Effect of mechanical activation on mullite formation in an alumina-silica ceramics system at lower temperature

David O. Obada
Department of Mechanical Engineering, Ahmadu Bello University, Zaria, Nigeria
David Dodoo-Arhin
Department of Materials Science and Engineering, University of Ghana, Legon, Ghana
Muhammad Dauda and Fatai O. Anafi
Department of Mechanical Engineering, Ahmadu Bello University, Zaria, Nigeria
Abdulkarim S. Ahmed and Olusegun A. Ajayi
Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria, and
Ibraheem A. Samotu
Department of Mechanical Engineering, Ahmadu Bello University, Zaria, Nigeria

Abstract

Purpose – This work aims to analyze the effect of mechanical activation on structural disordering (amorphization) in an alumina-silica ceramics system and formation of mullite most notably at a lower temperature using X-ray diffraction (XRD). Also, an objective of this work is to focus on a low-temperature fabrication route for the production of mullite powders.

Design/methodology/approach – A batch composition of kaolin, alumina and silica was manually pre-milled and then mechanically activated in a ball mill for 30 and 60 min. The activated samples were sintered at 1,150°C for a soaking period of 2 h. Mullite formation was characterized by XRD and scanning electron microscopy (SEM).

Findings – It was determined that the mechanical activation increased the quantity of the mullite phase. SEM results revealed that short milling times only helped in mixing of the precursor powders and caused partial agglomeration, while longer milling times, however, resulted in greater agglomeration.

Originality/value – It is noted that, a manual pre-milling of approximately 20 min and a ball milling approach of 60 min milling time can be suggested as the optimum milling time for the temperature decrease succeeded for the production of mullite from the specific stoichiometric batch formed.

Keywords Mullite, Mechanical activation, Amorphization, Agglomeration

Paper type Research paper

1. Introduction

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, catalyst converters, filters, optical devices and electronic packaging materials (Elmas *et al.*, 2013). Mullite is an alumino-silicate compound that is used extensively in traditional refractory applications. Most traditional ceramic products have mullite as part of their final phase composition, as they usually contain some clay and silicon as starting materials.

Mullite is becoming increasingly important in electronic, optical and high-temperature structural applications, because of its low dielectric constant, good transparency for mid-infrared light and excellent creep resistance. In conventional processing methods, mullite powders are shape-formed and sintered. This mullite is designated "sinter-mullite". The term sinter mullite describes a mullite which has been produced from its starting materials essentially by solid-state diffusion controlled reactions. Oxides, hydroxides, salts and silicates can be used as the starting materials. The Al_2O_3 content of sinter mullite is influenced by the sintering temperature, the duration of heat treatment, the initial bulk composition and the nature, grain size and efficiency of mixing of the starting materials. Mullitization takes place by solid-solid or transient liquid-phase reactions of the starting materials by aluminum, silicon and oxygen atom interdiffusion (Souto *et al.*, 2009).

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

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increases, resulting in a decrease in the reaction temperature (Behmanesh *et al.*, 2008). Different processes can remarkably influence the reactivity of the solids. Particularly, the mechanical treatments are important as long as they can help to produce the changes in the texture and structure of the solids. In many cases, these alterations in the structure cause certain modifications in the phases formed with a thermal treatment of the solids that were mechano-chemically treated (Tamborenea *et al.*, 2004; Mazzoni *et al.*, 1991).

Mullite has been synthesized in many ways, such as simple sintering of alumina and silica powders, sol-gel method, co-precipitation, hydrothermal and chemical-vapor-deposition processes. The mullitization temperature is as high as 1,600°C for the conventional fabrication method, i.e. the solid-state reaction of high-purity alumina and quartz (Souto *et al.*, 2009; Dong *et al.*, 2008; Viswabaskaran *et al.*, 2002). These findings are obviously without mechanical milling. In their work, Elmas *et al.* (2013) mechanically activated powder mixtures of alumina and quartz in a planetary mill for 2 h. Both non-activated and activated samples were sintered at different temperatures (1,250, 1,300, 1,325, 1,350 and 1,375°C) for 1, 2, 3 and 5 h, and the formation of a mullite phase was examined with an X-ray diffraction (XRD) analysis. It was determined that the mechanical activation increased the quantity of the mullite phase. For activated precursors milled for 60 min using a planetary ball mill as reported, it was found that at a temperature of 1,375°C, the mullite phases increased significantly.

Fotoohi and Blackburn (2013) investigated three milling methods (ball, ring and planetary) and the effects of mechanical action and milling times on the formation of cordierite powders at different temperatures. Sintering at 1,000°C for 2 h resulted in the development of significant mechanically assisted phase transformations specifically related to formation of mullite in the most highly activated materials. Mullite transformation to pre-cordierite mineralogy and the formation of magnesium aluminum silicate were also found to be dependent on the degrees and methods of mechanical processing. Planetary milling resulted in the highest densification of the material, which when sintered at 1,300°C for 2 h produced a ceramic body rich in cordierite composition.

Wu *et al.* (2013) reported a homogeneous coating on mullite particles where the mullitization occurs completely as low as 1,250°C. Homogeneously coated sol transforms to liquid binder during sintering to form an interlocking structure, which leads to a remarkable improvement in mechanical properties and thermal alkali corrosion resistance. The authors were of the opinion that producing porous ceramics by this method brings a lot of advantages including pure phase product and simple technique. Moreover, it can be widely used in an industrial exhaust filter area. The mullitization temperature is of interest in this present study.

Kirsever *et al.* (2015) showed the XRD patterns of sintered samples heated at 1,200, 1,250, 1,300, 1,350, 1,400 and 1,450°C for 1 h. When the samples were sintered at 1,200°C for 1 h, the quartz and alumina have been noted to be the major phases. The mullite phase appeared as the sample was sintered at 1,300°C for 1 h. When sintering temperatures were elevated to between 1,300 and 1,450°C, the intensity increased and the much sharper X-ray reactions of mullite were observed. It was found that quartz and alumina reacted completely and had mainly converted to mullite phase at 1,450°C. It is worthy of note that in their study, no mechanical activation was to the best of our knowledge reported to disorder the structure of the materials, hence the high temperatures reported in main conversion to mullite.

Baitalik *et al.* (2015) in their work observed the role of mullite source on the properties of final ceramics by using two sources of mullite (commercial mullite and synthesized mullite through sol-gel route). Porous SiC ceramics were prepared by sintering powder compact of mullite coated SiC/SiC + mullite particles in air at 1,300°C for 3 h keeping the mullite content same. Notably, sintering at this temperature of 1,300°C kept the mullite content intact.

In this work, the effect of mechanical activation on structural disordering (amorphization) in an alumina-silica ceramics system and formation of mullite most notably at a lower temperature were analyzed using XRD and SEM. Another objective was to focus on a low-temperature fabrication route for the production of mullite powders.

2. Materials and methods

The starting raw materials used were kaolin (Kankara, Nigeria), alumina (Sigma Aldrich: analytical grade), alumina hydroxide (Sigma Aldrich: analytical grade) and silica gel (Sigma Aldrich). These materials were wet-mixed during the applied milling processes based on weight ratios that satisfy the stoichiometric compositions in formation of mullite according to equation (1):

$$3Al_2O_3 + 2\ SiO_2 + 4.07\ H_2O \rightarrow \text{Mullite} + \text{Water} \quad (1)$$

The stoichiometric mullite ($3Al_2O_3 \cdot 2SiO_2$) was dispersed (equal percentage in weight) in distilled water, pre-milled manually in a ceramic mortar for approximately 20 min before wet milling with ceramic balls (Ø10 mm) for varying periods (30 and 60 min). The green bodies were compacted without using additives or binders. The rectangular compacts were then sintered at 1,150°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 (1,150°C) covered the area where most of the decomposition, phase transformation and reactions were expected to occur (Fotoohi and Blackburn, 2013).

Table I 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. Samples with codes CD1 and CD2 were ball-milled (tumbling action) at 30 and 60 min, respectively, and fired at 1,150°C.

The as-milled sintered samples were examined using XRD analysis (Philips X'Pert, PAN analytical B.V., Almelo, The Netherlands) to investigate mullite formations. The chemical composition of starting materials was carried out using the X-ray florescence (XRF) technique. Scanning electron microscopy (SEM) analysis was conducted using an ultra-high vacuum and high-resolution FEI, XL-30 scanning electron microscope for the morphological analysis of activated and

Table I 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)	100	0 min, CD0	NA
Ball mill	Ceramic balls (Ø10 mm)	100	30 min, CD1	1,150°C
Ball mill	Ceramic balls (Ø10 mm)	100	60 min, CD2	1,150°C

non-activated mixed powders. Table II gives the batch formulation of stoichiometric mullite (100 Wt.%).

3. Results and discussion

The XRF and XRD of starting materials used in this study are presented. Beneficiated kaolin, aluminum hydroxide, alumina and silica gel were batch-formulated according to stoichiometric equations as stated earlier for mullite-based composite ceramics. Table III gives the elemental composition of starting materials used in this study.

The XRD patterns for all starting materials are as shown in Figures 1–5. Figure 1 shows the reduction in the intensity of the quartz at Braggs' angle of 26.65 for the beneficiated kaolin. This is attributed to reduction in the concentration due to washing away during the beneficiation process.

Table II Batch formulations of stoichiometric mullite

Raw material (mullite)	Amount in composition (Wt.%)
Kaolin, $Al_2(Si_2O_5)(OH)_4$	31.55
Alumina, Al_2O_3	21.04
Aluminum hydroxide, $Al(OH)_3$	27.61
Silica, SiO_2	19.80
Total	100

Table III Chemical composition of starting raw materials

Element	wt % (Kaolin)	wt % (Alumina)	wt % (Alumina hydroxide)	wt % (Silica gel)
Si	59.5886	0.1125	ND	99.102
Na	0.0618	0.055	0.1721	ND
Mg	0.0759	ND	ND	ND
Al	38.528	99.425	99.823	0.1125
P	ND	ND	ND	ND
S	0.0043	ND	ND	ND
Cl	ND	ND	ND	0.5081
K	1.4389	ND	ND	ND
Ca	0.0414	ND	ND	ND
Ti	0.0283	ND	ND	ND
Mn	0.0343	ND	ND	0.0522
Fe	0.1495	ND	ND	0.0146
Zn	ND	ND	ND	ND
Rb	0.0084	ND	ND	ND
Zr	0.0073	ND	ND	ND
Ba	0.0296	ND	ND	ND
Co	ND	ND	ND	0.1971
Ni	ND	ND	ND	0.0134
Ga	0.0037	ND	0.0044	ND

Note: ND–not detected

Figure 1 XRD pattern of beneficiated Kankara kaolin

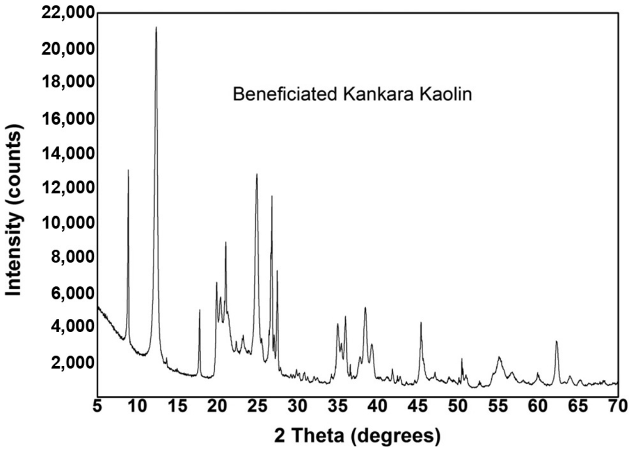


Figure 2 XRD pattern of aluminium hydroxide

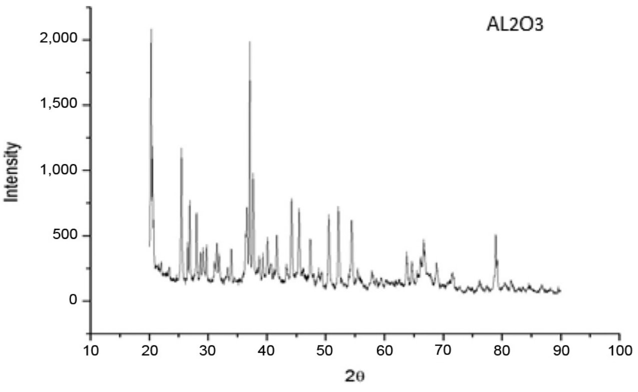


Figure 3 XRD pattern of alumina

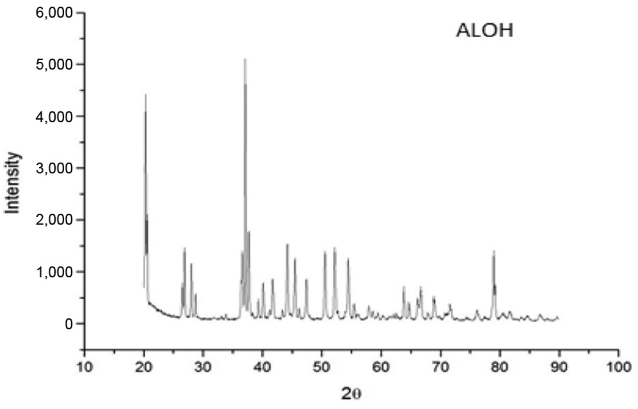


Figure 4 XRD pattern of silica gel

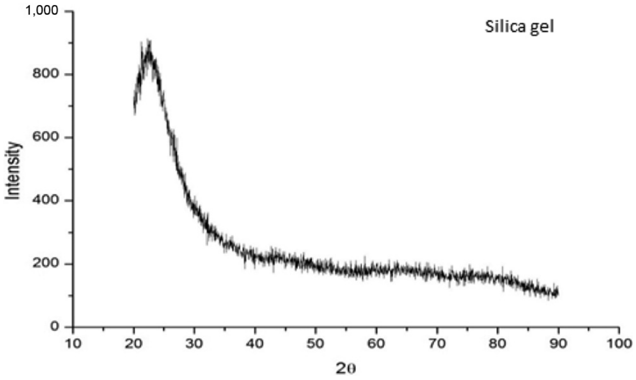
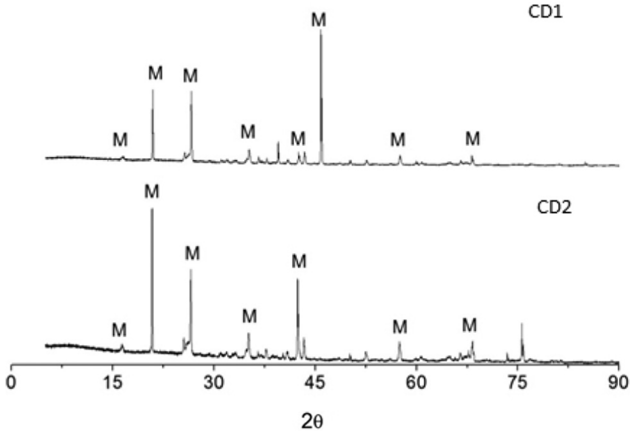


Figure 5 XRD patterns of sintered mullite batch precursors



Figures 2 and 3 show the characteristic XRD peaks of mixed phases of aluminum hydroxide and pure alumina which could be observed at Bragg's angles of 20.4, 27.9, 38.0, 40.3, 48.7 and 64.80. The peaks at Bragg's angles 27.9, 38.0, 48.7 and 64.80 were the characteristic peaks for the boehmite phase of aluminum hydroxide and alumina, while peaks at 20.4, and 40.3 were due to the bayerite phase of aluminum hydroxide (Du *et al.*, 2009). It can be observed that peaks were not noticeable between Braggs' angles of 30-35 in Figure 2 in comparison to Figure 3; this can be attributed to the percentage composition in terms of alumina content in the two samples.

Figure 4 shows XRD patterns of silica gel. As expected, the characteristic peak of quartz is observed at Braggs' angle of 26.65. The XRD pattern of the silica gel shows the powder is mostly amorphous in nature. However, the broad peak around Bragg's angle 22.8 may be attributed to crystalline silica.

The XRD pattern of pure mullite-based ceramic batch composition sintered at 1,150°C for 2 h has been shown in Figure 5, where CD1 and CD2 represent the samples with 100 per cent mullite composition ball milled for 30 min and 60 min and fired at 1,150°C for 2 h, respectively. All the samples show the presence of mainly mullite phases only. No other impurity could be detected in the XRD analysis.

A comparison of the peaks from the two diffraction patterns shows that all the diffraction peaks change after mechanical activation. This reflects the partial amorphization and structural disordering in alumina and silica (quartz). Mechanical activation has already been reported to amorphize materials (Balaz, 2008). Without sufficient milling, the precursor powders would remain largely unmixed, and as a result of inefficient contact between particles, the intermediate phase transitions could largely be inhibited. Differences in 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 kaolinite, alumina, aluminum hydroxide and silica 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. When the heat treatment was undertaken at 1,150°C, powder which had been milled with greater intensity showed higher levels of alumina-quartz decomposition and corresponding growth of mullite. It is assumed that a better mechanically induced transformation after sintering the powders will be the formation and subsequent removal of mullite, suggesting that the mullite reaction should occur at lower temperatures in powders, which is the case in this study. It is obvious that if ball milling is used, then mullite remains under all conditions. This finding is a further confirmation of mechanically promoted phase transformation. Mullite as a decomposition product of kaolinite is expected to form above 1,000°C (Chen *et al.*, 2003), and mechanical activation seems to have improved mullite formation after the material is sintered at 1,150°C for a 2-h dwell time.

Comparatively, with the results obtained in this study at lower temperature, Wu *et al.* (2013) reported a homogeneous coating on mullite particles where the mullitization occurs completely at as low as 1,250°C. The result in this present study showed mullitization at a lower temperature of 1,150°C, which is due to the intensive milling applied to the precursors of starting materials. Elmas *et al.* (2013) showed the XRD patterns of non-activated and activated quartz-alumina mixture powders fired at 1,250°C and 1,375°C for 60 min. It was found that the intensity of the mullite phase in the activated sample increases. On the other hand, when they were sintered at 1,375°C for 60 min, the mullite content increased. The mullitization temperature recorded occurred at even higher temperature as compared to the mullitization temperature, which was as low as 1,150°C, as achieved in this study. Their study adopted the planetary ball milling in activating precursors of starting materials at the milling time of 60 min. The present study used a pre-milling approach before adopting the ceramic ball milling approach using the tumbling action to activate precursors of starting materials for 30 and 60 min, respectively. This may have systematically induced to a larger extent the structural disordering of the starting materials, hence enhancing their surface areas and reducing significantly their particle sizes. This in turn increases their reactivity and hence reduces the mullitization temperature. According to Kirsever *et al.* (2015), when the samples were sintered at 1,200°C for 1 h, the quartz and alumina were noted to be the major phases. The mullite phase appeared as the sample was sintered at 1,300°C for 1 h. When sintering temperatures were elevated to between 1,300 and 1,450°C, the intensity increased and the much sharper X-ray reactions of mullite were observed. It was found that quartz and alumina reacted completely and had mainly converted to mullite phase at 1,450°C. It is worthy of note that in their study, no mechanical activation was performed to disorder the structure of the materials, hence the high temperatures reported in conversion to mullite. Hence, mechanical activation as reported in this study is key to achieving a much lower mullitization temperature. Baitalik *et al.* (2015) in their study sought to keep mullite content same in an SiC/SiC + mullite composite structure in air at 1,300°C for 3 h. Notably, sintering at this temperature of 1,300°C kept the mullite content intact. No information of intense milling was recorded for this study, hence the relatively high temperature needed to keep the mullite content in the composite intact.

From the foregoing, it is interesting to note that the pre-milling and ball milling approach using the tumbling action as employed in this study ensured to a large extent the structural disordering of starting raw materials, thereby lowering significantly the mullitization temperature.

Fotoohi and Blackburn (2013) reported shorter and longer milling times than the ones presented in this study. For the ball mill approach, they considered 60, 300 and 600 min; for the ring mill approach, 2, 5 and 10 min; and for the planetary mill, 10, 20 and 50 min for three batch-formulated samples. The ball milling adopted for a milling period of 60 min, as investigated by Fotoohi and Blakburn (2013) after sintering at 1,000°C, led to a body rich in enstatite and amorphous silica phases. It was apparent that the milling route and the duration of milling strongly influenced the phase development at this sintering temperature. Ring milling for short periods resulted in mullite formation but when milled for longer, magnesium aluminosilicate (MAS) dominated the traces mainly because it was a magnesia-alumina-quartz ceramic system. A slightly different phase composition was observed when applying each milling. In the planetary-milled samples as reported, for sample milled for 50 min, mullite and spinel phases were still found in relatively high proportions associated with the MAS phase. Comparatively, this present study which considered a ball milling approach with milling times of 30 and 60 min, respectively, at a temperature of 1150°C produced mainly mullite phases when analyzed by the XRD. This is in agreement with findings of Fotoohi and Blackburn (2013) when the ring milling approach was used. However, at our sintering temperature and milling times, results show mainly mullite phase formation.

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.

As illustrated in Figures 6 and 7, short milling times only helped in mixing of the precursor powders and caused partial agglomeration; this was observed in sample CD1. Longer milling times, however, resulted in greater agglomeration in CD2. 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 kaolinite and 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.

Figure 6 SEM image of starting raw materials (CD0) at 200×

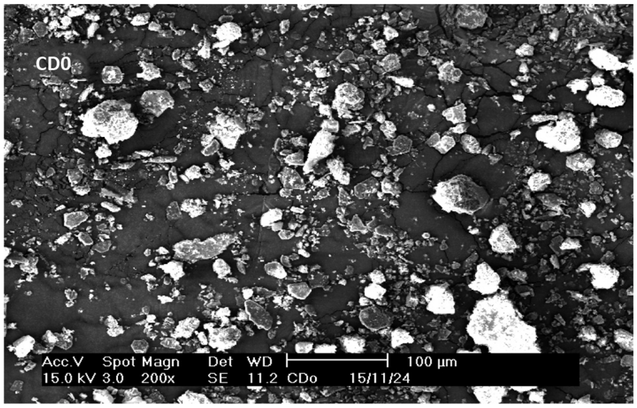
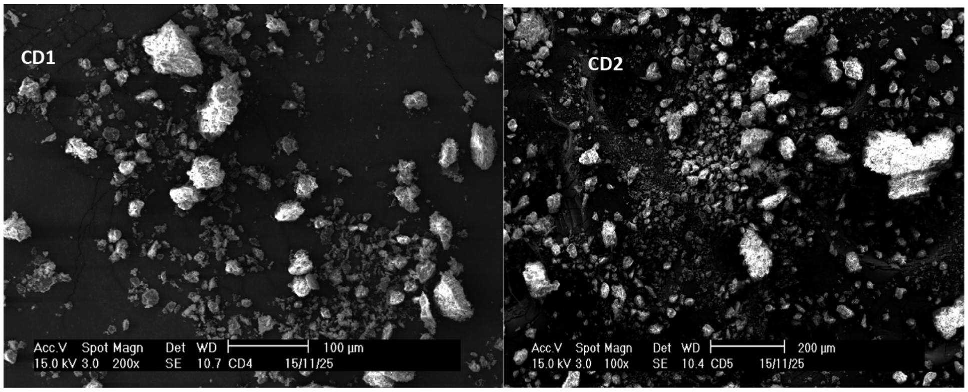


Figure 7 SEM images of mullite powders (CD1 and CD2) at 200×



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.

After a successful low-temperature route fabrication of mullite powders, it is critical to note that for this study, a manual pre-milling of approximately 20 min and a ball milling approach of 60 min milling time can be suggested as the optimum milling time for the temperature decrease succeeded for the specific batches. It is noted that the tumbling action of the ball mill and the obvious reduction in sizes and agglomeration of particles of precursor materials during intensive milling are significant variables which affect both the milling time and sintering temperatures toward mullite production.

4. Conclusion

The effect of mechanical activation on mullite formation in a batch mix system was studied by using XRD and SEM. The mechanical activation caused amorphization and structural disordering of the silica-alumina mixture. The application of energy milling allowed a change in the structure performance of batch mix, so the content of mullite was increased with mechanical activation. It is noted that, a manual pre-milling of approximately 20 min and a ball milling approach of 60 min milling time can be suggested as the optimum milling time for the temperature decrease succeeded for the production of mullite from the specific stoichiometric batch formed.

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Corresponding author

David O. Obada can be contacted at: obadavid4@gmail.com