PREDICTION OF STRESSES GENERATED DURING SINTERING OF A CONSTRAINED THIN FILM

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ABSTRACT

Residual stresses generated during sintering of ceramic based fuel cell components can lead to cracking or delamination. Often the processing conditions are optimised by trial and error. An analytical plane stress model has been developed to describe the microstructural changes (e.g. density, grain size) that the individual ceramic layers undergo during constrained sintering. The model has been calibrated with sintering data for powders under free and constrained conditions. While the model accurately predicts the variation of relative density during sintering and the final average grain size, the predicted stresses are considerably higher than those measured experimentally. This discrepancy is interpreted in terms of the approximate relationships used to describe the variation of elastic properties with density and to calculate stress from curvature measurements.

INTRODUCTION

Planar solid oxide fuel cell (SOFC) membranes are generally made by a powder route. In a self-supported planar design [1], the 50 μm thick anode layer is first screen-printed onto a previously sintered 150 μm electrolyte and then sintered at about 1400°C. The 50 μm cathode layer is then screen-printed onto the other side of the electrolyte and sintered at about 1200°C. However, in the case of supported designs [2], where a thick porous ceramic support is used as the load bearing structure, ~30 μm anode and ~10 μm electrolyte are first screen-printed onto the support and then sintered together at about 1500°C. Thereafter, the ~40 μm cathode layer is printed over the electrolyte and then sintered at about 1100°C. In either of these designs, the electrodes are not free to shrink during sintering. Such constrained sintering occurs when either a layer is being sintered on a rigid support or when two or more layers having significantly mismatched densification rates are co-sintered. In self-supported design, only the electrodes experience in-plane constrained sintering while in the supported ones all the three layers undergo in-plane constrained sintering.
Constrained sintering can lead to micro-crack formation, interface delamination and permanent distortion of the positive-electrolyte-negative (PEN) structures [3, 4]. Currently, sintering conditions for the PEN structures are optimised by trial and error. This results in a long product development cycle and the material behaviour under different processing conditions cannot be predicted. Thus, it is important to devise a systematic constitutive based approach which can describe the microstructural changes (e.g. density, grain size) which the individual layers of the PEN structures undergo during sintering.

In the recent past several attempts have been made to experimentally measure and develop constitutive models to describe free and constrained sintering [5-11], most of which ignored the effect of initial density and grain size and their subsequent evolution during sintering thus the predictions were not realistic [7-9]. A mechanistic model presented by Cocks et. al. [12, 13] but based on that suggested by Besson et al. [5, 6] is used as the basis for this work. The formulation relies on two internal state variables related to the evolution of the microstructure during sintering, namely the average grain size and the mean relative density. Different equations control their evolution during the various stages of sintering.

The purpose of this paper is to develop an analytical plane stress sintering model which can accurately predict the evolution of relative density, average grain size and stress state under both free and constrained sintering conditions. To illustrate the predictive capability of the analytical plane-stress formulation before the ongoing sintering experiments on PEN structures are complete, the material parameters have been calibrated from the experimental observations reported by Choe et al. [14], who conducted a number of tests on free and constrained sintering of gold circuit paste, measuring the evolution of relative density with time and initial and final average grain size. This paper will show that their observed retardation in the densification kinetics cannot be explained on the basis of reported stress measurements.

SINTERING DATA

Choe et al. [14] made a 63 ± 2 μm thick DuPont gold circuit paste film on a 0.5 mm-thick 6 mm by 6 mm square alumina substrate by multiple screen-printing. A portion of the film was then peeled off forming a free standing film leaving the remaining portion to be sintered under constrained condition. For stress measurement, a 25 μm gold film was applied on a 25 μm Si substrate. Exact details of the experimental procedure and measurement technique is given elsewhere [14]. The in-situ curvature measurements during constrained sintering were carried out at 750°C.
The driving force for sintering is the decrease in surface area and hence overall surface energy of the system. Sintering rate thus depends on initial particle size (the smaller the particles the higher the sintering rate), initial packing density (denser packing implies greater contact area and hence faster sintering), sintering temperature (higher temperature means lower required activation energy for deformation and hence faster sintering rate) and surface energy of the particles (higher surface energy results in higher sintering rates). Table 1 gives the main features of various stages of sintering [15].

Two internal state or microstructural variables describe the sintering behaviour of the ceramic: the relative density (\(\rho\)) and average grain size (\(L\)). The constitutive formulation can be expressed in terms of the total strain rate component, \(\dot{\varepsilon}_{ij}\), as given in Eq.1, where \(\dot{\varepsilon}_{ij}^e = \dot{\varepsilon}_{ij}^e(\sigma, \rho, L)\) is the inelastic strain rate component and \(\dot{\varepsilon}_{ij}^p = C_{ijkl}\dot{\sigma}_{kl}\) the elastic strain rate component (\(\dot{\sigma}_{kl}\) denotes the stress rate component and \(C_{ijkl}\) the compliance coefficients of the material). The flow rule is given by Eq.2 [6].

\[
\dot{\varepsilon}_{ij} = \dot{\varepsilon}_{ij}^e + \dot{\varepsilon}_{ij}^p \tag{1}
\]

\[
\dot{\varepsilon}_{ij}^e = \frac{\dot{\varepsilon}_{ij}^e}{\sigma_o} \left( \frac{L_o}{L} \right)^z \left[ \frac{1}{2} \hat{c}(\rho) \delta_{ij} + 3\hat{f}(\rho)(\sigma_m - \sigma_o) \delta_{ij} \right] \tag{2}
\]

\(\dot{\varepsilon}_{ij}^e\) is the equivalent creep rate of the material under a stress \(\sigma_o\) (defined by the ratio of surface energy \(\gamma\) to the initial average grain size \(L_o\)) for a fully dense material of average grain size \(L_o\), \(\delta_{ij}\) are the deviatoric stress components, \(\delta_{ij}\) is the Kroneker delta, \(\sigma_m\) is the mean normal stress (\(\sigma_m = 1/3\sigma_{kk}\)), \(z\) is a material constant reflecting the sensitivity of deformation response to grain size and \(\hat{c}(\rho)\) and \(\hat{f}(\rho)\) are dimensionless empirical functions of the relative density, \(\rho\). In the limiting case for \(\rho = 1\), \(\hat{c}(\rho) = 1\) and \(\hat{f}(\rho) = 0\). The sintering potential, \(\sigma_s\), is either set to \(2\gamma/L\) for all the stages of sintering [9] or defined as a function of the relative density \(\rho\) and the grain size \(L\) as given in Eq.3(a-c) [16] for the different stages of sintering. The evolutionary equations for the internal variables \(\rho\) and \(L\) are needed to complete the formulation. Both are functions of relative density, stress state, grain size and temperature (Eq.4). Precise forms for the functions \(\hat{c}(\rho)\), \(\hat{f}(\rho)\), and the evolutionary equations for different stages of sintering can be found in [12, 13].
Table 1. Various stages of sintering and its main features.

| Stage  | ρ Range             | Variables ρ and L | Remarks                      |
|--------|---------------------|-------------------|------------------------------|
| Stage 1a | < 0.6              | ρ > 0; L = 0      | Interconnected pores         |
| Stage 1b | 0.6 ≤ ρ ≤ 0.95     | ρ > 0; L > 0      | Interconnected pores         |
| Stage 2  | 0.95 ≤ ρ ≤ 1       | ρ > 0; L > 0      | Pores pinch-off              |
| Stage 3  | ρ = 1               | ρ = 0; L > 0      | Pores isolated within grains |

\[ \sigma_s = \frac{6\gamma \rho}{L} \left( \frac{2\rho - \rho_0}{1 - \rho_0} \right) \] for stages 1a and 1b of sintering

\[ \sigma_s = \frac{4\gamma}{L} \left( \frac{1 - \rho}{6} \right)^{-\frac{1}{3}} \] for stage 2 of sintering

\[ \sigma_s = 0 \] for stage 3 of sintering

\[ \dot{\rho} = \dot{\bar{\rho}}(\rho, \bar{\sigma}, L, T) \]

\[ \dot{L} = \dot{L}(\rho, \bar{\sigma}, L, T) \]
MODELLING CONSTRAINED SINTERING

The above constitutive model can be used to describe the sintering behaviour of a ceramic porous green film (Layer 1 in Fig.1) on a rigid substrate. During the sintering process, the porous layer is constrained from shrinking freely on its plane. The material densifies only by shrinkage normal to the substrate which in turn produces in-plane stresses in the film.

As shown in Fig.1, during free sintering the film shrinks at the same rate in all the three directions hence the strains are equal. This will produce stress-free film. However, during sintering of a film (Layer 1 in Fig.1) on a rigid support (Layer 2 in Fig.1), the shrinkage occurs only in the direction normal to the X1X2 plane, i.e. \( \dot{e}_{11} = \dot{e}_{22} = 0, \dot{e}_{33} \neq 0 \). Furthermore, due to thin nature of the film the shear strain rate components as well as the out of plane stress are all assumed to be zero.

For the above constrained sintering condition, Eq.1 can be expressed as in Eq.5. Here, \( E_p \) and \( v_p \) are the elastic modulus and Poisson’s ratio of the porous sintering material, respectively. For an isotropic film sintering under in-plane constrained conditions, \( \sigma_{11} = \sigma_{22} \) and \( \sigma_{33} = 0 \), and the equivalent stress becomes, \( \sigma = \sigma_{11} = \sigma_{22} \) and the mean hydrostatic stress, \( \sigma_m \), is as given in Eq.6.

\[
\dot{e}_{ij} = \frac{1+v_p}{E_p} \sigma_{ij} - \frac{v_p}{E_p} \sigma_j \delta_{ij} + \dot{e}_i^c
\]  

\[
\sigma_m = \frac{2}{3} \sigma
\]

Note that for free sintering, all \( \sigma_{ij} = 0 \) hence \( \dot{e}_{ij} = \dot{e}_i^c \) and the sintering potential \( \sigma_s \) will constitute the only driving force.

RESULTS AND DISCUSSION

The material parameters for the model described above were calibrated from the free sintering data of gold circuit paste at 750°C [14]. The values are given in Table 2.
Table 2. Value of various material parameters calibrated from Choe et al.'s [14] experimental free sintering data when the sintering potential is defined by Eq.3.

| $\rho_0$ | $L_0$ | $\gamma$ | $\dot{\varepsilon}_0$ | $\dot{L}_0$ | $\sigma_0 = \sqrt{\frac{\rho}{L_0}}$ |
|---------|--------|---------|----------------------|-------------|-----------------------------|
| 0.32    | 2      | 1.39    | 2.5                  | 1.8         | 0.7                         |

Assuming that the dominant creep mechanism remains essentially the same during both free and constrained sintering, constrained sintering behaviour can then be predicted using Table 2 parameters. The predicted evolutionary curves for relative density and average grain size during free and constrained sintering of gold circuit paste are shown in Fig.2a and 2b. A comparison between the predicted and the measured variation of relative density during the course of the sintering experiment are also shown in Fig.2a. Clearly there is reasonably good agreement between the model prediction and the experimental data. It can be seen that there is about 15% decrease in relative density during constrained sintering (Fig.2a). Choe et al [14] did not measure the variation of average grain size during sintering but visually compared the microstructures of final grain size for free and constrained sintered samples at different temperatures than 750°C to conclude that the grain sizes were nearly identical. Our model predicts the final average grain size after sintering at 750°C to be 8 $\mu$m after free sintering and 6 $\mu$m when sintered under constrained conditions (Fig.2b). Such a small difference in grain size would indeed be difficult to resolve through comparison of SEM micrographs and can be assumed to be nearly the same.

$$\sigma = \left[ \frac{kE_2d_2}{6(1-v^2)d_0} \right] \left[ \rho \left( \frac{d_2\rho}{d_2\rho + d_0\rho_0} \right) \right] \left[ \rho \right]^{\frac{2}{3}}$$  \hspace{1cm} (7)

Figure 3a shows a comparison between the equivalent stress (for plane stress condition in-plane stress is equal to equivalent stress) predicted by the model and those calculated from in-situ curvature measurement on a constrained sample during sintering at 750°C. As previously discussed, no stresses are induced during free sintering and this is shown in Fig.3a. However, it can be seen that while the predicted and the measured in-plane stresses for constrained sintering exhibit similar trends, their values are significantly different. The main reason for this discrepancy is the way Choe et al. [14] convert their curvature measurements into stress values. In their work, a modified Stoney formula (see Eq.7) was used to estimate the in-plane stresses. Stoney's formula was developed for a film which is much thinner than the substrate. Even though Choe et al. [14] modified it to take into account the fact that the film and the substrate are of the same thickness, their
The maximum in-plane stress measured by Choe et al. [14] develops after ~15 minutes of sintering whereas the model predicts such peak to occur only after 4 minutes. Since the in-plane stresses develop due to the sintering layer not being allowed to shrink by the rigid substrate, the maximum stress would be expected when the densification rate (\(\dot{\rho}\)) as in Eq.4) is maximum. Furthermore, as elastic properties depend on the density of the layer, one would expect the peak in-plane stress to develop when the combination of density and densification rates is maximum. A sensitivity study is underway to further investigate this discrepancy.

Use of an over simplified relationship to estimate the in-plane stresses during constrained sintering would explain the low level of stresses reported by Choe et al. [14] which, by their own admittance, are not large enough to explain the observed tenfold rate-retardation in the film. Thus, our predicted maximum equivalent tensile stress in the constrained film sintered at 750°C of about 2.6 MPa is more realistic. However, plane stress condition implies this value should be an upper limit. Further, the analysis shows that the stresses are very sensitive to elastic properties and a different relationship to describe the variation of stiffness and Poisson's ratio with density may lead to different numerical values. It is important to note that the variation of in-plane stress with sintering time is similar to that of the sintering potential (Fig.3b). This should be expected since the sintering potential physically is the apparent stress for sintering and is compressive in nature, whereas the constrained sintering stress opposes the sintering potential and is hence tensile. Once the sintering stress become equal to the sintering potential, densification stops and stress relaxation is possible thereafter only through shear densification. Thus, the higher the sintering potential, the higher the sintering stress induced by the process will be. The constrained sintering stress, however, can never exceed the sintering potential unless there is an externally applied pressure.

From the above discussion, it is clear that with adequate data (i.e. relative density and grain size evolution with sintering time), this model can easily be extended to predict stresses in each of the PEN layers during sintering for both self-supported and supported designs. An extension of this work to predict the stresses in two-layered systems where both layers are sintering at different densification rate will be presented elsewhere [17].

CONCLUSIONS

In this work, it has been shown that a constitutive modelling approach can be used to accurately predict the evolution of microstructural parameters, such as relative density and grain size, during sintering of PEN components for SOFCs. The difference in the values of predicted and measured in-plane stresses was interpreted in terms of the possible
limitations of the relationship used to convert measured curvature data into stress. It could also be the result of the way the evolution of the elastic modulus with relative density is defined in this model. The stresses predicted by the model can explain the tenfold densification rate-retardation observed experimentally.

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Free Sintering
\[ \varepsilon_{(1,1)} = \varepsilon_{(2,2)} = \varepsilon_{(3,3)} \]

Fully Constrained Sintering
\[ \varepsilon_{(1,1)} = \varepsilon_{(2,2)} = 0, \quad \varepsilon_{(3,3)} \neq 0 \]
\[ \varepsilon_{(1,1)} = \varepsilon_{(2,2)} = \varepsilon_{(3,3)} = 0 \]

Fig. 1 Schematic diagram showing different types of sintering conditions.

Fig. 2 Variation of (a) relative density and (b) average grain size during sintering. Experimentally measured relative density data for 750°C is shown for comparison.
Fig. 3 Variation of (a) the equivalent stress and (b) the sintering potential during sintering. Calculated in-plane stress data from curvature measurements for constrained sintering at 750°C is also shown in (a) for comparison.

LIST OF SYMBOLS

\( T \) = temperature
\( L_0 \) = initial grain size
\( \dot{L}_0 \) = initial grain size rate
\( \rho_0 \) = initial relative density
\( \dot{\rho}_0 \) = initial relative density rate
\( \dot{\varepsilon}_{ij} \) = strain rate component
\( \dot{\varepsilon}^e_{ij} \) = inelastic strain rate component
\( \dot{\varepsilon}^c_{ij} \) = Equivalent creep strain rate at \( \sigma_0 \)
\( \bar{\sigma} \) = equivalent stress
\( \sigma_m \) = mean triaxial stress
\( \delta_{ij} \) = Kroneker delta
\( \nu_p \) = Poisson's ratio of porous material
\( \nu_2 \) = Poisson's ratio of layer 2
\( d_0 \) = initial thickness of layer 1
\( c(\rho) \) and \( f(\rho) \) are functions of \( \rho \)

\( L \) = average grain size
\( \dot{L} \) = grain size rate
\( \rho \) = relative density at time \( t \)
\( \dot{\rho} \) = relative density rate
\( \dot{\varepsilon}^e \) = elastic strain rate component
\( \varepsilon^c_{kk} \) = volumetric creep strain
\( \sigma_0 \) = stress = \( \gamma/L_0 \)
\( \sigma_s \) = sintering potential or sintering pressure
\( S_{ij} \) = deviatoric stress
\( E_p \) = stiffness of porous material
\( E_2 \) = Young's modulus of layer 2
\( d_2 \) = thickness of layer 2
\( \kappa \) = curvature of bilayer 1 and 2
\( \gamma \) = surface energy