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Effect of Milling Time and Microwave Sintering on Microhardness and Electrical Properties of Nano and Micro Structured Cordierite

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ABSTRACT

The purpose of this research is to investigate the mechanical and electrical properties of nano structured cordierite. Nano grain size powders were synthesized through mechanical activation by high-energy ball milling of the starting powders containing 34.86 wt% Al_2O_3, 51.36 wt% SiO_2, and 13.78 wt% MgO. Samples were prepared by conventional and microwave sintering at 1390°C. SEM observations illustrated the equiaxed nano-grains of cordierite with an average grain size of 40 nm for samples sintered in microwave. With the increase of milling time, samples sintered at 1390°C in microwave furnace obtained higher micro-hardness and density than those sintered at temperature in conventional furnace. Sample milled for 30 h and sintered in microwave furnace at 1390°C obtained the maximum dielectric constant of 5.5±0.1.

1. INTRODUCTION

Cordierite has a low dielectric constant (ε=5–6), high resistivity (ρ>1012 Ωcm), elevated thermal and chemical stabilities and very low thermal expansion coefficient (α=1–2×10-6 ºC-1) [1-3]. With these properties and low processing costs, cordierite can be a potentially available material to be used instead of the alumina substrates, traditionally employed in the electronic industry. However, cordierite materials are difficult to sinter by solid state process [3-6]. Some attempts have been made to improve the sintering of cordierite by applying sintering aid [6–10] or using cordierite powders with favorable sintering behavior [9–15]. Adding sintering aid leads to decrease in the temperature of cordierite formation and increase in the density of the sintered materials, but it increases the thermal expansion coefficient and dielectric constant. Hence, the preparation of a homogeneous and fine cordierite powder which can be sintered without sintering aids is considered to be highly desirable [8–15].

Microwave heating (MWS) is for sintering ceramic materials for its uniform and speedy heating capability from the direct absorption of energy into the materials [16]. In addition, the increasein densification rate has been observed in some ceramic materials by sintering in a microwave furnace [16-20]. The mechanical activation process is another way to overcome the kinetic/diffusion constraints, arising from separation of particles in a dry powder mixture.

In this research we report the effects of microwave heating on mechanical and electrical properties of stoichiometric cordierite compositions activated for 1, 10, 20, and 30 h. The microstructures, electrical and mechanical properties of the microwave-sintered samples were compared with conventionally sintered samples.

2. EXPERIMENTAL PROCEDURES

Table 1 reports the chemical composition of MgO (d_{50} =0.3-0.4 mm), Al_2O_3 (d_{50} =0.5-0.8 μm), and SiO_2 (d_{50} =0.1-0.8 μm) used as the starting materials. The stoichiometric proportions of the raw materials were blended by milling in a plastic bottle using alumina balls and ethanol as a milling media for 1 h.

The mechanical activation of mixed powders was performed using a high-energy ball mill consisted of the alumina ball to powder mass ratio 15:1. The planetary mill pots were rotated at about 270 rpm. Powder mixtures were ground for 10, 20 and 30 h.

At different milling times the weight loss of alumina balls was measured before and after milling. The weight

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loss of alumina balls after 10, 20 and 30 h of milling, was 3.77, 5.65 and 7.11 g, respectively.

TABLE 1. The chemical composition of starting materials

	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	Na_2O
Silica	>99	tr.	tr.	tr.	<0.04	--
Alumina	≈0.08	≈99.8	≈0.06	≈0.02	≈0.02	≤0.1
Magnesia	0.02	0.01	98	0.005	0.005	--

The rectangular samples were fabricated by uniaxial pressing of powders at 220 MPa using a steel die with dimensions 0.5cm×0.5cm×2.5cm.

Comparison between two various heat treatments for sintering of samples was carried out using both microwave furnace (2.45 GHz and 900W) and electrical furnace in air at 1390°C. The details of microwave processing have been mentioned in Ref [17]. The mean rate of heat in microwave and electrical furnaces was about 37 and 10°C/min, respectively.

Porosity and bulk density of the sintered samples were calculated through the Archimedes method (ASTM C373-88) at ambient temperature. Vickers (Hv) microhardness of the sintered specimens were evaluated by a microhardness tester (Model: MVK-H21) using an indentation load of 100 g for a dwell time of 15 s. Each experiment was repeated at least five times to confirm the repeatability of the results. Dielectric constant and dielectric loss tangent measurements were made on disk shaped samples with 10 mm in diameter and 2 mm thickness. The parallel surfaces of samples were silver painted. The dielectric constant (ε) of the specimens were calculated from the measurements of the capacity (Eq. (1)).

$$\varepsilon = Cl/A\varepsilon_0 \quad (1)$$

Where ε_0 is the vacuum permittivity (F/Cm), A the area of the sample (Cm^2), l the thickness (Cm) and C (F) the capacity. Capacity and dielectric loss tangent were measured at room temperature and 1 MHz. The phase evaluation of the sintered samples were investigated by X-ray diffraction (Siemens, D500 system) method using CuKα radiation in the range 2θ=10-80. The morphology and microstructure of powder and etched samples was investigated by VEGA\\ TESCAN scanning electron microscope. More details of the experimental procedure have been brought elsewhere [21].

3. RESULT AND DISCUSSION

Figure1. shows the morphology of the powder mixtures of cordierite composition milled for different times. The mixture milled for 1 h (Figure 1a) consists of the starting powders distributed uniformly. The morphology of powder milled for 10 h (Figure 1b) shows some particles that have retained their shapes as well as some grounded particles gathered around bigger ones. Further attrition is observed in the powder milled for 20 h; the presence of spherical particles accompanied by heterogeneous agglomerates is also observable (Figure 1c). After 30 h of milling (Figure 1d), more particles have been grounded. The SEM micrographs with a higher magnification have been brought in Ref [21].

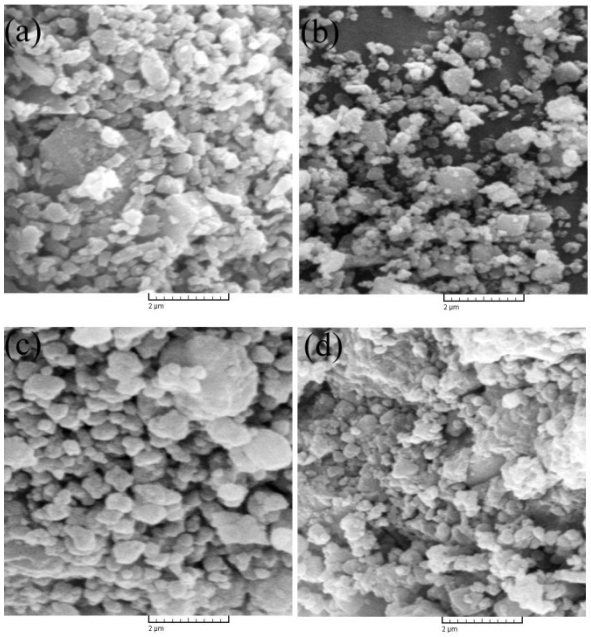

Figure 1. Scanning electron microscopy of mixtures (a) without milling and activated for (b) 10 h, (C) 20 h and (d) 30 h.

Figures 2. and 3. show the bulk density and porosity of the sample which sintered at 1390°C in both microwave (MWS) and conventional furnaces (CS) and milled for different times, respectively. From these figures, it can be concluded that microwave sintered samples lead to higher density and lower porosity compared to conventional sintered samples and with both heating methods, the increase in milling time increases density and decreases porosity of sintered samples. The behavior of sitering as a function of temperature was studied in the previous work [21].

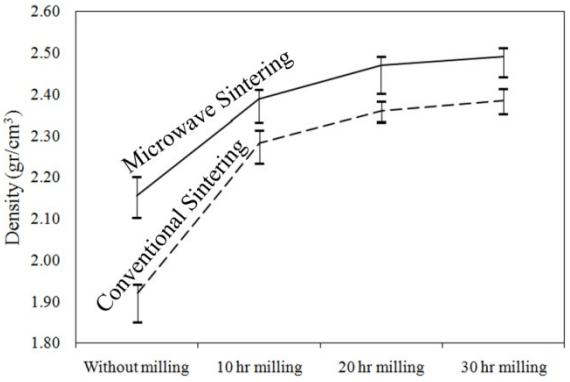

Figure 2. Density of mixtures activated for different times and sintered at 1390ºC in microwave (MWS) and conventional furnace (CS).

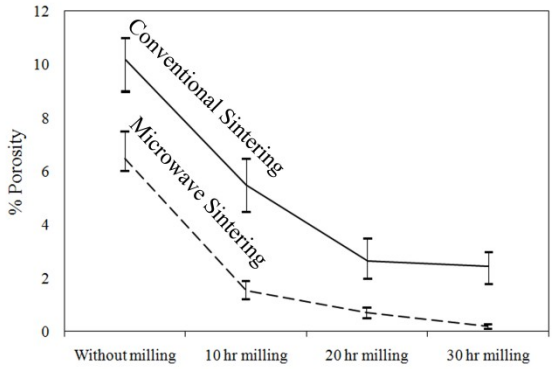

Figure 3. Prosity of mixtures activated for different times and sintered at 1390ºC in microwave (MWS) and Conventional furnace (CS).

Microwave radiation reduces the diffusion barrier of ions and accelerates diffusion of grain boundary and densification rate [18, 19].

XRD patterns of the samples milled at different times and sintered at 1390°C (Figure 4.) confirm that cordierite (File 01-085-1722) was the only crystalline phase in all the sintered specimens. Crystallization behavior of cordierite was investigated in the previous work [21].

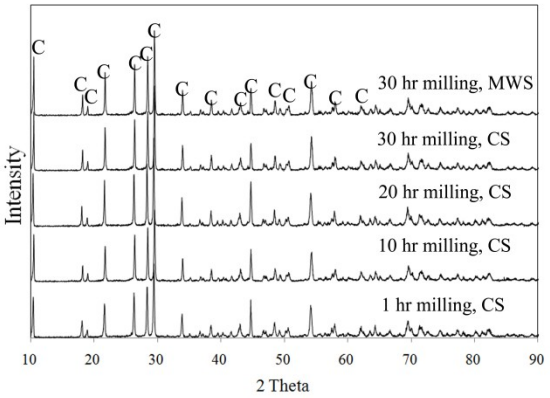

Figure 4. XRD patern of samples activated for different times and sintered at 1390°C in microwave (MWS) and conventional furnaces (CS).

Comparison between microwave and conventional sintering results (Figures 1. and 4.) showed that cordierite ceramics with higher crystallinity and density can be obtained by microwave sintering process without soaking. Mechanical activation produces changein the structure of the powders and causes the particle size reduction. A reduction of the particle size allows the crystallization rate increases.

Figure 5. illustrates the micro-hardness results as a function of milling time of MWS and CS specimens sintered at 1390°C. For each time of milling, the micro-hardness values of the MWS samples are higher than those of the CS samples; since the driving force for densification and crystallization is very high in specimens sintered in microwave furnace compared to conventional furnace. The results of microhardness test showed that with increasing the milling time from 1 to 30 h, the micro-hardness values of MWS and CS samples sintered at 1390°C increased from 546±28 to 1089±51 HV and from 498±23 to 818±52 HV, respectively.

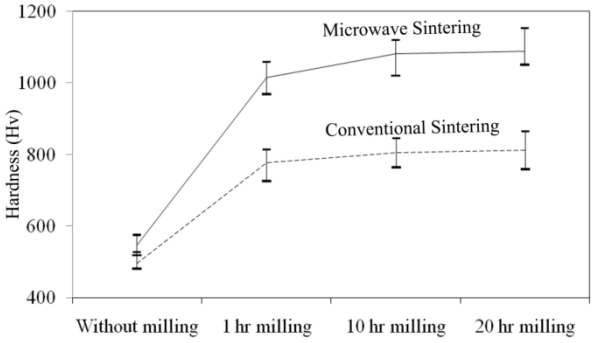

Figure 5. Micro-hardness of samples activated for different times and sintered at 1390°C in microwave (MWS) and conventional furnaces (CS).

With both heating methods, mechanical activation of precursor oxides led to the increase of density and microhardness and decrease of porosity of the sintered samples.

In Figure 6. the dielectric constant changes with milling time for the MWS and CS samples sintered at 1390°C are shown. The observed behavior can be attributed to the decrease in porosity of sintered samples by increase of milling time of both heating methods.

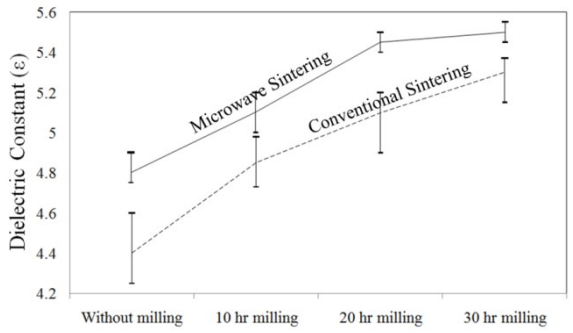

Figure 6. Dielectric constant (ε) mixtures activated for different times and sintered at 1390ºC in microwave (MWS) and Conventional furnace (CS).

In Figure 7. dielectric loss tangent versus milling time for both heating methods is shown. As this figure shown, the dielectric loss tangent reduces by increasing milling time. Figures 6. and 7. show the dependence of dielectric properties on porosity. In both heating methods, the dielectric loss tangent increases with the increase of porosity. Figures 8. and 9. present SEM micrographs of MWS and CS specimens milled for 30 h and sintered at 1390°C, respectively.

Figure 8a. indicates that 10 h of milling is not enough time and leads to the formation of an inhomogeneous

sample with a relatively high open porosity. Figure 7b. shows nearly equiaxed nano-grains of cordierite with an average grain size of 40 nm after 30 h of milling. Mechanical treatments led to the fine and uniform microstructure.

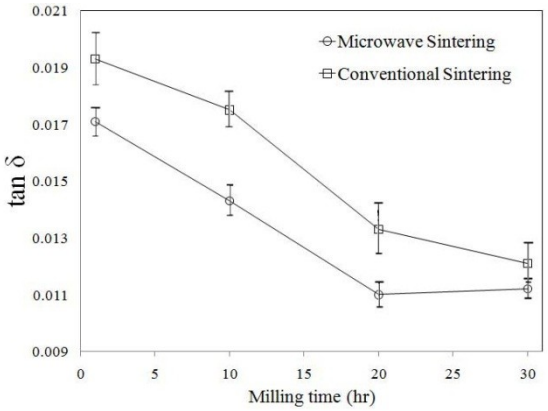

Figure 7. dielectric loss tangent versus milling time for samples sintered at 1390ºC in microwave (MWS) and Conventional furnace (CS).

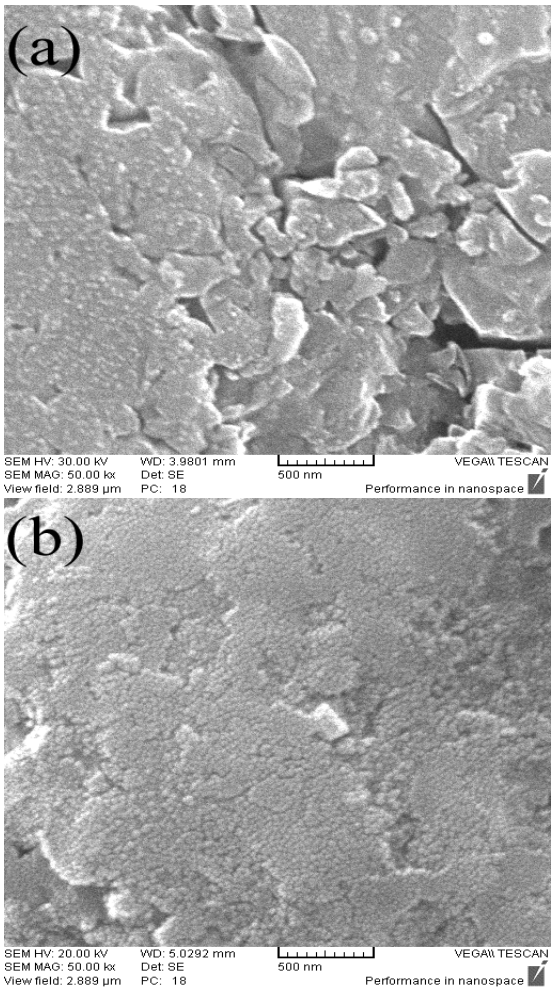

Figure 8. SEM micrographs of (a) 10 and (b) 30 h milled samples sintered at 1390°C in microwave furnace.

Comparison between Figures 8. and 9. reveals that when microwave heating is used rather than conventional heating, more homogeneous microstructure with a narrow grain size distribution can be obtained. This is due to the fact that in microwave heating the sintering time is much shorter than that in conventional heating, and hence, there is not enough time for the grains to grow and one finds much finer microstructure in microwave sintered products. In previous work [21], the distribution of porosity was more obvious in a lower magnification.

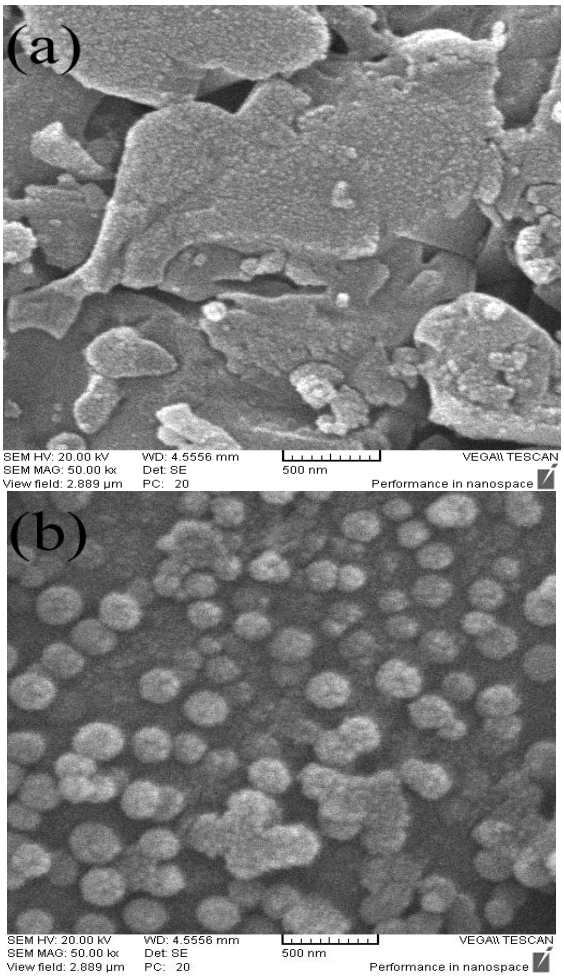

Figure 9. SEM micrographs of (a) 10 and (b) 30 h milled samples sintered at 1390°C in conventional furnace.

4. CONCLUDING REMARKS

The results of this work reveal that the mechanical activation of the alumina, magnesia and silica mixtures improves electrical and mechanical properties of microwave-sintered samples compared to conventionally sintered samples.

After 30 h of milling, samples sintered at 1390°C in microwave furnace (without soaking) and conventional furnace (held for 2 h) obtained a high density of 2.49

g/cm^3 (98.4% of the theoretical density) and a low density of 2.38 (91.5% of the theoretical density), respectively. Results showed that the loss tagent of microwave sintered samples decreased compared to conventional sintered samples.

Milling process and microwave sintering improved mechanical and electrical properties of samples؛ the microhardness of samples milled for 1 and 30 h and sintered at 1390°C increased from 546±28 to 1089±51 Hv in microwave sintering and from 498±23 to 818±52 HV in conventional sintering, respectively.

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