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Journal of the European Ceramic Society 24 (2004) 2067–2072
www.elsevier.com/locate/jeurceramsoc

Design and development of a chamotte for use in a low-clay translucent whiteware

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Received 8 November 2002; received in revised form 13 May 2003; accepted 25 May 2003

Abstract

In the design of a translucent whiteware it was intended to combine the best features of bone china and hard porcelain, i.e. to be aesthetically pleasing and to have the resistance to edge chipping of the former with the scratch resistance of the type of glaze used on the latter. The design envisaged producing a whiteware from two chamottes, each having the same composition but with different median particle sizes, and only a small amount of clay (~10 to 15%) to minimise the firing shrinkage and its anisotropy. In the design of the chamotte composition, anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) was selected to be the major phase and mullite ($3Al_2O_3{\cdot}2SiO_2$) and glass the minor phases. A further design requirement was to have high crystalline ($\geqslant$70%) and low glass ($\leqslant$30%) contents to enhance the fracture toughness of the whiteware. Anorthite was chosen as the major phase because its refractive index would be similar to that of the glass phase, which enhances translucency, and its thermal expansion coefficient (TEC) allows the TEC of the whiteware to match that of some glazes made with high-silica contents. Mullite was found to reduce sagging during glost firing.

Keywords: Anorthite; Mullite; Prefiring; Translucent whiteware; Whiteware

1. Introduction

A novel whiteware for use in high-quality hotels and restaurants has been designed and made using a low-clay content.[1–3] The clay content was kept low, at ~10 to 15%, to minimise the deleterious effects of anisotropic firing shrinkage that occurs in conventional whitewares[4,5] as a consequence of the clay particles becoming preferentially aligned during forming and spray drying. The replacement of part of the clay was effected by introducing a prefired body, i.e. a chamotte. In fact, in the present case two chamottes having different median particle sizes but the same composition were used: one was coarser with a median size of ~10 μm and the other finer at ~1.5 μm. Together with the micron to submicron clay these chamottes produce a well-packed body to reduce firing shrinkage. A typical composition might be 50% coarse chamotte, 38% fine chamotte and 12% clay. This paper deals with the compositional design of the chamotte.

The novel whiteware was designed to combine the best features of bone chinas and hard porcelains, i.e. to be aesthetically pleasing and to be suitable for severe service conditions. Both bone china and hard porcelain are white and translucent. Bone chinas are highly crystalline materials[6] which are resistant to edge chipping.[7] Strengths (MORs) of ~100 MPa[6,8] and a fracture toughness of ~2 MPa $m^{1/2}$ (Ref. [9]) have been measured. Unfortunately, the glazes used on bone chinas tend to be more easily scratched than those on hard porcelains. Hard porcelains are highly glassy and their edges tend to chip easily. They are expected to have lower toughness values and strengths than bone chinas: a K_{1c} value of ~1.2 MPa $m^{1/2}$ (Ref. [9]) has been measured and reported MORs are typically in the range 39 to 69 MPa.[8] However, the glazes on hard porcelains, which are rich in silica, are both chemically highly durable and abrasion resistant. Hence, the novel whiteware needed an appearance comparable with bone chinas or hard porcelains, to be chip resistant like bone china and to be

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0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00359-5

coated with a glaze similar to those applied to hard porcelains.

2. Design requirements for the chamotte

The coarse and fine chamottes form up to ~90% of the whiteware. Consequently, for the whiteware to be very white and translucent the chamottes must be very white and translucent. To allow the novel whiteware to have comparable toughness and strength to bone china, it was considered that the chamotte should be highly crystalline, i.e. have a low glass content, and the chamottes and whiteware should have low porosities. This is because glasses have low K_{1c} values in the range 0.7–0.9 MPa $m^{1/2}$ (Ref. [10]) and porosity reduces K_{1c}.[11]

The whiteware should be resistant to sagging at the temperature required to glaze it (glost firing). Since the glaze is likely to be rich in silica, so that it is resistant to being scratched, the glost temperature is likely to be greater than ~1250 °C and possibly up to 1350 °C. As an assumption, it was considered that resistance to sagging would require the coarse chamotte to resist deformation during glost firing.

3. Concept design for the chamotte

As a first approach it was considered that the chamotte should be composed mainly of anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) with glass present as a minor phase to effect densification. Anorthite has properties that should allow many of the design requirements of the whiteware to be met.

Anorthite has a refractive index of 1.58,[12] which is expected to be close to that of the glass phase at ~1.5. This should facilitate the attainment of translucency for the chamotte and the whiteware provided both can be made dense.

To make a translucent chamotte that is very white requires the colouring impurities in the starting materials to be at low levels. The starting materials also needed to be cheap. It was considered that these requirements could be met by making the chamotte by a mixed-oxide approach from low iron and titanium containing limestone ($CaCO_3$), quartz (SiO_2) and aluminium trihydroxide ($Al(OH)_3$) (Table 2). The limestone and quartz, as minerals, are cheap. Although aluminium trihydroxide is a chemically refined material it is fairly cheap because it is made in vast quantities in the Bayer process in which aluminium is made from bauxite. By making chamottes rather than final bodies from the starting materials, the high shrinkage and porosity caused by evolution of CO_2 and H_2O would not be a problem.

It was proposed to produce dense, well-reacted chamotte particles by a combination of mixing, firing and milling. The starting materials would be mixed in a mill to disperse agglomerates and reduce the sizes of the particles. This is to reduce the distances ions have to diffuse during calcination for the starting materials to interact fully. The mixture should be fired so that the finer pores shrink and vanish even if this causes the growth of the larger pores. When the chamotte is milled, growing cracks will be attracted towards the larger pores, so that the milled particles should be denser than the unmilled product.

Anorthite has an average thermal expansion coefficient (TEC) of $\sim 4.3\times10^{-6}/°C$.[13] This should allow the whiteware to have a TEC that matches that of the glaze.

Sagging behaviours during the densification and glost firings, if these are carried out separately, are not well understood. Clearly, a liquid phase is required during sintering to effect densification but this will also allow the whiteware to deform under its own weight by facilitating the slippage of the crystalline grains past one another. An experimental study was required to find a chamotte composition that would densify well but would be resistant to sagging in at least the glost firing.

4. Compositional development of the chamotte

4.1. Experimental trials

In preliminary studies, it was found to be necessary to add magnesium to the starting materials to produce fired materials that would densify and become translucent. It was added in the form of $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$. It has been shown by using the FACT[14] program (Facility for the Analysis of Chemical Thermodynamics) for the compositions examined in the $MgO–CaO–Al_2O_3–SiO_2$ system, that magnesium resides wholly in the liquid phase at the sintering temperature.

Given that a dense, white, translucent body ought to be produced with an anorthite/glass mixture made with starting materials having low contents of colouring impurities, a chamotte composition was sought that would result in the whiteware sagging little during glost firing. As an assumption, it was considered that this would require the coarse chamotte to resist deformation during this firing. Consequently, the sagging behaviours of prefired test-bars prepared with different compositions were examined. These compositions are given in Table 1.

The starting materials had the compositions or impurity contents shown in Table 2. The Loch Aline quartz was finely ground with a median particle size of ~2.4 μm. The limestone was supplied by Redland Minerals Ltd. It was a coarsely agglomerated powder with a median particle size of ~5 μm. The aluminium trihydroxide was supplied by Alcan (DH 101 grade) and was coarsely agglomerated. This material was batched

Table 1
Nominal compositions and sagging values of chamottes

Codes	$CaCO_3$ (%)	$Al(OH)_3$ (%)	SiO_2 (%)	$MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ (%)	Amount of mullite[a] (%)	Amount of sagging (mm)
M-1	25.28	35.21	37.25	2.26	–	6.3
M-2	25.00	38.90	33.60	2.50	–	11.4
M-3	24.40	38.05	32.85	4.70	–	12.8
M-5	23.50	37.75	34.20	4.55	–	6.2
M-6	20.40	39.30	37.90	2.40	6.9	1.2
M-7	20.15	39.60	37.90	2.35	7.7	1.0
M-8	19.95	39.85	37.85	2.35	8.4	0.9
M-12	19.70	40.35	37.60	2.35	9.5	0.8
M-16	19.35	40.35	37.95	2.35	10.1	0.7
M-14	19.55	41.00	37.15	2.30	10.6	0.6
M-17	19.35	40.60	37.70	2.35	10.4	0.5

[a] Mullite content computed at 1350 °C using the FACT program.

Table 2
Chemical composition of raw materials

Chemical species (%)	Limestone	Aluminium Trihydroxide	LA quartz
SiO_2	0.24	0.01	99.6
Al_2O_3	0.04	65.0	0.10
Fe_2O_3	0.02	0.008	0.03
TiO_2	0.00	0.00	0.01
CaO	55.9	0.02	0.01
MgO	0.19	0.00	0.01
K_2O	<0.01	0.00	0.01
Na_2O	<0.03	0.25	0.01
Combined H_2O	0.00	34.5	0.00
L.O.I	43.6	0.05	0.00

The magnesium carbonate hydroxide pentahydrate had no cationic impurities in higher concentration than the detection limits.

as-received to produce chamottes, but for the test-bars for the sagging trials it was heated to 250 °C prior to batching to remove the water. The magnesium was in the form of magnesium hydroxide carbonate and was supplied by Merck.

Batches of 1 kg of starting materials were wet mixed/milled for 3 h in a 5-l porcelain pot containing 70 alumina balls ~15 mm in diameter. The powder was mixed with 1.3 l of water. After mixing, the slurry was dewatered in plaster of Paris sinks and subsequently oven dried at 110 °C. The powder cakes were broken up in a porcelain mortar with porcelain pestle to form a powder. This was granulated by first spraying with a fine mist of water droplets and then by agitating the damp powder. The granulated powder was shaken on a sieve with a 700 μm aperture and the granules that passed through were retained for use. The oversized granules were broken up, re-granulated and sieved.

To produce the chamottes, the sub 700 μm granules were poured into alumina crucibles but not compacted. The loosely packed material was fired at 1350 °C for 3 h to form friable cakes. A Lenton Thermal Design (UK) Ltd. chamber kiln was used. This was heated at 3 °C/min. to the soaking temperature by silicon carbide elements. The calcined cakes shrank away from the sides of the alumina crucibles and did not stick to the crucible bases. The cakes were first broken-up by rubbing one cake against another. The coarse powder produced was crushed using a porcelain pestle in a porcelain mortar and powder passing through a 250 μm aperture sieve retained for milling to produce the coarse and fine chamottes.

Samples of some compositions were given heat treatments with higher temperatures but with considerably shorter soaking times. Such heat treatments would be appropriate for a commercial manufacturing process using a rotary kiln. To observe whether such an approach would be feasible, the chamotte material was fired in contact with high-alumina, refractory brick, of the type used to line rotary kilns, to see whether it would react and adhere.

Some calcined granules were mounted in epoxy resin to be ground and polished to see whether the mixing/milling and heat treatment had produced material from which it would be possible to produce dense particles of a sufficiently large size on milling to make the coarse chamotte. The specimens were polished using 6, 3 and 1 μm diamond pastes after being ground on silicon carbide papers. Specimens were examined using optical microscopy. The crystalline phases were revealed by etching in a 5% HF solution to remove the glass phase followed by examination using scanning electron microscopy with a CAMSCAN microscope.

To check whether the starting materials had been fully consumed during calcination, the calcined material was X-rayed. Powdered calcined samples of the chamottes were scanned from $2\theta = 5$–70° at 1°/min using RIGAKU 2000 DMAX diffractometer in $Cu_{K\alpha}$ radiation. The diffractometer was calibrated with a silicon standard before use.

To produce the test-bars for the sagging trials, moist granules of the starting materials, made with reactive alumina, were pressed at 40 MPa in a steel die to produce rectangular bars 120 mm×20 mm×3.5 mm. These bars were fired at 1350 °C for 3 h, in the Lenton chamber kiln, supported on beds of alumina powder. They were then refired at 1280 °C for 3 h supported only at their ends with their central spans, 85 mm long, unsupported. The sagging was measured by positioning an accurately ground steel bar 85 mm long symmetrically against the test-bar and measuring the maximum gap between the test-bar surface and the steel bar.

Some discs 31.5 mm in diameter and 3 mm thick of a few of the compositions in Table 1 (M3, M5, M6, M17) were pressed at 40 MPa using the starting material batch made with as-received aluminium trihydroxide. These were fired at temperatures from 1320 to 1420 °C with soaking times of 3 h to see how the materials densify. The densities after firing were determined from the

volume of the discs and their masses. The volumes were calculated from the diameters and thicknesses measured with a micrometer to ±0.02 mm and the masses measured using an electronic balance with a precision of 0.0001 g.

The thermal expansion coefficient of one chamotte (M17) was measured relative to fused silica using an in-house constructed dilatometer. Dense cylindrical rods were made using the technique of Jarcho et al.[15]

The colours of some chamottes and two commercial bone chinas were compared using a Lambda 2 spectrometer (Perkin-Elmer Co.) in the reflection mode with a light source, D_{65}, that approximates to average daylight. The spectrometer operates on the CLAB colour space system[16] in which the colour descriptors are Δa^* and Δb^*. The equipment measures the differences in the indices ΔL^*, Δa^* and Δb^* between the object and a white standard, where ΔL^* compares the brightness values.

4.2. Results

The results of the sagging trials are shown in Table 1. The compositions up to M5 did not form mullite and in those from M6 to M17 mullite developed. This is predicted using the FACT program.

An X-ray trace, Fig. 1, for M17 shows the presence of mullite and a polished and etched specimens of M17, Fig. 2, shows the presence of mullite needles. In the x-ray trace for M3, no mullite peaks are observed (Fig. 1) and in a polished and etched section, Fig. 3, no mullite needles were seen.

Quantitative x-ray analysis was carried out on M 17.[17] It was found that this material contained

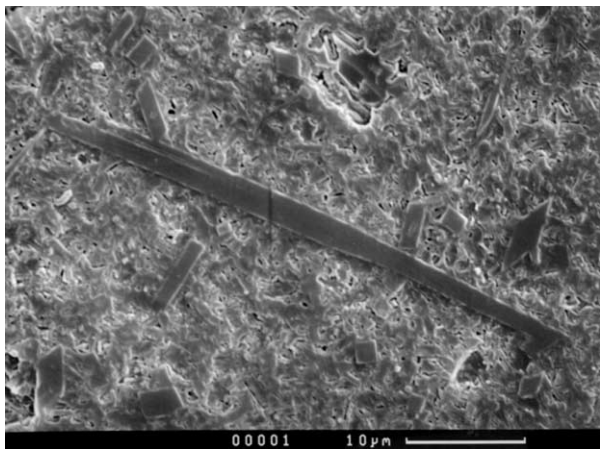

Fig. 2. The microstructure of M-17 composition at 1350 °C.

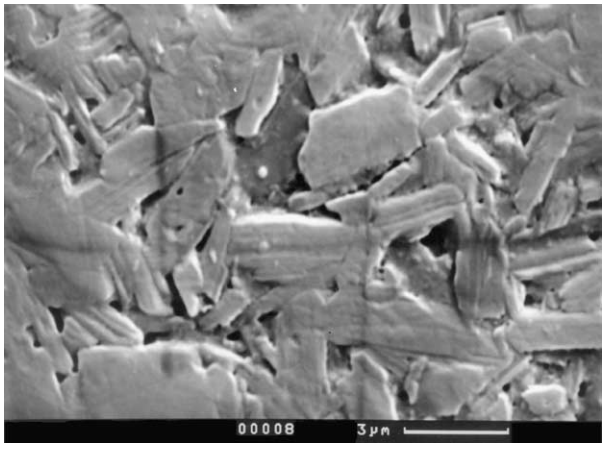

Fig. 3. The microstructure of M-3 composition at 1350 °C.

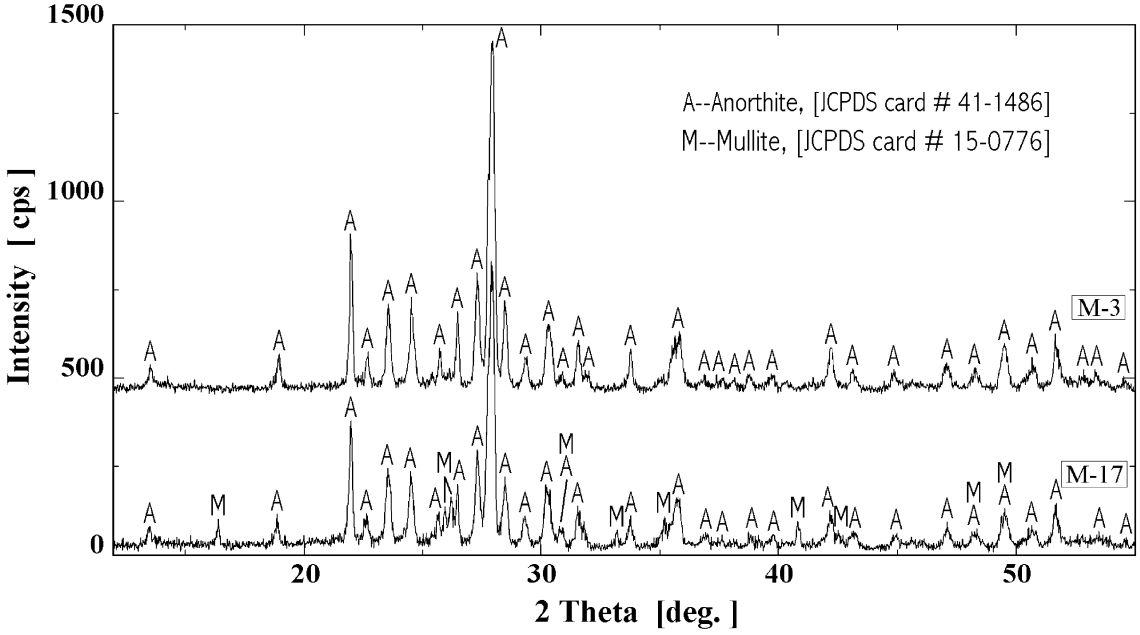

Fig. 1. XRD traces of M-3 and M-17 compositions showing anorthite and mullite formation labelled as A, M, respectively.

~76% anorthite and ~8% mullite with the remainder being glass.

The densities and shrinkage values for discs of M3, M5, M6 and M17 are shown in Fig. 4.

In Fig. 5, the pore structure of granules of M17, calcined at 1350 °C for 3 h, is shown.

The average thermal expansion coefficient of M17 chamotte over the temperature range 50–850 °C was estimated to be $\sim 4.5\times10^{-6}$/°C.

The colour difference map for four chamottes and two commercial bone chinas is shown in Fig. 6.

4.3. Discussion

From studies on sagging during refiring at 1280 °C (Table 1) and from the densification behaviour (Figs. 4 and 5), it appeared that the M17 composition combined low sagging with good densification and so was chosen for the chamotte composition.

Although sagging behaviour is not well understood, it appears that sagging during refiring is strongly reduced if mullite needles form. These randomly positioned and orientated needle-shaped crystals appear to impede the deformation of the chamotte under its own weight. From the predicted equilibrium mullite content from the FACT program, it appears that this impediment increases with mullite content increasing. No mullite should form in compositions M1–M5, which sag substantially. Composition M3 is an example from this group and both X-ray data and scanning electron microscopy are in accord with the prediction of no mullite formation.

The M17 chamotte densified well at 1350 °C with a 3 h soak, although the material was not significantly overfired to some 30 °C higher, as shown in Fig. 5. The finer pores appeared to have been removed from the granules fired at 1350 °C for 3 h so that essentially pore-free particles for the coarse chamotte should be produced by milling. It was demonstrated that a similar result could be obtained using a heat treatment of

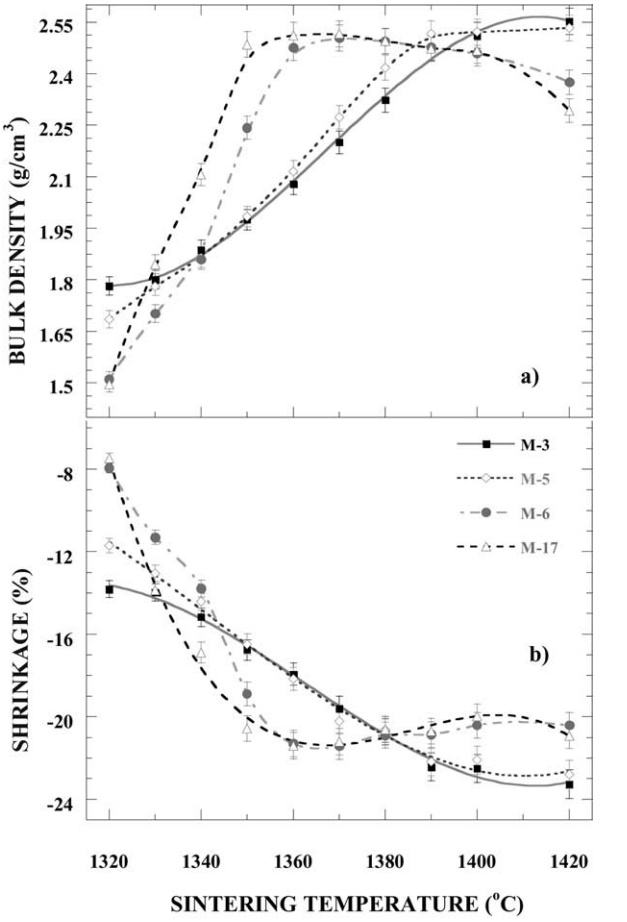

Fig. 4. (a) Densification behaviour of chamottes. (b) Shrinkage behaviour of chamottes.

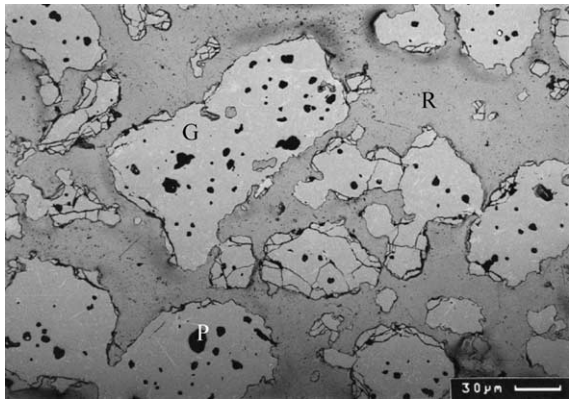

Fig. 5. The pore structure of granules of chamotte sintered at 1350 °C for 3 h and embedded in resin. G, P, R indicate granule, porosity and resin, respectively.

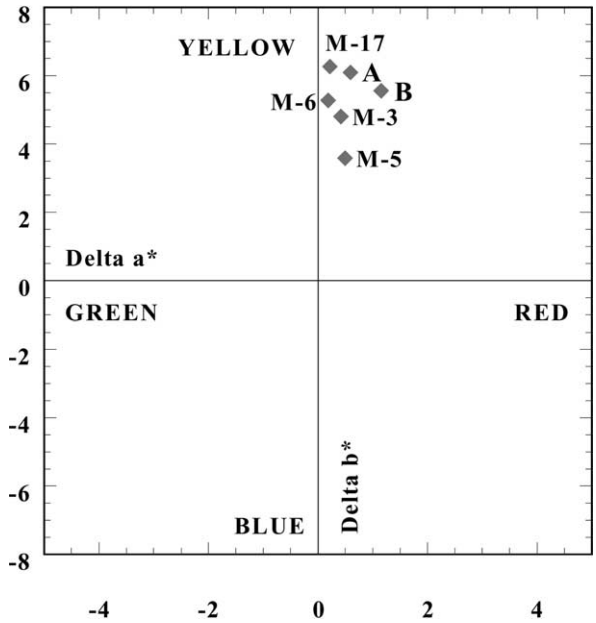

Fig. 6. The colour difference map for various chamottes and commercial bone china products A and B.

1415 °C for 15 min. It was found that mixtures of the starting materials fired at this temperature in contact with high-alumina brick did not noticeably react or adhere to the brick. This heat treatment would be suitable for calcination to be carried out in a rotary kiln lined with high-alumina brick for commercial production. It is envisaged that a mixed/milled slurry of the starting materials in water could be pumped into a rotary kiln in a manner similar to that used for making barium and strontium hexaferrites.

The M17 chamotte was found to have a colour similar to bone china as shown in Fig. 6. This has allowed whitewares made with M17 to have an appearance similar to that of bone china.

The TEC of the M17 chamotte, of $\sim 4.5\times10^{-6}/°C$, has allowed whitewares made with this chamotte to have a TEC that matches certain high-silica glazes.

5. Conclusions

A chamotte produced from cheap starting materials using a mixed-oxide route has been designed that enables all the chamotte requirements to be met. It has been shown that it should be possible to produce this calcined material in a rotary kiln. The chamotte has anorthite as its major phase (~76 wt.%) with mullite (~8 wt.%) and glass (~16 wt.%) as minor phases. Whitewares made with the chamotte have a similar appearance to bone china and a TEC that allows high-silica glazes to be applied. The glass phase allows the body to be densified to yield a translucent material. The mullite crystals act as creep inhibitors.

Acknowledgements

The authors would like to acknowledge the help given by Dr. A. Watson of Leeds University for calculations using the FACT thermodynamic program.

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