

Introduction

Current developments in solid oxide fuel cells (SOFCs) are focused on reducing the operating temperature below 800 °C. Though, the reduced operating temperature promotes durability of cells and decreases stringent demands on peripheral components, the electrical conductivity of electrolytes decreases following Arrhenius law. To solve this problem two different ways are possible: a) reducing the thickness of conventionally used yttria-stabilized zirconia (YSZ) electrolyte by using nanostructured particles as feedstock or b) by using an electrolyte with improved ionic conductivity for intermediate temperature (IT)-SOFCs. Conventional sintering of electrolytes is performed over several hours at temperatures above 1400 °C. Plasma sprayed electrolyte layers of conventional and of nanostructured YSZ, sintered in the temperature range of 800 to 1520 °C, are investigated.

The nanostructured YSZ particles after spraying maintained nanostructure. Nanostructure material assisted in enhancing the kinetics for sintering and grain growth. The coatings of both materials were under compressive stresses. However, it was observed that the sintering of free-standing coatings differed from that of coatings on substrates which was explained by theory of constrained sintering. A detailed comparison of sintering behaviour under constrained and non-constrained conditions for conventional and nanostructured YSZ was developed. Sintering properties, microstructure, and conductivity of sprayed and sintered YSZ electrolyte layers were investigated by Scanning electron microscopy (SEM), 4-point dc method, and by mercury intrusion porosimetry.

Experimental Procedure

Raw powder:

- 8 mol% YSZ (ZrO₂-Y₂O₃ 85/15; fused; H.C. Starck, LOT 03/75-24), -22.2+5.6 μm
- 10 mol% YSZ nanostructured powder (Nanox™ S4017, LOT#: IMCD293YSZ10; Inframat Advanced Technology), 60 to 90 nm, agglomerated to 5 to 20 μm particles.

Substrates:

- Steel for receiving free-standing electrolytes. (Treatment of as-sprayed layers with hydrochloric acid)
- Alumina strips for electrical conductivity measurements and for constrained sintering experiments at temperatures above 1000 °C.
- Steel for constrained sintering experiments at and below 1000 °C.

YSZ layers prepared by plasma spraying were sintered freely and under geometrical constraint in the temperature range of 800 to 1520 °C in Ar (flow rate: 100 ml.min⁻¹), holding time 6 hours. Dilatometry (Netzsch 402C™) characterised the densification of the sprayed, free-standing samples. Samples for constrained sintering were sintered in an electrical resistance furnace. Heating and cooling rates were both 5 °C.min⁻¹. Coatings morphologies were characterised by SEM (ZEISS LEO 982 „GEMINI“). Porosity and pore size distribution were obtained by mercury intrusion porosimetry (PASCAL 140 and PASCAL 240 devices from Fison Instruments up to pressures of 2,000 bar). Conductivity measurements were performed by 4-point dc method at 800 °C, under synthetic air (7 l.h⁻¹).

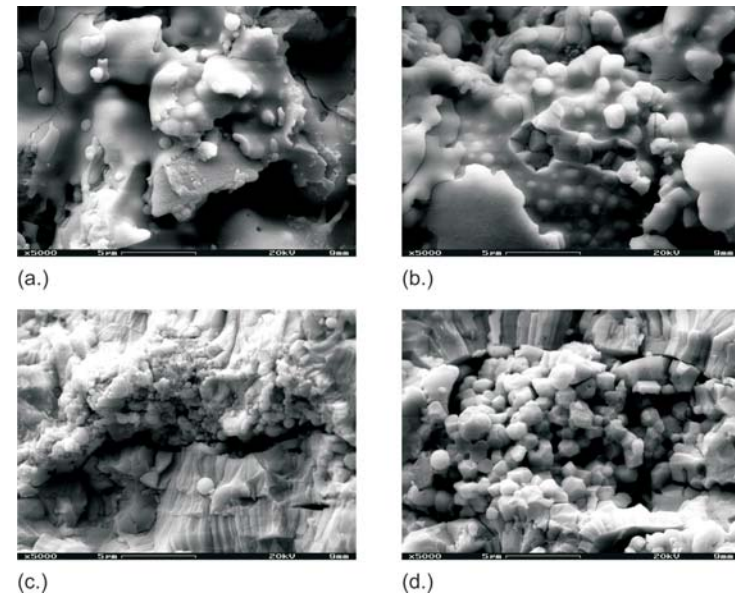


Fig.1. SEM micrographs of conventional and nanostructured as-sprayed YSZ,

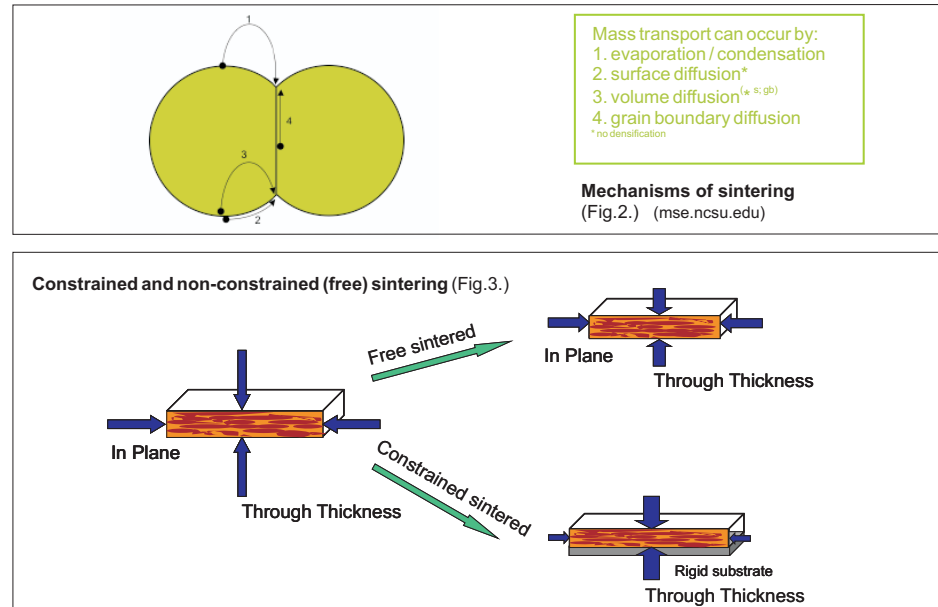
(a.) surface of YSZ_{conv}
(b.) surface of YSZ_{nano}

(c.) cross-fractional surface of YSZ_{conv}
(d.) cross-fractional surface of YSZ_{nano}

Sintering

Coble's sintering model is the most famous one, dividing the sintering process into three stages defined by shape characteristics.

- Initial stage (stage I):** Interparticle contact area is small, and increases from zero to 0.2 of the cross-section area of the particle. During the initial sintering stage neck formation and neck growth, which are leading to particle coarsening, will take place due to several mass transport mechanisms (i.e., evaporation/condensation, grain boundary or lattice diffusion). If in the initial stage shrinkage occurs, the rate will only be low.
- Intermediate stage (stage II):** Continuous pore channels with 3-grained edges. In this stage, density increases from 65 to 90%. Material is transported via pores diffusing away from, and atoms diffusing towards pore channels.
- Final stage (stage III):** Pore channels pinched off and isolated. Must have high defect mobility of this stage is to be achieved. Larger pores at grain boundaries between two grains decrease in size and can split into smaller sub-pores. At the grain boundary edge among three or more grains, the pore size decreases gradually.



Mass transport can occur by:
1. evaporation / condensation
2. surface diffusion*
3. volume diffusion (* = gb)
4. grain boundary diffusion
* no densification

Mechanisms of sintering (Fig.2.) (mse.ncsu.edu)

Constrained and non-constrained (free) sintering (Fig.3.)

Results and Discussion

- Experiments were run in the dilatometer under Ar flow, because in SOFCs a metal substrate is used, to measure the shrinkage behaviour of free-standing samples during sintering.
- Linear shrinkage is defined as the change in length dL divided by the initial length L₀ of the geometrical model.
- Shrinkage in the thickness direction (z) is less.
- Similar CTE (coefficient of thermal expansion) curves were measured till 900 °C.
- Lower dL/L₀ of YSZ_{nano} compared to YSZ_{conv} during heating above 900 °C indicates initiation of densification at lower temperature for nanostructured deposit.
- Temperature at which thermal expansion balanced the densification by sintering (appeared as maxima): 1326 °C for YSZ_{conv}, 1302 °C for YSZ_{nano}.
- The temperature at which densification by sintering exceeded thermal expansion (after maxima in curves): 1355 °C for YSZ_{conv} and 1315 °C for YSZ_{nano}.

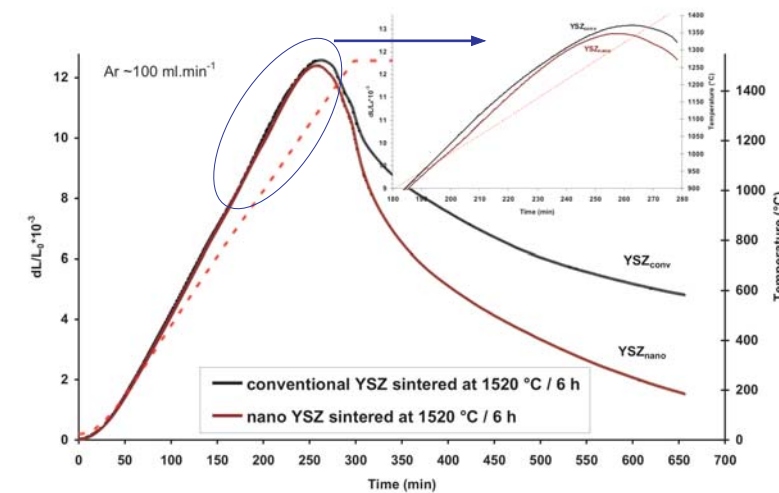


Fig.4. Dilatometer data of YSZ_{conv} / nano layers; heating rate 5 °C.min⁻¹, holding time 6 h at 1520 °C; Included figure: curve maxima in detail

- Sintering rates indicate start of stage I of sintering at temperatures below 900 °C.
- Cracks healing and inter-splat diffusion are observed in SEM micrographs of YSZ_{nano} / conv, both sintered at 1000 °C.
- Both effects were observed already at 800 °C during fuel cell operation in plasma sprayed YSZ electrolyte layers due to stage I of sintering where evaporation/condensation, grain boundary or lattice diffusion results in such microstructural changes.
- Shrinkage decreases linearly at 1000 °C isothermal heating, suggesting the possibility of stage I of sintering, which leads to only low shrinkage.

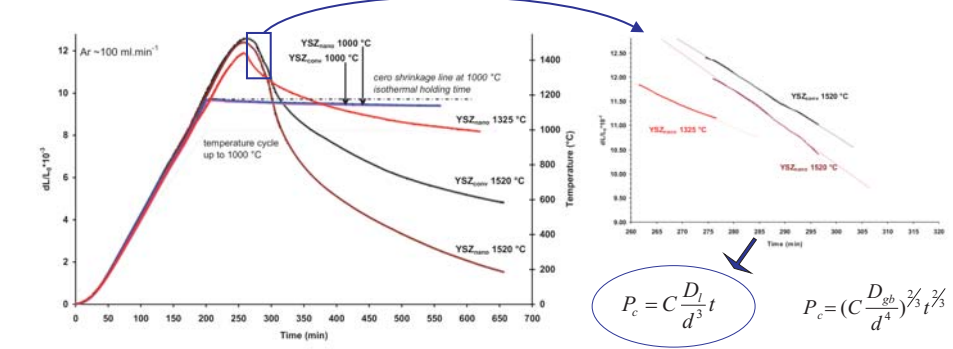


Fig.5. Dilatometer data of free standing YSZ_{conv} / nano samples sintered at 1000 °C, 1325 °C, and 1520 °C; right diagram: detailed curve with trend line; reflecting the intermediate stage of sintering

$$P_c = C \frac{D_l}{d^3} t$$

$$P_c = \left(C \frac{D_{gb}}{d^4} \right)^{2/3} t^{2/3}$$

P_c fractional porosity,
C concentration coefficient,
d edge length,
D_l lattice diffusion coefficient,
D_{gb} grain boundary diffusion coefficient,
t time

During sintering of a ceramic coating on a rigid substrate, the coating is under the driving force from sintering and the constraint from the rigid substrate. Tensile stresses develop in the coating in a direction parallel to the substrate while the shrinkage takes place mostly normal to the substrate.

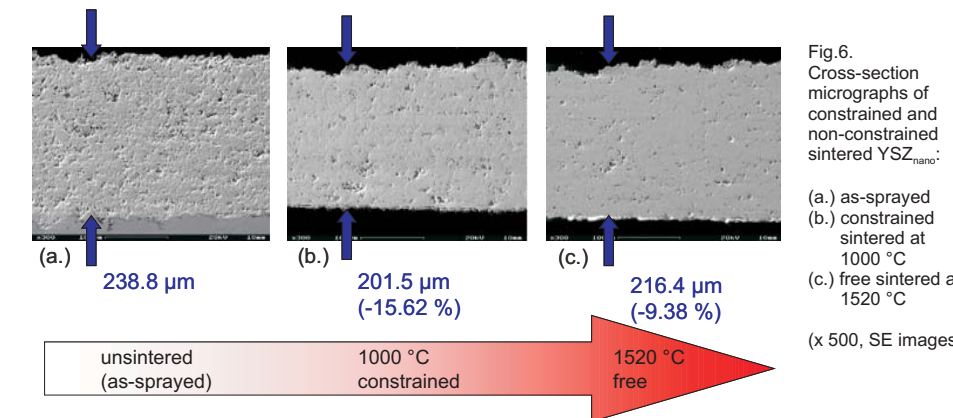


Fig.6. Cross-section micrographs of constrained and non-constrained sintered YSZ_{nano}:

(a.) as-sprayed
(b.) constrained sintered at 1000 °C
(c.) free sintered at 1520 °C
(x 500, SE images)

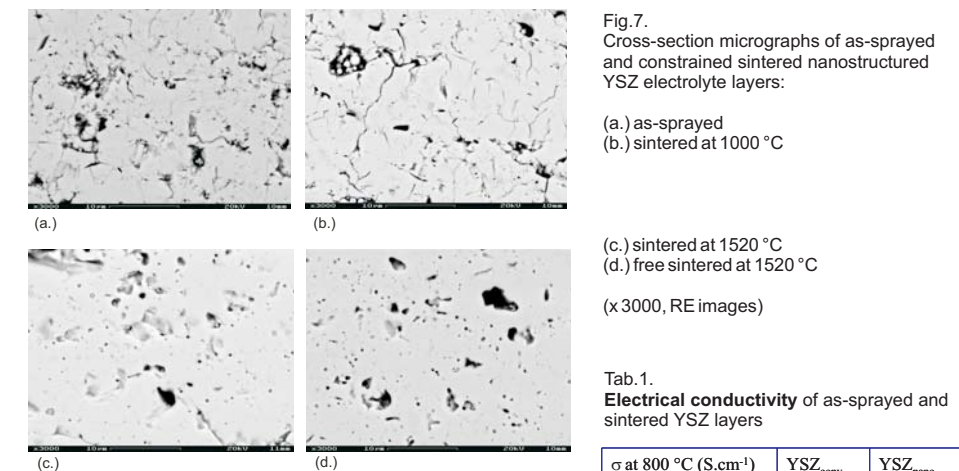


Fig.7. Cross-section micrographs of as-sprayed and constrained sintered nanostructured YSZ electrolyte layers:

(a.) as-sprayed
(b.) sintered at 1000 °C
(c.) sintered at 1520 °C
(d.) free sintered at 1520 °C
(x 3000, RE images)

Tab.1. Electrical conductivity of as-sprayed and sintered YSZ layers

σ at 800 °C (S.cm ⁻¹)	YSZ _{conv}	YSZ _{nano}
As-sprayed	0.021	0.013
Sintered at 1520 °C	0.068	0.016

Summary

- Initiation of densification of YSZ_{nano} at lower temperature compared to YSZ_{conv} (Lower dL/L₀).
- Higher shrinkage rate of YSZ_{nano} layer compared to YSZ_{conv} is due to different particle sizes of the powder feedstock.
- Cracks healing and inter-splat diffusion started at temperatures as low as 1000 °C.
- Lattice diffusion is the dominant effect in stage II of sintering.
- Lamellar microstructure in as-sprayed samples reduces electrical conductivity of YSZ electrolytes. Sintering of as-sprayed electrolyte layers at sufficient temperature increases electrical conductivity.