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Short communication

Light emission during electric field-assisted sintering of electroceramics

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Abstract

Electric field-assisted sintering has been shown to occur in ion, electron conducting as well as in insulating polycrystalline ceramics. Considerable linear shrinkage with microstructure control at temperatures lower than the conventionally utilized has been attained mainly in oxide ion conducting zirconia-based solid electrolytes. Some mechanisms, based on localized Joule heating and enhancement of defects diffusion, have been set forth to explain the sudden volume reduction in those ceramics. The results here reported contribute to the understanding of what happens *during* electric field-assisted sintering, by evidencing the occurrence of light emission simultaneously to the quasi instantaneous specimen shrinkage. An experimental setup with an optical fiber inserted in a dilatometer furnace allowed for light emission detection simultaneously to the electric current pulse in zirconia-yttria and also in tin dioxide specimens upon electric field-assisted sintering.

Keywords: Electric field assisted-sintering; Flash sintering; Light emission; Zirconia; Tin dioxide

1. Introduction

Electric field-assisted sintering has been applied to electroceramics since it was recently reported that high density and small average grain sizes might be achieved by applying a dc or ac electric field to polycrystalline yttria-stabilized zirconia solid electrolytes at temperatures lower than that usually required.[1] The technique has been successfully used in several electroceramic materials, mainly oxides.[2–25] Several attempts have been set forth to understand the underlying mechanisms responsible for sintering with or without densification: besides Joule heating, which results from the electric current pulse derived from the application of the electric field, nucleation of defects has been also claimed to induce mass diffusion with consequent sintering.[5] Analysis of what happens when an electric current pulse crosses a polycrystalline sample has been reported by several authors,[17,26] but analysis and experimental evidences on how the electric field produces that electric current pulse are still lacking. Recently it has been pointed out that "there are three things really going on at the same time: electronic conductivity, mass transport and photoemission".[27] However, using three experimental methods, *in situ* atomic emission spectroscopy, direct visual observation, and ultrafast *in situ* voltage measurements, no evidence of plasma generated between particles was found during the spark plasma sintering (SPS) process.[28,29] We must point out that SPS employs low dc fields (few V cm^{-1}) and high currents (usually kA) through a *graphite die* containing the ceramic powder, whereas electric field-assisted sintering employs relatively high fields (100 V cm^{-1}) and low currents (mA–A) through *the specimens*.

Let us consider what happens, from the physical point of view, to a polycrystalline metal oxide pressed pellet under an external electric field. Before that, we have to take into account (i) the electrical behavior of the metal oxide (dielectric, ionic, electronic or mixed conductor), (ii) the temperature (it determines the electrical behavior and the concentration of point defects), (iii) the atmosphere (oxidizing, neutral or reducing) and (iv) the magnitude (might produce dielectric breakdown, bulk and/or surface motion of charge carriers) and the nature of the electric field (dc may polarize and/or transport charge as well mass, ac does not polarize and transports only charge). Moreover, a metal oxide green pellet consists usually of a number of strained particles pressed together. The application of a dc electric field might produce local dielectric breakdown inside the pellet (due to the

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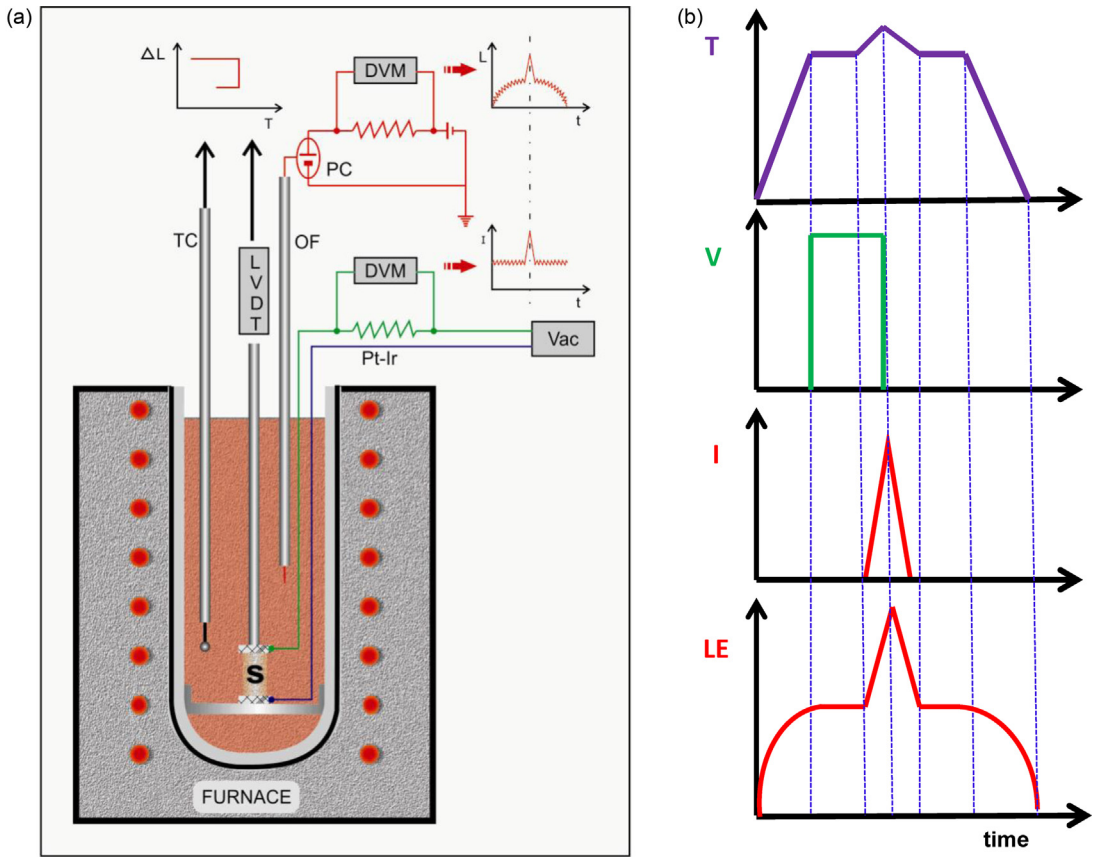

Fig. 1. (a) Experimental setup for simultaneous collection of shrinkage and light emission data from ceramic pellets upon electric field-assisted sintering. S—Sample, TC—thermocouple, LVDT—displacement transducer, OF—Optical fiber, DVM—Digital voltmeter, Vac—ac Power supply, PC—Photocell, I—electric current, t—time, L—Light emission, ΔL—Linear shrinkage. (b) Scheme of temperature, voltage, current and light profile during the electric field-assisted sintering experiment. LE—Light emission.

production of bound charges, which depends on the electric permittivity of the ceramic particles)[30] and electric discharges of the entrapped gas. The required physical conditions, namely, sufficient field strength, availability of gaseous ionic species, and sufficient high local temperatures are met.[27] Under these circumstances, photons might be emitted in the bulk as well as at the surface of the pellets. Now we get to the main objective here: to look for and to detect light emission *during* electric field-assisted sintering of electroceramics, whether it really occurs. Focus has been directed to two different electroceramics: cubic zirconia-yttria (oxide ion conductor) and rutile-tetragonal tin dioxide (electronic semiconductor).

To our knowledge, no experimental evidence had been published on photoemission during electric field-assisted sintering, besides the very recent paper by Lebrun and Raj,[31] where photoemission was detected during the increase in the electrical conductivity of flash-sintered zirconia: 3 mol% Y_2O_3, even in pre-sintered dense specimens. Optical emission spectra were recorded allowing for preliminary identification of the origin of the light pulse during flash sintering. Their explanation, which remains to be confirmed, was that photoemission and electrical conductivity in that ceramic are related to the concentration of electron-hole pairs. The main difference between their results and ours is the following: (a) their experiments allowed for collecting the spectral distribution of the emitted light and ours do not; (b) they carried out experiments only on yttria stabilized zirconia and we detected photoemission in both ionic conducting yttria stabilized zirconia and in electron conducting tin dioxide.

2. Experimental

Cubic ZrO_2: 8 mol% Y_2O_3 ceramic powder from Tosoh, Japan, hereafter 8YSZ, wasused. The powder was pressed uniaxially and isostatically under 46 MPa and 200 MPa, respectively, to ϕ5 mm × 5 mm thick pellets with green relative densities approximately 50%. tin (IV) oxide and manganese (IV) oxide from Alfa Aesar (99%) were used for preparing SnO_2:5 wt.% MnO_2 pellets by thoroughly mixing the stoichiometric amounts of the powders, uniaxially cold-pressing at 30 MPa and isostatically at 200 MPa.

Fig. 1a shows the experimental arrangement for detecting light emission inside the dilatometer furnace. A quartz optical fiber (ϕ3.18 mm, 1 m long) was inserted on a top aperture of the vertical furnace, and for preventing its thermal degradation its sensing tip was fixed down to approximately 15 cm from the sample holder. The light pulse emitted from the top surface of the ceramic sample could reach the optical fiber through the holes of a platinum mesh used as the top electrode. A photoelectric cell with terminal leads connected in series to a V_{dc}–R (3 V–20 k Ω) circuit was positioned on top of the outer tip of