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Modeling kinetics of distortion in porous bi-layered structures

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Abstract

Shape distortions during constrained sintering experiment of bi-layer porous and dense cerium gadolinium oxide (CGO) structures have been modeled. Technologies like solid oxide fuel cells require co-firing thin layers with different green densities, which often exhibit differential shrinkage because of different sintering rates of the materials resulting in undesired distortions of the component. An analytical model based on the continuum theory of sintering has been developed to describe the kinetics of densification and distortion in the sintering processes. A new approach is used to extract the material parameters controlling shape distortion through optimizing the model to experimental data of free shrinkage strains. The significant influence of weight of the sample (gravity) on the kinetics of distortion is taken in to consideration. The modeling predictions indicate good agreement with the results of sintering of a bi-layered CGO system in terms of evolutions of bow, porosities and also layer thickness.

Keywords: Modeling; Sintering; Bi-layer; Distortion

1. Introduction

Discretely graded ceramic multi-layers are considered to be promising material structures due to their performances in the development of various energy efficient electromechanical systems.[1,2] These structures are often produced by laminating different porous layers and then sintering them together (co-firing). During co-firing of multi-layers, different densification rates can cause development of stresses leading to defects like cracks and macrostructural distortions.[3–11] Asymmetric arrangement of layers usually relaxes the mismatched stress evolutions by warping and hence creating instabilities in the shape of the component. For example in the case of planar solid oxide fuel cell (SOFC) technologies, the deformations in the shape of the components/cells reduce successful stack assembly, and thus it is not desired. Therefore there is a growing interest for understanding how the intrinsic material properties can affect the evolution of distortion in order to reduce the stress development and to allow components to be produced with the desired shape after co-firing. In this study, this is studied through a combination of sintering experiments and mechanical modeling.

The introduction of continuum mechanics with linear viscous material model for porous structures can be seen as an important development in addressing the problem of shape distortions during co-firing of ceramic layers.[12,13] Since then there have been a number of reported works that deal with distortions in bi-layer ceramic systems. One of these is the work by Lu et al.[14] in which the continuum model of sintering is used to describe the kinetics of densification and curvature evolution, taking the effect of particle coarsening and grain growth into consideration. Lu et al. also considered the impact of pore size on the densification behavior of each layer into account. From beam theory, the stress and strain distributions along the section of the layers are known to be linear, but in the model by Lu et al. a uniform strain distributions are assumed over each layer, which may affect the accuracy of the model.

Detailed work on experimental observation of processing defects and the corresponding viscoelastic stress computation for constrained densification of alumina/zirconia hybrid laminates has been published by Cai et al.[3–15] After measuring the viscous properties of the constituent layers using cyclic loading dilatometry, Cai et al. were able to model the bow evolution of

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bi-layers in good agreement with experimental results. Cai et al. however did not consider the evolution of thickness of each layer during densification, which is significant in the case of highly porous layers.[8,16]

The linear distribution of strains with the corresponding evolution of thicknesses in each layer has been considered in the model suggested by Kanters et al.[1] Kanters et al. reported a good agreement of the model prediction of curvature evolution for two types of bi-layer samples made from nanocrystalline yttria-stabilized zirconia with different thicknesses.

Kang et al.[4] used the models proposed by Cai et al. and Kanters et al. to study a bi-layered system of gadolinium-doped ceria and a cermet of nickel oxide in a backbone structure of yttria stabilized zirconia. In both cases, they found a good agreement of distortion evolutions with the measurements during the sintering. In a similar way, Ollagnier et al.[8] compared the models of Cai et al. and Kanters et al. on bi-layers of porous and dense low-temperature co-fired ceramics (LTCC) with different initial thickness ratios. Unlike Kang et al., they found a significant discrepancy between the model predictions and the measurements of camber for which anisotropy of sintering parameters, effects of gravity and heating rates were suggested as a cause. Ollagnier et al. also showed the influence of ratio of initial thicknesses of the bi-layered system on the amount of camber after the sintering. The importance of gravity is also suggested by Mücke et al.[2] after their experimental observations on SOFC samples prepared from 8YSZ. Mücke et al. compared curvature evolutions of two samples sintered in vertical and horizontal positions. They observed reduction in the camber development in the case of horizontally sintered sample in which the effect of gravity is significant.[2]

Modeling the mismatch stresses and curvature of bi-layered structures with the help of experimental characterization of the viscous properties of each layer using cyclic load dilatometry has also been reported by Chiang et al.[5] and Ravi and Green.[9]

Often experimental characterizations of the viscous behavior of each layer are used to model the curvature evolution during the sintering process. This requires another set of creep experiments to independently measure the viscous behaviors of individual layers.[3–10] In most of the works reported, techniques like cyclic loading[5,9] and sinter forging[4] are usually used. Cologna et al.[17] also proposed another technique, called vertical sintering, in which the sample is allowed to sinter vertically under the influence of its own gravity. A similar way of determining the viscosity of each layer by measuring the maximum deflection rate for beams of porous materials that are allowed to deform under their own weight or under applied loads was also suggested by Atkinson et al. and Lee et al.[18,19] Alternative to these experiments, the capabilities of proven modeling approaches, like the Skorohod Olevsky Viscous Sintering (SOVS) model,[12,13] could also be used together with one sintering experiment conducted simultaneously for individual layers and asymmetric bi-layer so as to study the kinetics of densification in the free layers and shape distortions in the bi-layer system.

The effect of differential shrinkage is explained very well to be the factor controlling distortion. But as the studies by Mücke et al. and Ollagnier et al. showed the weight of the sample (gravity) also affects the rate of distortion by being an additional factor generating creep in the porous layers. Thus with all the important contributions from the works cited, it is still necessary to modify the modeling approaches so as to improve the accuracy of the predictions while maintaining them simple. The work by Frandsen et al.[16] from which the basis for the modeling approach adopted in this study, is built on a viscous analogy of classical laminate theory, where the effect of weight of the sample (gravity) on the distortion is considered.

The objective of this study is to present an alternative way of obtaining material parameters that control shape distortion from a single dilatometry experiment so as to model kinetics of densification and distortion in the bi-layer system. Improved modeling approaches are used in such a way that the effect of weight of the sample on the distortion evolution is considered to be another stress generating factor in addition to the differential shrinkage. Also the thickness evolutions in each layer are considered through the effective densification of each layer in the thickness directions. The approach is applied to obtain the kinetics of shrinkage and bow development during the sintering of porous and dense cerium gadolinium oxide, $Ce_{0.9}Gd_{0.1}O_{1.95-d}$ (CGO) layers with the help of analytical methods implemented in Matlab.

2. Cosintering model

The analysis is made based on continuum theory of sintering, which describes the macrostructural behavior of a porous body during sintering. It relates the external load to the strain rate by nonlinear viscous constitutive relationship.[12,13] The continuum model for linear relationship between the equivalent stress and strain rates is given by:

$$\sigma_{ij} = 2\eta_0 \left[\varphi \dot{\varepsilon}_{ij} + \left(\psi - \frac{1}{3}\varphi \right) \dot{e}\delta_{ij} \right] + P_L \delta_{ij} \tag{1}$$

where η_0 is the shear viscosity of the fully dense materials, φ and ψ are the normalized shear and bulk viscosities, P_L is the effective driving potential for sintering or sintering stress, δ_{ij} the Kronecker delta and $\dot{\varepsilon}_{ij}$ and $\dot{e}$ are the total and bulk strain rates respectively related to the stress tensor σ_{ij}.[12,13] The normalized shear and bulk viscosities are considered to be functions of porosity or volume fractions of voids in the porous body, θ, see Eq. (2). The effective sintering stress is the product of normalized sintering stress and local sintering stress, which is a function of surface energy per unit area, α, and grain size, G, in the form shown by Eq. (3).

$$\varphi = (1-\theta)^2; \ \psi = \frac{2}{3}\frac{(1-\theta)^3}{\theta} \tag{2}$$

$$P_L = \frac{3\alpha}{2G}(1-\theta)^2 \tag{3}$$

The porosity evolution is related to the volumetric densification strain using the principle of mass conservation as[12]:

$$\dot{e} = \frac{\dot{\theta}}{1-\theta} \tag{4}$$