JOURNAL OF MATERIALS SCIENCE **40** (2005) 3905–3909

Using granite rejects to aid densification and improve mechanical properties of alumina bodies

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The industrial use of waste materials in the ceramic industry has been widely investigated. This work describes the research carried out on the manufacturing of alumina bodies with granite reject additions. The reject was used as produced by a local industry that saws granite stones into blocks and slabs. This industrial process produces a significant amount of that reject, which is discarded in sedimentation lagoons, landfill areas or simply thrown in rivers, resulting in environmental pollution. Alumina and the granite reject were ball-mill mixed with 5 wt% manganese oxide and pressed under an uniaxial load of 20 MPa. Samples were subjected to thermal analysis (DTA, TG and dilatometry) and sintered in air at 1300 and 1350°C during 1 h in an electric furnace. Sintered specimens 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 (~300%) the cold mechanical properties of the alumina body.

1. Introduction

The sintering stage is the most important step in the fabrication process of any ceramic product, especially where energy costs are concerned. As is well documented in the literature for alumina [1, 2] and a variety of other systems [3, 4], to aid the sintering process (i.e. to sinter faster or at lower temperatures), the reactivity of the particles to be sintered must be increased (i.e. finer particle sizes), or sintering aids must be used. Early studies on the densification of pure alumina date back to the late 1950's [5, 6] and showed that restricting grain growth during sintering was essential to achieve a fully dense final material. On the other hand, the presence of small amounts of selected additives was found to alter the densification mechanisms and enable sintering at significantly lower temperatures [7]. These sintering aids promote sintering either by causing the development of solid solutions and lattice defects, or the development of a liquid phase, both favouring the diffusion processes necessary to sintering [8–10]. In those cases in which the properties of the sintered body are not unduly hindered by the use of sintering aids, this is still the easiest way of lowering the sintering temperature.

A number of researchers have studied the effect of various additives, such as MgO, CaO, MnO, TiO_2, SiO_2, Cr_2O_3, Fe_2O_3, Nb_2O_5, Y_2O_5 and γ-Al_2O_3, on the densification of non-reactive alumina powders [11–19]. The presence of those additives, singly or combined, improves the densification process and the cold mechanical properties of the sintered materials, while decreasing the sintering temperature, and can be used to control the microstructure (reduce the grain growth) of the alumina bodies. Those studies showed that the introduction of small amounts of such additives can reduce the sintering temperature of alumina from 1600 to *circa* 1400°C.

When the liquid-phase mechanism is the prevalent one, the general conclusion is that there is an optimum amount of each additive at a given temperature to reach maximum density and, the higher the temperature, the smaller the amount of additive needed. In this respect, the system Al_2O_3-TiO_2-MnO has caught the attention

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of the researchers [7, 11, 14]. Moreira and Segadães [20] explained the role played by combinations of manganese and titanium oxides, on the sintering behaviour of alumina, in terms of the equilibrium relationships in the system Al_2O_3-TiO_2-MnO: the sintering-aid effect of those oxides is mostly accomplished by a liquid phase mechanism, noticeable at temperatures above 1300°C. The phase equilibrium diagram also explained why those oxides, although not so adequate on their own, were particularly effective when present in equal amounts (total of ∼4 wt%).

With a liquid phase present at high temperatures, the resulting sintered alumina bodies might not be adequate for hot structural applications. But alumina is still the ideal material for cold abrasion/erosion applications (e.g. thread guides, spray nozzles), where it is important to be able to sinter at lower temperatures. In these cases, the high-temperature liquid phase can also improve the cold mechanical strength, an indirect measure of the abrasion resistance of the ceramic body [14, 18].

In other words, 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 alumina powders must be adequately "contaminated".

"Contamination" brings to mind growing environmental concerns about increasing production of industrial wastes and by-products, which, even when considered generally inert and non-hazardous, cannot be simply discarded and must be disposed of at a landfill site, at the very least. The use of industrial wastes in the ceramic industry, both as additives and as alternative raw materials, has been extensively investigated in the last decade [21–26] and is becoming common practice. Even if this is done in small amounts, the high production rates translate into significant consumption of waste materials. Moreover, some wastes (e.g. powerplant ashes, aluminium anodizing sludge, granite and marble rejects, foundry sands) are similar in composition to the natural raw materials used and often contain substances that are not only compatible but also helpful in the fabrication of ceramics.

Among the alumina-rich waste materials generated by industries in the north-eastern Brazil, marble and granite rejects produced in the cutting process of ornamental stones are becoming an worrying factor for industry owners and environmentalists alike, due to the growing amount of rejected mud that is continuously discarded into rivers and lagoons, likely leading to their environmental degradation [27]. The objective of this work is to study the prospective use of granite rejects and manganese oxide as additives and their effect on the sintering behaviour and mechanical properties of pure alumina, seeking a low temperature sintering material and a means to ameliorate and minimize the cutting mud negative impact on the environment.

2. Experimental procedure

Alumina APC-2011 SG (Alcoa, Brazil) with an average grain size of 2.3 μm was mixed with a constant amount (5 wt%) of MnO_2 (VETEC) and 10, 20 and 30 wt% of industrial granite reject. The granite reject was not beneficiated in any way (used as collected from the industry). The chemical composition of the reject was obtained by X-ray fluorescence (Shimadzu EDX-700). The various powder mixtures were dry-mixed for 4 h in a planetary mill with alumina grinding balls and were subjected to differential thermal analysis and thermogravimetry (Shimadzu DTA-50 and TGA-51, respectively).

The powders were uniaxially pressed into test bars ($50 \times 4 \times 4$ mm^3) under a load of 20 MPa. A dilatometric study (BP Engenharia RB-300) was carried out in air from ambient temperature up to 1350°C with a heating rate of 5°C·min^{-1}. Powder compacts were pressureless sintered at 1300 and 1350°C for 1 h in a tubular electric furnace, the heating and cooling rates being set at 5°C·min^{-1}.

The apparent density and porosity of the sintered samples were determined using the Archimedes water displacement method. Crystalline phases were identified by X-ray diffraction (Shimadzu XRD-600, 40 kW and 40 mA, in the 2θ range of 20 to 70° with a 2θ scanning rate of 2° min^{-1}). The mechanical strength of the sintered samples was determined as the average of four measurements for each composition, using a universal testing machine (Shimadzu Autograph, 250 kN) in a four-point bending geometry, with upper and bottom knives span of 40 and 20 mm, respectively, at a constant cross-head speed of 0.5 mm·min^{-1}.

The microstructure of sintered samples was studied on fracture and polished surfaces, by Scanning Electron Microscopy (Hitachi S-4100, at 25 kV, after carbon coating) and EDS.

3. Results and discussion

Table I gives the chemical composition of the granite reject, as determined by X-ray fluorescence (XRF). The material consists basically of SiO_2, Al_2O_3, Fe_2O_3 and CaO, with minor components like K_2O, MgO and TiO_2. With a sintering-aid role in mind, the reject obviously lacks MnO and the TiO_2 content might be insufficient. However, the high content of alkaline and alkaline-earth oxides (∼17 wt%), the usual fluxing agents in traditional ceramic compositions [21, 22, 24, 25], will likely help the development of a liquid phase during the sintering process. However, preliminary tests carried out with compositions containing alumina and various contents of the granite reject proved unfruitful. Similarly, additions of manganese oxide alone did not contribute to the mechanical strength of the sintered bodies. With both additives, improvements could be seen with 5 wt% MnO_2. Hence, a constant 5 wt% MnO_2 was added to all compositions here forth, together with the granite reject.

TABLE I Chemical composition of the granite reject, as determined by X-ray fluorescence

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

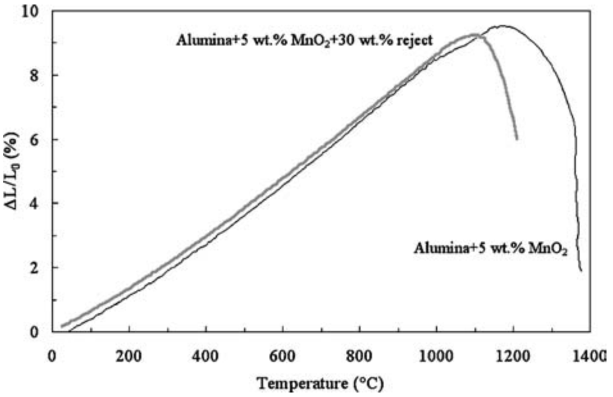

Figure 1 Effect of the additives on the dilatometric behaviour of alumina.

Fig. 1 compares the dilatometric curves obtained for the compositions containing 5 wt% MnO_2 and 5 wt% MnO_2 + 30 wt% reject. The effect of the additives on the onset of sintering can clearly be seen. When compared with data published in the literature for pure alumina [1, 2, 14], that temperature (viz. 1650°C) is significantly lower in the alumina + 5 wt% MnO_2 material (around 1200°C), being further reduced to 1100°C in the presence of the granite reject. This is a clear indication of the likely formation of a liquid phase between MnO_2 and the granite reject.

The composition 65 wt% alumina +5 wt% MnO_2 + 30 wt% reject was chosen to illustrate the typical thermal behaviour of the mixtures, which is shown in Fig. 2. The thermogravimetry (TGA) shows a series of weight loss steps from 250 to 1100°C, which can be attributed to the release of structural water and carbonates decomposition, essentially. Above that temperature, the weight loss recorded is probably due to oxygen loss from the manganese oxide, as the cation changes valency ($MnO_2 \Rightarrow MnO$) and equilibrates under the particular oxygen partial pressure isobar. In the DTA curve, an endothermic peak at ~250°C can be seen, corresponding to the first weight loss step in the TGA curve, followed by an endothermic event at ~800–900°C that matches the weight loss steps attributed to carbonate decomposition. The exothermic peak at 1217°C indicates the reaction between Al_2O_3, CaO and/or SiO_2 to produce new crystalline phases such as mullite and anorthite.

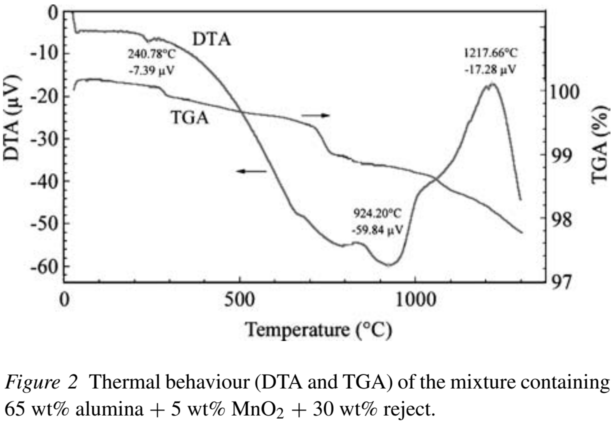

Figure 2 Thermal behaviour (DTA and TGA) of the mixture containing 65 wt% alumina + 5 wt% MnO_2 + 30 wt% reject.

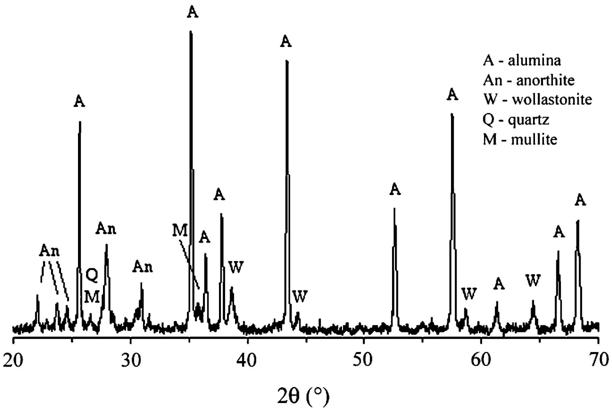

Figure 3 X-ray diffraction pattern of the sample containing 65 wt% alumina + 5 wt% MnO_2 + 30 wt% reject, sintered at 1350°C.

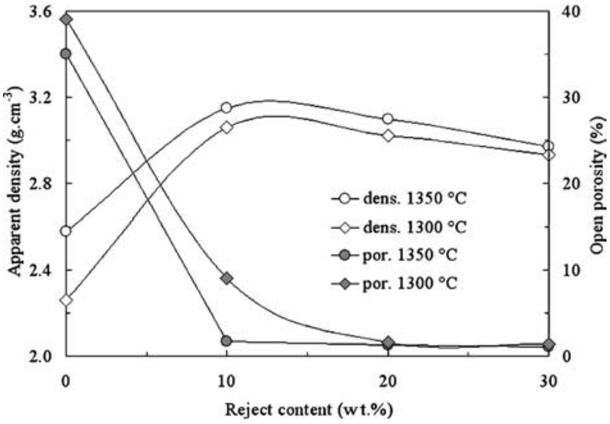

Figure 4 Effect of the granite reject content and the sintering temperature on the apparent density and the open porosity of samples containing alumina + 5 wt% MnO_2.

The major crystalline phases present in the sintered mixtures, identified by X-ray diffraction (XRD), were alumina, anorthite and wollastonite, accompanied by minor amounts of quartz and mullite. Fig. 3 shows the typical XRD pattern obtained (in this case, for the composition containing 5 wt% MnO_2 + 30 wt% reject, after sintering at 1350°C for 1 h). These results are in agreement with the chemical composition given in Table I and the thermal analysis results shown in Fig. 2.

Fig. 4 shows the changes in apparent density and open porosity of the samples containing alumina +5 wt% MnO_2, as a function of the added granite reject content and the sintering temperature. The densifying effect of the granite reject can clearly be seen, even at the lower sintering temperature (viz. 1300°C): apparent density changes from 2.2 $g{\cdot}cm^{-3}$ without the reject (alumina + 5 wt% MnO_2), to 3.1 $g{\cdot}cm^{-3}$ in the presence of 10 wt% reject. It is interesting to note that higher reject contents are somewhat detrimental to the densification and attenuate the beneficial effect of a higher temperature. This behaviour might be related to the easier formation of secondary crystalline phases, at higher reject contents and higher temperatures, rather than the straight vitrification of the liquid phase inside the alumina skeleton pores. Alternatively, even if higher reject contents lead to a larger quantity of liquid phase, its viscosity might not vary (decrease) enough to show a pronounced effect on the densification process. An entirely similar trend can be observed with the corresponding open porosity

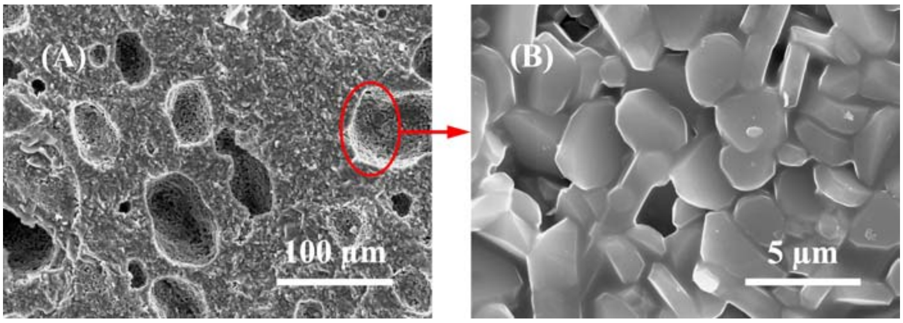

Figure 5 Typical microstructure of the fracture surface of samples sintered at 1350°C (in this case, 65 wt% alumina + 5 wt% MnO_2 + 30 wt% reject).

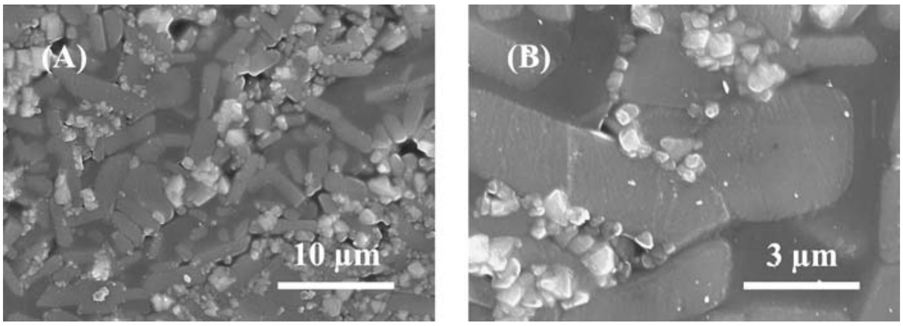

Figure 6 Typical microstructure of the polished surface of samples sintered at 1350°C (in this case, 65 wt% alumina + 5 wt% MnO_2 + 30 wt% reject).

values, as shown also in Fig. 4. Without the reject, a porosity of approximately 40% is reached at 1300°C, which is comparable to what would be expected for alumina sintered at that temperature without additives. The presence of 20 wt% reject at that temperature drastically reduces the open porosity to values of ∼2 % (at 1350°C, the same can be accomplished with 10 wt% reject). Given the relative density values obtained and the corresponding open porosities, the presence of a significant amount of closed pores is to be expected.

Fig. 5 shows the typical microstructure of the sintered samples (in this case, 65 wt% alumina + 5 wt% MnO_2 +30 wt% reject, sintered at 1350°C). These micrographs show a very fine alumina matrix (limited grain growth occurred during sintering) containing rather large closed (rounded) pores, homogeneously distributed (Fig. 5A). Fig. 5B shows in detail the inside surface of a large pore. Alumina grains display the usual thick hexagonal plate morphology and there are clear signs of the presence of a glassy (liquid) phase. Secondary phases, as identified by XRD, are not clearly seen. Those can be identified on micrographs of the polished surfaces, as illustrated in Fig. 6, and characterised by qualitative EDS. Fig. 6A shows a general view of the microstructure, with the lath like and also round alumina grains (light grey) containing iron and manganese in solid solution, a dark grey silicate phase, which is also a solid solution (possibly a glassy phase and/or anorthite), and a granular whitish phase rich in aluminium, manganese, iron and magnesium (possibly an aluminium manganate, with the other metal cations in solid solution). Table II shows the approximate composition (metal cations only) of those three phases, as obtained by qualitative EDS on microstructures such as shown in Fig. 6B.

Fig. 7 shows the effect of added reject on the cold flexural strength of the sintered samples. Even at the lower firing temperature (viz. 1300°C), the cold flexural strength increases ∼180% with the addition of 10 wt% reject, and remains approximately constant afterwards (i.e. for higher reject contents). This tendency is similar to that already observed for the apparent density and open porosity (Fig. 4). At 1350°C, although maximum density and minimum open porosity can be reached with the addition of ∼10 wt% reject, Fig. 7 shows that,

TABLE II Composition of the three phases found in the sintered microstructures, as determined by qualitative EDS

atom %	Na	Mg	Fe	Al	Si	Ca	Mn
Whitish grains	2.69	7 .61	11.96	53.52	4.97	–	19.25
Alumina grains	–	–	7.82	86.71	1.56	–	3.91
Silicate grains/glass	–	–	2.00	47.45	34.65	14.31	1.59

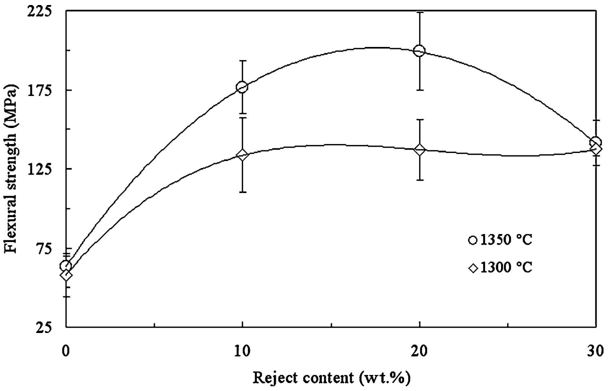

Figure 7 Effect of the granite reject content and the sintering temperature on the cold four-point flexural strength.

in terms of cold flexural strength of the sintered bodies, full benefit from the granite reject addition (an increase of ∼300%) requires the use of ∼20 wt% reject, as a direct consequence of the short firing time. These cold mechanical strength values are remarkable, considering the presence of the large closed pores in the microstructure (as shown in Fig. 5) and demonstrate how a presumably viscous liquid phase can be used to strengthen a porous microstructure.

4. Conclusions

A non-beneficiated industrial granite reject, produced in the cutting process of ornamental stones, was used in conjunction with small amounts of manganese oxide as a low temperature sintering additive for alumina powders. Sintered samples were found to contain well distributed closed porosity, all phases identified being solid solutions in higher or lower degree. The results obtained showed that the addition of 20 wt% granite reject can greatly enhance the sintering aid effect of 5 wt% manganese oxide and, upon firing at 1300°C, the samples density improves to above 3 g·cm^{-3} at a ∼2 % open porosity level. At 1350°C, due to the short firing time, full benefit, in terms of cold flexural strength of the sintered bodies (∼300% improvement), requires the addition of higher reject contents. These results suggest that the presumably viscous liquid phase that develops upon the granite reject addition acts as a low temperature sintering aid for the alumina matrix while preserving the closed porosity in the microstructure, which then translates into a remarkable improvement of the cold mechanical strength. Thus, the use of significant amounts of non-beneficiated granite reject as a low temperature sintering aid for alumina powders is rather promising and has the potential to ameliorate and minimize the cutting mud negative impact on the environment.

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Received 7 October 2004
and accepted 2 March 2005