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Microwave versus conventional sintering: Estimate of the apparent activation energy for densification of α -alumina and zinc oxide

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A comparative study between the conventional and 2.45 GHz microwave multimode sintering behavior of insulator (α -Al₂O₃) and semi-conductive ceramic (ZnO) was systematically investigated. The apparent activation energy of nonisothermal sintering was determined by way of the Arrhenius plot of densification data at constant heating rates (CHR) and the concepts of Master Sintering Curves (MSCs), respectively. During microwave densification process, the apparent activation energy was about 90 kJ/mol less than the value for conventional sintering of Al₂O₃ applying these two estimation methods. However, an opposite result was obtained in the case of ZnO, although its densification process had been also accelerated by microwave as well as Al₂O₃. The significant differences in activation energy give a good proof of the difference in diffusion mechanism induced by the electromagnetic field underlying microwave sintering.

Keywords: Microwave processing; Sintering; Activation energy; α -Al₂O₃; ZnO

1. Introduction

In order to achieve rapid heating, low sintering temperature and low processing cost, microwave-assisted process has received intensive interests for sintering various ceramic materials.¹⁻³ Thanks to the coupling between electromagnetic fields and materials, microwave sintering provides the possibility to heat volumetrically samples. As a result, the microwave energy is mostly absorbed within the bulk in many solids, leading to improved thermal efficiency and much higher heating rates. A homogeneous temperature distribution within the solid is subsequently achievable when microwave is used as a source of energy. Otherwise, high heating rates are useful to get low grain size and so to improve the properties of the products.

Homogeneous temperature fields are also beneficial to decrease the thermal stress into the sample being heat treated.

Enhanced densification behaviors were often reported in microwave process.^{4,5} A significant decrease in process temperature and density differences between microwave and conventionally sintered samples have been demonstrated, especially in the intermediate stage of sintering.⁶ The authors usually considered that the microwave electromagnetic field would accelerate the mass transport and then increase the densification rate, so-called “microwave effect”. However, the reason for microwave-enhanced diffusion is still debatable. Most of the works lack systematic comparison for ceramic materials between conventional and microwave sintering from a thermodynamic and kinetic point of view.

The apparent activation energy is an important thermodynamic parameter for sintering, this latter gives a clear insight of the different densification mechanisms being involved during sintering. The activation energy can be evaluated by several methods including the Arrhenius plot of the densification data

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measured under constant heating rate conditions (CHR) or in using Master Sintering Curve Concept (MSC), based on non-isothermal sintering.⁷⁻⁹ Both CHR and MSC methods assume that grain growth is only a density-dependent process. CHR method can give out the apparent activation energy evolutions for a given sintered density at different constant heating rates, while MSC method finds out the best fitting activation energy value of the whole densification process.

As functional ceramic materials, alpha-alumina and zinc oxide have gained much attention because of their wide range of applications. They have different dielectric properties, therefore their behavior under microwaves could be different. In the present work, we have used a systematic approach to compare the sintering behavior of α -alumina and zinc oxide during their conventional sintering and microwave sintering. The objectives of this investigation were to evaluate the sintering apparent activation energy of these two materials based on non-isothermal conventional and microwave sintering using CHR and MSC methods. Based on these data, the differences in densification mechanisms between these two heating techniques will be carefully examined.

2. Materials and methods

High-purity commercial α - Al_2O_3 powder (>99.99%, BWP-15, Baikowski International, France) with specific surface area of $19 \text{ m}^2/\text{g}$ was used as starting material. Cylindrical compacts (8 mm diameter \times 4.5 mm thickness for conventional sintering and 12 mm diameter \times 4 mm thickness for microwave sintering) were formed by uniaxial pressing at 400 MPa for conventional sintering and at 390 MPa for microwave sintering, respectively, in order to achieve a similar green density. The organic compound was removed by heating at $2^\circ\text{C}/\text{min}$ to 600°C with a dwell of 1 h in air, and weight losses after this process were about 1.7%. The average density of green bodies was $52.3 \pm 0.2\%$ of theoretical density (TD).

Concerning zinc oxide, high-purity commercial ZnO powder (>99.99%, 60 nm mean particle size, Alfa Aesar, Germany) was mixed with 1 wt% polyvinyl alcohol (Rhodoviol 4/125, Prolabo, France) in an agate mortar. Two set of samples were prepared respectively for the conventional and microwave multimode sintering. Both set of samples were shaped by uniaxial pressing at 110 MPa, followed by cold isostatic pressing (CIP) at 300 MPa. For the conventional sintering, initially ZnO powder was pressed into 7.5 mm diameter and 4 mm thickness pellets. For microwave sintering, ZnO powder was pressed into 11.5 mm diameter and 4 mm thickness pellets. Before sintering, the binder in the green ZnO pressed bodies was burned out by heating in air at $1.5^\circ\text{C}/\text{min}$ up to 500°C , with dwell duration of 1 h. All samples had a green density of $64.4 \pm 0.3\%$ of TD.

Conventional sintering experiments were carried out in air using a dilatometer (Setsys 16/18, SETARAM, France) at heating rates of 1.6, 4, 10 and $25^\circ\text{C}/\text{min}$, those heating rates being usual for both Al_2O_3 and ZnO. Individually, Al_2O_3 samples were heated up to 1550°C with a holding time of 5 min, whereas ZnO samples were heat treated up to 1050°C , without dwell.

Microwave sintering was performed in a 3 kW, 2.45 GHz multimode microwave cavity (GMP30K, SAIREM, France), the dimension of the cavity being $430 \text{ mm} \times 430 \text{ mm} \times 490 \text{ mm}$. A SiC ring was used as susceptor to initially hybrid heat samples, especially for low-loss alumina, at relatively lower temperature. The configuration of the overall process, including the microwave heating cavity and the temperature measuring system was previously reported by Zuo et al.⁶ Two infrared pyrometers (5G-1007 and 5R-3015, IRCON, USA) have been used to measure the temperature of the sample. In order to obtain the shrinkage curves, a CCD camera (SLC2050MTLGEC, 14-bit, 1600×1200 , SVS-VISTEK, Germany) records the changes in the radius of the sample during its heating. This contactless system allows the *in situ* measurement of the shrinkage during the overall microwave sintering process. Using this contactless method and conventional thermometry, the CHR and MSC approach has been implemented in both processes, conventional and microwave. In the case of Al_2O_3 , the temperature of sample was raised to 1550°C and held at this temperature for 5 min, with a various and controlled heating rates (10, 25, 50 and $100^\circ\text{C}/\text{min}$). In the case of ZnO, the same heating rates were used to achieve the maximum temperature of 1050°C .

Densities and densification rate were deduced from the final densities measured by Archimedes' method with absolute alcohol as the liquid medium and from the recorded shrinkage data. The final density was averaged from at least three measurements. The microstructures of sintered alumina samples were observed by Scanning Electron Microscopy (SUPRA 55, Carl Zeiss, Germany) on fractured surfaces. In the case of ZnO, SEM micrographs were taken on $1 \mu\text{m}$ polished and H_3PO_4 etched sample surfaces. Grain size measurements were carried out from SEM micrographs in using the following equation,¹⁰

$$G = 1.56 \times L \quad (1)$$

where G is the average grain size, L is the average grain boundary intercept length of nine random lines on two different micrographs of each sample. Each line accounts for about 30 grain interceptions.

3. Results and discussion

3.1. Comparison of densification behaviors between conventional and microwave sintering

The evolution of the density and the densification rate as a function of temperature during conventional and microwave sintering of Al_2O_3 and ZnO, at different constant heating rates, are shown in Fig. 1. A common phenomenon is observed on both samples (ZnO and Al_2O_3) sintered in either conventional or microwave sintering techniques: the densification curves shift toward higher temperature with increasing heating rate. This implies a thermally activated process.

The heating rate of $25^\circ\text{C}/\text{min}$ is common from conventional to microwave sintering technique. As a consequence, with identical thermal cycle, the sintering behaviors between

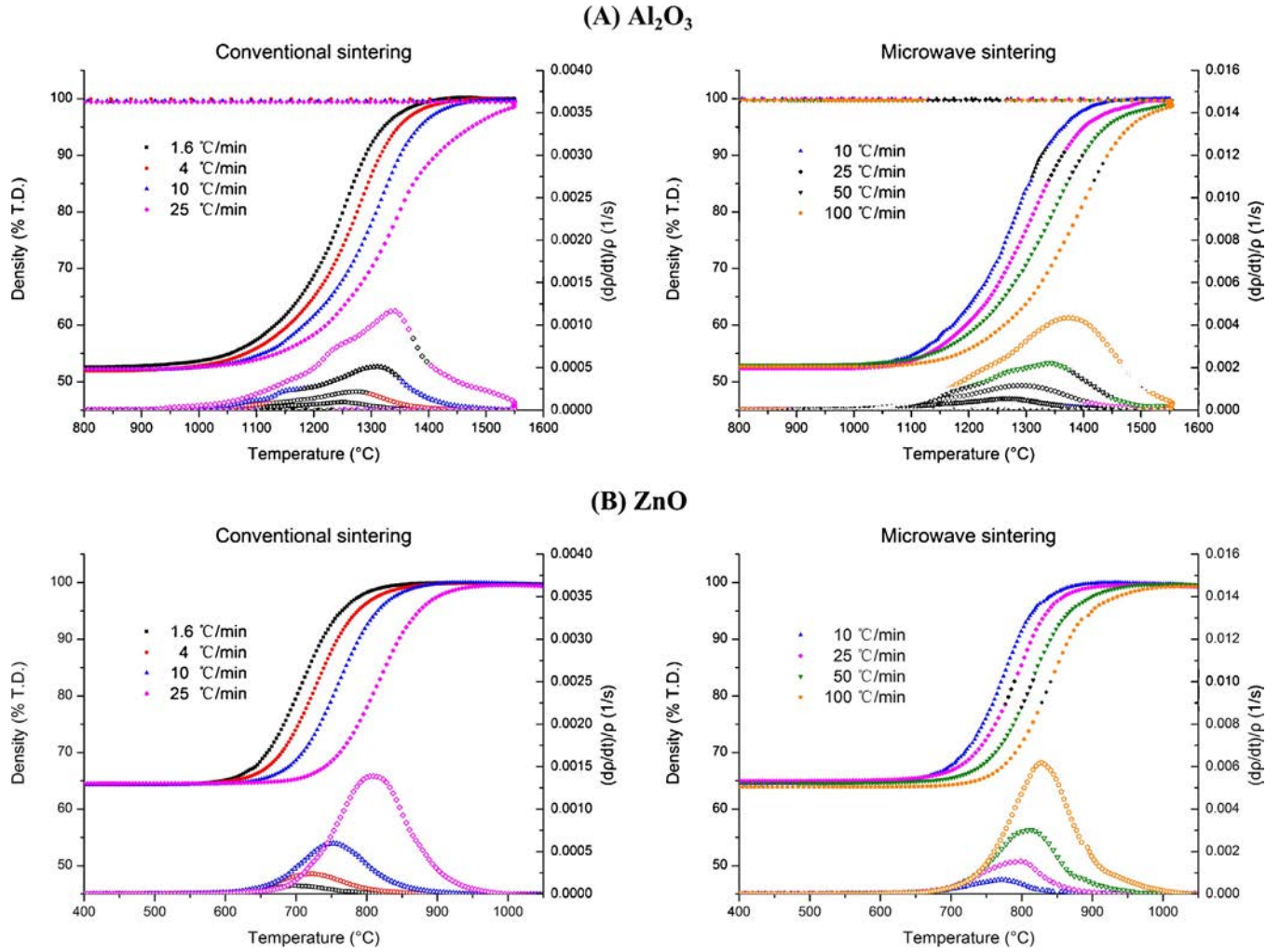


Fig. 1. Density and densification rate as a function of temperature during conventional (CS) and microwave (MW) sintering of Al₂O₃ (A) and ZnO (B), at different constant heating rates.

these two heating techniques can be directly compared, being given the fact that the temperatures are comparable from one to the other technique. According to Fig. 1, in the case of Al₂O₃ heated at 25 °C/min, microwave heating promotes the densification rate of the samples, and then reaches the top densification rate at 1293 °C, which is 46 °C lower than that obtained under conventional heating. For ZnO, a similar result is obtained, the densification rate peak is 12 °C lower under microwave heating than that observed on conventionally heated sample.

In order to better show the microwave enhancement on densification and its evolution, the curves of the density differences between microwave and conventionally sintered samples at the heating rate of 25 °C/min, (Density_{MW} – Density_{CS}) versus T , has been plotted in Fig. 2.

Based on Fig. 2, the maximal density differences achieve ~8% at 1335 °C and 815 °C, for respectively, Al₂O₃ and ZnO. These temperatures are in a range where intermediate sintering stage mostly takes place, for both materials. This clearly indicates that microwave-enhanced densification of Al₂O₃ and ZnO mainly occurs during the intermediate stage of sintering.

3.2. Evaluation of the activation energy of sintering

3.2.1. Method of CHR

3.2.1.1. Description of the CHR approach. The densification rate is given by the following equation:

$$\frac{d\rho}{dt} = A \frac{e^{-Q/RT}}{T} \frac{f(\rho)}{G^n} \quad (2)$$

wherein A is a material parameter, $f(\rho)$ is a function which depends only on the density, G is the grain size and n is the grain size exponent which depends on the dominant diffusion mechanism. Wang and Raj⁷ estimated the apparent activation energy Q of sintering by measuring the densification rate from the constant heating rate sintering experiments, and for same density values, using the following equation:

$$\ln \left(T \frac{d\rho}{dT} \frac{dT}{dt} \right) = -\frac{Q}{RT} + \ln[f(\rho)] + \ln A - n \ln G \quad (3)$$

Assuming that the grain size depends only on the density after sintering, Q can be determined for a given density interval

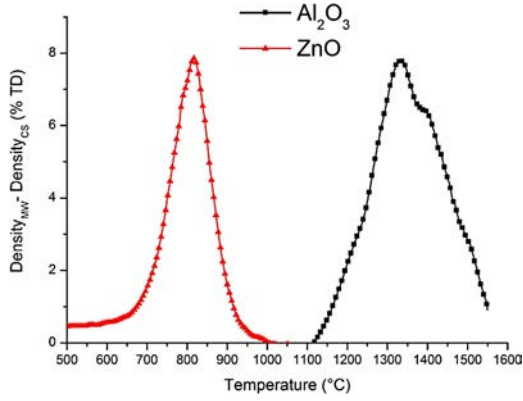


Fig. 2. Density difference variation between microwave (MW) and conventional (CS) heated samples versus sintering temperature.

from plots of the left-hand side of Eq. (3) vs $1/T$, for the different constant heating rates investigated.

3.2.1.2. Validity of application of the CHR method. The CHR method assumes that the grain size is only a density-dependent quantity.⁷ In order to use the CHR method with confidence, it is important to check if our data are consistent with this criterion. For doing this, a simple investigation of microstructural evolution has been carried out. In the case of ZnO, we have sintered in a conventional and microwave furnaces respectively two set of samples using different heating rates (1.6 °C/min for conventional sintering and 100 °C/min for microwave sintering), up to a density around 90% of TD. In this density range ($\leq 90\%$ of TD), it may be assumed that the intermediate densification stage mostly takes place. In the case of Al₂O₃, a sintering trajectory for the same starting powder used in this study has been reported (Fig. 3A), which indicates that there is no noticeable difference in the grain growth trajectory for samples sintered by any of the investigated methods or thermal cycles.¹¹ As observed from the Fig. 3B, for a given density below 90% of the TD, the ZnO sample density appears to be practically not dependent on the sintering history (heating rates/heating methods). For densities above 92%, samples sintered using both heating techniques exhibit well marked grain growth.

The microstructures of conventionally sintered and microwave sintered samples, of relative density around 90%, are shown in Fig. 4 as an example. To summarize, prior a density of 90% of TD, the grain growth for both materials follows a single path, depending on the density only, and not being affected by other parameters such as thermal sources or cycles.

3.2.1.3. Analysis of CHR data. As previously reported in the literature,⁶ microwave enhancement on densification mostly acts at the intermediate stage of sintering. Fig. 2, on which is plotted the density differences versus the heating mode and the temperature, confirms this already reported fact. Combined with the results shown in Fig. 3, the CHR method has been used over a relative density range of 60–85% of TD for Al₂O₃ and of 70–90% of TD for ZnO. The diagrams are shown in Fig. 5.

Table 1

Values of sintering activation energy estimated through the CHR and MSC methods. (CS: conventional sintering; MW: microwave sintering).

Method		Al ₂ O ₃	ZnO
CHR	Density range (% TD)	60–85	70–90
	CS (kJ/mol)	528 ± 22	221 ± 7
	MW (kJ/mol)	440 ± 8	307 ± 8
MSC	Density range (% TD)	55–99	65–99
	CS (kJ/mol)	538	214
	MW (kJ/mol)	434	289

According to Fig. 5, at each density, the four points obtained at four heating rates are well aligned. The apparent activation energy for densification at each density could be determined from the slope of the linear fit plotted in Fig. 5. For both conventional (full lines) and microwave sintering (dotted lines), the slope variation with the density is very small. This indicates that over the density range investigated (in the intermediate stage of sintering), the sintering is activated by a single dominant diffusion mechanism, for which a unique apparent activation energy is found. This is evidenced in both conventional and microwave processes. The average apparent activation energy values evaluated on conventional sintering are 528 ± 22 and 221 ± 7 kJ/mol for Al₂O₃ and ZnO, respectively, and 440 ± 8 and 307 ± 8 kJ/mol for those under microwave sintering (Table 1). For alumina, compared to the conventional process, the apparent activation energy for sintering is significantly lowered under microwaves, going from 528 ± 22 to 440 ± 8 kJ/mol. The opposite is found for ZnO, for which the apparent activation energy varies from 221 ± 7 kJ/mol (CS) to 307 ± 8 kJ/mol (MW). These unexpected results will be discussed later when moving to the MSC methods. Otherwise, it is worth to mention that, for a given density, the lines for microwave sintering slightly shift toward low temperatures, when comparing with those under conventional sintering. This is in good agreement with the fact that microwaves would enhance solid state diffusion phenomena.

3.2.2. Method of MSC

3.2.2.1. Description of the MSC concept. The apparent activation energies of conventional and microwave sintering processes were determined using the MSC concept. In this approach, the density ρ is plotted as a function of Θ , represented as:

$$\Theta(t, T(t)) \equiv \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (4)$$

where t is time, T is the absolute temperature, Q is the apparent activation energy for diffusion mechanism leading to sintering, and R is the gas constant. The right-hand side of Eq. (4) depends on the heating conditions of the materials. If there is single activation energy for which the functions:

$$\rho_i = f(\Theta_i) \quad (5)$$

(where i represents different thermal cycles) converge, then the fitted curve to the convergent ones is called Master Sintering Curve (MSC). In this case, the grain size should be independent

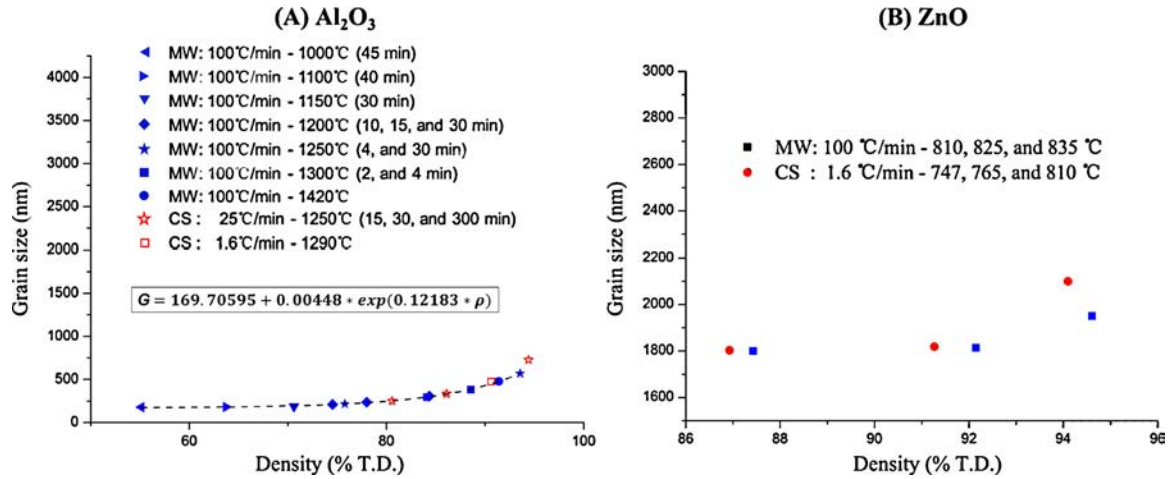


Fig. 3. Grain size (G) – Relative density (ρ) trajectory of microwave-sintered (MW) and conventionally sintered (CS) Al_2O_3 (A)¹¹ and ZnO (B) samples.

of the thermal history, and depends only on the density of the sample. The relationship between the ρ and the Θ is known as Master Sintering Curve.

3.2.2.2. *Construction of the MSCs.* In the present study, applying the theory of Eq. (4), the Master Sintering Curves for Al_2O_3 and ZnO powders were performed with the help of an automatic procedure developed at ENS Mines of St-Etienne. Based on the dilatometric data with different heating rates, this procedure can model the function which provides an optimal fit between the

densification parameter Φ and the $\ln \Theta$. The equation used to define the MSC is:

$$\Phi = \frac{\rho - \rho_0}{1 - \rho_0} = \frac{1}{\left(1 + \exp\left(-\frac{\log(\Theta) - a}{b}\right)\right)^c} \quad (6)$$

where ρ is the density, ρ_0 is the green density, and a , b and c are constants related to the curve. The MSCs of the two materials sintered with both methods were determined (Fig. 6).

In view of the MSCs shown in Fig. 6, it can be found that a good fitting was found based on the densification data recorded

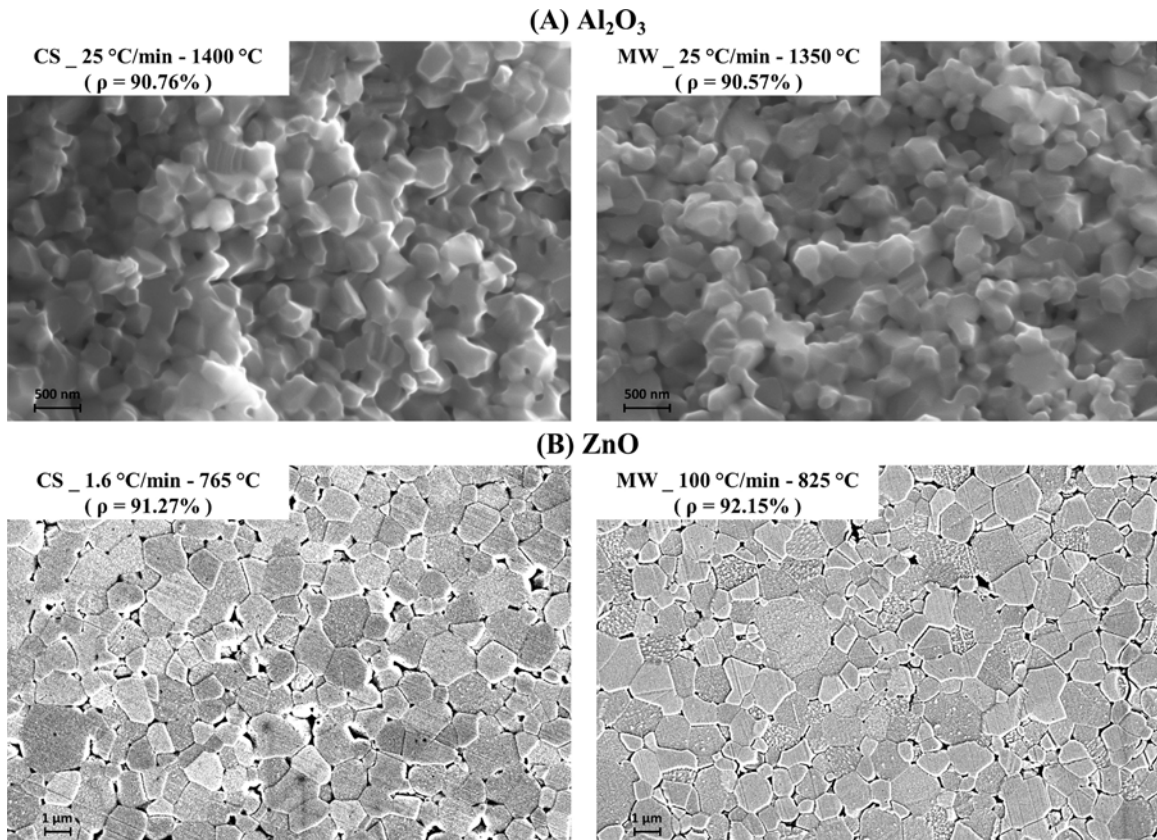


Fig. 4. SEM micrographs of conventionally sintered (CS) and microwave sintered (MW) samples, of relative density around 90%: (A) alumina, and (B) zinc oxide.

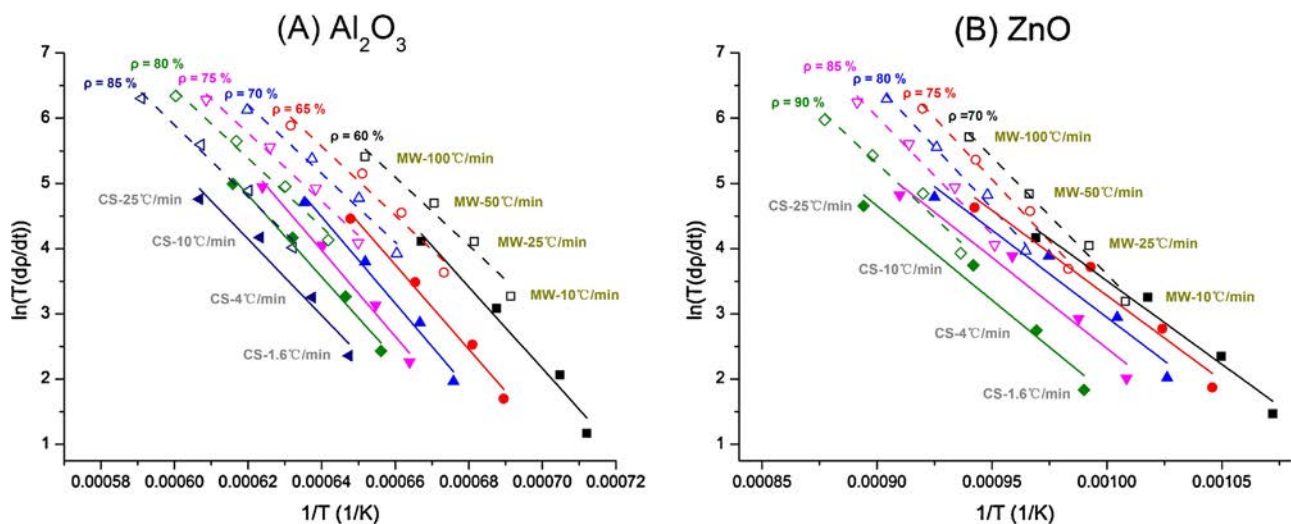


Fig. 5. Arrhenius plots of densification data to estimate the activation energy using different constant heating rates at given relative density, for the microwave and conventional sintering of (A) Al_2O_3 and (B) ZnO .

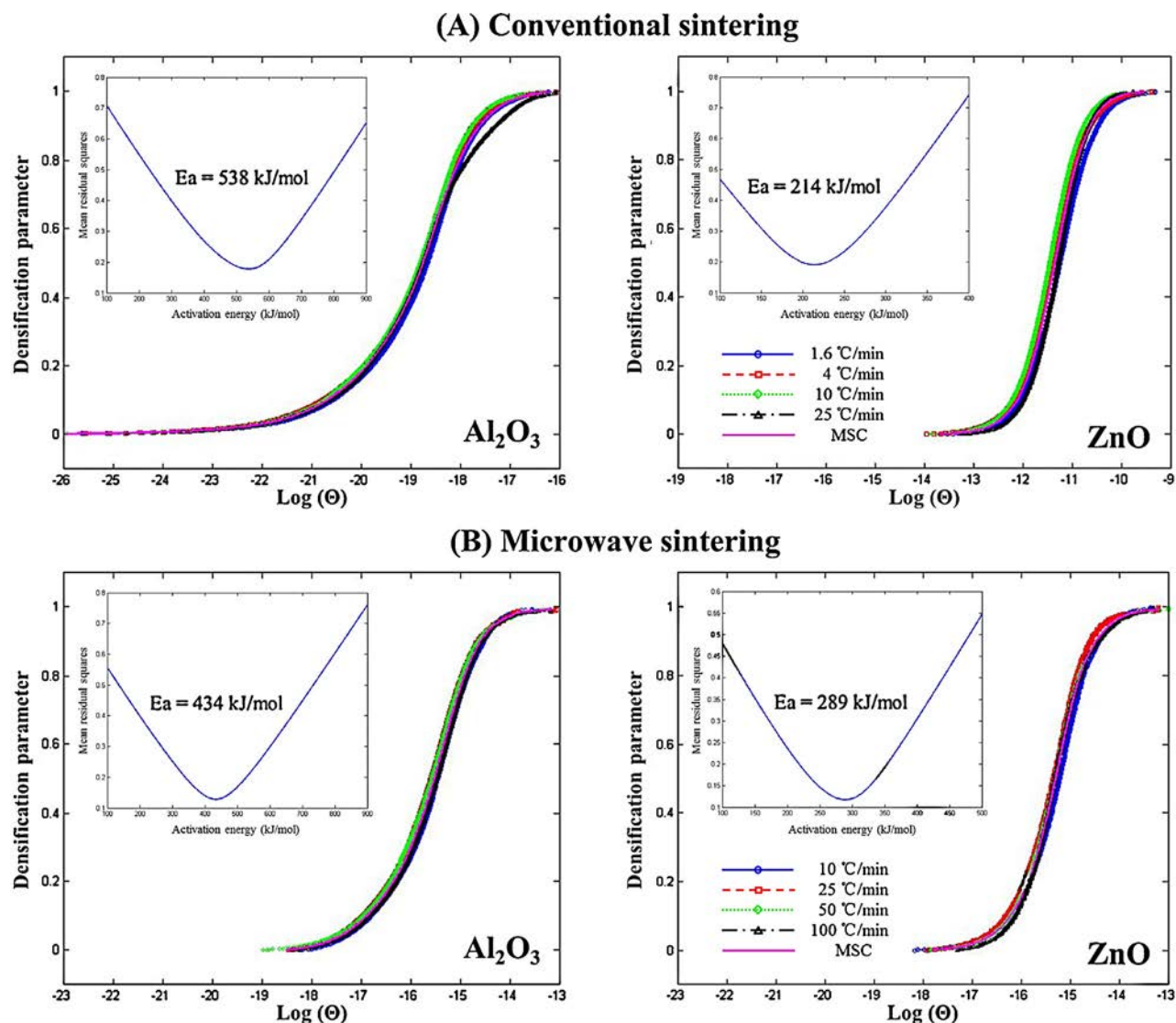


Fig. 6. Master Sintering Curves under conventional (A) and microwave (B) sintering of Al_2O_3 and ZnO for the whole stage.

at four different thermal cycles regardless the materials or the investigated process. Therefore, these activation energy values reported on Fig. 6, determined by minimizing the mean residual squares ($\Delta(\ln \Theta)$), are satisfactory and could be attributed to each material/process couple. The activation energies for conventional and microwave sintering of Al_2O_3 are 538 and 434 kJ/mol, respectively. For ZnO, these values are, respectively, 214 and 289 kJ/mol (Fig. 6 and Table 1). These values are mostly in good agreement with those obtained through the CHR approach and determined in the intermediate stage of sintering. The sintering activation energy determined by CHR method accounts for the intermediate sintering stage while that obtained through the MSC method, results from the entire densification stage, for which various diffusion mechanisms could be responsible for. It is reasonable to consider that the shrinkage stage corresponds mainly to the intermediate sintering stage. As a consequence, the roughly similar activation energy values obtained through these two calculation methods imply that the dominant diffusion mechanism in the whole densification process (MSC) is nearly the same with that in the intermediate stage of sintering (CHR).

3.2.3. Discussion on the densification microwave enhancement from the activation energy concept

Sintering is a process in which the mass transport plays the major role. From the thermodynamic viewpoint, the intrinsic driving force for sintering is the reduction of the total interfacial energy.¹² It depends only on the initial and final states of the thermodynamic parameters describing the overall process (temperature, curvatures, mass distribution within the solid, etc.), but does not depend on the path to reach those specific values. However, to make sintering happens, a minimum energy must be input to the system in order to jump the potential energy barrier which prevents atoms from diffusing within the solid. This minimum energy is so called “sintering activation energy”. The intermediate sintering stage was regarded as a density region where the densification occurs with minimal grain growth (Fig. 3). In this sense, the intrinsic driving force for sintering should be the same because the samples have almost the same grain size at a given density. However, the activation energy under microwave sintering significantly changed compared with that in conventional heating. This difference in E_a value during the stages of sintering when the grain size is not changing significantly, suggests that, the sintering process or the densification mechanism can be changed under electromagnetic field.

For both Al_2O_3 and ZnO, according to their densification behaviors, the presence of electromagnetic field slightly improves the densification process as seen on Figs. 1 and 2. The processing temperature is slightly lowered on microwave heating over conventional heating. For Al_2O_3 , this is in good agreement with the sintering activation energy, which is significantly lowered when microwave sintering is used compared to conventional sintering. In the paper of Zuo et al., it was assumed that the grain boundary diffusion is enhanced by an electromagnetic pressure during the microwave sintering of Al_2O_3 .¹¹ Based on this point of view, microwave should provide an external driving force to sintering system. In other words, additional

diffusivity is provided from “electromagnetic activation” rather than “thermal activation”. That is why the apparent sintering activation energy significantly decreases through microwave heating. In the case of ZnO, microwave sintering is accompanied by an increase of the activation energy compared to conventional heating. This seems to be contradictory with the experimental result that showed microwave densification enhancement of ZnO over conventional sintering (Figs. 1 and 2). However, the diffusion kinetic should be separately discussed from the energy activation for diffusion.

Grain boundary diffusion is usually regarded as the dominant mechanism controlling the intermediate stage densification in ZnO sintering. The apparent sintering activation energies found, in both heating processes are consistent with the values often reported for grain boundary diffusion governed ZnO densification.^{13,14} However, we must also note that the value underlying microwave sintering has significantly increased toward the value field established for lattice diffusion in ZnO. On the one hand, while the dominant densification mechanism is grain boundary or lattice diffusion, most materials densify through a mixture of densification mechanisms.¹⁵ On the other hand, we must also consider that ZnO is characterized by a good microwave coupling (loss factor $\tan \delta = 0.5$ at room temperature), different from Al_2O_3 .¹⁶ In this sense, maybe we can assume that: the contribution of lattice diffusion mechanism for ZnO densification could be relatively increased by electromagnetic field due to its significant response to microwave. That is to say, the microwave field and enhanced mobility of atom and vacancy could facilitate the material transport via lattice path during the sintering of ZnO. However, this hypothesis should be investigated in a future study in terms of kinetics.

Obviously, the main contribution of the MSC concept is the ability to predict the density of green powder compacts, processed using the same shaping conditions, over arbitrary thermal processing conditions.⁹ In this sense, the construction of MSCs for Al_2O_3 and ZnO under these two types of sintering is meaningful to design and interpret sintering experiments, to understand how changes in the heating profiles affect sintering behavior and microstructure, and to optimize the thermal cycles in order to maximize the density and minimize the grain size of samples. This will be the goal of our investigation in future.

4. Conclusions

In this work, a comparative study of densification behaviors of $\alpha\text{-Al}_2\text{O}_3$ and ZnO have been investigated under both conventional and microwave sintering. By the way of dilatometric measurement, the values of apparent activation energy, which can provide insight into dominant densification mechanisms and sintering kinetics, were estimated by applying CHR approach and MSC concept, respectively, at non-isothermal sintering conditions. This is the first attempt to thermodynamically compare conventional sintering and microwave sintering of two kinds of materials with different microwave responses by utilizing these systematic approaches.

The CHR method gave out the activation energy evolutions in the intermediate stage of sintering. At different densification

levels, the calculated values showed a very slight variation, corresponding to a unique mechanism controlling the densification in this stage. For the MSC approach, apparent activation energies were evaluated for the whole sintering process and in good agreement with the results obtained through CHR method.

Under conventional sintering, the apparent activation energies were about 510–550 and 210–230 kJ/mol for Al₂O₃ and ZnO, respectively. For microwave sintering, these values changed to 430–450 and 290–320 kJ/mol, respectively. As during microwave heating processing of a sample, different activation energy is required to reach the same stage of densification as during the conventional sintering. Combined with the enhanced densification behaviors for both materials, it suggests that electromagnetic field could change the diffusion mechanism in a special way depending on physical properties of materials.

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