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Improving the properties of low temperature sintered alumina bodies with granite reject additions

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Abstract. The use of industrial waste materials as additives in the manufacture of ceramic products has been attracting a growing interest from researchers in recent years and is becoming common practice. The continued depletion of natural resources throws a new light on the potential use of some industrial wastes and natural sub-products as full-fledged alternative ceramic raw materials. This work describes the research carried out on the low temperature manufacturing of alumina bodies using, as additive, granite reject as-produced by an ornamental stone processing industry that saws granite stones into blocks and slabs in Rio Grande do Norte, Brazil. This reject is produced in significant amounts and is discarded in sedimentation lagoons, landfill areas or simply thrown in rivers, resulting in environmental pollution. Samples containing up to 30 wt% granite reject and 5 wt% manganese oxide (constant) were uniaxially pressed and sintered in air in an electric furnace (1150-1350 °C, for 1 hour). Sintered test pieces were characterized by X-ray diffraction, apparent density, open porosity and flexural strength. The results showed that the addition of granite reject and manganese oxide enables low temperature sintering and remarkably improves the cold mechanical properties of the alumina body.

Introduction

Nowadays, the industrial activities produce a significant quantity of waste material that has some impact on the environment. Numerous studies have been carried out in order to use the industrial rejects in ceramic formulations [1-5]. From this point of view, the industrial reject materials can be classified in different types: as fuel wastes (high carbon content), as fluxing wastes, improving the densification of the material (glassy phase formers) and as plasticity-controlling wastes (shrinkage controllers). The results have shown that clay products, given their broad chemical composition range, can accommodate a variety of reject materials with no major sacrifice of their properties. Moreover, in some cases the reject can even aid the densification process, enabling sintering at a lower temperature [6-8].

The state of Rio Grande do Norte, Brazil, has an expressive ornamental stone cutting industrial activity (*e.g.* marble and granite) that produces a large amount of reject. This reject is disposed of in rivers and lagoons without treatment, causing a serious environmental problem. Marble and granite rejects show a non-plastic behaviour and are basically constituted by the same major and minor oxides present in common raw materials for the ceramic industry, which makes this material a good candidate to be used as additive or alternative raw material in the fabrication of ceramic products. Some works have shown the possibility of introducing the marble and granite powder produced during the stone cutting process in clays products, without degradation of properties [9-10].

In high-alumina ceramic products, the sintering process is the most important and expensive step of the fabrication process. It is well known that the addition of small amounts of certain additives (MgO, CaO, SiO_2, TiO_2, MnO_2, MnO, Nb_2O_5) to non-reactive alumina powders can decrease the sintering/densification temperature of alumina bodies from ~1600 to ~1400°C, largely reducing the energy costs of the process [11-13]. Basically densification can be improved by manipulating two mechanisms, both favouring the diffusion processes necessary to sintering: the development of solid solutions and lattice defects and the presence of a liquid phase during the sintering process. The latter has traditionally won the preference, particularly in those cases in which the product's end-use does not preclude the presence of a liquid phase (*e.g.* the product is not to be used for hot structural applications). When compared to pure alumina, the Al_2O_3-TiO_2-MnO system has shown a good improvement of the sintering behaviour [14-15]. The densification process in this system is mostly accomplished by the liquid phase mechanism, enabling a significant reduction of the sintering temperature of the alumina-based material. The presence of additives, singly or combined, can also be used to control the microstructure (*e.g.* reduce the grain growth), improving the cold mechanical properties of the high-alumina composition.

Alumina-based materials have been considered ideal for cold abrasion/erosion applications (*e.g.* thread guides, spray nozzles), where it is important to be able to sinter at lower temperatures but maintain the high cold mechanical strength, an indirect measure of the abrasion resistance of the ceramic body. In other words, it is important to make the most of the excellent room temperature mechanical properties of sintered alumina bodies and, simultaneously, to be able to save energy during the sintering process.

The granite reject produced in the cutting process of ornamental stones in the north-eastern Brazil is among the alumina-rich industrial waste materials and it is the objective of this work to study the possibility of its use as a sintering additive and its effect on the densification behaviour and mechanical properties of an alumina-based ceramic material.

Experimental Procedure

Alumina powder APC-2011 SG (Alcoa, Brazil), with an average particle size of 2.3 μm and specific surface area of 1.50 m^2/g, and a constant amount of 5 wt. % MnO_2 (Vetec, Brazil) were mixed with 10 to 30 wt. % of granite reject. The granite reject was collected directly from the ceramic industry and was not beneficiated. The chemical composition of the granite reject was determined by X-ray fluorescence (XRF, Shimadzu EDX-700). The powders were mixed in a ball mill and uniaxially pressed into rectangular bars (50 x 4 x 4 mm^3) under a load of 20 MPa. Powder compacts were pressureless sintered at temperatures ranging from 1150 to 1350 °C.

The apparent density and porosity of the sintered bodies were determined by using the Archimedes water displacement method. The crystalline phases present after sintering were identified by X-ray diffraction (XRD, Shimadzu XRD-600, 20-80° 2θ scanning range, 2° $2\theta.min^{-1}$ scanning rate).

The mechanical strength of the specimens (average of four samples for each value) was measured with a universal testing machine (Zwick, 2.5 kN) using a four point bending geometry, with upper and bottom span of 40 and 20 mm, respectively, at a constant cross-head speed of 0.5 $mm.min^{-1}$.

The microstructure of the sintered samples was studied on fracture surfaces, by Scanning Electron Microscopy (SEM, Shimadzu SSX-550, at 25 kV).

Results and Discussion

Table 1 gives the chemical composition of the granite reject, as determined by X-ray fluorescence. The material is mainly constituted by SiO_2, Al_2O_3, Fe_2O_3 and CaO, with minor concentrations of K_2O, MgO and TiO_2. The high content of alkaline and alkaline-earth oxides (~17 wt. %), the usual fluxing agents in traditional ceramic compositions, will likely help the development of a liquid phase during the sintering process. However, preliminary tests showed that a minimum 5 wt.% MnO_2 had to be added to the compositions, together with the various contents of the granite reject, to see improvements in the mechanical strength of the sintered bodies.

Table 1 – Chemical composition [wt. %] of the granite reject used in this work (XRF).

Al_2O_3	SiO_2	Fe_2O_3	CaO	K_2O	MgO	TiO_2	SrO	ZnO	MnO	V_2O_5
17.37	51.92	10.70	9.73	4.35	2.66	2.40	0.18	0.02	0.22	0.08

Fig. 1 shows the XRD pattern obtained for samples containing 65 wt. % alumina + 5 wt. % MnO_2 + 30 wt. % granite, sintered at 1150 °C and 1300 °C. The major crystalline phases identified were alumina, anorthite and wollastonite, accompanied by a minor amount of quartz. These results are in agreement with the chemical composition presented in Table 1. This analysis also showed that the temperature has not a marked influence on the observed crystalline phases.

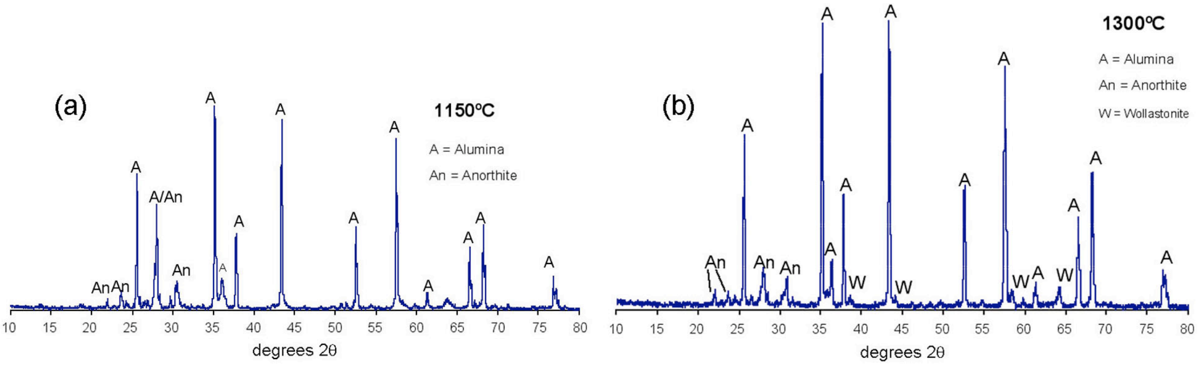

Fig. 1 – X-ray diffraction patterns of the sample containing 65 wt. % alumina + 5 wt. % MnO_2 + 30 wt. % granite reject, after sintering at: (a) 1150 °C, and (b) 1300 °C.

Fig. 2 shows the changes in apparent density (Fig. 2-a) and open porosity (Fig. 2-b) of the specimens containing alumina + 5 wt. % MnO_2, as a function of the granite reject content and the sintering temperature. Compared with pure alumina, the densifying effect of the granite reject is evident. Compared with the (alumina+MnO_2) composition, reject additions take the apparent density values from 2.2-2.3 to 2.9-3.0 g/cm^3, at 1300 °C, and from 2.4 -2.5 to 3.15-3.20 g/cm^3, at 1350 °C.

It is interesting to note that the density values are almost constant for any given temperature, regardless of the reject content. This result shows that the quantity of liquid phase does not play a significant role in the sintering process. The most important parameter is the presence of a liquid phase. The use of a higher amount of granite reject is expected to cause an increase in the quantity of liquid phase, but possibly its viscosity did not vary enough to show a significant effect on the densification process. Probably the material shows two concurrent mechanisms during the sintering process: the more abundant liquid phase is more effective in the dissolution/crystallization process towards the equilibrium (*e.g.* the reaction between Al_2O_3, CaO and/or SiO_2 to produce new crystalline phases such as anorthite, occurring above ~1200 °C), which consumes part of that liquid phase and eventually causes an increase in the viscosity. Maybe for this reason, the increase in the granite reject content causes no major changes on the apparent density.

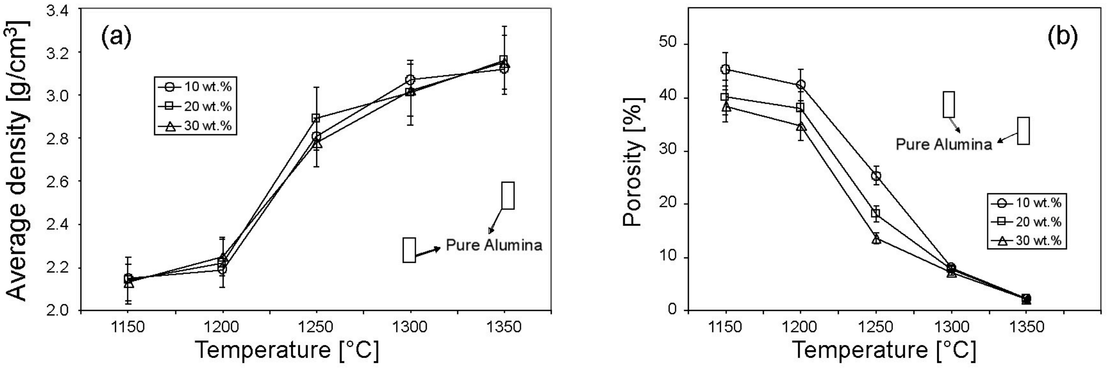

Fig. 2 – Effect of the added granite reject content and the sintering temperature on: (a) apparent density, and (b) open porosity, of samples containing alumina + 5 wt. % MnO_2.

Porosity values of the sintered samples show a similar behaviour (Fig. 2-b). The porosity level reached at 1300 °C without reject additions (~40%) can readily be obtained at ~1200 °C in the presence of the reject. At temperatures above 1300 °C the material shows a good improvement of the porosity values (<10%), which mostly depend on the sintering temperature.

Fig. 3 shows the effect of added granite reject content and sintering temperature on the cold flexural strength of the sintered material. At low sintering temperatures (*e.g.* 1150 and 1200 °C), the samples show strength values of 10-20 MPa, which is evidence that the material is not sintered yet. At temperatures above 1200 °C the densification process is improved and the sintered material shows much better strength values, which is in agreement with the results shown in Fig. 2.

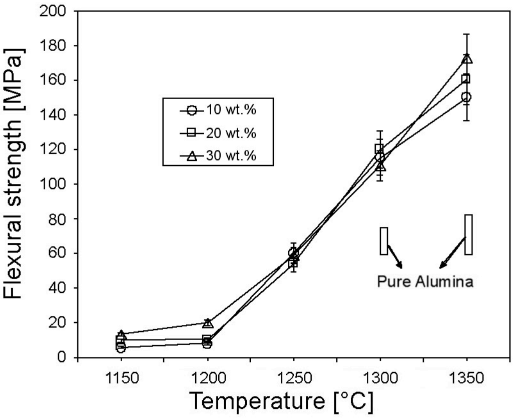

Fig. 3 – Effect of the added granite reject content and the sintering temperature on the flexural strength of samples containing alumina+ 5 wt. % MnO_2.

Compared with alumina without additives, the addition of granite reject leads to remarkable improvements (~300% at 1350 °C) in the cold flexural strength of the sintered material. Although the reject content does not seem to have much effect on the density and porosity of samples sintered at 1300-1350 °C, as shown in Fig. 2, Fig. 3 shows that the benefits in the cold flexural strength increase with the added reject content.

Fig. 4 illustrates the typical fracture surface, as observed by SEM, of samples containing 65 wt. % Al_2O_3 + 5 wt. % MnO_2 + 30 wt. % granite reject, after sintering at 1150 °C (Fig. 4-

a) and 1300 °C (Fig. 4-b). The sample sintered at 1150 °C shows a significant amount of porosity and neck formation between the particles is practically absent, which is a characteristic of the first stage of the sintering process. This microstructure explains the physical and mechanical properties of the low temperature sintered material, shown in Figs. 2 and 3. On the contrary, the samples sintered at 1300 °C show clear signs of vitrification, a very fine alumina matrix (limited grain growth occurred during sintering) and a higher degree of closed porosity (rounded pores), homogeneously distributed in the matrix. The higher densification degree observed is responsible for the better properties observed with the samples sintered at higher temperatures.

Further investigations are still under way aimed at furthering the study of the dependence of the properties of the MnO_2 and granite reject added alumina on the microstructure and the crystallization process.

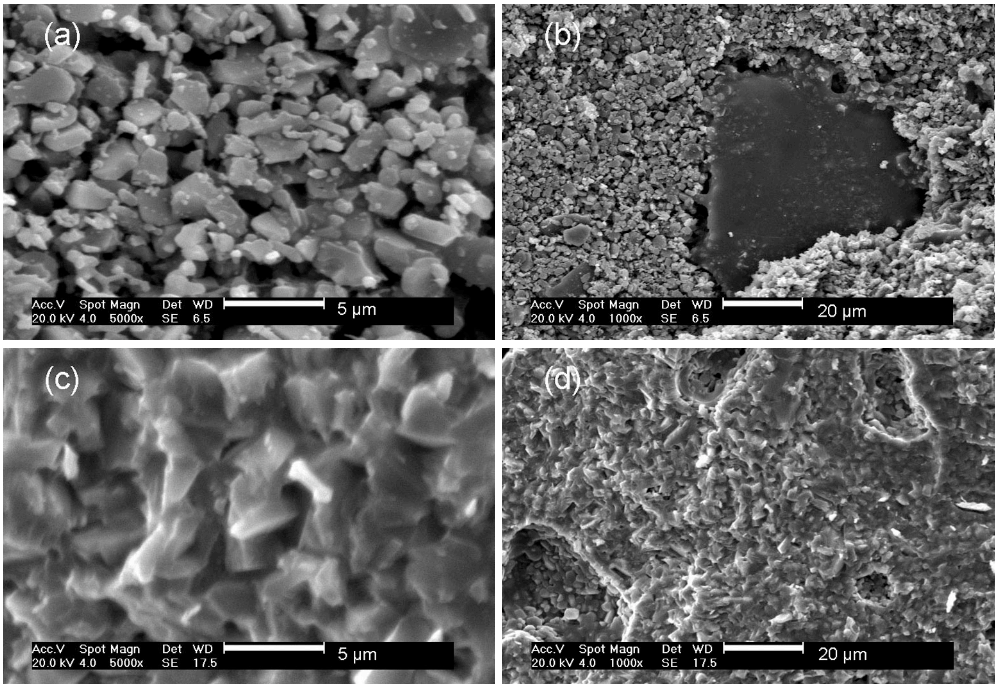

Fig. 4 – Typical microstructure of the fracture surface of samples sintered at: (a, b) 1150 °C, and (c, d) 1300 °C. Higher magnification micrographs are shown on the left (a, c).

Conclusions

A non-beneficiated industrial granite reject obtained directly from the cutting process of ornamental stones was used, combined with a constant 5 wt. % MnO_2 content, as a low temperature sintering additive for high-alumina ceramics. The obtained results show that the combination of those two materials led to a significant reduction in the sintering temperature of alumina, producing sintered bodies with much better values of porosity and density than those of pure alumina sintered at the same temperature. This pronounced effect was observed only at temperatures higher than 1250 °C. These results suggest that the presumably viscous liquid phase that develops upon the granite reject addition acts as an effective sintering aid and results in a remarkable improvement of the cold mechanical strength of the alumina-based composition. Thus, this use of significant amounts of non-beneficiated granite rejects throws a brighter light on the low cost production of alumina-based ceramic products and has the potential to ameliorate and minimize the cutting mud negative impact on the environment.

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