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Journal of Power Sources 105 (2002) 239–242

JOURNAL OF POWER SOURCES

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# Pulsed laser deposition of yttria stabilized zirconia for solid oxide fuel cell applications

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**Abstract**

Yttria stabilized zirconia (YSZ) films were grown by pulsed laser deposition (PLD) from a 8YSZ target using a KrF excimer laser source (248 nm). The films have been deposited under oxygen atmospheres on porous NiO/YSZ substrates heated from room temperature to 600 °C. YSZ films were obtained in the range of 1–2 μm thickness. The films have been investigated with respect to surface morphology, microstructure and film–substrate interface interaction. The film morphology varied from columnar to an irregular crystalline structure depending on the oxygen pressure and the substrate temperature. In all cases the films consisted of YSZ with the cubic fluorite structure. The formation of oxide layers under low oxygen pressures 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. The measured He leakage rates to analyze the gas tightness of the YSZ films have so far shown no improvements as compared with uncoated substrates.


*Keywords:* Solid oxide fuel cell; Yttria stabilized zirconia (YSZ) thin films; Pulsed laser deposition

## 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 750 to 650 °C, without reducing the electrochemical power density, yttria (8 mol% $Y_2O_3$) stabilized zirconia (8YSZ) electrolyte films of 1–2 μm thickness have to be realized [2]. Due to advantages such as being able to transfer the stoichiometry unaltered from the target onto the substrate, film-to-film reproducibility and single-phase purity, pulsed laser deposition (PLD) is an interesting tool to deposit ceramic thin films. Dense, crack-free and also epitaxial YSZ films have been deposited successfully by PLD on various substrates like polymethylmethacrylate (PMMA), polycarbonate (PC), glass (fused silica), Si(1 0 0) or sapphire [3–5]. In the present work, pulsed laser deposition was used to deposit thin 8YSZ films on porous NiO/YSZ anode substrates for fuel cell applications.

## 2. Experimental

The planar NiO/YSZ anode substrates were manufactured by the coat-mix process [1]. A less porous functional layer (NiO/8YSZ) of 10 μm thickness was applied on the pre-sintered NiO/YSZ anode substrate by vacuum slurry coating and sintered at 1400 °C for 4 h. The target used during the pulsed laser deposition was pressed and sintered from a commercial 8YSZ powder (Tosoh) and mounted onto a rotating holder in a vacuum chamber with a background pressure of $1 \times 10^{-5}$ mbar. The angle between target and substrate normal was 45°. The target-to-substrate distance was 30 mm. The substrate was mounted on a resistance heater ranging from room temperature to 600 °C with a heating and cooling rate of 15 K/min. A KrF excimer laser (248 nm) was used at a pulse energy of 220 mJ (fluence = 2.8 J/cm$^2$) and a repetition rate of 30 Hz. The incident angle between the laser beam and the target normal was 45°. YSZ thin films were deposited at 500 and 600 °C on the sintered substrates using oxygen as processing gas with pressures ranging from 0.01 to 0.5 mbar. The crystal structure of the films was analyzed by X-ray diffraction (XRD) using Cu Kα radiation. Scanning electron microscope (SEM) pictures and energy-dispersive X-ray analysis (EDX) were used to determine the morphology and the general composition of the deposited films. He leakage

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0378-7753/02/$ – see front matter 
PII: S0378-7753(01)00945-4

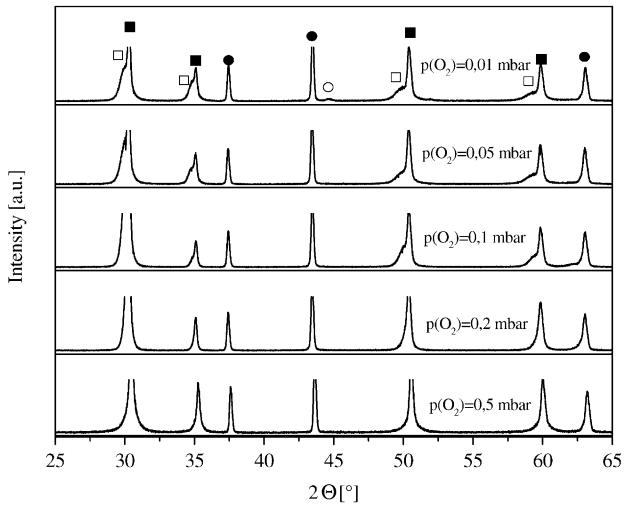


Fig. 1. XRD patterns of YSZ films on NiO/YSZ anode substrates deposited at different oxygen pressures. The symbols shown correspond to cubic-YSZ (■); tetragonal-YSZ (□); Ni (●); NiO (○).

rates were measured using a Balzers He leakage system (QualiTest HLT 260) to determine the gas tightness of the YSZ films.

## 3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the deposited YSZ films on NiO/YSZ substrates at 500 °C with oxygen pressures ranging from 0.01 to 0.5 mbar. In all cases the diffraction patterns showed the YSZ cubic phase with amounts of tetragonal phase at low oxygen pressures. At a low oxygen pressure of 0.01 mbar a partial reduction of NiO grains to Ni at the film–substrate interface was measured. Due to a higher binding enthalpy of $ZrO_2$ (263 kcal/mol) compared to NiO (57.3 kcal/mol) the NiO grains were partially reduced. The released $O^{2-}$ ions diffuse into the growing film using the oxygen vacancies of the YSZ substrate material and therefore YSZ was deposited even at low

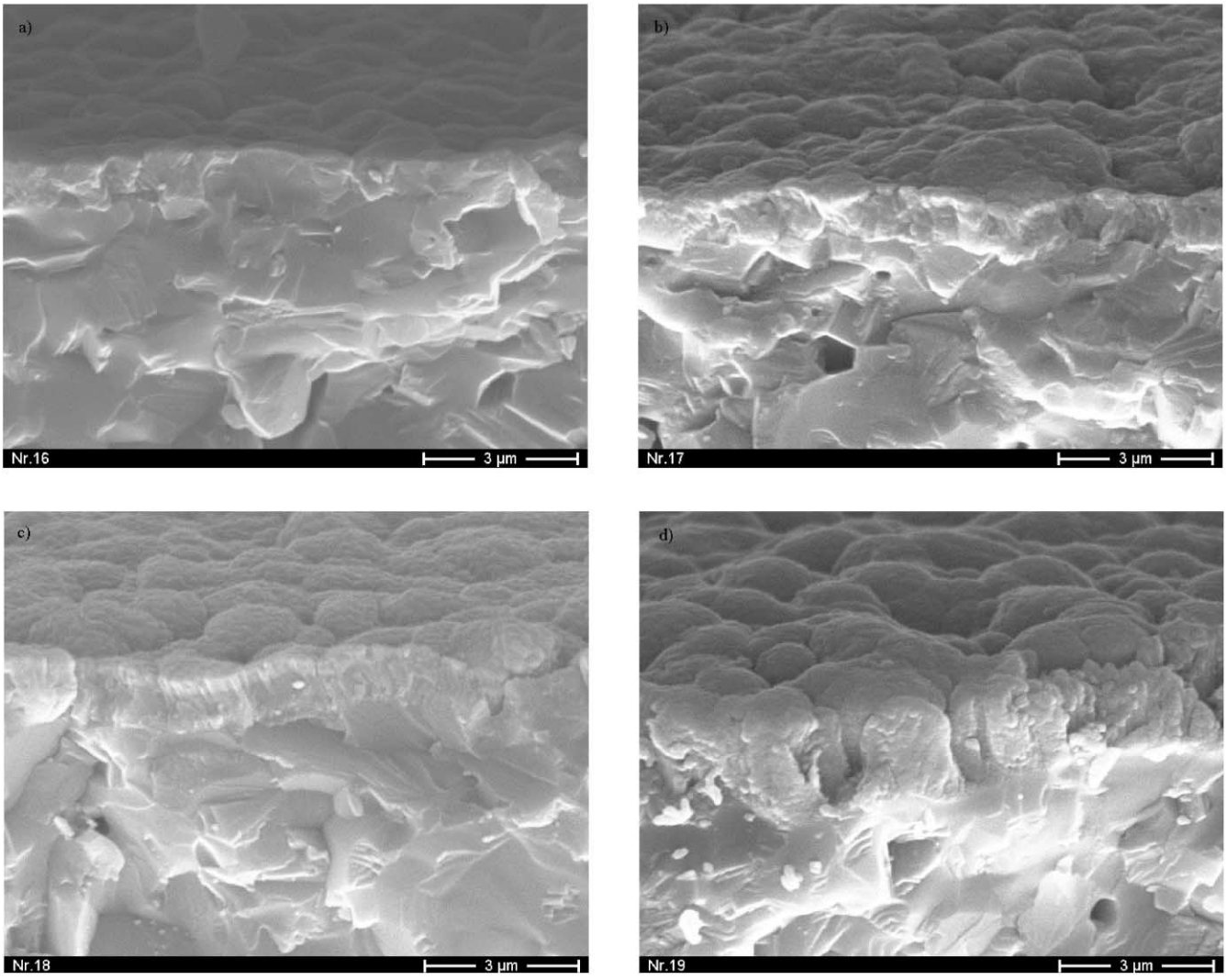


Fig. 2. SEM cross-section micrographs of YSZ films deposited with oxygen pressures of: (a) 0.05 mbar; (b) 0.1 mbar; (c) 0.2 mbar; (d) 0.5 mbar.

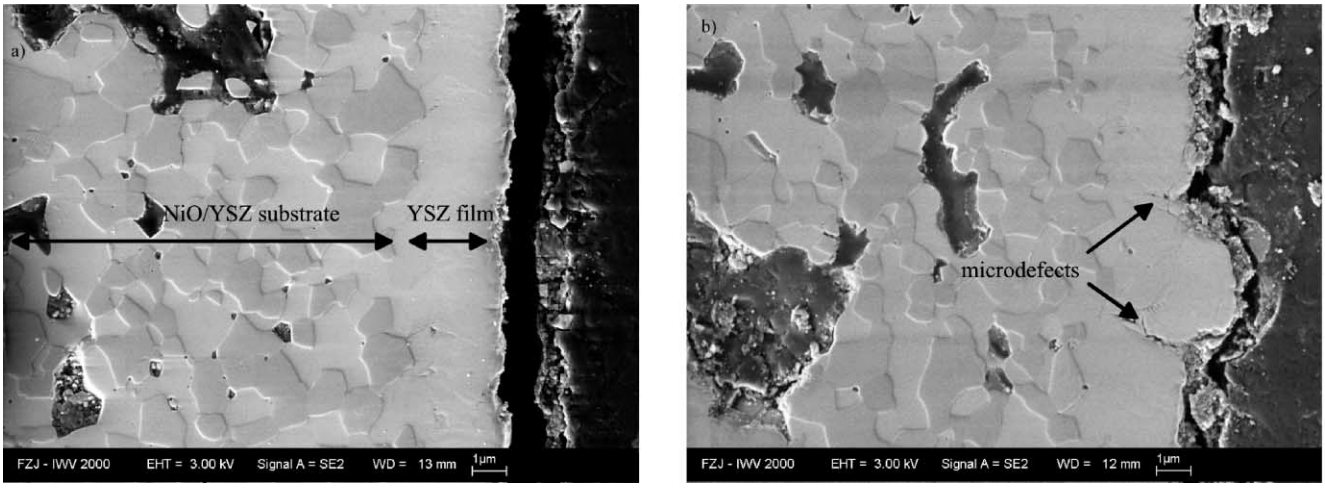


Fig. 3. SEM cross-section pictures of YSZ films: (a) without micro-defects; (b) with micro-defects caused by high surface curvatures of $1/R \approx 1\ \mu m^{-1}$.

Table 1
He leakage rates $L$ ($\times 10^{-4}$ mbar l/cm$^2$ s) of coated substrates depending on oxygen pressure during deposition and post-annealing temperatures

| $p(O_2)$ | $L_{as\ coated}$ | $L_{500\ °C}$ | $L_{700\ °C}$ | $L_{900\ °C}$ | $L_{1100\ °C}$ | $L_{1400\ °C}$ |
|---|---|---|---|---|---|---|
| 0.01 | 33 | 33 | 23 | 38 | 47 | 20 |
| 0.05 | 21 | 24 | 16 | 25 | 27 | 9 |
| 0.1 | 35 | 42 | 33 | 47 | 55 | 25 |
| 0.2 | 36 | 36 | 36 | 46 | 50 | 22 |

oxygen pressures. The tetragonal YSZ phase is due to low oxygen pressures during deposition whereas the fully oxidized cubic YSZ phase is deposited at oxygen pressures above 0.2 mbar. After post-annealing, the coated substrates at 1200 °C for 3 h in air, the tetragonal YSZ phase was completely transformed into the cubic YSZ phase. Also the partially reduced NiO grains were re-oxidized during post-annealing.

The morphology of the films in the sub-micrometer range was investigated by SEM. Fig. 2 shows the cross-sections of the samples corresponding to processing gas pressures ranging from 0.05 to 0.5 mbar. The films deposited with oxygen pressures of 0.5 mbar showed a high porosity. Dense and crack-free coatings were obtained with lower oxygen pressures. Films deposited at 0.05 mbar oxygen pressure showed a crystal size comparable to the crystal size of the substrate material. A higher oxygen pressure of 0.1 mbar led to the typical columnar structure [6]. Surface irregularities of high curvatures ($1/R \approx 1\ \mu m^{-1}$, $R$: radius of grain) induced micro-defects which led to higher He leakage rates (Fig. 3). YSZ films deposited at 600 °C showed no significant differences in the morphology with increasing oxygen pressure.

EDX mapping scans showed higher concentrations of Y and Zr in the film region compared to the concentrations in the substrate material. The amount of Ni dropped down to zero whereas the Ni concentration in the substrate was homogeneously distributed.

The He leakage rates of all coated substrates were in the same range as with the uncoated ones ($\approx 20 \times 10^{-4}$ mbar l/cm$^2$ s). Post-annealing treatments of the coated substrates in air at 500–1400 °C showed no improvements of gas t ightness compared to the as-coated substrates (Table 1). Fuel cells require a lower He leakage rate than $L = 1 \times 10^{-4}$ mbar l/cm$^2$ s as was shown in electrochemical tests [7].

## 4. Conclusions

Thin YSZ films with a thickness of 1–2 μm have been obtained by pulsed laser deposition on porous NiO/YSZ anode substrates at 500–600 °C for fuel cell applications. Low oxygen pressures during deposition induced dense YSZ films grown in cubic and tetragonal modification. At higher oxygen pressures cubic YSZ films were deposited in the typical columnar structure. All films showed no improvements towards gas tightness compared with uncoated substrates.

## Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft (DFG) under the contract numbers: Kr 516/22-2 and STO 382/1-2 is gratefully acknowledged.

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