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Flash Microwave Sintering of Alumina

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Abstract :

Conventional flash sintering is difficult to adapt to ceramics with a very low electrical conductivity like pure alumina. Alternatively, the latter can be heated by microwave/matter interaction due to dielectric losses. Microwave energy is also preferable as it allows a rapid contactless and volumetric heating that can be initiated by susceptors. This work presents the assembly designed for this purpose by using a 2.45 GHz single-mode microwave cavity and the original assembly of susceptors made from silicon carbide plates and a 3D printed zirconia crucible. Controlled thermal cycles ranging from 300 to 900 K/min were successfully applied while measuring the shrinkage during the flash sintering. Alumina pieces were successfully sintered up to 93-98 % in mere seconds, depending on the heating rates, and microstructures were discussed according to the microwave “flash” heating conditions originally applied.

Keywords : Flash sintering ; Alumina ; microwave sintering ; hybrid heating

I. Introduction

The flash sintering process has recently emerged as an advanced technique able to produce dense ceramic parts in a few seconds [1–4] . This method consists in applying a large voltage across a ceramic piece, which induces an electric power surge through it. The Joule’s effect results in an extremely fast heating of the granular compact and allows its rapid densification. This method has been initially developed for zirconia, taking advantage of the sudden increase of the electrical conductivity of this ceramic with temperature (Negative Temperature Coefficient behavior on the resistivity). The observed thermal runaway is the result of a combination of the applied high electric voltage, the temperature dependence of the electrical conductivity and the thermal losses which occur during the “flash” event[5–7]. This method implies the use of electrodes, and is mostly suitable for NTC type behavior ceramics. However, other materials, as alumina, have been tried these years[8]. In

conventional flash sintering, as pure alumina is a dielectric, it would require both high electric fields and temperatures to initiate the flash sintering, which is very challenging[9]. To overcome this issue, some authors employ some additives like MgO to increase the electrical conductivity of alumina[10]. In this communication, the aim is to replace the Joule heating process by an electrode-less microwave process adapted to alumina that couples with microwave energy at high temperatures where dielectric losses become high enough[11,12]. Flash microwave sintering has already been applied to low conductive ceramics at 24 GHz gyrotron frequency[13–15]. In this paper, a magnetron 2.45 GHz single-mode resonant cavity is designed to impose heating ramps ranging from 300 to 900 K/min. An original assembly of susceptors was used, made from silicon carbide and 3D printed zirconia materials. This new assembly opens the way of regulated “flash” sintering without the need of using any electrodes.

II. Materials and Method

In this study, Al₂O₃ powder from Baikowski (BMA 15 – Specific Surface Area 15m².g⁻¹, d₅₀=120 nm) was used as raw material. The 50% dense green samples (∅6mm, h5mm) were obtained by uniaxial pressing. The heating device consists in a 2.45 GHz single-mode TE₁₀₅ resonant cavity with a SAIREM microwave generator (magnetron GMP20KSM). The alumina sample is located in the middle of a container made by an assembly of SiC and 3D printed zirconia susceptors. They respectively initiate and impose a rapid heating behavior to the alumina sample. This container is surrounded by an aluminosilicate thermal insulation box (figure 1(a)). The temperature is measured by infrared pyrometer, pointing on the surface of the zirconia susceptor. Dilatometry measurements were also performed during microwave heating using an alumina pushrod leaning on the top of the sample, and an external displacement sensor (magnescapeDS830SLR)[16]. The impact of rapid and flash conditions on the sintering behavior of alumina has been studied through different PID regulated temperature cycles reported in figure 1b. After sintering, the density of each sample was measured in ethanol by Archimedes’s method. The determination of the grain size and the microstructure were obtained on polished surfaces using a scanning electron microscope JEOL 7200.

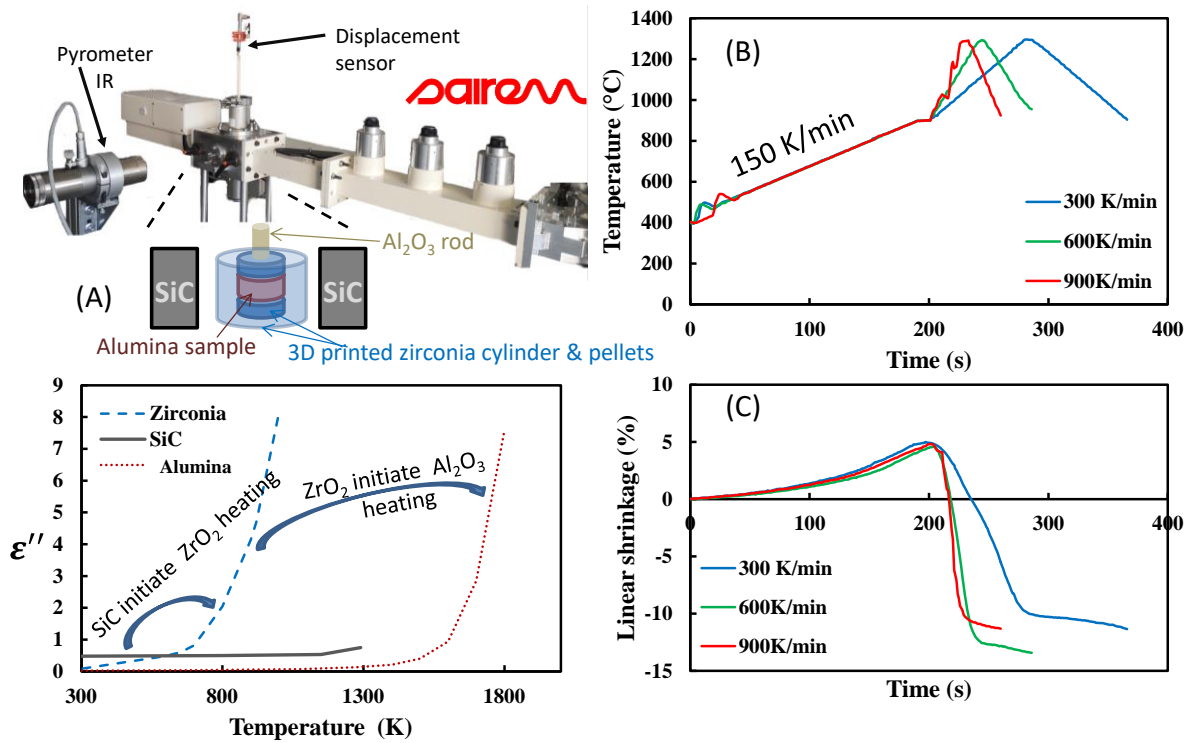


Figure 1. Scheme of microwave configuration and susceptors cascade heating strategy (A), experimental temperature cycles (B), shrinkage curves (C).

III. Results and Discussion

In this study, alumina sintering with heating rates ranging from 300 to 900 K/min has been studied. Some of the shrinkage curves versus time are plotted in figure 1c. All shrinkage curves are very similar, with a rapid densification of alumina as temperature rapidly increases. Those shrinkage curves clearly show that all materials are successfully sintered, with a final shrinkage value of ~10-15%. Even the material heated with the highest heating rate (900K/min) shows a final shrinkage of ~12 %, demonstrating that flash microwave sintering has been successfully achieved (for the latter, the total process time being 4 minutes, including the cooling time).

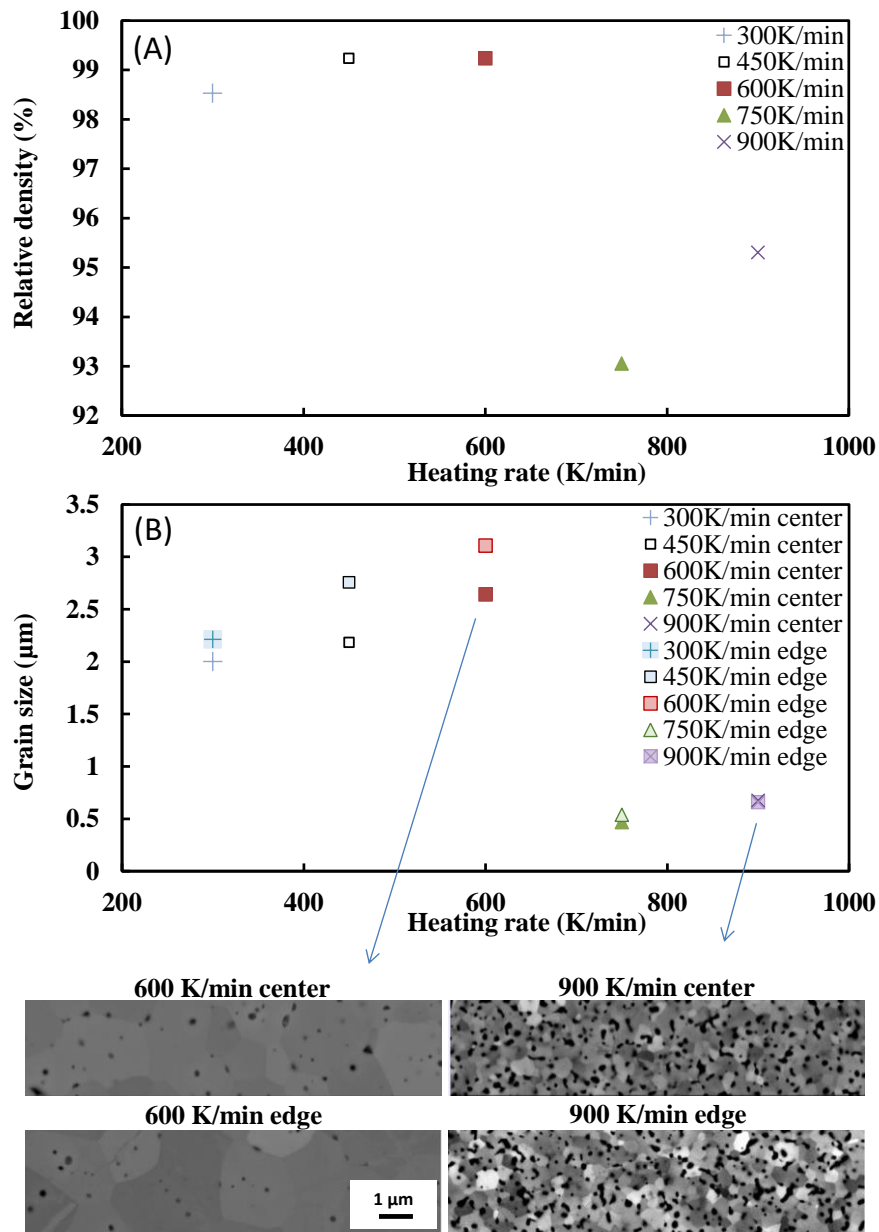


Figure 2. Graph of the relative density (A) and grain size (B) versus the heating rates of the tests.

Up to 600 K/min, relative densities are 98-99 % (see figure 2a). For the highest heating rates (750 and 900 K/min), density decreases down to 93-94 % (figure 2a). Simultaneously, the grain size increases up to 2-3 μm, for the lowest heating rates and remains low (0.5 μm) for the highest heating rates (≥ 750 K/min), as shown on figure 2b. When comparing the microstructures for the sample sintered at 900 K/min, no significant grain size heterogeneity can be observed between the center and the edges. Otherwise, the pores remain in the intergranular region and grains do not grow that much (grain size

going from ~ 120 nm for the starting powder to 500 nm when sintered). Actually, the microstructure reveals that the sintering is at the beginning of the final stage (porosities are closed) and that the porosity was located in intergranular region. The very fast heating rates do not allow the material to evolve towards a full dense microstructure. Moreover, the microstructure is similar regardless of the location – center and edges, suggesting that the temperature distribution field within the material is relatively homogeneous, despite the very fast heating cycle. For heating rates lower than 750 K/min, grain have rapidly grown, trapping the pores inside (figure 2b). This type of microstructure is often observed in ceramic sintered at too high temperatures. The grain boundary mobility is higher than pores mobility resulting in intragranular porosity[17]. Otherwise the zirconia crucible temperature is likely higher than the alumina temperature that causes a slightly coarser microstructure on the periphery. It is probably the same for the highest heating rates, but the heating process is too fast to be observed on the alumina microstructure (the center is similar to the edges). The sintering trajectory of similar powders of alumina (Specific Surface Area $13.7\text{m}^2\cdot\text{g}^{-1}$) is reported on figure 3. Black continuous line represents the alumina sintered conventionally by Bodisova *et al*[18] and blue dash line represents the alumina sintered with ultrafast high temperature by Kermani *et al*[19]. Our data (grain size *versus* density) obtained for various heating rates are also represented on the graph. Two comments can be made. First, the experiments below 750K/min converge towards the conventional trajectory. The grains are, however, slightly bigger than those obtained in the conventionally sintered material. This can be explained by the overheating of the ceramic, as shown by the intragranular porosity discussed previously. For the highest heating rates, experiments converge towards the ultrafast sintering. Grain size does not significantly change, while relative densities are still higher than 90% with no intragranular porosity. These experiments show that very high heating rates (> 750 K/min) help to retain fine microstructure even if adjusting the process parameters is still needed to improve the densification. Besides, microwave heating can be a relevant process to approach “flash sintering’ for thick dielectrics exhibiting very low NTC behavior.

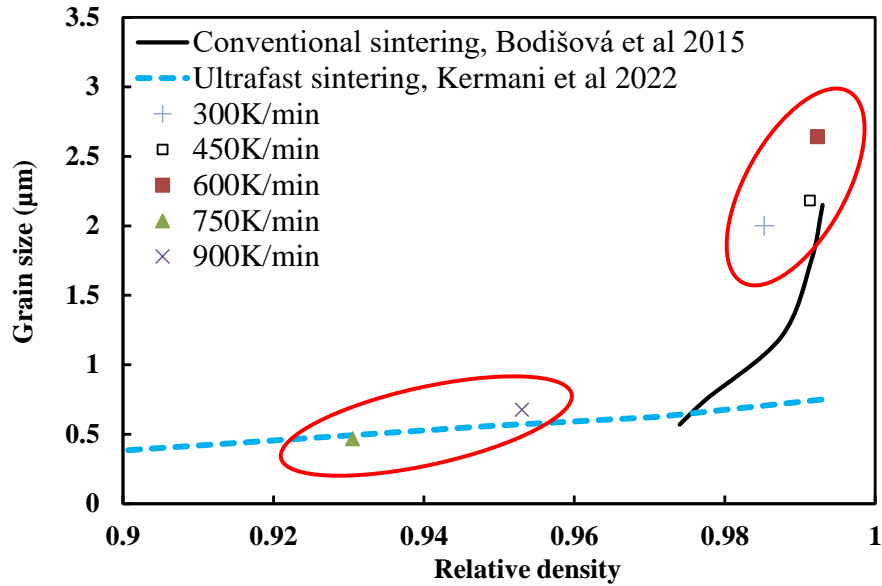


Figure 3. Sintering trajectories of the tests.

IV. Conclusion

An original assembly of susceptors made from silicon carbide plates combined with a 3D printed zirconia susceptor was designed and used to achieve PID regulated “flash” heating conditions (heating rates up to 900 K/min) in a 2.45 GHz microwave cavity. The as-designed assembly was used to sinter alumina disks with well-controlled heating ramps ranging from 300K/min to 900K/min. Such thermal cycles allow providing similar process times than those applied during flash sintering, except that the incubation stage is replaced by an ultra-rapid heating ramp. For alumina, typical flash sintering is very challenging due to its insulating behavior. On the contrary, taking advantage of the high temperature dielectric loss of alumina, hybrid flash microwave heating and sintering of alumina become possible. Experimentally, the shrinkage curves indeed indicate that the sintering of alumina has been completed for all investigated heating cycles. However, the best densities (>98%) are achieved for near 600 K/min with microstructures revealing grain growth and intragranular porosity. For the highest heating rates, densities achieve 93-94 % but intergranular pores are preserved, with low grain growth. Although the microstructure could be optimized, these experiments show that microwave heating can be a relevant process to approach “flash sintering” conditions for dielectrics.

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