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Characterisation of biscuit fired bone china body microstructure. Part II: Transmission electron microscopy (TEM) of glassy matrix

Alpagut Kara[a,*], Ron Stevens[b]

[a]*Department of Ceramic Engineering, Anadolu University, Eskişehir, Turkey*
[b]*Department of Engineering and Applied Science, University of Bath, Bath, UK*

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Abstract

In this second part of the study, electron transparent specimens of the biscuit fired bone china body were prepared for a conventional transmission electron microscopy (TEM) study. The crystalline phases present in the fired material were noted and particular consideration was given to determination of the nature and composition of the glassy phase. Compositional information on the phases was obtained using energy dispersive X-ray spectrometry (EDS) which was available in conjunction with TEM. Additionally, a simulated glass with a composition typical of that present in the bone china body was prepared and examined by TEM in order to compare its structure and chemistry with that of the glassy phase originally present in the bone china body.

Keywords: Biscuit firing; Bone china; Electron microscopy; Microstructure-final; Tableware

1. Introduction

Despite the fact that bone china has been manufactured for almost 200 years there is still controversy concerning the chemical reactions and physical processes that take place during biscuit firing. It is now generally accepted that fired bone china bodies consist of crystals of anorthite, β-tricalcalcium phosphate (β-TCP) and sometimes a small amount of quartz, embedded in a complex glassy matrix. Since the properties are dependent on the matrix phase it is important to quantify the variation of inhomogeneity in the glassy matrix. However, any direct experimental study of this phenomenon in the glassy phase is subject to difficulties.

Roberts and Beech[1] gave two hypotheses to fit the reaction between bone ash and china clay, both of which result in the formation of tricalcium phosphate and anorthite as detected previously by Wilde[2] in fired bone china bodies. However, they also stated that these hypotheses are simplifications, in the sense that they give too static a picture of what is essentially a gradual process, the reaction between the body constituents to give crystalline phases and glass. Consequently, the actual behaviour may occur somewhere between these two sets of conditions.

According to the first hypothesis, anorthite is formed solely from the excess calcium oxide in the bone ash surplus to the amount required to combine with the phosphorus pentoxide in the bone ash to form tricalcium phosphate. The excess clay then converts to mullite, which it is assumed, eventually becomes incorporated into the glassy phase with all the other raw materials. The reaction equation for this hypothesis is known as "the non-phosphate glass equation" and is written as follows:

$$\underset{\text{(bone ash)}}{[Ca(OH)_2.3Ca_3(PO_4)_2]} + \underset{\text{(china clay)}}{[Al_2O_3.2SiO_2]} \rightarrow \underset{\text{(tricalcium phosphate)}}{3Ca_3(PO_4)_2} + \underset{\text{(anorthite)}}{(CaO.Al_2O_3.2SiO_2)} + H_2O \quad (1)$$

According to the second hypothesis, all the calcium oxide in the bone ash is available for the formation of anorthite, by combination with the alumina and silica present in the china clay. The actual amount of anorthite formed is assumed to depend on the amount of alumina in the china clay. All the remaining calcium oxide in the body not accounted for, is assumed to form

* Corresponding author. Tel.: +90-222-3213550; fax +90-222-3239501.

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tricalcium phosphate, and all the other constituents, including excess phosphorus pentoxide from the bone ash, are considered to react to form the glassy phase. The equation for this hypothesis is known as "the phosphate glass equation" and can be written as follows:

$$\underset{\text{(bone ash)}}{3[Ca(OH)_2.3Ca_3(PO_4)_2]} + \underset{\text{(china clay)}}{6[Al_2O.2SiO_2]} \rightarrow \underset{\text{(tricalcium phosphate)}}{8Ca_3(PO_4)_2} \quad \underset{\text{(anorthite)}}{6[CaO.Al_2O_3.2SiO_2]} + P_2O_5 + 3H_2O \tag{2}$$

Based on the hypotheses above, it is possible to calculate the theoretical chemical composition of the fired bone china bodies and that of the glassy matrices. Glasses of the appropriate composition can then be made up separately, in order that their properties can be examined. However, which equation and which hypothesis prevails is still under debate.

2. Experimental

2.1. Experimental materials

2.1.1. Bone china body

Biscuit fired bone china pellets prepared in the first part (part I) of this study were also used for the preparation of specimens for the present TEM investigation.

2.1.2. Simulated bone china body glass

A simulated bone china body glass was prepared, using the theoretical composition suggested by Roberts and Beech[1] based on "the phosphate glass equation" [see Eq. (2)]. The calculated composition of the glass is given in Table 1. For the preparation of the glass batch, the required amounts of the analytical reagent grade carbonates ($CaCO_3$, K_2CO_3, Na_2CO_3) and oxides (MgO, Al_2O_3) were obtained from different commercial sources. Sodium hexametaphosphate ($(NaPO_3)_6$) was used as a source of phosphorus. Redhill flint (washed and processed high silica sand) with typically a 99.7% purity was the source of SiO_2, provided by Hepworth Minerals and Chemicals Ltd. (England). Prior to weighing, all the raw materials were thoroughly dried in an oven at ~110 °C. Subsequently, the calculated amounts of the raw constituents were weighed to an accuracy of better than ±1 mg on an analytical balance. The powders were then mixed and gently ground together in a mortar and pestle.

Table 1
The chemical composition of the simulated bone china body glass[1]

Oxide	Wt.%
K_2O	5.8
Na_2O	2.7
CaO	1.8
MgO	2.0
Al_2O_3	13.7
SiO_2	67.5
P_2O_5	5.8

During the melting of a glass batch, ideally the container should not react with the glass when in contact with it at high temperatures for long periods of time. This condition has been achieved by fabricating yttria stabilised zirconia crucibles using slip casting and sintering. Several crucibles were produced since the glass batch required more than one melting. Mixes rich in silica and low in alkali are well known for their high viscosity and inevitably require several sequential melts and longer melting times, interspersed with grinding, before a homogeneous glass is obtained. The use of zirconia crucibles for preparation of simulated bone china body glass has been reported previously.[3]

The glass batch mix was fired in the zirconia crucible in an air atmosphere at 1650 °C for 3 h in an electric chamber furnace (Model: Ultratherm 17/6, Pyro Therm, UK) heated with molybdenum disilicide heating elements. The molten glass was rapidly quenched in air and then crushed by pestle and mortar and if an undissolved part of the batch was observed, remelted. This procedure was repeated up to four times. Small sections were cut from the finished block of glass for further TEM work.

2.2. Transmission electron microscopy (TEM)

TEM studies were performed using a Jeol 200 kV analytical electron microscope using a side entry, single tilt holder. The bright field (BF) mode was employed to investigate in greater detail the morphology of crystalline and vitreous phases present in the biscuit fired bone china body and simulated bone china body glass. Particular attention was concentrated on the glassy areas. Chemical microanalysis of the phases were obtained using the EDS attachment of the instrument, an Oxford Instruments AN 10/25 Link microanalysis system, mounted without a window, allowing light elements such as sodium and oxygen to be analysed without difficulty. All images and EDS spectra were recorded using a 200 kV incident electron beam.

3. Results and discussion

3.1. Biscuit fired bone china

Fig. 1 is a typical bright field TEM image of the microstructure of biscuit fired bone china body. Several crystals, which are distributed unevenly in the glassy matrix, can be observed in the field of view. The EDS analyses of the crystals exhibiting twinning revealed that

they have a chemical composition close to that of anorthite, with additional small amounts of Na and K present. The presence of the same elements in the "anorthite" crystals had been shown earlier by the SEM analyses, in the first part of this study.

EDS analyses on the other crystals present in Fig. 1 showed that they were β-TCP. In addition, impurities

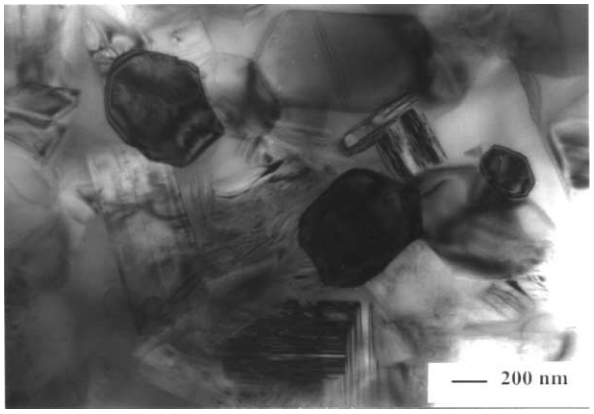


Fig. 1. A typical bright field TEM image of the general microstructure of the biscuit fired bone china body.

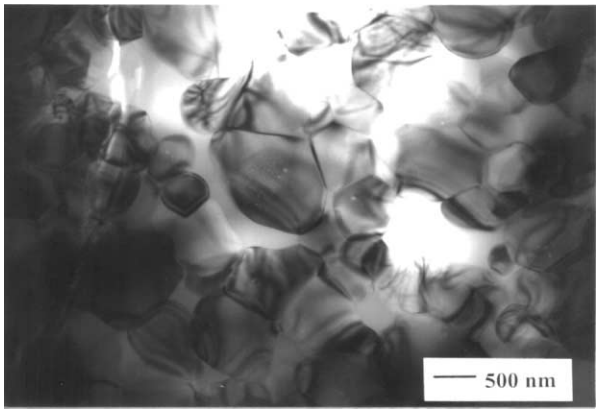


Fig. 2. A typical bright field TEM image of a group of β-TCP crystals.

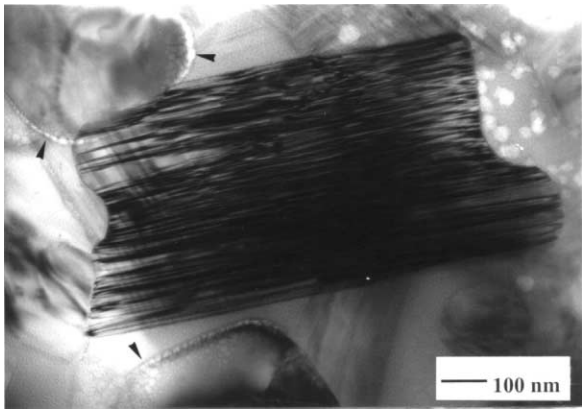


Fig. 3. A bright field TEM image of an anorthite crystal with extensive faulting.

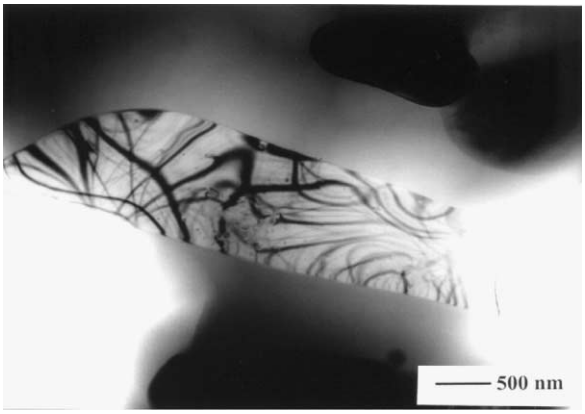


Fig. 4. A bright field TEM image of a quartz crystal in the glassy matrix.

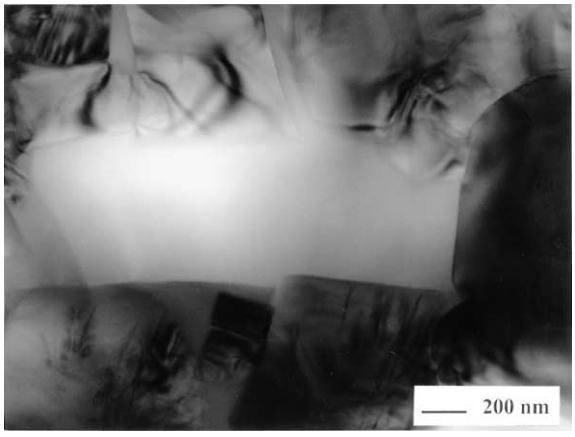


Fig. 5. A TEM image of the bone china body microstructure with a large glassy area.

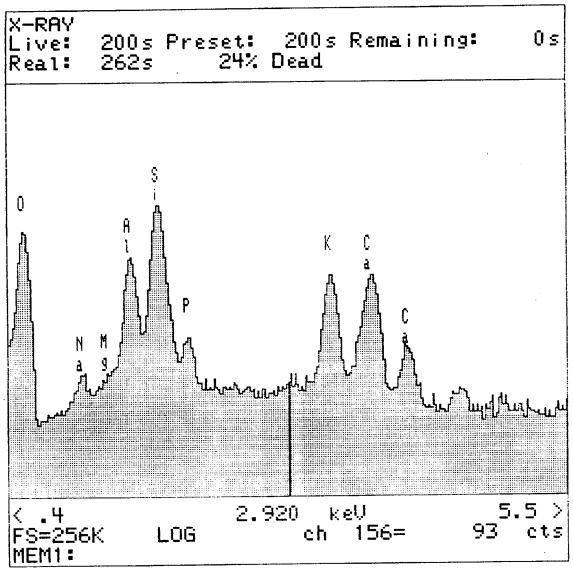
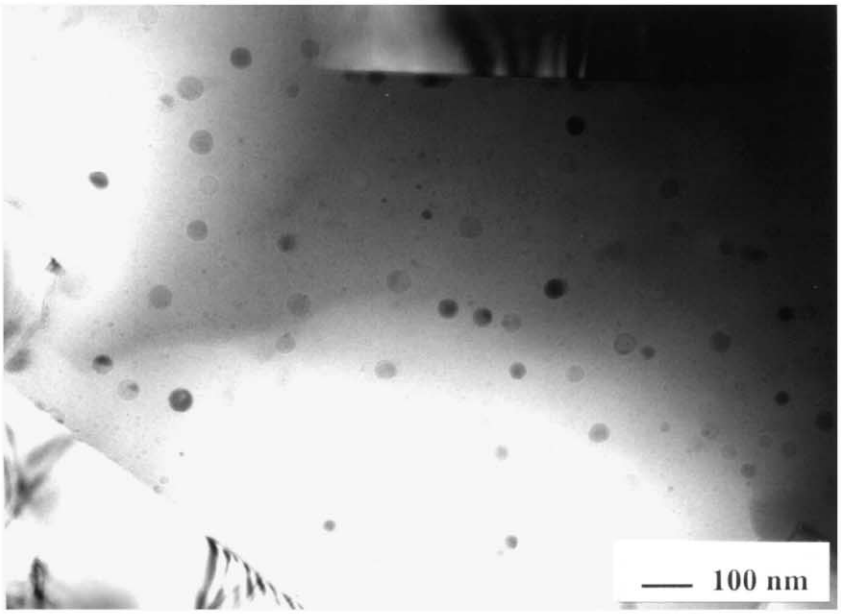
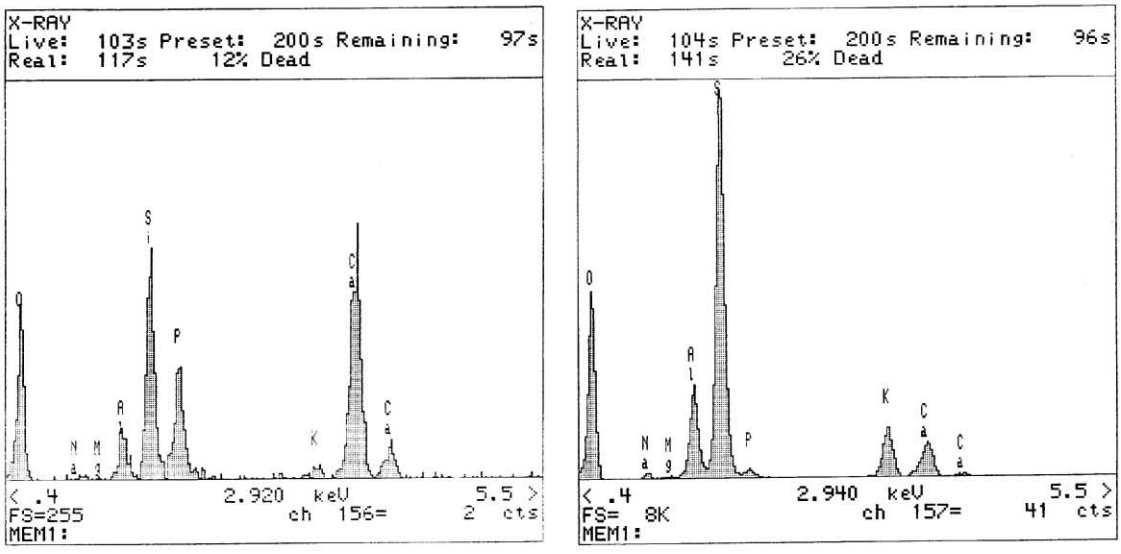


Fig. 6. A representative EDS spectrum of the large glassy area in Fig. 5.



(a)



(b) (c)

Fig. 7. (a) A bright field TEM image of the APS particles in the glassy phase; (b) and (c) the EDS spectra from an APS particle and the glassy phase in (a), respectively.

such as Mg and Na were also detected. It is suggested that the most likely source of these impurities would be the bone ash component of the raw materials.

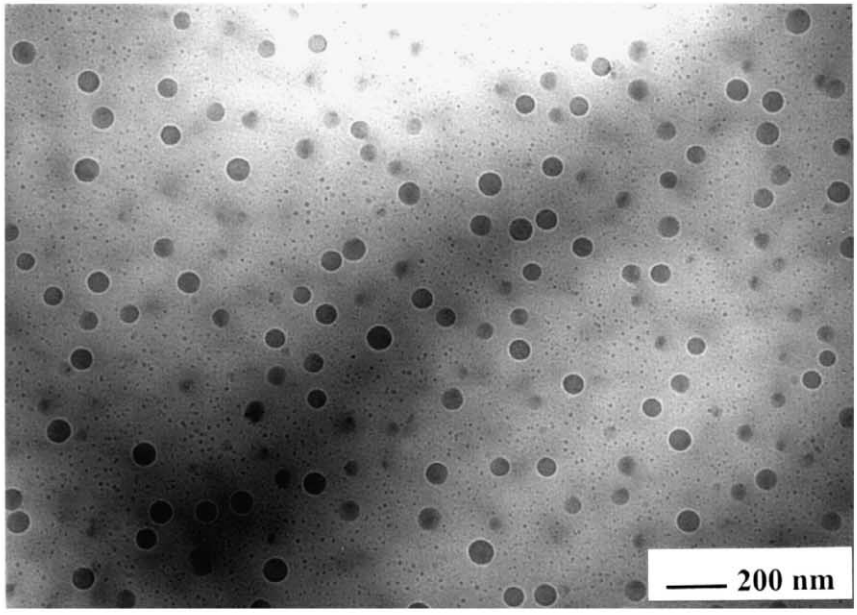
In regard to the distribution and morphology of the β-TCP crystals in the microstructure, they were generally observed to occur in groups, consisting of a few, to a large number of crystals bonded together. Earlier, this was also shown to be the case using SEM. Fig. 2 is a bright field TEM image taken from such an area. As can be seen, the individual crystals are mostly bonded together. In addition, the rounding of the grain boundaries in contact with the glassy matrix is evident in the image, which is an indication of the partial solubility of the crystals in the glassy matrix at firing temperature and a low value for the interfacial surface energy.

Fig. 3 depicts a high magnification bright field TEM image of an individual anorthite crystal. There is extensive faulting visible within the crystal, in the form of stacking faults and microtwins. Another interesting feature of this micrograph is the small bubble like structures

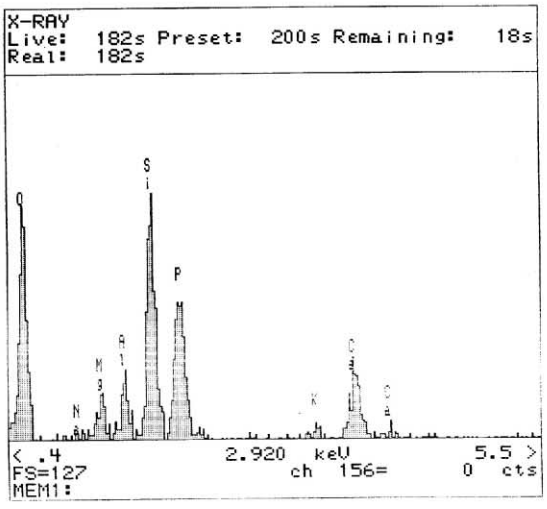
(marked with arrows) on the β-TCP grain surfaces. This is believed to be due either to the electron beam damage converting the irradiated area to an amorphous glass structure or to a similar process introduced by the specimen preparation method.

Fig. 4 shows a bright field TEM image of a single quartz crystal, the corners rounded by surface tension forces and partial solution in the glassy matrix. The presence of extensive diffuse dark curved lines (bend contours) within the crystal is due to local elastic straining under the electron beam heating. There are also several β-TCP crystals which can be distinguished just above the quartz crystal.

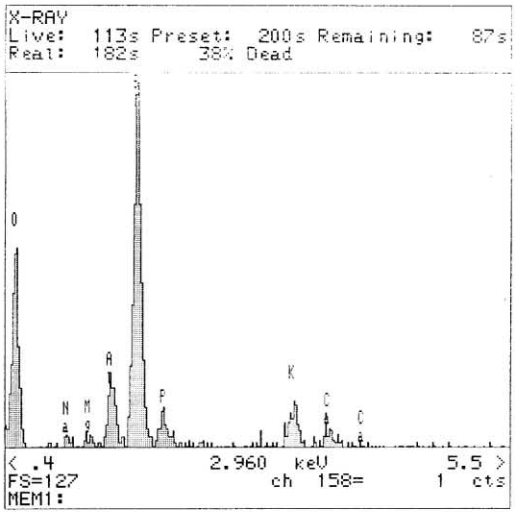
Fig. 5 is a TEM image of the microstructure of the bone china body showing multiple crystals in a glassy matrix. It was obtained by displacing the objective aperture slightly in order to increase contrast. As can be seen, the glassy phase is present in the middle of the image as a large rectangular area. There is also glassy phase present between the individual crystals. Fig. 6 shows the EDS spectrum taken from the glassy area in Fig. 5. One important observation is the presence of a significant P



(a)



(b)



(c)

Fig. 8. (a) A bright field TEM image of the simulated bone china body glass; (b) and (c) the EDS spectra from an APS particle and the glassy matrix in (a), respectively.

signal in the spectrum. In addition, significant amounts of Al, Si, K, and Ca with a smaller amount of Na is detected. An examination of other glassy areas by EDS also revealed the presence of the same elements but in varying proportions. In particular the presence of P in the glassy matrix provides supportive evidence for "the phosphate glass equation" given in Eq. (2), where the reaction between bone ash and china clay releases P_2O_5. Another important point worthy of mention is the absence of Mg in the glassy phase, as opposed to its presence in the simulated bone china body composition, suggested by Roberts and Beech[1] and used in this study (see Table 1).

Fig. 7(a) is another bright field image of another large glassy region surrounded by several crystals. The most striking feature of this microstructure is the presence of mostly spherical particles with a diameter of less than 50 nm distributed in the glass. The EDS analyses on the particles show that they are rich in Ca and P [see Fig. 7(b)]. The glassy phase, however, is rich in Al and Si [see Fig. 7(c)]. The spherical nature of most of the particles and the lack of distinct contrast is evidence of amorphous phase separation (APS) taking place as opposed to direct formation of a crystalline phase. Attempts to generate diffraction patterns from the separated phase were unsuccessful, again pointing to them being an amorphous phase. Further supporting evidence for the presence of APS in bone china comes from a study by Hill et al.[4] in which the carbon replicas of the polished and etched surfaces of biscuit fired bone china specimens were examined in TEM.

3.2. Simulated bone china body glass

TEM examination of the simulated bone china body glass indicated that amorphous phase separation (APS) is taking place in the glass. The slightly 'milky' appearance of the glass can be explained by the formation of the separate phases, which have different chemical compositions, but neither actually crystallises. The presence of phosphorus pentoxide and phosphates generally, encourages APS to take place in glass ceramics.[5] Thus, it is anticipated that APS would occur in the simulated bone china body glass, which has a high phosphorus content. Fig. 8(a) depicts a typical bright field TEM image of the P_2O_5 induced phase-separated microstructure of the simulated bone china body glass. As can be seen, the particles are spherical in shape and are somewhat random in size (below about 100 nm) and spacing. Note that each APS particle is surrounded by a bright fringe ('Fresnel' fringe) since the image is slightly out of focus.

An attempt was also made to chemically analyse the individual APS particles and the matrix phase. The main obstacle was the unstable nature of the APS articles under the electron beam heating, making imaging and chemical analysis difficult. Fig. 8(b) and (c) represents EDS spectra obtained from an APS particle and the glassy matrix shown in Fig. 8(a). The APS particles in the simulated bone china body glass are observed to be rich in Ca and P, as was the case for the APS particles observed randomly in the glassy phase of the biscuit fired bone china body [see Fig. 6(b)].

4. Conclusions

It has been demonstrated that direct examination by TEM of the crystalline and the glassy phases of the biscuit fired bone china body to be possible. Particular interest has centred around the nature and chemical composition of the glassy matrix phase, which bonds together the structure. TEM has enabled elucidation of the composition and structure of the glassy phase. EDS analyses on the different glassy areas revealed the presence of phosphorus in varying amounts, which provided supportive evidence for the hypothesis associated with "the phosphate glass equation". According to this hypothesis, the solid state reaction between bone ash and china clay releases P_2O_5, which was postulated to become incorporated into the glassy phase with other of the body materials not taken up in the reaction.

Another microstructural feature observed using TEM was the presence of spherical particles, with a diameter of less than 50 nm, distributed in the glassy phase. The spherical nature of the particles and lack of distinct contrast was taken as evidence of fine scale amorphous phase separation (APS) taking place in the glassy phase at some stage during the biscuit firing process. EDS analyses showed that the phase separated particles had high concentrations of Ca and P whereas the matrix phase contained comparatively high contrations of Si and Al. As previously stated, APS is widespread in glasses and is the dominant crystal nucleation mechanism in commercial glass ceramics. Phosphorus pentoxide and phosphates are known to promote APS in glass ceramics. Thus, APS is to be expected in the glassy phase of the biscuit fired bone china body. Further supporting evidence for the formation of APS in bone china comes from a study by Hill and his co-workers. They examined the carbon replicas of the polished and etched surfaces of commercially supplied biscuit fired bone china specimens using TEM and observed the presence of uniformly distributed APS particles with diameters ranging from 30 to 200 nm in the glassy phase. They suggested that the APS particles could well have a strong influence on the translucency of bone china, since the dimensional scale of APS occurs largely below light scattering wavelengths, which helps explain the exceptional translucency of bone china. When compared to Hill and his co-workers' results, the occurrence of the APS in the glassy phase of the biscuit fired bone china body in this study was, however, quite irregular. Only in a few cases were APS particles observed. This could be

explained by the inhomogeneous distribution of the glassy phase and its varying chemistry.

It is proposed that the greatest degree of inhomogeneity in the glassy phase is caused by the dissolution of the phosphate rich crystalline phases. Indeed, the partial dissolution of the crystalline phases in the glassy phase during the biscuit firing was illustrated by the electron microscopy studies. Peak temperature and soaking time together with total biscuit firing time are also important factors in dissolution behaviour of the crystalline phases. Moreover, it is suggested that the chemical composition of the glassy phase would be very dependent on the initial composition and the proportions of minor components, such as alkali metal oxides, which would further be concentrated in the glassy phase on crystallisation of anorthite and β-TCP. Also of interest was the unstable nature of the APS particles under the electron beam in TEM, giving rise to problems with imaging and chemical analysis. This could well be another reason for the unpredictable detection of the APS, since its dissolution under the influence of electron beam heating infers a degree of instability associated with a minimum of free energy of formation.

TEM investigation of the simulated bone china body glass clearly revealed its P_2O_5 induced phase-separated microstructure. This observation may be given as evidence for demonstrating the microstructural and chemical similarity of the simulated glass to the glassy matrix phase originally present in the bone china body, since the presence of APS with a similar chemistry was also observed in its microstructure. On the other hand, APS formation in the biscuit fired bone china body was found not to be a common occurrence, supposedly due to the inhomogeneous distribution and varying chemistry of the glassy phase. It should also kept in mind that the chemical composition of the simulated glass used in this study was only an approximation of the actual analysis based on the hypothesis of "the phosphate glass equation" which was assumed to go to completion. The glass composition was then calculated by the difference method for a particular bone china body with a known composition. Furthermore, this hypothesis gives no regard to the possibility that there may be some dissolution of the crystalline phases in the glassy phase during biscuit firing. Of further interest is the lack of MgO in the original glassy phase, as opposed to 2 wt.% present in the simulated glass.

A better understanding of the chemical reactions and physical processes that bone china bodies undergo during biscuit firing may well help to overcome the two major production problems; variations in translucency and high temperature distortion. Furthermore, such an understanding may be useful in developing shorter firing schedules, in developing new compositions with improved properties, based on alternatives to bone ash, which is a relatively expensive component.

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