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# Microwave sintering of cordierite precursor green bodies prepared by starch consolidation

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**Abstract**

This paper reports on a study of the microwave sintering behavior of green disks prepared by the starch consolidation forming method to produce cordierite-based porous materials. Green disks were formed by thermogelling the aqueous suspensions of talc, kaolin and alumina (29.6 vol.%) and potato starch (11.5 vol.%) at 75 and 85 °C for 4 h, drying and calcining. They were characterized by bulk density and apparent porosity measurements, and SEM. Microwave sintering was carried out at 1300 and 1330 °C for 15, 20 and 25 min, applying 50 °C/min. For purposes of comparison, an analysis of green disks prepared and calcined in the same conditions and conventionally sintered (1330 °C for 4 h) was also made. The materials were characterized by XRD, bulk density and apparent porosity measurements, and microstructurally analyzed SEM. The results were analyzed considering the behavior of starch in aqueous suspension at varying temperatures, and the experimental conditions of consolidation and sintering.



*Keywords:* D. Cordierite; Microwave sintering; Starch consolidation; Porous ceramics

## 1. Introduction

Porous ceramic materials are potential candidates for a broad spectrum of technological applications, e.g., catalyst supports, filters, gas sensors, combustion burners, and thermal insulators, among others [1,2]. Several new processing methods have been developed in recent years to meet the high demand of these materials with controlled porous microstructures [1–4].

Research today focuses increasingly on the study of methods that cause low environmental impacts. These methods include a new family of forming techniques (direct consolidation methods) to consolidate ceramic suspensions in nonporous molds (e.g., metal molds) without compaction or removal of water. Thus, a novel non-contaminating low-cost technique was developed, based on the gelling ability of starch aqueous suspension at temperatures of 55–85 °C, for use in the manufacture of porous ceramics. Starch acts as a consolidator/binder of ceramic particles and a pore former after consolidation by burn-out at high temperature [5–8]. During the gelatinization process, starch granules undergo rapid and irreversible swelling by water absorption [9], causing the ceramic particles to stick together and consolidate into a solid body. After applying heat treatments (burning and sintering), a porous material is obtained whose microstructure is dictated by the physical characteristics of starch granules (morphology and size), the amount of added starch and its behavior in warm water (i.e., starch swelling capacity, size and shape of swollen granules) [8,9]. This method has been successfully employed to produce porous bodies of alumina [10], cordierite [5], and mullite [11], among others. Cordierite ($2Al_2O_3 \cdot 5SiO_2 \cdot 2MgO$) is a potential candidate for use in thermal insulators, among other applications, because of its low thermal expansion coefficient ($\alpha = 1–3 \times 10^{-6}$ °C$^{-1}$) and thermal conductivity (1–2 W/mK) [12,13].

The removal of organic components by high-temperature burnout involves long heat treatments (200–700 °C) which must be carried out at very slow heating rates in order to favor the release of high amounts of gases, thus allowing for the

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development of materials with the fewest possible defects. The use of microwave energy to processing materials is a relatively recent development that has been gaining increasing importance in the field of materials research. Its main benefits are faster heating schedules and energy savings compared to conventional heating methods as those found in food processing [14–19]. Microwaves transfer energy directly into the material, where it is converted into heat through the interaction of atoms and molecules with the electromagnetic field, in ionic conduction, dipole relaxation, and photon–phonon processes [14–16,19]. Thus, microwaves provide uniform volumetric heating of materials, allowing for the application of high heating rates and considerably shorter processing times, eliminating numerous difficulties encountered in conventional rapid heating techniques [15,16]. In addition to volumetric heating, other features of microwave processing are the formation of reverse temperature gradients and heat flows compared to conventional heating processes [17]. The direct deposition of energy within the processed material reduces the consumption of energy when compared with refractory furnaces. Therefore, microwave processing offers the advantages of high heating rates, shorter processing times, and significantly lower energy consumption, particularly when compared to high-temperature processes, which involve enormous heat loss with increasing temperature [18]. An important feature that must be considered when microwave-heating a material is porosity, which is the main property of the cordierite under study here. Pore characteristics include the level of porosity, type of porosity, and pore distribution and morphology. Evidence of the interaction of microwaves with pores is clearly visible from the significant increase in loss tangent with increasing porosity in the material. However, it is difficult to quantitatively correlate the increase in loss tangent with porosity, since ceramic bodies may be constituted by other phases and have defects, besides pores [19].

This work involved a study of the microwave sintering of cordierite precursor green disks prepared by thermogelling of aqueous ceramic suspensions with potato starch at different temperatures to produce cordierite-based porous materials. The developed microstructures were analyzed in relation to behavior of the aqueous starch suspensions with temperature and experimental conditions of consolidation and sintering used. Moreover, the results were also compared with those obtained by the conventional sintering route.

## 2. Experimental

### 2.1. Characterization of the raw materials

A mixture of commercial kaolin (kaolin C-80, Stone Big CORP., Arg.), talc (Talc 40, China) and alumina (A2G Alcoa, USA) powders with particle sizes of <5 μm, was used as a cordierite precursor. Based on a qualitative X ray-diffraction analysis (Philips PW3710, Cu Kα radiation at 20 mA and 40 kW) of the raw materials, kaolinite ($Al_2Si_2O_5(OH)_4$, File 06-0221) was identified as the main crystalline phase, with traces of quartz ($SiO_2$, File 5-0490) and orthoclase ($KAlSi_3O_8$, File 31-0966) in the kaolin powder. The main mineral phase in the talc was $Mg_3Si_4O_{10}(OH)_2$ (File 19-0770), with traces of dolomite ($CaMg(CO_3)_2$, File 34-0517) and magnesite ($MgCO_3$, File 83-1461), while the only phase identified in the alumina powder was corundum ($\alpha$-$Al_2O_3$, File 42-1468). The cordierite precursor mixture was formulated based on its oxide compositions, which resembled that of stoichiometric cordierite ($SiO_2$ = 51.4 wt.%; $Al_2O_3$ = 34.8 wt.% and MgO = 13.8 wt.%), but with lower silica content and higher proportions of alumina and magnesia: 37 wt.% of kaolin, 41 wt.% of talc and 22 wt.% of alumina. Based on the global composition, 85.7 wt.% of cordierite and 14.3 wt.% of $Al_2O_3$·MgO spinel were estimated as the final phases in thermodynamic equilibrium.

Native potato starch commercially available in Argentina was used as a consolidator/binder and a pore forming agent. The real density (1.47 g/cm$^3$) was determined by He-pycnometry (Quanta-Chrome, USA). Particle size distribution (Malvern Instruments Ltd., UK) was determined from an aqueous suspension of starch containing a polyacrylic acid (Dolapix CE-64, Zschimmer & Schwarz, Germany) as dispersant and applying ultrasound for 15 min to disperse and stabilize the starch particles. The potato starch presented a bimodal distribution, with a low volume percentage of small granules possibly representing impurities or broken granules, a slightly larger mean particle diameter ($D_{50}$ = 47.8 μm) than the mean diameters of ceramic particles, and a high distribution width ($W = D_{90} - D_{10}/D_{50} = 1.3$; where $D_{90}$ and $D_{10}$ are the granule diameters for 90 and 10 vol.% of granules, respectively). The weight percentage of humidity (14.4 wt.%) was determined by thermogravimetric analysis (Shimatzu, TGA-50) at 10 °C/min up to 120 °C, in air. An analysis of the morphology of the dry starch by scanning electron microscopy (Jeol JSM-6460) showed granules with smooth surfaces and oval or spherical shapes. The pycnometric density ($\delta_{pic}^{P}$) of the precursor mixture determined by pycnometry in kerosene at 37 °C was 2.44 ± 0.06 g/cm$^3$. The behavior of aqueous starch suspensions as a function of temperature was studied in a previous work [20].

### 2.2. Preparation and characterization of green bodies

Green disks (13.0 mm diameter; 1.5–3.0 mm thick) were prepared by thermogelling aqueous suspensions of the cordierite precursor mixture (29.6 vol.%) and 11.5 vol.% of potato starch. The suspensions were prepared by: (a) mixing (impeller mixer) the ceramic powders in water (70.4 vol.%) with 1 wt.% of Dolapix CE-64 (Zschimmer & Schwarz, Germany) and 0.5 wt.% of sodium naphthalenesulfonate (both with respect to the ceramic solids content); the ceramic powders were added sequentially, beginning with kaolin, pausing for 24 h, followed by the talc and lastly the alumina; (b) homogenization in a ball mill for 2 h; (c) addition of starch and mixing (impeller mixer) for 3 min; and (d) degassing for 20 min. The suspensions were poured into cylindrical stainless steel molds (which were covered with Teflon tape to reduce water evaporation), heated in air at 75 or 85 °C for 4 h