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Influence of mixing on mullite formation in porcelain

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Abstract

Various forms of mullite occur in porcelains. *Primary* mullite forms from decomposition of pure clay. *Secondary* mullite forms from reaction of feldspar and clay and feldpar, clay and quartz. Which of these forms is strongly dependent on the extent of mixing of the body raw materials. Additionally, in aluminous porcelains *tertiary* mullite may precipitate from alumina-rich liquid obtained by dissolution of alumina filler. The size, shape and composition of the mullite crystals is controlled by the fluidity of the local liquid matrix from which they precipitate and grow, which itself is largely determined by the extent of mixing of the original powder batch. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Porcelains are vitreous (vitrified) ceramic whitewares used extensively in tableware, sanitaryware, decorative ware, electrical insulators and dental prosthetics. Vitrification indicates a high degree of melting on firing which confers low (often $<0.5\%$) porosity and high ($>40\%$) glass contents on fired porcelains. Porcelains typically have a triaxial formulation comprising about 50% clay, 25% flux and 25% filler. The *clay* acts as a binder for the other constituents in the green state, confers plasticity on the body for shaping and is usually kaolinite. The *flux* is a low melting phase that reacts with the other constituents and lowers the temperature of liquid formation in the system. This liquid permeates the microstructure leading to densification. Fluxes used commercially are alkali feldspars such as nepheline syenite ($KAlSi_3O_8$ and $Na_3KAl_4Si_4O_{16}$). The *filler* is reasonably stable at commercial firing temperatures and reduces distortion and shrinkage. It is often quartz sand or, in hotelware and electrical porcelains, additionally alumina. Firing bodies containing these 3 components results in a grain and bond microstructure consisting of coarse aggregate (filler) particles held together by a finer matrix or bond system that is almost fully dense[1–4]. It is the purpose of this paper to review microstructural studies of mullite formation in triaxial porcelains (including our recent work), highlighting the importance of mixing on the nature of the mullite formed in the bond system. Additionally, some comparisons will be made to mullite formation in pure clay systems and alumina-clay mixtures.

2. Experimental procedures

Commercial porcelain samples were provided by Wedgwood (Stoke-on-Trent, England). Model porcelain samples were prepared as previously described[5] using laboratory-scale mixing, ball milling and hand granulation. The milling procedures and scale of mixing of the commercial and model systems are known to be different. While details of the former are commercially sensitive, the spray drying techniques used would confer improved mixing compared to laboratory mixing techniques. Scanning electron microscopy specimens were polished using 6, 3 and 1/4 μm diamond pastes after grinding with silicon carbide powders and water. The polished surfaces were etched for 3 min in 5% HF solution and then gold/carbon coated before examination in a Jeol 6400 SEM operating at 20 kV.

3. Porcelain microstructures

Microstructural studies of porcelain include the early work of Lundin[1,2] and Schuller[3], while recently, modern microscopy and microanalytical techniques have been used to characterise the microstructures of commercial

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fully fired porcelains[4] and to examine microstructural evolution in a model porcelain system.[5] Early studies revealed the importance of the extent of mixing during the production of porcelain. Micro-regions of varying composition are present in the unfired ware, including pure clay agglomerates and feldspar-enriched regions. The size and extent of these regions is controlled by the raw powder particle size, level of agglomeration and degree of mixing. On heating, these regions react to form different types of mullite. Mullite crystals derived from the pure clay agglomerate relicts are cuboidal and are referred to as *primary* mullite since they form at the lowest temperature. Elongated needle-shaped mullite crystallising from the feldspar-rich melt is termed *secondary* mullite since it forms later in the firing process. A third form of mullite has been detected in porcelains containing alumina as filler termed *tertiary* mullite[4,6]. This is precipitated from alumina-rich liquid formed from dissolution of the alumina filler but has been observed only in minor quantities. Mullite derived by solution of alumina and reprecipitation has also been observed in kaolinite–alumina mixtures[7,8] although in those studies it was termed secondary mullite.

The general microstructural features of commercial porcelains are coarse quartz grains surrounded by solution rims of almost pure silica glass embedded in a much finer matrix system. Fig. 1 shows the typical microstructure of a porcelain containing primary and secondary mullite. The matrix is predominantly glass of varying composition being aluminosilicate in clay relict regions which also contain fine, cuboidal, *primary* mullite crystals and alkali (Na, K) aluminosilicate in flux penetrated regions which also contain larger, elongated *secondary* mullite[4]. This microstructure is a direct result of incomplete mixing but clearly is suitable for the purpose. Agglomerates of fine clay particles form predominantly primary mullite while those regions in which flux particles were mixed well with clay or where flux has penetrated clay agglomerates form secondary mullite. Fig. 1 shows several ~10 μm dia. regions showing secondary mullite presumably arising from similarly-sized raw flux particles.

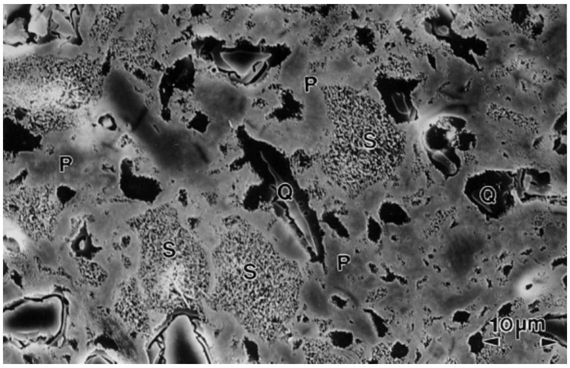

Fig. 1. Secondary electron SEM image of Wedgwood porcelain showing regions of primary mullite (P), secondary mullite (S), and quartz filler grains (Q) surrounded by dark rims of amorphous silica arising from their dissolution.

3.1. *Primary mullite*

The formation of primary mullite from the pure clay agglomerate relicts suggest such crystals will be identical to those formed from decomposition of pure clays. Comparison of the morphologies of mullites in recent studies[9,10] of pure kaolinite clays confirms this is the case. Cuboidal or low aspect ratio (1–3:1) mullite crystals form after firing at 1100–1200°C in pure kaolinite. Iqbal and Lee[5] observed cuboidal primary mullite forming in pure kaolin relicts at similar temperatures in their model porcelain. Since primary mullite forms from breakdown of pure clay to metakaolin (with formula $Al_2O_3{\cdot}2SiO_2$) it is expected to be close to a 2:1 Al_2O_3:SiO_2 mullite because it is observed to crystallise from a large proportion of silica-rich glass. It is not until temperatures above 1400°C that the aspect ratio of the mullite crystals derived from pure clay reaches about 10:1.[10] Silica-rich glasses are known to be particularly viscous so that mass transport and the potential for free growth of crystals at lower temperatures is limited. It is not until the liquid becomes fluid at high temperatures (>1400°C) that acicular, high aspect ratio, primary mullite can form.

3.2. *Secondary mullite*

Secondary mullite does not form from pure feldpar relicts since these contain insufficient alumina but from feldpar penetrated clay relicts or mixtures of fine clay, quartz and feldspar.[5] The reaction of feldspar (with e.g. formula $K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$) with metakaolin in intimately-mixed regions is likely to form a more alumina deficient mullite than decomposition of pure clay i.e. nearer 3:2 Al_2O_3:SiO_2 mullite since it has to access the alumina from the clay. Furthermore, because the surrounding liquid is now enriched in alkalis it will be far more fluid so that crystals once nucleated can grow rapidly and unhindered. This explains the more elongated morphology of secondary mullite than primary mullite formed at the same temperature within the same porcelain body.[5]

During their studies of microstructural evolution in model porcelains, Iqbal and Lee[5] observed that secondary mullites derived from areas of mixed fine clay; quartz and feldspar contained very high aspect ratio (30–40:1) secondary mullite crystals as well as lower aspect ratio (3–10:1) secondary mullites observed in feldspar penetrated clay relicts. This suggests an alternative notation for the types of mullite formed in porcelains is needed. Iqbal and Lee[5] suggest Type I for cuboidal low aspect (1–3:1) primary mullite derived from pure clay, Type II for 3–10:1 aspect ratio secondary mullite detected in feldspar-penetrated clay relicts and Type III for very high aspect ratio (30–40:1) secondary mullite needles. The elongated Type III mullite crystals occur in regions also containing Type II and are associated with a fluid matrix. This fluidity can arise from increased firing temperature or through the composition of the flux. Na_2O-rich feldspars produce a more fluid liquid and so larger needles than K_2O-rich fluxes in bodies fired to the same temperature. Fig. 2 shows the three types of mullite in a commercial porcelain while Fig. 3 shows schematically the relation between the morphologies of the types of mullite. The central part of Fig. 2 is a feldspar relict region (~50 μm dia.) suggesting the presence of a large flux particle in the original batch. As well as shape mullite crystal size changes increasing from regions containing Types I-III. This categorisation is important since increased strengths and toughnesses have been reported in porcelains containing increased amounts of high aspect ratio mullite.[11] Well-mixed porcelains or those using high alkali fluxes conferring high fluidity on the matrix might be expected to have higher proportions of the larger needles (Types II and III). The importance of matrix fluidity, and the potential for enhanced mullite growth in more fluid liquids arising from improved mixing, has been neglected in previous studies of porcelains.

Some authors have suggested that since primary mullite crystals form first in porcelains they can act as nucleation sites for secondary mullite crystals.[1–3] This seems a likely scenario although the definition of what is primary and secondary mullite then becomes blurred. The interface region in Fig. 2 between what is clearly primary (at the edge of the relict with a dense concentration of cuboidal mullite) and what is clearly secondary (in the centre of the relict with a low density of mullite) may well be such a region.

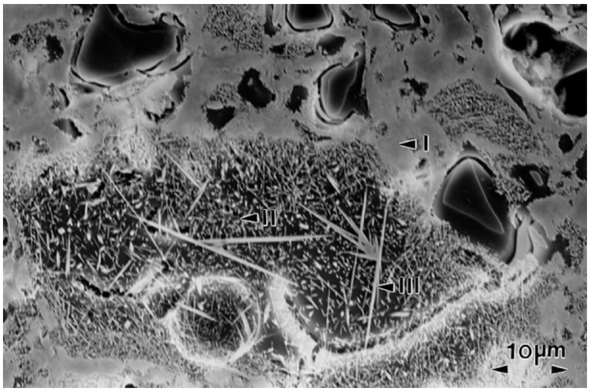

Fig. 2. Secondary electron SEM image of Wedgwood porcelain showing the 3 types of mullite.

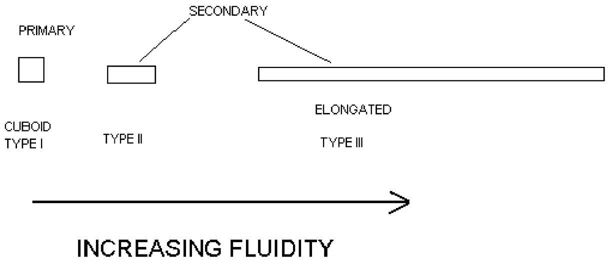

Fig. 3. Schematic diagram of mullite morphologies in porcelains.

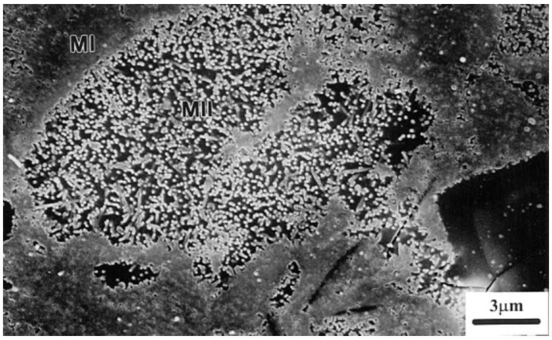

Fig. 4. Secondary electron SEM image of model porcelain fired to 1300°C containing secondary mullite predominantly as Type II(MII).

3.3. *Comparing commercial and model porcelains*

Fig. 4 shows the microstructure of a model porcelain fired to a similar temperature to the commercial sample of Fig. 2 and whose microstructural development on firing has been fully characterised.[5] The model porcelain contained many fewer elongated (Type III) mullites than the commercial porcelain and Fig. 4 indicates that the secondary mullite in the model porcelain is predominantly Type II. This suggests that the flux used in the commercial system is more effective since it has provided a more fluid liquid at equivalent temperatures enabling the secondary mullite needles to grow larger (Type III in commercial but only Type II in model porcelains). This highlights the important role of the flux in vitreous ceramic microstructures.

4. Conclusions

Forms of mullite occurring in typical porcelains are:

1. *Primary* mullite from decomposition of pure clay.
2. *Secondary* mullite from reaction of feldspar and clay and feldpar, clay and quartz. Additionally, in aluminous porcelains
3. *Tertiary* mullite may precipitate from alumina-rich liquid obtained by dissolution of alumina filler.

The size and shape of mullite crystals is to large extent controlled by the fluidity of the local liquid matrix from which they precipitate, and in which they grow, which itself is a function of its temperature and composition. The composition of this local liquid is determined by the extent of mixing of the porcelain raw materials and the role of the flux is critical.

Acknowledgements

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