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Phase analysis and microstructure evolution of a bone china body modified with scrap addition

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Abstract

Properties of a commercial bone china body containing varying amount of fired scrap of same material (0–12%) was studied and attempt was made to correlate the same with respect to phase analysis and microstructural evolution. Despite numerous studies on bone china by several authors, knowledge is still insufficient about the chemical reactions taking place among the various raw materials leading to very narrow firing range. In commercial production of bone china wares, loss during biscuit firing is significantly high. In this study attempt has been made to utilize a portion of the fired scrap in a commercial bone china composition and the effect of the same on the formation of the constituent phases has been tried to correlate with the properties developed. Phase analysis of the matured specimens revealed that there was gradual decrease in β-Tri calcium phosphate (β-TCP) content while increase in glassy phase was observed with progressive incorporation of scrap. Scrap incorporated body resulted in early maturity of the specimens as well as development of a very dense microstructure. Presence of scrap did not alter the anorthite phase content. The microstructure consisted of distinct regions of agglomerated spheroidal β-TCP and lath shaped anorthite crystallites in a heterogeneous calcium aluminosilicate glassy matrix.

Keywords: Scrap; Anorthite; β-Tri calcium phosphate

1. Introduction

Bone china is a highly specialized product whose properties critically depend on the quality of the raw materials used. This is also to be kept in mind that selection of raw materials and their proportions particularly the bone ash, processing parameters particularly firing atmosphere, maximum temperature attained and the soaking time have strong influence in the development of microstructure which in turn influence the ultimate thermo-mechanical properties of the products. In this process it must be considered the kinetic limitations, development of the phases and complexities of the microstructure. The appealing characteristics of bone china are in its whiteness, translucency, highly lusterous glaze and decoration capability coupled with high strength. Such attractive combination of properties enables bone china as one of the world's most attractive and expensive types of tableware. Despite the fact that bone china wares have been manufactured for the last 200 years there is still controversy concerning the chemical reactions that take place during biscuit firing.

The typical composition of a modern commercial bone china is 25 wt% clay, 25 wt% fluxing material and 50 wt% bone ash [1,2]. However, in actual production units the compositions vary from plant to plant. Clay minerals are introduced as white burning kaolins which provide the desired plasticity for shape forming. Potash feldspar is commonly used as a flux. Bone ash (cattle bones after processing are calcined at around 1000 °C) consists predominantly of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$. It may be noted that poorly calcined bone impairs the rheological properties of the slip and may lead to both a reduced firing range and increased fired porosity [3]. Bone ash in bone china bodies decomposes into β-tricalcium phosphate $[Ca_3(PO_4)_2]$, lime (CaO) and water (H_2O) at around 775 °C via the reaction [4]

$$Ca_{10}(PO_4)_6(OH)_2(s) \rightarrow 3\beta\text{-}Ca_3(PO_4)_2(s) + CaO(s) + H_2O(g) \quad (1)$$

Lime reacts with meta kaolin from clay relicts to form anorthite $[CaAl_2Si_2O_8]$ via the reaction

$$Al_2O_3{\cdot}2SiO_2(s) + CaO(s) \rightarrow CaAl_2Si_2O_8(s) \quad (2)$$

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St Pierre [5] showed that bone china may be represented by a ternary system of $Ca_3(PO_4)_2$–$CaAl_2Si_2O_8$–SiO_2 with a eutectic at 11% tricalcium phosphate, 51% anorthite and 38% silica with a melting temperature of 1290 ± 5 °C. However, in practice, equilibrium is never attained in commercial bone china products because specimens fired slowly to temperatures above 1250 °C sag and are commercially useless. Sagging or deformation again depends on the firing schedule as well as geometry of the body [6].

Production of bone china ware has never been an easy process and the body requires close control of a number of processing parameters. A significant constraint is caused by the narrow vitrification range, generally of the order of 15–25 °C. In this respect, the biscuit firing temperature is critical and needs to be carefully controlled. The firing schedule of commercial bone china bodies varies from manufacturer to manufacturer and depends very much on location of ware in the kiln as well as on the type of kiln [4]. In actual practice biscuit firing is carried out at a temperature in the range of 1220–1260 °C with around 3 h of soaking at the peak temperature [1,7]. The firing schedule may vary from 13 to 17 h depending on the raw materials used and their relative proportions [8,9]. Firing temperature and soaking time are the two most important parameters [10–12] for controlling the translucency in the unglazed bone china wares. A temperature in excess of 20 °C above the optimum maturing temperature can lead to over firing and distortion of the wares. In commercial production biscuit firing loss due to deformation of wares may go up to 20% or even more unless stringent quality control measure is taken in every processing stage. In order to obtain a longer firing range without impairing the quality of bone china it is suggested to use higher proportion of bone ash at the expense of china clay in the composition. However, this will reduce the plasticity of the mass, thereby making the shaping operation even more difficult. In any case substantial quantity of biscuit fire loss is experienced in commercial production which in turn causes loss in raw materials, energy and manpower.

Recycling of scrap or production waste has become very important as a result of increased production leading to generation of more wastes and their impact on the environment in general. The possibility of recycling wastes allows the achievement of important goals related both to storage of raw materials as well as safeguarding the environment. The incorporation of wastes into the mix composition involves at least two environmental advantages: first, reuse and/or recycling partly solve disposal problems, and second, the consumption of natural raw materials is reduced. Traditional ceramic bodies such as tiles and bricks essentially have a wide range in composition and such products can tolerate the presence of different types of waste materials rather well, even at higher percentages [13,14]. Pagani et al. [15] recommended the use of vitreous china scrap in sanitaryware production. However, bone china has a very typical composition and slight variation of body composition may cause deleterious effect on the ultimate properties of the product and may led to production of wares of no commercial value. The present study is directed towards determining the possibility of incorporation of fired scrap from the same production unit in the body composition and to understand the effect on green as well as fired properties.

2. Experimental

2.1. Sample preparation

Commercial bone china body (green), in the form of cups and mugs, was collected from a bone china ware manufacturing unit in India. Rejected biscuit fired pieces were also collected from the production line and the same was used as fired scrap. In addition to these, two varieties of china clay (Rajmahal china clay [white variety], Jharkhand, India and Nim-ka-Thana china clay, Rajasthan, India), feldspar and ground bone ash were also collected for parallel evaluation.

Five different body mixes (compositions B_0 to B_{12}) were used (Table 1). In the compositions biscuit fired bone china ware scrap was progressively incorporated, up to 12%, in the green body. The fired scrap was wet ground separately in a pot mill for 24 h to get the desired fineness (residue less than 1% on 250 mesh BS sieve). All the batches were mixed separately and wet ground in a pot mill for 6 h to get the desired mixing. The slurry obtained was sieved and made into casting slip after adjusting the rheological properties of the slip to the desired level. Slip was adjusted with requisite doses of electrolyte (sodium hexa meta phosphate, Loba Chem., India and Dispex N40 deflocculant, Allied Colliods, UK) and the rheological properties were controlled with pint weight (weight of 500 ml. of slip in g), fluidity and thixotropy. Fluidity and thixotropy were measured with Gallenkamp Universal Torsion Viscometer using a bob of 11/16 in. diameter and 32 SWG wire. Specimens were made by slip casting method in plaster of paris moulds. Rectangular bars of 150 mm × 15 mm × 4 mm were cast. The specimens after drying and finishing were fired between 1100 °C and 1250 °C at a temperature interval of 50 °C in an electric furnace. The average heating rate was 2.5 °C/min and the specimens were allowed a soaking for 2 h at the respective firing temperature before the furnace was switched off for cooling.

2.2. Measurements

Chemical analysis of the raw materials was carried out following standard procedure. The particle size distribution of different ground body mixes was determined using Malvern Particle Size Analyser, Model 2602 LC adopting laser diffraction technique. All the experiments were carried out using 63 mm lens and under identical conditions.

Table 1
Batch compositions (wt%).

Batches	Bone china green body	Bone china pitcher
B_0	100	0
B_3	100	3
B_6	100	6
B_9	100	9
B_{12}	100	12

Table 2
Chemical analysis of the raw materials used.

Oxide constituents (wt%)	Rajmahal china clay (white)	Nim-ka Thana china clay	Feldspar	Ground bone ash	Bone china pitcher
SiO_2	48.87	47.11	66.81	5.70	33.90
TiO_2	0.93	Tr	0.08	Tr	0.33
Al_2O_3	34.39	37.42	18.08	0.48	16.17
Fe_2O_3	0.87	0.67	0.24	0.10	0.41
CaO	1.42	1.62	1.03	50.61	26.12
MgO	Tr	Tr	0.23	0.46	0.27
Na_2O	0.10	0.41	1.69	0.61	0.63
K_2O	0.23	0.20	10.94	0.06	2.08
P_2O_5	na	na	na	39.71	19.36
LOI	12.83	12.84	0.58	2.16	0.45

The fired specimens were subjected to physical tests viz. linear shrinkage, flexural strength, apparent porosity, bulk density and relative density. Bulk density and percent apparent porosity were measured using the conventional water displacement method following Archimedes principle. True density of the specimens was determined from respective powdered material using specific gravity bottle. Relative density was determined using the standard equation (relative density = bulk density/true density). Flexural strength (3 point bending) was determined in a universal testing machine, Instron 5500R with a crosshead speed of 2 mm/min. For each specimen eight (8) bars were tested and average was taken and reported.

In order to measure the extent of deformation of respective specimen at the temperature of maturity, bars of 150 mm × 20 mm × 4 mm were separately fabricated and allowed to fire at the maturing temperature 1250 °C for 2 h (average heating rate 2.5 °C per min.) supported only at their ends with their central spans, 90 mm long, unsupported and suspended. Sagging was measured by comparing the test bars with a ground standard steel bar of 90 mm long symmetrically positioning against the test bar and measuring the maximum gap between the test bar surface and the reference steel bar.

Microstructure was studied by SEM analysis on selected sintered samples (polished and etched with 5% hydrofluoric acid for 3 min) using a LEO-S 4301 apparatus.

Concentration of crystalline phases were estimated for some matured selected samples from X-ray diffraction (XRD) line profile analysis using Rietveld analysis by X'Pert High Score Plus software (PANalytical). The XRD patterns of the samples were recorded in X'Pert Pro MPD diffractometer (PANalytical) operating at 40 kV and 30 mA using Ni filtered CuK_α radiation. The XRD data were recorded in step-scan mode with step size $0.02^\circ(2\theta)$ from 6° to 70°. Standard (a known amount of a pure crystalline phase) calcium fluoride was added to the sample to calculate the weight percentage of vitreous and crystalline phases in the sample using Rietveld analysis by X'Pert High Score Plus software (PANalytical). The quality of fitting was assessed from difference plots as obtained from Rietveld analysis by comparing observed diffraction patterns with the simulated patterns and also "Goodness of Fit" which varied from 1.70 to 2.76 among different samples.

3. Results and discussion

The results of the chemical analysis of the raw materials have been presented in Table 2. The chemical analysis results indicated that both the china clay samples were of normal type, SiO_2 and Al_2O_3 were the major constituents with low Fe_2O_3 (0.87% in Rajmahal clay and 0.67% in Nim-ka Thana clay) and alkali ($K_2O + Na_2O$) content. Low Fe_2O_3 content of the clay is an essential criterion for selection in a bone china body. XRD analysis (Fig. 1a and b) confirmed that the clay samples were essentially kaolinitic. Both the china clays contain Muscovite and quartz in varying proportions. Total alkali ($K_2O + Na_2O$) content of the feldspar sample was 12.63% with predominant contribution of K_2O. XRD analysis (Fig. 1c) indicated that microcline was the major phase in the sample of feldspar with little proportion of albite and muscovite. Ground bone ash was essentially calcium phosphate. Contamination during grinding might be the reason for appreciable SiO_2 content (5.70%) in the bone ash sample. Analysis of scrap indicates that around 50% bone ash was possibly used in the body composition.

The particle size distribution of different body mixes is presented in Table 3. There was very little difference in the distribution of fine particles among the mixes studied.

The preparation of a casting slip with good rheological properties for bone china bodies is a critical operation. The rheological behaviour of the slips, measured at a constant density and at a constant temperature of 30 °C, showed that the fluidity and the thixotropy of all the slips were substantially unchanged with increasing scrap content up to 12%. The same uniformity was also obtained for mechanical resistance, with an MOR of around 1.9 MPa for all the green bodies containing varying proportions of scrap.

The variation in percent fired linear shrinkage with increasing scrap content is presented in Fig. 2. From the curves it may be observed that there was insignificant effect on fired linear shrinkage up to 1150 °C with gradual increase in scrap content and beyond this temperature there was steady increase in the linear shrinkage with increasing scrap content up to 12%. Maximum shrinkage was reached for all the specimens at 1250 °C. However, at 1250 °C the curve more or less flattened indicating that fired linear shrinkage is practically independent of the scrap content in the specimens at least up to

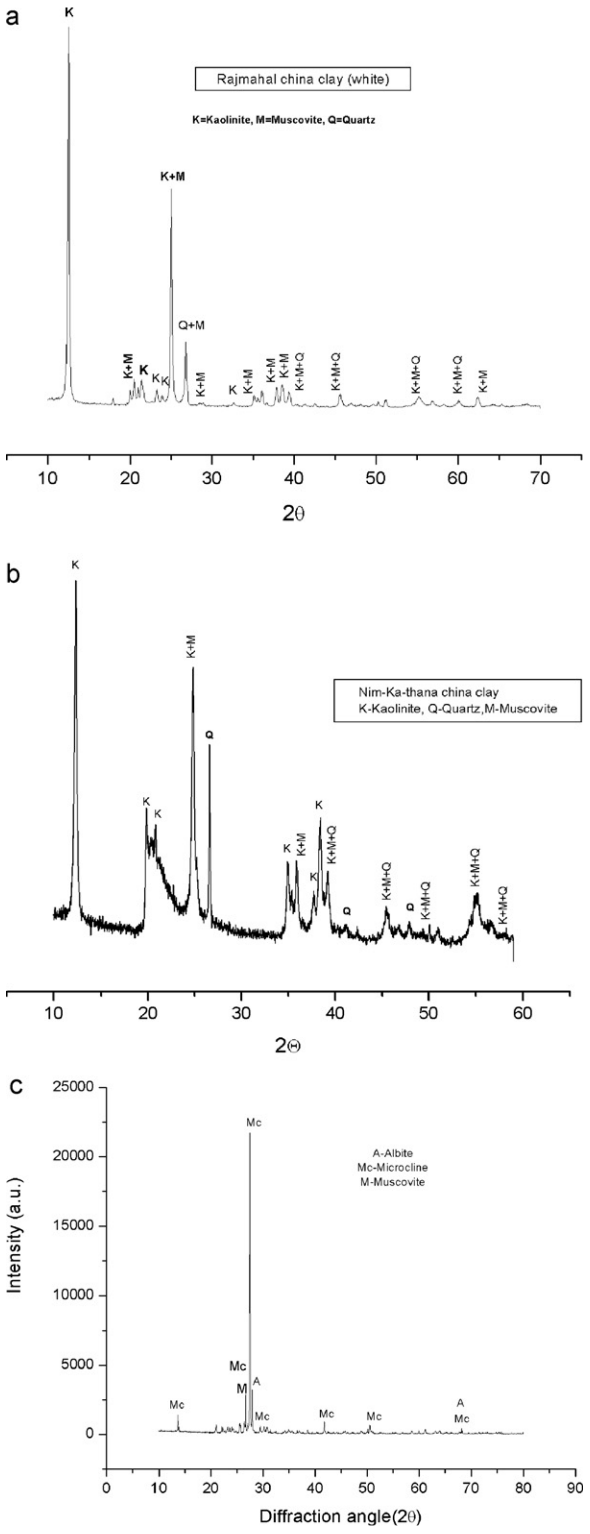

Fig. 1. (a) XRD analysis of Rajmahal china clay (K: Kaolinite Q: Quartz; M: Muscovite). (b) XRD analysis of Nim-ka-Thana china clay (K: Kaolinite Q: Quartz; M: Muscovite). (c) XRD analysis of feldspar (Mc: Microcline, A: Albite).

12% (11.39% for specimen without scrap to 11.64% for specimen with 12% scrap).

Table 3
Physical properties of different green bodies.

Properties	Body mixes				
	B_0	B_3	B_6	B_9	B_{12}
Particle size distribution, d_{50}, μ	7.33	7.37	7.46	7.43	7.51
Particles finer than 10 μ	72.23%	73.36%	73.96%	73.81%	74.49%
M.O.R., MPa	1.93	1.89	1.87	1.87	1.88

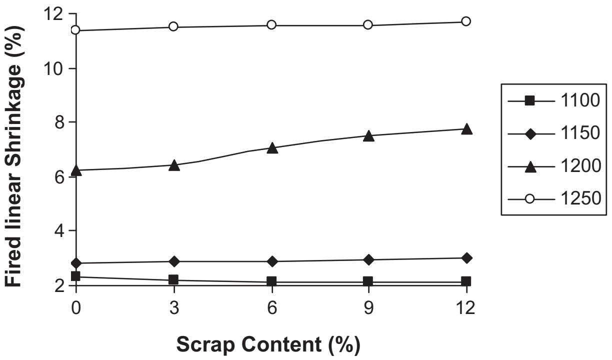

Fig. 2. Variation of fired linear shrinkage with increasing scrap content.

The variation in apparent porosity (AP) with firing temperature is furnished in Fig. 5 The figure reveals that all specimens containing scrap (B_3 to B_{12}) reached below 0.5% A.P. at 1250 °C indicating almost complete vitrification at this temperature. However, specimen without scrap showed an apparent porosity value of 1.33% at this temperature. Possibly shorter firing schedule under experimental condition did not allow the specimen to attain complete densification even at 1250 °C. This further indicated that presence of fired scrap actually reduced the vitrification temperature and the specimens containing scrap matured early than that of the normal body (B_0). Fired scrap and the bone china body are expected to have similar type of chemical compositions, however, presence of glassy phase in the scrap (being already fired at the maturing temperature) is expected to play a significant role in effecting early maturity of the specimens containing scrap. The vitrification characteristic of a bone china body is very important to the firing process and the fired product and this is best determined by maintaining minimum possible open porosity. A fired bone china body not fully matured will impair the translucency and make the products susceptible to crazing because of high moisture expansion [3]. The higher firing temperature is limited by the body either becoming distorted or bloated and making the products unusable. The effect of pitcher is not very pronounced up to the firing temperature of 1150 °C, however, at 1200 °C the AP values reduced from 22.79% for specimen of normal bone china body (B_0) to 11.32% for specimen of bone china body containing 12% scrap (B_{12}).

The changes in flexural strength of the specimens with increasing scrap content and with varying firing temperature are shown in Fig. 3. As expected, an increasing trend in flexural strength was observed with increasing firing temperature as

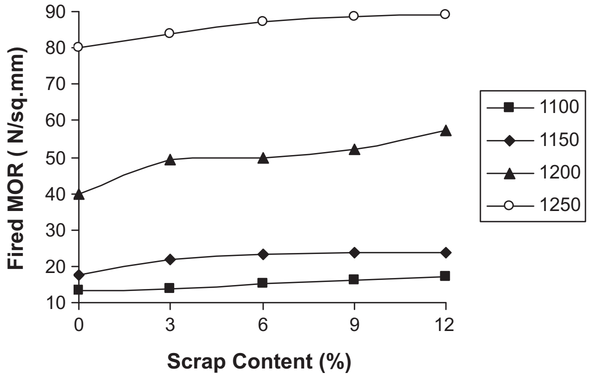

Fig. 3. Variation of fired modulus of rupture with increasing scrap content.

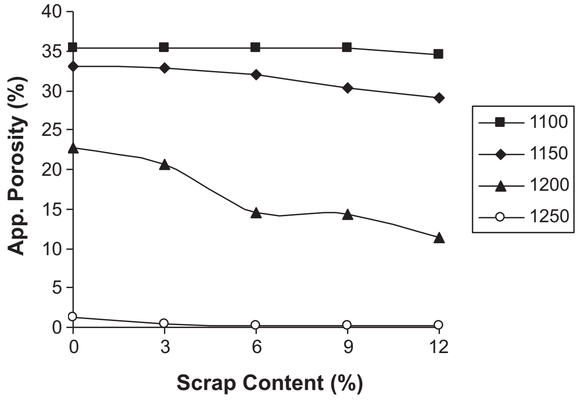

Fig. 5. Variation of apparent porosity with increasing scrap content.

well as increase in scrap content. As observed earlier, specimens of mixes containing scrap always showed higher flexural strength irrespective of temperature and a maximum value of 89.18 MPa at 1250 °C was attained with mix containing 12% scrap. The results are quite obvious as bending strength in ceramics increases exponentially with decreasing porosity, very much dependent on the amount of liquid phase present at the firing temperature and that, the denser the fired bodies, the higher the bending strength [16–18].

Variation in bulk density of specimens fired up to 1250 °C (Fig. 4) also showed the similar trend and increased with increasing scrap content. The highest bulk density value (2.64 g/cm^3) was observed with specimen B_{12} (containing 12% scrap) matured at 1250 °C. The maximum bulk density was recorded at the same temperature at which MOR was also highest, as observed by other [17], although working in different system. Taking the glassy phase already formed in the scrap into account, it may be inferred that more intensive sintering and attainment of higher density in the scrap incorporated compositions are due to the formation of higher proportion of liquid phase at the temperature of maturity.

To discuss the degree of densification, relative density rather than bulk density must be considered because the contents of the crystal constituents differ in the compositions. Fig. 6 shows the relative densities of the compositions fired at 1250 °C. Almost all the matured specimens attained around 93% relative density except the standard body B_0 (91.81%). The relative density of vitrified specimens reached the maxima at the highest firing temperature and a value of 93.90% was obtained with specimens containing 12% scrap at 1250 °C. Specimens of bone china body without scrap reached a relative density value of 91.81% at 1250 °C. When the bone china body becomes fully matured on firing, the remaining open porosity will preferably be below 0.5%, but there will also be a residue of closed pores which varied from 8.19% (B_0) to 6.10% (B_{12}) and thus support the observations of other researchers [19]. In general at the point of vitrification all the open pores have become sealed and closed pores tend to form. The decrease in closed porosity is desirable and this is caused probably as a result of the surface tension forces in the glassy phase causing the closed pores to shrink to an equilibrium size at which the gas pressure inside the pores balances the surface tension forces. The minimum closed porosity corresponds to the maximum bulk density. It may be inferred that better biscuit firing results was obtained with bone china body containing scrap.

The extent of warpage of the respective specimens at the temperature of maturity (1250 °C) has been presented in the Fig. 7. There was no difference in the sagging value with specimens containing up to 6% scrap and beyond this progressive increase in sagging value was observed with increasing scrap content reaching a maximum (17 mm) with specimen containing 12% scrap. Sagging behaviour may be correlated with the volume of liquid formation as well as the viscosity of the liquid. A liquid phase is essentially required

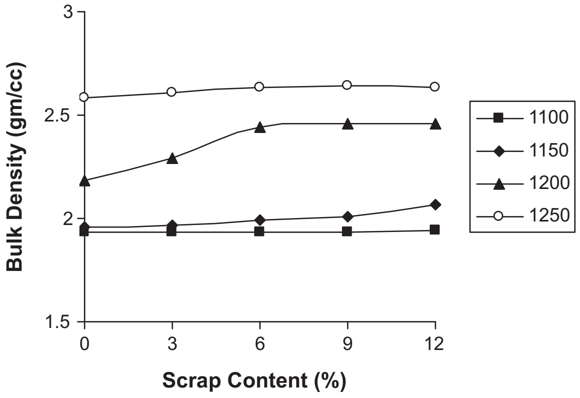

Fig. 4. Variation of bulk density with increasing scrap content.

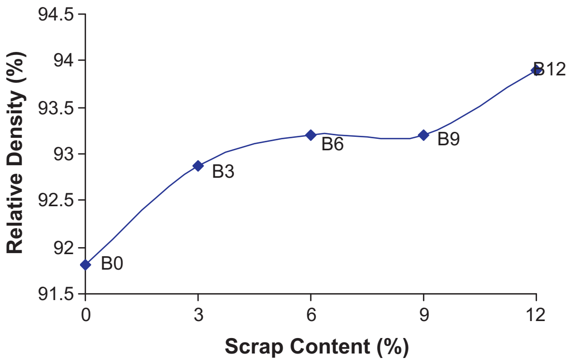

Fig. 6. Variation of relative density with increasing scrap content.

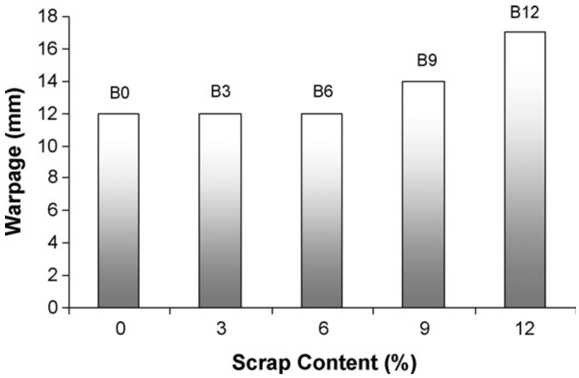

Fig. 7. Extent of warpage of the specimens with increasing scrap content on the temperature of maturity.

during sintering to effect densification but this will also allow the wares to deform under its own weight by facilitating the slippage of the crystalline grains past one another. Ratio of solid to liquid alters rapidly with temperature change in the region close to bone china composition [5]. It is expected that with progressive incorporation of scrap beyond 6% more liquid would be formed resulting in lowering of the solid/liquid ratio and thereby increasing the sagging tendency.

XRD analysis of bone china body (B_0) matured at 1250 °C (Fig. 8) indicated that anorthite and β-TCP (β-tri calcium phosphate) were the major crystalline phases present in the fired body with a small amount of quartz phase. It may be mentioned that the peaks from the β-TCP and anorthite phases frequently overlap in the spectrum, due to the similarity in their crystal lattice spacings. The results conform well to those obtained by Iqbal et al. [4] who discussed in details the constituents of bone china body fired at various temperatures ranging from 30 °C to 1500 °C. The observed small intensity of α-quartz peaks at the temperature of maturity (1250 °C) indicated that either quartz was not externally added in the original bone china body or it got dissolved at this temperature. The results further indicate that bone china body is highly crystalline, containing less than 40% glassy phase. Low porosity and high crystalline phase content will make bone china wares highly resistant to chipping [20] which have great commercial value.

Previous studies of bone china bodies contained limited microstructural analysis. The microstructure of bone china are known to contain β-TCP, anorthite, α-quartz and calcium aluminosilicate glass [6]. However, the morphologies and the distribution of these phases have been little investigated using modern microstructural techniques. The analysis of phases of bone china body (B_o) as presented in Table 5 conforms well to the results furnished by others [4,21]. With gradual incorporation of scrap in the body, gradual decrease in the β-TCP phase was observed reaching a minimum (33.15%) with body containing 12% scrap (B_{12}) while there was progressive increase in glassy/amorphous phase. The glassy phase was increased by around 20% when 12% scrap was incorporated in the bone china body. The increase in glassy phase with increasing scrap content has been reflected in the results of apparent porosity (Fig. 5) values of the specimens and scrap containing bodies showed early maturity. This also resulted in the augmentation of the densification process and attainment of maximum relative density with specimen containing 12% scrap. The results further indicated that there was very little variation in the content of anorthite phase with increasing scrap content although marginal increasing trend was observed (24.75% for B_0 to 26.33% for B_{12}). Around 1% quartz phase was observed in all the specimens analyzed. Interestingly no mullite phase was observed thus supporting the results of other workers [4,5,9,19,20]. In general bone china body contains 25–35% china clays and on firing to temperature around 1250 °C mullite phase is likely to crystallize out. The absence of mullite phase may be caused by the highly reactive CaO released from bone ash and the subsequent reaction of CaO with metakaolin to form anorthite which is possibly more favourable and faster than formation of mullite. Iqbal et al. [6] postulated that Al_2O_3/SiO_2 ratio in anorthite and metakaolin is 1:1, and that the formation of anorthite might be more feasible stoichiometrically than mullite with an Al_2O_3/SiO_2 ratio $\geq$3:2.

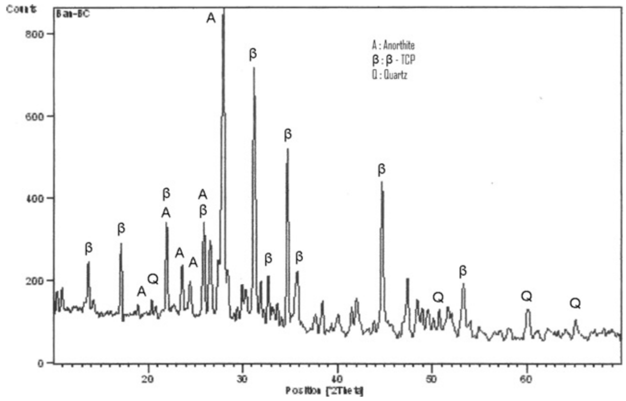

Fig. 8. XRD analysis of bone china body B_0.

The thermal expansion coefficient (TEC) of the bone china body (α_{30-500}) was found to be 8.40×10^{-6} per °C and the same decreased to 8.26×10^{-6} per °C with specimen (B_9) containing 9% scrap (Table 4). Comparison of thermal expansion of the standard bone china body (B_0) with the specimen containing 9% scrap (B_9) has been presented in Fig. 9. The reduction in thermal expansion coefficient value of the specimen containing scrap may be attributed to the reduction in the amount of β-TCP crystalline phase (Table 5), which has relatively higher TEC value. The observation again supports the results of phase analysis (Table 5).

The scanning electron photomicrographs of polished and chemically etched specimens of some selected compositions heated at 1250 °C is shown in (Fig. 10a and b) and (Fig. 10c and d). Very little differences in microstructure among the specimens were observed as all the specimens contained more

Table 4
Thermal expansion of selected matured specimens.

Specimen	Coefficient of thermal expansion (per °C × 10^{-6})		
	α_{30-500}	α_{30-700}	$\alpha_{30\text{-}900}$
B_0	8.40	8.65	9.01
B_9	8.26	8.46	8.78

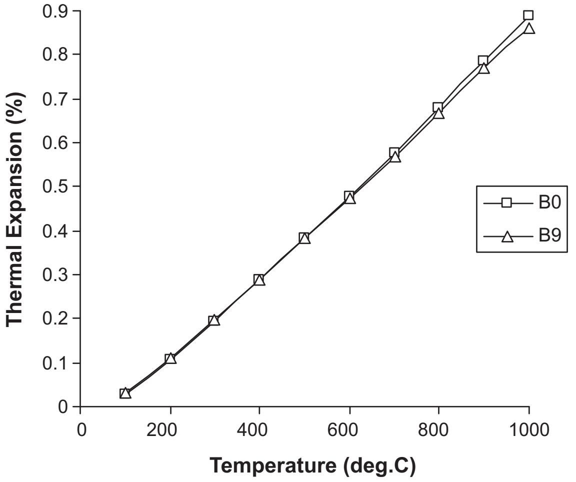

Fig. 9. Comparison of thermal expansion of a standard bone china body B_0 with that modified (B_9) with incorporation of 9% scrap.

Table 5
Phase analysis of specimens matured at 1250 °C.

Specimen	Phases present			
	Anorthite	β-TCP	Quartz	Amorphous
B_0	24.75	40.63	1.30	33.32
B_3	25.28	38.75	1.40	34.57
B_6	26.22	36.70	1.60	35.48
B_9	26.32	35.03	1.10	37.55
B_{12}	26.33	33.15	1.10	39.42

or less similar constituents. General microstructural features of bone china could be observed. The microstructure appeared very dense containing spheroidal β-TCP and lath shaped anorthite crystals (Fig. 10b) conforming to the observations of other researchers [4,19]. Very dense structure above 1200 °C suggests that highly reactive lime liberated during decomposition of bone ash as per Eq. (1) is likely to diffuse into the feldspar relicts leading to the formation of liquid phase. Silica discarded from clay relicts also gets dissolved in the melt resulting in calcium potassium aluminosilicate glass. It may be seen from the $CaO–P_2O_5–Al_2O_3$ ternary phase diagram that liquid phase can form at around 900 °C in the P_2O_5 richer field $CaO{\cdot}P_2O_5–Al_2O_3{\cdot}P_2O_5–Al_2O_3{\cdot}3P_2O_5$ [4]. However, P_2O_5 was never detected throughout the glassy phase, which was also observed by others, pointing towards possible formation and crystallization of β-TCP from the melt during cooling at the expense of P_2O_5 [4]. This may also be noted that according to Eqs. (1) and (2) the bone ash decomposes into β-TCP and CaO and this CaO in turn is utilized to form anorthite with clay and the decomposition or dissolution of β-TCP into the melt forming low melting phosphate glass is unlikely.

Discrete areas of anorthite are difficult to pick out, possibly because it is formed from very fine grained clay. It may also be possible that the crystals got dissolved in the melt at the firing

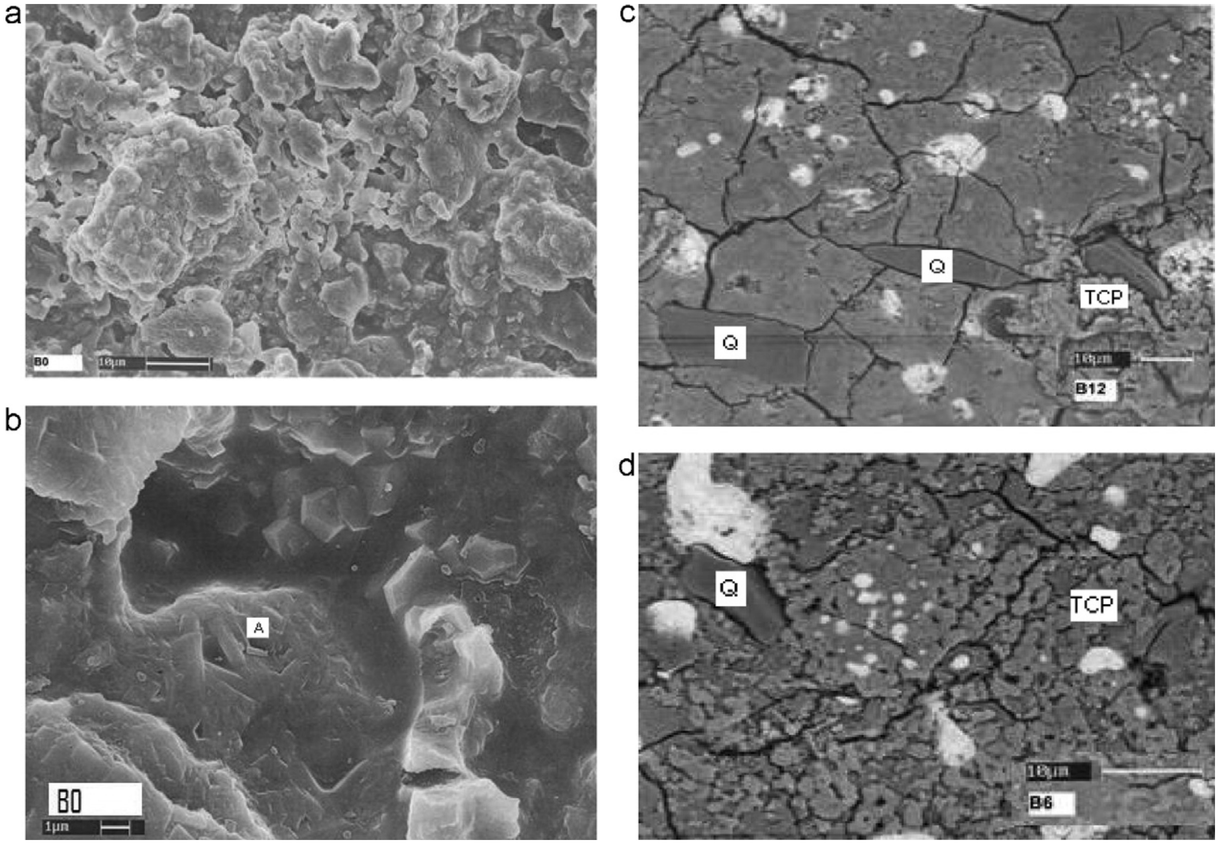

Fig. 10. (a) SEM micrographs of polished and etched specimens of bone china body fired at 1250 °C. (b) SEM micrographs of bone china body (B_0) showing the anorthite crystals. (c) SEM micrographs of B_{12}. Quartz crystals with cracks are visible. (d) SEM micrograph of B_6. Nodular β-TCP crystals are conspicuous.

temperature [6] or by the etchant. The observation of rather non-homogeneous distribution of anorthite and β-TCP crystals in the matrix revealed the non-equilibrium crystallization which may be related to the extent of mixing of the starting materials [6]. Iqbal et al. [4] also postulated the variation in viscosity of the liquid of heterogeneous composition surrounding the β-TCP crystal in explaining the differences in β-TCP crystal sizes from region to region. It may be assumed that distribution of bone ash in the green bone china body was not homogeneous; some regions contained only agglomerates of pure bone ash while in others it was mixed with clay and feldspar relicts. Consequently, the liquid forming in different regions has variable composition and viscosity.

Quartz crystals below 10 μ sizes are visible in Fig. 10c and d. It is interesting to notice that the sharp corners of some quartz crystals have been rounded by partial solution of the corner regions into the glassy matrix during biscuit firing supporting the observations of Kara and coworker [19]. The region close to the residual quartz grains is the glassy solution rim. The analysis revealed that the glass composition was silica rich adjacent to quartz crystal and varied in composition throughout the remaining microstructure. In addition there is a microcrack present around the periphery of larger quartz crystals (Fig. 10c). Such microcracks are due to differential thermal expansion stresses arising as a result of the thermal expansion mismatch on cooling between the quartz grains and surrounding glassy solution rim. The dark areas represent the closed pores, which are of a range of different shapes and sizes.

The chemically etched specimens were found to contain severe cracks throughout the microstructure. It may be that the glassy phase would be under stress due to the thermal expansion mismatch between the crystals of β-TCP and anorthite [6]. Microcracks have possibly developed in the highly stressed glass during polishing and etching. No significant microstructural difference was observed among the specimens of bone china body (B_0) and those containing scrap with different proportions.

4. Conclusion

The commercial bone china body containing scrap showed improved fired properties and around 10% increase in MOR values were obtained with matured specimens containing scrap in comparison to that of normal body while very little effect was obtained with fired shrinkage values. Phase analysis revealed that there was gradual decrease in β-TCP content while increase in glassy phase was observed with progressive incorporation of scrap. Presence of glassy phase in higher proportion in the scrap incorporated body resulted in early maturity of the specimens as well as development of a very dense microstructure. This also resulted in specimens with lower porosity and higher mechanical properties. Presence of scrap did not alter the anorthite phase content. Coefficient of thermal expansion of bone china specimen was found to decrease when modified by incorporation of scrap as β-TCP content was decreased with increasing scrap content.

SEM investigation of the polished and chemically etched specimens revealed complexity in the nature and distribution of the crystalline and the glassy phases in the microstructure. The microstructure consisted of distinct regions of agglomerated spheroidal β-TCP and lath shaped anorthite crystallites in a heterogeneous calcium aluminosilicate glassy matrix. Small proportion of angular α-quartz was also observed. Glassy phase was rich in silica in the vicinity of quartz grains while in other portions the composition was calcium alumino silicate containing K_2O. P_2O_5 was never detected in the glass suggesting that whole of P_2O_5 coming from bone ash was utilized in the development of β-TCP crystallites. There was practically no difference in microstructure between the bone china body and the modified one containing scrap at least up to 12%. Thermal expansion mismatch induced cracks were observed throughout the microstructure irrespective of the specimens studied. Though it may be recommended that up to 12% scrap can be utilized in the commercial bone china body, however, 9% scrap addition is optimum without impairing the ultimate properties of the products.

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