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Microstructure and conductivity of 8.5YSZ thin films obtained by sol-gel processing

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Motivation

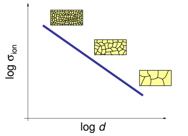
Ionic conducting 8.5 mol% Y_2O_3-doped ZrO_2 (8.5YSZ) is used as solid electrolyte in solid oxide fuel cells (SOFCs)

Trend: Reduction of operating temperature down to 500-700 °C

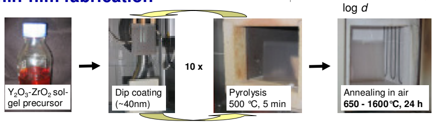
Problem: Ionic conductivity of microcrystalline 8.5YSZ too low in designated temperature range!

Idea: Enhancing ionic conductivity σ_{ion} of YSZ by decreasing mean grain size *d* ? [1]

***Project:* Investigation of the grain size effect on ionic conductivity in 8.5YSZ**



Thin-film fabrication



1. Dip coating of sapphire substrates in metal-organic sol-gel precursor [2]
2. Pyrolysis to burn out the organic fraction of the sol-gel [2]
3. Additional annealing to adjust the grain size in each single sample

→ **Series of YSZ thin films with varying mean grain size**

Experimental techniques

- Investigation of chemical composition / impurities as well as crystal structure and microstructure by transmission electron microscopy (TEM)
- TEM sample preparation using standard as well as focussed ion beam (FIB) techniques (**Zeiss Cross-Beam EsB 1540**)

200 keV Philips CM200 FEG/ST	200 keV LEO 922 OMEGA
• Conventional TEM (CTEM) • High-resolution TEM (HRTEM) • Selected-area electron diffraction (SAED) using imaging plates • Energy-dispersive X-ray spectroscopy (EDXS)	• Scanning TEM (STEM) + high-angle angular dark-field (HAADF) detector: Z-contrast imaging

Thin-film quality

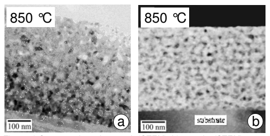


Fig. 1: a) Cross-section micrograph (CTEM), b) porosity (STEM)

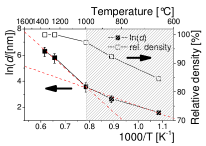


Fig. 2: Arrhenius plot ln(*d*[nm])/density [4]

- Thin films free of cracks with well-defined thickness/mean grain size (Fig. 1a) [3,4]
- Narrow-distributed grain size *d* (5 nm at 650 °C to ~ 1 µm at 1400 °C)
- Good adhesion on substrates
- Porosity in thin films annealed below 1250 °C (Fig. 1b)
- Size of pores ≈ mean grain size

Grain growth in nano-crystalline films (annealed below 1250 °C) limited by the presence of pores as indicated by the dashed lines in Fig. 2. [4]

Stoichiometry and purity

- Final Y^{3+} dopant concentration independent on the annealing temperature (Fig. 3)
- Quantification with respect to a TOSOH 8.5YSZ thick-film electrolyte: **8.27 +/- 0.33 mol% Y_2O_3** [4]

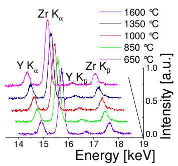


Fig. 3: EDX spectra of thin films normalized to Zr K$_\alpha$

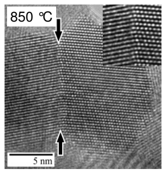


Fig. 4: Grain boundary (850 °C) (HRTEM)

No Si-/Al-rich glassy phases at the grain boundaries (HRTEM imaging + analytic methods)

Crystal structure and phases

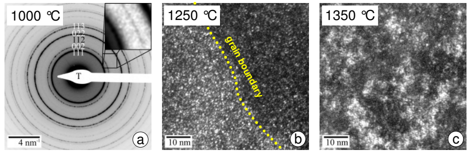


Fig. 5: a) SAED pattern of the thin film annealed at 1000 °C, b) and c) CTEM dark-field images visualizing tetragonal regions

SAED: weak additional {112} reflections (see insert in Fig. 5a)

→**Tetragonal phase ($a_t = c_t = a_c$) present in all prepared thin films**

Dark-field imaging with {112} intensity:

- Homogeneously distributed tetragonal regions in samples annealed ≤ 1250 °C (Fig. 5b)
- Size of precipitates 0.5-1 nm
- Concentration of precipitates independent of grain boundary/grain core (Fig. 5b)
- **Clustering** of tetragonal regions in specimen annealed at 1350 °C (Fig. 5c)

YSZ thin films not completely stabilized in cubic phase, microstructure strongly dependent on the final annealing temperature. [4]

Reference material

Microcrystalline 8.5YSZ SOFC-electrolyte substrates (TOSOH powder) [5]
as-sintered + homogenized ⟷ **annealed** (950 °C / 2000 h)

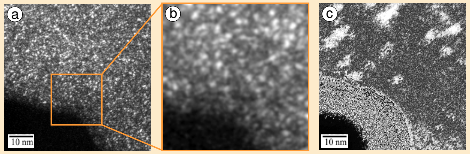


Fig. 6: CTEM dark-field images, taken using {112} reflections, of a) as-sintered 8.5YSZ, b) magnified region visualizing temporal fluctuations, c) annealed 8.5YSZ

As-sintered substrates:

- Tetragonal phase ($a_t = c_t = a_c$) clearly identified in 8.5YSZ [5]
- Microstructure similar to thin films annealed ≤ 1250 °C (Fig. 5b, 6a)
- Temporal fluctuation of tetragonal regions (Fig. 6b), suppression by LN_2-cooling

→ **No cation-diffusion based process!**

Annealed substrates:

- **Clustering** of tetragonal regions (Fig. 6c) + fluctuating regions [5]
- Slight variations (about ±10 at%) of Y-content observed on nano-scale applying electron energy loss spectroscopy (EELS)

→ **Decomposition?**

8.5YSZ not stabilized in cubic phase, fluctuating microstructure in as-sintered electrolytes, clustering of tetragonal regions during annealing at 950 °C. [5]

Phase diagram

Thin films annealed **≤ 1250 °C** + **as-sintered** 8.5YSZ substrates:

⊕ **Temporal fluctuation** of tet. regions
⊕ "Small" energetic gap between Gibbs free-energy functions of t''-/c-phase in wide range of Y^{3+}-content (Fig. 8 ◯)
→ Formation of metastable t''-phase

Thin film annealed at **1350 °C** + **annealed** 8.5YSZ substrates:

⊕ **Pinning + clustering** of tet. regions
⊕ No obvious growth
⊕ Local variation of Y content on nm-scale
→ Clustered tet. regions t''-phase? Decomposition at higher T, t? (*Driving force, mechanism, reason for Pinning*)

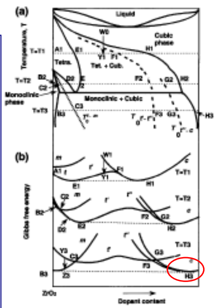


Fig. 8: a) Schematic metastable-stable phase diagram, b) corresponding Gibbs free-energy-composition diagram by M. Yashima et al. [6]

Conductivity

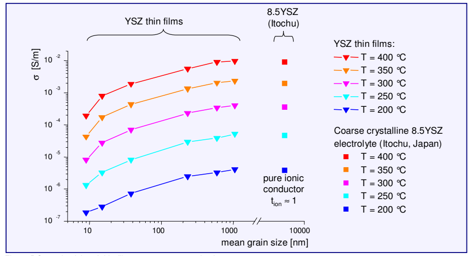


Fig. 9: DC conductivity of thin films versus mean grain size

DC conductivity:

- Coincidence of total DC conductivity of microcrystalline (1350 °C, 1250 °C) thin films with ionic conductivity of microcrystalline 8.5YSZ thick-film electrolytes (Itochu)
- Decreasing total conductivity with decreasing mean grain size

Impedance spectroscopy:

- Total resistance governed by grain boundary process (Fig. 9)

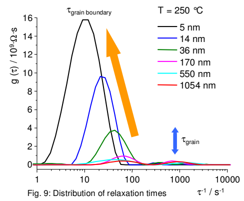


Fig. 9: Distribution of relaxation times

Summary

- YSZ thin films with 8.27 +/- 0.33 mol% Y_2O_3 prepared by sol-gel process
- Grain size (5 nm – 1 µm) / degree of porosity adjustable by annealing
- Residues of the sol-gel process / impurities in the thin films not detectable

Structure

- **YSZ thin films not completely stabilized in the cubic phase**: temporal fluctuations indicative for the existence of the **metastable t''-phase**
- **Clustering of the observed tetragonal regions** at higher temperature and longer time is still not completely understood. First EELS experiments on the nano-scale show slight fluctuations of the Y content.

→The presence of the tetragonal phase as well as the resulting microstructure have to be taken into account in modeling the electrical transport properties, since a strong influence of tetragonal nano-scaled regions in 8.5YSZ on ionic conductivity is observed! [5]

Conductivity

- Conductivity of microcrystalline YSZ thin films similar to standard electrolyte
- **Reduction of conductivity by decreasing the mean grain size down to nano-scale**, total resistance governed by grain boundary process!
- Clustered tetragonal regions as reason for degradation of bulk conductivity: *Y'_{Zr} and $V^{\bullet\bullet}_O$-depleted regions as scattering regions for O^{2-} hopping? Pinning of free $V^{\bullet\bullet}_O$ in clustered regions?*

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Acknowledgement

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