



# Flash sintering of alumina: Effect of different operating conditions on densification



Mattia Biesuz<sup>a,\*</sup>, Vincenzo M. Sglavo<sup>a,b</sup>

<sup>a</sup> Department of Industrial Engineering, University of Trento, Via Sommarive 9, 38050 Trento, Italy

<sup>b</sup> INSTM Research Unit, Via G. Giusti 9, 50121 Firenze, Italy

## ARTICLE INFO

### Article history:

Received 27 February 2016

Received in revised form 16 March 2016

Accepted 17 March 2016

Available online 22 March 2016

### Keywords:

Flash sintering

Alumina

Joule heating

Conduction

Activation energy

## ABSTRACT

Nearly pure  $\alpha$ -alumina samples produced by uniaxial pressing were flash sintered under electrical fields ranging from 500 V/cm to 1500 V/cm in experiments at constant heating rate. Sintering temperature significantly decreased with the applied E-field even down to  $\approx 900^\circ\text{C}$  at 1500 V/cm. The onset temperature for flash sintering can be successfully modelled as a function of the applied voltage. The sintering temperature is also shown to be strongly affected by the electrode materials used during the treatment: using silver or carbon electrodes the sintering temperature is about  $300^\circ\text{C}$  lower than when using platinum electrodes. In addition, the bulk density and porosity of the sintered alumina ceramic correlate strongly with the imposed current limit. Power dissipation was analysed before and during flash sintering; the activation energy for conduction was calculated in both cases, indicating that the process is based on ionic diffusion phenomena. Finally, we showed that during flash sintering the activation energy for conduction decreases, suggesting the occurrence of physical or structural modifications induced by current localization at the grain boundaries.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

The reduction of environmental, energetic and economic costs is today of major concern to the ceramic industry. Several recent studies [1–19] have shown that the application of an electrical field is very effective in reducing sintering time and temperature and so also energy consumption and  $\text{CO}_2$  emissions. In particular, at specific electrical field and temperature levels, so called flash sintering (FS) can be observed [1–19]. This phenomenon, which is accompanied by an abrupt increase in material conductivity, can reduce the sintering time to a few seconds and typically allows densification of ceramics at temperatures much lower than conventional. This sintering technique has been studied in many high temperature ionic conductor (YSZ [1–8], GDC [9]), protonic conductor ( $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-d}$  [10]), semi-conductors (SiC [11]), composites ( $\text{ZrO}_2$ - $\text{Al}_2\text{O}_3$  [12,13], CAS glass- $\text{Al}_2\text{O}_3$  [14]) and electrically conductive ( $\text{MnCo}_2\text{O}_4$  [15,16], LSCF [17,18]) ceramics.

Although there are various phenomenological explanations proposed for describing this unusual behaviour, the mechanisms leading to material densification are still unknown. Some proposed mechanisms involve local heating at the grain boundaries [1,19] or

the formation of Frenkel pairs [19,20] driven by the applied electrical field. Also Joule heating was suggested as responsible for the rapid densification; nevertheless, some experimental results have shown that the sample surface temperature is far lower than would be needed for conventional sintering in a few seconds [3,20]. Recently, Todd et al. developed a model indicating that a thermal runaway of Joule heating can induce an FS event [4]. Similar results were also independently obtained by Zhang et al. [21]. Todd also suggested that the temperature in the sample core upon FS can be much higher than that measured on the surface, although stating that “*the mechanistic details of densification remain uncertain*”. The problem is anyway still open and controversial.

Although FS has been demonstrated in several semi-conductive and conductive ceramics, very little work has been done on resistive materials. Cologna et al. made some experiments on high purity alumina and concluded that this could not be flash sintered. It was also shown that alumina completely changes its electrical behaviour if doped with 0.25 wt% MgO; and MgO-doped alumina was successfully flash sintered down to  $1260^\circ\text{C}$  [19].

In this work, we subjected 99.8% pure alumina to flash-sintering experiments in order to understand the possible conduction mechanisms and the densification behaviour in a widely used resistive oxide ceramic. We also intended to observe the influence of some

\* Corresponding author.

E-mail address: [mattia.biesuz@unitn.it](mailto:mattia.biesuz@unitn.it) (M. Biesuz).

operating conditions on FS, such as electrical field intensity, current density and electrode materials.

## 2. Experimental procedure

In this work we used nearly pure  $\alpha$ -Alumina (Almatis, CT 3000 SG,  $d_{50} = 0.6 \mu\text{m}$ ,  $d_{90} = 3.0 \mu\text{m}$ ) with nominal composition  $\text{Al}_2\text{O}_3$  99.8 wt%–MgO 0.04 wt%– $\text{Na}_2\text{O}$  0.03 wt%– $\text{Fe}_2\text{O}_3$  0.015 wt%– $\text{SiO}_2$  0.015 wt%–CaO 0.015 wt%. After adding 6 wt% distilled water, dog bone samples were produced by uniaxial pressing at 120 MPa. The thinner cross section of the pressed sample was  $3 \text{ mm} \times 3.3\text{--}4 \text{ mm}$ . Sintering tests were carried out in a Linseis L75 dilatometer with a constant heating rate of  $20^\circ\text{C}/\text{min}$ . We applied a DC field, using a Glassman EW series 5 kV–120 mA power supply, when the sample reached  $350^\circ\text{C}$  and this was maintained at constant value until the current limit was reached. The field and the current density ranged from 250 to 1500 V/cm and from 2 to 7 mA/mm<sup>2</sup>, respectively. We measured the current intensity and the voltage at 1 Hz using a multimeter (Keithley 2100). On reaching the current limit, we maintained the current flow for 2 min and then shut down the system.

The power supply connections to the samples were two platinum wires, forced into holes on opposite edges of the dog bone sample. To improve the electrical contact between these platinum electrodes and the ceramic, we used various conductive pastes. The first type, used for most experiments, was platinum-based (Sigma Aldrich). We also used silver paste (Agar Scientific) and carbon cement (Plano GMBH) for comparison.

The density of the sintered samples was measured by Archimedes' method using a balance (Gibertini) with sensitivity  $\pm 0.1 \text{ mg}$ . Only the constant-cross section part of the specimen between the two electrodes was used for the density measurements.

## 3. Results and discussion

### 3.1. Effect of current, voltage and electrode material

Fig. 1 shows the effect of the electrical field on the sintering behaviour of alumina for samples with platinum electrodes. First, we see immediately that the material considered can be flash sintered under an electric field (E-Field) in excess of 500 V/cm; if a voltage of 250 V/cm is applied, the shrinkage is limited.

The sintering temperature decreases significantly at higher E-fields, up to 1500 V/cm, when the material sinters at around  $920^\circ\text{C}$ . This shows clearly an anticipated sintering process if compared to the results collected by Cologna et al. on 0.25 wt% MgO-doped alumina [19]: the onset temperature for flash sintering (FS), in fact, decreases by  $120\text{--}230^\circ\text{C}$  (under the same field). This anticipated sintering process cannot be related to the different grain size [5], the powder we used being coarser ( $d_{50} = 0.6 \mu\text{m}$ ,  $d_{90} = 3.0 \mu\text{m}$ ) than that used by Cologna et al. (100–300 nm). In addition, we noted that the MgO-doped alumina used by Cologna et al. contains a larger amount of impurities (0.25 wt%) if compared with the material used here (0.20 wt%). This suggests that the anticipated FS phenomenon could be explained by some beneficial effect on corundum conductivity associated with the simultaneous presence of different chemical elements. Several authors have reported very limited cationic solubility in corundum [22–24], the solubility of magnesia at  $1720\text{--}1880^\circ\text{C}$  being only 75–175 ppm [24]. This means that almost all MgO contained in the powder used in the present work (and also in that used by Cologna et al.) produces the precipitation of a second resistive phase (periclase), which is not very effective for increasing the material conductivity. If different chemical elements are simultaneously added in amount larger than their solubility

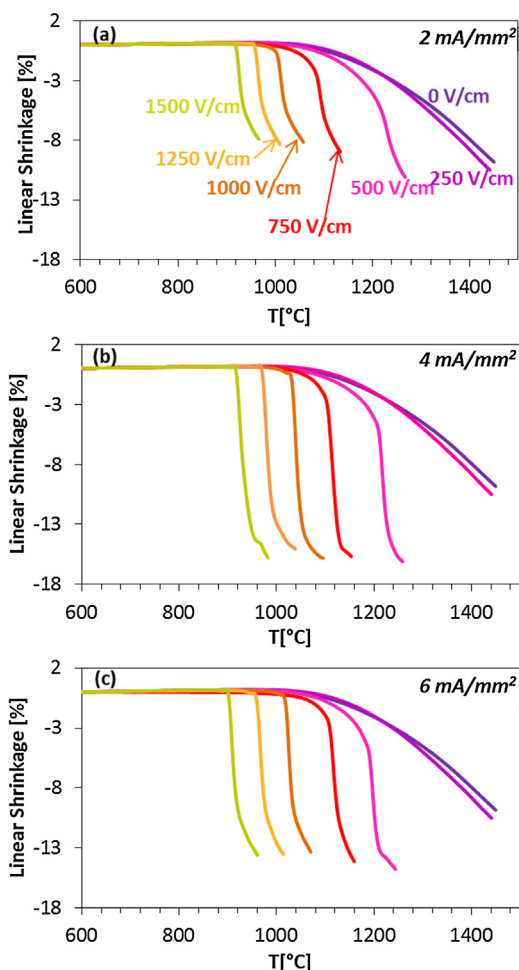


Fig. 1. Shrinkage curve for alumina sintered using Pt electrodes at various voltages and with nominal current densities of 2 mA/mm<sup>2</sup> (a), 4 mA/mm<sup>2</sup> (b) and 6 mA/mm<sup>2</sup> (c).

limit in alumina, it is reasonable to assume that the total amount of  $\text{Al}^{3+}$  that can be substituted by the doping cations is higher than what would be obtained by adding only MgO. In this solid solution, elements with oxidation number lower than 3 (e.g.,  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$ ) act as electron acceptors [25,26] and promote the formation of oxygen vacancies [26–28]; conversely, elements with oxidation number larger than 3 (like  $\text{Si}^{4+}$ ) behave as donors [25,26] and promote the formation of aluminium vacancies, as previously reported [28]. In this way, both ionic and electronic conductivity increase as a result of both greater vacancy concentration and narrower band gaps for electrons to jump in the conduction band, respectively.

Samples tested under low voltage (500–750 V/cm) exhibit two different densification mechanisms. The first occurs before reaching the current limit and is responsible for 3–6% linear shrinkage. The dilatometric plots show a characteristic downward concavity. The densification in this case is partially due to “conventional/thermal” sintering mechanisms. Nevertheless, we see that shrinkage increases with the applied E-Field: therefore, an electrical contribution to densification is also clearly present. For this reason, this sintering mechanism can be defined as Field Assisted Sintering (FAS).

The second part of the sintering process is characterized by an upward concavity in the dilatometric plots, occurring just after reaching the current limit. This is properly called flash sintering.

The samples tested under high voltage (1000–1500 V/cm), sinter at temperatures lower than  $1050^\circ\text{C}$  and therefore FS is responsible

Download English Version:

<https://daneshyari.com/en/article/1473459>

Download Persian Version:

<https://daneshyari.com/article/1473459>

[Daneshyari.com](https://daneshyari.com)