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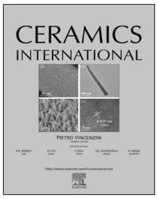

Effect of calcined colemanite additions on properties of hard porcelain body

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ABSTRACT

Utilization of calcined colemanite as a sintering aid in hard porcelain body, prepared by slip casting route using aqueous suspension containing mixtures of kaolin, quartz and potassium feldspar, was investigated. After calcination, colemanite powders were added to the admixture of porcelain by partial substitution with potassium feldspars in the range of 0–5 wt% to discover its influences on the densification and technological properties of the final product. Through optimization of process parameters of ceramic suspensions by using appropriate dispersing agents and facilitating densification by calcined colemanite addition, hard porcelain possess high strength was obtained. When relationship between the additive concentration with temperature was established, it is found that porcelain formulations resulted in substantial reduction of firing temperature about 50 °C without compromising its quality by 1 wt% calcined colemanite addition.

1. Introduction

Porcelain is a variety of dense, highly vitrified and translucent white-bodied ceramic fabricated from a formulation with essential components consisting of clay, feldspar and quartz [1–4]. The composition of typical hard porcelain is composed of 50% plasticiser, 25% fluxing agent and 25% filler. The plasticisers, is commonly kaolinite, play binding role for other ingredients in green body, provides plasticity and green strength during the forming stages of porcelain production. The fluxing material, is usually low melting alkali silicates such as feldspars, react with other constituents upon firing to form enough glassy phases at commercial firing temperature. The resulting glassy phase fills the porosity in the microstructure leading to densification of the body. The filler, possess no intrinsic plasticity like fluxes, is relatively stable at commercial firing temperatures and reduces the deformation tendency of body. Vitrification demonstrate a high level of melt which leads nearly zero ($< 0.5\%$) open porosity and a larger amount of glassy phase ($> 40\%$) in the microstructure of porcelains [4–6]. Vitrified porcelain bodies indicate a microstructure consisting of unreacted fillers bonded by mullite and glassy phases [1–4].

From the technological point of view, porcelains are characterized by excellent technological and functional features, especially such as low water absorption making it frost resistant and preventing liquid permeates; high mechanical properties making it functional for industrial and highly trafficked areas; endurance to chemical substances and cleaning agents, being easy-to-clean; it can be endowed with a broad spectrum of aesthetic possibilities [7]. The market continuously demands new products for wall tile, tableware and sanitary ware applications. Functional properties have stimulated research in to new materials with low costs in finished products. Following this tendency, the research carried out in ceramic materials in the last 50 years can be distinguished in two lines: i) synthesis of ceramics from new raw materials; and ii) decrease of the firing temperature. A further line of research is certainly based on the availability and quality of the raw materials. The second line has its origins in technical and economic reasons [8].

There are some technical and economic difficulties associated with the production of porcelain owing to the necessities for high purity raw materials and a larger amount of glassy phase in the bodies in order to obtain very low water absorption values in their microstructural design, compared to other traditional ceramics such as floor and wall tiles. These necessities have made the investigation of alternative raw materials inevitable and there have been numerous researches on alternative raw materials to be used in porcelain production [9].

Fluxing agents play a fundamental role in porcelain body due to the need to obtain low porosities in the finished product. Low porosity is achieved through the formation of a larger amount of liquid phases during firing, which result from the progressive melting of the fusible minerals used in the composition of the ceramic body. Thus, fluxing agents, which are determinants in defining the product's firing temperature and are responsible for the pyroplastic deformation the ceramic body undergoes during firing, strongly affect the resulting microstructural characteristics of the porcelain [10]. Therefore, improvement in the mechanical properties, translucency and lowering of the sintering temperature of porcelain products can be achieved by

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changing the constituent glassy phase [11]. Furthermore, initiatives have focused on use of alternative materials instead of available fluxing agent in the industry, due to provide productivity with a considerable reduction in energy cost. However, instability in the formed amorphous phase by melting of fluxes on firing state directly influences the technical properties of industrially produced ceramics [12]. In addition, lower fusibility of crystallized alkali-containing fluxes such as feldspar due to the high energy requirement for crystal structure's destruction is another major challenge [13].

In recent years, newly emerging researches have been performed to evaluate the feasibility of decrease firing temperature of porcelain by using additives. According to the relevant literatures, there are various studies involving employment of replacing potassium feldspar with soda-lime glass [14,15], glass waste [16], blast furnace slag [17,18], bentonite [19], scrap alkali silicate glass [20] and wollastonite [21]. The observed lower sintering temperature (by~100 °C) than feldspar based porcelain makes it an economical alternative as well [11].

Boron oxide-bearing minerals can technologically be considered as important alternative raw materials since they have a glass-forming character and have been used in the ceramic industry to reduce the melting point, lower the viscosity and decrease the thermal expansion of the glassy phase and hence increase thermal resistance, mechanical strength and chemical stability of the materials [9,22]. Nowadays, commercial borates, especially colemanite, find a wide variety of applications in ceramic industry [23]. Colemanite mostly used in textile type fiberglass, glass and ceramic industries and metallurgy. When used in textile type fiberglass industry, colemanite drops the melting temperature of the mixture, provides low viscosity at the melting temperature, prevents crystallization and positively affects the chemical and physical properties of final glass product. Colemanite reduces the melting point in glass industry and it is resistant to thermal shocks. In formulation of ceramic and enamel glazes, it provides a stable structure, homogeneous melting and low segregation. Since it is a solvent for almost all metal oxides, it is used as a fluxing agent in the metallurgy industry [24].

When boron minerals are exposed to heat, the mineral first loses crystalline water, followed by transformation of amorphous material or recrystallization into new phases [25]. Waclawska et al. (1998) report that colemanite structure involves enclosed water molecules within the structure and the internal pressure of its increases rapidly that cause an explosive water loss with increasing temperature [26]. This sudden release within the micropores induces a disruption of the framework with temperature increment [25,26]. For this reason, direct use of colemanite mineral is limited as a raw material in ceramic industry. The other issue is that deformation problems will be observed in the final products if boron containing minerals are used with high amounts in ceramic products when they preferred to densify in fast firing process [27]. Therefore, colemanite mineral should be calcined in order to prevent such problems before usage for sintering aid.

The heating rate, the most important parameter in decomposition of matter in shaped ceramic body, affects the fast firing conditions. Decomposition of colemanite by conventionally should be perform with very slow heating in order to avoid harmful effects of the severe water release within micropores of colemanite. Yildiz et al. [23] investigated the calcination of colemanite at the temperature range between 400 °C and 800 °C for a dwell time of 180 min by conventional route. Ediz et al. [27] also investigated the calcination of colemanite for a standing period of one hour at 500 °C by heating then cooling at the same rate (5 °C/min). The results obtained from the studies on colemanite calcination by conventional route as mentioned in these literatures revealed that the process is completed in a period of at least 3 h. Therefore, the slower heating rates gives longer processing times and it affect the fast firing conditions as negatively. Achieving shorter processing times than by convective heating can be accomplished using microwave energy, which generates heat by directly penetrate inside the exposed material and then throughout of its. Thus, the inverse thermal effect of microwave heating provides some excellent benefits such as fast volumetric heating of product's surface without overheating and removal of volatiles from materials without cracking. Because of these benefits, a shorter processing time is possible in calcination process by microwave assisting, in a fraction of the time it takes that of conventional route. The difficulties to coupling microwave and material at low temperatures can be improved by aid of a susceptor assisted microwave heating which raise the material's temperature up to coupling with microwave [28]. By considering mentioned reasons, it is thought to be an alternative approach use of microwave energy instead of conventional method in the calcination of colemanite before use in porcelain body.

The purpose of this research are to compare of both conventional and microwave techniques on the calcination of colemanite and to investigate the possibility of using of colemanite powders in hard porcelain production as an alternative fluxing agent with partial substitution the potassium feldspars. In accordance with these purposes, at first, calcination of colemanite by both heating techniques was performed. The calcined colemanite powders were added to the admixture of porcelain by partial substitution with potassium feldspars in the range of 0–5 wt%. The produced samples from resultant mixtures undergo heat treatment at a temperature between of 1250–1300 °C in order to discover its influences on the densification and technological properties of the final product.

2. Experimental studies

The ground colemanite under 75 μm used in present study was provided from Eti Mine Works (Turkey). The structural properties of as-received colemanite powder were examined by XRD, DTA-TG and BET analyses. Thermal analysis of colemanite samples was carried out using a simultaneous thermal analyser (Netzsch STA 449) at 10 °C/min in air atmosphere in order to establish the condition of conventional heating. An evaluation of methods for determining of microwave assisted heating condition was performed by volumetric and massive changes at different temperatures (450–700 °C). Phase analysis was performed by an X-ray diffractometer (Bruker-D8 Advance) to identify the present crystalline phases in the raw and calcined states of the samples. Characterizations of pore size of the samples were evaluated by gas adsorption (BET) analysis.

Comprehensive application based on heating techniques designed for calcination of colemanite was described as follows. In conventional approach, colemanite was treated in resistance heated furnaces to 450 and 700 °C at a ramp rate of 10 °C/min. The temperatures were selected in an interval between release of crystal water and the beginning of the amorphization behaviour, which are determined by the results of thermal analysis of the colemanite. In microwave assisted approach, colemanite was heated to the same temperatures by using a modified domestic microwave oven with different power levels (385, 539 and 700 W) in order to determine optimal power level in calcination process. Firstly, colemanite samples within crucible were put in a fiberboard box for thermally insulation. Two cylindrical shaped SiC susceptors were placed as symmetrically surrounding the crucible within the box. Then, susceptor integrated box was placed into the microwave chamber before processing. The variation of the temperature in the sample was observed using with TP-01 type K thermocouple which horizontally positioned in front of window of oven and focused on the crucible in the box.

The primary components for preparation porcelain in the present study were kaolin, quartz and potassium feldspar supplied from ceramic manufacturing companies in Turkey. The common properties of raw materials are shown in Table 1.

A basic formulation for hard porcelain comprising 50 wt% kaolin, 25 wt% silica and 25 wt% feldspar was prepared. In spite of the enormous wide range of application of feldspar as a fluxing agent in porcelain manufacturing, colemanite (calcium borate) was selected as