

Thermally-insulated flash sintering

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Abstract

The use of thermal insulation in flash sintering is proposed in this work. The results show that during conventional flash processes heat losses by radiation accounts for ~90% of the total energy input. Apart from being energy inefficient, heat losses have a negative effect on sample homogeneity. By employing insulating felts or powder beds these losses can significantly reduced while resulting in an improved densification. Analytical calculation, corroborated by experimental results, show an improvement up to 10% of the final density when a thermal insulation was employed.

Main body

Flash Sintering (FS) is a sintering technology, where an electric current is forced through a ceramic while it is heated in a furnace [1–4]. The flash phenomenon is characterized by the simultaneous observation of different effects: ultra-fast sintering, electrical resistivity drop and bright light emission; coupled with a thermal runaway of Joule heating [3,4]. The densification process is mainly controlled by the set current limit [5], which determines the peak and equilibrium sample temperature during FS [6].

The first and most commonly studied material is YSZ, which is characterized by many and uncommon effects upon FS. Among them, the activation of unexpected electronic conductivity [7,8], color changes [9,10], thermal gradients [9,11], abnormal grain growth in the electrodes regions[12] and phase transitions[13]. Despite the discussion about the “enhancing” role of electric current on sintering of YSZ is still an ongoing research topic [4,14–16]. Todd et al. have shown that Joule heating plays a pivotal role during the flash process, it triggers [17] and promotes densification [16] because of thermal runaway[18].

Starting from these basic considerations, the motivation of this letter is to understand whether or not 8YSZ densification upon FS might be enhanced by employing a thermal insulation, which prevent the heat to be dissipated from the sample toward the external environment. Apart from this, the proposed approach could allow to define in the future the intrinsic role of current on the densification, since a given temperature can be reached for different current densities values depending on the thermal insulation.

8YSZ powder (Tosho, Japan) was used in this work. Dog-bone-like samples, with gauge cross section $1.9 \times 3 \text{ mm}^2$ (as standard in previous works), were shaped by uniaxial pressing at 120 MPa using 5 wt% of B-1000 (Duramax) binder. Flash experiments were carried out in a vertical tube furnace at a constant temperature of 800°C on the pre-sintered samples (pre-sintering at 1100°C for 1 h, relative density ~45%). Two platinum wires, serving as electrodes, were forced within the holes present on the opposite side of the dog-bones and Pt-based paste was spread on the ceramic/metal interface to improve the electric contact. The Pt electrodes were connected to a DC 500V (Varied, RD-S5004T1) power source able to work in voltage and current control. The limiting voltage was set at 100 V/cm while different nominal current limits were used in the range 45 – 150 mA/mm². Once the system reached the current limit it was dwelled for 20 s, then the power source was shut down. Voltage and current were measured using data logging Module Nation instrument NI 9775 (acquisition frequency = 4 Hz). Different thermal insulating systems were used in order to reduce the radiative losses from the sample upon FS. These employed alumina felts (Morgan advanced materials, Kaowool 1600 Paper), alumina wool (Morgan advanced materials, super wool SW HT) and a 5 µm ZrO₂ power bed (Sigma Aldrich, grade 230693), as sketched in Figure 1. The density of the sintered samples was measured by Archimedes' method using an analytical balance with sensitivity 10⁻⁴ g. SEM micrographs of the samples sintered with 100 mA/mm² were taken on the external surface and in the sample center using (SEM, FEI inpect F50SU).

Table I reports some electrical data measured on the samples subjected to flash sintering without thermal insulation. The power dissipation and the sample temperature were calculated in the last 5 seconds of the flash process when a steady state is reached (i.e. no significant changes of current/voltage). The surface sample temperature (T_s) is estimated using the equation reported in [6] assuming an emissivity of 0.75 [16,17]. In absence of heat losses the Heating Energy (HE) follows:

$$HE = mC(T_s - T_0) \quad (1)$$

where m is the sample mass, C the specific heat (0.64 J/gK, substantially constant for $T > 800^\circ\text{C}$ [19]) and T_0 the furnace temperature. Comparing the HE with the total electrical energy input during the flash process, the energy effectively used for heating the sample represents is only about 10%, the other 90% being lost by radiation. Indeed, the efficiency would increase when working with larger sample (lower surface to volume ratio) or in “very short” flash processes which are more likely close to an “adiabatic” condition; but in any case it points out that strong losses take place during flash sintering, thus affecting the overall efficiency of the process. It is also worth mentioning that “very short” flashes, although being more energy efficient, are also characterized by very high power peaks which can damage the samples and cause hot spots [20,21]. The positive temperature coefficient of electrical conductivity along with surface heat losses could even accentuate the surface to core thermal gradients resulting in uneven microstructures.

A thermal insulation might reduce the losses and help to produce denser samples with a lower power dissipation. Using some heat transfer models we can estimate the surface temperature for a sample of radius R_1 embedded within an insulating medium of radius R_2 as:

$$T_{(R_1)} = \frac{WR_2}{kS_2} \ln(R_2/R_1) + T_{(R_2)} \quad (2)$$

where W is the electric power, k the thermal conductivity, and $T_{(R_2)}$ the temperature on the external surface of extension S_2 of the insulating medium (the derivation of Eq.2 is reported in “Supplementary material”). Eq. 2 refers to a stationary condition for an axial-symmetric problem.

Figure 2(a) shows a comparison between the estimated surface sample temperature with and without thermal insulation in terms of the overheating due to the application of the insulating medium. The curves refers to a 20 mm long cylindrical sample of radius $R_1 = 1.5$ mm with an applied power of 30 W. One can observe that (i) significant overheating can be obtained even when applying very thin insulating layers if their thermal conductivity is lower than 0.8 W/mK and (ii) if the employed material is not a good insulator the overheating becomes negative, in other words the application of an additional material around the sample causes a temperature drop. The thermal conductivity value at which this transition takes place depends on the insulating layer thickness and on the applied electric power as shown in Figure 2(b).

It is worth mentioning that refractory wools widely used in high temperature applications have a thermal conductivity at room temperature in the order of 0.05 W/mK, which however rapidly increases with temperature (about 0.3 W/mK at 1500°C) [22]. In any case, the “cooling” conditions reported in Figure 2 are very unlikely to be reach; therefore, their application should have a beneficial effect on the equilibrium sample temperature. Another important characteristic of the insulation system is that it should be flexible and able to follow the sample shrinkage during sintering.

Indeed, the overheating reported in Figure 2 are theoretical results which cannot be reproduced experimentally: such temperature values would cause a rapid degradation of the insulating medium which would lose its insulating properties. However, Figure 2 clearly points out that the use of a suitable experimental design could definitively improve flash sintering.

To validate the model, Thermally-Insulated Flash Sintering (TI-FS) experiments were carried out with the configurations reported in Figure 1. Figure 3(a,b) shows the relative bulk density and the apparent porosity as a function of the limiting current. One can observe that the materials treated by TI-FS are denser and less porous with respect to those treated with conventional flash process. The relative density in particular is improved by about 4-10% in TI-FS. Albeit the density variation is not huge, it is definitively significant and proves for the first time to our best knowledge that the densification upon FS can be improved by using very simple modifications to the traditional FS set-up. The density improvement upon TI-FS is indeed related to the reduction of the heat losses from the sample, which allow to achieve higher temperatures at a given electric current. This has a beneficial effect also on the energy consumption, which is reduced in the case of TI-FS (Figure 3(c,d)). A rough estimation of the sample overheating based on the comparison between the density measured with and without thermal insulation is reported in “Supplementary material”. Such results indicate that TI-FS lead to an average overheating of about 80°C with respect to conventional flash

process. Albeit no clear and significant differences can be pointed out between the different insulation systems, ZrO₂ powder bed slightly over-perform the others. It should be additionally mentioned that ZrO₂ powder bed is also expected to be more stable at high temperature since alumina felts and wool contain silica.

SEM micrographs are in agreement with the density results: Figure 4 shows that the material treated with TI-FS is denser and better sintered in comparison to the conventionally flashed one. The TI-FS sample evidences grain coarsening phenomena due to the increased temperature reached upon TI-FS. Moreover, Figure 4 shows some weak microstructural heterogeneities surface-core (specimen nominal cross section 1.9x3 mm²), more evident in the sample treated without thermal insulation. Temperature heterogeneities (surface-core) are expected to become significant [7] when working with larger components and the built up thermal stresses could affect the structural integrity of the samples. From this point of view, the use of thermal insulation may have a beneficial effect, reducing the losses from the surface and the induced thermal gradients. Additional micrographs are reported in "Supplementary material".

In summary we show that by employing a thermal insulation FS can be improved. The application of insulating media around the sample enhances densification, reduces the energy consumption and increases the efficiency of the process. The lower powers used in TI-FS may also have a beneficial effect on the final homogeneity of the sample, reducing the probability of hot spots-formation which are likely at high power densities[4].

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Figures

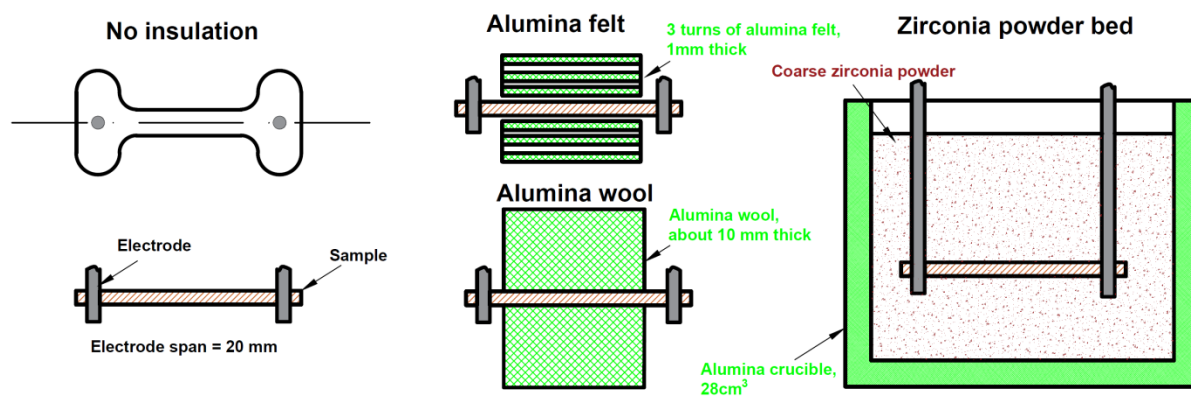


Figure 1: Flash sintering experimental set-up with and without thermal insulation.

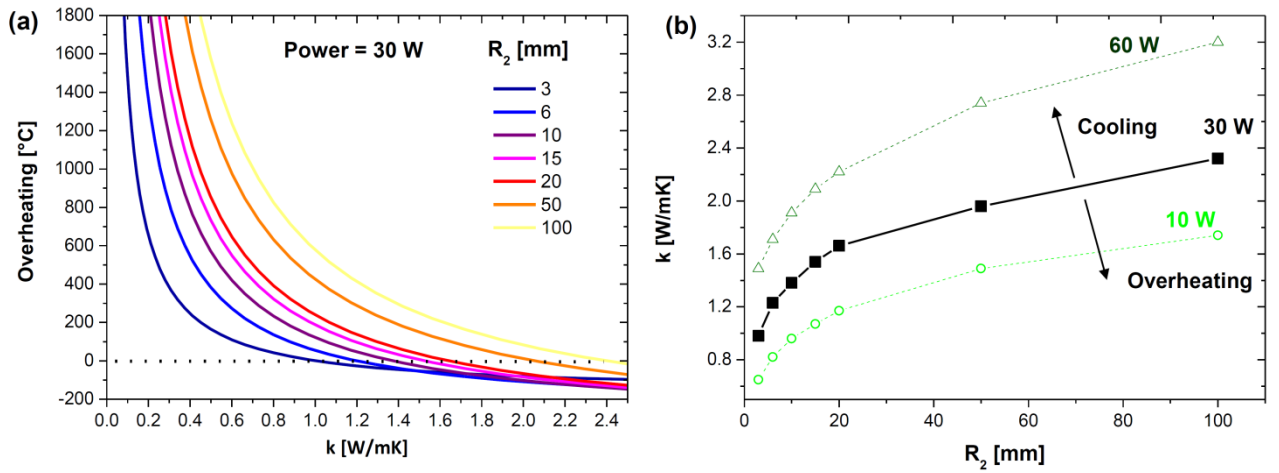


Figure 2: Surface sample overheating seen in presence of insulating medium having radius R_2 as a function of its thermal conductivity k (a). R_2 vs. k maps showing the conditions leading to an effective overheating or cooling depending on the thermal insulation of the sample (b). The analysis refers to the steady state of an axial-symmetric problem (sample 20 mm long with radius 1.5 mm, details in “Supplementary material”).

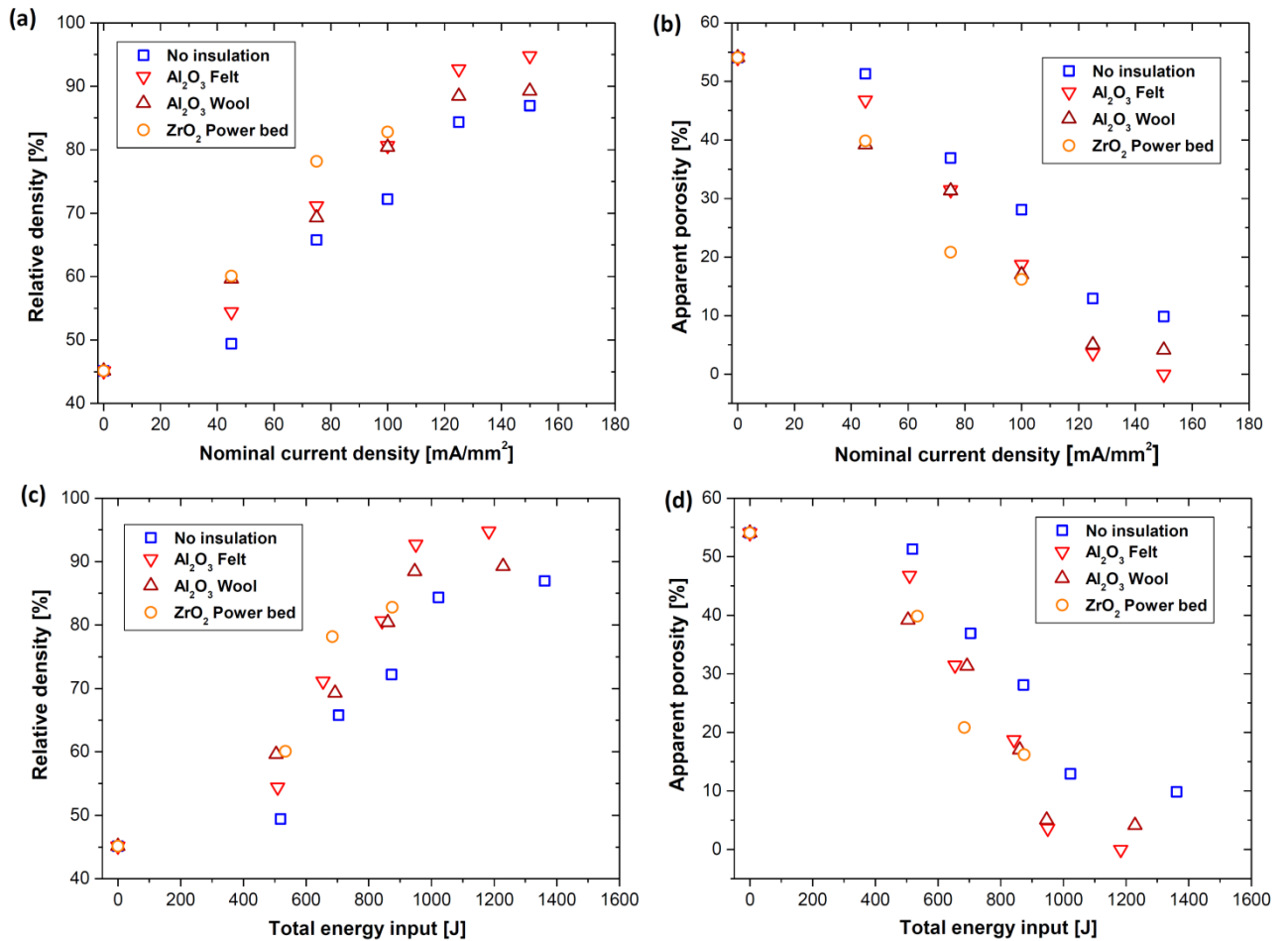


Figure 3: Relative (bulk) density (a,c) and apparent porosity (b,d) as a function of the applied nominal current limit (a,b) of the total energy input (c,d) upon FS (dwelling time in the flash state 20 s).

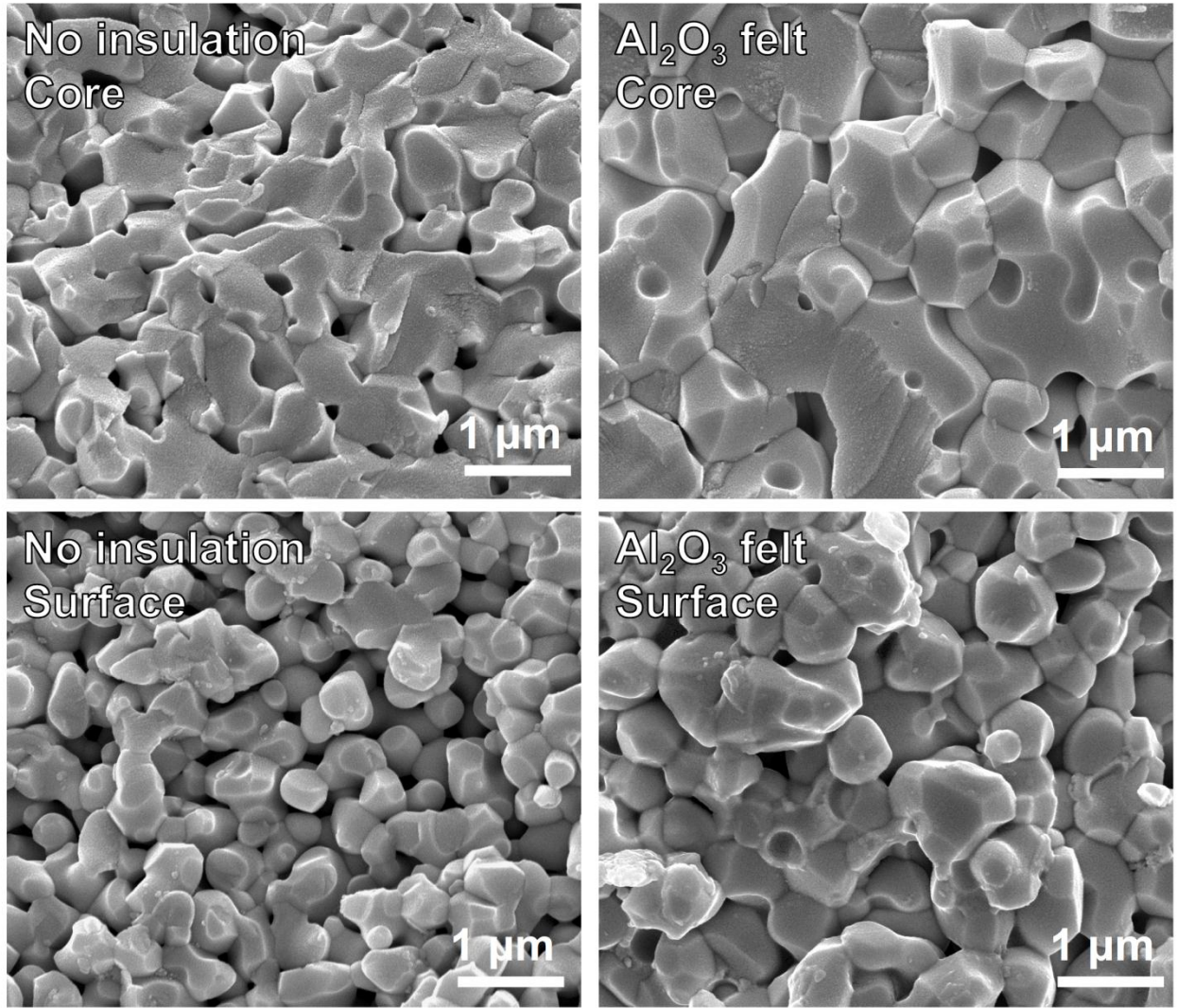


Figure 4: SEM micrographs of the fracture and external surface of samples treated with 100 mA/mm² for 20 s with and without (a,c) thermal insulation.

Table I: Flash sintering electric parameters recorded during the experiments without thermal insulation. The electric power and the sample temperature, T_s , were measured in the steady stage of FS (last 5 seconds of the experiments), efficiency refers to the ratio between the energy need to reach T_s in absence of any heat loss and the total FS energy input.

J [mA/mm ²]	Power [W]	T_s [°C]	Total energy input [J]	Heating energy [J]	Efficiency [%]
45	16	1085	519	56	10.9
75	21	1163	704	72	10.2
100	29	1337	873	107	12.2
125	34	1409	1023	121	11.8
150	54	1590	1361	157	11.5