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Dedicated to Professor Liviu Literat
On the occasion of his 85th birthday

SYNTHESIS AND CHARACTERIZATION OF CORDIERITE FOR DIESEL FILTERS

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ABSTRACT. Cordierite, $Mg_2Al_4Si_5O_{18}$, has a very low thermal expansion coefficient, thus a high resistance to thermal shocks as well as chemical stability at high temperatures. Accordingly, it is used in applications where high resistances to thermal shock are essential; such is the case of diesel particulate filters (DPF). This paper concerns the synthesis of cordierite by using the solid state reaction method starting from raw materials: kaolin, metakaolin and talc. The ceramics fired at 1300˚C and 1350 ˚C were submitted to chemical attack by an alkaline mixture (one mole Na_2CO_3 with 1.5 moles SiO_2) under so-called “less-severe” conditions, i.e., 900˚C and then under “severe” conditions at 1000˚C for 5 minutes. The SEM images evidence less corrosion in the first case, and slight corrosion features under the circumstance of the “severe” attack.

Keywords: *cordierite, ceramics, chemical attack*

INTRODUCTION

Cordierite ceramic has a high thermal shock resistance due to their low thermal expansion coefficient coupled with relatively high chemical and mechanical stability. These characteristics make it an important material for many applications such as heat exchangers for gas turbine engines, and honeycomb-shaped catalyst carriers in automobile exhaust systems. Because the natural mineral is not sufficiently pure, cordierite has to be synthesized. Cordierite powders can be prepared by the solid-state reaction, sol-gel technique,

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sintering and crystallization from vitreous state or consolidation of raw structure with organic materials and subsequent calcinations for obtaining a porous cordierite ceramic.

The solid state reaction is the most used method for applications of cordierite as honeycomb carrier because this technique allows formation of the monolithic structure with optimum mechanical and thermal shock resistance. However, a disadvantage of cordierite ceramic compositions prepared by this method is the close fired temperature range to the different eutectic points.

The particle size distributions of the precursor's oxides facilitate cordierite synthesis and favors crystallization of mineral phases. [1] Evolution of the crystalline phases in the cordierite synthesis with temperature and time allows controlling chemical and structural characteristics of final ceramic supports. [2]

Kaolin-based cordierite ceramics prepared by solid state reaction and thermal treated at 1350 ˚C gave the pure cordierite phase, good compressive strength and low thermal expansion coefficient being the suitable for using as catalyst support. [3]

Heat resistant ceramic materials based on cordierite with various mineralizing additives for obtaining the crystalline phases that ensure low values of thermal expansion coefficient have been reported. [4]

The cordierite can be obtained directly from oxides as well from other raw materials whose chemical composition sums up to that of cordierite. For this purpose, it can be used like raw materials: elementary compounds (pure oxides, hydroxides, carbonates); double compounds (kaolins, clays, talc, steatite, sepiolite); triple compounds (chlorite). [5-8]

One of the most extended applications of cordierite is as ceramic monolithic honeycomb supports. This structure is increasingly used in many reactor applications, such as petrochemical industry selective reduction of nitrogen oxides, selective hydrogenation of alcohols, automobile emissions control and control of volatile organic compounds. [9-12]

Ceramic substrates have been employed as automobile catalyst supports to facilitate the conversion of CO and HC emissions to CO_2 and H_2O by redox reaction. Cordierite ceramic honeycombs are currently considered as leading candidates for trapping and oxidizing the carbonaceous particulate emission from automobiles.

The corrosion resistance of cordierite remains an important issue in studies on cordierite as a material for particulate filters. During use, a DPF collects soot, i.e. carbon based particles from diesel combustion, as well as small amounts of components other than carbon and organic matter. These typically include compounds containing Ca, Mg, Zn, P and S originating from fuel or lubricating oil, as well as metals or metal oxides from wear of the engine or the exhaust gas system. The mechanism of the corrosion of single crystal natural Cordierite by sodium silicate ash was analyzed. [13]

In our work [14] the chemical attack on ceramics from powders obtained by sol-gel method was studied. The alkaline corrosion attack tests showed no damages of ceramics in the case of milder conditions, at 900 ˚C, and evidenced corrosion when the temperature in the diesel filters exceeds 1000 ˚C.

The goal of this study was to analyze the corrosion of the ceramics obtained by conventional method, solid state reaction, to test for alkaline chemical attack under severe or less-severe experimental conditions. The influence of the cordierite synthesis parameters from kaolin, metakaolinite and talc for a complete reaction of reactants, the grain size and thermal behavior of raw mixture were determined. From powders, ceramic materials were obtained by applying thermal treatment at various temperatures on pressed pellets, which were characterized from physical-chemical point of view, and have been tested for alkaline chemical attack under severe or less-severe experimental conditions.

RESULTS AND DISCUSSIONS

Grain size distribution of the mixture

The grain size distribution of the raw mixtures obtained by using the solid state reaction method is illustrated in figure 1. The sample shows a grain size interval between 0.010 and 0.179 µm, with an average of 0.049 µm. The typical curve evidences one grain size interval with following particles ratio:

17 % particles between 0.097 µm and 0.179 µm;
11 % particles between 0.010 µm and 0.028 µm;
78 % particles between 0.028 µm and 0.097 µm.

The decrease of particle sizes determines a more completed reaction of the solid reactants, it is in favour of faster firing rate. The small particle size also reduces the risk of phase separation during preparation of the mixture.

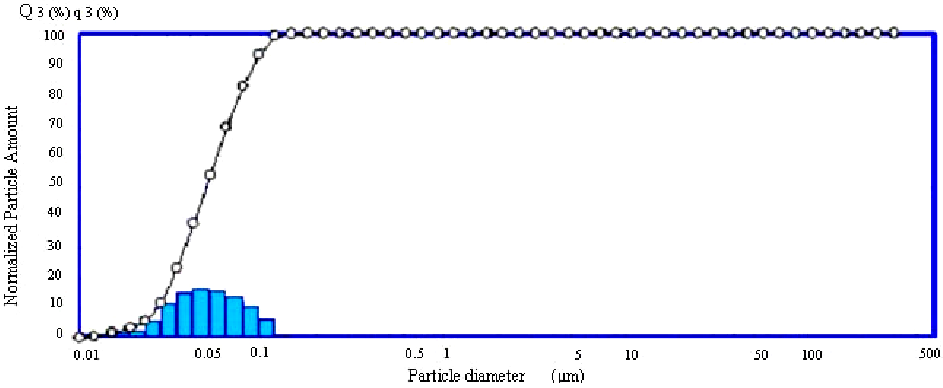

Figure 1. Particle size distribution of raw materials mixture

Thermal behaviour

Figure 2 shows the thermal differential (DTA) and weight loss (TG and DTG) curves for the raw materials mixture (kaolin, metacaolin and talc) until 1200 ˚C temperature under a heating rate of 10 ˚C/min.

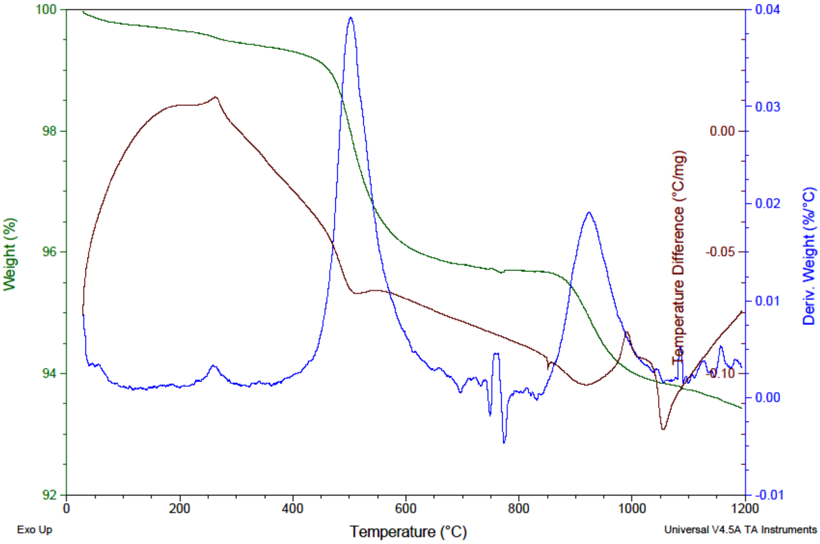

Figure 2. Thermal behaviour of raw materials mixture

The most important thermal effects evidenced in 20˚C – 1200 ˚C temperature interval are:

- In the 100-200 °C temperature range, an endothermic effect is due to elimination of the water adsorbed at the powder surfaces as a consequence of milling process;
- In the 200 – 300 °C temperature range, the sample shows a small exothermic effect accompanied by weight loss (about 0.5 %) as a result of oxidation of organic compounds;
- In the 400 – 600 °C temperature range the sample shows an endothermic effect accompanied by a weight loss (about 3 %) as a result of the dehydroxilation of kaolinite (transforming in metakaolinite at 450-500 °C) and elimination of OH^- groups from talc;
- In the 800-1200 °C temperature range the sample shows endothermic and exothermic effects as a result of decomposition of talc in magnesium metasilicate and silica oxide (at 600-1050°C temperature). Also the metakaolinite is transformed in spinel phase (at 900-1000 °C temperature), and after that in primary mullite. Talc is transformed in enstatite at about 1140 °C temperature. The weight loss in this interval is about 2 %.

X-ray diffraction

Figure 3 illustrates the X-ray diffraction of cordierite ceramic sample after thermal treatment at 1350 ˚C.

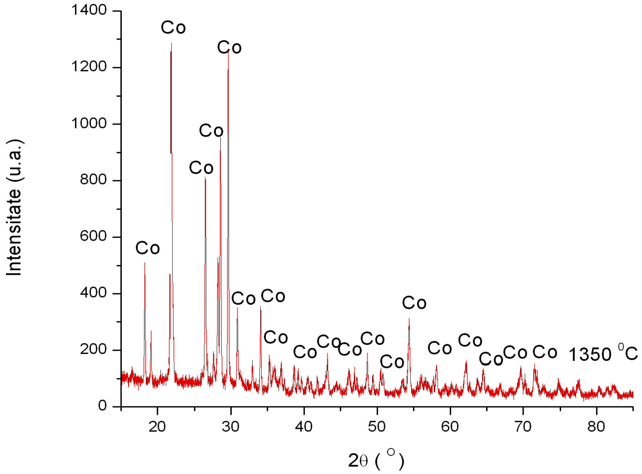

Figure 3. XRD pattern of ceramic sample fired at 1350 ˚C

The X-ray diffraction pattern of ceramic sample is dominated by the high temperature polymorph, α-cordierite. However, the relative lower intensity of the spinel and cristobalite index reflexes can be noticed. The presence of spinel and cristobalite might be explained as the result of an incomplete reaction the components in the system due to of an insufficient homogenization of raw materials. It is well known that the solid state reaction method has the disadvantage of an incomplete reaction between reactants. Thus, in final mineralogical composition can be found the intermediary compounds.

Compactness characteristics of ceramics

The compactness characteristics and relative size parameters in the case of the samples thermal treated at 1300 ˚C and 1350 ˚C, the heating rate being of 10 ˚C/min and maintaining 2 hours at maximum temperature are presented in Table 1.

Table 1. Compactness characteristics of ceramics

Sample	Firing temperature T_a[˚C]	Water absorption a [%]	Apparent density ρ_a [g/cm^3]	Apparent porosity P_a [%]	Firing shrinkage C_a [%]
I	1300	0.417	1.993	0.831	3.49
II	1350	0.210	2.071	0.434	3.7

It can be observed that open porosity is small for both samples. An increasing of temperature with 50 ˚C determines a decreasing of apparent porosity, as it is expected.

For an efficient diesel particulate filter is necessary a porous material. The higher values for porosity were registered for the sample sintered at 1300 ºC (0.831 %). The firing shrinkage does not vary significantly for the tested samples.

Thermal expansion

The thermal expansion coefficient of cordierite is low that recommend this material for various applications. This coefficient has been measured for ceramic samples sintered at 1300 ˚C and 1350 ˚C, the results being presented in Table 2.

Table 2. Thermal expansion coefficients for studied samples

Temperature [ºC]	Ceramics sintered at	
	1300 ºC	**1350 ºC**
	α E^{-6}/K	α E^{-6}/K
200	9.1	3.0
300	9.6	6.2
400	8	5.7
600	6.3	5.3
1000	4.7	3.9

It can notice that the lowest value of thermal expansion coefficient is $3.9\cdot10^{-6}$/K in the temperature interval of 20-1000 ˚C for the ceramic samples fired at 1350 ºC. In the case of ceramics thermal treated at 1300 ºC, the coefficient value in the same interval is higher ($4.7\cdot10^{-6}$/K) that can be explained by the compactness characteristics. The apparent porosity for samples fired at 1300 ºC is higher than porosity for samples at 1350 ºC.

The thermal expansion coefficient, in the 30-1000 ºC range as imposed by the standards for cordierite ceramics has to fall in the 2-4.5 range for the ceramics with maximum 0.5 % apparent porosity.

In conclusion, the ceramics thermal treated at 1350 ºC have the thermal expansion coefficient impose for cordierite ceramics and can be used in applications that require o high thermal shock resistance.

Resistance to corrosion of the cordierite ceramics

For testing the resistance to corrosion of the samples, a mixture of 1 mole Na_2CO_3 and 1.5 moles of SiO_2 was mixed that produced a reactive sodium silicate. The alkali-rich mixture was pressed as 6-mm pellets that were laid on the cordierite ceramics' surface. The Na_2O-SiO_2 system phase diagram evidences the presence of one eutectic at temperature of ~830˚C and an almost complete melting at ~950˚C. The sodium-rich melts are corrosive at temperatures significantly below 1000˚C. Due to this fact, one would expect that the cordierite ceramics undergoes alkaline attack during its use as filter for Diesel engines if in contact with alkali-rich ashes.

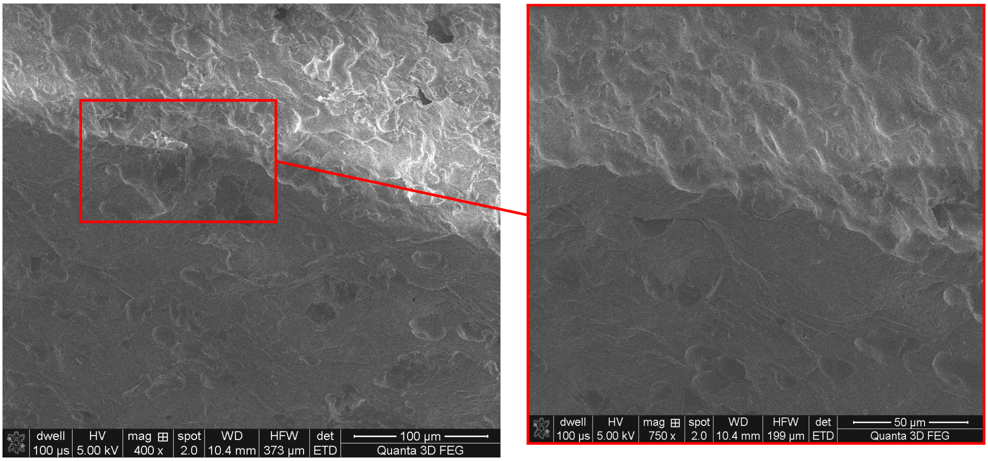

Figure 4. SEM image of the sample fired at 1350 ºC and corroded at 900 ºC

The tested cordierite ceramic was the sample sintered at 1350 ˚C. It was topped by the pellets containing alkaline mixture and was submitted to two experimental corrosion sets-ups. The first set-up was considered the milder version, thus the ceramics with alkaline pellets were fired at 900˚C for 5 minutes. For the second set-up, considered as intense chemical attack conditions, the samples were fired in a laboratory kiln at 1000˚C, for 5 minutes. The effects of the chemical attack on the ceramics were evidenced by scanning electron microscopy (SEM) (Figs. 4 and 5).

In the case of the milder experimental conditions, at 900 ºC the ceramic obtained from solid state reaction powders, is easily attacked by sodium silicate ash. In the superior side it is showed the ash and in the inferior side, the ceramic. At 1000 ºC, the ceramic sample is corroded by sodium silicate ash. This corrosion is presented in the SEM image, figure 5 (left). The chemical attack is very well evidenced in figure 5 (right). Thus, if the temperature in the diesel filters exceeds 1000˚C, corrosion of the cordierite ceramics occurs leading to increasing damage over time.

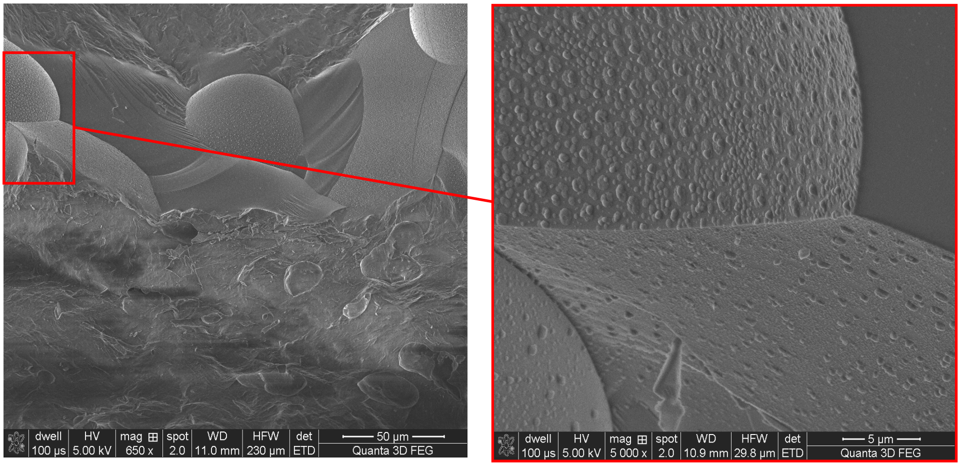

Figure 5. SEM image of the sample fired at 1350 ºC and corroded at 1000 ºC

CONCLUSIONS

The cordierite powders were synthesized by solid state reactions in the laboratory conditions. Cordierite ceramics were obtained by traditional route. Powders and cordierite ceramics were characterized.

The powders obtained by solid state method presents the nanometric particle sizes. The mean values for particle size of powders are 0.049 µm. The cordierite starts to crystallize after 1050 ºC according to the thermal analysis. The firing shrinkage presents normal values, due to densification of the material during the sintering, and the dehydration compounds from kaolin and talc. The compactness characteristics (water absorption, apparent density, apparent porosity), are changed with the sintering temperature. For an efficient diesel particulate filter is necessary a porous material. The higher values for porosity were found for the sample sintered at 1300 ºC. The thermal expansion coefficient presents lower values for the samples fired at 1350 ºC In conclusion, to reach a low thermal expansion coefficient, high temperatures are necessary or a longer plateau at maximum temperature.

The SEM images show that the ceramics is easily attacked by the sodium silicate ash, under less severe conditions, at 900 ºC. At 1000 ºC, the samples are corroded by the sodium silicate ash.

The best properties are presented by the sample fired at 1350 ºC, and corroded with sodium silicate ash at 900 ºC. It presented nanometer particle size, the optim values for water absorption and porosity, low thermal expansion coefficient. In terms of corrosion, it is easily corroded by sodium silicate ash under less severe conditions.

EXPERIMENTAL

The raw materials used were kaolin, metakaolin (dehydroxylated at temperature 650 ºC and time 5 h) and hydrated magnesium silicate (talc) [$3MgO\cdot4SiO_2\cdot H_2O$] (99.5%). Kaolin-based cordierite ceramics are prepared by the solid-state reaction by mixing a stoichiometric composition of kaolin, metakaolin and talc. The general processing diagram is presented in figure 6.

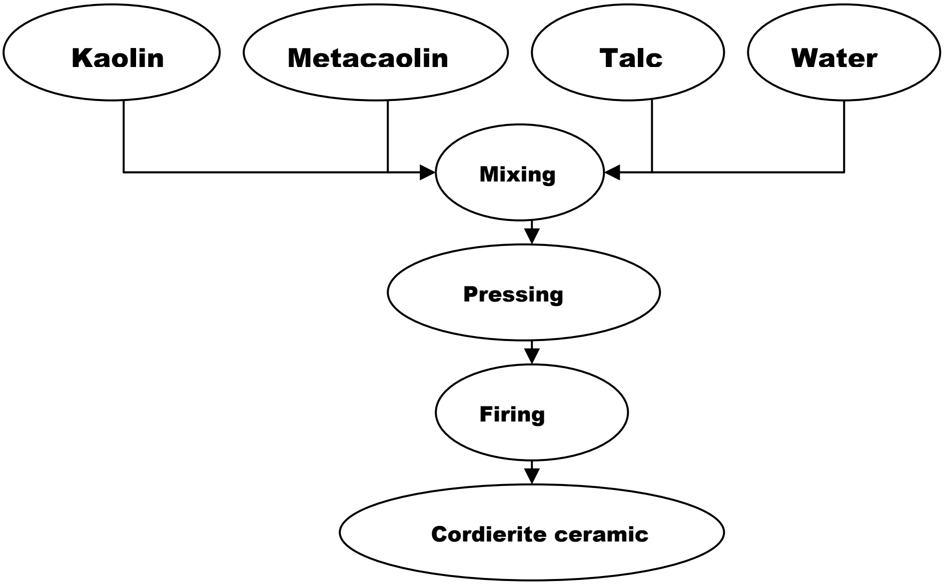

Figure 6. General processing diagram for obtaining cordierite ceramics

The raw materials are mixed in a ball mill at 200 rot/min for 4 h. The mixture is oven-dried at 115 ºC for 12 h and than pre-fired at 300 ºC for 3 h. The resulting powder was granulated and pressed as pellets with 28 mm in diameter and 2 mm thickness. The pellets were subsequently sintered at 1300˚C and 1350˚C with heating rate 10 ºC/min and plateau at maximum temperature 2 h, in a Nabertherm-type laboratory kiln.

The grain size distribution of raw mixture has determined by using a Counter Coulter WING-SALD 7101 unit; the thermal behaviour by using a SDT Q 600-type apparatus, and the thermal expansion coefficient with a L75H1400 dilatometer. The mineralogical composition was established based on the XRD patters measured on BRUKER D8 ADVANCE diffractometer with Cu $K_{\alpha1}$ (λ_{Cu1} = 1.540598 Å) radiation, Ni filter in order to eliminate the Cu K_{β} component, and Ge monochromator for eliminating the Cu $K_{\alpha2}$ component, on the 15–85˚ 2θ interval.

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