Field Assisted Sintering
FLASH SINTERING OF ALUMINA AND ITS MICROSTRUCTURAL EVOLUTION

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ABSTRACT
Alumina 99.8% pure was Flash Sintered under different fields and currents in the range of 500-1500 V/cm and 2-6mA/mm², respectively. It was shown that the considered material can be sintered down to 900°C and that the current density is controlling the shrinkage upon sintering. The analysis of the microstructure evolution pointed out that the porosity-grain boundary separation is enhanced by increasing the current.

INTRODUCTION
Field Assisted Sintering (FAS) represents a very promising route for consolidating ceramics at reduced time and temperature, with potential consistent decrease in energetic and environmental costs. Among FAS techniques, Flash Sintering (FS) allows to reduce, drastically, the sintering time to few seconds.

Flash Sintering has been studied in recent years on several semiconductive (YSZ1-5, GDC6, SiC7, ZrO₂-Al₂O₃ composites8) and conductive (MnCo₂O₄9, LSCF10) ceramics. Other insulating materials like high purity alumina and doped alumina have been tested and it has been shown that impurities play a crucial role upon field assisted sintering behavior11,12. In particular, it has been pointed out that the presence of different chemicals can reduce the onset temperature for FS.

Previous works have also shown that the application of an electric field may have a significant effect on the grain growth kinetics. The conclusions are anyway quite controversial and in some cases a retardation in grain growth was observed1,21,22 while in others an enhance growth kinetic was observed under the effect of high field22.

In the present work reactive alumina 99.8% pure was tested under different combinations of voltage/current limit with the purpose of identifying correlations between the microstructural features and the imposed electrical parameter. Moreover, the grain growth behavior upon conventional and field assisted sintering was studied.

EXPERIMENTAL PROCEDURE
α-alumina (Almatis CT3000SG, D₅₀ = 0.5 μm) with nominal composition (wt%) Al₂O₃ 99.8, MgO 0.04, Na₂O 0.03, Fe₂O₃ 0.015, SiO₂ 0.015, CaO 0.015 was used in the present work. The powder was shaped in dog-bone-like pellets by uniaxial pressing at 120 MPa with the addition of 6 wt% of water as binder. The cross section of the central part of the dog-bone green sample was 3x3÷4 mm². The samples were connected by two platinum wires to a DC power supply (Glassman EW series, 5 kV-120 mA) and to a multimeter (Keithley 2100), which allows to measure second-by-second the applied current and voltage. A drop of platinum paste was applied on the electrode for improving the electrical contact.

The samples were sintered in an alumina dilatometer (Linesis L-75) with a constant heating rate of 20°C/min and target temperature of 1450°C. A load of 0.8 N was applied to the sample by the dilatometer measuring rod. Once the sample reached 300°C, the power supply was opened and the system started to work under voltage control (250-1500 V/cm). Then, if the current limit was reached (2-6 mA/mm²), the current was let to flow for 2 min and finally the system was shut down.
For comparison, some samples were also conventionally sintered in the temperature range 1550-1700°C for different times (2-8 h) using a constant heating rate of 15°C/min.

The fracture surface of the samples (manually produced in the gage section at similar distance from the two electrodes) was analyzed by SEM (Jeol JSM 5500). The grain size was estimated by the linear intercept method. For each sample 12 measurements were taken.

RESULTS AND DISCUSSION

The dilatometric plots recorded during the FAS are reported in Fig 1. The dog-bone samples can be “flash sintered” here with fields higher than 500 V/cm. The sintering temperature is found to be definitely lower if compared with the results previously published on the same material with cylindrical samples\textsuperscript{12}. This is probably due to an improved metal-alumina electrical contact, which accounts for a reduced electrode resistance. Moreover, the onset temperature measured here under “flash sintering” conditions is lower than that found by Cologna et al. for 0.25 wt% MgO-doped alumina using a similar experimental set-up\textsuperscript{11}. It is very likely that the presence of different chemicals and impurities plays an important role on FS behavior. One possibility is that the presence of aliovalent elements may act as electron source/donor or may promote the formation of different lattice defects\textsuperscript{13-16}.

The dilatometric plots in Fig 1 show that the sintering temperature is drastically reduced down below 1000°C when fields in excess to 1000 V/cm are applied. In this case, the shrinkage occurs abruptly just after the current limit is reached. Conversely, under voltage equal to 750 V/cm or less, densification starts before the current limit is achieved and two main steps can be pointed out, the first corresponding to “thermal sintering” and the second associated to the “flash effect”. If a lower voltage is applied (250 V/cm) the E-Field effect is very limited.

![Figure 1: Dilatometric plot of field assisted sintered alumina with different voltage and current limit of 2 mA/mm\textsuperscript{2}. The shrinkage values are referred to the gage section.](image)

The current density is the key parameter controlling the sintering rate and the final density of the ceramic bodies. As shown in Fig 2 (a), the linear shrinkage (referred to the gage section) during the sintering process increases with the current. Moreover, one can notice that, if a low current is applied (i.e., 2 mA/mm\textsuperscript{2}), the final shrinkage is higher in the case of the samples sintered under low voltage (500-750 V/cm) with respect to those treated under higher filed. This could be the result of hybrid densification phenomena, where thermal-FAS sintering can not be
neglected. If higher current densities are imposed (i.e., 6 mA/mm$^2$), the densification is dominated by the flash sintering and all samples are characterized by similar linear shrinkage upon sintering.

The ratio between the shrinkage determined by FS and the total one is reported in Fig 2(b): if an E-field in excess to 1000 V/cm is applied, FS is responsible for the whole densification. Conversely, if the field is lower, a relevant part of the densification are due to thermal-FAST sintering, this effect becoming progressively less significant by increasing the current density.

![Figure 2](image.png)

Figure 2: (a) Linear shrinkage upon sintering as a function of the current density and (b) ratio between the shrinkage associated to FS and the total one.

The microstructural evolution is strongly related to the applied current. Some indicative SEM micrographs of the FS samples fracture surface are shown in Fig. 3. One can observe that the porosity becomes closed by increasing the current; in addition, very important grain growth phenomena are clear, especially considering that everything is happening in just 2 min. In the samples sintered with 2 mA/mm$^2$, the porosity is completely located at the grain boundary, while in those sintered with 6 mA/mm$^2$, a relevant amount of pores is isolated within the grains (Fig. 3(c)). This is due to the large grain boundary mobility during FS. Interestingly, also the fracture mechanism is changing from intergranular (low current) to mainly transgranular (high current, Fig. 3(c)), this pointing out different role of the grain boundary for variable current density. Conversely, no significant microstructural differences can be observed in the samples sintered under 0 and 250 V/cm. This can be accounted for by the fact that the sample sintered under 250 V/cm were not flash sintered and did not reach the current limit.

![Figure 3](image.png)

Figure 3: SEM micrograph of the FS samples fracture surface showing the microstructural evolution at different current density: 2mA/mm$^2$ (a), 4mA/mm$^2$ (b) and 6mA/mm$^2$ (c). The micrographs are referred to specimens treated with 1500 V/cm.
Figure 4 shows the average grain size as a function of the applied current under different voltage. It is possible observe that if the current is larger than 4 mA/mm², there is an abrupt increase in the grains dimension. Moreover, the applied voltage has very limited effect on the grain size. In other words, being the onset temperature for FS a function of the voltage, the effect of the furnace temperature (in the range 920-1200 °C) is very weak. Also the relative bulk density of the sintered body is reported in Figure 4 as a function of the applied current. One can notice that the densification of the material is strictly related to the current limit of the system, as it has been shown in a previous work.²³ For a more detailed discussion of this point see Ref.23.

The grain boundary is known to be a preferential path for both ionic¹⁷ and electronic conduction.¹⁸ Therefore, it is reasonable to assume that during FS there is a current concentration in these regions. One can speculate that, as a first and quite rough approximation, in the tested conditions the grain boundary temperature is proportional to the measured power dissipation. However, it was previously shown that during the steady stage of FS the power dissipation is, as a first approximation, proportional to current density¹²,²³. This is a result of the fact that, increasing the current limit, the sample gets hotter and the material resistivity decreases, this results in a non-ohmic behavior and the field is quite constant even is the current density is changing¹². Therefore, the present authors are going to speculate that the boundary temperature changes linearly with current density.

The well-known equation for modeling grain growth is¹⁹:

\[ G^n = G_0^n + K_0 \exp \left( -\frac{Q}{RT} \right) t \]  

where \( G \) and \( G_0 \) are the grain size at the end and at the beginning of the treatment, respectively, \( K_0 \) is a pre-exponential constant related the grain boundary mobility, \( Q \) the activation energy for diffusion across the grain boundary, \( R \) the universal constant for perfect gases, \( T \) and \( t \) the treating temperature and time, respectively. By using the assumption previously reported, Eq. (1) can be reduced to:

\[ G^n = G_0^n + K_0 \exp \left( -\frac{Q}{R C J} \right) t \]  

where \( J \) is the current density and \( C \) a constant. Being the treating time always the same (2 min), Eq. (2) can be written as:

\[ = G_0^n + A \exp \left( -\frac{B}{J} \right) \]  

where \( A \) and \( B \) are constant. By using Eq. (3), the experimental data were fitted by the least squares method and the best fit is:

\[ G^{0.128} = 0.39^{0.128} + 1.94 \exp \left( -\frac{13.7}{J} \right) \]  

where the grain size are in micron and \( J \) in mA/mm². The obtained fitting curve is shown in Fig. 5. It is interesting to observe that the value of \( G_0 \) (0.39 μm) is in good agreement with the powder size (\( D_{50} = 0.5 \) μm) and the value for \( n \) (0.128) is similar to that was previously calculated by Naik et al. for alumina-zirconia composites (0.12-0.13)²⁰.
The grain growth during conventional sintering was also studied by using Eq. (1). The best fit for modeling the grain size is:

\[
G = 4.3 \sqrt{0.3941 + 1.4 \times 10^{21} \exp \left( -\frac{92700}{P} \right) t};
\]

(5)

this means that for obtaining the measured grains size after 2 min FS, the grain boundaries should reach temperature in the range of 1508-1555, 1695-1733°C in samples sintered with 4 and 6 mA/mm², respectively. Such temperatures can be compared with the sample temperature as it can be estimated from the balance between the dissipated electrical and radiated power. The power balance is expressed by:

\[
V J E = S \sigma \varepsilon (T_s^4 - T_f^4)
\]

(6)

where V and S are the volume and the surface of the sample, respectively, \(\sigma\) the Stefan-Boltzmann constant, \(\varepsilon\) the emissivity and \(T_s\) and \(T_f\) the sample and furnace temperature, respectively. By using Eq. 6, the average sample temperature during the steady stage of Flash Sintering was estimated for 4 and 6 mA/mm² current density limit using emissivity equal to 0.5 and 0.7. The results, summarized in Table 1, show good agreement in the case of 4 mA/mm² current limit, while in the case of 6 mA/mm² the grain boundary temperature is higher than that calculated from the power balance. One possible explanation for this latter discrepancy can be the overheating at the grain boundary due to current concentration.
Flash Sintering of Alumina and Its Microstructural Evolution

Table I: Comparison between the average sample temperature ($T_s$), during the steady stage of Flash Sintering, estimated from the power balance (Eq. (6)) using different emissivity and the grain boundary temperature ($T_{GB}$) evaluated from the grain growth process.

<table>
<thead>
<tr>
<th>Current limit [mA/mm²]</th>
<th>$T_{GB}$</th>
<th>$T_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon=0.7$</td>
<td>$\varepsilon=0.5$</td>
</tr>
<tr>
<td>4</td>
<td>1508-1555°C</td>
<td>1430-1498°C</td>
</tr>
<tr>
<td>6</td>
<td>1695-1733°C</td>
<td>1503-1573°C</td>
</tr>
</tbody>
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CONCLUSIONS
On the basis of the results obtained in the present work some conclusions can be drawn:
I. Reactive alumina 99.8% pure can be flash sintered at temperatures as low as 900°C.
II. The current density controls the shrinkage upon sintering.
III. Flash sintering is associated to an evident grain growth phenomenon. By increasing the current, the porosity-grain boundary separation is enhanced.
IV. The grain size can be modeled by an exponential law as a function of the nominal current density.

REFERENCES
Flash Sintering of Alumina and Its Microstructural Evolution


