Effect of sillimanite beach sand composition on mullitization and properties of \( \text{Al}_2\text{O}_3-\text{SiO}_2 \) system

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Abstract. Mullite was developed by reaction sintering of sillimanite beach sand and calcined alumina. Two varieties of sillimanite beach sand viz. S and Z having different compositions were selected. Synthesis and properties of mullite were very much dependent on the sillimanite beach sand composition. Presence of higher amount of impurities in the Z-variety of sillimanite sand favours the densification by liquid phase formation. Presence of zircon in Z-variety increases the hardness and fracture toughness. Alumina addition improves the mechanical/thermomechanical properties of the samples. Mullite retains the usual orthorhombic habit of sillimanite. Rounded to sub rounded zirconia dispersed within the mullite matrix of the sample ZA is noticed.

Keywords. Sillimanite; mullite; beach sand; aggregate.

1. Introduction

Beach sand minerals did not gain so much importance till their counterpart rock minerals were available in abundance at an affordable price. With the depletion of rock minerals, demands for technology have gone up that would convert these minerals into value added products (Banerjee 1998; Tripathi and Banerjee 1998, 1999). In the \( \text{Al}_2\text{O}_3-\text{SiO}_2 \) system, the importance of mullite is well known for a long time. Stoichiometric mullite has a 3 : 2 molar ratio of \( \text{Al}_2\text{O}_3/\text{SiO}_2 \). It has (i) low thermal expansion, (ii) low thermal conductivity, (iii) excellent creep resistance, (iv) good chemical stability and (v) high oxidation resistance.

Generally mullite is occasionally found in nature, as its formation need high temperature and low pressure conditions. Sillimanite which is \( \text{Al}_2\text{O}_3\cdot\text{SiO}_2 \), occurred in nature in rock form. But the rock form sillimanite has been depleted/exhausted in many parts of the world. Placer deposits of beach sand sillimanite minerals occur in a number of coastal areas. Placer deposits are of two types, viz. beach placers and inland placers.

In India, sillimanite beach placer deposits are found in the eastern and southern coasts (Nagar 1995). In the present investigation, two varieties of sillimanite beach sand were selected. Efforts have been made to study the effect of sand composition on the mullitization and properties of the aggregates.

2. Experimental

Sillimanite beach sand was obtained from Indian Rare Earths Limited from two different regions (S-variety and Z-variety). S-variety and Z-variety of sillimanite were obtained from the eastern coast of Orissa and southern coast of Tamilnadu, respectively. Calcined alumina was obtained from the Indian Aluminium Company Limited, India. Batches were prepared with the above raw materials as well as by the addition of \( \text{Al}_2\text{O}_3 \) to convert the \( \text{SiO}_2 \) available into mullite as shown in table 1.

Batches were mixed and milled in a 750 cc attritor mill in water medium for 5 h. The ratio of charge to grinding media was maintained at 1 : 7. Slurries thus obtained were dried at 110 ± 5°C for 24 h, crushed to break the agglomerate, mixed with 5% PVA solution as binder and pressed into shapes. Rectangular bars of \( 60 \times 60 \times 6 \) mm were initially uniaxially pressed at 100 MPa and then isostatically pressed at 175 MPa. Bars were sintered in air at 1500, 1550, and 1600°C with 2 h soaking time. Sintering was done in an electrically heated furnace and the heating rate was maintained at 5°C/min. Sintered products thus obtained were characterized in terms of bulk density, apparent porosity, mechanical and thermomechanical properties and microstructure. Apparent porosity and bulk density of the samples were measured by conventional water displacement method using Archimedes’ principle.

High temperature flexural strength of the samples were measured at 1200°C by standard 3-point bending method. Samples which were sintered at 1600°C for 2 h were used to measure Young’s modulus, hardness and fracture toughness. Young’s modulus was measured by nondestructive Sonic method. Hardness and fracture toughness of samples were measured through Vickers’ indentation using a load of 49 N. X-ray powder diffraction pattern of the raw materials and fired products were obtained in an X-ray diffractometer using nickel filtered Cu–Kα radiation. Diffraction patterns were recorded in the Bragg’s angle 2θ.
range 10–55°. Microstructural analysis was done by scanning electron microscopy (SEM) using sputtered gold coating on fracture surface of the sintered samples.

3. Results and discussion

Chemical analysis of the raw materials are given in table 2. From table 2 it is seen that, the amount of ZrO$_2$, TiO$_2$ and alkali present in the S and Z-variety of sillimanite sand differ significantly. Both the sillimanite sands contain higher amount of silica than the stoichiometric amount. It was found that Z-variety contains ZrO$_2$ in the form of zircon (Banerjee 1998).

3.1 Densification

Degree of densification can be evaluated by means of bulk density of the sintered samples. Variation of bulk density with the sintering temperature is shown in figure 1. It is seen that sample Z achieved its highest bulk density of 3.04 g/cc at a sintering temperature of 1550°C (apparent porosity, 0.49%), whereas the sample S requires a temperature of 1600°C to achieve its highest bulk density. Alumina addition in the batch (SA andZA) requires higher sintering temperature for the same level of densification. At 1600°C the bulk density of SA and ZA is higher compared to respective alumina free samples (S and Z) due to the higher Al$_2$O$_3$ content. Apparent porosity of the Z samples sintered at 1500°C is 3.90% which is significantly lower compared to that of S sample (19.65%).

This is due to the presence of higher amount of alkali in sample Z which reduces the porosity by means of glass formation. Bulk density of all the samples except Z increases with sintering temperature up to 1600°C since Z has higher amount of impurities which help in liquid phase sintering at a lower temperature. In case of Z, bulk density reaches a maximum value of 3.04 g/cc at 1550°C and falls subsequently at 1600°C. Z has nearly eight times the alkali content than that of S sample. Its Fe$_2$O$_3$ and TiO$_2$ contents are two and twenty one times more, respectively than that of S. This results in the formation of excessive amount of glass, which is responsible for low BD of the sample Z sintered at 1600°C.

3.2 Mechanical properties

High temperature flexural strength is an important parameter for refractories selection. The high temperature strength of the refractory aggregates depends on the porosity, grain size, amount and nature of glassy phase. Variation of hot MOR at 1200°C of the samples with sintering temperature is depicted in figure 2. It is seen that, HMOR of the samples S and Z are primarily