Effect of specific absorbed power on microwave sintering of 3YSZ ceramics

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Abstract. Samples of 3 % yttria-stabilized zirconia (3YSZ) ceramics have been sintered to near full density with no appreciable grain growth using an ultra-rapid microwave sintering process. The sintering experiments were carried out on a 24 GHz / 6 kW gyrotron system for microwave processing of materials with automatic process control. By varying the properties of the thermal insulation surrounding the samples it was possible to vary the microwaves power required for heating. The final relative density of 3YSZ ceramic samples microwave heated at a rate of 50 °С/min to a temperature of 1400 °C without isothermal hold varied from 91.6 % when the specific absorbed microwave power was 4 W/cm³ to 99.4 % when the specific absorbed microwave power was 90 W/cm³. The specific absorbed power is therefore demonstrated to be the key parameter determining the achievable density in ultra-rapid field-assisted sintering processes.

1. Introduction

The effect of very rapid, so called flash sintering occurring when the sample is subjected to a dc or ac electric field, has recently attracted significant research interest. Authors of most recent studies associate the flash sintering effect with the development of an overheating instability in the materials [1–3]. This instability, commonly known as thermal runaway, is well known in the experiments on microwave heating of dielectric materials – in particular, on microwave sintering. A model explaining the growth of the instability was developed in [4–6]. The instability is observed during the heating of materials in which the effective electric conductivity grows with temperature, which creates a nonlinear positive feedback. It develops when the ratio between the specific power of microwave radiation absorbed per unit volume of material and the specific power of heat losses from its surface exceeds a certain threshold. A similar effect is apparently observed when the role of the volumetric power source is played by the Joule losses of the electric current flowing through the sample, as in the dc/ac flash sintering experiments. If the conductivity vs. temperature dependency and the parameters of the cooling process are known quantitatively, it is possible to calculate the parameters of the thermal instability. Such calculations were accomplished to determine the instability onset for the dc field-assisted sintering of ceramic compacts of various compositions: 3YSZ [2], 3YSZ and BaTiO₃ [7], ZnO [3], TiO₂ [8], Al₂O₃ [9], SrTi₅₋ₓFeₓO₃₋δ [10]. In the flash sintering experiments the measurable process parameters are the applied voltage, current, furnace temperature and the temperature at the sample surface. However, it is clear that the development of the thermal instability is determined not by separate electric parameters but rather by the relationship between the energetic characteristics of the heating process, viz. specific power of volumetric heat deposition and heat removal. An analysis of many experimental results on...
flash sintering [11] suggests that regardless of the type of electrical conduction in the material, the transition to rapid nonlinear increase in the electric conductivity of the materials occurs in a narrow range of specific power, 10...50 W/cm², while the values of the temperature and electric field strength vary widely (300...1300 °C and 10...1000 V/cm, respectively).

It follows from estimates [12] that the increase in temperature in the bulk of the samples during the development of the thermal instability may reach 800 °C relative to the temperature before the onset of sintering. However, according to [12] such an increase is insufficient to explain the observed ultra-rapid sintering by enhanced rates of thermally activated processes of solid-state diffusion mass transport. The exponential growth of the conductivity per se does not explain the accelerated sintering. Yet, the results of the flash sintering studies evidence that ultra-rapid densification is only observed when the specific power of Joule heating exceeds a certain threshold value - that is, when the thermal instability develops.

Recently, it has been shown that ultra-rapid or flash sintering is also observed during microwave sintering of ceramic materials such as Al₂O₃, Y₂O₃, MgAl₂O₄, and Yb(LaY)₂O₃ [13, 14]. It follows from these studies that a sharp acceleration of sintering occurs due to softening or melting of grain boundaries when the level of specific absorbed microwave power corresponds to the onset of thermal instability. In this paper the effect of the specific absorbed power is investigated in the process of microwave sintering of 3YSZ ceramics.

2. Experimental

Commercially available 3 % yttria-stabilized zirconia powder (TZ-3Y, Tosoh corporation, Japan) was used in the present work. According to the producer’s certificate, the powder has the following physical and chemical properties: crystallite size – 27 nm, particle size (D₉₀) – 0.6 µm, specific surface area – 16 ± 4 m²/g; impurity content (wt. %): Al₂O₃ ≤ 0.1, SiO₂ ≤ 0.02, Fe₂O₃ ≤ 0.01, Na₂O ≤ 0.04. The powder was used to fabricate plates by slip casting. The plates were dried for several days in air, then calcined for 2 hours at 800 °C in air. The samples in the form of discs, 12 mm in diameter and approximately 2.5 mm in height, were cut out from the plates. The green density of the samples was 49.5 % of the theoretical density. Two dimples for positioning thermocouple heads, 1 mm in diameter and 1.25 mm in depth, were drilled on the surface of the samples in the centre and 1 mm away from the edge.

The samples were heated in the applicator of a gyrotron system with a microwave power up to 6 kW at a frequency of 24 GHz equipped with a computerized feedback power control circuit [15]. The powder compacts were sintered in air at normal pressure. To limit heat losses from the samples undergoing microwave heating, two types of thermal insulation arrangements were used. In one case, the samples were placed in the centre of a cylindrical quartz crucible, 100 mm in diameter and 100 mm in height, which was filled with coarse alumina powder. In the other case, the samples were placed in a container fabricated from plates of highly porous, low microwave absorbing material Valox-1750 (Thermoceramica Ltd., Russia).

The samples were heated to a preset maximum sintering temperature chosen from the range 1100 – 1500 °C at a preset fixed heating rate (10, 15, 50, 100, 150 °C/min). The temperature was measured using B-type thermocouples. The process control was based on the reading of the thermocouple located in the centre of the sample. The heating was terminated when the preset maximum temperature was reached, i.e., sintering with zero hold time was performed. The microwave power was switched off automatically by the computer control system and the sample cooled down along with the thermal insulation surrounding it. For comparative study of densification the samples were heated conventionally in identical regimes using the resistive furnace “Thermoceramica-1700” (Thermoceramica Ltd., Russia).

The density of the sintered samples was determined by Archimedes weighing in distilled water with an estimated accuracy of ± 0.01 g/cm³. The microstructure of the sintered samples was studied by scanning electron microscopy (JEOL JSM-6390 LV). The phase composition of the sintered samples was analyzed using a Rigaku Ultima IV X-ray diffractometer.
3. Results and discussion

To analyze the influence of the specific absorbed microwave power on the process of densification of the material, series of heating runs were accomplished in identical regimes differing in the conditions of convective and radiative heat removal from the surface of the samples. The specific power spent on the heating of the samples, $P_v$, was determined from the energy balance equations, using the values of the heating and the cooling rates recorded immediately before and after the time instant when the maximum temperature was achieved and the microwave power was switched off \[13, 14\]:

$$P_v = \rho C \left( \frac{dT}{dt} \right)_+ + P_{hl} \quad P_{hl} = \rho C \left( \frac{dT}{dt} \right)_-$$

(1)

where $\rho$ is density, $C$ is specific heat capacity of the material of the sample, $P_{hl}$ is the power in heat losses, $(dT/dt)_+$ and $(dT/dt)_-$ are the rates of heating and cooling before and after the microwave power switchoff, respectively. The value of $P_v$ can be varied in experiments by either varying the heating rate (that depends on the input microwave power) or the cooling rate (that depends on the heat removal / thermal insulation conditions).

The variation of the heat removal conditions was implemented in this study by using two types of thermal insulation arrangements with considerably different thermophysical and electrophysical properties. It should be noted that within the approach adopted in this paper there is no need in knowing these properties in detail. The power in heat losses, $P_{hl}$, which is needed to derive the specific absorbed power, is characterized by measuring the cooling rate. This makes this method especially attractive from the viewpoint of practice. In fact, the absence of information about the microwave absorption coefficients of the thermoinsulating materials and their temperature dependencies, as well as the lack of data on their thermophysical properties make it not possible to calculate or estimate the heat removal characteristics. Moreover, even if such data were available, the calculations would be not much reliable because the 3D temperature fields in the objects undergoing heating are not known.

To illustrate the different properties of two thermal insulation arrangements, shown in figure 1 are the temperature data recorded during heating of the samples at a rate of 50 °C/min to a temperature of 1400 °C and subsequent cooling using the $\text{Al}_2\text{O}_3$ powder filling (a) and Valox-1750 plates (b) as thermal insulation. In the former case the cooling rate at the beginning of the cooling process was 70 °C/min, and in the latter case – 1360 °C/min.

The difference in the cooling rates under different thermal insulation conditions is associated with the difference in the temperature distributions formed due to the absorption of microwave radiation. In the case of $\text{Al}_2\text{O}_3$ powder filling, the microwave absorption in the powder layer with a thickness of about 4 cm results in its considerable heating. The measurements of the temperature difference between the centre of the sample and the point located 1 mm away from its edge give an idea of the temperature...
value at the side of the thermal insulation arrangement facing the sample. When the temperature of the sample is 1300...1500 °C, the temperature difference on the radial distance of 5 mm is 20 – 25 °C in the case of Al₂O₃ powder filling and about 100 °C in the case of Valox-1750 plates used as thermal insulation. In the latter case, the temperature gradients arising in the samples reach about 200 °C/cm, which sometimes resulted in partial cracking of the samples.

Listed in table 1 are the values of the specific absorbed power – estimated according to equations (1) and averaged over several experimental runs – for the processes of heating to temperatures 1100…1500 °C using different thermal insulation arrangements. For estimates it was taken that \( \rho \approx 6 \text{ g/cm}^3 \) and \( C \approx 0.7 \text{ J/g}^\circ\text{C} \).

| Heating rate, °C/min | Specific absorbed microwave power, W/cm³ |
|----------------------|-----------------------------------------|
|                      | Thermal insulation:                      |
|                      | Al₂O₃ powder (1300 °C ≤ T ≤ 1500 °C)     |
|                      | Valox-1750 plates (1100 °C ≤ T ≤ 1400 °C) |
| 15                   | 4                                        |
| 50                   | 8                                        |
| 100                  | 12                                       |

In the case of "less efficient" thermal insulation (Valox-1750 plates) the values of the specific absorbed power are more than an order of magnitude higher. It occurs that this results in considerably higher final densities of the sintered samples. For example, the density of 95.5 % achieved using the "less efficient" thermal insulation at a temperature of 1100 °C \( (P_v = 60 \text{ W/cm}^3) \) is only obtained at a temperature of 1450 °C when the "more efficient" thermal insulation \( (\text{Al}_2\text{O}_3 \text{ powder filling}) \) is used and the specific absorbed power is much lower \( (P_v = 4 \text{ W/cm}^3) \).

Shown in figure 2 are the dependencies of the relative density of the samples, sintered at different temperatures, on the specific absorbed power during heating. When the samples were microwave heated in the "more efficient" thermal insulation their relative density varied from 55.3 to 96.2 % of the theoretical value at variation of temperature from 1100 °C to 1400 °C. When the "less efficient" thermal insulation was used, the relative density varied from 95.5 to 99.4 % at the same variation of temperature. It should be noted here that 3YSZ ceramic samples with densities exceeding 99 % have been fabricated by ultra-rapid microwave sintering in the regimes without the isothermal heating stage at maximum temperature.

It can be argued that the levels of the specific absorbed power that are characteristic of the processes using the "more efficient" thermal insulation \( (2 \text{ W/cm}^3 \leq P_v \leq 12 \text{ W/cm}^3) \) are insufficient to trigger the thermal instability, whereas the levels of the specific absorbed power in the processes using the "less efficient" thermal insulation \( (60 \text{ W/cm}^3 \leq P_v \leq 120 \text{ W/cm}^3) \) do lead to the development of the instability. It occurs that the presence of the instability is a necessary condition of obtaining high final density in an ultra-rapid sintering process. This observation is consistent with the results of analysis of dc/ac field-assisted flash sintering experiments [11] which indicate that the development of thermal instability in various materials begins at specific absorbed power levels on the order of 10...50 W/cm³ and results in ultra-rapid ("flash") densification.

Shown in figure 3 are SEM images of the polished surfaces of the samples sintered under microwave heating at a rate of 50 °C/min to a temperature of 1400 °C in the "more efficient" thermal insulation (figure 3a, \( P_v = 12 \text{ W/cm}^3 \)) and "less efficient" thermal insulation (figure 3b, \( P_v = 120 \text{ W/cm}^3 \)). The average grain size in both samples is close to the initial grain size \( (D_{50} = 0.6 \text{ µm}) \). This demonstrates that near full density 3YSZ ceramics \( (\rho = 99.4 \% \rho_0) \) with practically no grain growth can be obtained by ultra-rapid microwave sintering without isothermal hold.
Figure 2. Relative density of the sintered 3YSZ samples vs. specific absorbed microwave power for different maximum temperatures and two types of thermal insulation – Al₂O₃ powder filling or Valox-1750 plates.

Figure 3. SEM images of the polished surfaces of the samples sintered under microwave heating at a rate of 50 °C/min to a temperature of 1400 °C: (a) in the "more efficient" thermal insulation (Al₂O₃ powder filling, \( P_v = 12 \text{ W/cm}^3 \)); (b) in the "less efficient" thermal insulation (Valox-1750 plates, \( P_v = 120 \text{ W/cm}^3 \)).
4. Conclusion
Near full density 3YSZ ceramics have been obtained by ultra-rapid microwave sintering without isothermal hold. Along with temperature, a critical parameter that characterizes the ultra-rapid sintering is the specific microwave power absorbed in the sample per unit volume. At a temperature of 1400 °C and the specific absorbed power about 90 W/cm$^3$ the achieved density of the sintered samples is 99.4 % of the theoretical value. Due to high heating rates and the absence of isothermal hold the average grain size in the sintered samples is practically equal to the particle size of the initial powder material (0.6 µm).

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