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DC Sputtering of yttria-stabilised zirconia films for solid oxide fuel cell applications

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Abstract

Yttria-stabilised zirconia (YSZ) thin films were dc-sputtered and investigated with respect to surface morphology, microstructure and film-substrate interface interaction. The films were deposited under argon/oxygen atmospheres on NiO/YSZ substrates heated to between 500 and 700°C. Dense and crack-free coatings were obtained in the thickness range of 1 to 10 μm. The film morphology varied from columnar to crystalline structure depending on the oxygen pressure and the substrate temperature. Whereas the coated films consisted of YSZ with cubic and tetragonal crystal structure under low oxygen atmospheres, the same deposition experiments on Al_2O_3 substrates revealed highly disordered layers of cubic YSZ. The formation of oxide layers on the NiO/YSZ substrates is due to a film-substrate redox interaction. The NiO grains close to the coating interface are partially reduced and serve as an oxygen source for the oxidation of the film. An exponential decay of the gas leakage vs. coating thickness was found.

Keywords: Films; Fuel cells; Yttria-stabilised zirconia (YSZ)

1. Introduction

The electrolyte thickness in anode-supported solid oxide fuel cell applications is about 10 μm.[1] In order to reduce the operating temperature from 800 to 650°C while maintaining the electrochemical power density, 8 mol% yttria-stabilised zirconia (8YSZ) electrolyte films of 1 to 2 μm thickness have to be produced[2] and cathodes with better electrocatalytic performance have to be applied.[3] Previous investigations have shown the successful deposition of YSZ films on various substrates such as steel, silicon, silica glass, platinum and also porous NiO/YSZ cermet by dc magnetron sputtering.[4,5] It was reported that dense and impervious YSZ films up to 16 μm thickness had been prepared in a single cubic phase structure. The porous NiO/YSZ substrate used was of relatively high porosity up to 32%.[5] The present work demonstrates the deposition of dc-sputtered 8YSZ electrolyte films up to 10 μm in thickness on substrates with similar porosity, but covered with a nearly dense NiO/YSZ functional layer.

2. Experimental

The planar NiO/YSZ anode substrates used in this study were manufactured by the coat-mix process.[1] A less porous NiO/YSZ functional layer of 5 μm thickness was applied to the presintered NiO/YSZ anode substrate by vacuum slurry coating[6] and sintered at 1400°C for 4 h. All films were deposited by dc reactive sputtering (Sputron, Balzers AG) using a metallic ZrY target (80:20 at.%) for deposition. The base pressure in the vacuum chamber was below 1×10^{-6} mbar, while the pressure of argon during deposition was 2×10^{-3} mbar. Substrates 50×50 and 25×25 mm^2 in size were used and heated to 700°C by halogen lamps. For comparison, additional coatings were prepared on polished alumina ceramics. YSZ films were deposited at 500 to 700°C using oxygen as the processing gas with pressures ranging from 0.65×10^{-4} to 6.0×10^{-4} mbar. A deposition rate of 1.56 μm/h was achieved with 60 W/cm^2 dc power on the target and about 200 mm distance between substrate and target. The crystal structure of the films was analysed by X-ray diffraction (XRD) using CuK_α radiation. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray spectrometry (EDX) were used to

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determine the morphology, the microstructure and the composition of the deposited films. The gas-tightness of the films was measured using a Balzers He-leakage system (QualiTest HLT 260). Sample thickness and roughness was measured by a Taylor–Hobson Talysurf 2 profilometer.

3. Results and discussion

Fig. 1 shows the XRD patterns of the deposited YSZ films on NiO/YSZ substrates at 500, 600 and 700°C with partial pressures of oxygen ranging from 0.65×10^{-4} to 6.0×10^{-4} mbar. In all cases, but much more pronounced at low partial pressures of oxygen, besides the cubic phase of YSZ (c-YSZ) the diffraction patterns also showed significant amounts of the tetragonal phase (t-YSZ). At an oxygen partial pressure of 2.3×10^{-4} mbar and below reflections of metallic Ni were detected. After postannealing of the coated substrates at 1100°C for 3 h in air, the tetragonal YSZ phase was completely transformed into the cubic YSZ phase.

The diffraction patterns of the films coated on polished alumina substrates showed the cubic YSZ phase at oxygen pressures $\geqslant 2.3\times10^{-4}$ mbar (Fig. 2). At lower oxygen pressures down to 0.65×10^{-4} mbar wider reflections of the YSZ pattern were measured according to smaller crystallites and/or increased disorder, and even an amorphous film was deposited as shown in Fig. 2(c). Without any oxygen supply the metallic phase of zirconium was deposited [Fig. 2(d)].

The thicknesses of selected YSZ films on NiO/YSZ and on polished alumina substrates obtained by profilometer measurements and by image analysis of SEM images are compared in Table 1. The film thickness showed not only a dependence on the deposition time but also on the oxygen pressure.

The roughness of the coated and uncoated substrates showed no significant differences. The roughness of the uncoated NiO/YSZ substrates was measured as $R_a = 0.3$ μm. The values of the coated NiO/YSZ substrates were in the same range. Both the coated and the uncoated alumina substrates showed a roughness value of $R_a = 0.025$ μm.

The morphology and microstructure of the films in the micrometer range was investigated by SEM. Fig. 3 shows the fractured and polished cross-sections of the samples listed in Table 1. In all cases crack-free, dense coatings were obtained. In the backscattering mode, the SEM images of the substrates showed light borders around the dark grey particles close to the film-substrate interface (Fig. 4). This was observed only on substrates which had been coated in atmospheres with low oxygen pressure and which showed a brown–black darkening of the substrate. This darkening spreads out with a fractal growth and may affect the whole surface at lower oxygen pressures. Optical microscopy images of polished cross-sections of substrates coated at low oxygen pressures showed a darkened region within the substrate down to a depth of 80 μm.

Because the darkening and the Ni reflections in the XRD patterns disappeared after heat treatment in air, it was assumed that a partial reduction of the NiO grains occurred during deposition. Therefore the light borders around the grains in Fig. 4 were interpreted as partially reduced NiO grains in the functional layers. The reduction of the NiO grains started at low oxygen pressures near the surface-film interface. Longer deposition times, higher deposition temperatures and lower oxygen

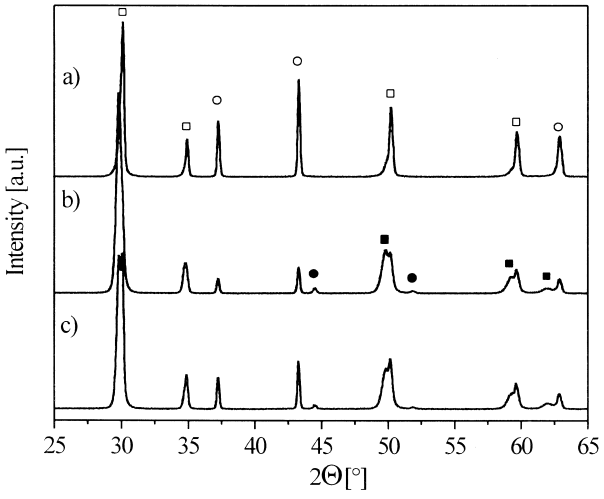

Fig. 1. XRD patterns of YSZ films on NiO/YSZ anode substrate deposited at different oxygen partial pressures and substrate temperatures: (a) 6.0×10^{-4} mbar at 500°C; (b) 2.3×10^{-4} mbar at 700°C and (c) 0.65×10^{-4} mbar at 600°C. The symbols shown correspond to c-YSZ (□), t-YSZ (■), Ni (●), NiO (○).

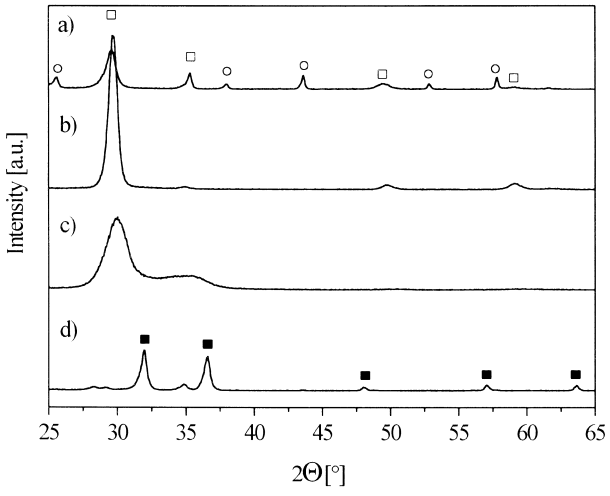

Fig. 2. XRD patterns of YSZ films on polished alumina substrates deposited at different oxygen partial pressures and substrate temperatures: (a) 6.0×10^{-4} mbar at 500°C; (b) 2.3×10^{-4} mbar at 700°C and (c) 0.65×10^{-4} mbar at 600°C; (d) no oxygen flow at 700°C. The symbols shown correspond to c-YSZ (□), Al_2O_3 (○), α-Zr (■).

Table 1
Thickness of YSZ films deposited on NiO/YSZ and on polished alumina substrates obtained by profilometer (d_{prof}) measurements and image analysis of SEM images (d_{SEM})

$p(O_2)$ (10^{-4} mbar)	$t_{deposition}$ (min)	$d_{prof–NiO/YSZ}$ (μm)	$d_{prof–alumina}$ (μm)	$d_{SEM–NiO/YSZ}$ (μm)
0.65	240	7.0	8.5	8.5
2.3	240	7.5	6.5	
6.0	210	1.5	1.5	1.2

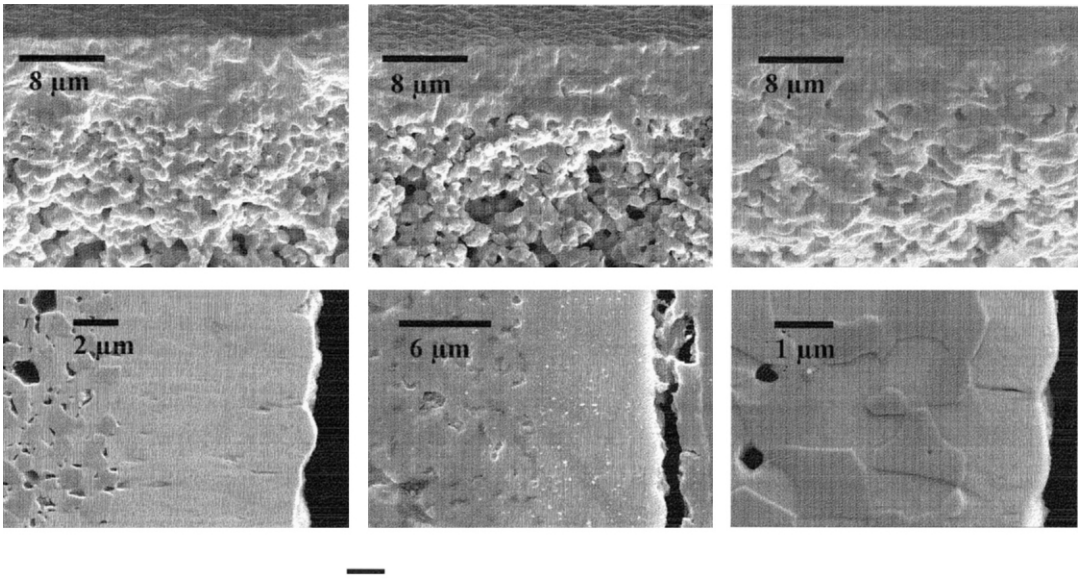

Fig. 3. SEM micrographs of fractured (top) and polished (bottom) cross-sections of YSZ films deposited with oxygen partial pressures of 0.65×10^{-4} mbar (left), 2.3×10^{-4} mbar (middle) and 6.0×10^{-4} mbar (right).

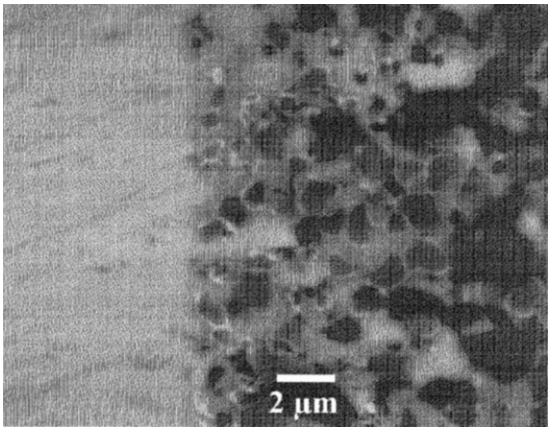

Fig. 4. SEM micrograph of polished cross-section of YSZ film (left) with partially reduced NiO grains (light borders around dark grey particles) in NiO/YSZ anode material (right).

pressures led to a thicker reduced zone. Indubitable proof of the partial reduction was achieved in a TEM investigation. The TEM images showed, on the one hand, the partial reduction of NiO grains along the grain boundaries with much better resolution (Fig. 5). On the other hand, the XRD pattern of Ni was obtained after X-ray microdiffraction.

The NiO grains were partially reduced due to a higher binding enthalpy of ZrO_2 (1100 kJ/mol) than for NiO (240 kJ/mol). The released O^{2-} ions diffuse into the growing film using the oxygen vacancies of the YSZ substrate material. Therefore YSZ was deposited even at low oxygen pressures whereas coatings under same conditions on Al_2O_3 revealed rather amorphous films (cf. Figs. 1 and 2).

The measured He-leakage rates of the coated NiO/YSZ substrates showed an exponential dependence on the film thickness (Fig. 6). The values for the as-coated samples were below the He-leakage rates of uncoated substrates ($\approx2\times10^{-3}$ mbar l/cm^2 s) but did not reach a level at which the gas-tightness is sufficient for SOFC application. However, post-annealing in air at 1100 to 1300°C, which corresponds to sintering temperatures of the SOFC cathode, showed improvements of gas-tightness compared to the as-coated substrates (Table 2). After post-annealing at 1300°C an improvement of the He-leakage rates by a factor of 2 to 10 was achieved. In the case of the substrates coated under low oxygen pressures the He-leakage rates were below $L=1\times10^{-4}$ mbar l/cm^2 s, which is required in electrochemical tests for fuel cells.[6]

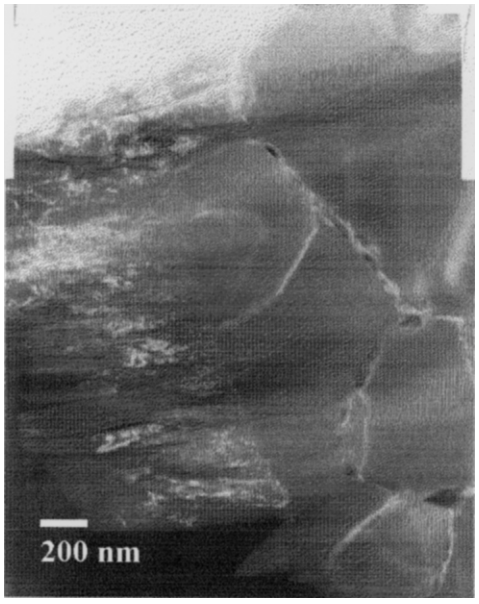

Fig. 5. Transmission electron microscopy image of partially reduced NiO grains along the grain boundaries at substrate-film interface.

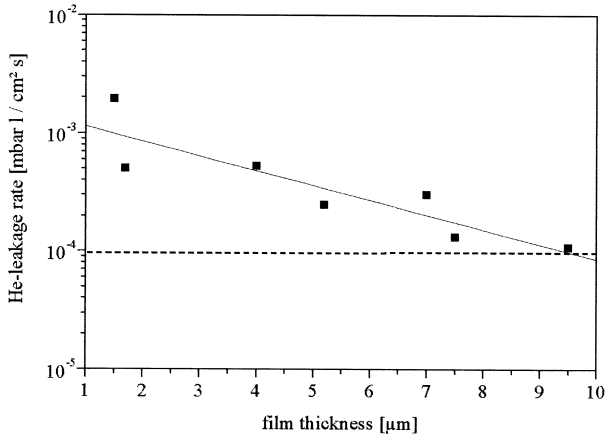

Fig. 6. He-leakage rates vs. film thickness of dc-sputtered 8YSZ films on NiO/YSZ substrates. The dashed line represents the gas leakage value which should be achieved for SOFC applications.

Table 2
He-leakage rates (L, in 10^{-4} mbar l/cm^2 s) of coated substrates depending on oxygen partial pressure during deposition and after post-annealing between 1100 and 1300°C

$p(O_2)/10^{-4}$ mbar	$L_{as\ coated}$	$L_{1100°C}$	$L_{1200°C}$	$L_{1300°C}$
0.65	1.3	2.1	1.3	0.6
2.3	3.0	1.0	1.6	0.3
6.0	19.3	48.0		11.0

4. Conclusions

Thin YSZ films with a thickness of 1.2 to 8.5 µm were obtained by reactive dc sputtering on porous NiO/YSZ anode substrates at 500 to 700°C for fuel cell applications. High oxygen pressures during deposition induced crack-free YSZ films grown in a cubic crystal structure. At lower oxygen pressures cubic and tetragonal YSZ films were deposited. Postannealed substrates showed single-phase cubic YSZ films and improvements towards gas-tightness by a factor of 2 to10 compared with as-coated substrates. Partial reduction of NiO to metallic Ni was observed during deposition, but is not critical for further SOFC processing.

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