



Improved densification and ionic conductivity in flash-sintered gamma-ray irradiated yttria-stabilized zirconia

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ABSTRACT

Experiments on electric field-assisted pressureless sintering were conducted, with a dilatometer connected to a power supply, in zirconia: 8 mol% yttria polycrystalline ceramics exposed to gamma radiation. During heating to 1000 °C, an electric field of 150 V cm⁻¹ was applied at room temperature up to a sharp thickness shrinkage occurred (flash sintering). It was found that the higher the imparted gamma radiation dose the higher the shrinkage. The shrinkage enhancement and the increase of the total ionic conductivity, when compared to non-irradiated sample, were probably due to the increase of oxygen vacancy concentration after exposure to gamma radiation.

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Sintering ceramic pieces to high density has been achieved primarily by heating green specimens for a certain time at a temperature below their melting point. The temperature and the time usually define the final density as well as the average grain size. Energy savings is achieved by decreasing the temperature and/or the time, for example, mixing the ceramic with low melting point sintering aids. Electric field-assisted sintering, either with or without applying pressure has been proposed as alternative techniques for producing dense samples at temperatures lower than those used in conventional sintering. Since the pioneering work of Cologna and Raj in 2010 on sintering ZrO₂: 3 mol% Y₂O₃ polycrystalline ceramics in few seconds (then the name “flash sintering”) by applying an electric field at temperatures well below that used in conventional sintering [1], several ceramic materials were flash sintered to high densities in relatively shorter temperatures and times usually without the grain growth that happens in conventionally sintered ceramics [2–6].

Yttria-stabilized zirconias (ZrO₂: 8 mol% Y₂O₃ - 8YSZ and ZrO₂: 3 mol% Y₂O₃ - 3YSZ) find application as solid electrolytes in solid oxide fuel cells and oxygen pumps (8YSZ) and in dental prosthesis (3YSZ). Both are electroceramics with conductivity predominantly ionic with about 1 eV activation energy, and oxygen vacancy is the charge carrier [7]. In yttria-stabilized zirconia, at temperatures lower than approximately 600 °C, oxygen vacancies are either free or bound to dopant ions forming cation-vacancy association (Y³⁺-V_O²⁻-Y³⁺ dipolar complexes), the former being responsible for the ionic conductivity σ ($\sigma = n \cdot q \cdot \mu$, n is the density, q the charge and μ the mobility of the charge carrier). The exposure

of a ceramic body to gamma-ray radiation may produce F-like color centers (one or two electrons trapped at an oxygen ion vacancy) [8] and increase the oxygen vacancy concentration by the production of displaced atoms [9]. The increase in the electrical conductivity of zirconia exposed to radiation (Radiation Induced Conductivity - RIC) have already been reported [10–13] and considered to be due to an increase of the oxygen vacancy concentration via two mechanisms: release of the oxygen vacancy by dissociation of the dipolar complexes [13,14] and displacement of oxygen atoms to interstitial position produced by internal bombardment by the gamma-ray induced Compton electrons [9].

The main idea behind this work was to evaluate whether the increase in oxygen ion concentration promoted by exposing yttria stabilized zirconia ceramics to gamma radiation could enhance their electric field-assisted flash sintering.

Commercial cubic yttria-stabilized zirconia powders, ZrO₂: 8 mol% Y₂O₃ (TZ-8Y, Tosoh, Japan), were uniaxially and isostatically cold-pressed at 50 MPa (Kratos press, Brazil) and 200 MPa (National Forge Co., Irvine, CA, USA), respectively, to produce ϕ 5 mm \times 5 mm thick pellets. A ⁶⁰Co gamma-cell was used to irradiate the samples during 2 min, 5 min and 10 min, yielding to the cylindrical ceramic pieces 22.9 Gy, 56.3 Gy and 112.1 Gy accumulated doses, respectively. Conventional sintering and electric field-assisted sintering were carried out in a vertical dilatometer (Unitherm 1161, Anter, Pittsburgh, PA, USA). For the electric field-assisted sintering the green 8YSZ pellet was positioned in the dilatometer sample holder between platinum disks, which were connected with platinum leads to an AC power supply (custom-made, 0–54 V, 0–6 A, 100–1200 Hz) [15]. The dilatometer furnace was programmed to 1000 °C/5 min with 10 °C min⁻¹ heating and cooling rates. A 150 V cm⁻¹ electric field, limiting the electric current to 1 A, was applied to the sample at room temperature, and turned off after

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2 min at 800 °C. The parallel surfaces of the sintered samples were observed in a scanning electron microscope (Inspect F50 FEG-SEM, FEI, Brno, Czech Republic). Impedance spectroscopy measurements were carried out from 5 Hz to 13 MHz, 20 frequencies per decade, 200 mV input signal, with an impedance analyzer (Hewlett Packard 4192A, USA) connected to a controller (Hewlett Packard 360, USA). Three cylindrical samples, with their parallel surfaces covered with

silver electrodes, were spring-loaded inside a sample chamber, which was inserted in a programmable tubular furnace (EDG, Brazil). A special software was used to collect the $[-Z''(\omega) \times Z'(\omega)]$ impedance data at 400 °C [16].

Fig. 1a shows dilatometric curves of electric field-assisted ZrO_2 : 8 mol% Y_2O_3 (8YSZ) polycrystalline pellets exposed to gamma radiation for 2, 5 and 10 min. An electric field of 150 V cm^{-1} was applied at room temperature and switched off 2 min after the shrinkage due to flash sintering starts. The temperature at which the shrinkage starts were 860 °C, 880 °C and 900 °C for 2 min, 5 min and 10 min exposure time, respectively, and the corresponding linear shrinkages were 11.3%, 13.3% and 14.5%, respectively. Fig. 1b shows dilatometric curves of a non-exposed and an exposed to 5 min gamma radiation 8YSZ specimens, the shrinkage being comparatively negligible for the former (0.2%) and 13.3% for the latter. Two are the heat sources in a dynamic flash sintering (application of an electric voltage during heating a polycrystalline ceramic specimen): the dilatometer furnace, where heat reaches the outside surfaces of the specimen, and Joule heating produced by the electric current pulses throughout the interparticle region (inside surfaces) of the specimen. This means that in that sintering technique the specimen shrinks continuously in the bulk as well as from the surfaces, being more efficient the bulk process according to several reports of sample center and near the border different microstructures [17]. One might consider that higher exposure time means higher gamma-ray doses and, consequently, increased F-center concentration, which are bleached continuously by the external (furnace) and internal (Joule heating) heat sources. This is shown in Fig. 1c, which is a zoom of the -0.6% – 0.6% thickness variation in the room temperature–850 °C range. Expansion of the thickness of the gamma-ray irradiated 8YSZ samples is detected, increasing for higher exposure time. The behavior of the non-irradiated sample is also plotted. A simple explanation, based on the annealing of F-like centers is here proposed: 1) during irradiation the ceramic sample is flooded with electrons released preferentially from the Y^{3+} ions due to their lower binding energy to the oxygen vacancies; 2) the electrons are trapped by the positively charged oxygen vacancies forming F centers (one electron per vacancy) and/or F centers (two electrons per vacancy); 3) the lattice parameter increases as the electrons are thermally released from the oxygen vacancies due to the increase of the coulombic repulsion force between the oxygen vacancies and the 3 impurity; 4) the sample expands. Fig. 1b shows the dilatometric curves from room temperature to 1000°C of an YSZ sample after 5 min gamma irradiation and a similar sample submitted to 150 V cm^{-1} . Under heating without the electric field, the shrinkage is negligible (0.2%) comparing to the shrinkage of the flash sintered sample (13.3%).

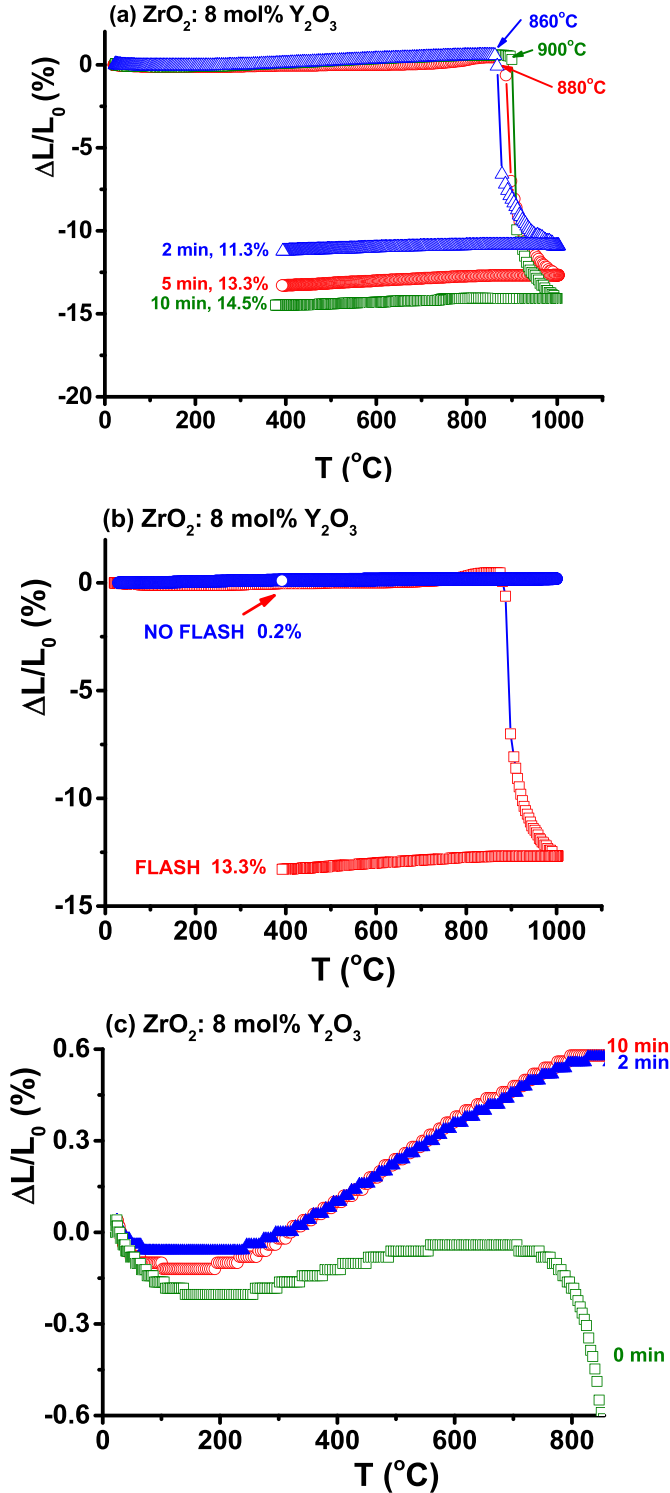


Fig. 1. Dilatometric curves of ZrO_2 : 8 mol% Y_2O_3 ceramic pellets (a) exposed to 22.9 Gy (2), 56.3 Gy (5) and 112.1 Gy (10) gamma irradiation, (b) an expanded view of (a) in the RT–850 °C, and (c) without and with application of 150 V cm^{-1} from room temperature to 800 °C after exposure to 56.3 Gy gamma radiation.

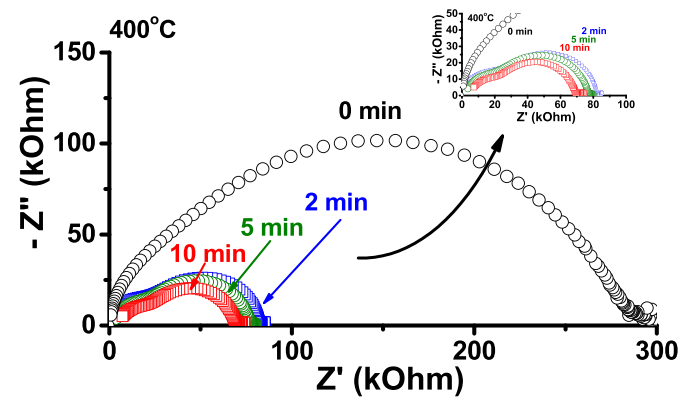


Fig. 2. Impedance spectroscopy plots of ZrO_2 : 8 mol% Y_2O_3 ceramic pellets exposed to 22.9 Gy (2 min), 56.3 Gy (5), and 112.1 Gy (10) gamma irradiation, all flash sintered at 900 °C under 150 V cm^{-1} , 1 kHz, 1 A limiting current. Temperature of measurement: 400 °C.

The next experimental step was to evaluate the electrical behavior of the gamma-irradiated samples. Fig. 2 shows $[-Z''(\omega) \times Z'(\omega)]$ impedance spectroscopy diagrams measured at 400 °C of $ZrO_2: 8 \text{ mol\% } Y_2O_3$ exposed to 22.9 Gy (2), 56.3 Gy (5) and 112.1 Gy (10) gamma radiation.

The diagrams are composed of two semicircles, one at low frequencies due to the intergranular (grain boundaries and pores) contribution and the other at high frequencies due to the intragranular (bulk) contribution to the electrical resistivity [18]. The larger was the gamma dose

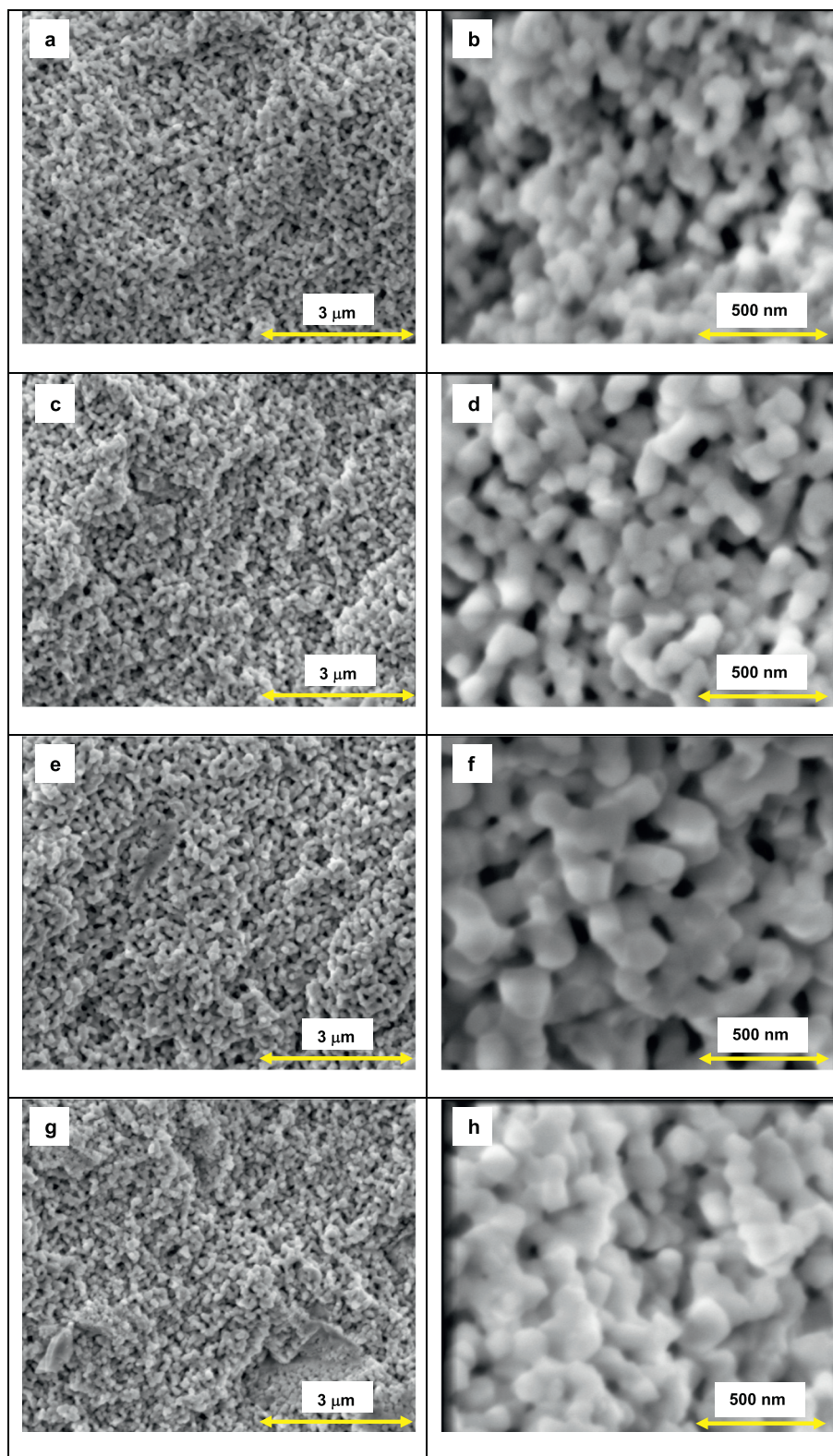


Fig. 3. Scanning electron microscopy micrographs of $ZrO_2: 8 \text{ mol\% } Y_2O_3$ sintered ceramic pellets without (a, b) and with exposure to 22.9 Gy (c, d), 56.3 Gy (e, f) and 112.1 Gy (g, h) gamma irradiation. Right figures: higher magnification.

the lower was the electrical resistance in agreement with the dilatometric results that shows that the samples are denser for increasing gamma radiation dose.

Fig. 3 shows scanning electron microscopy images of 8YSZ samples heated to 1000 °C without and with application of 150 V cm⁻¹ (cf. Fig. 1). Even though there is a slight increase of the average grain size, as usual in flash sintering experiments [19–22], the pore content decreases for increasing gamma radiation dose, in good agreement with the increase of the shrinkage level (Fig. 1) and the decrease of the electrical resistivity (Fig. 2).

In summary, gamma irradiation of zirconia-8 mol% yttria green pellets enhances the densification achieved by electric field-assisted (flash) sintering. Besides the shrinkage increase, there is an improvement of the ionic conductivity and a decrease of the pore content for increasing gamma radiation dose. As oxygen vacancies play a role on sintering stabilized zirconia, these effects were ascribed to the increase of the charge carrier (oxygen vacancy) concentration produced by ion displacements during irradiation. Gamma cells may be an efficient facility for improving flash sintering of electroceramics.

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