Modeling the evolution of stress due to differential shrinkage in powder-processed functionally graded metal–ceramic composites during pressureless sintering

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Abstract

Pressureless sintering of powder-processed functionally graded materials is being pursued to economically produce metal–ceramic composites for a variety of high-temperature (e.g., thermal protection) and energy-absorbing (e.g., armor) applications. During sintering, differential shrinkage induces stresses that can compromise the integrity of the components. Because the strength evolves as the component is sintered, it is important to model how the evolution of the differential shrinkage governs the stress distribution in the component in order to determine when the strength will be exceeded and cracking initiated. In this investigation, a model is proposed that describes the processing/microstructure/property/performance relationship in pressurelessly sintered functionally graded plates and rods. This model can be used to determine appropriate shrinkage rates and gradient architectures for a given component geometry that will prevent the component from cracking during pressureless sintering by balancing the evolution of strength, which is assumed to be a power law function of the porosity, with the evolution of stress. To develop this model, the powder mixture is considered as a three-phase material consisting of voids, metal particles, and ceramic particles. A micromechanical thermal elastic–viscoplastic constitutive model is then proposed to describe the thermomechanical behavior of the composite microstructure. The subsequent evolution of the thermomechanical properties of the matrix material during sintering is assumed to obey a power law relationship with the level of porosity, which is directly related to the shrinkage strain, and was refined to account for the evolving interparticle cohesion of the matrix phase due to sintering. These thermomechanical properties are incorporated into a 2-D thermomechanical finite element analysis to predict the stress distributions and distortions that arise from the evolution of differential shrinkage during the pressureless sintering process. Differential shrinkage results were verified quantitatively through comparison with the shape profile for a pressurelessly sintered functionally graded nickel–alumina composite plate with a cylindrical geometry, and the stress distribution results verified from qualitative observations of the absence or presence of cracking as well as the location in specimens with different gradient architectures. The cracking was mitigated using a reverse gradient at one end of the specimen, and the resulting distortions associated with the shape profile were determined to be no more than 15% reduced from the predictions. The effects of geometry were also studied out-of-plane by transforming the plate into a rod through an increase in thickness, while in-plane effects were studied by comparing the results from the cylindrical specimen with a specimen that has a square

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cross-sectional geometry. By transforming from a plate to a rod geometry, the stress no longer exceeds critical levels and cracks do not form. The results from the in-plane geometric study indicated that critical stresses were reached in the square geometry at temperatures 100 °C less than in the cylindrical geometry. Additionally, the location of primary cracking was shifted towards the metal-rich end of the specimen, while the stress distribution associated with this shift and the lower temperature for the critical stress resulted in secondary cracking.

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### 1. Introduction

Pressureless sintering is being used to fabricate powder-processed functionally graded metal–ceramic composites for high-temperature (e.g., thermal protection) and energy-absorbing (e.g., armor) applications (Chin, 1999). The components that are manufactured using this process can have complex geometries and gradient architectures. However, differences in the shrinkage of the powder mixtures often result in large stresses developing during the sintering process that can compromise the structural integrity of the component before the fully-sintered strength is achieved. However, the induced level of shrinkage stress depends directly on the level of differential shrinkage. The effects of various levels of differential shrinkage on the shrinkage stresses that develop in homogeneous WC–Co cylindrical specimen have been previously analyzed using finite element methods with experimental verifications of the sintered displacements (Gasik and Zhang, 2000). Exponential functions were used for mechanical properties, such as Young’s modulus and viscosity. The evolution of shrinkage stresses in functionally graded materials (FGMs) during the sintering process has also been investigated, based on a simple rule of mixtures for estimating material properties (Pines and Bruck, 2006). The sintering stresses for graded multilayer structures have been analyzed using plate theory, and a power law function for the density effect on the Young’s modulus (Shinagawa, 2003). All of these analyses are based on thermal elastic–viscoplastic analyses that assume the properties and the constitutive relations are functions of the mixture viscosity.

Attempts have been made to obviate the need for these analyses by reducing the level of differential shrinkage through the matching of shrinkage rates for the composites that are used in the gradient architecture (Watanabe, 1995; Winter et al., 2000). However, it is not possible to achieve perfect matching, so an optimum gradient architecture that reduces the level of differential shrinkage and minimizes the evaluated shrinkage stresses must still be predicted using an appropriate analysis. Therefore, it is necessary to develop appropriate models for predicting the evolution of stresses due to differential shrinkage in powder-processed functionally graded metal–ceramic composites during pressureless sintering in order to determine appropriate shrinkage rates and gradient architectures for a given component geometry to prevent cracks from initiating during the sintering process.

An important factor when analyzing the sintering behavior of functionally graded metal–ceramic composites is the accurate prediction of the change in thermomechanical properties and shrinkage at each temperature. The shrinkage is due to the decrease in pore volume and porosity with increasing time and temperature, while the thermomechanical properties are affected by the change in porosity as well as an increasing level of particle cohesion as the interfaces between particles are consumed. Thus, it has been a common practice to treat the effects of sintering on the thermomechanical properties of metal–ceramic composites by considering the thermomechanical properties to be a function of the relative density (Gasik and Zhang, 2000; Zhang and Gasik, 2002; Shinagawa, 2003; Moon, 1989; German, 1996).

In this research effort, a 2-D finite element analysis using a micromechanical thermal elastic–viscoplastic constitutive model has been developed to predict the evolution of stresses due to differential shrinkage and the corresponding final shape of plate and rod structures fabricated from functionally graded metal–ceramic composites. A similar analysis has been previously developed and experimentally verified for plasma-sprayed functionally graded coatings (Kesler et al., 1997). Nickel and alumina are used in the analysis as model materials because of the extensive thermomechanical characterization that has already been performed on them for
the development of thermal residual stress models for functionally graded metal–ceramic composites (Kesler et al., 1997; Bruck and Rabin, 1999; Williamson et al., 1993a; Rabin and Williamson, 1993). The powder mixture is considered as a three-phase material consisting of voids, metal particles, and ceramic particles. The shrinkage strains of the powder mixtures are directly related to the change in the level of porosity in the mixture. This change is then used to determine the evolution of the thermal elastic–viscoplastic constitutive behavior of the material. These thermomechanical properties are incorporated into a 2-D thermomechanical finite element analysis to predict the stresses that arise due to the evolution of differential shrinkage during the pressureless sintering process. In the model, the graded composite is divided into three regions: (1) a region near the pure metal considered to be a metal matrix with ceramic particles, (2) a region near the pure ceramic that is treated as a ceramic matrix with metal particles, and (3) regions of pure metal or pure ceramic. For the first two regions, a microscopic analysis is used. Conversely, the pure metal and ceramic regions are homogeneous, so a macroscopic analysis is used for the stress evolution of these regions. The model is used to predict the stresses that evolve during sintering in two different cross-sectional geometries: one square and one circular. The circular cross-sections were analyzed using a 2-D axisymmetric analysis, while the square cross-sections were analyzed using a 2-D plane strain analysis that has been found to closely approximate the exact solution associated with the 3-D geometry (Bruck and Gershon, 2002). To verify the model, the presence or absence of cracks and the final specimen profile due to differential shrinkage are directly compared with experiments from pressurelessly sintered functionally graded nickel–alumina plates with square and circular cross-sectional geometries.

2. Thermal elastic–viscoplastic constitutive model for powder mixtures

To develop the differential shrinkage model, a thermal elastic–viscoplastic constitutive equation for a particle-reinforced composite that accounts for the effects of micromechanical thermal stresses is employed (Asakawa et al., 1994; Noda et al., 1998). Since shrinkage is introduced during the sintering process, its effects on the total strain must be included in the original constitutive equation. The model assumes that the composite is macroscopically isotropic, consisting of brittle ceramic and ductile metal particles that are mixed to fabricate the functionally graded structure. In the composite system, the metal particles undergo elastoplastic deformations, while the ceramic particles deform elastically. Porosity is represented by the void volume fraction, with the change in porosity being directly related to the shrinkage. The porosity content in the green (before sintering) compacted structure is high, and exists in-between matrix particles and between the matrix particles and the reinforcement particles, as seen in Fig. 1. During the sintering process, diffusion between particles forms solid bonds that reduce the surface energy by reducing the interfacial area. With extended heating, the pore volume and porosity are further reduced as the matrix particles sinter between themselves and around the reinforcement particles, leading to isotropic shrinkage as shown in Fig. 1. During the sintering process, microstresses evolve due to the shrinkage of the matrix that can cause plastic deformation of ductile reinforcement particles or of a ductile matrix that further reduces porosity.
The current porosity during sintering, \( P \), is defined as the difference between the current density of the material, \( \rho \), and the theoretical maximum density, \( \rho_{\text{TMD}} \), divided by the theoretical maximum density. This relationship can be expressed as follows:

\[
P = \frac{\rho_{\text{TMD}} - \rho}{\rho_{\text{TMD}}}
\]  
(1)

For a homogeneous mass, \( m \), Eq. (1) can be rewritten in terms of the mass and associated volume, \( V \), as follows:

\[
P = 1 - \frac{m}{V \rho_{\text{TMD}}}
\]  
(2)

For a sintered material experiencing isotropic shrinkage, \( e_s \), the current volume can be represented as a function of the shrinkage and the original volume, \( V_o \), as follows:

\[
V = V_o \left(1 - e_s \right)^3
\]  
(3)

The mass can be expressed in terms of the initial porosity, \( P_0 \), the original volume, and the theoretical maximum density as follows:

\[
m = (1 - P_0) V_o \rho_{\text{TMD}}
\]  
(4)

Substituting Eqs. (3) and (4) into Eq. (2) yields the following expression which relates the level of porosity to the shrinkage:

\[
P = 1 - \frac{(1 - P_0)}{(1 - e_s)^3}
\]  
(5)

In general, the shrinkage strain, \( e_s \), varies with the temperature and matrix volume fraction, as well as particle size (Winter, 1999; Pines and Bruck, 2006a). The time-dependence of shrinkage for the matrix phase can be described using a Weibull power law time-dependent exponential equation, consistent with the Kolmogorov–Johnson–Mehl–Avrami kinetic theory of nucleation and growth, as follows (Pines and Bruck, 2006b):

\[
e_s(t, T(t)) = c_0 \left(1 - e^{-c_1 T(t)}\right)
\]  
(6a)

where the power law exponent, \( n \), also obeys a power law thermally-dependent exponential relationship as follows:

\[
n(T) = c_2 \left(1 - e^{-c_3 T^p}\right)
\]  
(6b)

In these equations, coefficients \( c_0, c_1, c_2, c_3 \), and exponent \( p \) are determined experimentally from a specimen composed of the pure matrix phase, and will depend on the particle size used for the matrix phase. The volume fraction of the matrix phase can then be used to determine the relative amount of shrinkage for the sintered composites. However, it has been determined that imperfect mixing in the composites will reduce the level of shrinkage by reducing the amount of matrix material that sinters. This reduction can be determined from the final porosity of the sintered composites (Pines and Bruck, 2006a). Therefore, the time-dependence of shrinkage for the composites, \( e_s^c(t) \), is determined as follows:

\[
e_s^c(t) = \frac{v_m v_s e_s^m(t)}{v_{\text{pure}}}
\]  
(7)

where \( v_m \) is the final volume fraction of the matrix phase in the composite, \( v_s \) is the volume fraction of the matrix phase that sinters in the composite, \( v_{\text{pure}} \) is the final volume fraction for the pure matrix material (i.e., \( 1 - P \)), and \( e_s^m(t) \) is the shrinkage of the matrix phase.

Since shrinkage is the result of a diffusional process, it is natural to incorporate other diffusional processes, such as stress-dependent creep, with the shrinkage relation given in Eq. (6) into a total time-dependent thermoplastic strain vector, \( \varepsilon_\tau^T(t, \sigma_k(t), T(t)) \), for the matrix material, as follows:

\[
\varepsilon_\tau^T(t, \sigma_k(t), T(t)) = \varepsilon_s(t, T(t)) \delta_i + \int_0^T n_{ik}^{-1}(T(\tau)) \sigma_k(\tau) \, d\tau \quad (i, k = 1, 6)
\]  
(8)
where \( \sigma_k(t) = (\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{12}, \sigma_{13}, \sigma_{23}) \) is the stress vector, \( \delta_k = (1, 1, 1, 0, 0, 0) \), and \( \eta_{ij} \) is the temperature- and porosity-dependent viscosity tensor determined from the following relation (Gasik and Zhang, 2000; Zhang and Gasik, 2002; Shinagawa, 2003):

\[
\eta_{ij}(P) = 3\eta(1 - P)^4 \begin{bmatrix}
(6.25P)^{-1} + 0.444 & (6.25P)^{-1} - 0.222 & (6.25P)^{-1} - 0.222 \\
(6.25P)^{-1} - 0.222 & (6.25P)^{-1} + 0.444 & (6.25P)^{-1} - 0.222 \\
(6.25P)^{-1} - 0.222 & (6.25P)^{-1} - 0.222 & (6.25P)^{-1} + 0.444 \\
0.333 & 0.333 & 0.333
\end{bmatrix}
\]

\( \eta(T) = c_1 d^3 T \exp(c_2/T) \)  

\( d(t)^3 = d_o^3 + \int_0^t c_3 \exp(c_4/T(\tau)) d\tau \)  

Eqs. (9a)–(9c) are phenomenological relations where \( c_1, c_2, c_3, \) and \( c_4 \) are constants that have been previously determined from experiments on a metal and ceramic system similar to the one used in this investigation, and \( d \) is the grain size. The values for these constants that were used in this investigation are shown in Table 1. Micrographs of the grain growth observed for the nickel used in this investigation can be seen in Fig. 2, and for pure alumina, 60 vol.% Ni, and 80 vol.% Ni sintered at 1350 °C with a 4 h hold in Fig. 3. The grain structure starts evolving from the 3 μm nickel particles and 0.4 μm alumina particles, and is on the order of 100 μm in the pure nickel and 5 μm in the alumina at the end of the sintering process. It is important to note that for this grain size of alumina, the effect of viscosity on the stress state is negligible, while for nickel the viscosity is at least 2 orders of magnitude less than alumina and has a more significant effect on the stress state and deformations at elevated temperatures (Rabin et al., 1998; Williamson et al., 1995). The presence of alumina particles in the nickel matrix will also reduce the grain size to around 10 μm and significantly reduce the effects of viscosity in the nickel-rich composites. The change in the porosity is also clearly evident in the micrographs, and is directly related to the shrinkage and the initial porosity through Eq. (5). The time-dependent effects on \( \eta_{ij} \) in Eq. (8) are determined by the thermal profiles, \( T(t) \), used for sintering. In matrix form, the thermoplastic strain vector can be written:

\[
[e^T_p(t, \sigma_k(t), T(t))]_{ij} = \begin{bmatrix}
[e^T_p]_1 & [e^T_p]_4 & [e^T_p]_5 \\
[e^T_p]_4 & [e^T_p]_2 & [e^T_p]_6 \\
[e^T_p]_5 & [e^T_p]_6 & [e^T_p]_3
\end{bmatrix}
\]

If the metal undergoes elastoplastic deformation in the metal matrix composites, the equivalent shear modulus and Poisson’s ratio, \( \mu'_0 \) and \( \nu'_0 \), must be introduced in the constitutive equation instead of \( \mu_0 \) and \( \nu_0 \):

\[
\mu'_0 = \frac{\mu_0}{1 + 3 \frac{\mu_0}{E}} \quad \nu'_0 = \frac{\nu_0 + \frac{3}{2} \frac{\mu_0}{E} (1 + \nu_0)}{1 + 2 \frac{\mu_0}{E} (1 + \nu_0)}
\]

<table>
<thead>
<tr>
<th>Constant</th>
<th>Nickel</th>
<th>Alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_1 )</td>
<td>3e15 Pa/K m³</td>
<td>8e14 Pa/K m³</td>
</tr>
<tr>
<td>( c_2 )</td>
<td>20000 K</td>
<td>45000 K</td>
</tr>
<tr>
<td>( c_3 )</td>
<td>1e−8 m³/s</td>
<td>1e−12 m³/s</td>
</tr>
<tr>
<td>( c_4 )</td>
<td>−30000 K</td>
<td>−30000 K</td>
</tr>
</tbody>
</table>

Table 1  
Constants for viscosity phenomenological relations
where $H'$ is the work hardening ratio of the matrix. When the matrix undergoes elastic–viscoplastic deformation, the thermal elastic–viscoplastic constitutive equation taking into consideration the temperature change can be written as (Shabana and Noda, 2001; Williamson et al., 1993b):

$$
d_{kk} = \frac{1}{3k_0(1 - \bar{\nu})A_h} \left[ \left\{ (k_1 - k_0)\bar{\nu} + k_0 \right\} \left\{ (1 - \bar{\nu})(1 - f_p - f_v) + (1 - \bar{\nu})f_p k_0 \right\} d\sigma_{kk} \\
+ \left\{ \alpha_0 - \frac{k_1 f_p}{A_h} (\alpha_0 - \alpha_1) \right\} 3dT + d[\sigma_p^{kk}] \right)
$$

and

$$
d_{ij}' = \frac{1}{2\mu_0(1 - v^* A_d} \left[ \{ (\mu_1 - \mu_0)v^* + \mu_0 \} \{ (1 - v^*)(1 - f_p - f_v) + (1 - v^*)f_p \mu_0 \} d\sigma_{ij}' + d[\sigma_p^{ij}] \right] \\
- \frac{\delta_{ij}}{3} d[\sigma_p^{kk}] 
$$

where

$$
A_h = (1 - f_p - f_v)\{ k_0 + (k_1 - k_0)\bar{\nu} \} + f_p k_1 \\
A_d = (1 - f_p - f_v)\{ \mu_0 + (\mu_1 - \mu_0)v^* \} + f_p \mu_1
$$

$d_{kk}$, $d_{ij}'$, $d\sigma_{kk}$ and $d\sigma_{ij}'$ are the hydrostatic and deviatoric components of incremental macroscopic strain and stress, respectively, $d\varepsilon$ is the incremental shrinkage, $dT$ is the incremental temperature change, $\alpha_1$ and $\alpha_0$ are the coefficients of thermal expansion of the particle and the matrix, and $f_p$ and $f_v$ are the particle volume fraction and the void volume fraction in the incremental process. The bulk modulus and the shear modulus of the matrix and the particles, $k_0$, $\mu_0$, $k_1$ and $\mu_1$, are given by
where \( E_0, E_1, \nu_0 \) and \( \nu_1 \) are Young's modulus and Poisson's ratio of the matrix and the particles, respectively. The Eshelby’s tensors for a spherical inclusion are denoted as

\[
\begin{align*}
\mathbf{E}_{0} & = 1 + \frac{\nu_0}{3(1 - \nu_0)} \\
\mathbf{E}_{1} & = \frac{2(1 + \nu_1)}{15(1 - \nu_0)}
\end{align*}
\]

for the hydrostatic component

\[
\begin{align*}
\mathbf{E}_{3} & = \frac{3k_0k_1f_p(1 - \bar{\nu})(\bar{\nu}_1 - \bar{\nu}_0)}{A_h} 3dT + 3k_0d[\mathbf{e}_{pp}^{T}]_{kk}
\end{align*}
\]

The incremental stress of the matrix and the particle, \( \mathbf{d}\sigma^m = (\mathbf{d}\sigma^m_{kk}, \mathbf{d}\sigma^m_{ij}) \) and \( \mathbf{d}\sigma^p = (\mathbf{d}\sigma^p_{kk}, \mathbf{d}\sigma^p_{ij}) \), are given by:

\[
\mathbf{d}\sigma^m_{kk} = \frac{k_0 + (k_1 - k_0)\bar{\nu}}{A_h} \mathbf{d}\sigma_{kk} + \frac{3k_0k_1f_p(1 - \bar{\nu})(\bar{\nu}_1 - \bar{\nu}_0)}{A_h} 3dT + 3k_0d[\mathbf{e}_{pp}^{T}]_{kk}
\]

\[
\mathbf{d}\sigma^m_{ij} = \frac{\mu_0 + (\mu_1 - \mu_0)\bar{\nu}}{A_d} \mathbf{d}\sigma_{ij} + \frac{\mu_0}{A_d} \left\{ d[\mathbf{e}_{pp}^{T}]_{ij} - \frac{\delta_{ij}}{3} d[\mathbf{e}_{pp}^{T}]_{kk} \right\}
\]

\[
\mathbf{d}\sigma^m_{kk} = \frac{k_1}{A_h} \mathbf{d}\sigma_{kk} + \frac{3k_0k_1(1 - f_p - f_v)(\bar{\nu}_1 - \bar{\nu}_0)(1 - \bar{\nu})}{A_h} 3dT
\]

\[
\mathbf{d}\sigma^m_{ij} = \frac{\mu_1}{A_d} \mathbf{d}\sigma_{ij}
\]
Again if the matrix is in the elastic state, \( \mu_0 \) and \( \nu_0 \) in all these equations reduce to their elastic counterparts \( \mu_1 \) and \( \nu_1 \), respectively. When the particle undergoes elastic–viscoplastic deformation in the ceramic matrix composites, \( \mu_1 \) and \( \nu_1 \), similar to those in Eq. (10), must be introduced in the constitutive equation instead of \( \mu_1 \) and \( \nu_1 \). The finite element formulations of these constitutive equations have been described previously but for this model initial strain vector is modified to include both thermal strain and shrinkage (Shabana and Noda, 2001). Additionally, the effects of porosity on the constitutive behavior of the composite were incorporated by treating the porosity has a third phase interacting with the fully dense metal–ceramic composite, thereby treating the powder mixture as a three-phase material consisting of voids, metal particles, and ceramic particles.

3. 2-D thermomechanical finite element analysis of shrinkage stresses in functionally graded plates

After developing the thermal elastic–viscoplastic constitutive model as a function of the evolving porosity of the pressurelessly sintered composites, a 2-D thermomechanical finite element model was used to analyze the shrinkage stress in functionally graded plate and rod structures. Fig. 4 shows the configuration of a typical functionally graded structure with a thickness \( h \) and width \( d \), and a gradient architecture consisting of eight layers with 0, 5, 10, 20, 40, 60, 80, and 100 vol.% Ni respectively. This represents a quadratic gradient that has been previously determined to be nearly optimal for reducing residual stresses in graded nickel–alumina composites (Williamson et al., 1993b). In order to create a particle material with discrete particle reinforcement, the powder size of the particle phase was approximately 1 to 2 orders of magnitude less than the matrix phase, as shown in Table 2. A binder was added after the composite powder has been fully mixed to hold the powders together before they are sintered. The binder used was Q-PAC 40 and the binder weight percentage for each layer is shown in Table 3. As the binder is burnt off and the powders consolidate, the binder volume fraction will increase the level of porosity accordingly in the analysis. To prevent oxidation of the nickel at high temperatures, the specimen is sintered under flowing argon.

Specimens with two different geometries are analyzed. First, a plate with a square cross-sectional geometry of 31.75 × 31.75 mm² and a thickness of 27.9 mm; second, a cylindrical plate with a diameter of 25.4 mm and a thickness of 27 mm. Additional thicknesses of the cylindrical specimens were also analyzed to determine the thickness effect on the mechanical behavior of functionally graded structures during the sintering process. Also, the omission of some layers and changing the order of layers were analyzed to see their effects on the redistribution of shrinkage stresses in the functionally graded structures. For each specimen, all layers have the same thickness. Referring to Fig. 4, \( h \) is the specimen thickness, while \( d \) is the side length and the diameter for the square and the cylindrical specimens, respectively.

The deformation of the functionally graded structure is assumed to be in the plane strain condition for the square cross-sectional geometry. The nickel undergoes elastic–viscoplastic deformation governed by the von
Mises yield condition and the isotropic hardening, while the alumina deformations are predominantly elastic. Due to the symmetrical free boundary conditions of the sintered specimen, the FEM model is developed for half of the specimen. The element used in the finite element analysis is an 8-node isoparametric element, and 2800 elements are used. The element size is refined near the interfaces between the layers to accommodate the concentration of stress. The smallest element size is $7.5 \times 10^{-6}$ m.

This model is more complex than previous efforts to predict stress distributions in functionally graded structures fabricated from sintering nickel and alumina powders, and has an additional complication in accounting for the effects of evolving cohesive strength on the behavior of matrix phases. In previous modeling efforts, the thermal residual stresses that develop as a fully dense graded materials cools from the sintering temperature have been studied using thermomechanical constitutive behavior predicted by modified rule-of-mixtures models without regard to the effects of porosity or evolving cohesive strength (Bruck and Rabin, 1999; Williamson et al., 1993b, 1995). The predicted constitutive behavior was later modified to include the effects of porosity on constitutive behavior and strength through a microstructural rule-of-mixtures formulation on the fully sintered graded materials, and its impact on the predicted thermal residual stress distribution was experimentally verified (Bruck and Rabin, 1999; Rabin et al., 1998). However, these models were not capable of predicting the evolution of shrinkage stresses during sintering since they did not account for the effects of the evolving cohesive strength. Therefore, it was necessary to determine a method for relating the evolution of thermomechanical properties for the matrix phase in the thermal elastic–viscoplastic constitutive model to the total shrinkage or porosity. Mechanical properties, such as the modulus of elasticity and strength that evolve during sintering have been previously determined to vary with porosity according to a power law description (German, 1996). It was also determined that this description could be refined by using an exponential description for the evolution of interparticular cohesion of the matrix phase due to sintering, $\chi$, as follows (Bruck et al., submitted for publication):

$$\chi = (1 - e^{c(\hat{p} - \hat{p}_s)})$$

(20)
where $\rho_i$ is the initial relative density, $\rho_s$ is the sintered relative density, and $\tau$ is a constant that was determined to be 12 for nickel and alumina. Therefore, the evolution of mechanical properties used in this investigation was determined by multiplying the power law description by the relation in Eq. (12).

For modeling the pressureless sintering process, a thermal profile is used for heating a specimen to 1350 °C, as shown in Fig. 5. In order to drive off the moisture, the temperature is held at 150 °C for half an hour. Also, another temperature hold at 400 °C for 2 h is used to drive the binder off. The heating rate never exceeds 4 °C/min, while the cooling rate is always less than 2 °C/min. Thus, isothermal conditions (i.e., no thermal gradients) are assumed when evaluating the stresses and strains that develop in the functionally graded structures.

### 4. Results and discussion

The first task was to measure the change in porosity for the metal–ceramic composites used in this investigation in order to determine the evolution of shrinkage strain and corresponding porosity for the thermal visco-plastic constitutive model. Initial and final porosities were obtained from volumetric measurements using Eq. (4) can be seen in Fig. 6. For the initial porosity, it can be seen that the higher value occurs for the pure nickel layer, while the lower value occurs for the 40 vol.% Ni layer. The pure alumina layer has a low value because of using bimodal alumina particles (85% of the mixture is 0.4 μm in diameter, and 15% is 18 μm). Previous research efforts have indicated that using a bimodal first layer provides better matching of thermal behavior for graded nickel–alumina composites (Winter et al., 2000). For the final porosity, on the other hand, the higher and lower values occur for the 60 vol.% Ni and pure nickel layers. Fig. 7 shows
the evolution in shrinkage strain with sintering time and the predicted behavior using Eq. (7). The predictions correlate well with actual measurements for each composition. The corresponding shrinkage data as a function of temperature can be seen in Fig. 8. As expected, the pure nickel layer has the highest shrinkage in Fig. 7 because it has sintered more, and has the maximum reduction in porosity due to sintering, as shown in Fig. 6. Since the 40 and 60 vol.% Ni layers have the minimum reduction in porosity due to sintering, they have minimum total shrinkage. Because a bimodal alumina with 15 vol.% large alumina particles was used for the pure alumina layer, it ends up with a slightly smaller level of shrinkage than the next layer, which has only 5 vol.% of large nickel particles and unimodal alumina.

After the evolution of the shrinkage strain and porosity was determined, the thermal elastic–viscoplastic constitutive model was incorporated into the finite element analysis using the properties of the fully dense metal and ceramic phases shown in Table 4. It is assumed in the finite element model that cracking occurs at a node on the surface of the specimen when the normal stress in the thickness direction normalized by the corresponding ultimate strength (a power law function of the porosity), is greater than unity. Fig. 9 shows the stress distribution at 900 °C along the thickness direction of a functionally graded cylindrical specimen with a green thickness of 27 mm before sintering. It can be seen that the stress exceeds the ultimate strength.
of the material at the interface between 60 and 40 vol.% Ni layers. Therefore, it is expected from this theoretical analysis that cracking occurs at this interface. The sintered specimen shown in Fig. 9 has cracked at the previously mentioned interface. It can be concluded from this figure that the location of cracking predicted by the finite element model is the same as experimentally observed.

Since the shrinkage difference between 60 and 80 vol.% Ni layers is larger than that between 80 vol.% Ni and pure Ni layers, as seen in Fig. 7, it is expected that the stresses may be reduced by replacing the pure nickel layer by a 60 vol.% Ni layer to create a gradient architecture with a reverse gradient at one end of the specimen. Fig. 10 shows the stress distribution in the thickness direction for the cylindrical functionally graded cylindrical specimen with a green thickness of 27 mm before sintering and with the pure nickel layer replaced by a 60 vol.% Ni layer. It can be seen that the maximum compressive stress during the sintering process in the nickel-rich end of the specimen is reduced and shifts into the 80 vol.% Ni layer, while the stress at the interface of the 40 and 60 vol.% Ni layers is reduced by approximately 60% at 900 °C. In general, the stresses during the entire sintering process are lower than the strength limits, therefore no cracking is expected. This agrees well with final configuration of the sintered specimen also shown in Fig. 10. The stress at 300 °C shown in the figure is the residual stress that remains in the functionally graded structure after cooling.

Out-of-plane geometric effects on the stress distribution were studied by increasing the specimen thickness to transform from a plate to a rod geometry. A functionally graded cylindrical rod specimen was fabricated with eight layers varying from pure Al₂O₃ to pure Ni over 40.5 mm instead of 27 mm. Fig. 11 shows the stress distributions for the 40.5 mm thickness cylindrical specimen at various temperatures during the sintering process. At 900 °C, the stress at the 40 and 60 vol.% Ni interface is reduced by approximately 30% and the peak stress is shifted to the 60 and 80 vol.% Ni interface. In general, the normalized stress never exceeds unity

<table>
<thead>
<tr>
<th>Property</th>
<th>Nickel</th>
<th>Alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus of elasticity</td>
<td>$E = 208$ GPa</td>
<td>$E = 380$ GPa</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>$v = 0.31$</td>
<td>$v = 0.28$</td>
</tr>
<tr>
<td>Yield strength</td>
<td>$\sigma_y = 148$ MPa</td>
<td>–</td>
</tr>
<tr>
<td>Ultimate strength in tension</td>
<td>$\sigma_{Ut} = 200$ MPa</td>
<td>$\sigma_{Ut} = 196$ MPa</td>
</tr>
<tr>
<td>Ultimate strength in compression</td>
<td>$\sigma_{Uc} = 200$ MPa</td>
<td>$\sigma_{Uc} = 2241$ MPa</td>
</tr>
<tr>
<td>Thermal expansion coefficient</td>
<td>$\alpha = 13.4 \times 10^{-6}/\text{K}$</td>
<td>$\alpha = 5.4 \times 10^{-6}/\text{K}$</td>
</tr>
<tr>
<td>Strain hardening parameter</td>
<td>$H' = 670$ MPa</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 9. Stress distribution at 900 °C for functionally graded cylindrical specimen with a green thickness of 27 mm before sintering. The normalized stress exceeds unity at the interface between 40 and 60 vol.% layers, which is where cracking occurred in the specimen shown in the center of the figure.
during the sintering process, which means that no cracking should occur. This agrees well with the experimentally sintered specimen shown in Fig. 11. Thus, gradient architectures can be designed to eliminate cracking by either reversing the gradient at the metal-rich end, or increasing the length (i.e., interlayer thickness).

In addition to qualitative verification of the stress distributions predicted by the finite element model by comparing the location and level of maximum stress with the cracking observed in specimens, it was also possible to quantitatively verify the deformations by comparing the shape profile of a sintered specimen with that predicted by the model. Fig. 12 illustrates the profile view of the 27 mm thickness cylindrical specimen with the reverse gradient and the profile predicted by the model, while Fig. 13 is a quantitative comparison of digitized profile data obtained from the specimen with the theoretical prediction. The distribution shown is for the gradient architecture consisting of two 60 vol.% Ni layers surrounding an 80 vol.% Ni layer. Not only does this distribution yield no cracking, but it also has a unique shape with a dual bulge in the nickel-rich region of the functionally graded structure rather than a single bulge in the middle of the composite. The results tend to correlate well, but there appears to be reduced distortion, up to 15% from predictions, experimentally measured in the 80, 40, and 20 vol.% Ni regions of the specimen. This reduced distortion would tend to indicate that either imperfections in the fabricated gradient architecture altered the stress distribution or the material in these regions may be yielding or creeping more than had been predicted by the thermal elastic–viscoplastic constitutive relations. It is important to note that the yield and creep behavior of these powder-processed materials are very sensitive to the evolution of porosity during the sintering process, and either the initial...
The porosity level may be greater than assumed or during processing of the graded specimen the porosity reduction is slower than predicted by the sintering model. Additional investigations could reveal the exact form of this mechanism by focusing more on the change in the evolution of the shrinkage profile for the graded specimen as a function of sintering temperature.

The effects of geometry were also studied in-plane by sintering specimens with square cross-sectional geometries of $31.75 \times 31.75 \text{ mm}^2$ and a thickness of 27.9 mm to compare with the cylindrical specimens. Fig. 14 shows the distribution of normalized stress along the edge of a specimen with a square cross-section at 820 °C, approximately 100 °C less than the cylindrical specimens. The distribution reveals that the stress reaches a critical value at the interface between 60 and 80 vol.% Ni layers, which is exactly where a large crack developed in the specimen, as shown in Fig. 15. However, there were smaller secondary cracks present near the interface between 10 and 20 vol.% Ni layers and the interface of the 40 and 60 vol.% Ni layers that were not present in the cylindrical specimen. Comparing the predicted stress distributions between the cylindrical and square-cross sectional geometries, it can be seen that the normalized stress is near or above 0.75 for every interface between 10 vol.% Ni and 100 vol.% Ni layers for the square cross-sectional geometry, but is only present between 20 vol. % Ni and 100 vol.% Ni layers in the circular geometry. The presence of the secondary cracks may be due to a shift in the stress distribution towards the alumina-rich end, which causes the peak normalized stress in these regions to exceed unity. The absence of these secondary cracks in the circular specimens may be due to the higher sintering temperature at which the primary crack forms, allowing for the cohesive strength of the composites to increase enough to maintain the normalized stress below unity. Modeling the effects of cracking on the redistribution of shrinkage stresses was not the focus of the current investigation.
5. Conclusions

A new thermomechanical model for predicting crack initiation and the final shape that arises from differential shrinkage during pressureless sintering of powder-processed functionally graded metal–ceramic composites has been developed. This model considers mixtures of metal and ceramic powders as a three-phase material consisting of voids, metal particles, and ceramic particles. The microstructure of the material associated with the mixture during sintering is used to determine the evolution of the thermal elastic–viscoplastic constitutive behavior using a micromechanical model of the composite material. The evolution of thermomechanical properties for the matrix phase during sintering is predicted by using a power law relationship between the properties and the porosity that was refined to account for the evolution of interparticular cohesion of the matrix phase due to sintering. The thermomechanical constitutive model was then incorporated into a 2-D thermomechanical finite element analysis to predict the stresses and deformations that arise from differential shrinkage. Predicted normal stresses in the direction of the thickness on the surface of the graded structure were normalized by the predicted strength to determine the location of crack initiation.

Fig. 14. Stress distribution at 820 °C predicted for a functionally graded specimen with a square cross-sectional geometry and a green thickness of 27.9 mm before sintering indicating peak normalized stresses exceeding unity at the interface between 60 and 80 vol.% Ni layers.

Fig. 15. Cracking evident at the 60/80 vol.% Ni interface in the functionally graded specimen with a square cross-section and a green thickness of 27.9 mm before sintering.

However, the current results clearly indicate that the model can provide guidance in understanding the effects of both the out-of-plane and in-plane specimen geometry on the crack initiation in order to mitigate these effects in the design of graded structures for applications such as armor plating.
To qualitatively verify the new model, the location of cracking in pressurelessly sintered nickel–alumina graded structures with circular cross-sections were compared with the location where the normalized stresses predicted by the model exceeded unity. These comparisons indicated that the location of primary cracks in the graded structures correlated well with the predictions. Using predictions from the model, a gradient architecture with a reverse gradient at one end of the specimen was fabricated to mitigate the cracking. Quantitative verification was obtained by comparing measured and predicted shape profiles for a gradient architecture that resulted in an uncracked specimen. These comparisons indicated reduced distortions of up to 15% between the measured and predicted deformations, where are most likely due to either imperfections in the fabricated gradient architecture or greater amounts of plasticity or creep deformation.

Using the new model, geometric effects on the evolution of shrinkage stresses during pressureless sintering were also investigated. Out-of-plane geometric effects were studied by modeling and fabricating cylindrical plate and rod specimens with different thicknesses. It was determined that by using a rod instead of a plate geometry, the stresses could be reduced to levels below the ones required to initiate cracking. In-plane geometric effects were studied by fabricating a plate specimen with a square cross-sectional geometry. It was determined that the square geometry produced a stress distribution that caused cracking at temperatures approximately 100 °C less than the cylindrical geometry and shifted the location of primary cracking from the 60 and 80 vol.% Ni interface to the 40 and 60 vol.% Ni interface. Additionally, secondary cracks were observed in the cylindrical specimens that were not the focus of the current modeling effort. These results clearly have important implications on the design of appropriate out-of-plane and in-plane geometries for functionally graded structures in applications such as armor plating.

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