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ScienceDirect
Journal of the European Ceramic Society 31 (2011) 1517–1521
www.elsevier.com/locate/jeurceramsoc

Short communication

Flash grain welding in yttria stabilized zirconia

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Received 27 January 2011; received in revised form 14 February 2011; accepted 18 February 2011

Abstract

Self-standing samples made of isostatically pressed powders of ZrO_2:8 mol% Y_2O_3 were submitted to AC signals of 60 and 1000 Hz. At temperatures of around 900 °C, a current density exceeding approximately 100 mA/cm^2 starts an avalanche process with a fast increasing current under constant voltage. It lasts about 60 s and it is preceded by an induction period of the order of 30 s. After that, the material is sintered as confirmed by impedance diagrams. Relative densities of 94% could be obtained.

Keywords: A. Sintering; B. Grain boundaries; C. Impedance; C. Ionic conductivity; D. ZrO_2

1. Introduction

In addition to obvious economical and technical incitements, the search for fast sintering techniques has been accelerated by the upsurge of an overwhelming interest in nanostructured materials. It is well established that fast sintering can be achieved without any substantial grain growth. This is the case with solid oxide ion conductors such as stabilized zirconia and doped ceria. Industrial equipment based on the spark plasma sintering (SPS) is commonly used for this purpose. Five recent review papers[1–5] give extensive details on the fast sintering techniques (also called electric current activated/assisted sintering technique – ECAS,[2] current-activated, pressure-assisted densification – CAPAD[4] or pulsed electric current sintering – PECS[5]) which have been applied to a large variety of materials. Dense, nanograined yttria stabilized zirconias have been successfully obtained using the SPS technique with commercial and improved equipments.[6,7] More theoretically oriented studies[8–12] of the oxide sintering mechanisms have recently shown that a DC or AC voltage applied during a conventional sintering process lowers the densification temperature by inhibiting the grain growth. A flash sintering of nanograin TZP has also been observed under DC polarization.[13]

Referring to fairly systematic investigations of the blocking of the ionic carriers by various microstruture defects in YSZ,[14,15] it has been concluded that the major part of the material resistance of a porous sample is located at the contacts between the grains. Therefore, applying a voltage to such a porous material will mainly generate a Joule effect at the contacts between the grains. It is likely to favor their welding. The analogy with the metal spot-welding may be misleading, but gives an image of the local heating effect at the microstructure level. Another common observation in the impedance characterization of the sintered oxide ion conductors is that contacts between the grains in the sintered bodies are also characterized by fairly important electric capacitances. Passing an AC current through such contacts would charge and discharge these capacitances and therefore move back and forth the adjoining ions which are the electric carriers. Under high AC current, this is likely to result in a heavy shuffling of the local ions and possibly also to a welding of the contacting grains.

The experimental finding reported here was observed during an attempt to implement this simple concept to YSZ. The observed phenomena will be called flash grain welding (FGW).

A specific experimental difficulty with the oxide ion conductors results from the very nature of their electric current carriers. Because of their ionic nature, they drain with them a certain amount of oxygen, defined by the Faraday law. As sketched in Fig. 1, under DC polarization, at the contact between the sample and the electric current collector negatively polarized,

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doi:10.1016/j.jeurceramsoc.2011.02.030

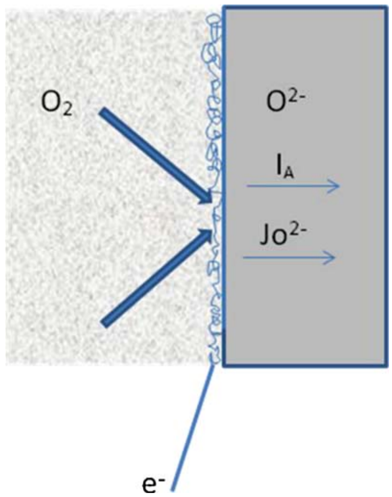

Fig. 1. Sample holder.

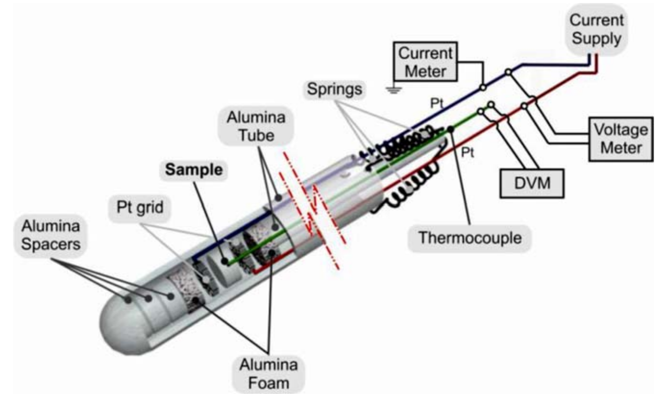

Fig. 2. Fluxes of matter associated with a direct current passing through the sample.

the balance of matter shows a deficit of oxygen. This can be compensated by the ions supplied by the so-called electrode reaction:

$$O_2(\text{air}) + 4e^-(\text{contact}) \rightarrow 2O^{2-}(\text{sample}) \quad (1)$$

Numerous experimental results, obtained for instance with fuel cells, show that an efficient compensation cannot be expected for current densities exceeding a few A/cm^2. When the compensation is not ensured, the sample is chemically reduced. This results in an additional, fairly high, electronic conductivity. This is the so-called blackening process. Experimentally, when this process starts locally, it initiates preferential current routes because of the important local electric resistance fall. It frequently ends in a kind of electrochemical spark through the sample. In the case of yttria stabilized zirconia, the first stage of blackening is reversible, and the material can be re-oxidized without major damage.[16] In the case of ceria, the reduction leads to the formation of large Ce^{3+} ions and to an expansion detrimental to the crystal integrity. In practice, with the high current densities expected to be used in flash welding, higher degrees of blackening are likely to be reached. Then the chemical reduction is no longer reversible. On subsequent re-oxidation, the material is mechanically weakened.

At the other current collector contact, positively polarized, where oxide ions are brought in, the situation is less crucial; excess oxygen simply outgases from the sample. Only under very high current densities, this can physically deteriorate the electric contact.

The conclusion from this sketchy analysis is that AC voltages should preferably be used to investigate the potentialities of the Flash Grain Welding. Passing an alternating current will alternatively re-oxidize the possibly reduced negative electrode sub-layer. To get a quantitative evaluation of the reduction risk, we can simply refer to the Faraday law which relates the oxygen flux $J(O_2)$ to the electric current I (see Fig. 1):

$$J(O_2) = \frac{I}{4F} \quad (2)$$

where J is expressed in mol/s and I in A. The Faraday constant F is approximately equal to 96,500 C.

A quantitative application of this equation indicates that each half cycle of a 50 Hz alternating current of 10 mA/cm^2 drains in and out 0.36 O^{2-} ion per (5 Å)^2 which is approximately the lateral surface of an elementary YSZ cell.

2. Experimental

Commercial powders (TZ-8Y from Tosoh, Japan) with 75 μm average size granules, composed of primary particles of 25 nm mean diameter, were used without further treatment. The samples were pressed, first uniaxially under 46 MPa and then isostatically under 200 MPa. After these pressings, the green relative densities were all close to 50%. To be able to use various equipments, two sets of dimensions were selected. A series of pellets have diameters of the order of 5 mm and a thickness of 3 mm. The other series has 7 mm and 3 mm, respectively. To improve the uniformity of the current distribution through the samples, their bases were covered with Pt paint (Degussa Demetron 308A).

The experimental setup diagram is shown in Fig. 2. The investigated sample is inserted between two current collectors made of either Pt foils or grids. To maintain the electric contact, a slight pressure of a few hundreds grams was ensured by springs and transmitted by an alumina plunger. This sample holder was simply introduced in an electric furnace whose temperature was regulated to within 2 °C. All the experiments were performed under air. A thermocouple type S was located close to the sample to qualitatively indicate any heating effect associated with the grain welding.

The impedance analyzer is a Hewlett Packard 4192A run by the Hydro-Quebec impedance spectroscopy software[17] in the 5 Hz to 13 MHz range.

As sources of polarizing current, we used: a DC power supply Tectrol model TCA 30-5; a variable transformer 60 Hz/25 A/220 V simply connected to the main line; a 1 kHz, 60 W homemade power supply.

The sample microstructure was examined in a scanning electron microscope Philips XL30.