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The master sintering curves for $BaTi_{0.975}Sn_{0.025}O_3/BaTi_{0.85}Sn_{0.15}O_3$ functionally graded materials

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Abstract

The most important aim in the design and processing of functionally graded materials (FGMs) is to produce devices free from any deformation. Smart choices of different combination of graded layers, as well as the heating rate during sintering, are important for the fabrication of high-quality FGMs. In this study, $BaTi_{0.975}Sn_{0.025}O_3/BaTi_{0.85}Sn_{0.15}O_3$ (noted as BTS2.5 and BTS15, respectively) FGM was used as a model system for the construction of master sintering curves (MSCs) and estimation of the effective activation energies of sintering for different BTS graded layers. The MSCs were constructed, for BTS2.5 and BTS15 graded layers in FGMs, using shrinkage data obtained by a heating microscope during sintering at four constant heating rates, 2, 5, 10 and 20 °/min. The effective activation energies were determined using the concept of MSC; values of 359.5 and 340.5 kJ/mol were obtained for graded layers BTS2.5 and BTS15, respectively. A small difference of the effective activation energies of chosen powders made it possible for us to prepare high-quality FGMs, without delamination, distortion or other forms of defects.

Keywords: Sintering; Composites; $BaTiO_3$ and Titanates; Diffusion; Master Sintering Curve

1. Introduction

Functionally graded materials (FGMs) belong to an attractive class of materials in which it is possible to obtain a gradient of properties that cannot be attained in any monophase materials. Continuous changes in the properties of these materials for instance: composition, grain size, porosity, etc., result in the gradient of their features such as mechanical strength and thermal conductivity. Over the years, FGMs have found applications in various functional materials, like piezoelectric ceramics,[1] thermoelectric semiconductors,[2] and biomaterials.[3]

Fabrication of FGMs by powder technology is accompanied by significant problems of components' shape distortion.[4] An important processing goal for FGMs is to obtain high-quality microstructure with desired grain size and density. During the thermal treatment, different graded layers in FGM show different shrinkage kinetics, i.e. different shrinkage rates and extents of shrinkage during sintering, as well as different final density. This phenomenon can lead to excessive shape distortion, warping, delamination, development of cracks and microstructural damage in the sintered FGMs. Therefore, it is desirable to predict the sintering process (shrinkage and anisotropy) for every graded layer in FGM and design sintering strategies to achieve high-quality FGM free from any form of deformation.

Here, we have chosen BTS2.5/BTS15 FGM as a model system for the construction of MSCs and estimation of the effective activation energies of sintering for graded layers of the FGM. BTS ($BaTi_{1-x}Sn_xO_3$) powders are very important in ceramic industries. BTS powders improve the dielectric behavior of barium titanate ceramics, i.e. the increase of the Sn content (up to 15 mol%)[5] in barium titanate ceramics decreases temperature of phase transformation, and also, increases dielectric constant.[3,5–7] Furthermore, BTS powders are important for practical applications in ceramic capacitors, as well as for FGMs (in the form of monolithic ceramics with an uniaxial gradient of piezoelectric and/or dielectric coefficients). BTS FGMs are very useful because they have a broad transition temperature and high dielectric constant in a wide temperature range.[5,8] The width of the transition temperature range for BTS FGM depends on the number of layers, as well as on the tin content in each of the graded layers.[5]

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The aim of the present study has been to construct a master sintering curve for BTS2.5 and BTS15 graded layers in BTS2.5/BTS15 FGMs, for pressureless sintering using a heating microscope. FGMs were designed and fabricated by the powder-stacking method and uniaxially pressing process, followed by sintering. The shrinkage of FGMs during sintering was investigated as a function of the tin contents in the graded layers and sintering conditions. With the help of MSCs of BTS2.5 and BTS15 graded layers in BTS2.5/BTS15 FGM we can estimate the effective activation energies of BTS components. Also, we can predict the densification behavior of BTS FGM and avoid deformations of the devices.

2. Construction of the master sintering curve (MSC)

Sintering is a complex process, involving the evolution of microstructure through the action of several different transport mechanisms.[9] One of the ultimate objectives for sintering studies is to be able to predict densification results under different thermal histories for a given processing method.

Sintering kinetics of most systems of industrial importance can be quantitatively predicted by the model proposed by Su and Johnson, in which the entire sintering process is successfully described.[10] They have reported that the geometric parameters related to sintering are often functions only of density for a given powder and green-body process, provided that one diffusion mechanism dominates in the sintering process.[10] Based on that report, the concept of a master sintering curve (MSC) has been developed to characterize the sintering behavior for a given powder and green-body process regardless of the heating profiles. Using MSC, densification behavior can be predicted under arbitrary temperature–time excursions following a minimal set of preliminary experiments. These predictions can be used in planning sintering strategies. So, it is possible to make quantitative predictions of the sintering process of practical powders and, based on this, design strategies to control sintering in order to achieve high-quality products. The master sintering curve is an approach that makes it possible. Finally, the MSC is a characteristic measure of the sinterability of a compact over a wide density range.

The master sintering curve can be derived from the densification rate equation of the combined-stage sintering model.[11] For the development of master sintering curves, the parameters in sintering rate equations are separated into (a) those related to the microstructure and (b) those related to time and temperature terms, on the opposite sides of the equation, then the two sides of the equation are related to each other experimentally.[10] If there exists only one dominant diffusion mechanism (either volume or grain boundary diffusion), the terms which define the microstructural evolution are independent of the thermal history and can be represented by,[10,12]

$$\Phi(\rho) \equiv \frac{k}{\gamma \Omega D_0} \int_{\rho_0}^{\rho} \frac{(G(\rho))^n}{3\rho \Gamma(\rho)} \mathrm{d}\rho \quad (1)$$

where k is the Boltzmann constant, γ is the surface energy, Ω the atomic volume, D_0 is the preexponential factor, ρ_0 is the green density of the powder compact, G is the mean grain diameter, n is the grain size power-law exponent (i.e. $n = 3$ for volume diffusion and $n = 4$ for grain boundary diffusion), Γ is the collection of microstructure scaling parameter.

The time and temperature dependent side of the equation can be represented as theta parameter, Θ,

$$\Theta(t, T(t)) \equiv \int_{0}^{t} \frac{1}{T} \exp\left(-\frac{E_a}{RT}\right) \mathrm{d}T \quad (2)$$

where t is instantaneous time, which is a function of temperature, E_a is the activation energy, R is the gas constant and T is the absolute temperature. For a constant heating rate, Eq. (2) can be written as:

$$\Theta(t, T(t)) \equiv \frac{1}{c} \int_{T_0}^{T} \frac{1}{T} \exp\left(-\frac{E_a}{RT}\right) \mathrm{d}T \quad (3)$$

where c is the heating rate and T_0 is the temperature below which no sintering take place.

$$\Phi(\rho) = \Theta(t, T(t)) \quad (4)$$

The relationship between the density (ρ) and Θ (Eq. (4)) is defined as the master sintering curve. For the construction of MSC, a series of runs at different temperatures (isothermal) or constant heating rate over a range of heating rates are needed. If the activation energy of sintering is unknown, it has to be estimated in order to obtain the master sintering curve.

For the construction of MSC, the integral of Eq. (2) and the experimental density should be known. Dilatometry was conveniently used to determine the shrinkage (density) of monolayered samples.[10,12–16] However, for multilayered samples dilatometer shows total shrinkage, not shrinkage of every single layer. So, in the case of multilayered samples heating microscope, using as an optical dilatometer, can be a suitable instrument for detailed quantitative studies of sintering kinetics of each layer.[4] To the best of our knowledge, the corresponding investigations of MSCs on graded layers in FGMs were not reported until now.

For the calculation of Θ, the activation energy for the sintering process must be known. If the activation energy is unknown, it can be estimated with good precision from Θ *versus* density (ρ) data. For this purpose, a particular value of activation energy should be chosen and ρ–Θ curves should be constructed for each heating rate. If the curves fail to converge, a new value of activation energy should be chosen and the calculations repeated. This procedure should be continued until all the curves converge, showing that the activation energy is the acceptable one for sintering. A curve can be then fitted through all the data points, and then the convergence of data to the fitted line can be quantified through the sum of residual squares of the points with respect to the fitted line. The best estimate of E_a will be the value of the minimum in the plot of the activation energy *versus* mean residual squares.