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Effect of spherical porosity on co-fired dense/porous zirconia bi-layers cambering

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ABSTRACT

Geometrical instability leading to cambering is recorded during co-sintering of zirconia dense/porous bi-layered planar structures. Sintering strain in the bi-layers rises mainly from mismatch between the different porosity volume fractions at the layers and their interface. In this paper, we analyze the model case of dense taped of 8 mol% Y_2O_3 -stabilized ZrO_2 laminated on *ca.* 400 μ thick 3 mol% Y_2O_3 doped zirconia porous tapes, with homogenous spherical porosity of 13 vol%, 46 vol%, and 54 vol%. Sintering stress during densification is evaluated from the shrinkage rates and viscoelastic behavior during sintering by thermo-mechanical analysis, using cyclic loading dilatometry. The camber development of the bi-layers is measured by *in-situ* optical dilatometry. In accordance with the model prediction, cambering can be controlled tuning the porosity while achieving a synergetic effect between densification and formation of open porosity at the bilayers.

1. Introduction

Planar design in solid oxide electrolysis cell (SOEC) and solid oxide fuel cell (SOFC) technologies is a widely chosen geometry because of its high-power density and low fabrication costs [1]. Multilayered structures are generally produced by conventional powder processing technologies, *e.g.* tape casting, screen printing, spray coating, lamination, and finally by co-firing to achieve consolidation [2,3]. However, co-firing of planar type fuel cells can have a critical effect on the final shape and integrity, sometimes resulting in shape distortion, cracks, and delamination [3–7]. In multilayered ceramics for SOFC and SOEC applications, material properties comprehension, such as stress and uniaxial viscosity, and the study of their development during the sintering process is essential for an optimal consolidation [8]. In co-fired ceramic structures, the sintering behavior is mainly controlled by the interfacial in-plane properties rather than the thickness properties. The interfaces at the different layers are sources of intense stresses that contribute to rather severe shape instabilities as cambering, curling and eventually to delamination [4]. Some sintering parameters, such as shrinkage rate of each material, viscosity, and curvature rate, in addition to microstructural properties, *i.e.* relative arrangement of ceramic particles and porosity, substantially affect the curvature evolution of the structure during co-firing [9]. These parameters can be also used to optimize the co-sintering. A fair prediction of shape evolution of the planar bilayers during sintering can be also carried out by different

models [10–17]. In particular, Cai's model prediction for sintering mismatch stress and camber development in bi-layered structure can be validated by *in-situ* monitoring of the laminates co-sintered [10,11].

One of the most common electrolyte materials in SOFC/SOEC technology is stabilized zirconia [18–20]. Ytria-stabilized zirconia is mainly used as dense electrolyte due to its high stability as pure oxygen ionic conductor at high temperatures [21]. Particularly, 8 mol% Y_2O_3 -stabilized ZrO_2 (8YSZ) is known for its fairly high oxygen ion conductivity at high temperature [11–13]. Zhao et al. reported of a LSF infiltrated 8YSZ cathode supported fuel cell produced by laminating three tape-casted ceramic green tapes, a highly porous thick support, a less porous thin interlayer and a dense thin film [22]. However, 3 mol% Y_2O_3 -stabilized ZrO_2 (3YSZ) has better mechanical properties, despite of its lower ionic conductivity, and for this reason it can be preferred as support or electrode material where a high porosity is needed since the electrocatalyst materials must be infiltrated. By contrast, 8YSZ is preferred as electrolyte material since the electrolyte mainly needs to have high ionic conductivity [23,24].

In order to optimize the time-consuming infiltration steps, a high porosity and a high pore volume are advantageous. Porosities around 50% are especially important for infiltration based electrode layers, which in SOFCs have high performances due to the large triple phase boundary [25,26]. Conversely, closed porosity is not desirable for these structures, since it cannot be infiltrated and the closed pores can still act as mechanical weak points [23]. Therefore, a compromise between

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strain and microstructure has to be achieved in bi-layered dense/porous structures.

In this work, three dense/porous bi-layered structures, obtained by laminating a dense and a porous layer with homogenous porosity of 13%, 46%, and 54% respectively, were investigated during sintering. Particularly, uniaxial viscosities of dense 8YSZ and porous 3YSZ layers were experimentally characterized by thermo-mechanical analysis (TMA) performing cyclic loading dilatometry [27,28]. Furthermore, during co-firing, the camber evolution of the three bi-layered structures was *in situ* monitored by means of optical dilatometry. The sintering mismatch stress of dense/porous bi-layered structures, influenced by the sintering shrinkage mismatch and the changing viscosity of individual ceramic layers, was calculated based on Cai's model for bi-layered laminates, as also reported in previous studies [10,11].

2. Experimental

2.1. Materials

Porous tapes of 3 mol% yttria stabilized zirconia (3YSZ, Tosoh, Japan) with final open porosity of 13%, 46% and 54%, and a dense tape of 8 mol% yttria stabilized zirconia (8YSZ, Tosoh, Japan), were manufactured by tape casting [29]. The formulation details of the tape casting slurries are reported elsewhere [15]. After drying, the thickness of each tape was around 200 μm . To obtain porous structures with highest possible pore volume/surface area ratio and with fewest possible notch-features (for the mechanical properties), spherical pore formers of PMMA were used. The fraction of porosity was evaluated from the bulk density (*i.e.*, the density including the volumes of the solid, open, and closed pores), which was measured with the mercury porosimeter in the low-pressure regime, where no mercury was intruded. By comparing the bulk density to the theoretical density of the solid, *i.e.* 3YSZ, a measure of the total porosity (open and closed) was obtained. The fraction of closed porosity was then deduced by subtracting the measured open porosity from the calculated total porosity. More details of measured open porosity, calculated closed porosity, and average pore size based on volume (d) are reported in Ref. [23]. Asymmetric bi-layered structures were fabricated by laminating porous 3YSZ and dense 8YSZ tapes; three laminated structures were finally obtained: 8YSZ/3YSZ_13%, 8YSZ/3YSZ_46%, and 8YSZ/3YSZ_54%. The total thickness for all three structures was around 400 μm .

2.2. Dilatometric measurement and samples characterization

Optical dilatometry (TOMMI; Fraunhofer Institut Silicatforschung ISC, Neunerplatz 2, D-97082 Würzburg, Germany) was used in this work for dilatometry characterization. This is a non-contact technique to investigate thermal processes [30] of tape-casted materials, specifically de-binding and sintering. For the samples used in this work the total shrinkage of the final ceramic bodies was in the range of 10% to 30%. This is usually accompanied by unpredictable changes of the planar shape and, depending on the amount of organic content, on the relative arrangement of the ceramic particles, porosity, etc. [3,21,9]. Optical dilatometry was carried out on two types of configurations, in terms of free sintering of individual layers and co-firing of bi-layers:

- "Bulky" samples: tight rolled and gently pressed tapes were used to measure the free sintering behavior of individual ceramic components [5].
- Asymmetric bi-layered laminates: 8YSZ tape was laminated with 3YSZ tapes, with porosity of 13%, 46%, and 54%, and cut into 20 mm x 5 mm rectangular samples. The thickness ratio between 8YSZ and 3YSZ was 1:1, the total thickness of each green bi-layered structure was $\sim 400 \mu\text{m}$. The bi-layered structures: 8YSZ/3YSZ_13%, 8YSZ/3YSZ_46%, and 8YSZ/3YSZ_54% were used to study the camber development during co-firing in a self-standing

configuration. All the samples analyzed in the optical dilatometer were fired continuously in air at a heating rate of $0.33 \text{ }^\circ\text{C min}^{-1}$ from room temperature to 500 $^\circ\text{C}$ and held for 4 h to ensure the burn out of all organics. Then the samples were sintered at a heating rate of $1 \text{ }^\circ\text{C min}^{-1}$ –1350 $^\circ\text{C}$ and kept for 2 h at 1350 $^\circ\text{C}$ [23]. Reported data refers only to the constant heating rate stage. The shrinkage and camber development for asymmetric bi-layered laminates were monitored *in situ* during the heating [5].

During the sintering, uniaxial viscosities of the porous and dense zirconia materials were estimated from cyclic loading dilatometry carried out by a thermo-mechanical analyzer (TMA 402 F1 Hyperion, Netzsch, Germany) on individual tape of ceramic material, as reported by Teocoli et al. [27,28].

After sintering at 1350 $^\circ\text{C}$ for 2 h, the microstructures of the three structures were determined using scanning electron microscopy (SEM; Hitachi TM1000, Tokyo, Japan) on mechanically polished cross sections.

2.3. Theoretical background

In an asymmetric bi-layered laminate, camber is frequently generated during co-firing due to the mismatch in sintering shrinkage of the individual materials. During co-firing, tensile stress is expected in the layers to lead to a higher densification rate. The stress distribution inside the bi-layered laminate is thus not uniform. Particularly, the tensile stress is expected to increase from the external of the layers to the interface of the asymmetric dense/porous laminates, and the stress can be only partially relaxed as the structure bends [21,22,9].

Densifying ceramic materials are modeled as a linear viscous continuum, except for the early stages of heating when the compacts are still elastic [31]. Due to the analogy between linear viscous and linear elastic deformation mechanisms [25,32], Cai et al. obtained the following equation for the normalized curvature rate \dot{k} [10,11]:

$$\dot{k} = \frac{d(h_p + h_d/r)}{dt} = \left[\frac{6(m+1)^2 mn}{m^4 n^2 + 2mn(2m^2 + 3m + 2) + 1} \right] \Delta \dot{\epsilon}, \quad (1)$$

where h_p and h_d are the thickness of the porous and dense layers, respectively; r is the radius of curvature; $m = h_p/h_d$ is the layer thickness ratio; n is the viscosity ratio between the layers and $\Delta \dot{\epsilon}$ is the strain rate difference between layers.

The maximum sintering mismatch stress, located at the interface of the asymmetric bi-layered laminates, can be calculated by [10,11]:

$$\sigma_{\max} = \left[\frac{m^2 n(4m + 3) + 1}{m^4 n^2 + 2mn(2m^2 + 3m + 2) + 1} \right] \hat{\sigma}, \quad (2)$$

in particular,

$$n = \frac{\eta_p/(1 - \nu_p)}{\eta_d/(1 - \nu_d)}, \quad (3)$$

where η_p and η_d are the uniaxial viscosity of the porous and dense layers, respectively; ν_p and ν_d are the viscous Poisson's ratio; $\hat{\sigma}$ is the nominal viscous mismatch stress, defined as $\hat{\sigma} = \Delta \dot{\epsilon} \cdot \eta_p$.

Moreover, using the normalized curvature rate \dot{k} , the nominal viscous mismatch stress can also be calculated by [10,11]:

$$\hat{\sigma} = \left[\frac{m^4 n^2 + 2mn(2m^2 + 3m + 2) + 1}{6(m+1)^2 mn} \right] \dot{k} \cdot \eta_p. \quad (4)$$

3. Results and discussion

3.1. Free sintering and viscoelastic characterization of individual layers

Green ceramic tapes were characterized by optical dilatometry under free-sintering conditions. Fig. 1a shows the shrinkage for dense

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