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Electric field-assisted sintering of tin dioxide with manganese dioxide addition

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

Center of Science and Technology of Materials Energy and Nuclear Research Institute Trav. R 400, Cidade Universitária, São Paulo, SP, Brazil

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Abstract

Green compacts of pure SnO_2 and with addition of 0.25, 0.5 and 1.0 wt.% MnO_2 were sintered by applying 100 V cm^{-1} at 1 kHz and limiting the current to 5 A during 5 min at 1100 and 1200 °C. The shrinkage was monitored precisely during the electric current pulses. The role played by the additive was clearly seen in the shrinkage data: the higher is the additive content the lower is the onset of the shrinkage and the higher is the attained final shrinkage level. Sintering experiments on cylindrical samples with 0.5 wt.% MnO_2 with different thickness-to-diameter ratio show that the lower is that ratio, the higher is the shrinkage level, showing that the imparted Joule heating play a key role in the mechanisms responsible for sintering. The total electrical resistivity, evaluated by impedance spectroscopy, depends on the maximum attained shrinkage level, due to pore elimination upon sintering.

Keywords: Electric field-assisted sintering; Tin dioxide; Impedance spectroscopy

1. Introduction

The importance of SnO_2 semiconductor ceramics is reflected by the wide range of application of this material, described in reviews on monolithic ceramics[1] as well as on hierarchical nanostructures.[2]

Tin dioxide (SnO_2), a semiconductor known to be difficult to sinter, was recently reported by the authors to be successfully sintered at 1100 °C when exposed to electric current pulses resulting from the application of ac electric fields.[3] Pure SnO_2 powder compacts do not get dense by conventional sintering because there is the predominance of an evaporation-condensation mechanism due to its high vapor pressure value.[4–6]

Manganese dioxide is reported to have very low solubility in tin dioxide; upon mixing and heating, the manganese cation is positioned in a very thin segregation layer surrounding the tin dioxide grains.[7] The sintering of tin dioxide with addition of manganese dioxide (melting point ~535 °C) was reported to create oxide ion vacancies at the grain interfaces and therefore to promote densification via vacancy-assisted grain boundary diffusion.[7–9]

Electric field-assisted sintering of SnO_2,[3] SiC[10] and TiO_2[11] semiconductors have already been reported. The common interest in those papers is the ability of that sintering technique to obtain sintered polycrystalline ceramic bodies either saving energy (lower sintering temperature, short sintering times) or attaining desirable microstructure features not easily reached by conventional approaches. Particle–particle contact promoted by Joule heating was considered the main reason for enhanced sintering of SiC.[10] Moreover, additives were found to be important for obtaining near full density SiC. Similar to the behavior of electric field-assisted sintered SnO_2,[3] bulky SiC specimens sinter better at the center than at the border. This could be due either to heterogeneous green microstructure or to the very fast sintering time (order of seconds, not enough to transfer heat through the whole sample). This problem could be circumvented by stacking the specimen between a material with low (thermal) conductivity. This density gradient is not reported by others[11–18], probably because their experiments were performed with relatively thinner specimens.

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

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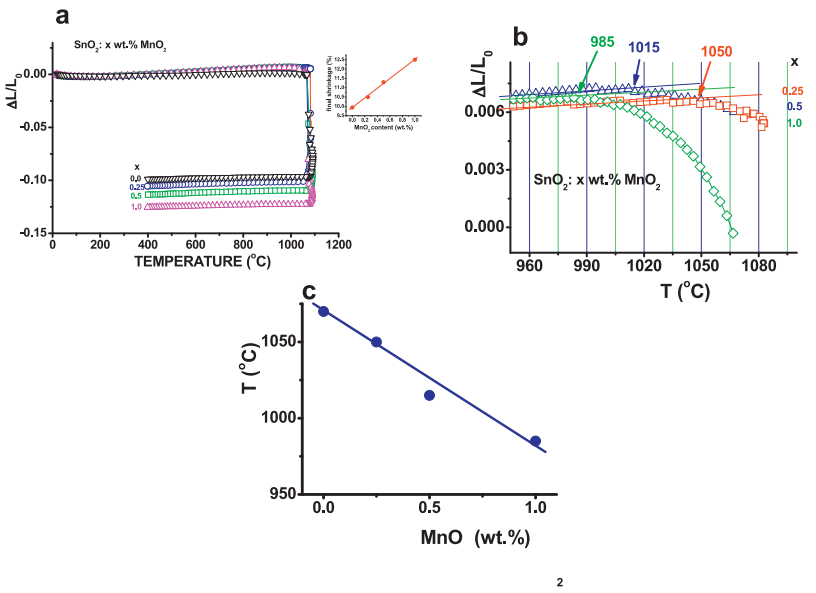

Fig. 1. (a) Dilatometric curves of ϕ 5 mm × 5.3 mm thickness SnO_2:x wt.% MnO_2, x = 0, 0.25, 0.5 and 1.0, green compacts upon heating to 1100 °C and application of 110 V cm^{-1}. Inset: final shrinkage dependence on MnO_2 content; (b) detail of increasing temperature data of (a); (c) onset temperature for shrinkage as a function of MnO_2 content.

In our previous paper we investigated two effects on the final densification of pure and SnO_2 + 2.0 wt.% MnO_2.[3] One is the limitation of the electric current through the sample under an ac electric field. This limitation is important to avoid a thermal runaway with a continuous increase in the electric current, which could even provoke the melting of the sample. The limit value to be chosen depends on the electrical behavior of the sample at the temperature the electric voltage is applied. The other effect is the use of manganese dioxide as a sintering aid. Briefly, it was shown that increasing the limit current from 1 A to 5 A, a shrinkage level of 20% is achieved, whereas without the sintering aid, the grains are welded together without significant densification.

Suitable processing procedures have to be taken into account for a successful sintering. Conventional sintering requires the knowledge of powder size, firing time, temperature, additives and atmosphere.[19] In the electric field-assisted sintering one has to consider further the electrical behavior of the specimen as a function of temperature.

Here, we evaluate the effect of the sintering aid content on the linear shrinkage level. Moreover, for a fixed amount of sintering aid (0.5 wt.% MnO_2) the influence of the sample dimensions (volume effect), important for the scale up of the electric field-assisted technique to actual ceramic pieces, was also investigated.

2. Experimental

SnO_2 obtained by calcination in air at 900 °C of SnO and MnO_2 (both Alfa Aesar 99.9%) were dried, weighed, mixed thoroughly in an agate mortar, and pressed (ϕ 5 mm to 3–5 mm thick disks) in stoichiometry contents to produce SnO_2:x wt.% MnO_2, x = 0, 0.25, 0.5 and 1.0 green compacts. Samples with 0.5 wt.% MnO_2 were prepared with different thicknesses to evaluate the effect of the thickness-to-diameter ratio on the final shrinkage under similar imparted electric field. The X-ray fluorescence analysis of electric field-assisted sintered pellets, performed in a Shimadzu EDX-720 equipment, showed that the manganese content is nearly the same as the nominal addition. The electric field-assisted sintering experiment was conducted in a laboratory setup described in detail elsewhere.[3,20] The sintering process occurs inside a dilatometer, which allows to monitor shrinkage while applying an electric voltage to the specimen. All electric field-assisted experiments were carried out in the same way: the dilatometer was set to increase the temperature from room temperature to 1100 or 1200 °C without any dwelling time, and to decrease the temperature to 200 °C. Heating and cooling rates were fixed to 10 °C min^{-1}. When the temperature of the dilatometer furnace reached 1100 or 1200 °C, an ac (1 kHz) electric voltage (usually corresponding to 100 V cm^{-1}) was applied to the specimen during 5 min. The electric current was limited to 5 A, a value we found to produce shrinkage in tin dioxide green pellets without visible deterioration.[3] The power surge was handled manually, the electric voltage as well as the maximum electric current being kept constant at each pulse. There was no automatic switching to electric current control as reported by other investigators.[21–23]

The sample was not allowed to cool down to the furnace temperature before the application of the next pulses in an attempt to force the shrinkage to the desired level or to the desired pulsing time (5 min, for example). The shrinkage level was monitored in the dilatometer and the voltage-current versus time data were collected in a data logger consisting of two (one for voltage and another for current) Fluke 8050A digital multimeters connected to a pc with a designed interface. The impedance spectroscopy analysis was carried out with a Hewlett Packard 4192A impedance analyzer in the 5–1.3 × 10^7 Hz frequency range in sintered specimens (with the parallel surfaces silver coated) positioned in a homemade sample chamber, which was