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Effect of pyrophyllite on vitrification and on physical properties of triaxial porcelain

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Abstract

Quartz was progressively replaced by pyrophyllite in a conventional porcelain mix with a composition of 50% clay, 25% quartz and 25% feldspar. The addition resulted in early vitrification and decreased thermal expansion of the sintered specimen. Addition of up to 15% pyrophyllite decreased the fired shrinkage by 6% and improved the fired strength by around 29% compared to the standard body. The gradual increase in flexural strength with incorporation of pyrophyllite was primarily due to the elimination of stresses in the structure with a decreasing quartz content as well as to the increasing amount of secondary mullite distributed throughout the matrix forming an interlocking network. However, the firing temperature and the generation of the correct amount of properly sized mullite needles are vital in achieving the desired strength. Pyrophyllite was found to dissolve in the melt in preference to quartz. Beyond the optimum proportion of pyrophyllite, a large volume of glass formed as well as large elongated pores distributed in the matrix resulting in deterioration of mechanical properties.

Keywords: B. Microstructure; D. Porcelain; Pyrophyllite; Quartz; Vitrification

1. Introduction

Triaxial white ware body essentially consists of 50% kaolinite clay, 25% quartz and 25% feldspar. Although quartz plays a significant role in the development of ultimate properties of the product as well as appropriate microstructure, only a small portion of it gets dissolved in the melt during firing while a significant amount remains unreacted. The unreacted quartz phase undergoes transformations during cooling and the resultant volume change leads to the development of stresses in the structure which adversely affects the mechanical strength as well as thermal shock resistance [1]. Chaudhuri [2] observed that thermal shock resistance of hard porcelain deteriorated with the increasing amount of quartz and glassy matrix while the same improved with increasing mullite content. The temperature at which quartz begins to dissolve and interact with surrounding materials is strongly affected by batch composition as well as particle size of quartz [3–5]. Cracks are commonly observed in and around quartz grains with sizes >20 μm resulting from large thermal expansion mismatch between crystalline quartz ($\alpha = 23 \times 10^{-6}\,K^{-1}$) and the glassy phase ($\alpha = 3 \times 10^{-6}\,K^{-1}$) in the temperature range 20–750 °C [4,6]. The stresses in the glassy phase create tensile force perpendicular and compressive force parallel to the grain boundaries [7]. Highest dissolution of quartz in the melt will reduce the tensile force between residual quartz and surrounding glassy phase [8].

Mullite is the only stable phase in the Al_2O_3–SiO_2 system at atmospheric pressure. The mullite phase is believed to play a significant role in the development of traditional and advanced ceramics [9,10]. Lieberman [11] observed that replacement of quartz by aluminium oxide in an electrical porcelain composition resulted in 100% increase in flexural strength. He correlated the increase in strength with the amount of mullite and corundum as well as the decrease in the number of micro cracks. Khandelwal and Cook [12] achieved 200% increase in transverse strength by adding 40% alumina to a vitreous china body. Increasing alumina

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and decreasing feldspar content increased the total crystalline content of the fired body [12]. Analysis of microstructures revealed a higher mullite content. Increased interlocking of the mullite crystals is thought to increase thermal shock resistance. On the other hand the same author compared the strength of two quartz bodies with different mullite contents and opined that it was not the mullite content but the microstructure (the quantity, size, size distribution and shape of various constituent phases) contributed significantly in the development of porcelain properties. Tkalcec et al. [13] observed that addition of talc up to 4% increased the quantity of mullite but reduced the MOR due to the increase in the quantity and size of pores in the fired bodies. Maiti and Kumar [14] observed that progressive replacement of quartz by sillimanite sand in a porcelain composition resulted in increased flexural strength and fracture toughness. Prasad et al. [15] replaced quartz and feldspar in a white ware composition with sericitic pyrophyllite ($K_2O + Na_2O$ 10.08%). Incorporation of 22.5% sericitic pyrophyllite resulted in increased fired strength while decreasing the thermal expansion. This was attributed to the presence of spherical shaped pores and the decrease in free quartz content. In another work of Bhasin et al. [16], the effect of pyrophyllite additions on sintering characteristics of fly ash-based ceramic wall tiles was studied. The impact strength and apparent density was found to increase with the increase in pyrophyllite content while decreased water absorption values were observed. Further, presence of pyrophyllite imparted improved thermal shock resistances. Rieger [17] observed that high-sericitic pyrophyllite has the ability to form mullite at comparatively low temperatures and interlocking grain structure of mullite results in greatly increased fired strength in vitrified bodies. In addition, high sericitic pyrophyllite also has the advantage of low-moisture expansion bodies, little shrinkage, and less warpage.

In the present study, quartz was progressively replaced by pyrophyllite in a normal porcelain white ware composition consisting of 50% clay, 25% feldspar and 25% quartz. Effect of such substitution on shrinkage, bulk density, porosity, thermal expansion, strength, phase evolution in relation to firing temperature was studied. Some selected samples were examined for micro-structural changes.

2. Experimental

The raw materials used in this investigation were china clay (Rajmahal, Bihar, India), plastic clay (Ranchi, Jharkhand, India), quartz, feldspar and pyrophyllite (Maharashtra, India).

The chemical analysis of the raw materials conducted by standard method is given in Table 1.

Batch (Table 2) was wet ground for 16 h in porcelain jars with porcelain balls up to a fineness of around 53 μm. The ground slurry was sieved, passed through a permanent magnet, dewatered and test specimens were extruded in a vacuum extruder in cylinders of 2 cm in diameter and 15 cm in length. The test specimens were dried and subsequently fired between 1150 and 1300 °C in an electric furnace with 2 h soaking at the respective peak temperatures.

Table 1
Chemical analysis of raw materials (wt.%)

Constituency	Pyrophyllite	China clay	Plastic clay	Quartz	Feldspar
SiO_2	59.51	48.87	58.38	98.11	66.81
TiO_2	0.26	0.93	1.15	Trace	Trace
Al_2O_3	30.43	34.39	25.54	0.41	18.08
Fe_2O_3	0.86	0.87	0.49	0.22	0.24
CaO	0.37	1.42	0.95	0.68	1.03
MgO	0.78	Trace	Trace	Trace	0.23
Na_2O	0.73	0.10	0.13	0.15	1.69
K_2O	1.95	0.23	0.63	0.07	10.94
LOI	5.40	12.83	12.24	0.19	0.58

Apparent porosity and bulk density of the specimens fired at different temperatures were measured by the water displacement method. Flexural strength in three-point bending stress was measured with an electromechanical universal tester (Instron 1195). The cross head speed was 1 mm/min and a span of 100 mm was maintained throughout the experiment. Flexural strength was measured using the formula = $8\ WL/\Pi D^3$, where W is the breaking load, L the span length, D the diameter of the cylindrical specimens.

Linear thermal expansion of the matured specimens was determined using an Orton Automatic Dilatometer (Bosch & Lamb, UK) at a heating rate of 2 K/min.

Major crystalline phases present in the matured specimens were identified by X-ray diffraction (XRD) using a Philips PW-1730 X-ray diffractometer. Microstructure was studied by SEM analysis on selected sintered samples using a LEO S-430i apparatus.

Concentration of crystalline phases was estimated by X-ray diffractometry in a Philips make X-pert Pro diffraction unit attached with secondary monochromator automatic divergence slit and Ni-filter was used to get monochromatic Cu Kα radiation. The instrument was run in step scan mode with step size (0.02) and time per step 8 s/step within the angle 5–75°. The collected data were refined using profit software. X-Pert plus and Quaser software based on Rietveld were used to calculate the percentage of mullite and quartz phases where standard mullite and quartz were used as reference materials.

Table 2
Body composition with progressive replacement of quartz with pyrophyllite (%)

Composition	China clay	Plastic clay	Feldspar	Quartz	Pyrophyllite
S-1	25	25	25	25	0
S-2	25	25	25	20	5
S-3	25	25	25	15	10
S-4	25	25	25	10	15
S-5	25	25	25	5	20
S-6	25	25	25	0	25