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Journal of the European Ceramic Society 34 (2014) 3103–3110

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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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Received 27 February 2014; received in revised form 27 March 2014; accepted 2 April 2014
Available online 1 May 2014

Abstract

A comparative study between the conventional and 2.45 GHz microwave multimode sintering behavior of insulator (α-Al_2O_3) 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 Al_2O_3 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 Al_2O_3. 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-Al_2O_3; 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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http://dx.doi.org/10.1016/j.jeurceramsoc.2014.04.006
0955-2219/

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 m^2/g was used as starting material. Cylindrical compacts (8 mm diameter × 4.5 mm thickness for conventional sintering and 12 mm diameter × 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 °C/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 ± 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 °C/min up to 500 °C, with dwell duration of 1 h. All samples had a green density of 64.4 ± 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 °C/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 mm × 430 mm × 490 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 thermodilatometry, 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 °C/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 μm 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 °C/min is common from conventional to microwave sintering technique. As a consequence, with identical thermal cycle, the sintering behaviors between