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The characterisation of paper composite porcelain in a fired state by XRD and SEM

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Abstract

Paper composite porcelain is widely used to produce artistic objects in ceramic art. The aim of this study is to characterise the microstructure and chemical compositions of paper composite porcelain since they determine the material properties. Interaction between paper filler, paper fibre, and the porcelain clay body in its fired state were investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The starting materials were kaolin, feldspar, quartz, hybrid copy/print waste paper, and other waste papers. XRD clearly shows that the paper composite porcelain bodies in the fired state mainly consist of α-quartz, mullite, anorthite and amorphous materials in a complex matrix. In the fired state, calcite from the waste paper's relict interface to kaolinite from porcelain. A transformation to anorthite in the microstructure of paper composite porcelain was indicated. In the microstructure, anorthite tubes were observed as fibrous structures in their fired state.

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Keywords: Waste paper; Calcite; Anorthite; Microstructure; Chemical analysis; Porcelain

1. Introduction

Porcelains are vitreous ceramic whitewares used extensively in tableware, sanitary ware, decorative ware, electrical insulators and dental prosthetics. Porcelains typically have a triaxial formulation comprised of 50% clay, 25% flux and 25% filler.[1] Firing bodies containing these three components results in a grain and bond microstructure consisting of coarse aggregate (filler) particles held together by a finer matrix or bond system that is almost fully dense.[2] Porcelain represents the foundation of the ceramics discipline and is one of the most complex ceramic materials. Composed primarily of kaolin, feldspar, and quartz, porcelains are heat-treated to form a mixture of glass and crystalline phases.[3]

The term "paper composite porcelain" stands for any kind of porcelain that is combined with paper. Paper composite porcelain is a type of paper clay[4] that mainly consists of plant-based fibre pulp and mineral additives. They are widely used to produce artistic objects in ceramic art. As a ceramic material, paper composite porcelain is a specialised product and is the basis for the most attractive and inexpensive types of ceramic art products, mainly due to its light weight, workability and its high strength in its green state.[5] Despite the wide use of paper composite porcelain by numerous ceramists over many years, the character of this material is still poorly determined. No detailed studies have been reported for the chemical components and microstructural interactions between the porcelain raw materials, paper filler, and fibres, which make up the paper composite porcelain body in its fired state. In spite of the commercial interest in developing paper composite porcelain, very little research has been conducted in this field. This leaves significant opportunities for investigation and study, particularly in the two topical areas of phase and microstructural evolution and mechanical performances, the main topics to be addressed here. According to Gault,[6] Juvonen,[7] and Lightwood[8] the paper fibre is burnt away and leaves the porous structure in the fired state of paper composite porcelain body that gives a lighter weight than ordinary porcelain bodies. The organic paper fibre cellulosics act as a binder in the paper composite porcelain body. However, the inorganic mineral additives as a filler from paper may not just burn away, but could change

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form while interacting with other porcelain raw minerals. As a result, a controversy about the formation and chemistry of constituent phases in a paper composite porcelain body, particularly the glass matrix phase in a fired body, remains.

The main goal of this paper is to investigate the microstructural formation and chemical analysis in paper composite porcelain bodies, highlighting the importance of mixing of the paper fillers and fibres formed in the porcelain bond system. Additionally, some comparisons have been made to porcelain body formations to purify the porcelain system. This study involves the characterisation of the interactions between paper filler, paper fibre, and the porcelain clay body during the production process in the fired state using XRD and SEM techniques. The aim is to obtain detailed and systematic information about the morphological and chemical characteristics of the resulting phases formed at the interfaces. This paper focuses on the complexities of the microstructure and the phase development in paper composite porcelain in a fired state.

2. Experimental procedure

2.1. Raw materials of porcelain

Porcelain has been studied as a mother body. The most relevant characteristics of porcelain are the following: it is composed of 50% kaolin, 25% feldspar and 25% quartz. The starting raw materials were kaolin (ECC International Standard Porcelain, Imerys Minerals Ltd., UK); the mineralogical composition is 84% kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) of 100% weight, whose chemical analysis approximates 48% silica (SiO_2), 36.5% alumina (Al_2O_3), and 12.5% H_2O. Particle size distribution is 70% $<2\,\mu m$ of weight %. FFF Finnish flotation feldspar (Partek Industry Mineral Ltd., Finland) of ceramic grade 200 mesh; the typical minerals are 47% potash feldspar ($K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$) and 42% soda feldspar ($Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$), whose chemical analysis is 67.2% silica, 18.3% alumina, 7.7% potash (K_2O) and 5.0% soda (Na_2O). The typical mineral composition of Finnish flotation quartz (Partek Industry Mineral Ltd.) of ceramic grade 200 mesh, is 96.5% quartz and 3.5% feldspar whose chemical analysis approximates 98.5% SiO_2 of high purity. Silica stone consisted of almost pure quartz, which is hereafter designed as quartz. The recalculated oxides of the raw materials are shown in Table 1.

Table 2
Composition of copy paper (wt.%)

Product: MultiCopy Original	
Short fibre pulp (beech)	36
Long fibre pulp (pine and spruce)	36
Precipitated calcium carbonate (PCC)	20
Starch	3.1
Optical brightening agent	0.6
Polymer	0.1
Neutral size agent	0.1
Retention agent (silicon dioxide, BMA)	0.1
Water	4.3

Source: declaration of content reported by Stora Enso Nymölla AB (2002).

2.2. Waste paper as additional raw material of paper composite porcelain

Starting waste materials were chosen among the numerous varieties in paper production. Two different hybrid waste papers were selected due to easy availability. The first is a hybrid copy/print paper waste (CP), and the second is other hybrid paper waste (HP) that mixes all types of paper. Both included coated and uncoated papers. Table 2 shows the chemical compositions of the copy paper used in this study. The mineralogical constituents of the two papers are approximately the same with the exception of kaolinite, and talc, which are included in HP. The mineral additives of the paper used in this study are kaolin (kaolinite, $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$), calcium carbonate (calcite, $CaCO_3$) and talc ($3MgO{\cdot}4SiO_2{\cdot}H_2O$). The mineral additives of paper, as fillers and coatings, are added to papermaking stock to improve properties such as opacity and smoothness, and often to reduce costs in paper production.[9] Kaolin and calcium carbonate are the most common mineral fillers of paper. Talc or titanium dioxides (TiO_2) are also used.

2.3. Sample preparation

Both hybrid waste papers (CP and HP) were reduced to pulp before being mixed with the porcelain powders. The waste paper was first soaked in hot water and beaten to disintegrate the fibres. Using a large mesh screen to get a pulp with 20% water, the porcelain powders were then added, and squeezed to get rid of excess water. The excess water was recycled as additional water when mixed with porcelain powders and paper pulp. The starting powders were mixed with various ratios in a planetary mixer for 3 h. The content of added water was 30 wt.%. Test samples were made of each test batch by free-hand pressing into a one-sided plaster

Table 1
Chemical compositions of the raw materials (wt.%)

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	P_2O_5	Rb_2O	MgO	Na_2O	K_2O	Loss of ignition	Total
Kaolin	48	36.5	0.68	0.02	0.07	–	–	0.30	0.10	1.65	12.5	99.82
Feldspar	67.2	18.3	0.13	–	0.5	0.14	0.07	<0.03	5.0	7.7	0.39	<99.46
Quartz	98.5	0.8	0.025	–	0.4	–	–	0.01	0.2	0.15	0.14	100.225

Table 3
Composition of a mother porcelain body (M)

Raw materials	Percentage (%)
Kaolin	50
Feldspar	25
Quartz	25

mould, and the open surface was smoothed with a splint. Test samples were dried for 48 h at room temperature. After air-drying at room temperature for 48 h, they were further dried in an oven for 24 h at 110 °C. Firing was carried out in an electric kiln (Nabertherm, Germany), heated with Kanthal A1 elements. The samples were fired once at pick temperatures of 1220, 1240, 1260, 1280 and 1300 °C. The firing temperature is fixed at 1300 °C because studio potters rarely use firing temperatures above 1300 °C and commercial paper porcelains are mainly produced for studio potters. The samples were heated up to 250 °C (90 °C/h), and the heating continued up to 600 °C (150 °C/h), and then the firing proceeded at full rate to a final temperature, with a dwell time of 5 min.

The mineralogical composition of the mother porcelain powders used is shown in Table 3. The ratio of dried fibre varies from 6.8, 14.6 and 39.8% in relation to the dry weight of porcelain powders.

The test batches were mixed with two different paper types (CP and HP) with three different paper ratios (50, 70 and 90% by volume; 6.8, 14.6 and 39.8% in weight), five different firing temperatures, a base porcelain body (mother porcelain, M) with no paper fibre added, and two different raw paper types. The formulations of paper composite porcelain bodies are shown in Table 4. The characterisation quality assurance was adopted according to ISO-8402.

It should be noted that one practical difficulty with the XRD work was to prepare representative specimens of the relevant interfaces. The paper fibres were not uniformly distributed in the samples. The unevenness of the surface and different depths of penetration made the assessment of the diffractogram a difficult task.

2.4. Experimental techniques

2.4.1. X-ray diffraction (XRD)

XRD was used for the qualitative determination of the crystalline phases present in the 1300 °C fired paper composite porcelain bodies, 1300 °C fired porcelain body, CP hybrid paper, and HP hybrid paper. This was performed using a Siemens D 5000 diffractometer operating at 45 kV and 45 mA. Monochromatic Cu Kα radiation, $\lambda = 0.154060$ nm, was employed. The X-ray scan was made over a range of 2θ values of 15–60° with data acquisition for 2.0 s at intervals of 0.05°. The X-ray intensities were recorded using a computer system and commercial software Diffract AT. Crystalline phases were identified by comparison with standard reference patterns from the Powder Diffraction File PDF-2 database sets 1–52, maintained by the International Centre for Diffraction Data (ICDD).

Table 4
Paper composite porcelain formulations (wt.%)

	MCP1	MCP2	MCP3	MHP1	MHP2	MHP3
Kaolin	46.60	42.70	30.10	46.60	42.70	30.10
Feldspar	23.30	21.35	15.05	23.30	21.35	15.05
Quartz	23.30	21.35	15.05	23.30	21.35	15.05
CP	6.80	14.60	39.80	–	–	–
HP	–	–	–	6.80	14.60	39.80

2.4.2. Scanning electron microscopy (SEM)

This study examined the microstructures of samples fired at different temperatures in order to understand developments and how cellulose from the waste paper changes the porcelain structure to the fibrous structure. The MCP and MHP samples were fired once at temperatures of 1220, 1240, 1260, 1280 and 1300 °C. The M sample was fired once at a chosen temperature of 1300 °C. The CP sample was prepared raw. Microstructural examination of the interfaces in surfaces were carried out using a CamScan S4-80DV analytical SEM equipped with Oxford Instruments EXL Link microanalysis system. This technique was used for a fired porcelain body, as well as fired paper composite porcelain bodies, to reveal their microstructures and to observe topographical contrast in the secondary electron imaging (SEI) mode. Gold coating of the specimens was carried out using an electron beam evaporation system (Model: S150B, Edwards High Vacuum Ltd., UK).

3. Results and discussion

3.1. X-ray diffraction (XRD)

XRD phase analysis of the components detected from the samples is shown Table 5.

Raw material compositions consisted of equal amounts of kaolin, feldspar and quartz in MCP1 and MHP1, MCP2 and MHP2, MCP3 and MHP3, respectively, with a variation in

Table 5
XRD analysis of the chemical components from samples

Samples	Phase
CP raw	Calcite, cellulose, maghemitite, sodium calcium silicate
HP raw	Calcite, cellulose, talc, kaolinite
M 1300 °C fired	α-Quartz, mullite, nepheline
MCP1 1300 °C fired	Anorthite, α-quartz, mullite
MCP2 1300 °C fired	Anorthite, α-quartz, mullite, albite, wollastonite
MCP3 1300 °C fired	Anorthite, α-quartz, mullite, albite, wollastonite, hematite
MHP1 1300 °C fired	Anorthite, α-quartz, mullite, albite
MHP2 1300 °C fired	Anorthite, α-quartz, mullite, albite
MHP3 1300 °C fired	Anorthite, α-quartz, mullite, albite, portlandite

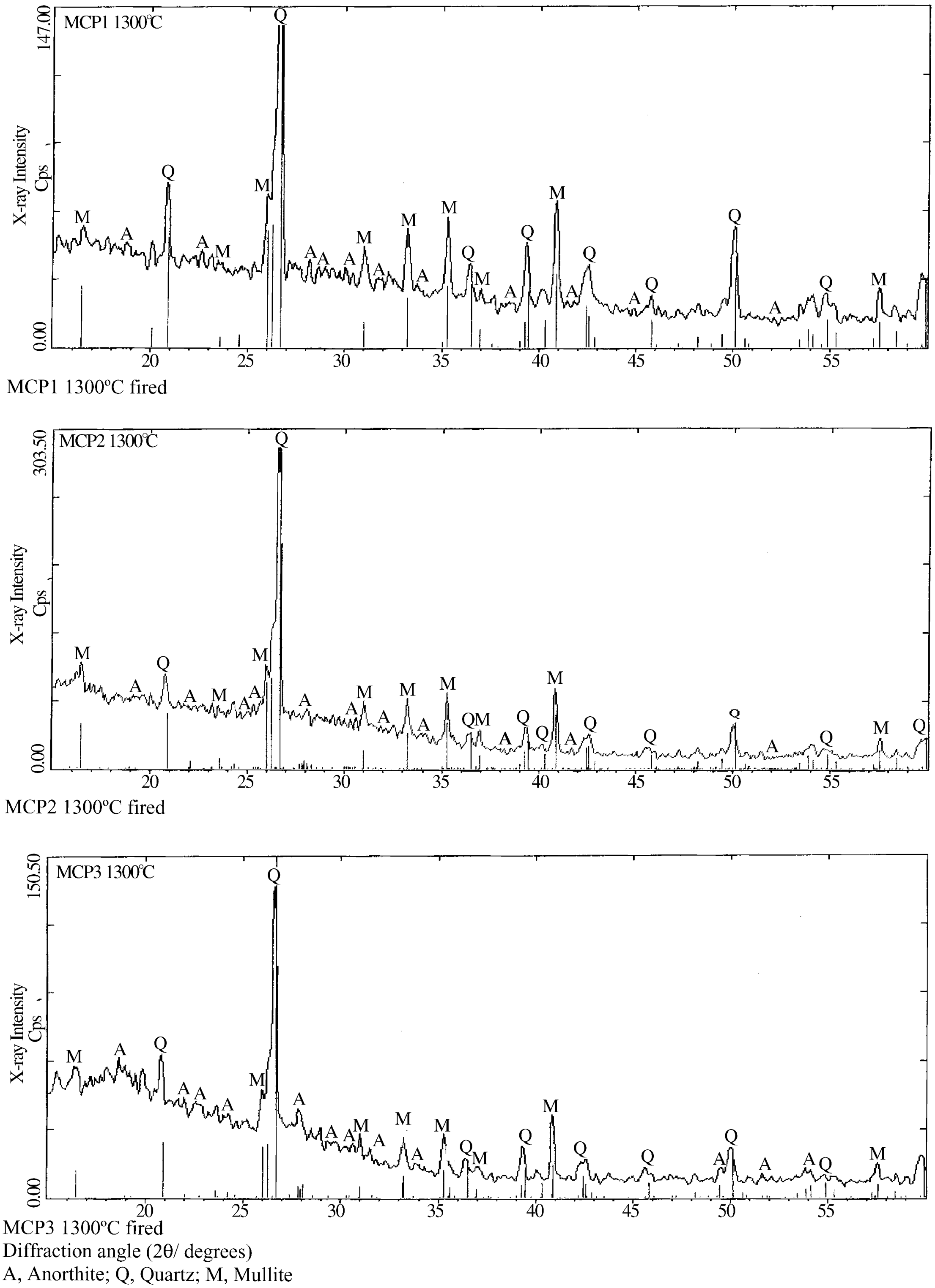
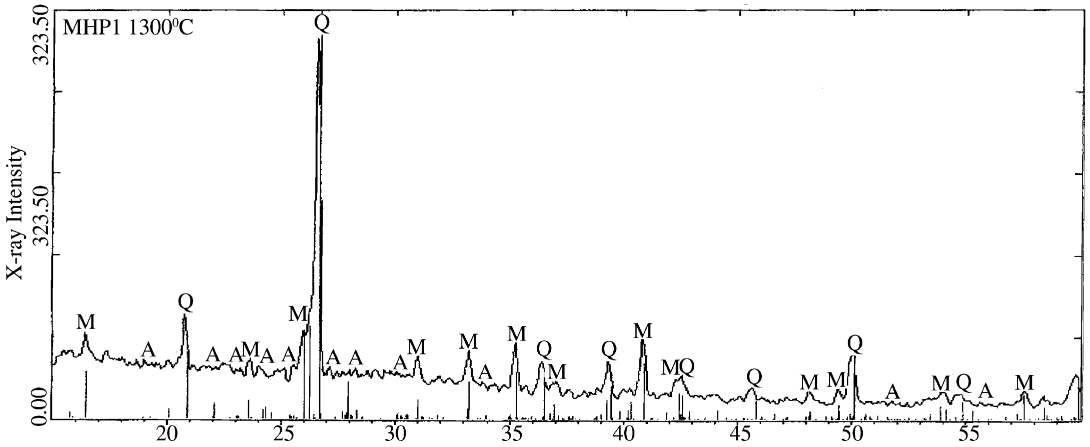
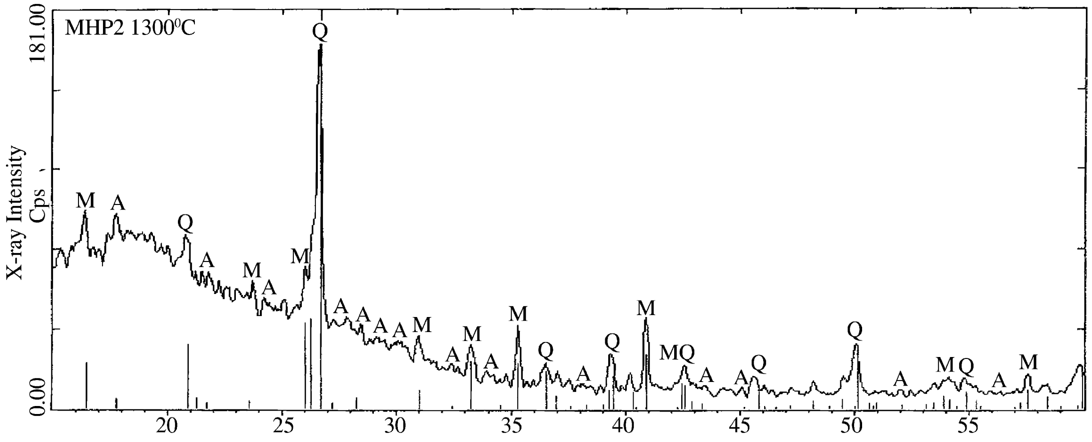


Fig. 1. X-ray diffraction patterns with various compositions in 1300 °C fired MCP bodies.

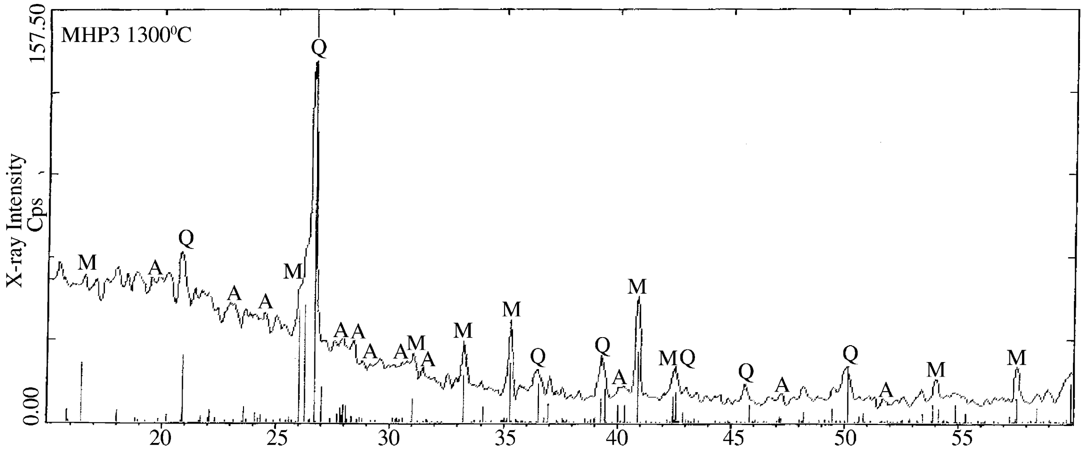
the CP and HP contents. Compositions fired at 1300 °C consisted almost totally of mullite ($3Al_2O_3{\cdot}2SiO_2$), α-quartz (SiO_2), anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) and an amorphous silica-rich phase. The increased amounts of CP or HP in sample batches are attributed to the increasing Ca contents as anorthite, wollastonite ($CaO{\cdot}SiO_2$) and portlandite ($Ca(OH)_2$) in samples. Representative XRD diffractograms of the samples are illustrated in Figs. 1–4. Examination of the peaks leads to the conclusion that the only major crystalline phases present in the fired paper composite porcelain



MHP1 1300°C fired



MHP2 1300°C fired



MHP3 1300°C fired
Diffraction angle (2θ/ degrees)
A, Anorthite; Q, Quartz; M, Mullite

Fig. 2. X-ray diffraction patterns with various compositions in 1300 °C fired MHP bodies.

bodies are mullite, α-quartz, and anorthite (marked as M, Q and A, respectively, in the diffractogram) despite the different amounts or the different types of paper contents in the bodies.

In Figs. 1–4, the major phases show the distinct peaks marked in the XRD patterns. The traces are also determined by XRD but the peaks are not marked in the patterns.

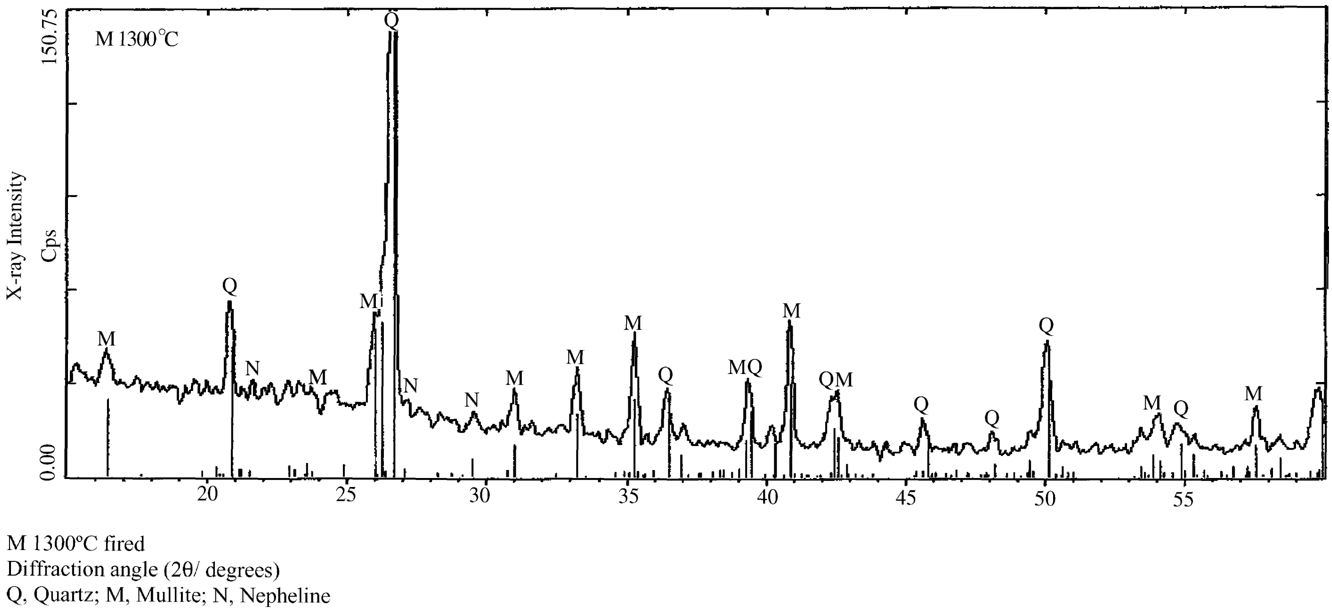


Fig. 3. X-ray diffraction pattern in 1300 °C fired M body.

Fig. 1 shows XRD patterns as a function of the composition in the fired MCP bodies heated at 1300 °C. The XRD patterns show that mullite, α-quartz, anorthite and amorphous materials are formed at all the MCP batch compositions. Wollastonite and albite ($Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$) are formed in MCP2 and MCP3 with larger amounts of CP than MCP1. Hematite (Fe_2O_3) is formed only in the MCP3 fired body with the largest amount of CP.

The increasing anorthite peak is directly proportional to the increasing amount of CP in the porcelain body. This is because more calcite is relict from CP, as shown in Fig. 1. The anorthite is formed by crystallisation from the glassy phase produced from the calcite, feldspar, quartz and kaolin. Anorthite was also synthesised from kaolin and CaCO3,[10] and SiO_2, $CaCO_3$ and Al_2O_3[11] α-quartz and mullite decreased inversely in proportion to increasing CP in a porcelain body. Major components of the MCP1 sample fired at 1300 °C are anorthite, α-quartz and mullite. Major components of the MCP2 sample fired at 1300 °C are anorthite, α-quartz and mullite, and its traces are wollastonite and albite. Major components in the MCP3 sample fired at 1300 °C, anorthite, α-quartz and mullite were identified with traces of hematite, wollastonite and albite. It is presumed that hematite is relict from print ink in CP. Compared with these profiles, no differences were observed except the intensity of diffraction peaks and some traces indicating changes in the relative amounts of these compounds. All MCP1, MCP2 and MCP3 samples fired at 1300 °C show anorthite, α-quartz and mullite as major phases.

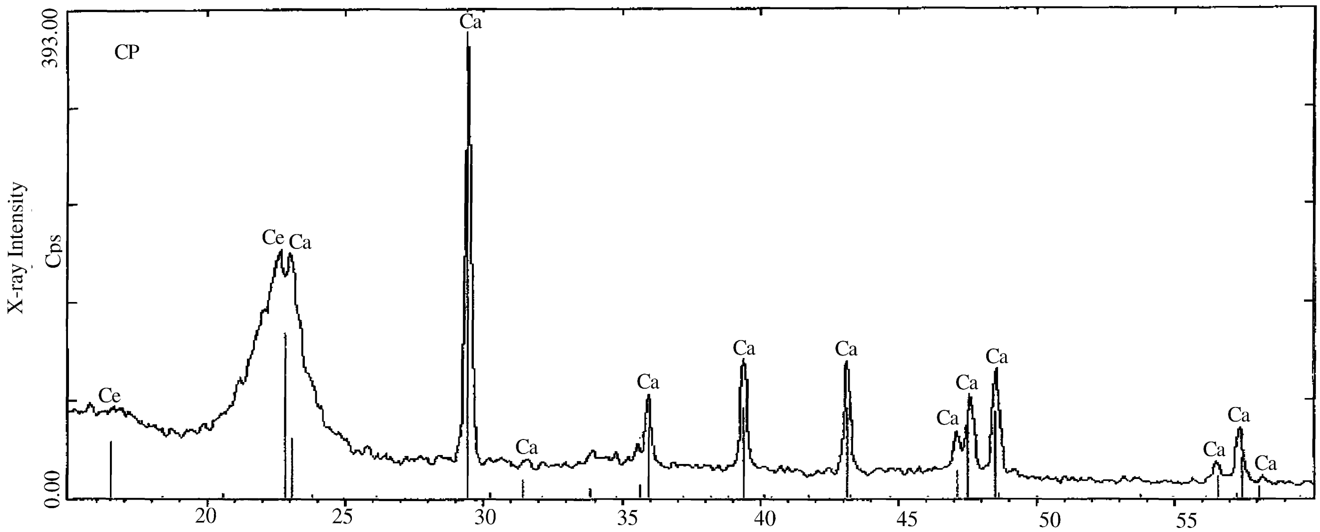
Fig. 2 shows the features of the MHP 1300 °C bodies with XRD patterns very close to those of MCP 1300 °C fired bodies, in which the major components anorthite, α-quartz and mullite are formed. The addition of HP as a substitute for clay forms anorthite in all the MHP fired bodies. Albite as a trace it is formed in all the MHP fired bodies. Portlandite, a trace, is formed only in the MHP3 fired body with the highest HP content. α-Quartz and mullite are a decreasing inversely in proportion to a larger amount of HP in a porcelain body. However, the anorthite increases directly proportional to the increases the amount of HP in a porcelain body because of the fact that more calcite is relict from paper. No portlandite is detected from MHP1 and MHP2.

The XRD analysis (Fig. 3) shows that M body fired at 1300 °C contains mostly α-quartz and mullite as major components. A trace is nepheline ($Na_2O{\cdot}Al_2O_3{\cdot}$2SiO2). Anorthite is not formed in the M body that clearly differs from the MCP and MHP bodies.

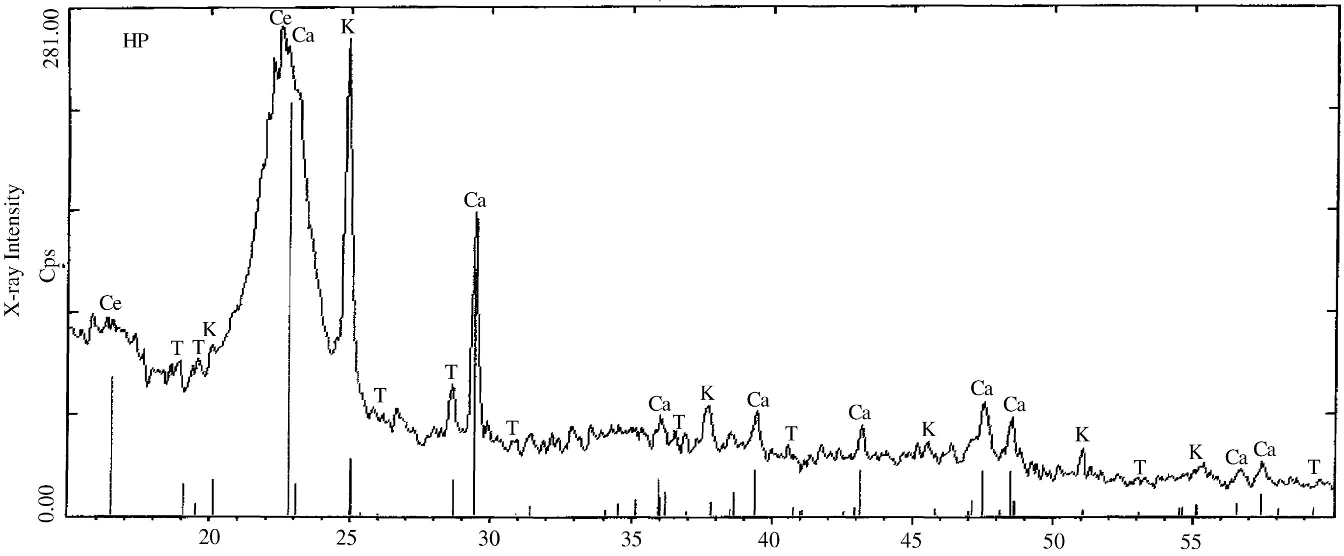
Fig. 4 shows the XRD patterns of the CP and HP raw samples. Major components of the CP raw sample are calcite and cellulose ($(C_6H_{10}O_5)_n$). Traces are maghemite (Fe_2O_3) and sodium calcium silicate ($Na_2O{\cdot}CaO{\cdot}SiO_2$). It is assumed that maghemite is relict from CP used as a pigment of print ink. This remains on MCP bodies even after 1300 °C fired as a trace. Sodium calcium silicate is an impurity from calcite. Major components of the HP raw sample are calcite and cellulose. Traces are talc and kaolinite.

3.2. Scanning electron microscopy (SEM)

SEM micrographs of the surfaces of the MCP and MHP samples containing different fibrous structures compared with M 1300 °C fired body, are shown in Fig. 5. The fibrous structures display strongly binding fibres, an interlocking of the fibres and construction of fibrous bridging. The surface morphologies of fired samples (M, MCP, MHP fired samples) and a fresh raw sample (CP raw) are examined



CP
Ca, Calcite; Ce, Cellulose

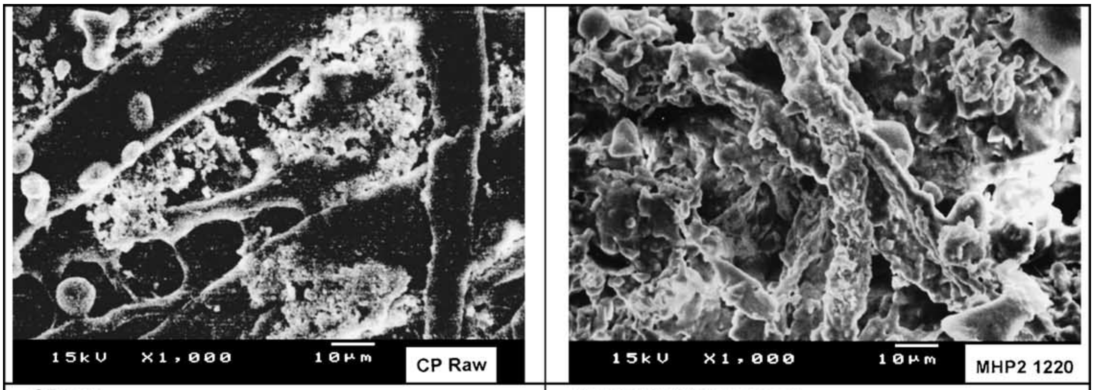


HP
Diffraction angle (2θ/ degrees)
Ca, Calcite; Ce, Cellulose; T, Talc; K, Kaolinite

Fig. 4. X-ray diffraction patterns in CP and HP raw samples.

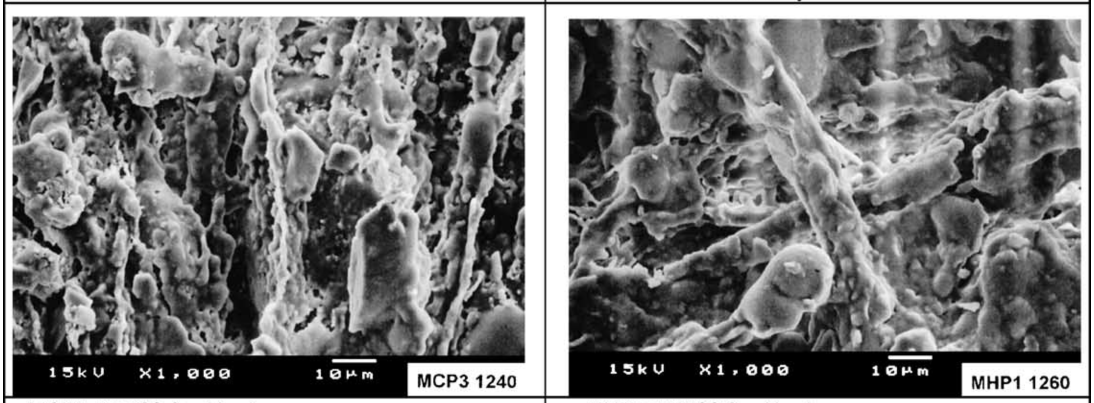
by SEM techniques. SEM examinations revealed that the fibrous structure decreases with increasing firing temperature. As shown in Fig. 5, the orientation of the fibrous structure is random in the composites. It is also observed that the fibrous structure distribution in the composites is not very homogeneous. Fig. 5 shows SEM photomicrographs of the base samples surfaces that were fired at 1220, 1240, 1260, 1280 and 1300 °C as an elevated temperature.

The micrographs, taken at different firing temperatures, show how the typical surface structure changes with increasing temperature, which are characteristic of all the compositions used in this work. The high porosity fibrous structure is clearly visible in the structure of 1220 °C fired MHP2 body fired at the lowest temperatures. At higher temperatures, the pores start to coalesce to form a closed porosity that is reduced between 1220 to 1240 °C in the MCP3 body. At the highest temperature, on MCP1 and MHP2 bodies fired at 1300 °C, the surface structures of the dense glassy matrix is formed and vitrified. However, the fibrous structures are still displayed at 1300 °C in MCP1 and MHP2 fired bodies, which illustrates the degree of the inhomogenity in its microstructure. The individual crystalline phases are rather unevenly dispersed in a glassy matrix. It is difficult to locate



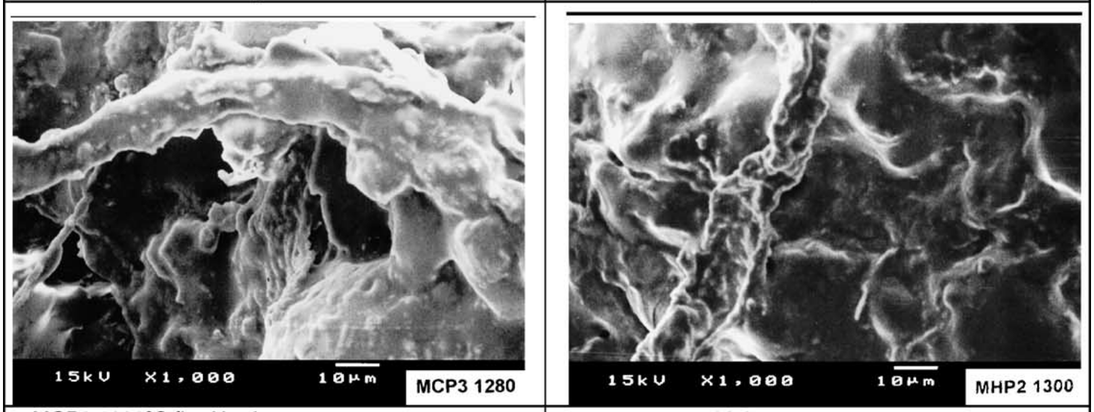
CP raw

MHP2 1220°C fired body



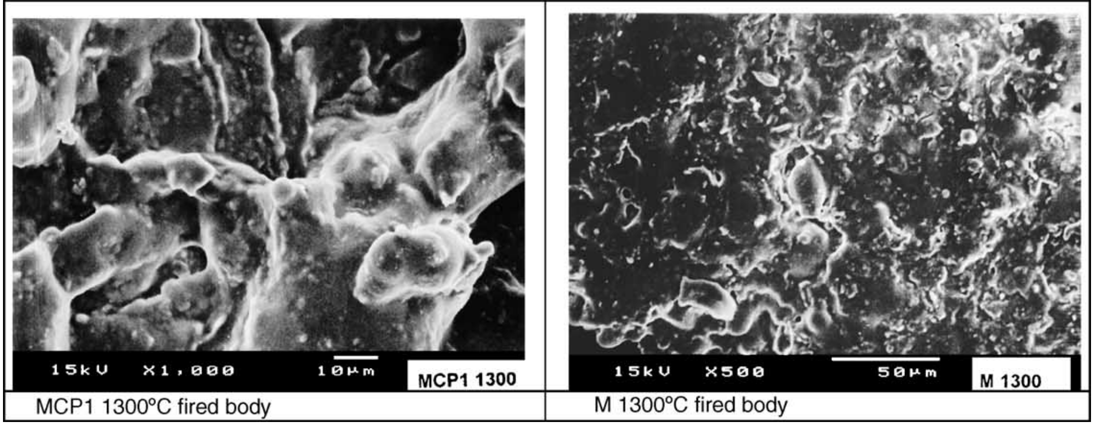
MCP3 1240°C fired body

MHP1 1260°C fired body



MCP3 1280°C fired body

MHP2 1300°C fired body



MCP1 1300°C fired body

M 1300°C fired body

Fig. 5. SEM photomicrographs of the base samples surfaces that fired at 1220, 1240, 1260, 1280 and 1300 °C as an elevated temperature.

the anorthite crystals in the fired MCP and MHP microstructure. On the other hand, the anorthite crystals are formed into anorthite tubes in the fibrous structures. The anorthite originates from the calcite component of waste paper, and the anorthite tubes are shaped from the cellulose fibrous structure from the CP and HP. In addition, it is believed that there may be some dissolution of anorthite crystals in the glassy phase at high temperatures. The M 1300 °C fired body shows the surface of the mother porcelain body without CP or HP. The microstructure of the 1300 °C fired M body has no fibrous structure, and clearly differs from the MCP and MHP bodies.

4. Conclusions

A microstructural investigation was conducted to determine if the addition of the selected waste paper would change the microstructure and chemical properties of paper composite porcelain in the fired state. After firing, the microstructure of paper composite porcelain bodies mainly consists of α-quartz, mullite, anorthite and amorphous materials; the grains held in a complex matrix. The chemical composition of raw recycled hybrid copy/print papers mainly consists of calcite, cellulose, and small amounts of maghemite and sodium calcium silicate. The chemical composition of other raw recycled hybrid papers mainly consists of calcite, cellulose, talc and kaolinite. Calcite as paper filler from the recycled papers melts with the kaolinite during the firing process. Their compositions transformed to anorthite in the microstructure of paper composite porcelain in a fired state. In paper composite porcelain, anorthite tubes as a fibrous structure are observed in fired bodies by SEM. The fibrous structures display strongly binding fibres, an interlocking of the fibres and construction in the fibrous bridging.

It is shown by the XRD that the only major crystalline phases present in the fired paper composite porcelain bodies are mullite, α-quartz, anorthite, and amorphous materials despite the different amounts or the different types of paper contents in bodies. The development of anorthite in the fired paper composite porcelain is caused by calcium carbonate from the waste paper that increases the heterogeneity in the formation of a porcelain body.

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