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Characterisation of biscuit fired bone china body microstructure. Part I: XRD and SEM of crystalline phases

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Abstract

As a ceramic material bone china is a highly specialised product and is the basis of the world's most attractive and expensive types of tableware, mainly due to its translucency, whiteness, bright glaze, decoration quality, and high strength. Despite numerous studies on bone china made by several authors over many years, insufficient is known even today about the chemical reactions and physical processes taking place between the various raw materials which make up the body, during biscuit firing. As a result, there is still controversy about the formation and chemistry of its constituent phases, particularly the glassy matrix phase. In this paper, part of an extended study, the biscuit firing process and the resultant microstructure of the bone china body, studied using a combination of techniques such as X-ray diffraction (XRD) and scanning electron microscopy (SEM), is reported. It is clearly shown that fired bone china body consists of crystals of anorthite, β-TCP, and also a small amount of quartz, rather unevenly dispersed in a complex glassy matrix phase. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Biscuit firing; Bone china; Microstructure; Phase composition; Tableware

1. Introduction

To date, bone china is a specifically English product. It was first developed and produced commercially by Josiah Spode II in Stoke-on-Trent around 1800 A.D. A short account of this invention is given by Rado.[1] It is believed that the development of bone china was stimulated by the desire at this time, of the English potters, to produce tableware and ornamental ware to match the whiteness, strength, and fine quality of the porcelain produced in China and Europe, particularly the Meissen product.[2] The particular characteristics of bone china that appeal are its whiteness, translucency, high glaze and decoration quality, and high strength. Such an attractive combination of properties results in bone china being one of the word's most attractive and expensive types of tableware.

Bone china is produced traditionally from the raw materials of bone ash, china clay, and Cornish stone. Compositions may vary from one company to another but the constituents can be grouped in the approximate weight ratios of 2:1:1. The minerals and oxides involved are listed in Table 1.

Production of bone china body requires close control of a number of processing parameters. A significant constraint is caused by the narrow temperature range allowable for vitrification, generally of the order of 15–25 °C. In this respect, the maximum biscuit firing temperature is critical and needs to be carefully controlled. Biscuit firing of bone china products is carried out in the region of 1220–1250 °C,[2] dependant on the precise chemical composition.

A typical unfired plastic bone china body will contain about 35% porosity, all of which is interconnected, i.e. in the form of open porosity. When the bone china body becomes fully matured as a result of firing, the remaining open porosity will be less than 1%, preferably below 0.5%, but there will also be a residue of closed pores giving a true porosity of about 8–10%.[4]

A survey of the relevant literature shows that the biscuit firing of bone china body has been studied by several authors over a period of many years and most have contributed significantly to the overall understanding of the system. However, despite these studies, little enough

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Table 1
Minerals and oxides involved in bone china manufacture[3]

Raw material	Mineral	Oxides	Wt.%
Bone ash	Hydroxyapatite	$Ca(OH)_2 \cdot 3Ca_3(PO_4)_2$	50
China clay	Kaolinite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	25
	Feldspar	$K_2O \cdot Al_2O_3.6SiO_2$	
Cornish stone	Quartz	SiO_2	25
	Mica	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2.2H_2O$	

is known even today about the chemical reactions and physical processes taking place between its various raw materials during biscuit firing process. As a result, there remains controversy about the formation and chemistry of its constituent phases, particularly the glassy matrix phase. It is now generally recognised that fired bone china bodies consist of crystals of anorthite, β-tricalcium phosphate (β-TCP) and sometimes a small amount of quartz embedded in a complex glassy matrix, which binds the microstructure together.

2. Experimental

2.1. Materials

The spray dried bone china body (Grade: BCG 400) for the present study was kindly supplied by Jesse Shirley & Son Ltd. (England). It is a new product and no data sheet was available at the time. It has a water content of ~2.5%. Raw material for the body is derived from a bone china body clay (Grade: BCP 4), with a typical chemical analysis as given in Table 2. The chemical composition of BCG 400 body is similar to BCP 4.

The spray dried bone china body was uniaxially pressed in a 20 mm diameter stainless steel die by means of a hand-operated hydraulic press at a suitable pressure, the peak pressure, 50 MPa, being maintained for 60 seconds. Following the pressing, the bone china pellets were placed in a drying oven at ~110 °C for at least 24 h until they reached a constant mass. After several firing trials at different firing temperatures for different soaking times and following measurements of the density and porosity values, a peak temperature of 1245 °C for 1 h soaking was standardised as the biscuit firing regime for the bone china pellets. The heating and the cooling rates were 75 and 200 °C/h, respectively. An electric furnace (Model: RHF 1500, Carbolite, England), heated with silicon carbide elements, was used for firing. The pellets were fired supported by an alumina grog spread on alumina plates.

Table 2
Typical XRF analysis of the BCP 4 grade bone china body clay [5]

Oxide	*Wt.%*
SiO_2	33.20
TiO_2	0.05
Al_2O_3	12.90
Fe_2O_3	0.24
CaO	25.90
MgO	0.72
Na_2O	1.27
K_2O	1.64
P_2O_5	19.50
ZnO	0.02
BaO	0.01
SrO	0.04
LOI at 1025° C	4.35

2.2. Experimental techniques

2.2.1. Etching

Both chemical and thermal etching techniques were used in this study. The chemical etching of polished biscuit fired bone china body was achieved by immersing in 5% hydrofluoric acid (HF) solution at room temperature for 120s. The thermal etching was carried out at 1150° C for 1 hour in an electric chamber furnace (Model: CWF 13/13, Carbolite, England), heated with coiled nichrome heating elements.

2.2.2. X-ray diffraction (XRD)

Prior to scanning electron microscopy studies, X-ray diffraction (XRD) was used for the qualitative determination of the crystalline phases present in the fired bone china body. This was performed using a Philips PW 1710 based diffractometer with a 40 kV generator voltage and a 25 mA current. Monochromatic CuK_α radiation, $\lambda = 0.154060$ nm, was employed. The X-ray scan was made over a range of 2θ values of 5–80° with data acquisition occurring for 1.0 s, at intervals of 0.02°. The X-ray intensities were recorded using a computer system and commercial software. Crystalline phases were identified by comparison with standard reference patterns from the Powder Diffraction File PDF-2 database sets 1–45, maintained by the International Centre for Diffraction Data (ICDD).

2.2.3. Scanning electron microscopy (SEM)

The SEM used was a Jeol JSM-6310 analytical scanning electron microscope fitted with Oxford Inst. AN 10/85 Link microanalysis system. A technique was developed to etch the biscuit fired bone china body to reveal its microstructure in relief and to observe the topographical contrast in the secondary electron (SEI) mode. There was also sufficient atomic number contrast to study the microstructure using back-scattered (BEI) mode on the polished surfaces. The EDS work was undertaken by withdrawing the beryllium window on the detector in order to increase the sensitivity of the system. A logarithmic scale display was chosen for presentation in order that the presence of the elements at low concentrations could be observed clearly on the display trace.

Gold coating of the specimens was carried out using a sputter coater (Model: S150B, Edwards High Vacuum Ltd, England). The carbon coating machine was Model: 12E6 (Edwards High Vacuum Ltd, England).

3. Results and discussion

3.1. Physical Properties

Values of bulk density and apparent porosity of the fired bone china body were measured using the water immersion method based on the Archimedes' principle, and with other physical properties are given in Table 3. When the bone china body is fully matured, the apparent porosity (accessible pore volume) will be less than 1%, preferably below 0.5%, but there will be a residue of closed pores giving a true porosity of about 8–10%. The apparent and true porosity of the fired bone china pellets fabricated in this study was found to be less than 0.5 and 10%, respectively, showing that the biscuit firing had been carried out successfully. Finally, translucency is a property of considerable importance from an aesthetic point of view, but its measurement is difficult and was considered to be outside the scope of this study. Generally speaking, if the bone china is properly fired, then its translucency is expected to be adequate. An initial visual examination of the fired bone china pellets indicated that they exhibited considerable translucency.

3.2. X-ray diffraction (XRD)

A representative XRD spectrum of the biscuit fired bone china body is illustrated in Fig. 1. Note that the spectrum has been normalised to its largest intensity peak. Examination of the peaks leads to the conclusion that the only crystalline phases present in the fired body are β-TCP and anorthite, with a small amount of quartz (marked as T, A, and Q in the spectrum respectively). It should also 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.

Table 3
The physical properties of the biscuit fired bone china body

Property	Bone china
Bulk density (g/cm^3)	2.58
Apparent porosity (%)	⩽0.5
True density (g/cm^3)	2.82[a]
Relative density (%)	91.5

[a] Provided by the supplier.

3.3. Scanning electron microscopy (SEM)

Fig. 2 displays a typical SEM image of the spray dried bone china body granules used in this study. The particles are roughly spherical in shape with an average diameter of ~200 μm, and each of which is assumed to consists of a very large number of individual particles of the body components. There is also a group of smaller spheres observable in the form of small granules often attached to the larger particles. As a result of the spherical shape and size, this powder flows easily into the die for uniaxial pressing. Most of the particles show hollow cores ("donut" shape), the dimple being the point where the hot core gas escapes during the last stages of drying. In addition, the granules have a smooth surface texture.

Fig. 3 is a typical BE image of the as polished surface of the biscuit fired bone china body, which illustrates the degree of the inhomogenity in its microstructure. The individual crystalline phases are rather unevenly dispersed in a glassy matrix. Atomic number contrast between the crystalline and glassy phases is evident in the image. Since calcium has the highest atomic number of the elements present in the body, it is inferred that the brighter areas are likely to contain higher amounts of

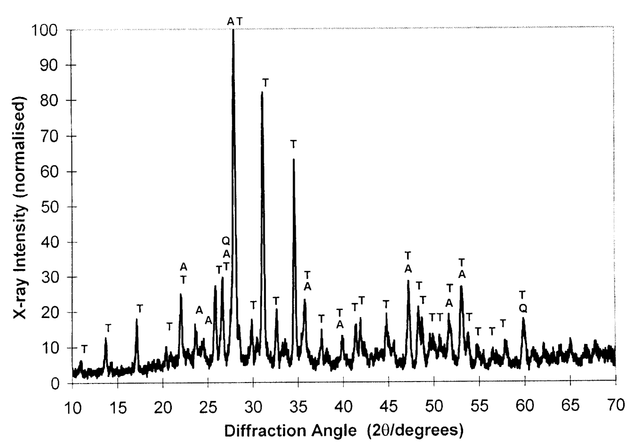


Fig. 1. A typical XRD spectrum of the biscuit fired bone china body. A, anorthite; T, B-TCP; Q, quartz.

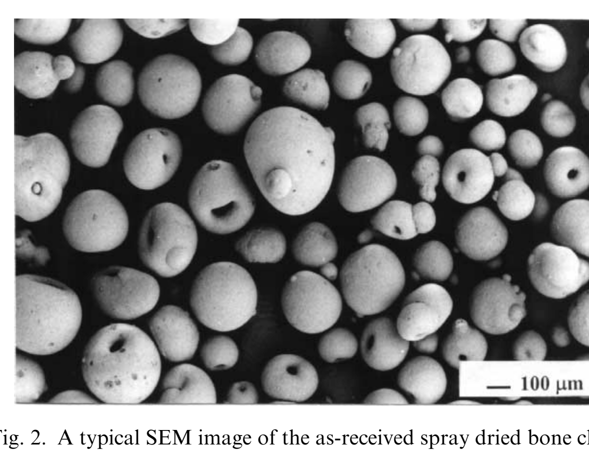


Fig. 2. A typical SEM image of the as-received spray dried bone china body granules.

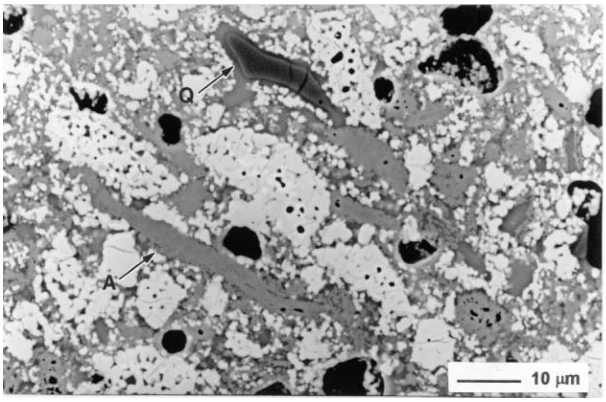


Fig. 3. A typical BE image of the biscuit fired bone china microstructure (as polished surface).

calcium. The EDS analyses on these bright areas confirmed that they represent the β-TCP phase. Discrete areas of anorthite are difficult to pick out, possibly because it is formed from very fine-grained clay which may be distributed uniformly. On the other hand, Fig. 3 does include a long anorthite crystal (marked as A) on the left hand side of the image. There is also a quartz crystal (marked as Q) present in the image. The dark areas represent the closed pores, which are of a range of different shapes and sizes. The large pores (above 10 μm) are believed to have originated from the remnant void structure of the packing of the spray dried granules developed during the uniaxial pressing. An additional feature observed in the microstructure is the presence of very fine porosity on the large β-TCP crystals. Fig. 4 gives the EDS spectrum obtained from the same region as shown in Fig. 3. As can be seen, all the main elements present in the bone china body were readily detected (see also Table 2).

SEM examination, following etching in 5% HF solution for 120 s, of the biscuit fired bone china microstructure, revealed that some of the glassy matrix was selectively attacked and removed by the etchant, clearly exposing the constituent crystalline phases. Fig. 5 depicts the SE image of such an etched area. The big crystal with small pores (marked as T) in the image is a β-TCP crystal. The EDS analysis shows that it contains mainly calcium (Ca) and phosphorus (P) with very small amounts of silicon (Si), aluminium (Al), magnesium (Mg), and sodium (N) (see Fig. 6 (a)). Several EDS analyses, in most cases carried out on different β-TCP crystals, also revealed the presence of these impurities. It is possible that the detection of such impurities may be in part due to signal interference from neighbouring areas. However, Na and Mg would be expected to be present as natural impurities and Si and Al as natural contaminants in calcined and ground bone ash. Of further interest, the β-TCP crystal in Fig. 5 appears to be made up of small individual crystals sintered and bonded together, rather than being a unique single crystal. Should this be a feature of the formation of the growth

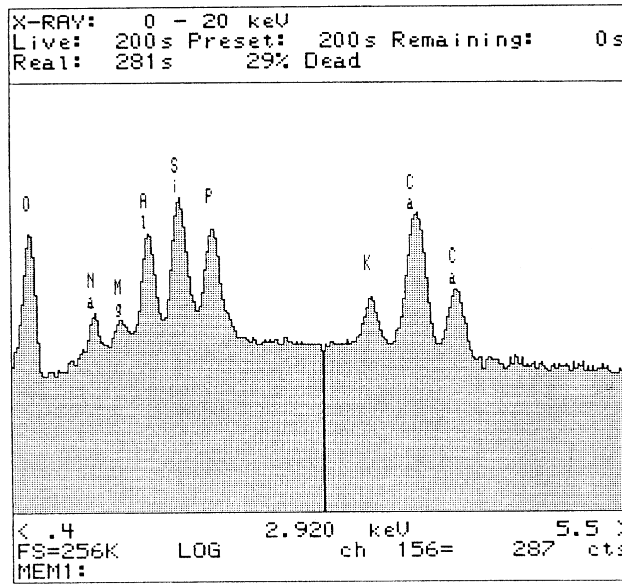


Fig. 4. A typical EDS spectrum of the biscuit fired bone china body.

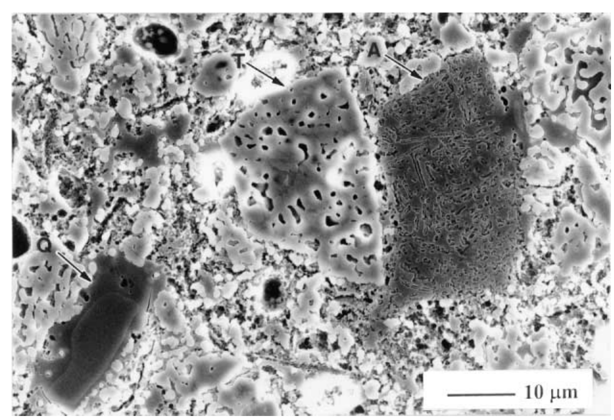
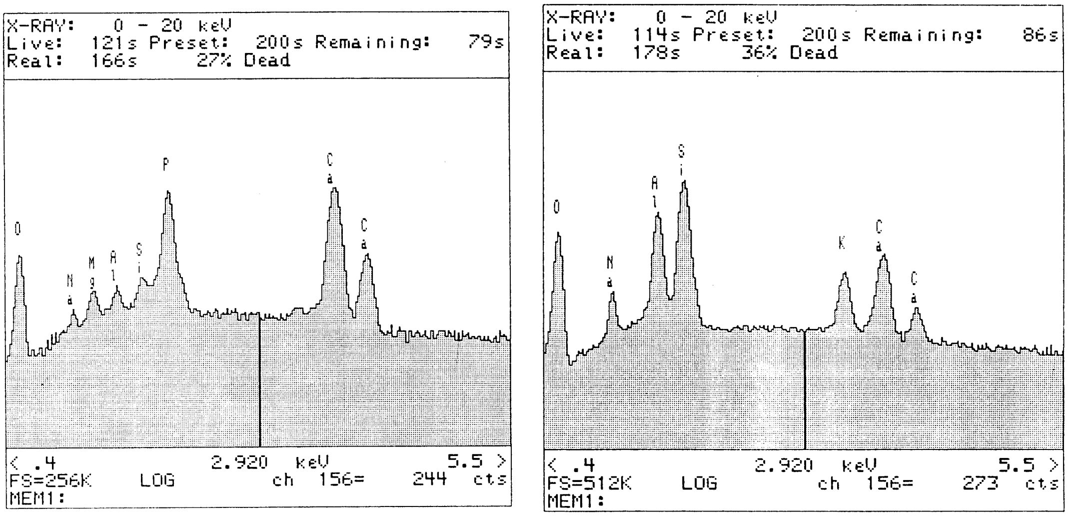


Fig. 5. A typical SE image of the polished and chemically etched microstructure of the biscuit fired bone china body.

during sintering of small agglomerates of β-TCP, it could account for the regions of small voids present in the larger crystals, their presence being due to the porosity residing between the original raw materials that formed the β-TCP.

As previously mentioned, it is difficult to locate the anorthite crystals in the fired bone china microstructure. In Fig. 5, the large crystal marked A is believed to be an anorthite crystal. As can be seen, it was lightly attacked by the etchant. The EDS analysis revealed the presence of Al, Si, and Ca with lesser amounts of Na and K (see Fig. 6 (b)). The same elements were also detected in varying proportions from other similar features in the microstructure. It is assumed that there may be some dissolution of anorthite crystals in the glassy phase at high temperatures.



(a) (b)

Fig. 6. (a) The EDS spectrum of the β-TCP crystal marked as (T) in Fig. 5; (b) the EDS of the anorthite crystal marked as (A) in Fig. 5.

Fig. 5 also contains a quartz crystal (marked as Q). It is noticeable that the sharp corners have been rounded by surface tension forces and by partial solution of the corner regions into the glassy matrix during the biscuit firing. The region close to the residual quartz grain is the glassy solution rim. In addition, there is a circumferential microcrack present around the quartz crystal in the image. Such microcracks are to be expected since differential thermal expansion stresses may arise as a result of the thermal expansion mismatch on cooling between the quartz grains and surrounding glassy solution rim during the β to α transformation of quartz.

The microstructure of the biscuit fired bone china body was also investigated using SEM after being thermally etched at 1150°C for one hour soaking time. It was found that thermal etching is a more effective technique than the chemical etching for revealing the grain boundaries of β-TCP crystals distributed in the microstructure. Fig. 7 illustrates such a polished and thermally etched region. As can be seen from the image, there is a large β-TCP crystal, which is actually made up of a number of separate crystals in the middle, with a circumferential microcrack surrounding the feature. Again the fine pores can be seen between the individual crystals. Moreover, the presence of individual β-TCP crystals with different grain sizes embedded in the glassy phase is quite evident. There is also a quartz crystal visible on the top right hand corner of the image. Again a small microcrack can be seen around the quartz crystal, which is limited to the periphery of the crystal.

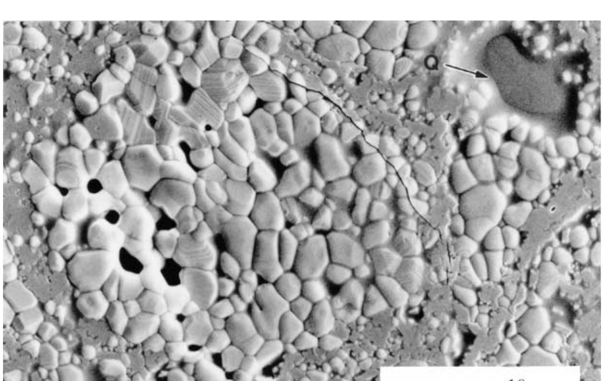


Fig. 7. A typical SE image of the polished and thermally etched microstructure of the biscuit fired bone china body.

4. Conclusions

In this part of the programme, the pressing and the biscuit firing of the spray dried bone china body granules was carried out successfully. The firing schedule was standardised at 75 °C/h rise in temperature plus 1 h soaking time at 1245 °C peak temperature. The density and porosity values obtained through this heat treatment schedule were well within commercial requirements. A visual examination of the fired pellets also indicated that they exhibited considerable translucency.

SEM investigation of the polished and chemically etched surfaces of the biscuit fired bone china pellets revealed considerable complexity in the nature and distribution of the crystalline and the glassy phases in its microstructure. It was also shown by the XRD studies that β-TCP, anorthite and a small amount of quartz were the only crystalline phases present in the bone china body at the firing temperature employed.

An interesting experiment attempted during this study was to thermal etch the biscuit fired bone china body followed by examination using SEM. It was found that thermal etching was a more effective technique than the standard chemical procedure for revealing the distribution of β-TCP crystals in the microstructure.

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