Using bone ash as an additive in porcelain sintering

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Abstract

Calcined bovine bone (CBB) is generally used to manufacture high-quality porcelain known as bone china. In these products, the amount of bone ash is about 50%. However, it is known that CBB, in small quantities added to raw materials such as feldspars, can reduce the *liquidus* temperature and thus promote liquid-phase sintering. The purpose of this study was to evaluate the potential use of bone ash as a sintering promoter of porcelain made by a classical triaxial system. Hard porcelain was prepared with 0, 1, 2, and 5 wt% CBB and sintered at temperatures ranging from 1100 to 1400 °C. For the sample containing 2% CBB, the sintering temperature was reduced by 50 °C relative to 0% CBB, while the sample's tensile strength was the highest among all samples. Two mechanisms could be observed during porcelain sintering depending on CBB quantities: for 1 and 2% of CBB, the mullite formation determined the final shrinkage without changes on initial sintering temperatures; for 5% the initial sintering temperature was decreased by liquid formation.
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1. Introduction

Porcelain has unique characteristics that distinguish it from other kinds of china, such as high mechanical strength, firing temperatures above 1350 °C, porosity below 0.3%, and high whiteness and translucency [1]. Porcelain is a ceramic material of the alumina–silica–alkali oxides (primarily K_2O) ternary system, and is produced by sintering a mixture of kaolin, feldspar, and quartz at a composition close to 50:25:25, respectively [1,2]. Plastic clays can replace part of the kaolin content to increase the mechanical strength and plasticity of green bodies. Albite or orthoclase are usually used as flux and contain high sodium or potassium oxide content, respectively [1,2]. Less common raw materials used as fluxes include phyllite, pegmatites, and, more recently, phonolites, soda-lime scrap-glass and slag [3–11]. However, different types and proportions of fluxes can modify the firing temperature and final mechanical resistance of the products. For this reason, orthoclase is generally used as a flux for porcelain [1].

The characteristic particulars of the glass phase formation process during porcelain firing restrict the use of new flux compounds in china. Because porcelain consists generally of a 70% glassy phase and a 30% crystalline phase, the viscosity of the glassy phase and the amount of the crystalline phase control the pyroplastic deformation resistance of these materials [12]. Calcite and dolomite can be used to accelerate the melting of feldspars and to reduce the firing temperature without significantly changing the pyroplastic deformation behavior. However, carbonates have, as a significant drawback, the formation of CO_2 at temperatures above 900 °C. For ceramic materials produced by a single firing or rapid thermal cycles, the formation of gases at high temperatures can cause performance-affecting defects in the end products.

Calcium phosphate can be used as an alternative to carbonates for reducing the melting temperature of feldspar

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in porcelain. Calcined bovine bone (CBB), or bone ash, use is restricted to amounts of about 50% [2] in the manufacturing of bone china, making bone china generally more durable and translucent than kaolin-based porcelain [13].

The reactions of calcined bovine bones (CBB) were extensively studied by Iqbal et al. [14,15]. Although the article deals with the microstructural evolution of phosphatic porcelain, most of the chemical reactions between the CBB, kaolin, quartz and feldspar should be similar despite the low proportion of CBB used as a sintering additive of hard porcelain. As shown previously, CBB is mainly hydroxyapatite and alone is stable until 1000 °C [15,16]. However, CBB decomposes to β-TCP and calcium oxide at temperatures higher than 775 °C probably due to the presence of metakaolin [15]. The lime originated from the hydroxyapatite decomposition was supposed to react with clay materials to give a new anorthite phase at temperatures next to 800 °C and liquid phase was detected only for $T > 900$ °C [14]. Gas bubbles were supposed to be the origin of the anomalous density decreases when sintering temperatures are higher than 1200 °C [14]. Bone china sintered at 1245 °C by 1 h has a final composition of crystalline grains of anorthite, β-tricalcium phosphate and small amounts of quartz immerse in a glassy matrix [17].

Closed porosity were observed above 1280 °C for porcelain stoneware tiles as a consequence of the increase of pressure of the gas inside the closed pores, which tends to expand the pores when glass viscosity decreases [18]. Thermal analysis of porcelain stoneware (50% kaolinitic clay, 40% feldspar and 10% quartz) showed the endothermic transformation next to 550 °C is due to both clay dehydroxylation and $\alpha \rightarrow \beta$ quartz transformation and the exothermic reaction next to 1000 °C was attributed to mullite crystallization [18]. Mullite, quartz and glass were found after sintering at 1280 °C simultaneously to the decrease of the mechanical properties [18]. Therefore, the best results of strength were obtained at 1270 °C which reached 34 MPa [18].

The main thermal transformations during porcelain firing were described by Carty and Senapati [1] and can be summarized as: 550 °C—dehydroxylation of kaolinite; 573 °C—α to β-quartz inversion; 700–1000 °C—alkali feldspar transformation to sanidine and depends on the sodium: potassium ratio; 950–1000 °C metakaolin transforms to a spinel-type structure; 990 °C—amorphous silica liberated during the metakaolin decomposition; 990 °C—a eutectic melt of potash feldspar with silica (depends on the type of feldspar); next to 1200 °C melt becomes saturated with silica-quartz dissolution ends and quartz-to-cristobalite transformation begins [1]. The kinetic of mullite formation could be affected by the viscosity of liquid phase formed during metakaolin decomposition [19,20]. Marinoni et al. showed that the premature glass formation due to the substitution of some feldspar by soda-lime glass in the porcelain formulation accelerated the mullite growth reaction kinetics [21].

Despite the abundance of cattle in Brazil, CBB has rarely been exploited as a raw material in the ceramic industry, and the production of bone china is relatively unknown in Latin America. CBB is primarily hydroxyapatite, which in combination with kaolin and feldspar, could form glasses [22]. Unlike most kaolin porcelains, bone china contains amorphous and crystalline phases—approximately 30 and 70%, respectively. While the amorphous phase is rich in SiO_2 and Al_2O_3, but also contains K_2O and CaO, the crystalline phase is mainly calcium phosphate [2]. CBB could therefore be used to change the *liquidus* temperature [23–25], promote liquid phase formation, and reduce the sintering temperature via liquid phase sintering.

The purpose of this study is to verify the effect of small quantities of CBB on the sintering, microstructure, and properties of traditional kaolin-based porcelain. Porcelain containing 0, 1, 2, and 5 wt% CBB was sintered at temperatures ranging from 1000 to 1400 °C.

2. Materials and methods

Water absorption and flexural strength were measured for all samples, and the degree of the decomposition and/or phase formation was determined by X-ray diffraction using the Rietveld method. Microstructural information was obtained by scanning electron microscopy (SEM), and chemical analysis was carried out using energy dispersive X-ray spectroscopy (EDS).

A 2:1:1 base porcelain composition of kaolin, to orthoclase, to quartz, respectively, was provided by Porcelanas Teixeira Company. The raw material was initially milled in an industrial ball mill for 24 h. CBB in amounts of 1, 2, and 5 wt% was introduced to the base composition by milling in a laboratory ball mill for 24 h with porcelain grinding elements. A reference sample without CBB was milled under the same conditions. Details of the powder preparation are given elsewhere [16]. The autoclaved material was then calcined at 700 °C, and ground in a laboratory ball mill. The raw material was dispersed using a commercial sodium polyacrylate, and specimens with a standard size of $80 \times 30 \times 3$ mm were obtained by slip casting in a plaster mold.

The specimens were heated at a rate of 2 °C/min from room temperature to the sintering temperature in a muffle furnace. The maximum sintering temperatures ranged from 1100 to 1400 °C in 50 °C increments without any soaking time. Three-point bend testing of the sintered samples was performed using a Kratos® universal machine with a support span of 40 mm. Deformation was carried out at a rate of 6 mm/min until fracture. Water absorption was measured in each sample by initially determining the dry weight at 110 °C, and then determining the wet weight after immersion in boiling water for 2 h and then cooling. Sintering studies were performed in a dilatometer (BP Engenharia–RB 115) by heating at 2 °C/min to 1200 °C, without residence time, in flowing air (1 atm).

The samples characterized by X-ray diffraction (XRD) were ground in an agate mortar to eliminate any preferred orientation that may have developed during firing. The patterns were carried out in the range of 10 to 70° 2θ, with a step size of 0.03° and a counting time of 30 s per step, using a PANalytical X'Pert PRO diffractometer equipped with a X'Celerator detector operating with Cu-$K\alpha$ radiation using similar analysis