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Microwave technique: An innovated method for sintering β-eucryptite ceramic materials

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Abstract. Microwave sintering has emerged in recent years as a new, fast, cheap and green technology for sintering a variety of materials. The main advantages of microwave heating can be summarized as follow: reduced processing times, energy costs and environmental benefits. Nevertheless, understanding how this specific heating drives to obtain ceramic materials with a combination of unique, structural and functional properties is the big challenge.

The present work shows the different and improved properties achieved with β-eucryptite nanocomposite ceramic materials by microwave heating compared with the conventional method. Microcracking evolution in addition to the microstructure of the sintered materials along the several thermal cycles has been studied. Mechanical properties changes observed can be related to this process.

Thus, the microwave technique is a promising tool for sintering new materials by controlling the composition of the phases, chemical reactivity and nanostructure, using up to 70% less energy in the whole sintering process than conventional heating. This technique becomes part of the new and innovative technologies "eco-green".

Introduction

Lithium aluminum silicates (LAS) have attracted widespread attraction over the last several decades primarily due to their negative, low or even zero coefficient of thermal expansion (CTE). This makes them suitable for a variety of applications like large mirror blanks for telescopes, optical windows and thermal shock resistant structures [1]. Some studies have paid attention on the dimensional stability behavior of these materials over time, with no loads or variable environmental conditions, but there is not previous literature on the subject regarding mechanical and thermal properties over time in use. Hysteretic temperature effects can have a significant cumulative effect on a structure due to the large number of thermal cycles the material may experience in its operational lifetime.

β-eucryptite ($LiAlSiO_4$) is one of the prominent members of the LAS ceramic family, which exhibits a highly anisotropic CTE, which leads to a negative average crystallographic CTE [2]. This thermal expansion anisotropy produces large thermal residual stresses that cause spontaneous

microcracking in β-eucryptite materials. Microcracking, and therefore thermal expansion, has been shown to depend on the grain size of β-eucryptite [3]. Specifically, when the grain size is larger, the extent of microcracking is greater, leading to a large negative CTE, and vice versa. Within this framework, the current study aims to understand the effect of microcracking on the mechanical properties, such as hardness and Young's modulus, of dense β-eucryptite materials. The samples were fabricated through two different methods, conventional and microwave sintering at 1200 ºC. In the present investigation, microcracked structures of β-eucryptite were produced via repeat thermal fatigue cycles, heating-cooling in an electric furnace.

Materials and Methods

β-eucryptite solid solution powders were synthesized for this study following the route proposed in a previous work (see [4] for details). The chemical compositions of the LAS powder correspond to a Li_2O:Al_2O_3:SiO_2 relation of 1:1.1:2.5 (Compositions LAS8 in [4]). Green samples were prepared by cold isostatic pressing (CIP) at 200 MPa of pressure (15 mm height, 10 mm diameter). The green density was approximately 1.2 g cm^{-3}, i.e. 49% of theoretical density (2.39 g cm^{-3}). Green samples were sintered in air by conventional heating process in an electrical furnace (Thermolynetype 46100, Thermo Fisher Scientific, USA) at 1200 ºC with 10 ºC min^{-1} of heating rate and 2 h of holding time.

A single mode cylindrical cavity operating in the TE_{111} mode with a resonant frequency of 2.45 GHz was selected as the heating cell for microwave sintering. The *E* field vectors are perpendicular to the cavity axis with the maximum electric field magnitude at the center, where the samples are located. A movable short-circuit at the bottom of the cavity permits to track the cavity heating mode resonant variations caused by changes in the dielectric constant of the heated test sample during the sintering process. A rectangular waveguide is used to launch microwaves to the cylindrical cavity through a coupling aperture. A switching power supply (Magdrive1000) circuit for driving a magnetron (Panasonic 2M244, 1200 W) operating at 2.45 GHz delivers a continuous variable 1 kW of microwave power. A compact isolator (Valvo VZU1234 isolauncher) protects the magnetron from undesirable reflections. Incident, reflected and absorbed microwave energy, as well as complex impedance of the cylindrical cavity, is measured by a waveguide reflectometer [5]. The temperature of the sample is monitored by an infrared radiation thermometer (Optris CT-Laser LT, Germany), which is focused on the test sample via the small circular aperture in the wall of the cavity. The emissivity of the LAS material at different temperatures was calculated previously. The samples were sintered at 1200 ºC in air with a heating rate of 100 ºC min^{-1} with a short holding time of 10 min at the maximum temperature. The bulk density of the sintered samples was measured by Archimedes' principle by immersing the sample into water based liquid (ASTM C373-88).

Thermal fatigue cycles were carried out in an electric furnace made for this purpose (Energon S.L., Spain). The oven has a platform that goes up and down allowing the rapid heating and cooling of the samples. Figure 1 shows the thermal fatigue oven and the tests cycles that have been carried out. The samples were heated to 400 °C for 10 minutes and cooled with cold air immediately. The cycle number chosen was 400.

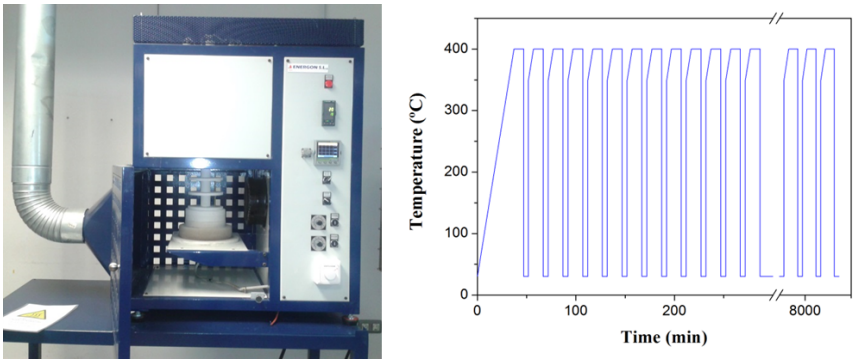

Figure 1: Thermal fatigue furnace and the tests cycles.

Nanomechanical properties such as hardness and Young's modulus of samples were obtained by nanoindentation technique (Model G200, MTS Company, USA). Tests were performed under maximum depth control, 2000 nm, using a Berkovich diamond tip previously calibrated with silica. The contact stiffness (*S*) was determined by Continuous Stiffness Measurement technique (CSM) to calculate the profiles of hardness (*H*) and elastic modulus (*E*) [6]. Amplitude was programmed to 2 nm with 45 Hz of frequency. A matrix with 25 indentations was performed for each sample. In order to ensure the quality of the tip throughout the work, pre- and post- calibration procedures were performed for this indenter ensuring the correct calibration of its function area and correct machine compliance. Previous to the nanoindenter testing, the samples were prepared by metallographic techniques. After cutting, the surface was lapped and then polished, with a final step with 0.25 μm diamond paste.

The crystalline phases of the bulk ceramic composites were determined by X-ray diffraction (XRD, BRUKER AXS D5005, Germany). The measurements were performed in the 15º-70º range and the step size and time of reading were 0.02º and 0.3 s, respectively.

The fracture surface sections of the samples have been observed using a field emission gun scanning electron microscope (FESEM, HITACHI S-4800, Japan).

Results and discussion

The relative densities of sintered samples obtained by conventional sintering at 1200 ºC with 2 hours holding time (CS 1200-2h) and microwave sintered at 1200 ºC during 10 min (MW 1200-10) were 88.9% and 98.6%, respectively. The density of MW sample enhances up 9% compared to CS sample. The rapid sintering of samples by microwave is attributed to the enhanced densification rate due to mechanisms such as particle rearrangement and breaking up of agglomerates aided by faster heating rates. The power produced by the microwave source can be spent entirely on heating the product, without needing to heat the massive furnace elements. Therefore, much higher heating rates are achievable with microwaves, which is one of the most important factors in many processes. Along with the evident energy savings and reduction in process duration (30 min in MW vs. 360 min in CS), high rates of microwave heating help improve the densification, resulting in final materials with finer and less defective microstructures and enhanced functional properties [7].

The phase composition of raw material and sintered samples were studied by XRD. In all cases, glass-free materials have been obtained, the major phase identified corresponds to a solid solution of β- eucryptite (PDF file #870602 and 251183, Figure 2).

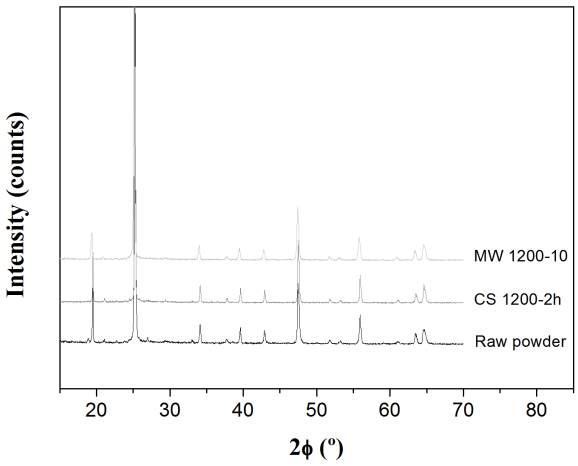

Figure 2: Diffractogram of the raw powder and sintered materials**.**

Figure 3 shows the FESEM fracture surface of β-eucryptite samples sintered by conventional and microwave methods at 1200 ºC, before and after thermal fatigue cycles. CS sample (Figure 3a) shows higher porosity compared to MW sample (Figure 3b). This fact is evidently in agreement

with the above density values discussed. There is a clearly difference in the grain size between samples obtained by conventional or non-conventional sintering. The mean values measured are present in Table 1. During microwave heating, the energy is transferred electro-magnetically to the material and not as a thermal heat flux, enabling the material to be heated at fastest rates and shortest sintering times. The sintering occurs due to a self-heating of the material and the maximum temperature is found in the core of the material. The most energetic area is located within grain center, therefore, the grain boundary diffusion and subsequent formation of sintering neck is less favored. This effect can lead directly to the second stage of the sintering process; densification and microstructural change [8], skipping the first phase, which causes the neck between grains and thickening.

Other significant difference observed in Figure 3 is the microcracking phenomenon. Before subjecting the samples to thermal fatigue cycles, microcracks were observed in the CS sample (Figure 3a), nevertheless, MW sample is free of them (Figure 3b). It is widely accepted that microcracks depend on the grain size of β-eucryptite, and there is a critical grain size below which microcracks do not occur [3,9-11]. For example, it has been reported by Pelletant et al. [9] that the critical grain size for having spontaneous microcracking is located below 2.8 μm. Bruno et al. [10] found that different grain sizes induce microcracking at different temperatures (~500 ºC for large grains, 20-30 μm, and 300 ºC for medium grain sizes, 5-10 μm). Shyam et al. [3] demonstrated that the grain sizes <4 μm of β-eucryptite material is nominally free of microcracks. Others studies revealed that prolonged sintering time introduced microcracks in the sintered sample [2].

The grain size observed in Figure 3a for the CS sample (3.4 μm) is close the critical value reported by different authors and, therefore, microcracks are indeed present in this sample. In this work, two different sintering techniques, with a notorious difference of dwell time, heating source and heating/cooling rates have been used. The microwave process inhibits the final grain size and this fact is a reason to produce free - microcracking β-eucryptite materials.

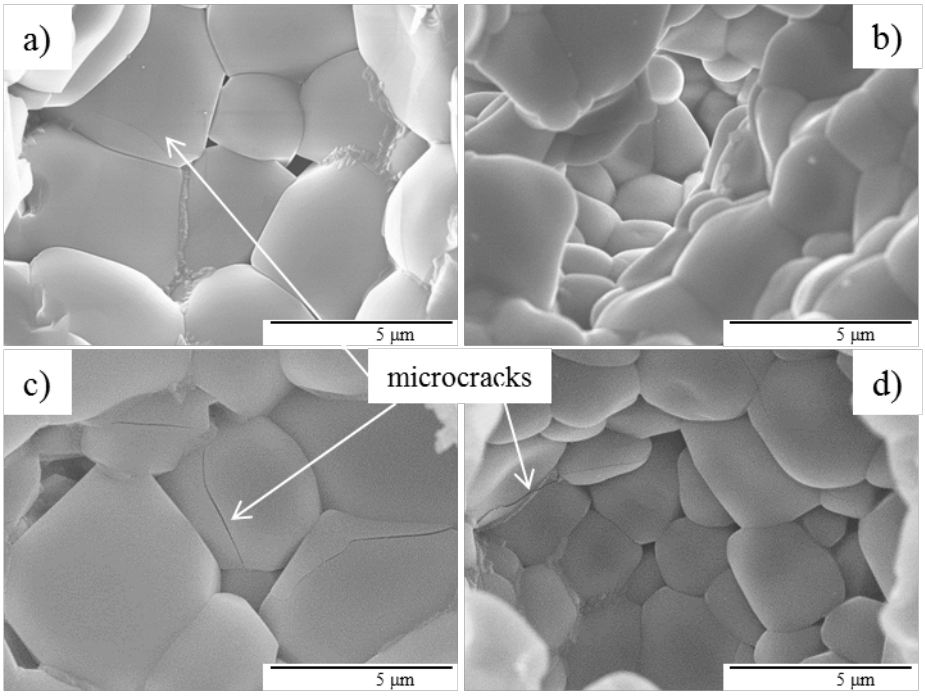

Figure 3: FESEM images of fracture surface of samples sintered by CS 1200-2h: a) without thermal fatigue cycles and c) with 400 cycles of thermal fatigue; and sintered by MW 1200-10: b) without thermal fatigue cycles and d) with 400 cycles of thermal fatigue.

In order to study the mechanical properties of β-eucryptite materials over time in use, several thermal fatigue cycles have been carried out. Both samples, CS 1200-2h and MW 1200-10, have been heated and cooled in an electric furnace during 400 cycles (Figure 1). As it can be seen in

Figure 3c and Figure 3d, microcracks are now present in both samples. Thermal fatigue has induced these microcracks. It is well-known than β-eucryptite materials have low or even negative coefficient of thermal expansion upon heating from room temperature because the expansion along the crystallographic a and b axes is cancelled by the contraction along the c axis [12]. Some reports document that the microcracks caused by thermal expansion anisotropy originated stresses often result in anomalous thermal expansion coefficients. Thermal misfit strains, due to the high thermal expansion mismatch and anisotropy, may reach sufficiently high values to cause spontaneous microcracking [13]. The microcracks continuously heal and close upon heating and, upon cooling. Microcracks reopen only when the thermal stresses exceed the grain strength of the material. Microstresses are driven by crystal thermal expansion anisotropy and are proportional to the temperature different from the stress-free, high-temperature, microcrack reopening occurs only below a certain temperature, as Bruno et al. explain [10].

In our work, thermal stress has been purposely induced by thermal cycle treatments. On the one hand, in the CS sample after 400 fatigue thermal cycles, microcracks have grown, causing more grain ruptures (Figure 3c). On the other hand, MW sample (Figure 3d), with smaller grain size and none microcracks observed as sintered, has been microcracked. In spite of the fact, this may be due that during microwave process the heating and cooling is very fast and this produces residual stress between the grains that may cause spontaneous microcracks in β-eucryptite materials after they are submitted to thermal fatigue.

Mechanical properties of CS and MW samples, before and after thermal fatigue, are summarized in Table 1. The hardness and Young's modulus values are averaged from 250 nm to 1500 nm of depth. Lower mechanical values obtained in CS sample without thermal cycles, are due to the low density and its microcracks [3]. The appearance of microcracks in the microstructure of the MW sample after thermal fatigue are not reflected in lower mechanical properties values.

Experimental results presented in this paper suggest that it is necessary to study the influence of the observed microcracking growth in the coefficient thermal expansion property and to determinate the variations in the elastic properties of β-eucryptite.

Table 1: Grain size and mechanical properties of sample before and after thermal fatigue.

Sintered technique	Thermal fatigue cycles	Grain size (μm)	Young's Modulus (GPa)	Hardness (GPa)
SC 1200-2h	0	3.4 ± 0.9	70 ± 11	4.1 ± 1.1
SC 1200-2h	400	3.9 ± 1.0	77 ± 9	4.2 ± 1.0
MW 1200-10	0	2.2 ± 0.7	93 ± 4	6.2 ± 0.5
MW 1200-10	400	2.1 ± 0.9	90 ± 5	6.1 ± 0.7

Conclusion

The mechanical behavior of the β-eucryptite materials obtained by different sintering techniques, conventional and microwave sintering and submitted to thermal fatigue cycles, has been investigated. Microwave sintering has a lot of benefits in terms of mechanical properties and microstructural design, as well as in terms of speed in the process. β-eucryptite materials sintered by the microwave technique show a full density with a small grain size compared to the specimens sintered by conventional methods. Microcracks evolution is noticeable in the samples obtained by conventional process. The development of microcracks, after the thermal fatigue cycles in the microwave sintered samples, has not modified the obtained values for hardness and Young' modulus of the samples.

Acknowledgements

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