

Effect of bauxite addition on densification and mullitization behaviour of West Bengal clay

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Abstract. The effect of bauxite addition on the densification and mullitization of reaction sintered bauxite–clay mixture had been studied in the temperature range 1400–1500°C. The maximum bulk density (2.89 g/cc) and minimum apparent porosity (0.58%) was achieved by addition of 50 wt% bauxite. The impurities present in bauxite and clay formed liquid phase which helped in particle diffusion to aid densification. The X-ray diffraction of sample fired at 1500°C showed cristoballite phase gradually disappearing and at the same time mullite and α -Al₂O₃ phase appearing at a higher level of bauxite addition. The *in situ* nascent alumina formed was reactive that facilitated the formation of secondary mullite by solution precipitation mechanism. The presence of bauxite also changed the morphology of the mullite particles. Two types of mullite were distinctly observed in the SEM photographs: elongated primary mullite and equiaxed secondary mullite.

Keywords. Bauxite; kaolinite; reaction sintering; primary mullite; secondary mullite; cristoballite.

1. Introduction

The phases in the system, Al₂O₃–SiO₂, are constituents of many ceramic products. This system is important not in the conventional ceramic products but it is of interest in the advanced ceramic products. Mullite occurs very rarely in nature. Mullite is the only stable phase in the binary system, Al₂O₃–SiO₂ (Klug *et al* 1990; Pask 1990). Mullite is becoming increasingly important in electronic, optical and high temperature applications (Pask *et al* 1991). Low density ($\rho = 3.17$ g/cc), low thermal conductivity ($K = 2$ Wm⁻¹ K⁻¹), low thermal expansion coefficient ($\alpha_{20/200^\circ\text{C}} = 4 \times 10^{-6}/^\circ\text{K}$), low dielectric constant ($K = 6.5$ at 1 MHz) and excellent mechanical properties at high temperature (strength in excess of 400 MPa at 1200°C) and low creep rate make mullite ceramic a promising candidate for advanced electrical and structural applications (Schneider and Eberhard 1990; Boch and Chartier 1991). Extensive efforts have been made to synthesize mullite powders (Nurishi and Pask 1982; Okada *et al* 1991; Rezaie *et al* 1997; Amutharani *et al* 1999) and to prepare dense sintered bodies, these methods involve very high cost starting materials and powder processing and are not cost effective for large scale production. The use of kaolinitic clay, kaolinitic clay and alumina or sillimanite as starting materials are cheaper alternatives. The kaolinite (Al₂O₃·2SiO₂·2H₂O) is one of the most used starting materials for aluminosilicate based ceramics due to its common occurrence and good availability. The mullite is formed at elevated tem-

perature from kaolinitic clay. But the amount of silica in the clay is much higher than that of stoichiometric mullite (3Al₂O₃·2SiO₂). This silica combined with the impurities present in the natural clay, forms a glassy phase and cristoballite in addition to the formation of mullite at a temperature higher than 1000°C. The cristoballite may also transform to a glassy phase with other impurities when kaolinite is fired above 1500°C. The presence of large amount of glassy phase has a detrimental effect on the mechanical properties of mullite prepared from kaolinite.

The amount of the excess silica in the kaolinite can be utilized by the addition of alumina to produce mullite. The addition of alumina can, therefore, enhance the mullite phase eliminating the glassy phase to improve the mechanical properties. During kaolinite firing, cristoballite was formed from amorphous silica exsolved during the primary mullite formation (Liu *et al* 1991).

The presence of sufficient alumina began to react with silica-rich liquid favouring the formation of mullite and therefore, retarding or inhibiting the cristoballite formation, depending on the extensiveness of the alumina–liquid reaction (Liu and Thomas 1994). Regarding the role of alumina in the formation of mullite, it was suggested (Chen *et al* 2000) that alumina is inert to the formation of primary mullite up to <1300°C. In the temperature range 1300–1500°C, the amount of mullite increases rapidly and the amount of alumina decreases rapidly instead. The increase in mullite amount in this temperature range is contributed by the formation of secondary mullite by dissolution of alumina to silica-rich glass and precipitation of secondary mullite.

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Most of the above works on the reaction sintering between alumina and kaolinitic clays were dealt by the synthetic, pure variety aluminas. But in the present work, natural Indian bauxite was used as the source of alumina. Here an attempt has been made to study the effect of bauxite addition on the densification, mullitization and microstructural development.

2. Experimental

The clay (Birbhum District of West Bengal), as one of the principal raw materials, was crushed and beneficiated as per standard method of removal of any adhering impurities (Grimshaw 1971). The other important raw material was bauxite (Saurashtra District of Gujarat), crushed, demagnetized and ground. The physical and chemical characteristics of the raw materials are described in table 1. The amount of bauxite was varied from 10–70 wt%. The batch composition along with sample code followed in this study is given in table 2. The requisite amounts of clay and bauxite were mixed and ground thoroughly in wet condition for 2 h. The slurry was dried at 110°C. The dried powder was granulated after mixing with water and sieving through BS 30 mesh. The granules were uniaxially pressed at 600 kg/cm² into 25 mm diameter discs. The pressed samples after drying at 110°C for overnight were sintered at 1400°, 1450° and 1500°C for 2 h soaking at the sintering temperature.

Table 1. Chemical and physical properties of the principal raw materials.

Constituent oxides	Clay	Bauxite
SiO ₂ (%)	45.52	2.81
Al ₂ O ₃ (%)	36.10	60.00
TiO ₂ (%)	1.56	1.70
Fe ₂ O ₃ (%)	1.72	1.85
MgO (%)	Trace	trace
CaO (%)	0.53	trace
Na ₂ O (%)	0.67	trace
K ₂ O (%)	0.75	trace
LOI (%)	13.25	32.17
Crystalline phases present:		
Major	Kaolinite	Gibbsite
Minor	–	Anatase
DTA peaks		
Endothermic (°C)	530°	360°
Exothermic (°C)	973°	–
Mean particle size (µm)	3	–

Table 2. Batch composition and the sample code used in the study.

Sample code	B0	B10	B30	B50	B70
Clay (wt%)	100	90	70	50	30
Bauxite (wt%)	0	10	30	50	70

The bulk density and apparent porosity were measured by water displacement method using Archimedes' principle. The phase analyses of the raw materials and sintered samples were done by X-ray powder diffraction using Ni filtered CuK α radiation. Microstructural analyses by scanning electron microscope was performed on fractured surface after chemical etching with 40% HF for 30 s followed by thoroughly washing with alcohol and water mixture. The SEM analysis was also done on the mirror polished surface after thermochemical etching.

3. Results and discussion

The chemical and physical analyses of the raw materials are described in table 1. The chemical analyses of the

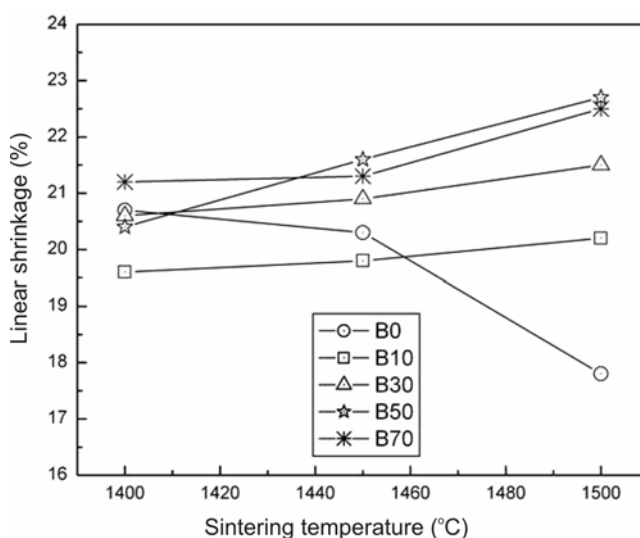


Figure 1. Linear shrinkage as a function of sintering temperature.

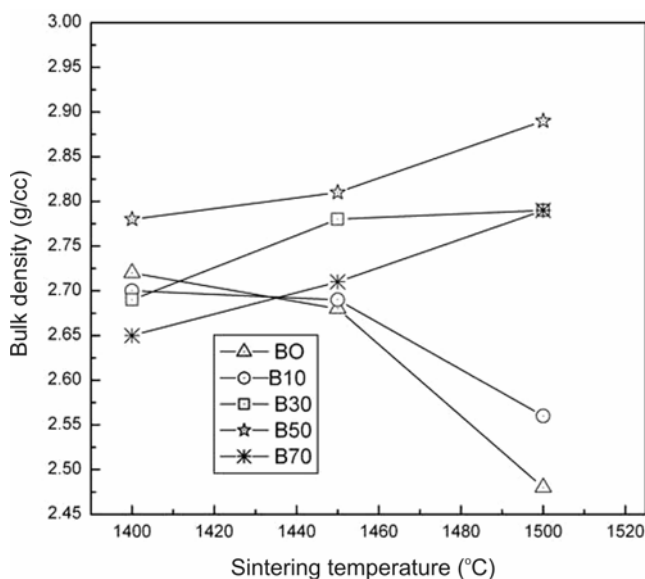


Figure 2. Effect of firing temperature on bulk density of reaction sintered mullite samples.

clay shows that the silica to alumina ratio is 1.26 close to that of pure kaolinite (1.18). The bauxite contains silica, titania and iron oxide as important impurities. The X-ray diffraction pattern of both raw materials corroborates the results of the chemical analysis. The main phases present in the clay and bauxite are kaolinite and gibbsite, respectively. Anatase is the minor impurity phase present in bauxite. The differential thermal analysis showed that the clay had characteristic endothermic peaks at 530°C due to the dehydroxylation of kaolinite leading to the formation of metakaolin (Rezaie *et al* 1997; Viswabaskaran *et al* 2003). The exothermic peak at 973°C is due to the formation of 2 : 1 mullite and spinel from metakaolin (Johnson

et al 1982; Rezaie *et al* 1997; Viswabaskaran *et al* 2003). The bauxite also showed an endothermic peak at 360°C due to the dehydroxylation of gibbsite (Kloprogge *et al* 2002).

The pressed samples were fired at 1400°, 1450° and 1500°C for 2 h. The percent linear shrinkage as a function of sintering temperature is shown in figure 1. The linear shrinkage of the bauxite containing samples increases with firing temperature indicating the presence of bauxite helped to densify the samples at high temperature. The maximum shrinkage was observed with the B50 samples at 1500°C for 2 h.

The bulk density (BD) and apparent porosity (AP) as a function of firing temperature is plotted in figures 2 and 3. The samples without bauxite (BO) had maximum BD (2.72 g/cc) at 1400°C with minimum apparent porosity (0.58%). Its value decreased with increasing sintering temperature. The same was observed with 10% bauxite samples. This decrease in bulk density may be due to the dissociation of Fe₂O₃ present in the clay into FeO and oxygen which is considered to be responsible for bloating in whiteware body at high temperature (Chen *et al* 2000). The opposite trend was observed in the high bauxite containing samples. With increasing temperature the BD was also increased. The maximum BD with minimum AP was achieved in 50% bauxite containing samples. The presence of alumina in the bauxite containing samples dilutes the effect of ferric oxide as it can dissolve into mullite at high temperature (Brownel 1958; Johnson and Pask 1982). It was found that the solid solution limit of Fe₂O₃ in a synthetic mullite was 7.7 wt% at 1300°C. Fe³⁺ ions can substitute for Al³⁺ ions due to the similarity in ion size and charge. The impurities present in the bauxite and clay formed higher amount of the glassy phase which facilitated particle diffusion (Bakr and Naga 2002). The *in situ* nascent alumina formation from bauxite was more reactive to be dissolved in glassy phase along with cristoballite to form secondary mullite by solution precipitation technique (Liu *et al* 1991). The amount of glassy phase was decreased as the secondary mullite consumed the silica from the glassy phase (Chen *et al* 2000).

The X-ray diffraction pattern of the powdered samples fired at 1500°C are shown in figure 4. The cristoballite phase is observed with 10% bauxite samples but no cristoballite peaks were observed with other bauxite containing samples. This observation confirmed that the nascent alumina derived from bauxite in 30 wt% and higher samples was more reactive and sufficient to dissolve in glassy phase along with cristoballite to form secondary mullite by solution precipitation technique with enhancing densification (Liu *et al* 1991). The reduction of glassy phase in the bauxite containing samples, the absence of cristoballite and the increase in secondary mullite were responsible for the high BD with high bauxite batches at high temperature. The amount of *in situ* alumina (10 wt% batch) was insufficient to form secondary mullite after dissolu-

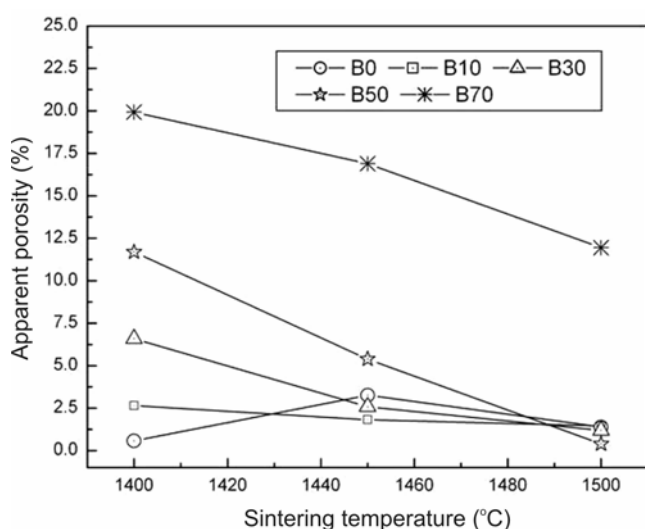


Figure 3. Apparent porosity as a function of sintering temperature.

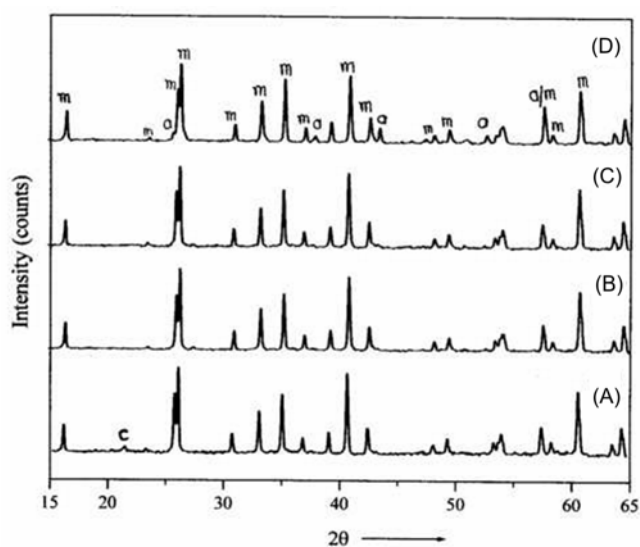


Figure 4. XRD patterns of reaction sintered mullite fired at 1500°C: (A) B10, (B) B30, (C) B50 and (D) B70 (m, mullite; c, cristoballite and a, α -alumina).

tion of cristoballite due to which few cristoballite phases were identified in the XRD. The mullite phase was also observed in all the cases and the mullite peak intensity gradually increased. At 70% bauxite in addition to mullite phase, α - Al_2O_3 phase also appeared. The 50% bauxite was near the stoichiometric mullite composition and beyond this the excess alumina was crystallized as corundum (α - Al_2O_3) phase.

The SEM microstructure of B0 sample fired at 1500°C is shown in figure 5. Considerable growth of mullite crystals are observed. The grains have rounded edges with distinct needle shape. The fully-grown crystals of high aspect ratio are identified. The microstructure is very similar to that obtained by Gnanam *et al* with South Indian clay (Viswabaskaram *et al* 2003).

Figure 6 is the SEM of bauxite containing samples fired at 1500°C for 2 h. The microstructure shows mullite grain morphology appearing to be a bimodal structure of larger elongated primary mullite crystals with high aspect ratio and smaller, more equiaxed secondary mullite (Liu *et al* 1991; Sainz *et al* 2000). The larger mullite crystals with higher aspect ratio corresponded to the primary mullite nucleated in kaolinite and grown in firing. The smaller mullite crystals are secondary mullite nucleated from the transitory liquid phase formed by the dissolution of *in situ* alumina from bauxite (Chen *et al* 2000). Figure 6a is the fired sample of B10 batch showing the higher amount of primary mullite and lower amount of secondary mullite grown from the alumina-rich glassy phase. Formation of mullite from the glassy phase can be noticed. Figure 6b is the microstructure of the sintered sample of B30 batch revealing the increasing amount of equiaxed secondary mullite formed from alumina-rich glassy phase. The elongated grains are primary mullite.

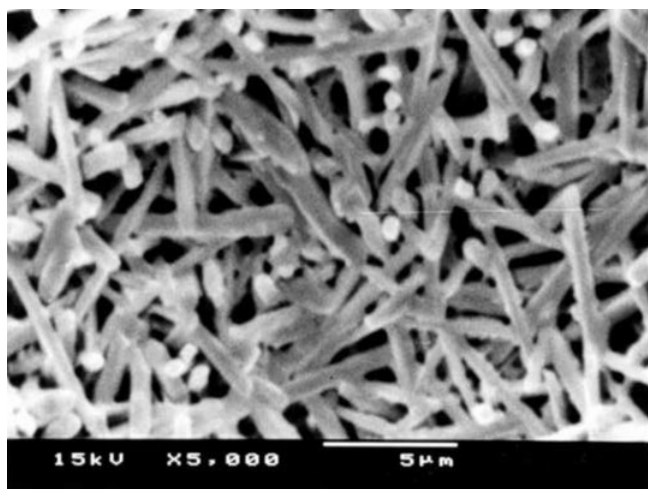


Figure 5. Secondary electron image of mullite without bauxite (B0) sintered at 1500°C after chemical etching of fractured surface.

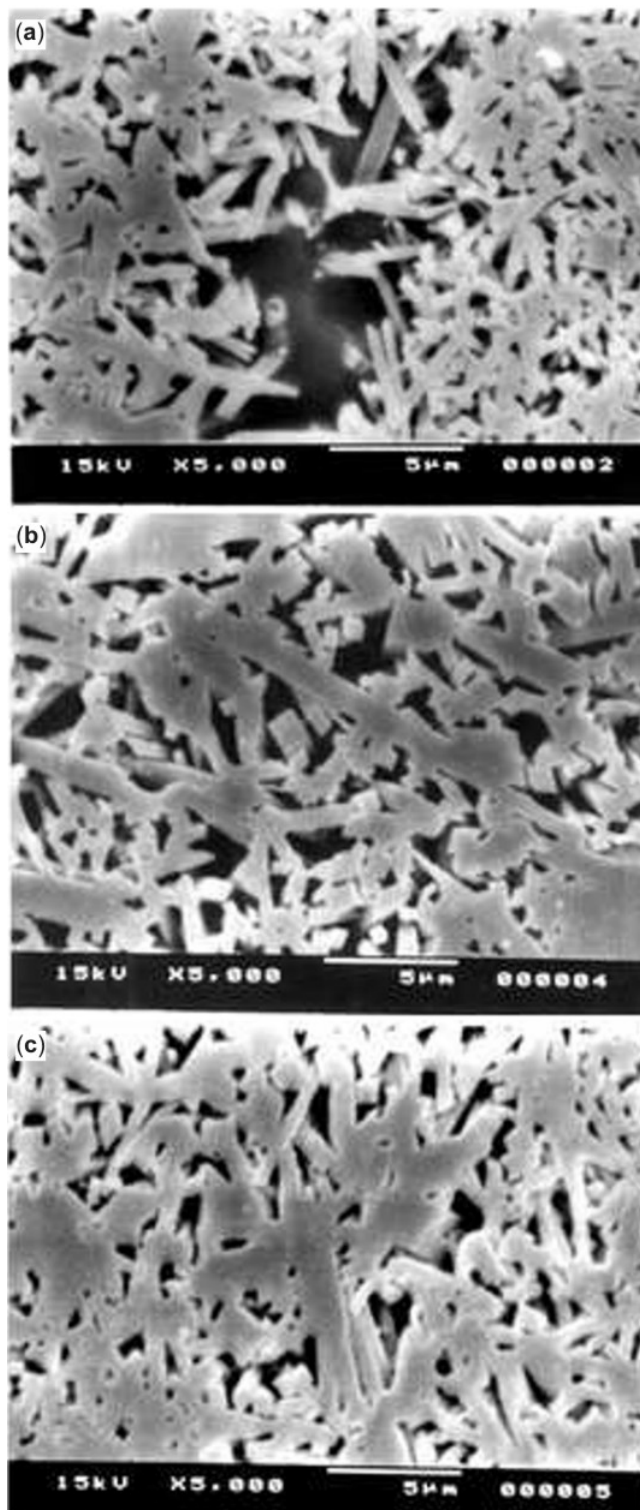


Figure 6. Scanning electron microstructure of mullite with different bauxite contents sintered at 1500°C after thermochemical etching of polished surface: (a) B10 showing the presence of primary mullite and formation of secondary mullite from glassy phase (black area), (b) B30 showing the presence of primary and secondary mullite with uniform distribution of glassy phase (black area) and (c) B50 shows the compact microstructure consisting of primary and secondary mullite with minimum glassy phase. For sample codes, see table 2.

The glassy phase is uniformly distributed. In figure 6c the bauxite containing sample (B50) sintered at 1500°C for 2 h is shown. The amount of secondary mullite is much higher than the previous two microstructures. The glassy phase is small and the microstructure is compact which corroborates with the BD value. With increasing bauxite content the amount of glassy phase decreased with increase in the secondary mullite content in place of primary one. The nascent alumina (from bauxite) can act as the nuclei for the formation of secondary mullite grains. The increase of bauxite increases the amount of nuclei and decreases the amount of glass, the size and aspect ratio of mullite grains are thus reduced (Chen *et al* 2000).

4. Conclusions

The present study demonstrated that mullite can be prepared by reaction sintering of kaolinitic clay and bauxite. The presence of bauxite helped to densify the material at low temperature. The impurities present in the bauxite and clay formed glassy phase that facilitated the material diffusion to favour the densification. On the other hand, the *in situ* alumina formation from natural bauxite was reactive enough to form secondary mullite by solution precipitation technique.

With increase in bauxite content the amount of secondary mullite increased in lieu of glassy phase and cristoballite which ultimately enhanced the bulk density and optimized the BD at 50 wt% bauxite. Two types of mullite were distinctly observed in the microstructure: larger, elongated primary mullite from kaolinite and smaller, equiaxed secondary mullite by solution precipitation technique from alumina and silica rich glassy phase. The increase in the alumina content increased the amount of mullite nuclei and decreased the amount of glass, the size and aspect ratio of mullite were thus reduced (secondary mullite).

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