Microstructural Characterization of Clay-Based Ceramics with the Addition of Granite Residues

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Abstract. Million tons of ornamental stones residues are produced every year. Most of this residue is disposed without any kind of processing or treatment. Moreover, disposal occurs without a prospective of reuse or recycling. The incorporation into ceramics is a possible alternative for part of this residue. Clay-based ceramics have high capacity of incorporation of industrial residues. This work aimed to conduct a microstructural characterization of clay-based ceramics with incorporation of granite residues in the composition of the ceramic matrix. Specimens were produced with the addition of 0, 10, 20 and 30 wt. % of granite residues. The specimens were prepared by uniaxial pressing and sintered at temperatures of 1050 and 1200°C. For the microstructural analysis were carried out by scanning electron microscopy and X-ray diffraction. The results indicated that the incorporated ceramics sintered at 1200°C presented higher densification and lower porosity as compared with those sintered at 1050°C.

Introduction

In the last decades, the ornamental stone sector has experienced increasing industrial activities in Brazil. The Brazilian Association of the Ornamental Stone Industry (ABIROCHAS) estimated that in the year of 2016 more than 9.3 million tons of ornamental stones were produced [1]. Moreover, during the process chain for production of these kinds of stone, which includes the extraction as well as the processing, are generated residues. It was estimated that approximately 2 million tons of fine residues per year were generated [2]. These residues are deposited, most of the times just outside the industry, resulting in the occupation of an extensive area of open space and also contributing to environmental pollution. For this reason, studies that point to a solution to this problem, be it the reuse, recycling, processing or proper disposal of these residues are necessary [3]. In this scenario, ornamental stone residues use is presented as an economical and environmentally sustainable alternative, which provides a definitive destination for this kind of waste. Consequently, in recent years several studies have been carried out aiming to present possible applications for these types of residues [4–6]. Alexandre et al [7] studied the incorporation of limestone residues from the processing of marble in soil-cement blocks. They showed that the addition of residues for the preparation of soil-cement blocks improved the compressive strength, water absorption and durability, especially for the 30 vol% of residues incorporation into the mixture. Pedroti et al [8] investigated the ideal composition of clay bodies incorporated with residues from granite processing for the production of press-molded ceramic blocks. It was observed that the incorporation of 17 vol% of granite residues would result in strength of 30 MPa and water absorption of 15%. Torres
et al [9] studied the influence of adding granite stone residues to produce roof tiles. Their results showed that sintered products incorporating the sludge exhibited enhanced or similar properties in comparison to those conventionally used. Water absorption lower than 6%, bending strength of about 14 MPa and 38 MPa for the green and sintered product, as well as a lower pyroplastic deformation index were some of the properties reported [9].

This work aims to study the microstructural characterization of ceramics clays with the incorporation of granite residues. Actually, this work presents a continuity of previous works, where the ceramic clay added with granite residues were used for the production of rustic wall tiles [10] as well as high temperature ceramics [11]. In this last study, the addition of granite residues substantially improves properties such as water absorption and flexural strength.

Methodology

Kaolinitic clay as well as granite residues were used as raw materials in this investigation. Kaolinitic clay was supplied by the ceramic industry Ceramica Rodolfo Azevedo Gama, located in the city of Campos dos Goytacazes, state of Rio de Janeiro, Brazil. Granite residues were collected from an ornamental stone industry in the city of Cachoeiro de Itapemirim, state of Espírito Santo, Brazil. Such residues were generated from the sawdust processing of the granite blocks by multi-wire technology. Table 1 presents the chemical composition of the clay ceramic as well as the granite residues, as reported elsewhere [10, 12].

![Table 1. Chemical composition of the raw materials (%wt)](Table 1. Chemical composition of the raw materials (%wt))

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>Materials</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>MnO</th>
<th>LoI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granite Residues</td>
<td>77.9</td>
<td>11.9</td>
<td>1.2</td>
<td>4.4</td>
<td>3.5</td>
<td>0.6</td>
<td>0.09</td>
<td>0.09</td>
<td>traces</td>
<td>0.05</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Clay Ceramics</td>
<td>43.6</td>
<td>25.6</td>
<td>10.4</td>
<td>1.6</td>
<td>traces</td>
<td>0.15</td>
<td>0.66</td>
<td>1.55</td>
<td>0.25</td>
<td>0.11</td>
<td>15.2</td>
<td></td>
</tr>
</tbody>
</table>

*LoI: Loss on Ignition

The materials in as-received condition were dried in a stove at 110 °C for 24 hours. After this first processing stage the materials were milled and sieved until a maximum particle size of 0.854 mm was obtained. Specimens were prepared with the amount of granite residues of 10, 20 and 30 wt%, denominate C10W, C20W and C30W, respectively, and a reference specimen was also produced without the addition of granite residues, denominate C0W. For production of specimens, the bodies were prepared with 8 wt% of moisture. The sintering of the products were carried out in two different temperatures the first at 1050 °C and the second at 1200 °C, both for about 3 hours.

The fracture analysis of the specimen’s surface was performed by scanning electron microscopy (SEM). Secondary electrons were used to verify the surface morphology, as well as the electron energy dispersion spectroscopy (EDS), to identify the chemical composition of fragments. The mineralogical characterization was carried out by X-ray diffraction (XRD) in a model Endeavor Bruker diffractometer, with CoKα radiation and 20 angle varying from 5 to 80°.

Results and Discussion

Figs. 1 to 3 exhibit the microstructure of the clay ceramics with the addition of 10, 20 and 30 wt. % of granite residues, C10W, C20W and C30W respectively, as well as the reference sample, C0W, without the incorporation of granite residues in its composition. The sintering temperature used in the production of these specimens was 1050 °C.

Figs. 1 (a) and (b) present the microstructure for the C0W sample sintered at 1050 °C. One can see a relatively rough microstructure composed of partially adhered fine particles that are related to the clay matrix. These characteristics are commonly observed for kaolinitic clays sintered at this temperature [13]. Figs. 1 (c) and (d) show the C10W microstructure. One can notice that this microstructure is very similar to those observed in Fig. 1 (a) and (b), exhibiting a slightly adhesion of small particles and the rough microstructure.
Fig. 1: Micrographies of the fracture region of clay ceramics sintered at 1050 °C: (a) C0W 400x, (b) C0W 1000x, (c) C10W 400x and (d) C10W 1000x.

Fig. 2 (a) and (b) present the microstructure for the C20W sample sintered at 1050 °C. One can observe the formation of a liquid phase that adds a further complexity to the sintering process. Although due to the sintering temperature it was not possible to detect a total densification of the materials. Moreover, either the viscous glass or the amount of liquid existing were enough to flows under the action of the capillary forces in the pores to fill up the porosity of the body [14].

Fig. 2: Micrographies of the fracture region of C20W sintered at 1050 °C: (a) 400x and (b) 1000x.

Figure 3 (a) and (b) exhibit the C30W microstructure sintered at 1050 °C. It is clear that the higher amount of granite residues in the composition of this specimen had a major impact in the microstructure of the material. One should notice the presence of aggregate particles and heterogeneity as well as micro-cracks in the quartz particle.

In Figs. 4 to 6 the microstructural characterization is analyzed for all conditions prepared and sintered at 1200 °C. In Fig. 4 (a) and (b), exhibiting the microstructure for the C0W condition sintered at 1200 °C, one sees that the behavior is quite similar to that shown for the same condition but with lower sintering temperature, Fig. 1 (a) and (b). In Fig. 4 (c) and (d), one realizes that there is the presence of a liquid phase in the sintering process but, once again, not in enough amount to fill out the porosity of the ceramic body.
Fig. 3: Micrographies of the fracture region of C30W sintered at 1050 °C: (a) 400x and (b) 1000x.

Fig. 4: Micrographies of the fracture region of clay ceramics sintered at 1200 °C: (a) C0W 400x, (b) C0W 1000x, (c) C10W 400x and (d) C10W 1000x.

For condition C20W, Fig. 5 (a) and (b), as well as condition C30W, Fig. 6 (a) and (b), one sees a greater formation of liquid phase and vitrification phenomenon, which is a complex case of viscous sintering in clay-based materials; already observed [14]. Moreover, the morphology of the porosity could be analyzed, with round as well as angular pores. The high amount of porosity is probably due to the shrinkage of the granite residues and, also, to the imprisonment of gases during the processing of the material.

Fig. 5: Micrographies of the fracture region of C20W sintered at 1200 °C: (a) 400x and (b) 1000x.
Figs. 7 (a) to (d) show the EDS analysis result chart for C20W and C30W. Elements such as Al, C, Ca, Fe, K, Na, Si, O and Ti were reported, also to C0W and C10W. According to the results in Table 1, elements such as Fe and Ti might be associated with the kaolinitic clay matrix. Na and K can be associated with the granite residues. Furthermore, Al and Si are related to both the matrix as well as the granite residues.

XRD analysis showed that the ceramics, with or without the granite residues, present the same crystalline phases and exhibit traces of quartz, hematite and mullite. Quartz is a phase existing in the clay as well as in the granite residues, hematite is a dehydrated iron hydroxide, also associated with the natural clay and mullite is originates from the kaolinite [15]. In the C0W and C10W ceramics sintered at 1200°C cristobalite, which is the SiO₂ allotropic form, has also been identified. For the C20W and C30W sintered at 1050°C condition feldspath was also observed.

**Summary and Conclusion**

- During the firing process, the granite residues acted by forming a liquid phase. The formation of this liquid phase occurred due to its composition, with the presence of alkaline oxides known as fluxing agents and contributes to the ceramic sintering. This fact was even more evident in ceramics sintered at 1200 °C.
- Ceramics added with 20 and 30 wt% of granite residues sintered at 1200°C, presented higher amount of liquid phase. Thus, greater formation of vitrification phenomenon occurred.
• Ceramics sintered at 1200ºC presented higher densification and lower porosity in the microstructure in comparison with those sintered at 1050ºC. This is proposed due to the higher firing temperature.
• The addition of granite residues can be used in the production of ceramics, with great benefits, such as the reduction of raw materials, reduction of the amount of residues to be disposed, use of the waste as raw material and the mitigation of environmental impact.

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References


