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FABRICATION OF MULLITE-CORDIERITE BASED COMPOSITE POWDERS FROM A SECONDARY SILICA SOURCE

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ABSTACT: A stoichiometric cordierite-mullite composite formulation has been prepared by mechanical activation from indigenous kaolin, talc, alumina, aluminium hydroxide and a new secondary silica source (silica gel). Phase formation behaviour of the samples has been studied from the XRD patterns of the sintered samples. The XRD analysis showed mullite and cordierite as phases for samples sintered at 1150°C and 1300°C for a soaking period of 2hrs. A comparison of the peaks formed shows that all the diffraction peaks change after mechanical activation. This reflects the partial amorphization and structural disordering in alumina, magnesium and quartz. It can also be noted that at 2 theta angle of 10.4° where characteristically cordierite peaks are formed, samples CD3a and CD3b show signs of cordierite peaks. SEM studies showed those different milling times as expected resulted in powders with different particle sizes, shapes, and most importantly degrees of agglomeration.
Keywords: Cordierite, mullite, amorphization, mechano-chemistry

1. INTRODUCTION

Cordierite ($2MgO_2Al_2O_3_5SiO_2$) is one of the important phases of the $MgO–SiO_2–Al_2O_3$ system. Cordierite ceramics have low thermal expansion coefficient, excellent thermal shock resistance, low dielectric constant, high volume resistivity, high chemical durability, high refractoriness and high mechanical strength. Therefore, they are widely used as honeycomb-shaped catalyst carriers in automobile exhaust systems, as substrate material for integrated circuit boards and as refractory materials [1-6]

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is an important ceramic phase in conventional ceramics such as tableware, construction ceramics and refractories, advanced high-temperature structural materials, heat exchangers, catalytic converters, filters, optical devices and electronic packaging materials. However, mullite suffers from its relatively low fracture toughness which limits its application in industrial use [7-9]

Cordierite ($2MgO. 2Al_2O_3. 5SiO_2$) and mullite ($3Al_2O_3. 2SiO_2$) composites have become an important, worth noticing ceramic because of its wide range of applicability. It has been used as refractory materials because it can withstand the fast firing techniques for development of ceramic products. They have in recent years also attracted much attention as substrate material as cordierite has low average thermal expansion coefficient [10].

Mechanical activation of starting materials is a promising method for precursor preparation. The particle size reduction, which increases the contact surfaces between the particles, is a direct consequence of milling. Also, the energy of the system increases, resulting in a decrease in the reaction temperature[11]

Nigerian kaolin deposit was estimated to be over 3 billion metric tons [12]. The need to harness this abundant mineral for synthesis mullite and cordierite based ceramic powders which can

serve as substitute for the imported ones cannot be over emphasized. Efforts to produce mullite and cordierite based ceramic powders using indigenous kaolin in Nigeria as a starting raw material have yielded little or no progress due to inadequate research in this area.

A lot of research has been carried out in the area of mullite and cordierite based ceramics. A study by Awanoet.al,[13], involved the use of grinding after sol-gel process. The agitator was maintained at 115 rpm for 24 hrs. As a result of their study, the ground powder crystallized from the amorphous and through the intermediate phases to a cordierite single phase at 1250°C for 1 hr. Kurama and Ay[14], proposed the use of two different sources of MgO and grinding times to form cordierite.The samples were sintered at 1200°C for 2 hrs. They concluded that the intensity of the cordierite peaks varied with grinding time. Obradovicet al[15], carried out mechanical activation on the starting mixtures containing 5.00 mass% TiO_2 in a high-energy ball mill for 10 minutes. The compaction pressure varied from 0.5 to 6tcm-2 (49–588 MPa). The sintering process was performed at 1350°C for four hours in the air atmosphere. According to the results presented in their study, the XRD analysis has shown a different phase composition in the sintered samples pressed under two limit pressures. The cordierite phase is the dominant phase.

Hence the objective of the present research is to study the suitability of indigenous raw materials, a new secondary silica source for the production of ceramics in addition to other materials of analytical grade to fabricate mullite-cordierite based composite ceramics for industrial applications. Hence this paper seeks to report the process including the preliminary results obtained. Therefore, the specific objectives of this research are as follows:

» Development of mullite-cordierite based ceramics using silica gel as a new secondary silica source
» Characterization of the starting raw materials by the XRF and XRD
» Characterization of the developed ceramic composite powder by XRD and SEM.

Finally, the major contribution of this research work is the potential of the fabricated ceramic powders to serve as a substitute for the imported ones.

2. MATERIALS AND METHODS

The starting raw materials used were kaolin (Kankara, Nigeria), talc (Ghana), alumina (Switzerland: analytical grade) alumina hydroxide (analytical grade) and silica gel (Ghana). These materials were wet mixed during the applied milling processes based on weight ratios that satisfy the stoichiometric compositions in formation of cordierite and mullite. Table 1 shows the batch formulation of cordierite (100wt %) mullite (100wt %) and cordierite-mullite composite (50 wt%-50wt %)

Table 1: Batch formulations of cordierite, mullite and cordierite-mullite ceramics

Raw material (Cordierite)	CD (wt%)	ML(wt%)	CD-ML (wt%)
Kaolin, $Al_2(Si_2O_5)(OH)_4$	21.74	31.55	26.64
Talc, raw, $Mg_3(Si_2O_5)_2(OH)_2$	39.24	NIL	19.62
Alumina, Al_2O_3	11.23	21.04	16.14
Aluminum hydroxide, $Al(OH)_3$	17.80	27.61	22.71
Silica, SiO_2	9.99	19.81	14.89
Total	100	100	100

CD-Cordierite; ML-Mullite; CD-ML- Cordierite- Mullite Ceramics

The stoichiometric cordierite ($2MgO_2Al_2O_3_5SiO_2$) and stoichiometric mullite ($3Al_2O_3 \cdot 2SiO_2$) was dispersed (equal percentage in weight) in distilled water and wet milled with ceramic balls (Ø10 mm) in a ball mill for varying periods (30 and 60 minutes). The green bodies were compacted without using additives or binders. The rectangular compacts were then sintered at 1150°C and 1300°C. Heating and cooling cycles in the furnace were set at 5°C/ min before and after a 2-h dwell time. The temperature range (1150°C – 1300°C) covered the area where most of the decomposition, phase transformation and reactions were expected to occur.

Table 2 gives the details of the milling experiments as well as sample coding for the ground material. Sample CDO (unmilled reference) was prepared with no tumbling action in the ball mill to avoid any intensive mechanical action on the powders, while CD1 and CD2 was ball milled at 30 and 60 minutes respectively and fired at 1150°C.CD3 (a) and CD3 (b)was ball milled at 30 and 60 minutes respectively and fired at 1300°C. The as-milled sintered samples were examined using X-ray diffraction analysis (XRD; Philips X'Pert, PAN analytical B.V., Almelo, The Netherlands) to investigate the phase transformations.The chemical composition of starting materials was carried out using the Xray florescence technique. Scanning electron microscopy

analysis was conducted using an ultra-high vacuum and high resolution FEI, Xl-30 scanning electron microscopy for the morphological analysis of activated and non-activated mixed powders.

Table 2: Mechano-chemical milling test conditions and sample coding

Machine Type	Grinding Media	Approximate grams of powder used in one test	Milling time and relevant sample coding	Sintering Temperature
Ball Mill	ceramic balls (Ø10 mm).	100grams (50g CD,50g ML)	0min, CD0	NA
Ball Mill	ceramic balls (Ø10 mm).	100grams (50g CD,50g ML)	30min, CD1	1150^{0}C
Ball Mill	ceramic balls (Ø10 mm).	100grams (50g CD,50g ML)	60min, CD2	1150^{0}C
Ball Mill	ceramic balls (Ø10 mm).	100grams (50g CD,50g ML)	30min, CD3 (a)	1300^{0}C
Ball Mill	ceramic balls (Ø10 mm).	100grams (50g CD,50g ML)	60min, CD3 (b)	1300^{0}C

CD-Cordierite; ML-Mullite

3. RESULTS AND DISCUSSION.

The XRF of starting materials used in this study are presented. Beneficiated kaolin, aluminium hydroxide, talc, alumina and silicagel were batch formulated according to stoichiometric equations as stated earlier for mullite-cordierite based composite ceramics. Table 3 gives the elemental composition of starting materials used in this study. It is shown that talc provides a source of magnesia (19.807%) and silica gel is a huge source of silica (99.102%) based on the formula of cordierite ($2MgO.\ 2Al_2O_3.\ 5SiO_2$) and mullite ($3Al_2O_3.\ 2SiO_2$). The beneficiated kaolin gives a silica-alumina ratio of 1.54, while alumina and aluminium hydroxide which is obviously a source of alumina gave alumina of 99.425% and 99.823% respectively.

Table 3: Chemical Composition of Starting Raw Materials.

Element	% Conc (Talc)	% Conc (Silica gel)	% Conc (Kaolin)	% Conc (Alumina)	% Conc (Alumina hydroxide)
Si	53.675	99.102	59.5886	0.1125	ND
Na	1.0206	ND	0.0618	0.055	0.1721
Mg	19.807	ND	0.0759	ND	ND
Al	17.9501	0.1125	38.528	99.425	99.823
P	0.0342	ND	ND	ND	ND
S	0.0048	ND	0.0043	ND	ND
Cl	0.0164	0.5081	ND	ND	ND
K	2.3939	ND	1.4389	ND	ND
Ca	0.0331	ND	0.0414	ND	ND
Ti	0.5766	ND	0.0283	ND	ND
Mn	0.0524	0.0522	0.0343	ND	ND
Fe	3.108	0.0146	0.1495	ND	ND
Zn	0.0046	ND	ND	ND	ND
Rb	0.0086	ND	0.0084	ND	ND
Zr	0.0212	ND	0.0073	ND	ND
Ba	0.0448	ND	0.0296	ND	ND
Co	ND	0.1971	ND	ND	ND
Ni	ND	0.0134	ND	ND	ND
K	ND	ND	1.4389	ND	ND
Ga	ND	ND	0.0037	ND	0.0044

Figure 1 show XRD patterns of silica gel which is the secondary source of silica used in this study as a starting material.. As expected, the characteristic peak of quartz is observed at Braggs' angle 26.65^0.The XRD pattern of the silica gel shows the powder is mostly amorphous in nature. However, the broad peak around 22.8^0 may be attributed to crystalline silica.

3.1 Structural changes in the activated and non –activated precursor batch powders

The X-ray diffraction analysis activated mixture powders as batch formulated is given in Figure 2. The formulated powder mixtures were fired at 1150^{0}C and 1300^{0}C. The XRD pattern of starting batch precursors which were not mechanically activated is as presented in Figure 1. It can be observed that peaks of quartz were more pronounced than other starting materials. A comparison of the peaks from Figure 3 shows that all the diffraction peaks change after mechanical

activation. This reflects the partial amorphization and structural disordering in alumina and quartz. Mechanical activation has already been reported to amorphize materials [16]. It can also be noted that at 2 theta angle of 10.4 where characteristically cordierite peaks are formed, sample CD3a and CD3b show signs of the peak formed at that angle.

The XRD pattern of different cordierite-mullite composite samples sintered at 1150°C and 1300°C, for 2 hours has been shown in Figure 2 where CD1 represents the sample with a composition of 50% mullite and 50% cordierite ball milled for 30 minutes and fired at 1150°C, CD2 represents the sample with composition of 50% mullite and 50% cordierite ball milled at 60 minutes and fired at 1150 °C and CD3 (a) and CD 3 (b) represents the sample with composition 50%mullite and 50% cordierite ball milled at 30 and 60 minutes and fired at 1300 °C respectively. All the samples show the presence of cordierite and mullite phases.

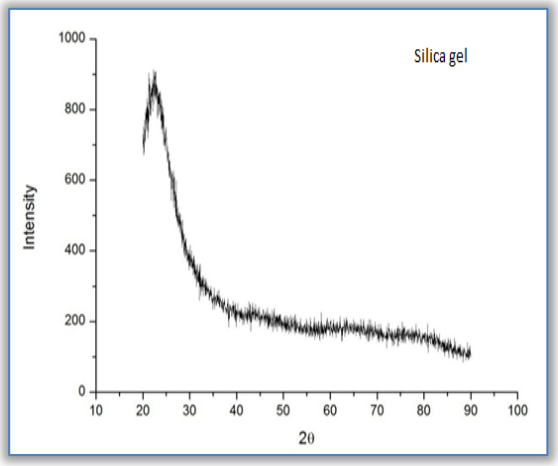


Figure 1: XRD pattern of Silica gel.

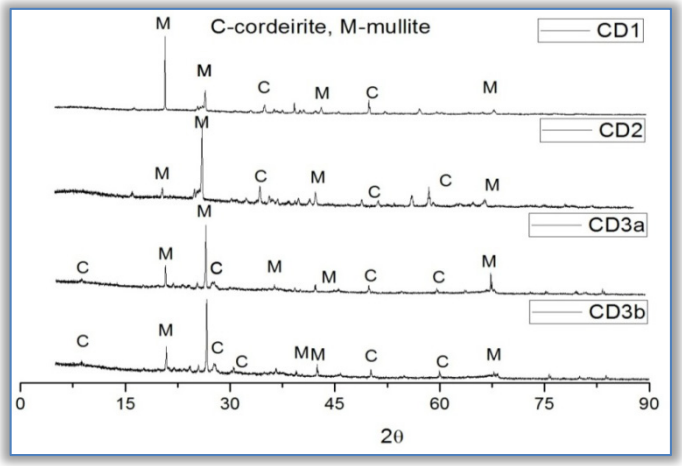


Figure 2: XRD patterns of sintered mullite - cordierite batch precursors

The morphology and size distribution of the precursor as well as the ground powders were evaluated with SEM. Differences in shape and size of the individual powders and relatively high degree of agglomeration were found to be major obstacles in achieving accurate size measurements. Different milling times as expected resulted in powders with different particle sizes, shapes, and most importantly degrees of agglomeration.

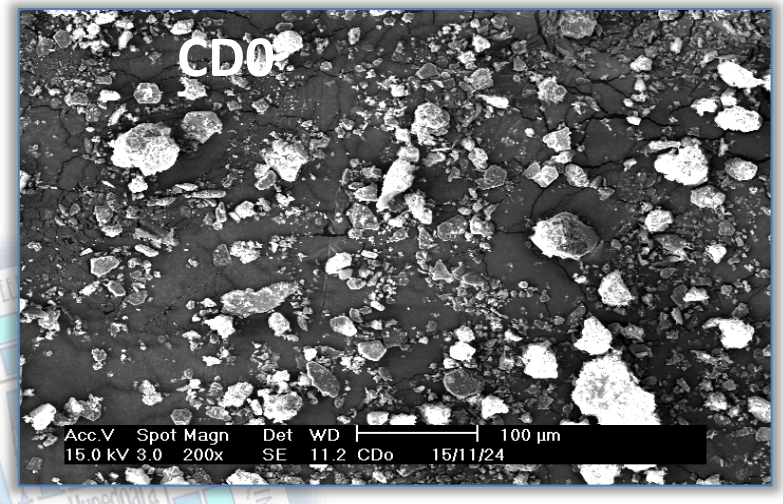


Figure 3: SEM image of starting raw materials (CD0) at 200x.

As illustrated in Figure 3, SEM images of starting raw materials showed no agglomeration of particles, this is of the obvious milling of no mechanical activation. Samples CD1 and CD3(a) as shown in Figures 4 and 5 showed that short milling times only helped in mixing of the precursor powders and caused partial agglomeration. Longer milling times, however, resulted in greater agglomeration in samples CD2 and CD3 (b) as shown in figures 4 and 5.

When the milling times are extended, agglomeration was observed to increase possibly as a result of increases in surface energies and the development of defects and amorphization. Complete amorphization was not achieved using the applied milling method and times; however, differences in microstructure and reaction products did develop during the sintering process,

indicating that the milling method induced different degrees of damage to the starting powder system. The reaction sintering of talc, kaolinite, and boehmite (from alumina) is a complex process, with various intermediates being created and consumed before the final structure is generated. These transformations occur at different temperatures depending on the grinding method and the duration of grinding. A better indication of the mechanically induced transformation after sintering the powders, however, was the formation and subsequent removal of mullite (CD1- CD3B), suggesting that the mullite reaction occurs at lower temperatures in powders which had undergone more intensive and/or longer milling.

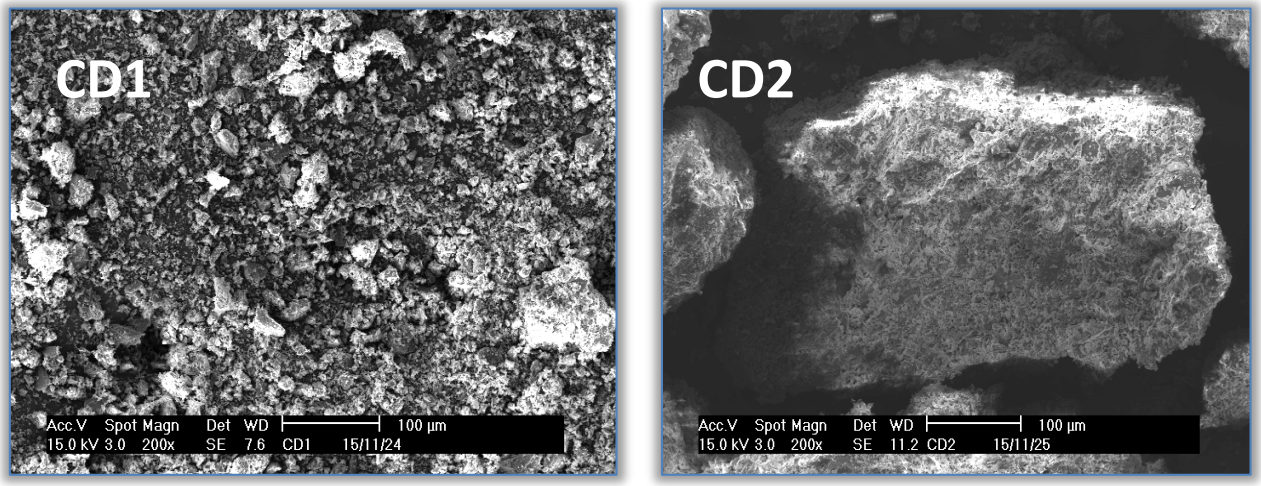


Figure 4: SEM images of sintered mullite-cordierite powders (CD1 and CD2) at 200x

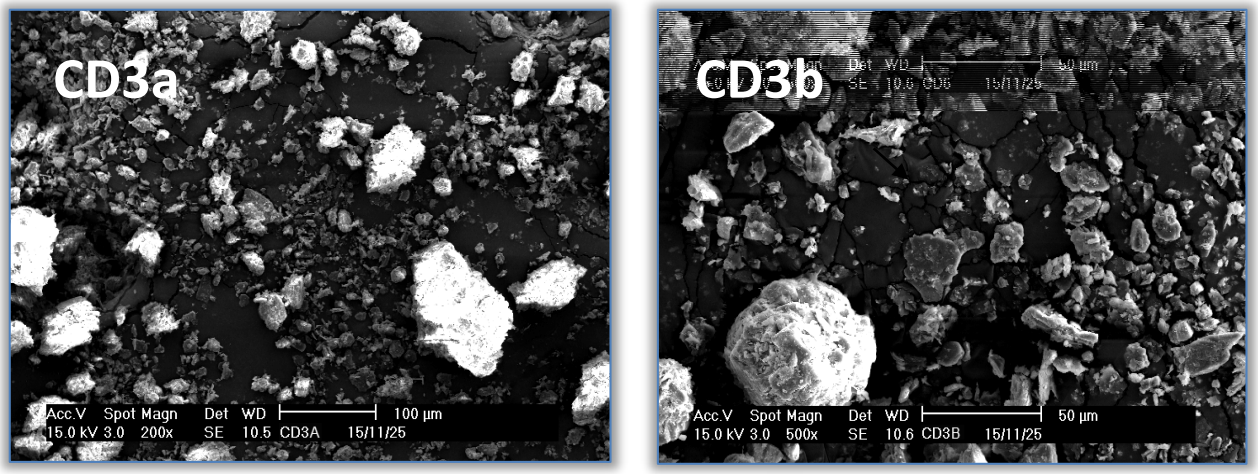


Figure 5: SEM images of sintered mullite-cordierite powders (CD3a-CD3b) at 200x

As can be observed from the SEM images, imageresults show that extended ball milling promoted the structural decomposition of talc and kaolinite as well as the formation of enstatite and amorphous glassy phases (silica and metakaolin or premullite) during heat treatment for samples CD1-CD3B. Relatively large dark-colored grains were observed in the SEM images, yet corundum or other alumina phases were not identified in the XRD analysis, suggesting an amorphous character. There are many intermediate products of the structural change in γ-alumina (derived from boehmite and decomposition of kaolinite) that makes identification difficult in a multi component material such as the one under consideration. Ball milling even after short milling times resulted in sintered samples showing complete decomposition of talc and a reduction in glassy phases by formation of magnesium aluminosilicate (MAS). Grain growth through the consumption of smaller grains to form new phases was also evident especially in SEM image of (CD2). In general, the more intense the milling, the fewer phases were identifiable in the sintered samples. Occasionally large grains were seen to emerge from the background, and these had elongated rectangular shapes.The high Si bearing Mg-Al silicates which developed at 1150^{0}C were often more defined in shape with rectangular or polyhedral cross sections. They grew in size and became more homogenous in composition with increased milling, for example, in CD3 (b) as shown in Fig. 5. Increasing the milling time caused larger pores to be formed in the sintered bodies which usually formed along the boundaries of large and growing phases.

4. CONCLUSIONS

The effect of mechanical activation on the fabrication of mullite-cordierite formation in a batch mix system was studiedby using XRD and SEM. The mechanical activation caused amorphization and structural disordering of the magnesia-silica-alumina mixture. The application of energy milling allowed a change in the structure performance of batch mix, so the peaks of mullite-cordieritecomposite powders were increased with mechanical activation.It was confirmed that the sintering of stoichiometric mixture of kaolinite, talc, alumina, aluminium hydroxide and silica gel without the addition of sintering aids at 1150^{0}C and 1300 ^{0}Ccan produce mullite-corderite phase ceramic powders and can proceed to a characteristic cordierite phase transformation, provided sufficient (mechanochemical) energy is used in their preparation through intensive milling and increased sintering temperatures.

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