O U R N A L O F

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Microstructural characterization of sanitaryware, the relationship spinel and mullite

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Sanitaryware reference industrial experimental compositions have been formulated, formed by slip casting and subsequently sintered in a laboratory electric furnace. Microstructural evolution was followed by HRTEM, BSE, X-ray diffraction and infrared spectroscopy. Thermal evolution of raw materials shows dehydroxylation of kaolinite, transformation to spinel and mullite, and transformation of α -quartz into β -quartz. Principal discussions are focused on the spinel and mullite evolution in the 900-1300 °C temperature range. Evidence of the phase trans formation from spinelto mullite were found in single crystals characterized locally by fast Fourier transformand lattice fringe d spacing accounting for the coexistence of nanometric mullite with the cubic spinel phase. Back scattered electrons (BSE) in topographic mode have been used to show the presence of the spinel type intergrowth plates within the sanitaryware microstructure. Aspect ratio calculations and interplanar analysis of the distances shows less characteristic planes of spinel as mullitization and vitrification progresses, mullite planes increase up to 1250 °C and decrease at 1300 °C.

Key words: Spinel, Mullite, Sanitaryware, Microstructure, Hrtem, Infrared spectroscopy.

Introduction

Stoneware used for sanitaryware manufacture is traditionally formed by slip casting a fine grained paste that renders a porosity of less than 0.5%. A common problem in this industry is a high rate of rejects up to 20%, mainly caused by flaws and porosity which can be related to the raw materials and processing conditions that impact on the microstructure of the final ware and in particular the presence of the crack stopper mullitic phaseevolution [1, 2]. In general large and bulky sanitaryware triaxial compositions are similar to those of vitreous tiles, although sanitaryware contains higher proportions of non-plastic clay, feldspar and quartz. Such higher compositions obviously require different processing conditions, i.e. higher firing temperatures and longer soaking times than tiles and this in turn leads to higher mullite contents in the final product [3, 4]. During the firing, kaolinite Al₂Si₂O₅(OH)₄ decomposes without change of its crystal shape, so the primary mullite firstly formed is pseudomorphic to kaolinite. Kaolinite undergoes a series of phase transformations upon heating in air [5]. Endothermic dehydroxylation occurs within 550-600 °C to produce disordered metakaolin Al₂Si₂O₇.

though continuous hydroxyl loss (–OH) is observed up to 900 °C [6, 7]. Further heating to about 980 °C converts metakaolin to a defect aluminum-silicon spinel, $Si_3Al_4O_{12}$, which is sometimes also referred to as a gamma-alumina type structure according to the reaction:

$$2Al_2Si_2O_7 \rightarrow Si_3Al_4O_{12} + SiO_2 \tag{1}$$

The spinel-type phase can be produced by a topotactic transformation of metakaolinite. Further heating causes the spinel phase $(Si_3Al_4O_{12})$ to nucleate and transform to mullite, $3 \text{ Al}_2\text{O}_32 \text{ SiO}_2[1, 5]$. It has been reported for triaxial bodies the alkalis migrate from the eutectic melt into the pseudomorphic mullite phase giving rise to secondary mullite that exhibits an idiomorphic crystal habit, forming long tiny needles within the liquid phase [8, 9]. This suggests that primary mullite crystals formed at the external surface of pure clay agglomerates could grow out and transform into secondary mullite crystals if they are near a liquid phase [4, 10]. The kaolinite mullite reaction series has been controversial for a long time (Brindley (1954) [11], Okada (1986) [12], Sonuparlak (1987) [6], Srikrishna (1990) [13], Carty and Senapati (1998) [1], Lee (1999) [10] and Chakraborty, (2003) [14] and one of the reasons for this is the small crystal size and poor crystallinity of the main phases involved. One of the issues often disputed is about the reaction mechanisms proposed for the 980 °C exothermic peak that has often

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been related to the complete decomposition of metakaolinite or to the formation of one or more of spineltype phases, amorphous silica and mullite phases [11, 14]. It is the aim of the present study to describe the phase relations encountered in sintered sanitaryware reference industrial compositions, placing particular emphasis on the application of high energy, high penetrating power of backscattered electrons and high resolution transmission electron microscopy (HRTEM) to disclose the relationship of the spinel-mullite nanostructures that may eventually influence the properties of ceramic triaxial compositions.

Materials and Methods

Sanitaryware reference experimental compositions were prepared out of clay, feldspar and quartz (50:40:10 wt %), the specimens were formed by slip casting and sintered in an electric furnace. Samples were fired up to 1300 °C at a 10 Kminute⁻¹ heating rate in an electric furnace. Microstructural evolution and phase transitions were analyzed by differential thermal analysis (DTA), infrared spectroscopy (IR), Raman spectroscopy, nuclear magnetic resonance (NMR), X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). DTA tests were carried out in a New Castle instrument Model Q600 running up to 1300 °C, at a 10 Kminute⁻¹, with 100 cm³minute⁻¹ nitrogen gas flow. In-situ shrinkage was recorded by a Theta dilatometer Model 3230, up to 1300 °C at a 10 Kminute⁻¹heating rate. The samples were dried for 48 h in air and then at 110 °C for 24 h in an electric furnace. Heating in the specimens was carried out with rates of 10 Kminute⁻¹, to 600, 1000, 1050, 1100, 1150, 1200, 1250 and 1300 °C and kept at the maximum temperature for 120 minutes and the cooling rates were also 10 Kminute⁻¹.

For SEM analysis, specimens were previously polished to a mirror surface by standard techniques and chemically etched with a 5% HF solution in order to dissolve the glass and reveal the mullite phase. A Jeol JSM-6400 SEM, at 15 kV coupled with an energy dispersive Xray spectrometry (EDS) detector (Bruker AXS Inc. XFlash 4010), was used for microstructural observations in order to distinguish the various phases and their chemical composition. 0.1 Micrometers sintered specimen thin sections were prepared by standard TEM polishing techniques for HRTEM examination on vitrified samples, using a Philips TECNAI 20 super Twin, at 200 kV. A TENSOR 37 series FT-IR (Bruker Optics Inc), was performed to obtain infrared spectra by ATR technique (with ZnSe crystal), spectra were accumulated over 64 scans at 2 cm¹ resolution. Deconvolution of peaks and the area bands in the spectra analyzed, was calculated by an Origin software peak-fitting module (Microcal Software, Inc.) and a PeakFit V4.00 software (AISN INC).

Results and Discussion

Identification of phases

Fig.1 shows DTA for an experimental sample sintered up to 1300 °C at 10 Kminute⁻¹. An endothermic peak at 150 °C, is due to the removal of physically adsorbed water followed by dehydroxylation of kaolin at 494 °C. The broad endothermic band around 580 °C is due to the $\alpha \rightarrow \beta$ quartz transformation. The exothermic peak at about 990 °C is due to the transformation of metakaolin to spinel-type structure and mullite according to the literature [1, 14]. The 1200-1300 °C endothermic effect during sintering is due to the formation of a liquid phase derived from the feldspar component in the intermediate stage of densification. It will be apparent that the DTA behavior is similar to published data on vitreous tiles except by the more pronounced DTA endothermic slope at vitrification temperatures due to the reportedly body higher liquid phase content, according with dilatometric study discussed in previous work [7].

Phase evolution for sanitaryware reference experimental compositions subject to increasing heating temperature can be systematically followed by IR, as shown in Fig. 2. Spectra present substantial band changes in intensity, width and position with temperature. The 3693, 3653 and 3620 cm⁻¹ triple peaks could be assigned to OH stretching arising from inner and inner surface OHbonds in the kaolinite; At the same time kaolinite exhibited the Si-O and Si-O-Al intense stretching bands lying at 1114 and 1004 cm⁻¹, as well as 912 cm⁻¹ attributed to Al-OH [15]. Two doublets bands at 1101, 1050 and 798,773 cm⁻¹ are assigned to quartz. The 1111, 1033, 1005, 779 and 719 cm⁻¹ signal correspond to anorthoclase feldspar. Up to 500 °C no significant changes are observed in the IR spectra. At 600C the bands at 3693, 3653 and 3620 cm⁻¹ are clearly modified and disappear due to dehydroxylation of kaolinite. On the other hand, the most intense band centered at 1034 cm⁻¹ reflects the increasing of Si-O-Si, Al-O-Al



Fig. 1. DTA for experimental sanitary ware sintered up to 1300 °C at 10 Kminute⁻¹.



Fig. 2. IR Spectra of experimental sanitary ware specimens fired at various temperatures for 30 minutes. Note dehydroxylation of kaolin at 600 °C, quartz dissolution at high temperatures and thermal phase evolution on the deconvoluted spectra (right).

bonds along with the formation of new Si-O-Al ones while the characteristic Al-OH vibration mode at 933-910 cm⁻¹ disappears. The formation of metakaolín is markedly weakened in accordance with typical XRD measurements. Asymmetric stretching vibrations of Si-O bonds in the SiO₄ network at 1070-1030 cm⁻¹ are attributed to the glass phase at 1100 °C. The shoulder around 940 cm⁻¹ can be ascribed to symmetric stretching vibrations of Si-O bonds, while that at 750-790 cm⁻¹ corresponds to the symmetric vibrations of the Si-O-Si or Si-O-Al bonds according with the literature [16-19]. Characteristic mullite bands also appear at 1100 °C, for the 1131, 994 cm^{-1s} spectral region corresponding to the tetrahedral Aliv-O bands. At 1150 °C, the major change in the spectra corresponds to the decrease of the 1034 cm⁻¹ absorption for the disolution of quartz. After the thermal treatment at 1200 °C, as may be seen by the same figure, sanidine bands decrease their intensity and are slightly displaced toward higher wave number reflecting the increasing liquid phase. The increasing amount of glassy phase can be seen by the increasing intensity on asymmetric stretching vibrations for the Si-O-Si bonds at 1074 cm⁻¹.Deconvoluted bands for the mullite show an increasing amount of the mullite phase up to 1250 °C. A higher definition of the bands is observed at 1250 °C, which turned out to be secondary mullite. The partial dissolution of mullite in the liquid phase at 1300 °C is denoted by a decrease in intensity of the mullite bands, according whit DRX and SEM analysis. This effect is important since 1250 °C is a key temperature that corresponds to a turning point in physical properties (showed in fig.3). The increasing amount of glassy phase can be seen by the increasing intensity of the asymmetric stretching vibrations for the Si-O-Si bonds at 1074 °Ccm⁻¹.

Mechanical Properties

Fig. 3 shows the temperature dependence of bulk density, rupture modulus (*MOR*) and microhardness (HV) during the intermediate and final sintering stage. It is seen that maximum values of bulk density, MOR



Fig. 3. Temperature and time variation of the bulk density, rupture modulus (*a*), apparent porosity andmicrohardness (b), during sintering process.

and HV are reached at 1250 °C (e.g. 2.39 g/cm³, 40.57 MPa and 693 HV respectively) and decrease at higher temperatures. The increment of the temperatures at 1250 °C led to an increase in the properties. This increase can be explained by a decrease of the porosity and the increment in acicular mullite. Bending strength depends on the crystalline phase content and is directly related to the increment of mullite and glass. Bloating also occurred at higher temperatures and led to an elevation of the apparent porosity and a decrease in the density and rupture modulus. Linear contraction, rupture modulus and bulk density were also maximized at 1250 °C and 120 minutes, this temperature and time was considered to be ideal to obtained optimum firing profile reported in previous work [7]. Between 1100 °C and 1150 °C a considerable decrease in the porosity



Fig. 4. a) SEM image taken from a large specimen area, densified up to 1100 °C and subject to the glass dissolving action of HF. b) SEM image at 1150 °C attacked with HF. Is seen in the figures residual porosity, quartz (Q), primary mullite (PM), secondary mullite (SM) and a vitreous matrix (VM).



Fig. 5. Secondary and backscattered electron micrograph composite image for sanitary ware specimen fired at $1150 \,^{\circ}$ C. (a) clay relict within the general sanitary ware composition, (b) clay relict higher magnification, showing large and fine scale globular mullite. (c y d) Is a COMPO and TOPO BSE modes of the globular area. Note the coexistence of fine scale globular mullite with spinel plates (single crystals) at 60 $^{\circ}$ to each other (dark area).

occurs, coinciding with the beginning of vitrification. A considerable decrease in the porosity therefore also begins. At 1250 °C the bodies become more vitrificated and the pores close, and the porosity decreases significantly.

Spinel to mullite phase transformation

Fig.4-a, is a SEM image taken from a large specimen area, densified up to 1100 °C and subject to the glass dissolving action of HF; it shows residual porosity, quartz (Q), primary mullite (PM) and a vitreous matrix (VM). Pure clay relicts at 1100 °C contained small globular mullite crystals, while clay-feldspar relict regions contained longer mullite crystals. In fig. 4-b at 1150 °C, formation of γ -Al₂O₃ and primary mullite was observed in pure clay relicts, according with high resolution transmission electron microscopy results, while in feldspar-fluxed regions, acicular mullite crystals were more developed. Is demonstrated that mullite crystals grow from the outer surface of the clay relict into the glass matrix, suggesting that primary mullite may act as a seed for the nucleation of secondary mullite as discussed also by Schneider [8, 9].

The relict at 1150 °C showing in the micrograph of fig. 5-a presents a submicron horizontal stratum that contains even finer globular primary mullite. Fig. 5-b is micrograph at higher magnification at 10,000 X. Fig. 5-c is a SEM image in a compositional backscattered electron signal mode (COMPO-BSE) in the same area and Fig. 5-d is a topographic backscattered electron signal mode (TOPO-BSE). BSE signals shows very fine detail, of globular mullite arranged in hardly resolved lines that run diagonally against the gray background of the picture. In addition, the spinel phase is strikingly seen forming plates like precipitates at 60 ° on the upper part of the micrograph which is rendered visible by the higher penetration power of the backscattered electrons. Such precipitates may align energetically favorable low index spinel planes in a similar arrangement that is commonly seen in other cubic systems.

Microstructure details in the glassy matrix and crystalline phases were studied by TEM and HRTEM as shown in fig. 6 and 7. The TEM bright-field (BF) imaging in fig. 6 reveals that the acicular mullite crystals (AM) at 1150 °C. The AM crystals were randomly oriented and dispersed in a glassy matrix that was evidenced by the diffusive halo in the corresponding selected-area electron diffraction pattern (SADP) shown in the Fig. 7. In this study, mullite crystallized almost simultaneously with spinel phase formation, according with the results in HRTEM (images in fig. 7 and 8). The existence of nanocrystals of spinel and mullite were found disseminated within the glassy phase. Measured interplanar distances at 1100 and 1150 °C, correspond to the (040), (130), (311) and (321) planes for the mullite orthorhombic structure (JCPDS No 15-776) and (400), (440) and (220) plane for ã-alumina (JCPDS No 29-0063). From these micrographs it is clear that the spinel phase exhibits lightly distorted pseudo hexagonal habit and the characteristic spinel (220) planes gradually changed into an orthorhombic mullite structure in which the (130), (311), (321) and (040) planes are clearly seen. Lattice fringes of mullite have strong contrast with their predominant spacings of about 1.9-2.8 Å. By contrast the spinel phase (JCPDS No 29-0063) exhibits



Fig. 6. Bright-field TEM image showing the acicular mullite crystals (AM) in glass matrix at 1150 °C.



Fig. 7. HRTEM sample sintered at 1100 $^{\circ}$ C, showing mullite and γ -alumina (dark contrast) immerse in the porcelain glassy matrix (light areas). FFT inset shows (400) γ -alumina and (040), (311) and (321) mullite planes crystallizing out of the glass at 1100 $^{\circ}$ C.

an average of 1.97 Å out of 20 fringes in 15 different images. The spinel-type phase differs from mullite by its weaker contrast and smaller grain size, about 5 nm in diameter. These lattice fringes that generally belong to rounded spinel grains were seen to be connected to the mullite fringes (see Fig. 7). The upper right side of the fig. 7 shows an FFT of the whole micrograph from which weak intensity rings show poorly crystalline spinel and mullite phases. Analysis of interplanar distances in different zones, shows less characteristic planes of spinel as mullitization progresses, mullite planes increase up to 1250 °C and decrease at 1300 °C, according whit SEM and IR spectra.

Fig. 8 HRTEM sample sintered at 1150 °C, showing the coexistence of spinel and mullite phases, the upper part of the figure is mullite, the lower part is spinel. The mullite crystals thus formed tend to have texture in that the c-axis lies out of the plane. This is understandable in terms of the fact that metakaolinite consists of sheets of alumina and silica tetrahedra and the mullite forms on these sheets. The c-axis is the smallest dimension of the mullite unit cell. Therefore,



Fig. 8. HRTEM sequential images showing the spinel to orthorhombic mullite phase transformation on a single crystal. (a) Large view of mullite single crystal; (b) High resolution area, single crystal exhibiting phase transformation i.e. a globular spinel at the lower part of the crystal and growing acicular mullite at the upper part; (c) High resolution area of the gradual lattice transformation of mullite, (c-1) marked area, (c-2) corresponding FFT and (c-3) inverse FFT from the marked area; and (d) High resolution area at the low part of the crystal, (d-1) marked area, (d-2) corresponding FFT and (d-3 and d-4) inverse FFT's from the marked area.



Fig. 9. SEM images showing microstructure of a triaxial ceramic body. a) HF etched sample at 1200 °C disclosing porcelain phases: quartz (Q), vitreous matrix (VM), primary (PM) and secondary mullite (SM); b) higher magnification, showing large and fine scale globular mullite immerse in vitreous matrix. (c) HF etched sample at 1250 °C disclosing secondary mullite (SM); (d) SEM image sample at 1300 °C showing bloating effect. Note the coexistence of fine scale globular mullite with a 2/1 of the Al₂O₃/ SiO₂ content and secondary mullite with approximately 3/2.

energetically it would be favourable for it to lie perpendicular to the plane of the meta-kaolinite sheets.

The SEM micrograph confirms the formation and the dissolution of secondary mullite in etched specimens with HF at higher temperatures. Fig. 9 shows SEM images of an etched polished section of ceramic bodies sintered at 1200 °C, 1250 °C and 1300 °C. Fig. 9-a shows a quartz, granular (primary) mullite, which is seen to form in the clay particles subsequently

becoming seeds for acicular mullite growth showing in Fig. 9-b at upper amplification. Semiquantitative EDS revealed that the Al_2O_3 : SiO₂wt% ratio for primary (MI) mullite was 2 : 1 (Fig. 9-b); for secondary mullite, the ratio was 3 : 2 (Fig. 9-c). The dissolution of mullite is confirmed by the aspect ratio of the mullite acicular crystals. The acicular crystals aspect ratio increases considerably at 1250 °C whit an approximately aspect ratio of 18. Finally at 1300 °C, the mullite dissolution is observed showing aspect ratio of 10. This dissolving effect of mullite into the glass and therefore the partial disappearance of the mullite reinforcing phase may bring about a detrimental effect on the physical properties of porcelain. Fig. 9-d shows large rounded pores within the microstructure due to the onset of bloating in specimens fired up to 1300 °C.

Conclusion

The application of HRTEMfast Fourier transform and d-spacing fringe measurements on nanocrystalline regions allowed to observe the spinel to mullite gradual transformation within single crystals immersed in the glass phase of triaxial compositions at vitrification temperatures. High energy backscattered electrons on the topographic mode proved useful to image cubic spinel crystallographic plates at 60 ° to each other on the micro scale. That findings may help to better understand the nature of the coexistence of the spinelmullite phases at temperatures higher than the 980°C exothermic peak as well as to confirm the existence of the cubic spinel single crystals in kaolin derived triaxial ceramic systems. Analysis of interplanar distances shows less characteristic planes of spinel as mullitization and vitrification progresses, mullite planes increase up to 1250 °C and decrease at 1300 °C.

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