contribution of solids fraction to retain the structure of the gel formed by carrageenan, because a larger fraction of particles provides a denser packing inside the cavities of the network and contributes to increase the strength.

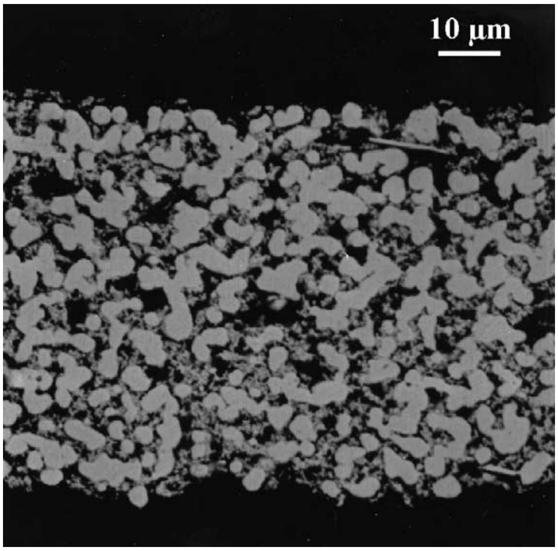

Fig. 8. Low magnification SEM micrograph of a 60 μm Ni-YSZ self-supported film obtained after a thermal treatment of 1200 °C for 1 h.

Metal–ceramic films were treated in air at 800 °C for 1 h to promote graphite burning out leading to a self-supported material. Carbon-free films were treated in reducing N_2/10% H_2 atmosphere at 1100, 1200, 1300 and 1400 °C for 1 h, to evaluate the microstructural evolution. Fig. 6a–d show the SEM microstructure of the materials obtained at each temperature. Micrographs show that zirconia is homogeneously distributed in a porous nickel matrix. As temperature rises nickel grains grow, so that the size at 1400 °C is twice that at 1100 °C. Zirconia starts to develop sintering necks from 1200 °C (Fig. 7), while nickel at this temperature forms an interconnected three-dimensional network as observed in the micrograph. A 60 μm thick self-supported layer is obtained with an open structure, where nickel grains are connected from one face to another and homogeneously bounded by zirconia grains, as it can be seen in the SEM picture of Fig. 8.

In summary, self-supported Ni-YSZ films have been obtained by EPD in water with the addition of carrageenan that promotes the consolidation by thermogelation on cooling during withdrawal.

4. Conclusions

We have demonstrated the viability of the aqueous electrophoretic co-deposition process on the shaping of metal–ceramic thin films. In a first step of the process, stable suspensions of Ni and Ni-YSZ have been prepared to moderate solids loading (up to 17 vol.%) by dispersing with 1 wt.% polyacrylic-based dispersant and TMAH at pH 10. There was also demonstrated that gelation contributes to the films forming, so carrageenan addition has been also adjusted in order to provide an adequate consolidation of the shaped coatings. Finally, self-supported films have been obtained after the graphite burn-out. EPD tests were performed at constant intensity conditions maintaining the electric field below 1 V cm^{-1} in order to prevent extensive bubbling near the electrode. Porous sintered films with 60 μm in thickness and homogeneous distribution of the phases have been obtained after a thermal treatment of 1200 °C for 1 h.

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