Viscous Poisson's ratio, bulk and shear viscosity during electrical field assisted sintering of polycrystalline ceria

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Abstract

Uniaxial viscous Poisson's ratio, bulk and shear viscosities were measured by discontinuous sinter-forging without and with alternating current electric fields under the same conditions, i.e. by keeping the sample temperature constant. This precaution enables the exclusion of any macroscopic Joule heating. Major findings are: (i) viscous Poisson's ratio increases with the relative density, with and without electric field; (ii) viscous Poisson's ratio increases with the presence of electrical fields; (iii) changes in the viscous Poisson's ratio can be correlated to a clear decrease in shear viscosity, which can be attributed to an easier grain boundary sliding under electric field.

Keyword

Ceria, electric field assisted sintering, viscous Poisson's ratio, shear viscosity, bulk viscosity

The application of electric fields for the sintering of inorganic materials has raised great interest, since it offers a new approach for processing materials difficult to sinter conventionally and enables to reduce both sintering time and temperature [1-4]. Broader application of this technique requires a better understanding and a self-consistent description of the process. The continuum mechanics formalism has been used to predict the conventional sintering behavior of co-fired multi-layers [5-8], as well as powder compacts of complex shape and with density gradients [9-10]. Until now, the effect of electric fields has neither been systematically investigated nor modeled. The influence of moderate AC electrical fields (and induced current flowing through the sample) on viscous Poisson's ratio as well as the bulk and shear viscosity were determined and investigated here for the first time, allowing for a more complete understanding of the possible mechanism occurring during field assisted sintering.

Sintering behavior of ceramic bodies can be predicted using viscous analogy in the frame of continuum mechanics. The governing equations for an isotropic, linear viscous specimen in cylindrical coordinate system are provided as follows:

$$\dot{\epsilon_r} = \dot{\epsilon_f} + \left(\frac{1}{E_p}\right)\left[\sigma_r - \upsilon_p(\sigma_\theta + \sigma_z)\right] \tag{1}$$

$$\dot{\epsilon_z} = \dot{\epsilon_f} + \left(\frac{1}{E_p}\right)\left[\sigma_z - \upsilon_p(\sigma_\theta + \sigma_r)\right] \tag{2}$$

where σ_z, σ_θ and σ_r are the axial, hoop and radial stress, respectively. $\dot{\epsilon_f}$ is the free strain rate without any constraints. υ_p and E_p are the viscous Poisson's ratio and the uniaxial viscosity, respectively. In the case of a uniaxial stress state, the corresponding stress and strain state should be $\sigma_z \neq 0$, $\sigma_\theta = \sigma_r = 0$. Hence, Eq. (1 - 2) can be reduced to:

$$\dot{\epsilon_r} = \dot{\epsilon_f} - \left(\frac{\upsilon_p}{E_p}\right)\sigma_z \tag{3}$$

$$\dot{\epsilon_z} = \dot{\epsilon_f} + \left(\frac{1}{E_p}\right)\sigma_z \tag{4}$$

Therefore, the viscous Poisson's ratio is described as follows:

$$\upsilon_p = \frac{\dot{\epsilon_f} - \dot{\epsilon_r}}{\dot{\epsilon_z} - \dot{\epsilon_f}} \tag{5}$$

According to Eq. 5, the experimental approach to obtain uniaxial Poisson's ratio is challenging since it involves the subtraction of two measured small rates. With this in mind, a more robust approach was applied to obtain the viscous Poisson's ratio, as shown for low temperature cofired ceramics (LTCC) materials [11]. The relationship between volumetric densification rate, $\dot{\epsilon_v}$, and the driving force can be expressed as follows:

$$\dot{\epsilon_v} = 2\dot{\epsilon_r} + \dot{\epsilon_z} = \frac{1}{K_p}\left(\frac{\sigma_z}{3} + \Sigma\right) \tag{6}$$

Where K_p is the bulk viscosity and the driving force consists of two parts: Σ, the sintering potential and σ_z, the external applied stress. Because the sintering potential gives the free sintering rates without any constraints, Eq. 6 can be expressed as:

$$\dot{\epsilon_v} = 3\dot{\epsilon}_v^f + \frac{1}{K_p}\frac{\sigma_z}{3} \tag{7}$$

Similar to the determination of uniaxial viscosity [6], the bulk viscosity can then be obtained through the inverse of the slope of the plot $\dot{\epsilon_v}$ vs. $\frac{\sigma_z}{3}$. Together with the uniaxial viscosity E_p from our previous work [12], the viscous Poisson's ratio can be calculated according to the following equation:

$$\upsilon_p = \frac{3K_p - E_p}{6K_p} \tag{8}$$

Finally, the shear viscosity, G_p, can also be calculated according to the following relationship:

$$G_p = \frac{E_p}{2(1+2\upsilon_p)} \tag{9}$$

On the other hand, the above deduction also implies that the viscous Poisson's ratio, υ_p, is related to both bulk viscosity and shear viscosity under constant temperature as follows [13]:

$$\boldsymbol{\upsilon_p} = \frac{\boldsymbol{3K_p - 2G_p}}{\boldsymbol{2(3K_p + G_p)}} \tag{10}$$

Uniaxial viscous Poisson's ratio exhibits a close to linear dependence on relative density, ranging from about 0.1 at green density to 0.5 at 100 % of theoretical density, as shown by Zuo *et al.* [14-15] on alumina, Okuma *et al.* [16] on calcium aluminosilicate (CAS) glass and Samuel *et al.* [12] on $YBa_2Cu_3O_{6+x}$. The most accepted technique used to determine viscous Poisson's ratio is called discontinuous sinter-forging technique [7,14]. It offers not only an accurate measurement of axial strain rate as well as radial strain rate, but can also alleviate the anisotropic effect brought by the application of uniaxial load. Besides experimental measurements, theoretical models were proposed accordingly. Zuo [15] compared his results with several theoretical models designed for the prediction of viscous Poisson's ratio, and found out that it fitted well with semi-empirical models, such as Rahaman's model [17] as well as Venkatachari and Raj's model [18]. However, Wakai *et al.* [19] pointed out the lack of underlying physics of these models due to the ignorance of grain boundary sliding.

The discontinuous sinter-forging technique was applied using a custom-made loading dilatometer, which has been introduced elsewhere [6,20]. A commercially available 10 mol.% yttria doped ceria (10YDC) nanocrystalline powder (CerPoTech, Tiller, Norway) was used. The as-delivered powder was calcined and milled to have a more homogeneous particle size distribution. The nanocrystalline powder turned to submicron powder with median (d_{50}) average particle size of 150 nm (based on laser diffraction results). Cylindrical specimens were first uniaxially pressed at 100 MPa and subsequently cold isostatically pressed at 300 MPa. The obtained cylinders of 10YDC were 14.804 mm ± 0.9 % in height and 9.39 mm ± 0.6 % in diameter, yielding a relative green density of 62 % ± 2 %. The samples were heated with a heating rate of 30 K/min and held at isothermal furnace temperature from 1188 °C to 1208 °C. The subsequent measurements of the sintering parameters started after the isothermal temperature was reached.

All the "free" sintering experiments of this work were conducted under a minimal load of 10 N (i.e. 0.15 MPa) to maintain the contact between the electrodes and the specimen. All these measurements were conducted under three different electrical fields at the beginning of the experiment: E_{rms} = 0 V/cm, 14 V/cm and 28 V/cm with a frequency of 50 Hz. The moderate increase of the electrical field strength due to the reduction of sample height has already been discussed elsewhere [12]. Discontinuous sinter-forging cycles were performed on samples 'freely' sintered to a desired density of 70 %, 75 %, 80 % and 85 %, and then subjected to a constant load resulting in a pressure of 1.2 MPa and 2.4 MPa according to the specimen dimension at the beginning of the experiment. This mechanical load was applied within a 3 % increase of relative density. At least 20 sinter forging experiments were done, including two complete free sintering experiments.

After the discontinuous sinter-forging experiments, the final relative density was validated through Archimedes' method. Some samples were ground and then polished to a 50 nm finish. Subsequently, the samples were thermally etched at a temperature

50 K lower than the sintering temperature for 1 hour. Finally, the samples were investigated using a scanning electron microscope, Zeiss Ultra55 (Carl Zeiss Microscopy, Oberkochen, Germany). Further, SEM images were imported into an image processing software (analySIS pro, Olympus Soft Imaging Solutions GmbH, Münster, Germany), applying a grain segmentation method for grain size analysis with a factor of 1.6 [21]. This factor was used for estimating the average 3D grain size from the mean 2D grain size. Pores were also analyzed to quantify their properties. At least 1000 pores were investigated per sample. The pore orientation was quantified using the concept of cumulated pore lengths [22-23] in which the weighted pore length was analyzed as a function of the pore orientation angle.

On the base of our previous work [12], we could show that, at a given sample temperature, the uniaxial viscosity (related to kinetics of densification) decreased with increasing electric field and the sintering stress (related to the thermodynamics of sintering) increased. Significant effects could be observed for electric fields well below those required to induce any flash sintering. In this work, bulk viscosity, shear viscosity and viscous Poisson's ratio were calculated as a function of relative density according to Eq. (7 - 9). The resulting curves of bulk viscosity are shown in Figure 1 and the viscous Poisson's ratio in Figure 2. Both bulk viscosity and Poisson's coefficient increase along with the relative density, but change oppositely according to electrical fields. The as-determined viscous Poisson's ratio increases from 0.11 at the relative density of 70 % to 0.24 at the relative density of 85 % under E_{rms} = 0 V/cm. In the case of E_{rms} = 14 V/cm, the viscous Poisson's coefficient increases from 0.12 to 0.27 in the range of 70 % to 85 %, while for E_{rms} = 28 V/cm, the viscous Poisson's ratio increases from 0.19 to 0.31 within a relative density range from 73.5 % to 85 %.

The measured viscous Poisson's coefficient from our work is lower than both Chang's work [5] and Zuo's work [15]. Wakai *et al.* discussed the dependence of viscous Poisson's ratio of the same relative density on different factors and concluded that viscous Poisson's ratio decreased with increasing coordination number, ratio of grain boundary energy to surface energy as well as non-dimensional viscosity, as follows:

$$\boldsymbol{\eta}^* = \boldsymbol{\eta}\frac{\boldsymbol{\Omega\delta D_{gb}}}{\boldsymbol{kTr^2}} \quad (11)$$

where η is the microscopic viscosity, δ is the grain boundary thickness, D_{gb} is the grain boundary diffusion coefficient, T is the temperature, Ω is the atomic volume and r is the particle radius [19]. With this in mind, the difference can be attributed to either the experimentally approved segregation of yttrium at the grain boundary [24] or the inhomogeneous powder compacts with large agglomerates and relative small particles. These two factors can influence not only the ratio between the grain boundary energy and surface energy but also the grain boundary sliding, which subsequently affects the uniaxial Poisson's ratio.

Figure 1: Bulk viscosity as a function of relative density using discontinuous sinter-forging.

Figure 2: Uniaxial viscous Poisson's ratio as a function of relative density using discontinuous sinter-forging. Comparison of the measured viscous Poisson's ratio under different electrical fields of our work with the viscous Poisson's ratio of alumina, gadolinium-doped ceria (the line was added to guide the eye).

Figure 3: SEM pictures and pore orientation distribution of samples after discontinuous sinter forging experiments under 2.4 MPa, a) 0 V/cm; b) E_{rms} = 14 V/cm; c) E_{rms} = 28 V/cm, with the arrow denoting the load direction.

Various attributes need to be considered for the analysis of viscous Poisson's ratio, such as temperature, grain size and possible anisotropic microstructure induced by the applied stress and electric field. As already discussed in our previous paper [12], there is hardly any difference in grain size between the different samples within the density range considered. Moreover, the highest sample temperature in the axisymmetric plane of the sample was kept the same with and without electrical fields by lowering the furnace temperature to compensate the macroscopic Joule heating effect induced by the current flowing through the specimen. Ollagnier *et al.* [11] pointed out that even though the thermodynamic boundaries for isotropic bodies are $0 < \upsilon_p < 0.5$, the Poisson's ratio between -1 and 1 is possible for anisotropic material. Zuo et al. [10,14] pointed out that biased microstructure with preferred pore orientation along the load direction is the main cause of a negative viscous Poisson's ratio determined from continuous sinter-forging experiments. Chang et al. [5] also showed a dramatic increase of viscous Poisson's ratio up to values higher than 0.6 for Gd-doped ceria (GDC) with relative density higher than 84 % and related the result to the anisotropy of the material. Therefore, it is also important to confirm whether or not the microstructure remained isotropic in our case. Exemplary micrographs and pore orientation diagrams are given in Figure 3, where a mechanical pressure of 2.4 MPa was applied on the specimens with a relative density of 80 % under different electric field strengths. These data prove that discontinuously sinter forged samples remain isotropic after the experiments, which is required for the evaluation of sintering parameters characteristic of an isotropic material, as assumed theoretically according to Eq. (3 - 4).

Therefore, it is conceivable to conclude that the observed difference of the viscous Poisson's ratio under electrical fields can not be attributed to above mentioned variables. According to Eq.10, the viscous Poisson's ratio can be formulated as a function of bulk viscosity and shear viscosity. Riedel et al. [25] developed a method to estimate bulk viscosity and shear viscosity of isotropic porous materials from the knowledge of microstructure. The densification process is related to the microscopic motion of individual particles. The normal velocity vector to the grain boundary is proportional to the grain boundary diffusion coefficient, while the tangential velocity is linked to the microscopic viscosity. Wakai et al. [16] analyzed how shear viscosity and viscous Poisson's ratio depend on grain boundary sliding, local structure, and relative density. When grain boundary diffusion is the dominating mechanism during sintering, bulk viscosity is dependent on grain boundary diffusion coefficient, and shear viscosity depends on both grain boundary diffusion coefficient and grain boundary sliding, which is characterized by the non-dimensional viscosity, η^*: As shown in Figure 1 and Figure 4, both bulk viscosity and shear viscosity decrease with the application of electric field. Since bulk viscosity is inversely proportional to the grain boundary diffusion coefficient [19], the experimental result suggests that the grain boundary diffusion coefficient is enhanced by the application of electric field. The slight change in the bulk viscosity indicates that this enhancement by the electrical fields is not very significant. When the grain boundary sliding occurs freely ($\eta^* = 0$), the shear viscosity depends on grain boundary diffusion only, so that the effect of electric field should be the same with that for bulk viscosity. However, the comparison of Figure 1 with Figure 4 shows that the influence of electric fields on shear viscosity is more significant than that on bulk viscosity. The result implies following statements: (i) Non-dimensional viscosity is positive; (ii) Non-dimensional viscosity decreases with electrical fields, because shear viscosity increases with η^* [16]. Therefore, the increase in viscous Poisson's ratio observed under electric field can be related to the decrease in η^*, even though there should be a slightly increase in the grain boundary diffusion coefficient on the base of decreasing bulk viscosity with electrical fields. The decreasing non-dimensional viscosity could be related to decreasing microscopic viscosity, which is related to the grain boundary structure or a microscopic temperature gradient. Both can be possibly influenced by the electrical fields. To clarify further this point, the exact influence of electrical field on the constitution of the grain boundaries and associated space charge layers will be investigated in a further work.

Figure 4: Shear viscosity as a function of relative density using discontinuous sinter-forging.

To conclude, by carrying out discontinuous sinter-forging experiments under moderate AC electric fields and constant sample temperature in order to exclude any Joule effect, we could show for yttrium-doped ceria that:

(1) No microstructural anisotropy is induced by the loading conditions, assuring reliable strain data for determining Poisson's ratio.

(2) Bulk viscosity of 10YDC increases with densification and slightly decreases under electric field.

(3) Viscous Poisson's ratio as well as the shear viscosity is significantly influenced by moderate electric fields. This effect might be related to a modification of the grain boundary properties and an easier sliding under electric field.

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