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Dilatometric study of anisotropic sintering of alumina/zirconia laminates with controlled fracture behaviour

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ABSTRACT

Al_2O_3 and ZrO_2 monoliths as well as layered Al_2O_3/ZrO_2 composites with a varying layer thickness ratio were prepared by electrophoretic deposition. The sintering shrinkage of these materials in the transversal (perpendicular to the layers, i.e. in the direction of deposition) as well as in the longitudinal (parallel with layers interfaces) direction were monitored using high-temperature dilatometry. The sintering of layered composites exhibited anisotropic behaviour. The detailed study revealed that sintering shrinkage in the longitudinal direction was governed by alumina (material with a higher sintering temperature), whilst in the transversal direction it was accelerated by the directional sintering of zirconia layers. For interpretation of such anisotropic sintering kinetics, the Master Shrinkage Curve model was developed and applied. Crack propagation through laminates with a different alumina/zirconia thickness ratio was described with the help of scanning electron microscopy and confocal laser microscopy.

1. Introduction

Layered ceramic composites (laminates) can be prepared by various techniques like tape casting, slip casting, or electrophoretic deposition (EPD). EPD is an experimentally simple and cheap method enabling the formation of deposits from stable suspensions. EPD is a powerful method for the preparation of ceramic laminates [1,2], but also of monoliths [3] or structural composites such as particle mixed composites and functionally gradient materials [4–6]. In the last decades, ceramic laminates have been one of the main areas of focus for material scientists particularly for their crack deflection behaviour [7,8].

Internal stresses are responsible for unique crack propagation in ceramic laminates [9]. The tension arising during sintering is usually described by the constrained sintering model. Unfortunately, this model is designed for the sintering of one layer on a rigid substrate [10]. However, laminate composites consist of hundreds of individual layers supporting each other. Constrained sintering causes hindering of sintering and very often the generation of cracks, or crack like defects [11,12]. Additionally, internal stresses that are due to a mismatch in the coefficient of thermal expansion (CTE) are generated during cooling as well [11].

The magnitude of residual tensile stress (σ_r) in the ZrO_2 layer can be calculated using the following relation [9,13].

$$\sigma_{rZrO_2} = \frac{(\alpha_{ZrO_2} - \alpha_{Al_2O_3}) \cdot \Delta T \cdot E_{ZrO_2}}{1 - \upsilon_{ZrO_2}} \cdot \left(1 + \frac{d_{ZrO_2}}{d_{Al_2O_3}} \cdot \frac{E_{ZrO_2} \cdot (1 - \upsilon_{Al_2O_3})}{E_{Al_2O_3} \cdot (1 - \upsilon_{ZrO_2})}\right)^{-1}, \quad (1)$$

where d is the layer thickness, α is the coefficient of linear thermal expansion, ΔT is the difference between the sintering and the current temperature, ν is Poisson's ratio, and E is the modulus of elasticity. Stress in the Al_2O_3 phase can be obtained analogously. In contrast with ZrO_2, stress in the alumina layer is compressive. The stresses are directed parallel with the interfaces.

For a better understanding of the fracture properties of ceramic laminates, the detailed study of crack propagation in laminates with various values of internal stresses appears appropriate. It follows from Eq. (1) that internal stresses can be designed by the proper choice of thicknesses ratio of individual layers. To tailor the thicknesses of the layers in the final laminate, the exact control of the deposition kinetics as well as sintering shrinkage is needed. Since the detailed study of deposition kinetics was presented in our previous papers [1,14], the goal of this work is the study of sintering behaviour carried out with the help of high-temperature dilatometry [15].

The concept of Master Sintering Curve (MSC in the following) is a good engineering tool for optimizing and predicting the sintering

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process which can also be used for the determination of sintering activation energy [16]. The MSC model was derived under conditions of validity of some geometrical and physical conditions [16] and it is used in the form of relation between density and function Θ (describing the thermal history of the sintering with the help of parameter Q):

$$\frac{k}{\gamma\Omega D_0}\int_{\rho_0}^{\rho}\frac{(G(\rho))^n}{3\rho\Gamma(\rho)}d\rho \equiv f(\rho) = \int_0^t \frac{1}{T}\exp\left(-\frac{Q}{RT}\right)dt \equiv \Theta, \quad (2)$$

where γ is the surface energy, Ω is the atomic volume, k is the Boltzmann constant, R is the gas constant, T is the thermodynamic temperature, G is the mean grain size, D_0 is the coefficient of a diffusion process (only one dominant diffusion process is considered), Γ represents scaling parameters that relate different geometric features as the driving force of sintering and the mean diffusion distance to the grain size, t is the time, ρ is sample density, Q is the activation energy of sintering, and n has a value of 3 (for volume diffusion) or 4 (for grain boundary diffusion).

Not only does the construction of MSC require several sintering experiments performed at different heating schedules, but also time consuming mathematical iteration. Recently, some mathematical approaches enabling the easy construction of MSC from few dilatometric sintering experiments have been published [17,18], shown by the dramatic rise of references being made to MSC in the literature. The basic MSC model has already been modified for many special purposes. An and Han [19,20] extended the MSC model to pressure-assisted sintering and Enneti et al. to field-assisted sintering [20,21]. An et al. [22] and Raether et al. [23] used the MSC model for construction of sintering kinetics diagrams. Di Antonio et al. [24] and Wang et al. [25] showed that MSC can be extended to all Arrhenius type equations. Recently, Song et al. [26] and Pouchly et al. [27] showed that MSC can also be used for the description of sintering behaviour when the change of the controlling sintering mechanism has to be taken into account.

The limitations of the MSC model arise when a more complicated sintering material is examined. For example, in the case of a lamellar composite, the shrinkage is not isotropic [28], and therefore the geometrical assumption of the MSC model is not fulfilled [29]. The densification curve of the sample cannot be calculated from one-dimensional dilatometric shrinkage. Hence, the second goal of this work is modification of the MSC model from density related to shrinkage related. Such a modified MSC can then be applied to lamellar composites with the aim to use the results of such analysis for the description of processes which occur during sintering.

For this study, the Al_2O_3/ZrO_2 laminates prepared by EPD were chosen since the authors have much experience with the preparation of these laminates with strongly bonded layers. Using sintered composites with various layer designs, the crack propagation was demonstrated and discussed.

Table 1
Ceramic powder materials used for electrophoretic deposition.

Material	Manufacturer	Grade	Mean particle size[a] [μm]
Al_2O_3	Malakoff Ind., USA	HP-DBM	0.47
ZrO_2	Tosoh, Japan	TZ-3YS-E	0.14

[a] Values were calculated from specific surface area given by the producer.

2. Experimental

2.1. Electrophoretic deposition

For preparation of ceramic monoliths and laminates, alumina and tetragonal zirconia (stabilized by 3 mol% of Y_2O_3) powders were used. Detailed information about ceramic powders is shown in Table 1. Suspensions contained 15 wt.% of alumina or zirconia, 12.75 wt.% of monochloroacetic acid (99%, Aldrich, Germany) used as a stabilizer and 72.25 wt% of the dispersion medium – 2-propanol (p.a., Onex, Czech Republic).

Electrophoretic deposition was performed in an electrophoretic glass cell with the constant current mode of 5 mA. The distance between stainless steel electrodes with an effective area of 18.2 cm^2 was set to 26 mm. In order to prevent particles from settling on the bottom of the EPD cell, the suspension was repeatedly stirred every 5 min during electrophoretic deposition. The repeated transfer of the deposition electrode from the alumina to the zirconia suspension (and vice versa) enabled the preparation of ceramic laminates with about 100 alternating alumina and zirconia layers with a thickness ratio of 2:1, 1:1, and 1:2 (denoted as Z33, Z50, and Z67, respectively). The precise control of deposition kinetics enabled the preparation of ceramic laminates with well defined thicknesses of individual layers [30]. For comparison, alumina (denoted as A), and zirconia (denoted as Z) monoliths were prepared during 90 min and 140 min long depositions, respectively. A detailed description of all prepared deposits is given in Table 2. All deposits were dried after the deposition for at least 24 h at room temperature. After the drying, the deposits were annealed at 800 °C/1 h in air.

2.2. Sintering of ceramic samples and constructing of the modified MSC

The sintering of the test samples was done in a contact high-temperature dilatometer (L70/1700, Linseis, Germany), where the sample shrinkage was in-situ monitored both in the transversal direction (perpendicular to alumina/zirconia interfaces, i.e. parallel to the direction of deposition) as well as in the longitudinal one (parallel to alumina/zirconia interfaces, i.e. perpendicular to the direction of deposition). Samples were cut from the deposits in the shape of prismatic bars, with a cross-section ca 4 × 4 mm, height ca 10 mm (longitudinal sample) resp. ca 5 mm (transversal sample).

The coefficient of thermal expansion (α) of all the samples was calculated according to Eq. (3):

$$\alpha = \frac{\varepsilon_{room} - \varepsilon_{T\max}}{(T_{room} - T_{\max})\cdot 100}, \quad (3)$$

Table 2
Characteristics of deposited and sintered samples.

Laminate	Al_2O_3/ZrO_2 thickness [μm/μm]	ZrO_2 content [vol%]	Green density [%TD]	Final density [%TD]	Grain size Al_2O_3/ZrO_2 [μm/μm]	Final shrinkage	
						T [%]	L [%]
A	50/0	0	62.0	99.40	1.3/-	17.5	14.2
Z33	50/25	33.3	57.3	99.20	1.6/0.6	22.7	14.9
Z50	50/50	50.0	55.0	99.57	1.2/0.4	24.2	15.4
Z67	25/50	66.7	52.7	98.02	1.6/0.6	27.2	16.1
Z	0/50	100	48.0	99.92	-/0.3	22.4	21.4

Note: T = transversal, L = longitudinal.

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