

Dolomite, wollastonite and calcite as different CaO sources in anorthite-based porcelain

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Abstract

Anorthite-based porcelain was fabricated by using ball clay, quartz, alumina, feldspar and three different sources of CaO as raw materials. The effect of CaO sources such as dolomite, wollastonite and calcite on the mechanical, thermal and aesthetical properties of anorthite-based porcelain was investigated. X-ray diffraction (XRD) and scanning electron microscopy (SEM) studies were also carried out to analyze the microstructure. Anorthite was formed as major phase in all the samples fired at their optimum sintering temperatures (1200, 1215 and 1230 °C). The sample with dolomite had the highest bulk density but the smallest flexural strength due to formation of substantial glassy phase. The maximum flexural strength (~ 110 MPa) was reached in the sample containing wollastonite, which was mainly attributed to the favorable microstructure. Anorthite as the single crystalline phase was found in the sample with calcite and the sample showed the lowest thermal expansion coefficient and the highest whiteness, which was similar to bone china in appearance. © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: D. Porcelain; Anorthite; CaO sources

1. Introduction

Bone china is a highly specialized product in terms of its appearance; being exceptionally white and translucent makes it the world's most expensive type of tableware [1]. Typical composition of bone china is about 50 wt% animal bone ash, 25 wt% china clay and 25 wt% Cornish stone or feldspar [2]. After sintering, the phases in the fired body generally consist of 40 wt% β -tricalcium phosphate (β -Ca₃(PO₄)₂), 30 wt% anorthite (CaO · Al₂O₃ · 2SiO₂), and 30 wt% calcium aluminosilicate glass phase [3,4]. So, bone china is a highly crystalline ($\sim 70\%$) whiteware that exhibits good resistance to edge chipping and a high flexural strength value of ~ 100 MPa [5,6].

However, the glaze applied to bone china is easily scratched and the fired body thermal shock resistance is poor. The former is due to its alkaline rich glaze and the latter is attributed to mismatch of thermal expansion coefficient (TEC) of different phases in the fired body. The TEC of anorthite [7] from 20 to 500 °C is $\sim 4.3 \times 10^{-6}$ K⁻¹.

The TEC of glass phase detected in bone china from 20 to 350 °C is calculated to be $3\text{--}4.5 \times 10^{-6}$ K⁻¹, while the approximate TEC of β -tricalcium phosphate from 50 to 400 °C is 12×10^{-6} K⁻¹ [8]. Apparently, β -tricalcium phosphate crystalline phase has a negative effect on thermostability of bone china. Meanwhile, anorthite has a refractive index of ~ 1.58 [9], which is close to that of the glass phase (~ 1.5) [10]. That is, anorthite crystalline phase can increase translucency performance of bone china. Therefore, anorthite-based porcelain can be used in tableware to improve heat stability and decoration quality.

In recent years, many studies [10–15] have been undertaken to develop anorthite-based porcelain to replace traditional porcelain (including bone china and hard porcelain). Capoglu [10–12] designed low-clay translucent whiteware, which was produced from prefired materials and a small amount of clay at 1370 °C for 3 h. The low-clay whiteware consisted of anorthite, mullite (3Al₂O₃ · 2SiO₂) crystalline phases and glassy phase with high crystalline to glassy phase ratio. Taskiran [13,14] also reported a new porcelaneous stoneware, which was obtained from a mixture of wollastonite, alumina, quartz, magnesia and ball clay by powder pressing and sintering at 1225 °C. The material had anorthite

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as its major phase with corundum, cristobalite and glass as minor phase.

In addition, aluminous cement ($\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$), limestone (CaCO_3), colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), wollastonite ($\text{CaO} \cdot \text{SiO}_2$), calcite (CaCO_3) and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) can all be used in the production of anorthite-based porcelains as a CaO source [16–20]. Meanwhile, the production of anorthite ceramics was studied with different sources of CaO such as $\text{Ca}(\text{OH})_2$, CaCO_3 , marble powder and gypsum mold waste by Kurama [21]. However, the above mentioned study only aimed to produce dense anorthite ceramics from different CaO sources, and there was little attention paid to the microstructure and the other properties. For tableware, the applicability and decoration quality is very important for its marketing. So, not all calcium-containing minerals are appropriate for the manufacture of anorthite-based porcelain for daily use. In China, dolomite, wollastonite and calcite are rather abundant, and are cheaper than other calcium-containing minerals. In a previous study [22], the preparation of anorthite-based porcelain was fabricated using calcite as a source of CaO. The present work, which is a part of an extended research program, aims to elucidate the influence of dolomite, wollastonite and calcite on the microstructure and technological properties of anorthite-based porcelain, including sintering character, flexural strength, thermal expansion and appearance quality.

2. Experimental procedure

2.1. Raw materials

Ball clay and quartz were used as starting raw materials. Dolomite, wollastonite and calcite were chosen as different

CaO sources. Feldspar was used to obtain dense porcelain body at a relatively low temperature. The high content of CaO decreases the liquid phase viscosity of the porcelain at high temperatures, which makes it particularly easy to generate shape distortion of the porcelain bodies. To resist high-temperature deformation, a small amount of industrial alumina is added as a source of aluminum to increase the viscosity of high-temperature melted liquid. The starting raw materials were purchased from Guangdong Sitong Group Co. Ltd. (Chaozhou, China). Table 1 shows the chemical composition of raw materials.

2.2. Sample preparation

Compositions were prepared on the basis of the approximate stoichiometric anorthite compositions with different CaO sources (dolomite, wollastonite and calcite) and were labeled as A, B and C (Table 2), respectively. These powders were wet mixed and milled in a planetary mixer with zirconia ball millstone for 6 h. The particle size distributions of the milled slurry were analyzed by a BT-9300S model laser diffraction particle size analyzer (Dangdong Bettersize Instruments Ltd., China). The result is given in Fig. 1. It can be seen that all samples have approximate results with similar log-normal distribution presenting one maximum point. Meanwhile, the particle sizes are less than 10 μm , which are centered at 1–5 μm .

The slip casting was used for forming, which could obtain green body with high-strength [19]. Slips were cast in a plaster mold into rectangular blocks of 60 mm \times 60 mm \times 10 mm dimensions. The consolidated rectangular blocks were removed from the mold after 45 min. Natural drying time of the consolidated specimens was determined

Table 1
Chemical composition of raw materials.

Raw materials	Constituents (wt%)								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	L.O.I
Ball clay	48.61	36.14	0.21	0.14	0.16	0.21	0.98	0.24	12.7
Quartz	98.38	1.02	0.03	0.01	0.08	0.02	0.07	0.04	0.23
Alumina	–	≥ 99.0	–	–	–	–	–	–	–
Feldspar	65.56	18.85	0.08	0.02	0.23	0.03	12.39	2.28	0.56
Dolomite	1.32	0.45	0.04	0.03	29.90	19.41	0.02	0.36	48.46
Wollastonite	50.13	0.92	0.20	0.02	44.80	0.82	–	–	3.21
Calcite	3.02	0.61	0.04	0.01	53.98	2.13	0.04	0.11	39.82

Table 2
Composition of the investigated samples A, B and C (wt%).

Sample	Raw materials						
	Ball clay	Quartz	Alumina	Feldspar	Dolomite	Wollastonite	Calcite
A	20	14	21	–	45	–	–
B	20	7	15	18	–	40	–
C	20	20	12	18	–	–	30

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