Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 34 (2014) 915–923

www.elsevier.com/locate/jeurceramsoc

Electric field-assisted flash sintering of tin dioxide

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

Center of Science and Technology of Materials, Energy and Nuclear Research Institute, Travessa R 400, Cidade Universitária, S. Paulo, SP 05508-900, Brazil

Received 23 August 2013; received in revised form 20 September 2013; accepted 23 September 2013
Available online 16 November 2013

Abstract

SnO_2 green pellets were submitted to ac electric fields at temperatures below 1350 °C. Electric current pulses occurred and a substantial modification was found in the microstructure of the pellets after application of 80 V cm^{-1} at 900, 1100 and 1300 °C. Similar experiments were carried out in SnO_2 mixed to 2 wt.% MnO_2. The linear shrinkage of the pellets was monitored with a dilatometer during the application of the electric field. Scanning electron microscopy micrographs of the pellets show the grain structure evolution after the electric current pulses. The larger is the electric current flow through the SnO_2 pellet, the larger are the shrinkage and the average grain size. Even though sintering occurs without significant densification in SnO_2, the welding of the grains is evident. The apparent density of green pellets of SnO_2 with MnO_2 addition sintered at 1100 °C increased 110% with the application of 80 V cm^{-1}, 5 A.
© 2013 Elsevier Ltd. All rights reserved.

Keywords: Flash sintering; Tin dioxide

1. Introduction

Tin oxide is an n-type semiconductor with application in many devices such as chemical sensors,[1–3] solar cells, displays and batteries.[4–6] Pure SnO_2 does not densify upon heating because of the predominance of the evaporation–condensation mechanism.[7] For sintering SnO_2 bulk ceramics from powders, sintering aids are required for avoiding the decomposition of SnO_2 to SnO at temperatures higher than 1300 °C.[8–10] The relative densities of a SnO_2 green pellet and of pellets sintered at 1000, 1100, 1220 and 1300 °C were reported as 49.8, 49.8, 49.9, 49.7 and 49.8%, respectively.[7] It is a common practice the mixing of sintering aids to achieve dense SnO_2, for example by liquid phase sintering with the addition of Li_2CO_3 or CuO.[7,10] Aliovalent cations have been proposed to form solid solutions, creating lattice defects and thereby promoting densification upon sintering by solid state diffusion.[8,10] Relative densities of 95% of the theoretical density and even higher values were obtained upon sintering SnO_2 with MnO_2 addition for a $Mn/(Mn+Sn)_{atomic}$ cation ratio equal to 4×10^{-3}.[11–13]

One of the more important recent developments on sintering ceramic materials involves the application of an electric field on heating a green pellet without applying pressure. The first reports on this new sintering technique showed that either dc or ac electric fields inhibited grain growth.[14,15] In ionic conducting ceramics, low dc electric fields were found to enhance the sintering rate and the plastic deformation.[16] Afterwards larger electric fields (>40 V cm^{-1}) were applied with significant densification in few seconds of Y-TZP[17] and Y-FSZ[18,19] at temperatures lower than 1000 °C. Flash sintering has been applied recently to many green pellets of different electrical behavior: alumina insulator,[20] Co_2MnO_4 electronic conductor,[21] cubic and tetragonal yttria-stabilized zirconia ionic conductors,[22–26] strontium-doped barium cerate protonic conductor,[27] ceria ionic conductor,[28] strontium titanate semiconductor[29] and polymorphic silicon carbide semiconductor.[30] Theoretical aspects (mechanism and grain growth) have also been reported.[22,24,31,32] Most of the experiments, independent on the attributed physical mechanism, reach the same general feature: the application of a dc or ac electric field with suitable magnitude promotes densification during sintering at temperatures which depend on the studied compound, but is always lower than the conventional sintering temperature. Recently the welding of the grains in yttria-stabilized zirconia was proposed to occur when an ac field is applied to these ceramics in the electrolytic region, namely, in

* 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).

0955-2219/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jeurceramsoc.2013.09.017

the ionic conduction regime.[18] The welding of the grains happens in a singular current pulse (few seconds' half-width) and was ascribed to an intense Joule heating by the flow of an electric current through the inter-particle region of the green pellet. The increase in the inter-particle temperature might also promote densification and grain growth due to heat transfer to the bulk of the particles. This welding promotes a large decrease in the intergranular blocking of charge carriers, seen as a large reduction of the impedance spectroscopy arc at low frequencies, which represents the electrical resistivity of the grain boundaries. Even though Joule heating might occur, a full explanation of the mechanisms responsible for flash sintering and/or flash grain welding is still lacking.[22,24,31–33] Experiments were reported of flash sintering under constant electric fields or current densities,[34] with materials with different average particle sizes,[35] under continuous application of an electric field during heating and on the effects of the applied field and temperature on the incubation time for flash sintering,[36] and on application of very high electric fields.[37] This method of sintering has been applied with success to dog bone shape, cylindrical shape and tape-casted ceramics.[38] Few works deal with technological application of this sintering method, specifically for solid oxide fuel cells.[19,21,39,40]

Here we have to point out the main difference between flash sintering and flash grain welding: during a flash sintering experiment, either a dc or an ac field is applied; during a flash grain welding experiment, on the other hand, only an ac field is applied through the specimen, to promote charge but not mass transfer. Application of ac fields avoids depletion of ionic species inhibiting stoichiometry deviation, which produces, for example, the blackening effect in zirconia.[41–43] In ceramic materials with poor sinterability, like Gd-doped $BaCeO_3$, the application of an ac electric field promoted negligible changes in densification, although the grain boundary conductivity substantially improved.[27] That result along with those measured in granules of yttria-stabilized zirconia[25] show that the primary effect upon application of an ac electric field on an ionic conductor is the welding of the interfaces. In spite of the recognized success of this novel sintering technique, some important questions remain unanswered. It seems that the application of this technique to ceramic materials with poor sinterability like pure alumina[20] and silicon carbide[30] *without* sintering aids exerts minor effects on both microstructure and densification.

In this work, the effects of an ac electric field on sintering SnO_2 and SnO_2 mixed to MnO_2 were investigated at temperatures below the decomposition temperature of SnO_2.

2. Experimental

Tin (IV) oxide and manganese (IV) oxide from Alfa Aesar (99%) were used. The purity of the tin oxide powder was ascertained by X-ray fluorescence analysis (Shimadzu EDX-720) and the distribution of particle size was evaluated by laser scattering in a Cilas granulometer. SnO_2: 2 wt.% MnO_2 was prepared by thoroughly mixing and homogenization in an agate mortar. The SnO_2 and the SnO_2: 2 wt.% MnO_2 powders were uniaxially cold-pressed in ϕ 5 mm × 5–7 mm thickness at 30 MPa with steel dies and isostatically at 200 MPa. The structural phase was determined by X-ray diffraction measurements in a Bruker-AXS model D8 Advance X-ray diffractometer with Cukα radiation (40 kV, 40 mA), 20–80° 2θ range, 0.05° step size, 3 s per step. For crystallite size evaluation using Scherrer equation,[44] the measurements were performed in the 51–53° 2θ range, which corresponds to the (2 1 1) reflection of SnO_2 (JCPDS 41-1445), 0.01° step size, 10 s per step.

The microstructure of fracture pellet surfaces, without any coating, was examined in a field emission gun scanning electron microscope (FEG-SEM FEI Inspect F50). Density was determined by measuring the weight and dimensions of the compact before and after sintering. The theoretical density (TD) was considered to be 6.993 g cm^{-3}.[8]

The experimental setup for simultaneously applying ac/dc voltage and monitoring shrinkage was described elsewhere.[26] Briefly, it consists in a vertical dilatometer (0.5 μm precision) with Pt electrical connections from both flat surfaces of cylindrical pellets to a homemade 30–60 V, 1–10 A ac power supply operating in the frequency range 500–1000 Hz. The applied electric voltage turns off when the electric current reaches a pre-set value in the 1–10 A range. Multiple electric current pulses may be applied by turning on the applied voltage. The shrinkage of the specimen is monitored in the dilatometer and the voltage–current data is collected in a pc-controlled homemade data logger. Sintering has been carried out at 900, 1100 and 1300 °C dilatometer temperatures without and with 80–100 V cm^{-1} (1 kHz) pulses with the electric current limited either to 1 A or 5 A.

3. Results and discussion

The analysis of the distribution of particle size of the commercial SnO_2 powders, which purity was determined as 98.6% by fluorescence X-ray analysis, shows that it is composed primordially of agglomerated particles with approximately 1 μm average size. The average crystallite size, estimated by X-ray diffraction was 373 nm.

3.1. SnO_2

Fig. 1a–c shows dilatometric curves of SnO_2 green pellets exposed to 5 min sequential electric current pulses at temperatures close to 900 °C, 1100 °C and 1300 °C, respectively. In the figures, the dilatometric curves of samples just heated and cooled in the dilatometer without the application of an ac field are also shown. Shrinkage due to the application of the electric field is evident. Heating the green SnO_2 pellet to 900 °C produces no appreciable densification (44.5%TD, green density 41.8%TD). The application of 80 V cm^{-1} with 1 A limiting current at ~900 °C leads to negligible but measurable 5% longitudinal shrinkage. Just heating to a larger temperature, 1100 °C, produces an expected small shrinkage of 0.2% (45.2%TD), which changes to 5.6% upon the application of the electric field. A further 200 °C increase in the temperature to 1300 °C does not show substantial increment in shrinkage. The shrinkage limits attained were 5.0%, 5.6% and 5.8% at 900 °C, 1100 °C

Download English Version:

https://daneshyari.com/en/article/1475032

Download Persian Version:

https://daneshyari.com/article/1475032

Daneshyari.com