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An experimental setup for shrinkage evaluation during electric field-assisted flash sintering: Application to yttria-stabilized zirconia

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Abstract

Analyses of electrochemical impedance spectroscopy plots and dilatometric curves of ZrO_2:Y_2O_3 (YSZ) green compacts upon sintering show the possibility of choosing the shrinkage level of the green pellet by passing a current flash through the interparticle regions. The experiments consisted on inserting a YSZ green compact in a dilatometer sample holder, connecting either to a power supply or to an impedance analyzer, and monitoring the shrinkage upon sintering with and without applying an ac voltage in the 800–1000 °C temperature range. This procedure allows taking the sample from the first to the second sintering stage in few seconds without the occurrence of significant grain growth.

Keywords: Flash-sintering; Dilatometry; Impedance spectroscopy; FEG-SEM; Yttria-stabilized zirconia

1. Introduction

In the last few years many experiments have been reported on the non-traditional sintering behavior of several ceramic materials, particularly coupling the effects of heat to the effect of applying either dc or ac electric field.[1–13] Electric current activated/assisted sintering, also named spark plasma sintering (SPS), requiring simultaneous application of pressure, has been also extensively studied.[14] Considerable shrinkage has been obtained by a new technique named flash sintering by Raj and co-workers by simply applying an electric field at temperatures well below the temperature required for attaining full density.[1–9] Bearing in mind that ionic conductivity in oxide solid electrolytes has contributions to charge transport in the bulk (grains) and in the interfaces (mainly grain boundaries), the application of a short ac voltage pulse at frequencies leading to a flow of an electric current preferentially through the grain boundaries could weld the grains via Joule heating. This idea was applied to promote primarily grain welding in yttria-stabilized zirconia[15] and in gadolinium-doped barium cerate solid electrolytes.[16] Mass transport as well as charge transport might be considered, taking into consideration the nature of the applied electric field. The electrical behavior of the ceramic material as well as its geometrical dimensions and shape have to be taken into account for the suitable choice of the electrical parameters, namely the electric power and voltage, important for the occurrence of an electric current flash across the sample to be sintered. The distribution of particle size, the average particle size, the particle shape, the packing procedure, the pore average size and content and the green density are also parameters to be considered for a successful sintering, because they are decisive on the electrical power to be delivered to the sample and also on the available pathways for the electric current across the sample. The impedance spectroscopy technique, considered a powerful technique for the analysis of the electrical behavior of ceramics, is of utmost importance for the evaluation of the bulk and interfaces (mainly grain boundaries) electrical resistivities before, during and after sintering. The experimental setup for partially or fully flash (5 s) sintering ceramic materials to chosen shrinkage values, consisting of a dilatometer connected either to a power supply or to an impedance analyzer, are here described in detail along with the results on yttria-stabilized zirconia solid electrolytes after conventional (at 1500 °C) and electric field-assisted (800–1000 °C, 80–150 V/cm, 500–1000 Hz) sintering.

2. Experimental

Commercial ZrO_2:8 mol% Y_2O_3 ceramic powders from Tosoh, Japan, consisting of spray-dried granules of nanosized particles with $16 \pm 3\ m^2/g$ surface area, were used in this study.

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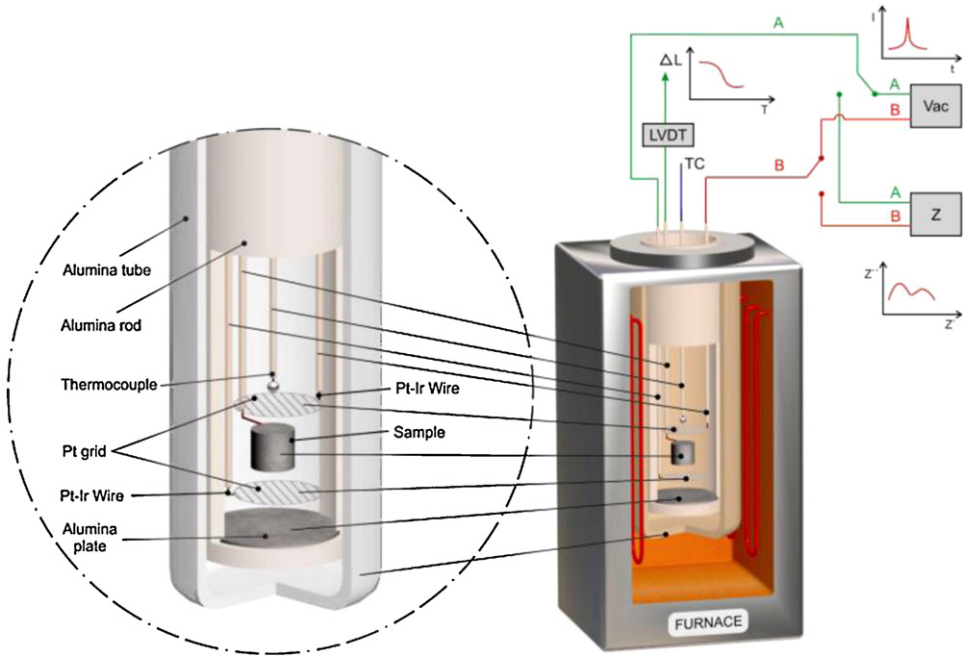

Fig. 1. Sketch of the experimental setup for dilatometric measurements, application of voltage (Vac) and impedance spectroscopy data collection (*Z*) of green ceramic pellets. LVDT: linear variable differential transformer; TC: Pt-Pt10%Rh thermocouple; ΔL: linear shrinkage.

The powders were uniaxially cold-pressed in ϕ5 mm × 5 mm thickness at 10 MPa with steel dies and isostatically at 210 MPa. Green densities were typically 45% TD.

The experimental setup for flash-sintering green pellets consisted on a pc controlled vertical dilatometer (Anter 1161, ambient to 1650 °C, minimum linear displacement detection level 0.5 μm) with the sample holder connected, via alumina-insulated platinum wires, to a homemade power supply designed to apply ac voltages up to 70 V in the frequency range 500–1080 Hz. Fig. 1 shows a schematic drawing of the whole experimental arrangement for measuring the shrinkage/expansion simultaneously to the application of a ac voltage to produce the flash sintering and the connections to a Agilent 4294A impedance analyzer for collecting impedance data in the 40 Hz to 110 MHz range with ac voltage signal in the 100–200 mV range. Impedance spectroscopy measurements were also carried out inside a sample chamber inserted in a tubular furnace in sintered specimens after removal of the platinum paste and deposition of silver paste.

A flash-sintering experiment consists in positioning the green pellet on top of a Pt grid in the bottom of the vertical dilatometer sample holder, placing another Pt grid on top of the green pellet, gently positioning the alumina pushrod on top of the Pt grid, and resetting the digital gauge coupled to the pushrod. The dilatometer sample holder slides then vertically inside the dilatometer furnace. In the sequence the temperature profile (heating and cooling rates, temperature dwellings) is settled, a voltage being applied when the sample reaches an electrical resistance value suitable for passing an ac current through the interparticle regions. Obviously this value depends on the material to be submitted to flash. For the yttria-stabilized zirconia green pellets used in our experiments this value is in the kΩ range. A flash of current, typically 0.1–0.5 A for a 1–10 kΩ sample resistance flows through the sample along with several paths, which depend on the packing structure of the green body. The flash, which lasts few seconds before the voltage is manually turned off, produces enough Joule heating to weld the packed particles and eventually to densify the sample. The densification depends on the values of the applied voltage and frequency, attained ac current, the pulse half-width, the number of applied pulses, and, very important, to the green microstructure (particle morphology, average particle size, particle consolidation). Experimental studies on the evaluation of these contributions are underway.

The sintered specimens, either by applying an ac voltage in the 800–1000 °C range or conventionally in a furnace, were polished with diamond paste (sequentially with 15, 3, 1 μm average particle size) and thermally etched for observation in a FEI Inspect F50 FEG-Scanning Electron Microscope.

3. Results and discussion

Dilatometric results of the effect of the application of an ac voltage during sintering a ϕ = 5 mm × 5 mm thick 8YSZ green pellet are shown in Fig. 2. One sample was heated up to 800 °C and submitted to an ac voltage (80 V/cm, 1000 Hz). After approximately 15 s an electric current is triggered and manually stopped when it reaches approximately 150 mA. If the voltage is not turned off, the current increases continuously and melting of the specimen might occur due to local Joule heating. It occurred indeed in previous experiments, before we noticed that hundreds of mA is the limit to avoid the 8YSZ sample melting. In the example shown in Fig. 2, the final shrinkage with only one current pulse is 350 μm, approximately 25% of the shrinkage the specimen reaches when conventionally sintered at 1500 °C. Subsequent flashes of current could be applied

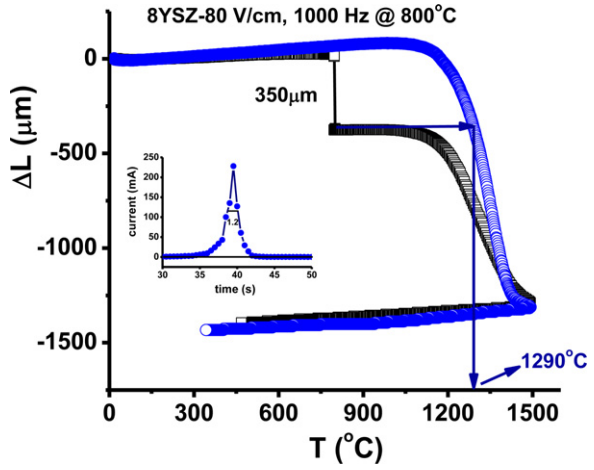

Fig. 2. Dilatometric measurements of 8YSZ cold-pressed ceramic pellets up to 1500 °C with (flash-sintering) and without the application of an ac voltage at 800 °C. Inset: current versus time electric current flash.

to the sample to obtain further shrinkage levels. In the experiment here discussed, after the flash the sample is heated up to 1500 °C and cooled down to room temperature to compare the shrinkage behavior with a similar sample (same material, same dimensions, same pressing conditions) conventionally sintered in the dilatometer up to 1500 °C. To the limit of the programmed temperature as well as during cooling down, both curves merge precisely within the experimental error of the dilatometer gauge.

The electric current through the specimen during the flash procedure shown in Fig. 2 is collected as a function of time and is plotted as an inset in Fig. 2. The flash profile shows that the half-width is only 1.2 s. This flash is sufficient to promote at 800 °C a shrinkage level equivalent to the one attained after a conventional sintering at 1290 °C, shown by the arrows in Fig. 2, i.e., a jump from the first to the second stage of sintering.

Additional information may be gathered by the experimental setup by collecting impedance spectroscopy data before and after the application of the flash sintering procedure. Fig. 3 shows the results of the following experiment with a 8YSZ green pellet: heating rate 10 °C/min up to 1500 °C; when the sample temperature reaches 500 °C, the impedance data $[-Z''(\omega) \times Z'(\omega)]$ is collected in the impedance analyzer. The impedance plot (one of the insets in figure) shows a semicircle typical of pressed pellets with the overlapped contributions due to the bulk and the interfaces, mainly pores, with a total resistance of 70 kΩ. When the sample temperature reaches 800 °C, the impedance data is collected again. Its shape is similar, with a lower value of the total resistance (15 kΩ). The sample is then connected to the power supply and the flash sintering procedure is carried out: 120 V/cm at 1000 Hz is applied to promote a current flash, which is monitored by the voltage drop across a 10 Ω resistance in series with the sample. When the value of this voltage reaches 1 V (∼100 mA current), the applied voltage is turned off and the flash is finished. Subsequent flashes may be applied, but requiring higher voltages because even though the sample resistance is lower (due to partial sintering), less easy paths for the current are available due to the closure of the interparticle region (pore elimination). Finished the flash, with the shrinkage being monitored in the dilatometer, the power supply is disconnected and the impedance analyzer is connected again to evaluate the effect of the flash on the electrical behavior. The effect on the impedance data is striking: the impedance diagram is now composed of at least two semicircles, the low frequency one due to interfaces (grain boundaries and pores) and the high frequency one due to the bulk (grains) of the sample. The total resistance decreased from 15 kΩ to 930 Ω (16 times), 680 Ω due to the

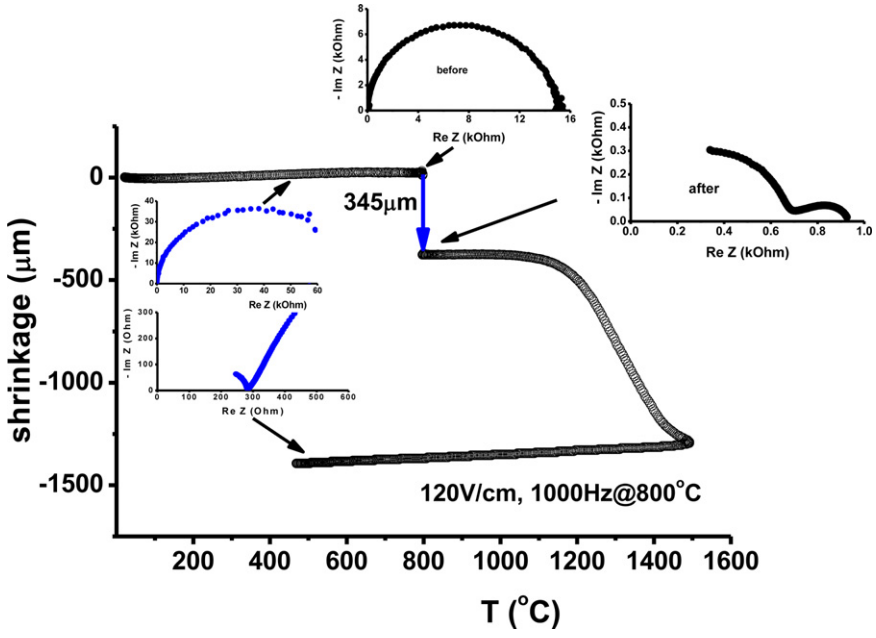

Fig. 3. Dilatometric measurement of a 8YSZ cold-pressed ceramic pellet with application of 120 V/cm, 1000 Hz, at 800 °C during 5 s. Insets: impedance spectroscopy diagrams measured at 500 °C and 800 °C before and after the voltage flash.

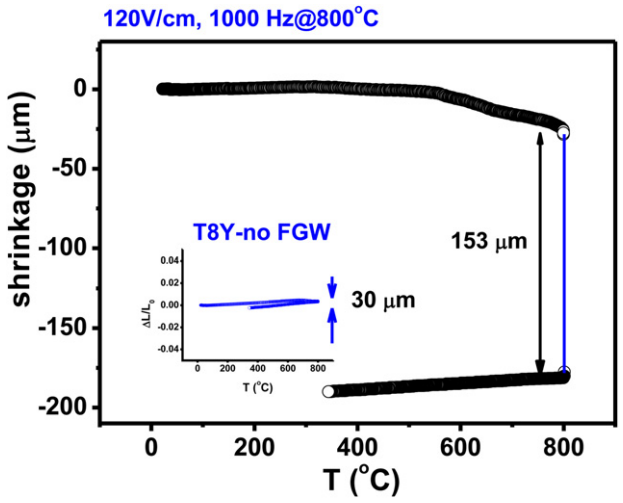

Fig. 4. Dilatometric measurements of 8YSZ cold-pressed ceramic pellets up to 800 °C with and without (inset) the application of 120 V/cm, 1000 Hz.

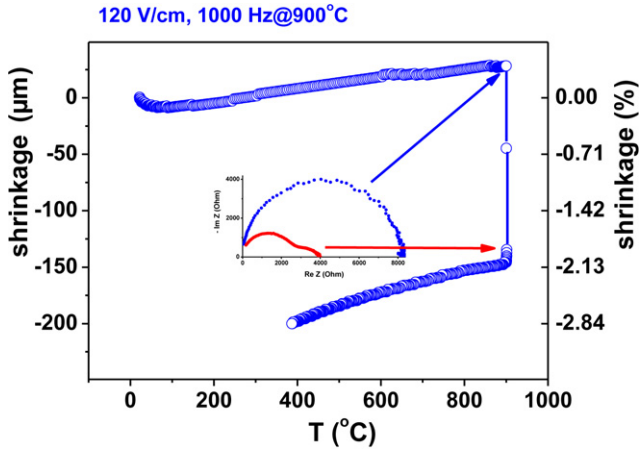

Fig. 5. Dilatometric measurements of 8YSZ cold-pressed ceramic pellets up to 900 °C with application of 120 V/cm, 1000 Hz. The arrows point to the temperature the impedance diagrams (inset) were measured.

bulk and 250 Ω to the interfaces. After that, sintering proceeds with the habitual pattern. The impedance data are again collected when the temperature reaches 500 °C. The total resistance of the sample is determined as 280 Ω (of the same order of magnitude reported for spark plasma sintered 8YSZ[17]), to be compared with 70 kΩ (250 times higher) measured at the same temperature in the green pellet. Minor differences in these resistance values may be expected due to the varying dimensions of the samples in each situation. The temperature of 500 °C was chosen because is the temperature belonging to the electrolytic region (oxide ion conduction) of 8YSZ.

A different way to see the effect of the ac current flash during a dilatometric measurement is by performing the experiment without further heating the specimen to the third sintering stage. In this case, an ac voltage is applied to the 8YSZ specimen at 800 °C and the specimen is cooled down to room temperature. The specimen was heated up to 800 °C and 120 V/cm was applied for 10 s. The results are shown in Fig. 4. The specimen shrank 153 μm, the voltage was turned off and the specimen was cooled down. A similar specimen was subjected to the same thermal cycle and the shrinkage was recorded. The total shrinkage without the electric current flash was 30 μm, showing that the thermal effect on shrinkage is 5 times lower than the thermal + electric field effects.

Fig. 5 shows another similar experiment, now with the ac voltage applied at 900 °C, the inset depicting figures of the impedance diagrams (details in Fig. 6) measured before and after the flash. Eventual small differences in the dilatometric profiles in Figs. 5 and 6 are due to the platinum grid spring-loaded to the specimen.

The experimental setup with the impedance analyzer connected to the sample during the dilatometric measurement allows for collecting impedance spectroscopy data at any temperature. As the data collecting time of the impedance analyzer for the whole frequency range (40 Hz to 110 MHz) is approximately 21 s in the HP4294A impedance analyzer and the heating rate is 10 °C/min, the temperature of the sample varies less than 1% during the impedance spectroscopy measurement. Fig. 6 shows $[-Z''(\omega) \times Z'(\omega)]$ impedance diagrams of the 8YSZ ceramic pellet measured at 710 °C before the application of the ac voltage (total resistance ~40 kΩ) and when cooling down after turning off the voltage that provoked the electric current flash (~2.3 kΩ). Besides the large difference in the total resistance, the impedance diagram measured before the flash has only one semicircle representing the contributions of the packed

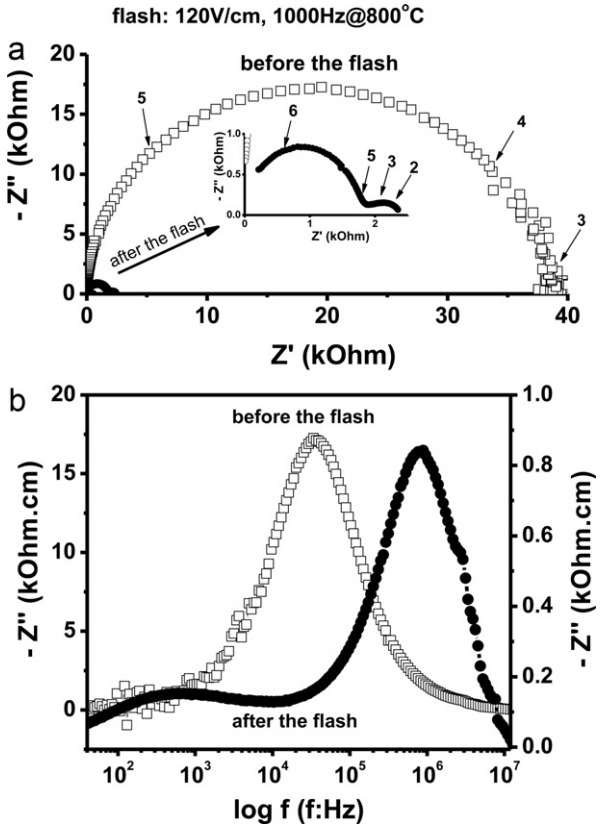

Fig. 6. Impedance spectroscopy (a) and Bode (b) diagrams of 8YSZ pellets after heating to 710 °C and measured at 710 °C after the application of 80 V/cm, 1000 Hz, at 800 °C. The numbers with pointing arrows are the logarithm of the frequency (Hz) of the applied 200 mV ac signal.

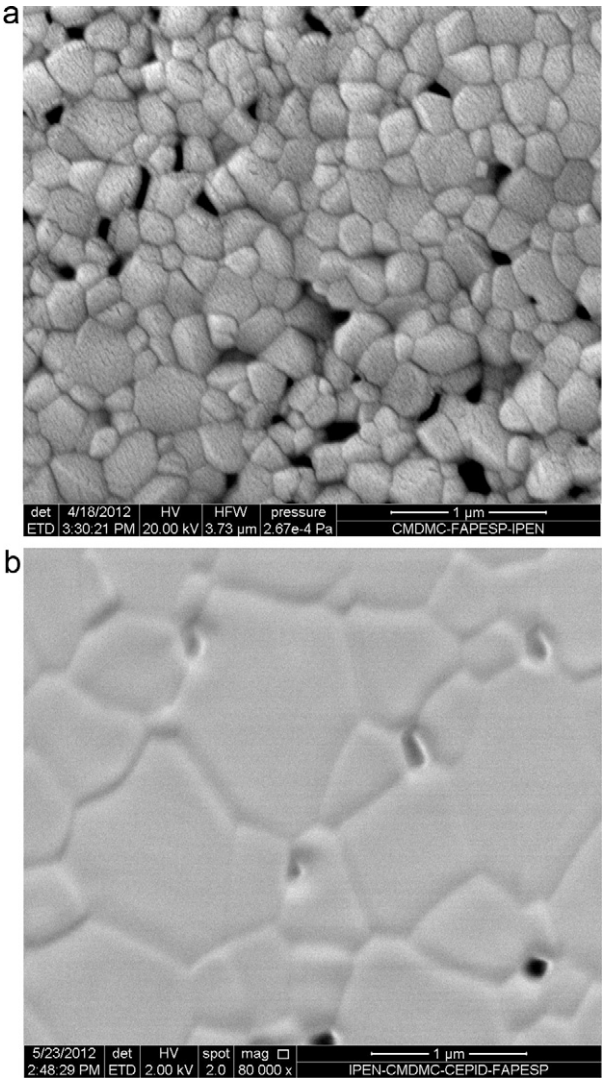

Fig. 7. FEG-SEM micrographs of a polished and thermally etched 8YSZ pellet surfaces. (a) Specimen exposed to 120 V/cm, 1000 Hz, at 800 °C during 5 s. (b) Specimen sintered at 1300 °C.

particles and the interfaces – mainly pores, because the specimen is still in the first sintering stage. The impedance diagram measured after the flash, on the other hand, shows two well defined semicircles, typical of specimens in the second stage of sintering, with contributions to the electrical resistivity due to the bulk (now grains and not only particles) and to interfaces (now mainly grain boundaries and not dominated by pores). The Bode diagrams, which allows for better viewing the frequency dependence of the electrical response, are also shown (Fig. 6b).

Another feature of the flash sintering is the final submicron microstructure in comparison with the microstructure of conventionally sintered specimens. Fig. 7a shows a FEG-SEM image of a polished and etched surface of a 8YSZ green pellet after flash sintering during 5 s with application of 120 V/cm at 800 °C. According to Fig. 2, this flash sintering procedure is equivalent, in terms of attained shrinkage level, to a sintering temperature of 1290 °C. Even though Joule heating promotes sintering, in this experiment the attained equivalent temperature is lower than the temperature of maximum retraction (the inflection point in the dilatometric curve). Moreover, the time the Joule heating acts inside the sample is too short to promote grain growth. The average grain size is below 500 nm and intergranular pores are visible, probably due to both the localized fast firing pathways in the green pellet and that only 25% of the maximum possible specimen shrinkage. The FEG-SEM image of a 8YSZ pellet sintered at 1300 °C is shown in Fig. 7b. The difference between both images is striking. Conventional sintering produces samples with much larger grains due to the collective heating effect over the whole pellet (approximately 4 h total time inside the furnace with 10 °C/min heating and cooling rates). Similar results have already been ‘ reported.[1,3,7,11]

4. Conclusions

An experimental facility, consisting on a vertical dilatometer, a ac power supply, an impedance analyzer and a data logger, was used to carry out in situ impedance spectroscopy measurements before and after flash sintering ceramic green pellets. Dilatometric experiments were carried out in the first stage of sintering ZrO_2:8 mol% Y_2O_3 ceramic pellets with and without the application of an ac voltage at a frequency corresponding to the response of the intergranular region of the pellet. The shrinkage level may be substantially increased upon application of the ac voltage, provoking the passage of an electric current through the interparticle region of the pellet. Joule heating is probably the main responsible for the large densification attained by the stabilized zirconia pellets. The impedance spectroscopy technique was successfully used to evaluate the oxide ion resistivity decrease upon flash sintering. Flash sintering promotes densification but inhibits grain growth due to the short elapsed time of the current flash through the ceramic sample. Even though we report results in an electroceramic material, a solid electrolyte, the technique does not preclude its application to other ceramic materials, provided proper experimental arrangements are available.

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