Effect of TiO₂ on Mullite Formation in Mixture of Nigeria Sourced Kaolinite and Calcined Alumina

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Abstract:
In this study, the effect of TiO₂ when added to a mixture of Nigerian sourced of kaolin and calcined alumina powder (50:50) was investigated. The influence of Ti⁴⁺ ion on the physico-mechanical property (apparent porosity, bulk density and modulus of rupture), phase and microstructural evolution was studied at sintering temperature of 1600 °C when mullitisation has been maximized based on previous reports. The sintered samples showed considerably high porosity of about 16 %, a slight reduction of about 5 % in porosity was observed on TiO₂ addition. There was no appreciable change in the bulk density due to TiO₂ doping, but the modulus of rupture (MOR) reduced appreciably from 43 MPa to 36 MPa on TiO₂ doping. As shown by the XRD, mullite was seen as the major phase with negligible cristobalite phase for the undoped sample. The TiO₂ doped sample displayed mullite as major and corundum as minor phases. There appeared more mullite phases in the doped sample than the undoped sample indicating a higher percentage of mullite formation. The microstructural study shows the presence of acicular mullite with round edges and good aspect ratio. The presence of inter-granular and intra-granular pores in TiO₂ doped samples might have contributed to the reduction in strength observed at 1600 °C.

Keywords: Kaolin; Sintering; TiO₂ doping; Mullite; Porosity.

1. Introduction

Mullite ceramics (3Al₂O₃·2SiO₂) have been in use as a refractory for a long time due to its outstanding properties [1-2]. Some of these outstanding properties include; excellent thermal and chemical stability, high refractoriness and low creep rate [3-4]. The aluminosilicate mullite also has a low coefficient of thermal expansion and a very high thermal shock resistance [5-6]. Its usage and applications in high temperature industrial process and refractory applications have made the demand for this aluminosilicate increase day by day. It is the only material that has ability to exist in its fixed crystalline state from room temperature up till around 1880 °C [3, 7]. The aluminosilicate mullite is rather synthesized than mined due to its rareness in nature as there is no known abundant natural deposit. The first discovery of mullite was from a natural deposit on an island called Mull, located West of Scotland. This place of discovery brought about the name “mullite” [1]. Kaolin is formed, in most cases, due to the weathering of pegmatites and micaceouschist. The formation process undergoes reaction sequences such as hydrolysis, desilication and hydration [8]. According to the geological survey of Nigeria, there exist a lot of clay deposits

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across the length and breadth of the country [9]. Also, large quantities of sedimentary and secondary deposition clay have been found in Ekiti and Ogun state, Nigeria.

Geologically, these clays were found to belong to the refractory clay group after some scientific studies were carried out [10]. The chemical composition and physical properties of these kaolin deposit will determine its industrial application. Kaolinitic clay is a major raw material used in the production of various forms of ceramic products with specific valuable and desirable properties coupled with diverse application [11]. Solid state sintering of kaolin and reactive alumina is one of the most ingenious and cost effective method of mullite formation and synthesis [12-15].

In our previous work Ajanaku et al. [16], the suitability of Nigeria sourced kaolin for mullite production has been established. Also, in another of our work Aladesuyi et al. [17], mullitisation was maximized using the mixing ratio of 50:50 alumina: Nigeria sourced kaolin at 1600 °C. Mullite ceramics can incorporate transition metal ions into their interstices as dopants [2]. The amount of the respective transition metal ions incorporated depends on certain factors. The main factors responsible for the amount of transition ions incorporated are the method of synthesis, mullitisation temperature and the environment of synthesis [18]. Atomic radii and oxidation states of the transition metal ions also determine the extent of incorporation [19]. The transition metal has the ability to get into the Al$_2$O$_3$ tetrahedral or into the AlO$_6$ octahedral of the mullite. These transition metal ions rearrange the local ligand symmetry, interact with the silica layer and destabilize the aluminate matrix which leads to accelerated phase transformation. Addition of transition metal ion as dopant does the following during mullite synthesis; (i) reduce the temperature of mullite formation (ii) enhance grain growth and (iii) improves physico-mechanical properties [18, 20]. The choice of TiO$_2$ as a dopant in this investigation is as a result of the relatively small atomic radius of Ti$^{4+}$ and also the ability of TiO$_2$ if added within the solubility limit (1 - 4.1 %) to promote densification [21].

In this present study, an attempt was made to determine the influence of Ti$^{4+}$ in a mixture of 50:50 Nigerian kaolin and calcined alumina on the phase and microstructural evolution of mullite during sintering at different temperatures.

2. Materials and Experimental Procedures

Kaolinitic clay was obtained from Abule Onikosin road in Abeokuta area of Ogun state, Nigeria as described in our earlier work [16]. Chemical grade calcined alumina obtained from Almatis was used for this present study. Chemical grade TiO$_2$ was obtained from Klinscatter laboratory limited. The elemental composition of the kaolinite clay and their characteristics have also been described in our previous work, Ajanaku et al. [16] as shown in Table I. The SiO$_2$ and Al$_2$O$_3$ contents were determined volumetrically, CaO and MgO were determined complexometrically, Fe$_2$O$_3$ and TiO$_2$ spectrophotometrically (LAMBDA-45, Perkin Elmer, USA) while CaO and K$_2$O by flame photometry (PFP-7, Jenway, UK). The loss of ignition (LOI) was obtained by heating gravimetricaly to about 800 °C. The clay and high purity alumina was mixed in the ratios of 50:50 and kept in airtight containers. Distilled water was added to each of the samples to form slurry in the ratio 1:10, and each of the batch compositions were milled in a high energy pot milling machine for about five hours. Zirconium alloy balls were used as the grinding medium in the pot mill. The same procedure was repeated with the addition of TiO$_2$ (4 % in weight) as a dopant. The mixed slurry was taken in a porcelain container for the respective clay-alumina composition and dried slowly in an electric oven at 110-120 °C for a period of 24 hours. The dried masses were powdered, thereafter water of about 5-6 wt.% was added to each of the dried powder and then the moistened powder was uniaxially pressed in a rectangular mould (65 mm × 14 mm × 5 mm) at a pressure of 350 Kg/cm$^2$ using a hydraulic press. Sintering of the rectangular bars of the
TiO$_2$ doped clay alumina was carried out in a high temperature carbolite furnace at a heating rate of 10 °C/hours for a soaking time of 2 hours at the temperature 1600 °C, when mullitisation has been maximized as determined in our earlier work, Aladesuyi et al. [17]. The percentage apparent porosity (A.P) and bulk density (B.D) of the sintered compacts were determined by standard methods. The modulus of rupture (MOR) was obtained using the universal testing machine (INSTRON 5500R, UK). The batch composition, 500 g each of the kaolin-alumina samples is shown in Table II.

**Tab. I Chemical composition of processed kaolinite [16].**

| Constituents (wt%) | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | TiO$_2$ | CaO | MgO | Na$_2$O | K$_2$O | LOI |
|-------------------|---------|-------------|-------------|---------|-----|-----|--------|--------|-----|
|                   | 59.26   | 24.04       | 3.87        | 1.46    | 0.39| 0.14| 0.74   | 0.3    | 9.4 |

**Tab. II Batch compositions of the samples.**

| Batch | Clay (g) | Al$_2$O$_3$ (g) | TiO$_2$ (g) |
|-------|----------|-----------------|-------------|
| A1    | 250      | 250             | -           |
| A2    | 250      | 250             | 20          |

The minerological phases of the processed clay were determined using X-Ray diffractometer [PAN Analytical]. The XRD data were recorded in step-scan mode with step size 0.05°(2θ) and step time 75 sec from 10-80°. For the SEM analysis, the compacted samples were grinded and polished using Silicon carbide powder and diamond paste respectively. Afterwards, water and acetone were used in cleaning the surface of the samples and they were gold coated using Edwards, Scancoat. ‘OXFORD’ equipment was used for the EDAX analysis.

3. Results and Discussion

3.1 Physico-mechanical properties of the doped (A2) sample

The porosity, bulk density and modulus of rupture of the TiO$_2$ doped and undoped kaolin-alumina compact was determined at firing temperature of 1600 °C (when mullite formation have been maximised) as shown in Fig. 1(a-c). The reduction in porosity can be explained on the basis of the stability in electronic configuration of titanium at oxidation state 4 and also the spherical charge distribution of Ti$^{4+}$. Therefore, the incorporation of Ti$^{4+}$ into mullite interstitial can be said to be based on its ionic size only and not the oxidation state or electronic configuration. Since the ionic size of Ti$^{4+}$ is fairly small, there is a high tendency of the ions locking itself into the mullite interstitial and also providing a liquid phase that will enhance mullitisation and reduce porosity.

There is not much difference in the bulk density of the doped mullite sample when compared to the undoped, which may be attributed to poor densification due to the inhomogeneous grain growth and unreactive alumina that was still present in the melt. At a temperature of 1600 °C, mullitisation has reached the maximum and the bulk density of the doped compact was a little bit higher than the undoped compact.

The modulus of rupture of the compact does not improve on doping rather it decreases. Although the cation size of Ti$^{4+}$ suggests preference for octahedral coordination [2, 21] but the deviating oxidation state of Ti$^{4+}$ is less favorable despite the fact that ionic radii is close to that of Al$^{3+}$, because there is need for a simultaneous tetrahedral substitution of Si$^{4+}$ and Al$^{3+}$ so as to allow for compensation of the excess positive charge. Therefore, the Al$_2$O$_3$ - TiO$_2$–SiO$_2$ spinel formed at maximum mulitilisation will have lesser strength and lower
density despite the low porosity due to the deviating oxidation states of TiO$_2$. The decrease in strength could also be as a result of the inhomogenous grain growth and poor interdiffusision of the Al$^{3+}$ and Si$^{4+}$ ions during sintering.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{Variation in (a) % apparent porosity (AP), (b) bulk density (BD) and (c) modulus of rupture (MOR) of sintered TiO$_2$ doped (A2) and undoped (A1) samples at 1600 °C.}
\end{figure}

3.2 Microstructural study

As shown in the SEM image (Fig. 2), there exist the presences of acicular mullite with round edges and good aspect ratio. As seen in the SEM image of the doped mullite (Fig. 3), there occurs a change in morphology of the mullite from equiaxed to acicular upon doping. This an indication of the presence of more secondary mullite [22]. Due to its stable electronic configuration coupled with a spherically charged distribution Ti$^{4+}$ incorporation is essentially based on atomic radii and not other factors like oxidation states and reaction conditions. However, the atomic radii of Ti$^{4+}$ is relatively small. This allowed for adequate
incorporation into the mullite lattice which reduced viscosity and enhanced grain growth development. The EDAX micrograph of TiO$_2$ doped mullite aggregates at 1600 °C sintering temperature is shown in Fig. 4.

![Fig. 2. SEM image of undoped (A1) kaolin-alumina sample sintered at 1600 °C.](image1)

![Fig. 3. SEM image of TiO$_2$ doped A2 samples heated at 1600 °C.](image2)

![Fig. 4. EDAX images of TiO$_2$ doped A2 samples at 1600 °C heating temperature.](image3)
3.3 Phase identification of doped (A2) samples

Fig. 5 shows the XRD pattern of both the undoped and TiO$_2$ doped mullite sample at 1600 °C. The XRD patterns showed major phases of mullite without any trace of quartz and negligible trace of cristobalite. The absence of quartz and negligible trace of cristobalite is an indication of secondary mullite formation and that mullitisation has been maximized with raw material ratio of 50:50 kaolin-reactive alumina. Although both pattern looks similar but the length of peaks of the TiO$_2$ doped are more intensive when compared to the undoped. In addition, the doped nullite has more mullite phases when compared to the undoped indicating that mullite formation increased appreciably in the doped sample. Also at around 20 (26) as shown in Fig. 5 there is the presence of two splitting pattern, the presence of this splitting pattern is a proof that there was an abrupt conversion primary mullite 2Al$_2$O$_3$SiO$_2$ to secondary mullite 3Al$_2$O$_3$.2SiO$_2$ [23-25]. The more pronounced splitting pattern at 20 (26) of the doped sample as shown in the XRD is an indication of lattice insertion [1, 23, 26]. The conversion to secondary mullite also reflected in the physico-mechanical properties of the doped compacts at 1600 °C.

It is clear from the Figure that mullite phase evolution is enhanced by the presence of TiO$_2$ additives. This evolution of mullite phase observed in the doped samples can be explained on the basis of liquid state assisted sintering [17, 27-28]. Incorporation of TiO$_2$ into SiO$_2$ brought about a reduction in viscosity of the melt at high temperature. This drop in viscosity enhances the diffusion kinetics. In addition, the alumina interdiffusion into siliceous matrix is also accelerated due to the increase in liquidity of the matrix.

![XRD pattern of undoped (A1) and TiO$_2$ doped (A2) clay-alumina samples sintered at 1600 °C (M- mullite, Co- corundum, C- cristobalite).](image)

4. Conclusion

The following conclusions were made on the basis of this study:

- The TiO$_2$ doped samples displayed a higher degree of mullite formation when compared to the undoped as revealed by the XRD. This can be explained on the basis of liquid assisted sintering.
The doped mullite aggregates showed negligible change in bulk density and reduction in the modulus of rupture despite the reduction in apparent porosity. This is attributed to the deviating oxidation state of Ti$^{4+}$.

The modulus of rupture of the doped samples reduced due to inhomogenous grain growth and presence of inter-granular pores associated with solid state sintering. With the information gathered, other methods of synthesis other than sintered mullite can be employed so as to obtain a better densified mullite.

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мулит као главну и корундум као споредну фазу. Више је мулиптне фазе у допираним узорцима него у недопираним. Микроструктуре показују присуство игличастог мулиита облих ивица. Присуство интер- и интра-грануларних пора у узорцима са TiO₂ су допринеле редукцији чврстоће примећене на 1600 °C.

Кључне речи: каолин, синтеровање, допирање TiO₂, мулит, порозност.

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