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Shrinkage control of yttria-stabilized zirconia during ac electric field-assisted sintering

R. Muccillo *, E.N.S. Muccillo *

Center of Science and Technology of Materials – CCTM, Energy and Nuclear Research Institute – IPEN, Travessa R 400, Cidade Universitaria, São Paulo, SP 05508-900, Brazil

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Abstract

Yttria-stabilized zirconia pellets were easily and accurately sintered to a predetermined sintering level, including near full density, in an experimental arrangement consisting of a vertical dilatometer and an ac adjustable power supply. Conventional and electric field-assisted sintering steps can be combined, starting from temperatures above 800 °C and applying 1000 Hz alternating electric fields in the range 80–160 V cm^{-1}. A systematic comparison of the microstructures and impedance diagrams of samples conventionally and electric field-assisted sintered to the same density levels shows that the non-conventional sintering method gives significantly small grains in agreement with previous observations. The results show that this sintering method can be applied to produce materials partially sintered at any desired shrinkage level.

Keywords: Sintering; Dilatometry; Impedance; Microstructure; ZrO_2

1. Introduction

Electric field-assisted sintering without application of a mechanical stress of polycrystalline ceramic materials, mostly investigated on zirconia–yttria compounds, is under intense investigation. Sintering a pre-formed ceramic body in a few seconds, with low cost equipment, is highly attractive. As the basic mechanisms responsible for this short time and low temperature sintering are not yet fully explained, it is essential to take into account the exact role of the intrinsic and extrinsic parameters, and to vary these parameters to evidence potential experimental artifacts. As intrinsic parameters we define here the applied ac with varying frequencies or dc electric fields, which may act at the interfaces or in the bulk, and the extrinsic parameters as those related to the specimen geometry and electrical conductivity, temperature, etc., which determine the power dissipation and the electric current density.

Earlier studies on tetragonal zirconia polycrystals (3YSZ) emphasized the enhanced sintering rate due to dc or ac electric field application.[1] In that case, the ac electric field was found to be more effective than a dc field to reduce the sintering temperature and the final average grain size. For yttria fully stabilized zirconia (8YSZ) a reduction of the sintering temperature needed for the densification onset was explained as a consequence of its relatively higher ionic conductivity.[2] The primary action of the ac electric field on green compacts was found to be the welding of the grains/particles.[3] Depending on the nature of the material under investigation and the experimental parameters, the result of the application of an electric field to a ceramic compact may be restricted to this stage of welding of the grains.[4]

In spite of the short sintering time for densification with application of an electric field, an impressive reduction of the sintering temperature of fully stabilized zirconia was reported when high voltages were applied.[5] The electric current density was also claimed to play an important role for the success of this method of sintering: relatively very low current densities (1 mA mm^{-2}) show no effect, i.e., do not provoke shrinkage, whereas current densities 65 times larger result in appreciable shrinkage. Moreover, the interruption of the current flow stops the shrinkage and

* Corresponding authors. Tel.: +55 11 31339203; fax: +55 11 31339276.
E-mail addresses: muccillo@usp.br (R. Muccillo), enavarro@usp.br (E.N.S. Muccillo).

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sustaining the current in the electrolytic region leads to a large increase in densification kinetics.[6] Another interesting reported feature is that the densification curve shows no difference in experiments with the application of the electric field during heating up the samples or at a fixed temperature.[2] Examination of the microstructure of electric field-assisted sintered cubic stabilized zirconia evidenced a limitation of this technique. The high electric currents changed the main fracture mechanism from the intragranular to the intergranular mode in a clear demonstration of grain boundary weakening, namely, susceptible to fracture.[7]

Various recent successful attempts have also been made to demonstrate that this sintering method can be applied to several electroceramics, such as Y_2O_3-stabilized ZrO_2,[2–9] MgO-doped Al_2O_3,[10] Co_2MnO_4,[11] Gd_2O_3-doped $BaCeO_3$,[12] SiC,[13] Gd_2O_3-doped CeO_2,[14] $SrTiO_3$,[15] SnO_2,[16] and Y_2O_3.[17]

In the reported works, the main differences in the experimental approach refer to the specimen shape and the applied electric field (ac or dc). In some experiments either an electric field was applied during the sample heating or a suitable electric field was applied at a constant temperature, where the sample electrical conductivity is estimated to be sufficient to enable an electric current pulse to produce the electric field-assisted sintering. In the first case, the current pulse is triggered when a certain temperature and therefore an adequate sample electrical conductivity is reached. In the second case, when an appropriate voltage is applied and when an incubation time has elapsed.[10] Both cases have been currently reported as "flash sintering" because the elapsed time for the completion of the shrinkage lasts few seconds.

There is a continuous discussion in the scientific literature on the advantages of short-time sintering of ceramics as compared to traditional high temperature/large dwelling times. The former allows producing fine-grained ceramics, whereas in the latter grain growth is unavoidable. Sintered ceramics with small average grain size should present enhanced mechanical properties.[18] The question now, with the fairly recent electric field-assisted sintering, flash sintering, fast sintering, SHS-quick processing sintering and others, how those techniques may produce specimens with enhanced mechanical properties at relatively low temperatures and short times. There are few papers dealing with the evaluation of the mechanical properties in fast sintered ceramics.[19]

Here, the recently reported experimental facility was used to continuously control the sample shrinkage resulting from the electric current pulses.[8] Using this technique, multi-step sintering including electric current pulse sintering steps were developed, allowing for tuning the desired specimen shrinkage level. These results represent additional experimental data to contribute to understand the mechanisms responsible for the electric field-assisted sintering of electroceramics.[10,20,21]

2. Experimental procedure

All samples were prepared with the commercial powder (cubic ZrO_2:8 mol% Y_2O_3 TZ-8Y from Tosoh, Japan, hereafter 8YSZ) composed of 25 nm particles agglomerated into 75 μm spherical granules. The dried powders were pressed uniaxially under 46 MPa and then isostatically under 200 MPa. The green relative densities were approximately 50%. The cylindrical samples were about 5 mm in diameter and thickness approximately 5 mm. To improve the uniformity of the electric current distribution through the samples, their parallel surfaces were covered with chloroform-diluted platinum paint (Degussa Demetron A308).

A pc controlled vertical high temperature dilatometer (Anter model 1161, Pittsburgh, USA) was used. Even though the dilatometer may be operated under controlled oxidizing and reducing atmospheres, all the experiments were performed under static air. It can be operated up to 1600 °C with 1 μm sensitivity. This equipment allowed us to continuously monitor the sample shrinkage and to perform in situ electric field-assisted sintering experiments. Four platinum wires isolated in a 4-holes alumina capillary connected these current collectors either to the power supply or to the impedance analyzer. The dilatometer thermocouple measured the average local temperature close (∼5 mm) to the sample, which could be visualized in the pc monitor. Further details may be found elsewhere.[8]

For the electric current intensity measurement and recording, a variable (helipot) resistance was inserted in the current circuit. This equipment easily enables to continuously adjust the electric field intensity and time profiles.

The experimental sequence consists first in setting the temperature profile of the dilatometer (dwelling temperatures and time, heating and cooling rates).When the dwelling temperature is reached, the power supply is connected to the sample, and the voltage is turned on up to the occurrence of the electric current pulse and the consequent attained shrinkage level. The shrinkage behavior is continuously visualized in the digital gauge of the dilatometer. In this way, by varying the applied voltage, we can adjust the shrinkage rate and stop the densification at any level, monitoring the gauge.

The experimental procedure consisted in: (a) to produce a shrinkage level by adjusting the applied electric voltage magnitude (10–65 V), promoting the electric current pulse; (b) to stop the shrinkage advance at any pre-selected level, simply by interrupting the supplied voltage; (c) to trigger subsequent electric current pulses inducing additional shrinkages; (d) to progressively approach the full densification, avoiding a sample overheating, (and therefore limiting the grain growth); (e) to combine conventional sintering and electric field-assisted sintering steps.

Polished (16, 5, 3 and 1 μm average particle diamond paste) and thermally etched non-metalized surfaces of the electric field-assisted and conventionally sintered specimens were observed in an Inspect F50 FEI FEG-SEM microscope. Some of these polished specimens were mounted with Buehler epoxi thermoset and had the Vickers hardness evaluated in a Buehler Macro Vickers 5112 Hardness Tester with 150 N load during 15 s.

The $[-Z''(\omega) \times Z'(\omega)]$ impedance spectroscopy data, before and after the electric field-assisted sintering, were obtained with a 4192A Hewlett Packard impedance analyzer with a 362 HP controller in the 5 Hz–13 MHz frequency range $[f = (\omega/2\pi)]$ under a voltage amplitude of 200 mV and at temperatures in the oxide ion conductivity region.