

Elaboration of cordierite ceramic starting from Algerian clays

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Abstract— Cordierite ceramic are elaborated by mixing a Algerian kaolin which is located in “Djebel Debbagh” region in the Algerian east, and hydroxide of magnesium. This kaolin named “DD3”, contains a large tenor of manganese oxide ($MnO > 1.34\%$) what gives a blackish colouring to this clay, which limit its utilization in luxury porcelain and sanitary ware where brightness and whiteness are required. However DD3 is composed mainly by kaolinite and gibbsite which is also bearer of alumina. Fusible compound such iron and alkalis are less than 1 %. Elaboration of cordierite is carried out by mixing magnesium hydroxide to DD3. Fumed Silica powder is added to respect the stoichiometric composition of cordierite. Magnesium hydroxide is prepared by precipitation from $MgCl_2$ and NH_4OH . The mixtures with various compositions of DD3 kaolin and magnesium hydroxide are pressed to give samples in form of pastilles, and sintered at temperatures ranging from 1200 °C to 1350 °C to determine the ceramics properties such apparent and specific density, linear shrinkage, water absorption. Formation of Cordierite phase and structural changes are investigated by X-ray diffraction (XRD), simultaneous thermal analysis (DTA-TG), and thermal dilatometry.

Keywords-component; Elaboration, cordierite, kaolin

I. INTRODUCTION

Cordierite is a magnesium aluminium silicate which is the main phase of the $MgO-Al_2O_3-SiO_2$ system; the stoichiometric formula is $(2MgO.2Al_2O_3.5SiO_2)$. Cordierite materials have very interesting properties for many industrial applications. Cordierite ceramics possesses an extremely low thermal expansion; low thermal conductivity, and high mechanical strength, these properties gives an excellent thermal shock resistance. Its refractoriness is appreciable; safety temperature used is above 1200 °C. Refractory applications concern several products such kiln furniture, molded honeycomb-like catalyst supports in auto emission reduction devices, thick films, porous ceramics, insulators, high frequency insulators, high performance resistors, special furnace shapes, heating element supports, exhaust catalyst supports, burner tubes, refractory setters and substrates, welding tapes, heaters, thermocouples, and appliance insulators. Cordierite ceramics possesses also, low values of dielectric constant, and dielectric loss which allow applications in electronic industry such as substrates, packaging, and multichip module (MCM).

The conventional methods for synthesis of cordierite ceramics include the solid-state sintering of MgO , Al_2O_3 and SiO_2 purest oxides in ratios corresponding to the stoichiometric chemical composition of cordierite $(2MgO.2Al_2O_3.5SiO_2)$ [1-2], but also extensive researches are developed to synthesize cordierite from cheaper raw materials such clays and talc [3-4]. In industrial production of cordierite ceramics such as for refractory application, natural raw materials are often used such Kaolin, talc, feldspar, sepiolite, gibbsite, and magnesia. To respect the stoichiometric composition formula of cordierite, one adds alumina [5], calcined alumina and silica powder [6], magnesium compounds [7].

This study presents our investigations of elaboration of cordierite ceramic starting from a abundant Algerian kaolin for developing its valorization. The Algerian kaolin which is named “DD3” comes from a deposit which is located in “Djebel Debbagh” region, in the Algerian east [8-9]. DD3 kaolin has a blackish coloring, that which limits its utilization in luxury porcelain, sanitary ware where, and paper where brightness and whiteness are required [10].

II. MATERIALS AND METHODS

II.1. Starting materials

(1) The DD3 kaolin is composed by mainly by kaolinite over 80 % weight, the other minerals are represented by gibbsite which bearer of alumina, and by todorokite which gives blackish color to that raw material (Fig.1). The chemical composition (table 1) shown that kaolin is very rich in alumina ($Al_2O_3 > 38\%$), and the alkaline metal oxide content in the kaolin was extremely low ($Na_2O + K_2O < 0.10\%$). The ignition loss value exceed 17 wt. %, it's constituted mainly by H_2O because DD3 kaolin is poor in carbonates, the amount of earth-alkaline oxides (CaO and MgO) is very low ($< 0.50\%$). The simultaneous thermal analysis (TG /DTA) shows the characteristics peaks of kaolin. Two endothermic peaks at 142.1 °C and 536 °C, first peak corresponds to elimination of interlayer molecules H_2O of halloysite, and second peak to the dehydroxylation of kaolinite, which is transforms into metakaolinite. Exothermic peak observed at 986.7 °C can be attributed to the spinel $\gamma-Al_2O_3$ and or mullite which are

formed from the reaction between the constituents of metakaolinite [10-12]. Dehydration of gibbsite is observed at 436.2 °C (DDTA peak) with weight loss of 2.94 %. Minor weight loss (0.78 wt. %) at high temperature can be attributed by the dehydration of todorokite ((Ca,Mn) Mn₅O₁₁.4H₂O) which transformed to hausmannite (Mn₃O₄) [8].

Thermal behaviour is study by dilatometer (402 PC NETZCSH), this analysis shows that kaolin undergoes a three contractions (Fig.3). (i) At 504.1 °C with a small contraction -2.74 % which is attributed to dehydroxylation of kaolinite, (ii) at 850 °C with -7.61 % is attributed to the reorganisation of metakaolinite to give spinel or mullite, (iii) and at 1066 °C with -9.72 % which can be attributed to mullite crystallisation. The dilatometric DD3 kaolin compoment does not shows the characteristic expansion α to β of quartz at 573°C, DD3 kaolin is very poor on free silica.

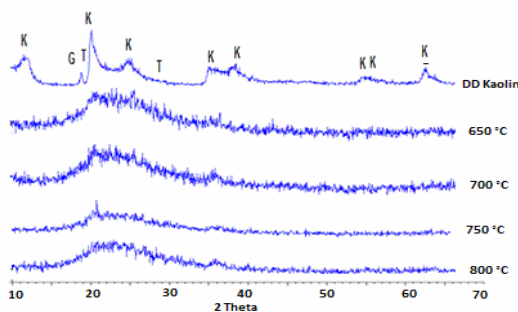


Fig.1 : X-ray diffraction for kaolin powder and for calcined kaolin

Table 1:
Chemical composition of DD kaolin

Oxide	Mass %	
	DDn	DDc
SiO ₂	41.97	50.56
Al ₂ O ₃	38.00	45.78
MnO	1.34	1.61
CaO+MgO	< 0.50	<0.60
K ₂ O+Na ₂ O	<0.10	<0.12
Fe ₂ O ₃	<0.05	<0.06
SO ₃	<0.05	<0.06
TiO ₂	<0.01	<0.12
I. loss	17.00	-

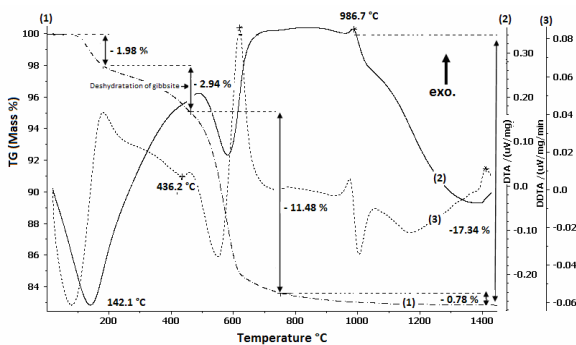


Fig.2 : DTA/DDTA and DTG of DD3 kaolin

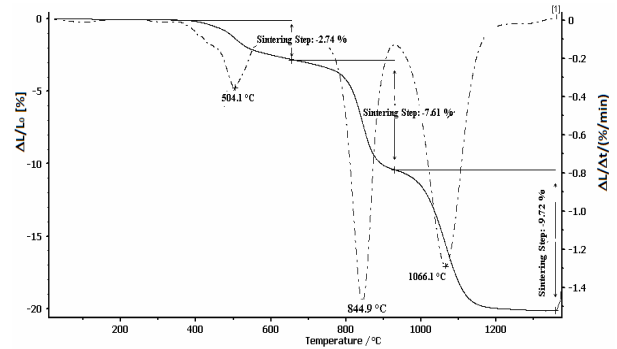
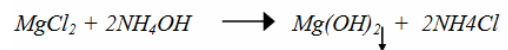


Fig.3 : Linear shrinkage and sintering shrinkage rate of DD3 kaolin from room temperature to 1400 °C

(2) The magnesium hydroxide (Mg(OH)₂) is precipitated from magnesium chloride solution with ammonia solution according the reaction (1). Ammonia is added in excess (+10%) to guarantee the totality of the chemical reaction, and then the suspension is washed with distilled water several times for eliminate excess from ammonia. After decantation the magnesium hydroxide is dried at 100 °C for be used in the starting mixture of cordierite.



(3) Fumed Silica powder is added to respect the ration of stoichiometric composition of cordierite (2MgO.2Al₂O₃.5SiO₂).

2.2. Procedure of elaboration of cordierite ceramic

Two compositions are prepared, (1) starting from kaolin with two mixtures from DD3<40 μm, and from DD3<25 μm, and (2) one mixture (DDc) from the calcined kaolin at 800 °C (metakaolin). Every mixture is composed from magnesium hydroxide, and silica powder in a molar ratio of (2MgO.2Al₂O₃.5SiO₂), is dispersed at wet state under magnetic agitation. After drying the mixture, samples were uniaxially pressed at 20- 50 MPa to form a disk of diameter 40 mm, and of thickness 5 mm. The green compacts were fired in air from room temperature up to 1350 °C at a rate of 5 °C/min in air.

2.3. Characterisation

The crystalline phases of cordierite formed were identified by XRD analysis using a Cu-tube diffractometer (Philips X' PERT, PW3040). DTA-TG (NETSCZH 409 PC), and thermal expansion analysis (NETSCZH 402) were also used to examine the crystallization and the sintering of cordierite respectively. The chemical composition is determined by an XRF analysis (Philips X' PERT). In order to examine the thermal behaviours, and optimal formation of cordierite phase, green specimens were analysed by simultaneous thermal analysis (NETSCZH 409 PC), and by thermal dilatometer analysis (NETSCZH 402). Ceramics properties such apparent density (δ_a) is determined from the weight and volume, total porosity (P_t) is calculated starting the ration of densification (δ_a/δ_s), and water absorption (W.A.) of

samples were determined by common means for to complete our study.

2.4. Results

The simultaneous thermal analysis DTA-TG of starting mixtures of cordierite shows: the crystallisation of cordierite phase is not clear in the case of DDc mixture (Fig. 4), one observed 3 exothermic peaks; at 999 °C can be attributed to mullite crystallization, 1150 °C, and 1316 can be attributed to indialite phase.

In the case of DD40 and DD25, the crystallisation of cordierite is clear and net; at ~970 °C for μ cordierite and at ~1200 °C for α cordierite (indialite).

The sintering shrinkage thermal behaviour of starting mixture which carried out by dilatometer analysis with 5°C/mn (NETSCZH), it's observed two sintering shrinkage, first shrinkage can be attributed to μ cordierite, and second shrinkage to α cordierite crystallisation and sintering of ceramic.

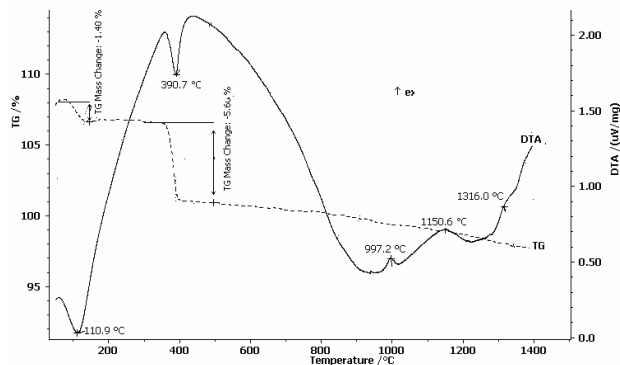


Fig.4 : DTA curve of DDc starting mixture of cordierite

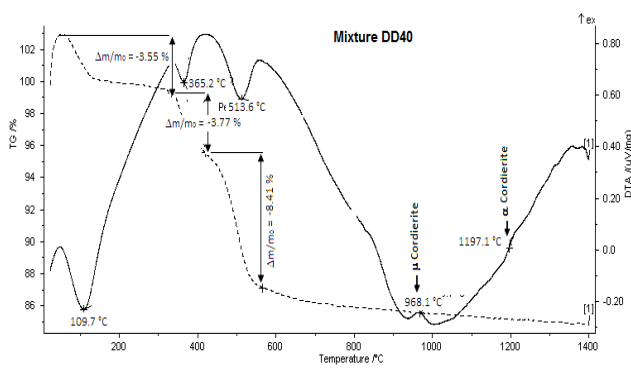


Fig. 5 : DTA-TG curve of starting DD40 mixture of cordierite

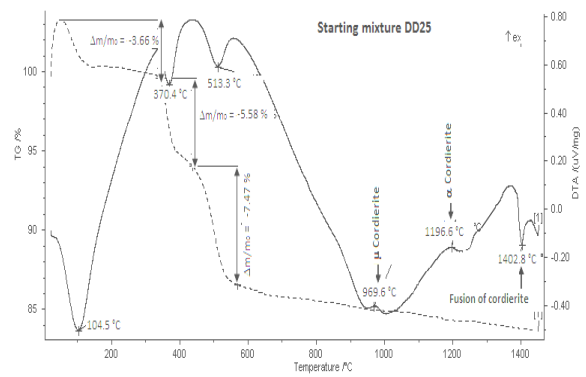


Fig.6 : DTA-TG curve of starting mixture DD25 of cordierite

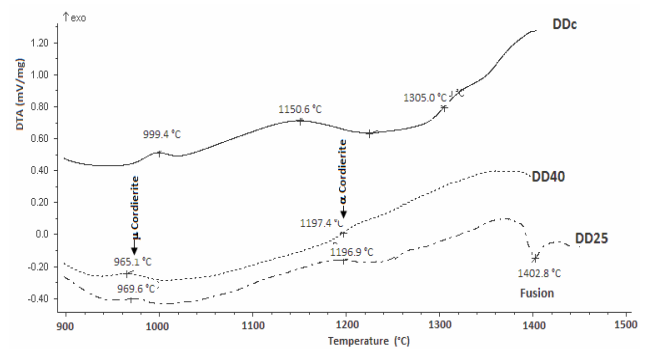


Fig.6 : DTA curves of 3 starting mixtures of synthesized cordierite

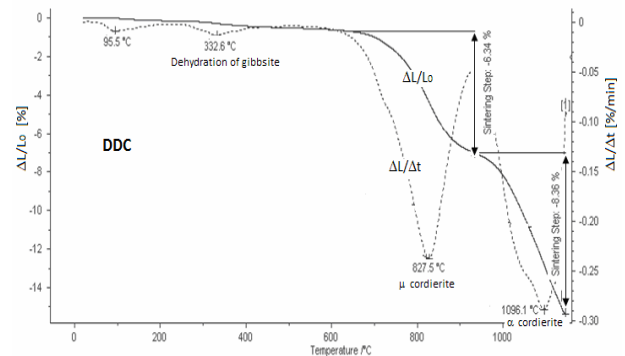


Fig.7 : Thermo-dilatation curve of starting mixture of cordierite (DDc)

The XRD analysis of DD25 mixture which is sintered at 1350 °C/ 2 hours shows that material is mainly composed by cordierite; all the XRD peaks are attributed to the α cordierite phase.

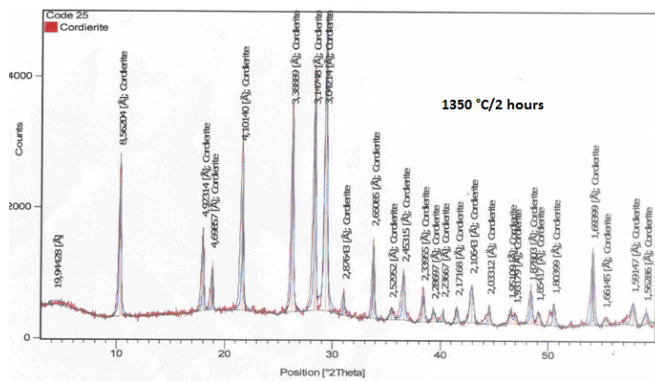


Fig. 8 : XRD analysis of DDc cordierite powder

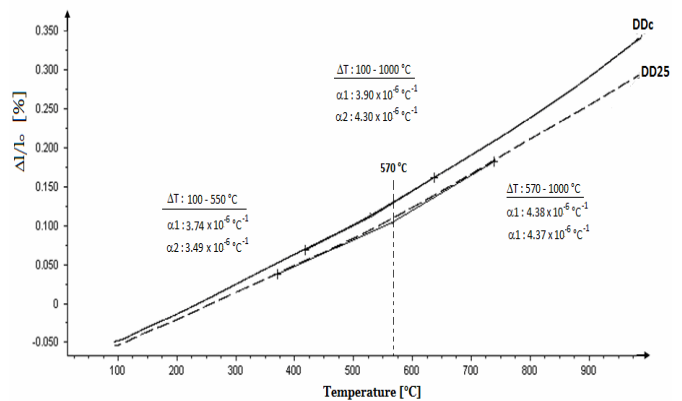


Fig. 8 : Thermo-dilatation of ceramic of cordierite

The results of ceramic properties are reported in table II, one observed better densification is carried out from starting mixture based kaolin. The densification of ceramics ($\delta\alpha/\delta s$) increases with the decrease in the size of particle of the starting powder.

TABLE II:
CERAMICS PROPERTIES OF SYNTHESIZED CORDIERITE

Mixtures	Firing properties 1350 °C/2 hours				
	($\delta\alpha$)	(δs)	($\delta\alpha/\delta s$)	[1-($\delta\alpha/\delta s$)] %	W.A %
DD63	2.23		87.45	12.54	8.15
DD40	2.25	2.55	88.23	11.76	7.45
DD25	2.30		90.20	9.80	5.45
DDc63	2.25		88.23	11.76	7.45
DDc40	2.28	2.55	89.41	10.60	5.45
DDc25	2.35		92.16	7.84	5.00

The thermal expansion coefficient (TEC) is lower than $4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ from 100 °C to 1000 °C. This value is lower than theoretical TEC of cordierite, may be because the densification is lower also (< 90 %).

3. Conclusion

In this study cordierite ceramic are elaborated starting a Algerian kaolin and hydroxide of magnesium, to assure the stoichiometric composition of cordierite, fumed silica powder is added. Magnesium hydroxide is prepared by precipitation from MgCl_2 and NH_4OH . The crystallisation of cordierite phase is appeared at 970 °C, and it's complete at 1350 °C by formation of α cordierite.

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