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Microwave sintering of pure and TiO_2 doped $MgAl_2O_4$ ceramic using calibrated, contactless in-situ dilatometry

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ABSTRACT

This work describes the development of a contactless dilatometry system for simultaneously measuring the shrinkage and the temperature during microwave sintering of materials in a 2.45 GHz single-mode cavity. An original temperature calibration method has been developed using a monochromatic Infrared pyrometer, taking into account that the apparent emissivity depends on the temperature. Different calibration oxide materials were selected according to their melting points to determine the temperature dependence of the thermal emissivity. This parameter was then used to get the most accurate temperature values over the entire processing temperature range. Afterwards, microwave sintering kinetics and microstructures of pure $MgAl_2O_4$ and TiO_2-doped spinel material were studied and compared to those of conventionally sintered samples. It was shown that there was no significant difference in the densification behavior of the pure spinel material compared to the conventionally sintered material. On the contrary, the shrinkage curve of the microwave sintered TiO_2-doped spinel was found to be shifted to lower temperature compared to the conventional shrinkage curve. This result occurs due to likely species diffusivity enhancement provided by a specific coupling between microwaves and point defects, such as $[Ti^{4+}\text{-}V''_{Mg}]$ pair dipoles.

1. Introduction

In recent years, microwave energy has been successfully used for processing many materials, including the synthesis of oxides [1] or the sintering of materials [2]. This technology is known to be faster and greener than conventional technologies involving infrared radiation heating sources (electrical or gas furnaces). It is also well established that, considering the penetration depth of the microwave electrical field ('E') – a few centimeters in most oxide materials, the heat is generated within the volume of the sintered material. This is a great advantage over conventional infrared heating since it also contributes to the high efficiency of the microwave thermal process. However, up to now, the main issues that prevent the microwave technology from being widespread on an industrial scale are the control of the temperature (conventional thermocouples cannot be used as they may interact with the microwaves) and the control of the materials dimensional changes during the process. This is even more true when high temperature sintering processes are involved and the materials final microstructure must be carefully controlled. In the literature, only a few papers have reported the overall control of the sintering process under microwave heating. Marinel et al. [3] first described the in-situ measurement of the shrinkage during microwave sintering of CuO, using a triangulation method based on a laser telemeter. However, in this preliminary work, the temperature was not calibrated and the shrinkage measurement method was not contactless, implying that the sample needed to be subjected to a small pressure. In the same way, Kutty et al. [4] used a conventional thermo-mechanical dilatometer to study the microwave sintering of hydroxyapatite in a multi-mode microwave cavity. In 2011, Zymelka et al. [5] developed a novel method to simultaneously measure the change in the samples shrinkage and surface temperature over time. The shrinkage measurement was based on the contour detection of the sample, detected by a high resolution CCD camera. The measurements were carried out continuously by using both a CCD camera and an IR pyrometer during the microwave heating. The great advantage of this new method comes as a result of the contactless shrinkage measurement and the calibration of the temperature using metallic germanium turnings (Tm ~ 938 °C), which calibrate the emissivity based on the germanium's melting point. The basic method to calibrate the

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apparent emissivity of the sample in its environment is to place a small turning of a calibration material on top of the samples surface. The pyrometer is focused on the surface of the sample (in the vicinity of the turning) and a CCD camera allows the turning to be observed in real time. When the turning melts, the emissivity of the pyrometer is tuned to fit the melting point of the calibration material. This method is very effective, provided that the calibration material does not react with the sample, assuming that both the sample and the calibration materials are at the same temperature. This holds to be even more true if the calibration material has similar dielectric properties to the material being heated (same or close absorption behavior). More recently, Zymelka's method was improved and used to study the microwave sintering of alumina and zinc oxide [6] in detail, with palladium (Pd, melting point ~1550 °C) turnings being used as calibration materials. Zhu et al. also applied Zimelka's method to study the sintering of Ni-CuZn ferrites [7] using a multimode microwave cavity. In these experiments, the multimode cavity made use of SiC susceptors in order to provide hybrid heating to the sample. Specific instrumentation was developed and published recently by Croquesel et al. [8] to measure both the shrinkage and temperature of the sample during microwave sintering in a 2.45 GHz single-mode microwave cavity. In this paper, they used an original assembly that made use of both a thermocouple and infrared pyrometer (based on an induction heating process), to calibrate the emissivity of the sintered material as a function of its temperature [9]. In this design, no calibration material was used. This work presents the development of specific instrumentation to simultaneously measure the shrinkage and the temperature of oxide ceramics being directly microwave sintered in a 2.45 GHz single-mode cavity. The originality of this work lies first on the use of four novel oxide calibration materials in order to determine the temperature dependence of the emissivity. In doing so, a very reliable temperature calibration is expected. Secondly, the as-developed method allows direct microwave sintering to be studied and to follow up the shrinkage of the material in real time without the necessity to subsequently handle data, which is very useful to follow up the densification progress of the materials and control the final microstructure. This method will be applied to study the shrinkage behavior of the microwave sintering of both pure spinel and TiO_2 doped spinel material. The aim of doping the spinel phase with TiO_2 is to generate point defect concentrations [10] and, as a result, to investigate the microwave sintering behavior of both TiO_2-doped and un-doped $MgAl_2O_4$. According to several recent papers [11–13], the increase of point defect concentration may result in enhancing the effect of the microwaves on the diffusion mechanism.

2. Experimental

2.1. Sample preparation

In this study, a commercial high purity $MgAl_2O_4$ spinel powder (Baikowski, France), with a specific area of 30 m^2/g and a median particle size D_{50} of 200 nm, was used as a starting material. The main impurities in the spinel powder (PS: Pure Spinel), given by the supplier, are (in ppm): Si (20), Na (10), Fe (10) and Ca (5). A powder with an addition of 0.25 wt% TiO_2 rutile (DS: Doped Spinel) (Chempur, APS: 30–40 nm, SSA $>30\ m^2$, Germany) was also prepared to study the effect of TiO_2 on the densification and microstructural properties of spinel. Kim et al. [14] reports the beneficial effect of this additive in quantities above 1 wt%. Nevertheless, secondary phases ($TiAl_2O_5$) can be observed on the doped sample's microstructures. The mixture of the titanium oxide and spinel powder was milled by attrition milling for 30 min in liquid solution (ethanol 40% and butanone 60%) with alumina balls (Ø=2 mm). An organic binder (Butvar B – 98 – Sigma – 0.3 wt%) was added to facilitate the shaping of pellets. The mixture of powder and binder was thoroughly mixed in a Turbula (T2C Model) for 3 h and subsequently dried under IR lamps. The binder was removed by heating at 2.5 °C/min up to 400 °C with a dwell of 2 h in air. The same protocol was used for the un-doped spinel powder. Cylindrical samples (12 mm diameter and 3 mm thickness) were shaped by uniaxial pressing at 100 MPa, followed by cold isostatic pressing (CIP) at 750 MPa. The apparent density of the green material was 1.90 g/cm^3, which is roughly 53% of the theoretical density (3.578 g/m^3).

Samples coming from each batch of powder (PS and DS) were sintered at 1450 °C for 30 min using a heating ramp of 10 °C/min. Conventional sintering experiments were carried out in air using a dilatometer (Setsys 16/18, SETARAM, France). Microwave sintering was performed in the monomode microwave (2.45 GHz; Sairem, France, GMP20KSM) equipped with a CCD camera which allows to visualize the sample during the experiments.

2.2. Microwave set-up

Microwaves are generated by the microwave source (1) working at 2.45 GHz and delivering a power of up to 2 kW (SAIREM 20 KSM) (Fig. 1A). Afterwards, the microwaves are transmitted through a normalized TE10 rectangular wave guide (WR-340) which is ended by a TE10M single mode applicator (2). This cavity was tuned in TE103 mode by adjusting the length between the iris (3) (not visible in the photograph) and the piston (4) (not visible in the photograph). More details could be found in Refs. [15,16]. An infrared monochromatic pyrometer (5) is used for measuring the

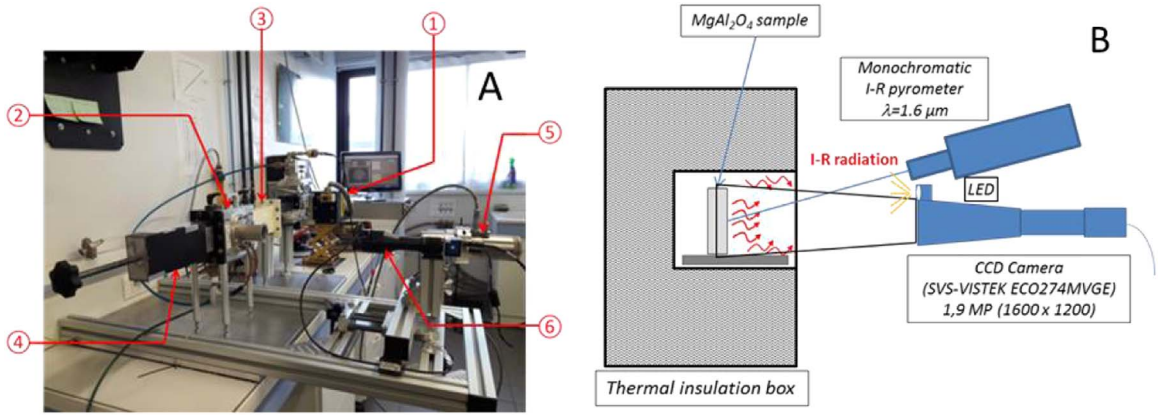

Fig. 1. (A) Photograph showing the overall microwave apparatus used in this study; (B) scheme representing the sintering cell used in the single mode cavity.

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