The microstructure of vitrified kaolin ceramic tapes has been studied via scanning and transmission electron microscopy (SEM and TEM). The sintered samples contained crystalline phase of predominantly stoichiometric mullite (3Al₂O₃·2SiO₂), which consisted of high aspect ratio, acicular crystals that are often referred to as secondary mullite. These crystals were interlocked and embedded in an aluminosilicate glass matrix of inhomogeneous composition. The glass matrix contained an average of ~3.63 wt% K as determined by energy-dispersive X-ray analysis (EDS), whose composition could be approximated to 5.5Al₂O₃·16SiO₂·0.1MgO·0.3K₂O·0.15TiO₂·0.12Fe₂O₃. The acicular crystals have approximately the stoichiometric composition of Al₂O₃·SiO₂ = 3:2. They have grown along a specific crystallographic orientation along the [001] axis. The crystal growth front exhibited faceting on the (110) planes with microfacetting on both the (100) and (010) planes.

I. Introduction

The crystal structure of mullite is orthorhombic, which belongs to the space group Pbam (No. 55). It consists of AlO₆ octahedral chains, parallel to the c-axis, which are cross-linked by the (Al,Si)O₄ tetrahedral chains. With a large range of solid solution, its chemical composition can vary from 3Al₂O₃·2SiO₂ to 2Al₂O₃·SiO₂ (often referred to as the 3:2 and 2:1 limits, respectively), where the nonstoichiometry is accommodated by oxygen vacancies generated extrinsically.

Triaxial porcelain bodies acquire significant strength and toughness through the formation of mullite during sintering as a result of vitrification. Mullite crystals are categorized by the chemical composition (i.e., nonstoichiometry), and the crystal morphology including both shape and size. Mullite formed from kaolin clay alone is termed primary mullite (M(I)) while that formed from reaction of inhomogeneous composition. The glass matrix contained an average of 5Al₂O₃·16SiO₂·0.1MgO·0.3K₂O·0.15TiO₂·0.12Fe₂O₃ (of scaly appearance) and secondary M(II) (of granular shape).

Further, mullite crystals produced in clay–feldspar relicts are secondary mullite (M(II)) with several morphologies, such as the granular, cuboidal, acicular, or needlelike. Primary mullite crystals, produced from alumina-rich glass at a later stage of crystallization, have sizes smaller than those of M(I) crystals. The aspect ratio of M(II) crystals depended on the viscosity of the eutectic liquid that varied with the alkali content (e.g., Na₂O versus K₂O) of the initial powder. The cuboidal M(I) crystals appeared to have rounded corners as well as faceted surfaces (Fig. 3 in Iqbal et al., further defined secondary mullite in the fine clay, feldspar, and quartz matrix as type-II and type-III categories based on the aspect ratio. They were observed from both model and commercial triaxial porcelain bodies vitrified at temperatures above 1400°C. Tertiary mullite crystals, produced from alumina-rich glass at a later stage of crystallization, have sizes smaller than those of M(I) crystals.

II. Experimental Procedure

Kaolin powder (Akima-35) was supplied by Associated Kaolin Industries Berhad (Ipoh, Malaysia). The powder containing kaolinite and minor amounts of α-quartz and mica is similar to those used by Castelein et al. Its composition, determined via the inductively coupled plasma mass spectrometry (ICP-MS) is SiO₂ (48.6 wt%), Al₂O₃ (35.7 wt%), K₂O (1.2 wt%), Fe₂O₃ (0.9 wt%), TiO₂ (0.4 wt%), MgO (0.2 wt%), CaO (0.1 wt%), and BaO (0.1 wt%).

Green tapes of ~400 μm thick were cast, using a doctor-blade, from a slurry of 20 wt% solid containing 2 wt% Na₃PO₄ (sodium phosphate) dispersant, 2.5 wt% poly(vinyl alcohol) (PVA) binder, and poly(propylene glycol) (PPG) plasticizer in equal quantity. The cast tape has shrunk to a thickness of ~100–150 μm thick after drying. Thin squares of 1.0 cm × 1.0 cm were stamped from the dried tape, placed in a covered alumina setter, and sintered at 1000°C, 1500°C, and 1600°C for 1 h at a heating rate of 5°C·min⁻¹.
were derived from the dehydroxylation of kaolinite to metakaolin.\(^7\)
The liquid eutectic may also originate from the combination of amorphous Al\(_2\)O\(_3\)–SiO\(_2\) with the trace impurity of K\(_2\)O (~3.6 wt%\(^{13}\) detected by EDS) and Na\(_2\)O (not detected by EDS). Although sintering of kaolin–Al\(_2\)O\(_3\) mixtures, rather than just kaolin, was investigated by Chen et al.,\(^{13}\) precipitation of secondary mullite from glassy phase containing Al\(_2\)O\(_3\)–SiO\(_2\)–K\(_2\)O in which a similar amount of 3.06 wt% K\(_2\)O detected by EDS was reported. Nevertheless, fine M(I) crystals\(^7\) have not been detected under TEM in the present work and that is probably due to its scarcity.

The growth direction of M(II) crystals along [001] having the low surface energy plane on (110) when precipitating from a eutectic liquid can be certain. Treating the crystal structure as pseudotetragonal with \(a\) (0.955 nm) \(\approx b\) (0.969 nm), the faceted planes can be addressed as [110]. Microfaceting also occurred on [100] and [010] on M(II) crystallization from the melts resulting in the corrugated growth front along both longitudinal and lateral directions (Fig. 5). The “cuboidal” mullite crystals were distinctively faceted crystallographically, similar to those in Figs. 5 and 7 shown by Iqbal et al.\(^7\) The faceting along (110) from their TEM observations, similar to Figs. 4(a–c), could have been determined, but not reported by them. The crystals of the “cuboidal” shape, usually adopted to describe the small and faceted M(I) crystals,\(^7\) are most likely to be M(II), particularly when they are immersed in a glassy matrix.\(^4\)–\(^9\) The identified acicular nature, the facetting, and the stoichiometry determined by microanalysis all suggest that they are unambiguously M(II) crystals (Figs. 4(a–c)) when viewed from the long morphologic axis, or [001], along which the mullite crystals are grown axially.

Eutectic liquid is necessary for the precipitation of M(II) in vitrified kaolin, i.e., sintered by vitrification. The amount of liquid formed at sintering temperatures, and the duration at which the crystallization has taken place, will determine the chemical composition and the aspect ratio of M(II). Consequently, the aspect ratio (that differentiates type II from type III\(^9\)) was controlled by position and the aspect ratio of M(II) during the crystallization has taken place, will determine the chemical composition, form at sintering temperatures, and the duration at which the crystallization has taken place, will determine the chemical composition and the aspect ratio of M(I). Therefore, a glassy matrix is necessary for the precipitation of M(II)

V. Conclusions

Ceramic tapes prepared from a commercial kaolin powder, sintered at 1500\(^{\circ}\)C and 1600\(^{\circ}\)C, have been characterized by the microstructure of interlocking acicular, secondary mullite (M(II)) crystals embedded in a glassy matrix. The M(II) crystals growing axially along [001] from liquid eutectic melts of compositions lying in the Al\(_2\)O\(_3\)–SiO\(_2\) and K\(_2\)O–(Na\(_2\)O)–Al\(_2\)O\(_3\)–SiO\(_2\) systems. They have exhibited crystallographic facetting on the corrugated (110) planes with microfacetting on (100) and (010) planes. This suggests that the plane of low solid-to-liquid surface energy in the stoichiometric M(II) crystals.

References


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