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Residual stresses and strength of multilayer tape cast solid oxide fuel and electrolysis half-cells

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HIGHLIGHTS

- Bending strength of MTC half-cells with 3 and 4 layers.
- Influence of loading orientation with respect to the plies of MTC half-cells.
- Influence of the number of layers on the strength due to residual stresses.
- An identification of the weak points inside the half-cells.
- Guidelines to reduce the residual stresses.

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ABSTRACT

The cost-effectiveness of Solid Oxide Cells production can be improved by introducing "multilayer-tape-casting" (MTC: sequential casting of the layers) and co-sintering of the half-cells. MTC additionally results in more homogeneous layers with strong interfaces. However, the thermal expansion coefficient (TEC) mismatch between the layers, cumulated from high temperature, induces significant residual stresses in the half-cells. Furthermore, it has been observed that MTC half-cells with 4 layers (MTC4: support, fuel electrode, electrolyte and barrier layer) are sometimes more fragile to handle than those with 3 layers (MTC3: without barrier layer). The bending strength of MTC3 and MTC4 under various loading orientations (electrolyte on the tensile or compressive side of the loading) is compared. The analysis, by taking residual stresses into account, shows that the strength of the half-cells with the electrolyte on the compressive side corresponds to the strength of the support. With the loading in the other direction (electrolyte on the tensile side), the origin of the failure is in a different layer for MTC3 (fuel electrode) and for MTC4 (barrier layer). In order to decrease the tensile residual stresses, especially in the outer barrier-layer, possible changes to the layer properties are discussed and some optimization guidelines proposed.

1. Introduction

Various processes can be used to produce solid oxide electrolysis cell and solid oxide fuel cell (SOCs) half-cells (Nickel Oxide – 3 mol % Yttrium Tetragonal Zirconia Polycristals: NiO-3TZP, Nickel Oxide – 8 mol% Yttrium Stabilized Zirconia: NiO-8YSZ, 8 mol% Yttrium Stabilized Zirconia: 8YSZ and in some cases an additional $Ce_{0.9}Gd_{0.1}O_{1.95}$ layer: CGO10). Among the classical processes for the component formation and sintering, some involve up to 6 or 7 steps to obtain the layered half-cells (see e.g. Ref. [1]) including for example: tape-casting of support (NiO-3TZP), spraying of fuel electrode (NiO-8YSZ), spraying of electrolyte (8YSZ), sintering at high temperature, spraying of barrier layer (CGO), sintering at a lower temperature.

Using multilayer tape-casting (MTC) reduces the number of steps to obtain the various half-cells to two steps including tape casting of the 3 or 4 layers (depending on the type of half-cell) together (NiO-3TZP, NiO-8YSZ, 8YSZ and eventual additional CGO) and co-sintering [2,3]. It may also lead to more homogeneous layers [2]. Minimizing the number of processing steps will reduce the cost significantly, and hence MTC constitutes a promising route to reduce the manufacturing costs of SOCs [4,5].

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The thermal expansion coefficients (TECs) of CGO, NiO-8YSZ and NiO-3TZP are similar (see Table 3). However, the 8YSZ layer has a significantly smaller TEC. Due to the mismatch between the TECs of the different layers, the multilayer samples are not in a stress-free state at room temperature before the mechanical tests. Some layers are already in strong tension and others in compression [3,6–8]. These high residual stresses (especially tensile residual stresses) can result in a SOC, which is more fragile in handling (smaller apparent strength), e.g. during stacking. Furthermore, we find in laboratory practice that half-cells with 4 layers are sometimes more fragile and delicate to handle that half-cells with 3 layers. This could also be attributed to a change in the residual stresses state.

The residual stresses in multilayers can be determined by a number of different ways. A direct measure of the strain can be done using high temperature strain gages [9] or X-ray diffraction [3,8–13]. It is also possible to determine the residual stresses by measuring the stress relaxation due to removal of material by hole drilling or focused ion beam or due to nano-indentation [9,14]. Another commonly used technique is to measure the curvature of the multilayer and to use the thermo-mechanical properties of the layers to get the differential strain and/or a theoretical reference temperature corresponding to a stress-free state [6,7,13,15–18]. Residual stresses and their impact on multilayer strength has already been studied on bi-layer SOC materials [6,8,13,15,19,20] showing that depending on the loaded layer, the residual stresses could effectively strengthen the layers under compressive residual stresses and weaken the layers under tensile residual stresses. The relationship between residual stresses and strength for MTC half-cells with 3 or 4 layers has however not yet been reported in literature.

The strength of the components can be measured in different ways leading to global or local tensile solicitation of the sample, such as uniaxial tensile testing [16,20] 4-point bending [21,22], ring-on-ring bending test [15,19] and ball-on-ring bending test [17,23,24]. The influence of the residual stresses can be quantified by tensile testing or conveniently by bending with the electrolyte on the tensile or compressive side and comparing the measured strength.

In this work, the strength of multilayer samples (3 and 4 layers) was tested by a biaxial flexure experiment (ball on ring [23]) under two loading directions: 1) with electrolyte on the tensile side (support on top) or 2) on the compressive side (support at the bottom). The sample failing strength and the origin of the failure were analyzed in each condition.

The influence of small changes in the properties of the layers on the residual stresses (especially in the additional CGO barrier layer in 4 layers half-cells) is then analyzed and discussed to arrive at suggestions on how to mitigate risk of failure by layer design.

2. Experimental

2.1. Sample preparation

We prepared two types of multilayer half-cells for this study. Both were prepared by "Multilayer-Tape Casting" (MTC: sequential casting of the layers in green state, see Fig. 1) and then co-sintered at ~1300 °C under a loading ceramic plate of 180 g to restrain the curvature from the sintering shrinkage mismatch [25]. The half-cells contained respectively three layers (MTC3: NiO-3TZP support, NiO-8YSZ fuel electrode and 8YSZ electrolyte) or four layers (MTC4: idem MTC3 with additional CGO10 barrier layer).

Table 1
Average geometrical properties of MTC layers based on micrographs of MTC3 and MTC4 cells.

Material	MTC3		MTC4	
	Thickness (μm)	Porosity (%)	Thickness (μm)	Porosity (%)
NiO-3TZP	328 ± 5	10 ± 2.5	321 ± 5	10 ± 2.5
NiO-8YSZ	13.9 ± 0.5	2 ± 1	12.9 ± 0.5	2 ± 1
YSZ	4.1 ± 0.25	0	8.7 ± 0.25	0
CGO10			6.3 ± 0.5	5 ± 1

Table 2
Material parameters for the composite sphere model (E_0 and ν_0 are the Young modulus and Poisson ratio at 0 porosity).

Material	E_0 (GPa)	b_E	ν_0	Error (%)	References
CGO10	200	1.016	0.33	±1.34	[43]
8YSZ	190	1.076	0.308	±1.12	[43]
NiO-8YSZ	209.5	0.46	0.32	±1.40	[44]
NiO-3TZP	217	1.0	0.333	±1.50	[17]

In each case, the cell total thickness was around 350 μm with small variations (±5 μm) of the layer thicknesses from sample to sample. The layers thickness and porosity were determined from micrographs of the samples (Fig. 2). The small thickness variation observed from sample to sample is assumed to be due to a thickness variation of the support. The average thickness and porosity of the individual layers are presented in Table 1.

The main difference between MTC3 and MTC4 samples is the addition of a CGO10 layer in MTC4 half-cells and the increased thickness of the YSZ layer in MTC4 half-cells. The average thicknesses and porosity of the fuel electrode (NiO-8YSZ) and support (NiO-3TZP) are comparable for both types of samples.

From each sintered half-cells, 25-30 discs of Ø 20 mm and 1 long strip of 100 × 5 mm^2 were cut by laser.

2.2. Measurement of curvature profile

As a result of the uneven expansion of the layers and consequent residual stresses, the multilayer samples are curved. The deflection of MTC3 and MTC4 cells has been measured with a profilometer Vantage 2 from Cyber Technologies on the long strips samples (100 × 5 mm) cut in the center of the half-cells.

2.3. Measure of strength by ball on ring

The Ball-on-Ring (BoR) set-up is used to determine the strength of ceramic materials under a bi-dimensional loading. The set-up has been described in Ref. [17]. It is a biaxial bending experiment composed of 3 main parts (Fig. 3): the ring of radius $R_r = 8$ mm, the sample disc of radius $R_d = 10$ mm and the flattened ball of radius $R_b = 2$ mm and of contact area radius $L_b = 1.79$ mm. With this configuration, the stressed area is far from the sample edge, thus avoiding the influence of cutting on the strength.

The BoR set-up (Fig. 3) was placed in an Instron machine (Model 1362) with a load cell of 250 Nm. The load was applied by a piston on the upper ball with a constant displacement rate of 0.2 mm/min.

For each type of half-cells, 50 to 60 samples were broken at room temperature: half of them with the support at the bottom (electrolyte on the compressive side of the loading in MTC3-sb and MTC4-sb) and the other half with the support on top (electrolyte on the tensile side of the loading in MTC3-st and MTC4-st).

3. Theory and calculation

3.1. Material parameters from literature

Material parameters of SOEC and SOFC (Solid Oxide Electrolysis and Fuel Cells) materials are widely reported [26]. Therefore, the