Prediction of Initial Shape of Functionally Graded Ceramic Pre-Forms for Near-Net-Shape Sintering

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Abstract: Sintering of macroscopically inhomogeneous ceramic components is always accompanied by shape distortions due to the difference in shrinkage rates of powder elements. The objective of the present investigation is the theoretical determination of initially distorted shapes of the green bodies needed to provide near-net-shape sintered components. Calculations are based on a finite element implementation of the continuum theory of sintering. In this theory, sintering is considered as a creep under the influence of the compressive “sintering stress”. To predict the initial shapes of the components the “inverse” numerical procedure is used when the component is assumed to swell from the final shape to the initial one under the influence of the pressure equal (with the exception of sign) to the sintering stress.

Keywords: Functionally Graded Material; Shape Distortion; Continuum Theory of Sintering.

Резюме: Спекание макроскопически неоднородных керамических образцов как правило приводит к их короблению из-за разности скоростей усадки различных элементов образца. Целью настоящей работы является теоретическое предсказание такой начальной формы неоднородной заготовки, которая в результате спекания обеспечивает заданную конечную форму изделия. Вычисления основываются на конечно-элементной реализации континуальной теории спекания. Спекание рассматривается как результат получения материала под воздействием давления спекания. Для вычисления начальной формы заготовки используется специальная процедура “обратного хода времени” в которой рассматривается разбухание образца от заданной конечной формы к искомой начальной под воздействием давления обратного давлению спекания.

Ключевые слова: Функционально-градиентный материал; искажение формы; континуальная теория спекания.

Садржај: Синтеровање макроскопски нехомогених керамичких компонената увек је праћено кривљењем облика због разлике у брзинама скупљања различитих елемената праха. Циљ овог истраживања је теоретско предвиђање таквог полазног облика нехомогеног узора, које после синтеровања обезбеђује задати крајњи облик производа. Прорачун су засновани на имплементацији коначних елемената континуалне теорије синтеровања. У овој теорији синтеровање се разматра као клизање "напрезања синтеровања" под притиском. За прорачун полазног облика
испреска примењује се специјални поступак "инверзног тока времена" у оквиру кога се разматра ширење узорка од коначног облика ка траженом полазном под дејством притиска супротног дејству напрезања при синтеровању.

Кључне речи: Функционално градијентни материјал; дисторзија облика; континуална теорија синтеровања.

1. Introduction

Functionally graded materials are macroscopically inhomogeneous materials with the inhomogeneity deliberately adjusted to the pre-supposed applications. Powder consolidation is the main route for the production of this type of composites. Free sintering is the cheapest method to impart strength to powder bodies. Unfortunately, sintering of macroscopically inhomogeneous components leads, as a rule, to distortions due to a non-uniform shrinkage of different powder elements. Various methods of cutting, grinding, polishing are used to render the necessary final shape of components after sintering. For ceramics, this finishing stage is a rather expensive operation. It seems reasonable to use initially distorted green bodies to provide near-net final shape after sintering. In general, machining of porous pre-forms is much a simpler operation then finishing of dense components. Moreover, some of the modern technologies of the formation of graded pre-forms can provide almost any pre-set initial shape for them. For example, the components considered in the present investigation are formed by electrophoretic deposition of powders [1]. The deposition can provide a wide range of ceramic pre-forms for subsequent sintering. Functionally graded pre-forms are obtained by electrophoretic deposition of a mixture of different powders from electrolyte suspension with concentrations of constituent powders varied with time. As a result, the concentration profile in a composite green body mirrors the history of the concentration evolution in the suspension.

2. Numerical Procedure

The numerical approach for the prediction of initial shapes of components is based on a finite element implementation of the continuum theory of sintering. From the macroscopic point of view, shrinkage during sintering can be treated as a linear creep of a porous body under the influence of the internal compressive pressure, which is usually termed as “sintering stress” or “Laplace pressure” and it is denoted as $P_L$ [2]. If the initial shape and the composition of a powder body are known, the theory of sintering can predict its final shape. The traditional statement of the modeling problem gives some insight about origins of distortions during sintering. However, from the practical point of view, the statement of the problem has to be opposite: final shapes of components are known and initial shapes have to be found. To solve this problem it seems natural to consider the “inverse” process of swelling of components from the final to initial shape under influence of the pressure - $P_L$. This is the main idea of the approach.

As a result of the calculations, the initial shape corresponding to a certain level of the mean initial density can be readily found, but initial density will be distributed non-uniformly in the volume. The use of pre-forms with a non-uniform density distribution is not possible from the practical point of view. To obtain the initial shape of green bodies with a uniform
density distribution, an iterative procedure is used. After the first step of the inverse calculations the next step is the direct modeling of powder sintering with the initial shape of the pre-form taken from the previous step. Initial density is taken uniformly distributed throughout the volume. The calculations are carried out up to the density about 95%. As a result of the calculations, density distribution in the component is obtained. At the next step, the inverse calculations from the given final shape are used again, but the starting density distribution is taken from the previous direct step. The mapping of density distribution from the distorted to the undistorted final shape can be readily carried out if the same finite element mesh is used for all steps of the iterative procedure without remeshing. In this case the natural correspondence is established between elements of the green body during all stages of the procedure. In such a manner at the beginning of the inverse step the density of the corresponding element from the foregoing direct step is attributed to every element. The iteration procedure is repeated until the condition of practical convergence for the initial shape of the component is met. Earlier this procedure has been used for the prediction of optimum initial shapes of powder components during HIP [3].

The procedure can be applied only if the sintering stress and the constitutive behavior of the powder body are known. In the present investigation, sintering of pre-forms made of a mixture of alumina and zirconia is considered. These two powders have about ten times difference in particle sizes. The difference in the grain size will be considered as a main contribution into the non-uniform sintering of a functionally gradient composite. The sintering stress is sensitive to the powder size and, as a result, in the case of a mixture of powders with different sizes it becomes a function of concentrations of constituents.

3. Evaluation of the Sintering Stress for a Two-Component Mixture of Spherical Particles

A general formula for the sintering stress is given in [4] as:

\[
P_L = -\frac{1}{V_e} \int \sigma_0 m_i j_i dL ,
\]

where repeating indices mean summation, \( V \) is the volume of the powder, \( L_p \) is the overall combination of the perimeters of all contacts between particles, \( \vec{m} \) is the unit vector normal to \( L_p \) within the local plane of the contact, \( \vec{j} \) is the diffusion flux, \( \sigma_0 \) is the value of the normal stress on \( L_p \), \( e \) is the specific rate of the volume change. The stress \( \sigma_0 \) can be assessed as

\[
\sigma_0 = \gamma K ,
\]

where \( K \) is the sum of the principal curvatures on \( L_p \), \( \gamma \) is the specific surface energy. The curvature \( K \) at the edge of the neck between two equal spherical particles can be estimated as [5]:

\[
K = \frac{\alpha R}{x^2} = \frac{2}{x} \sin \frac{\psi}{2} ,
\]

where \( \alpha \) is a constant, \( x \) is the neck radius, \( \psi \) is the dihedral angle. In the ensuing assessments contribution of the second term in the right-hand side of (3) will be considered to...
be negligible. For the sintering of particles with different radii, the curvature $K$ can be estimated as follows [6]:

$$K = \alpha \frac{2R_s R_l}{x^2 R_l + R_s},$$  \hspace{1cm} (4)

where $R_s, R_l$ are the radii of the small and large particles, respectively.

The diffusion flux in (1) can be found through the shrinkage rate $w$ [5]

$$m_i j_i = w x$$  \hspace{1cm} (5)

where $w$ is the rate of approach of one particle toward the other. The shrinkage rate, in turn, can be evaluated through the rate of the volume change

$$w = \frac{1}{3} e R_i + R_s,$$  \hspace{1cm} (6)

After substitution (6), (5) and (2) into (1), the formula for the sintering stress assumes the form

$$P_L = -\frac{2\pi \alpha \gamma}{3V} \sum R_i R_2,$$  \hspace{1cm} (7)

where summation is taken place over all necks between particles. Parameters $R_i, R_2$ are the radii of the particles forming particular neck. According to (7) the sintering stress does not depend on radii of necks between particles. For the unit volume of powder, formula (7) gives

$$P_L = -\frac{\pi \alpha \gamma (1 - \Theta)}{3} \left[ \frac{\varphi_s}{4 \pi R_s^3} \left( R_i^2 n_{sl} + R_i R_s n_{si} \right) + \frac{\varphi_i}{4 \pi R_i^3} \left( R_s^2 n_{il} + R_i R_s n_{il} \right) \right],$$  \hspace{1cm} (8)

where $\varphi_s, \varphi_s$ are the volume concentrations of large and small particles, respectively; $n_{sl}$ is the coordination number of small particles in contact with large particles, $n_{si}, n_{il}, n_{il}$ are defined in a similar way, $\Theta$ is the porosity. The values of the coordination numbers were taken from [7]. The coordination number of the small particles with respect to large particle neighbors can be found in the form

$$n_{sl} = S_a N_{sl},$$  \hspace{1cm} (9)

where $S_a$ is so-called fractional area of large particles

$$S_a = \frac{\varphi_i}{\varphi_i + (R_i/R_s) \varphi_s},$$  \hspace{1cm} (10)

and $N_{sl}$ is the coordination number if small particle has contacts only with large particles:

$$N_{sl} = \frac{0.5 N_s (1 + c_{sl})}{1 + c_{sl} - \left( c_{sl}^2 + 2c_{sl} \right)}.$$  \hspace{1cm} (11)

Parameter $N_s$ is the assumed average coordination number for a packing of spheres of the same size. In the present calculations it was taken equal to 6. Parameter $c_{sl} = R_s / R_l$. 
Coordination numbers \( n_{sl}, n_{ll}, n_{ls} \) can be found from the formulas (9)-(11) by interchange of indices.

The final result after substitution of the coordination numbers is the following

\[
P_L = -\frac{\alpha\gamma(1-\theta)N_c}{4} \left[ \frac{\varphi_s c_{ls}}{R_s(\varphi_s + c_{ls}\varphi_s)} \left( \varphi_s + \frac{\left(1 - \frac{\sqrt{3}}{2}\right)\varphi_s(1 + c_{ls})}{1 + c_{ls} - \sqrt{1 + 2c_{ls}}} \right) + \frac{\varphi_l c_{sl}}{R_l(\varphi_s + c_{sl}\varphi_l)} \left( \varphi_l + \frac{\left(1 - \frac{\sqrt{3}}{2}\right)\varphi_l(1 + c_{sl})}{1 + c_{sl} - \sqrt{1 + 2c_{sl}}} \right) \right],
\]

where \( c_{ls} = R_l/R_s \). The sintering stress as a function of volume concentrations of small and large particles for different ratios of particle sizes is given in Fig. 1.

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**Fig. 1** Sintering stress as a function of volume concentration of small particles.

4. Evaluation of Bulk Viscosity for a Mixture of Alumina and Zirconia

According to the experimental results [8] the average densification rate \( \dot{\rho} \) during sintering of mixture of alumina and zirconia can be approximated in the following form

\[
\dot{\rho} = A \frac{\exp\left(-Q/R_gT\right) f(\rho)}{T} \frac{R^4}{f(\rho)}
\]

where \( \rho \) is the relative density of the powder, \( A \) is a constant, \( T \) is the temperature, \( R_g \) is the gas constant, \( f(\rho) \) is the function of density. Experimental data [8] for the activation energy \( Q \) in the numerical examples were approximated as
\[
Q = \begin{cases} 
440 + 5200\varphi_{ZrO_2}, & \varphi_{ZrO_2} < 0.05 \\
700, & 0.05 \leq \varphi_{ZrO_2} \leq 0.95 \\
615 + 1700(1 - \varphi_{ZrO_2}), & \varphi_{ZrO_2} > 0.95 
\end{cases} \text{ kJ/mol} 
\] 
(14)

where \( \varphi_{ZrO_2} \) was the volume fraction of zirconia. The function \( f(\rho) \) was taken from Ref. [2] in the form
\[
f(\rho) = \frac{1 - \rho}{\rho}. 
\] 
(15)

According to Ref. [6], the sintering rate for powder compacts with particles of the same size can be transformed into a more general case of the sintering rate of powder compacts with a bi-modal particle size distribution by an introduction of the effective particle size
\[
R = R_c \chi(c_{sl}, \varphi_s), 
\] 
(16)

where
\[
\chi = \frac{c_s^3 (1 - \varphi_s)^2 + \varphi_s (1 - \varphi_s) (1 + c_{sl}) c_{sl} + \varphi_s^3}{c_s^3 (1 - \varphi_s)^2 + 0.5 \varphi_s (1 - \varphi_s) (1 + c_{sl}) ^2 c_{sl} + \varphi_s^2 c_{sl}}. 
\] 
(17)

Substitution of Eqs. (14) and (16) into Eq. (13) provides an assessment of the densification rate during sintering of a mixture of powders for any concentrations of constituents.

The bulk viscosity \( K_v \) of a powder compact can be obtained as a ratio of the sintering stress and the rate of the free sintering densification.

\[
K_v = -\frac{P_s \rho}{\rho}. 
\] 
(18)

The ratio of the shear viscosity to the bulk viscosity of powder elements was taken equal to \( 1.5 f(\rho) \) [2].

5. Numerical Examples

As a numerical example for the modeling, the sintering of a composite femoral ball head was considered. The femoral ball head is the part of the ceramic prosthesis of a hip joint (Fig. 2).
For increasing hardness of the ball, it has been proposed to use a thick graded alumina-zirconia coating on the surface of the zirconia core. Zirconia inside the ball head has to provide high fracture toughness of the component and alumina has to improve hardness of the surface. According to the experimental data [8], a mixture of zirconia and alumina is sintered much slower than pure zirconia, and as a result a considerable distortion of the component takes place (Fig. 3).

The zirconia-alumina graded coating was modeled as a thick outer layer with equal volume concentrations of alumina and zirconia. The iteration procedure based on the combination of the "consolidation" and "swelling" steps was used for the prediction of the initially distorted geometry of a green body needed for the near-net final shape after sintering (Fig. 4). In the calculations, FEM implementation of the continuum theory of sintering [2] was used.

The initial shape of the green body, which is necessary to provide the flat surfaces of a disk after sintering, is given in Fig. 5. Another example is sintering of a laminated round disk consisting of equal layers of zirconia and a mixture of alumina with zirconia in equal volume concentrations. The radius-to-height ratio of the disk is 5:1.
Fig. 5 Initial shape of a bi-layered round plate.

6. Conclusions

In many cases, functionally graded ceramic components have unique properties that cannot be reached in macroscopically homogeneous materials. However, consolidation of a macroscopically non-uniform powder green bodies as a rule leads to a final shape which is significantly different from the initial one. The problem of the distortion during sintering can be circumvented by the use of initially distorted green bodies. The numerical procedure for the prediction of the initial shape of green bodies is put forward. The procedure is based on the use of the “inverse swelling” from the final to the initial shape. The same procedure can be used for the prediction of initial shapes of composite powder green bodies for the production of near-net-shape components by HIP or Sinter-HIP.

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References