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Ceramics International 34 (2008) 593–597
CERAMICS INTERNATIONAL
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Properties of sintered mullite and cordierite pressed bodies manufactured using Al-rich anodising sludge

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Received 17 May 2006; received in revised form 24 August 2006; accepted 18 December 2006

Abstract

Mullite and cordierite based refractory ceramic materials were produced from formulations based on an industrial Al-rich sludge derived from the wastewater treatment of the aluminium anodising process. Some common ceramic raw materials, like ball clay, kaolin, diatomite and talc, were also added. Cylindrical samples processed by uniaxial dry pressing were sintered at different temperatures (between 1300 and 1650 °C, 1 h soak at each temperature) to study the ceramic properties.

The fired properties of materials was evaluated (firing shrinkage, water absorption, bending strength, thermal expansion coefficient, refractoriness and SEM microstructure) and demonstrated that optimal properties were obtained at 1650 °C for mullite and 1350 °C for cordierite.

Keywords: D. Mullite; D. Cordierite; Al-anodising sludge; Ceramic properties

1. Introduction

Aluminium anodising and powder surface coating processes are commonly used techniques to protect metallic bodies from corrosion and to achieve some aesthetic effects, such as colouring. These processes consume large quantities of water and generate large amounts of sludge (about 100,000 metric tonnes per year in EU countries). The sludge consists mainly of colloidal aluminium hydroxide; sodium or calcium (generated from neutralising solutions), and aluminium (used as flocculating agent) sulphates; water (up to 85 wt.%). The anodising waste is classified as non-hazardous [1–3]. The difficulties in reducing sludge volume, by filter-pressing, the high transportation costs for disposal (22–30US$/tonne) and the lack of industrial applications; have resulted in the accumulation of waste in special landfills. Attempts to search for potential market outlet applications in the cement, ceramics, and paper-producing industries are spurious and do not consume more than 20% of the generated amount [1,4].

On the other hand, predictable high alumina contents of the calcined sludge and its compositional constancy over time make them very attractive for recycling processes; such as by recovering aluminium-based compounds, beneficiating the alumina-based materials, or incorporating the alumina materials in other products. Sludges have been used in several inert matrixes, such as concrete, glass and ceramics [4–7].

Some of those studies suggest that recycling of Al-rich anodising sludge in mullite ($3Al_2O_3{\cdot}2SiO_2$) and cordierite ($2Al_2O_3{\cdot}5SiO_2{\cdot}2MgO$) refractory bodies might represent a good environmental outlet [8,9]. In that sense, several studies have been conducted first to fully characterise the waste; then to design promising compositions by using the sludge alone or mixed with natural/commercial raw materials (clay, kaolin and talc), or by-products (diatomite) [10,11]. Mullite-based ceramics exhibit important properties: high thermal resistance (incongruent melting at 1890 ± 10 °C), low linear thermal expansion coefficient ($\alpha = 5.0 \times 10^{-6}\ K^{-1}$, between 20 and 800 °C), excellent creep resistance ($\varepsilon > 10^{-10}\ s^{-1}$ at 1200 °C) and high bending strength (360–370 MPa) [12–14]. Cordierite-based ceramics have high electrical resistivity ($>10^{14}\ \Omega$ cm), very low linear thermal expansion ($\leq 2 \times 10^{-6}\ K^{-1}$, between 20 and 800 °C) and good bending strength (62–92 MPa) [15].

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doi:10.1016/j.ceramint.2006.12.005

The main purpose of the present study is to make dry pressed mullite and cordierite ceramics refractory materials based on pre-calcined Al-anodising sludge and to evaluate the performance of these materials. In addition, the sintering process was studied to optimize desired physical properties, since they are strongly dependent on the microstructural development [16].

2. Experimental

The Al-sludge was generated in the wastewater treatment unit of an anodising or surface coating industrial plant (Extrusal, S.A., Aveiro, Portugal). It represents reasonably well the type of waste generated in the anodising industry. It was used after calcination at 1400 °C for 1 h. Its full characterisation is detailed elsewhere [8,10] with an average chemical composition listed in Table 1.

Two different formulations (named M [mullite-based] and C [cordierite-based]) were prepared, combining the Al-sludge with ball-clay (BM-8, Barracão, Portugal), kaolin (Mibal-B, Barqueiros, Portugal), a previously calcined diatomite (at 600 °C, from Anglo-Portuguese Society of Diatomite, Óbidos, Portugal) and talc (Luzenac, France) in the proportions given in Table 2. Diatomite is a low-value by-product from sand quarries and is generated in high amounts in the Centre region of Portugal. Table 1 also gives the chemical composition of all these components.

Starting aqueous suspensions of Al-sludge mixtures having a solids load between 30–35 wt.% were deagglomerated and mixed by wet ball milling for 15 h. The slurries were then partially dehydrated in plaster moulds up to a water content of about 20 wt.%, then dried at 110 °C for 24 h. The dried cakes were then processed to powders by grinding in porcelain jar mills for 15 min. Circular and rectangular green bodies were shaped from the ground powders by uniaxial pressing at 32 MPa (sample dimensions: $\phi = 25 + 3$ mm thickness, and 200 mm × 20 mm × 5 mm, respectively).

The pressed bodies were then fired between 1350 and 1650 °C and 1300–1380 °C for M and C compositions, respectively. The firing schedule involved heating and cooling rate of 5 °C/min with 1 h soak at the maximum temperature. Apparent density of the fired materials was determined by the Archimedes method (Hg immersion), while the water absorption was determined from the weight differences between the as-fired and water saturated samples (immersed for 2 h in boiling water). Flexural strength (Lloyd Instruments LR 30K) and dilatometric analysis (Netzsch 402 EP) was measured on sintered samples. Mineralogical characterization to determine the main crystalline phases that formed during firing was determined by XRD (Rigaku Denk Co., Japan). Microstructural study (SEM-Hitachi S4100) of fired samples was conduced on etched materials (5 (v/v) HF solution for 3–5 min). The complete procedure used to prepare and evaluate the materials is schematically shown in Fig. 1.

Table 2
Tested batch formulations (wt.%)

Mixture	A-sludge	Kaolin	Ball-clay	Diatomite	Talc
M	42.0	15.0	15.0	28.0	–
C	25.0	–	–	32.0	43.0

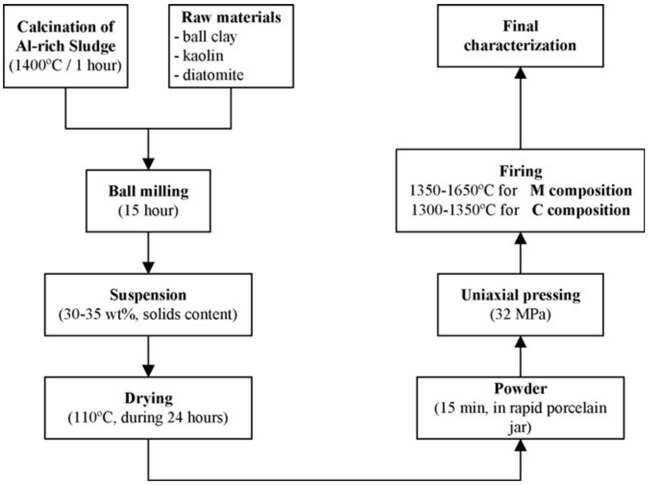


Fig. 1. Testing procedure for samples.

The refractoriness of sintered samples was predicted by evaluating the high temperature deformation of bars under a known applied load (0.5 or 1.5 MPa) at high temperature (1200 and 1280 °C for 2 h), as shown in Fig. 2. The common practice of the refractory-making industry for the two type materials studied assumes that a good performance corresponds to high temperature deformation values lower than 10 and 20% at 1200 and 1280 °C, respectively [17].

3. Results and discussion

Fig. 3 shows the thermal expansion behaviour through 1300 °C of dried M and C bodies. The sintering process seems

Table 1
Chemical compositions of raw materials determined by XRF and EDS (Al-sludge and diatomite)

Raw material	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	LoI
Al-sludge[a]	4.54	–	87.2	0.72	0.36	1.37	–	0.79	–	5.06	–
Kaolin Mibal-B[b]	47.0	0.20	37.1	1.10	–	0.10	0.15	–	2.00	0.20	12.2
Ball-clay	53.3	0.80	28.7	2.27	–	0.23	0.11	–	1.85	0.09	11.9
Diatomite[c]	92.3	–	1.40	1.80	–	1.80	-	–	2.70	–	–

LoI, loss of ignition at 1000 °C.

[a] Calcined at 1400 °C for 1 h.

[b] As given by the supplier.

[c] Calcined at 600 °C for 2 h.

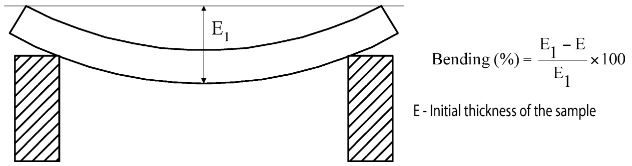


Fig. 2. A schematic representation of the high temperature bending test.

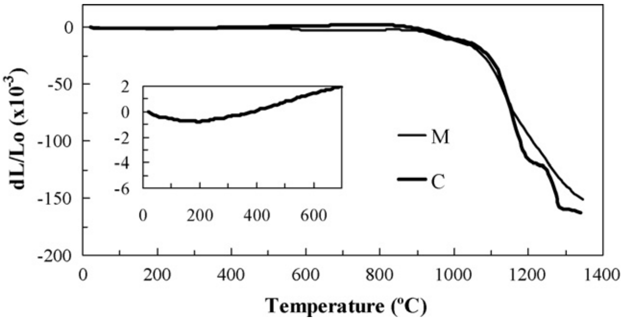


Fig. 3. Thermal expansion curves for dried M and C compositions. Inseted picture gives a detailed view of the expansion behaviour of the C sample.

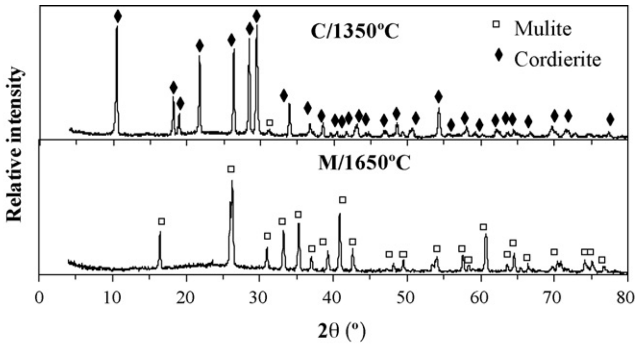
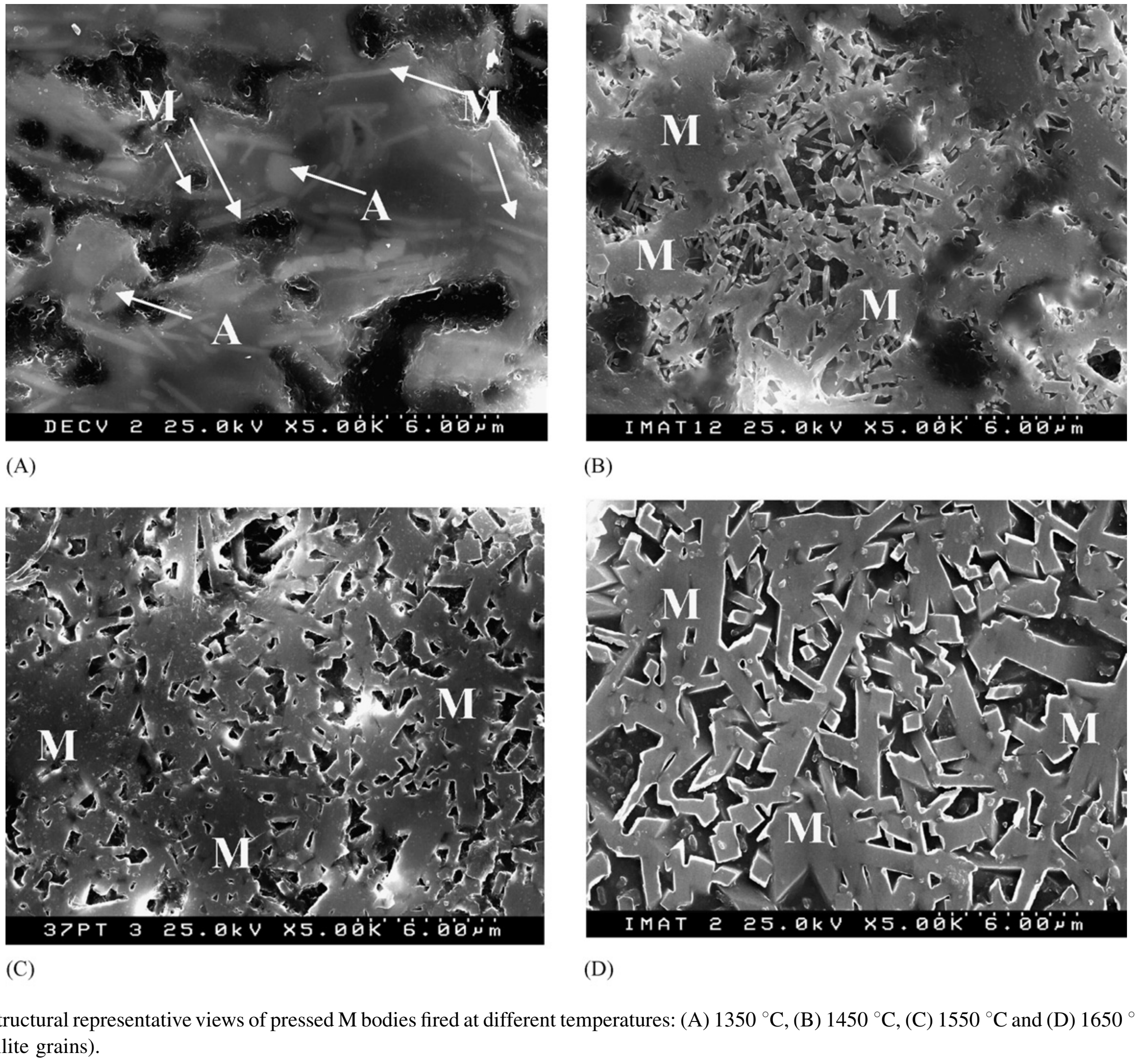


Fig. 4. XRD spectra of M and C samples fired at the maximum sintering temperature of C = 1350 °C and M = 1650 °C.

to start at a similar temperature in both compositions (1000–1100 °C), at least by assuming the point where the sample tends to shrink. Then, the comparative behaviour of C and M materials tend to diverge, with C showing a higher shrinkage rate, compatible with the expected formation of a higher relative amount of liquid phase. This may be explained by a higher concentration of active fluxing agents, such as magnesium compounds, and with a corresponding lower quantity of refractory-type Al-sludge in the C samples.



(A)

(B)

(C)

(D)

Fig. 5. Microstructural representative views of pressed M bodies fired at different temperatures: (A) 1350 °C, (B) 1450 °C, (C) 1550 °C and (D) 1650 °C, (A, alumina grains; M, mullite grains).

Table 3
Room temperature properties of M and C samples sintered at different temperatures

Composition	Sintering temperature (°C)	Total shrinkage (%)	Water absorption (%)	Apparent density (g/cm^3)	Bending strength (MPa)
M	1450	15.4 ± 0.2	9.7 ± 0.7	2.13	35 ± 3
	1550	16.4 ± 0.3	7.5 ± 0.9	2.23	38 ± 3
	1650	19.0 ± 0.8	0.7 ± 0.3	2.50	59 ± 3
C	1300	11.9 ± 0.5	9.8 ± 0.5	1.93	35 ± 3
	1350	13.0 ± 0.2	4.2 ± 0.8	2.07	41 ± 2

The X-ray diffraction patterns (Fig. 4) of the M + C samples sintered at the maximum temperature (C = 1350 °C, M = 1650 °C) shows that mullite is the single crystalline phase formed in composition M. At lower temperatures (e.g. 1350 °C), mullite is already observed, but the presence of some precursor phases, such as quartz and alumina may be still visible [18].

As previously mentioned, M samples were sintered at temperatures between 1350 and 1650 °C. Fig. 5 shows the microstructural evolution of samples versus sintering temperature. From Fig. 5, it is possible to confirm the presence of prismatic mullite grains in contact with a glassy phase that fulfils the interparticle space. At 1350 °C, some cubic grains are still visible, which belong to an alumina precursor phase, as revealed by XRD. Small needles of mullite and a glassy phase composed the microstructure, while the number/dimensions of open pores were reasonably high (Fig. 5(A)). At 1450 °C, only mullite crystals were observed (as confirmed by XRD and EDX), and the porosity strongly decreased (Fig. 5(B)). Between 1550 and 1650 °C the growth of mullite crystals occurred along with a decrease in porosity. This is confirmed by the strong decrease of water absorption values in Table 3. At the maximum temperature, the densification process is almost complete (absorption value below 1%), and the bending strength reaches 59 MPa, a value lower those reported (360–370 MPa) for pure mullite [12]. The lower strength is due in part to the presence of a glassy phase (concentrating fluxing agents), and to differences in material processing.

XRD of the C sample sintered at 1350 °C (Fig. 4) confirms that cordierite is the main crystalline phase formed, and that traces of mullite were formed. Sintering was conducted in a narrower range (1300–1350 °C) than that of M composition due to the powerful fluxing character of C additives. At 1300 °C, the porosity was still reasonably high (water absorption of about 10%), with cordierite the dominant phase, as shown in Fig. 6. The relative amount of glassy phase in C bodies sintered at 1350 °C is very high, as shown in Fig. 6(B), which indicates that the maturation/densification process is near completion. In fact, heating samples to 1380 °C causes clear signs of overfiring, as revealed in similar compositions [18]. The equilibrium phase diagram of the system Al_2O_3–SiO_2–MgO [19] shows an eutectic at 1355 °C involving tridymite (SiO_2), protoenstatite ($MgSiO_3$) and cordierite phases; justifying the sudden increase of the amount of glassy phase at 1350 °C. The presence of impurities in the actual formulations, namely fluxing elements such as Na and K, might also increases glass content, promoting overfiring. The measured mechanical strength at the peak values (see Table 3) are close to those reported for commercial cordierite [15].

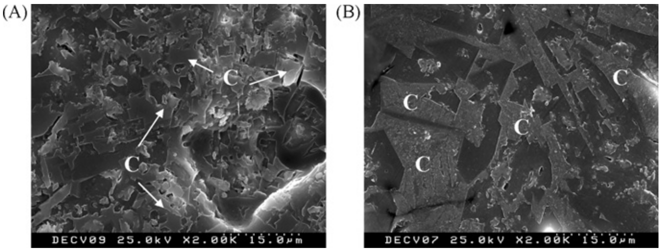


Fig. 6. Microstructural representative views (polished surface) of pressed C bodies fired at different temperatures: (A) 1300 °C and (B) 1350 °C (C, cordierite grains).

Dilatometric tests were conduced with sintered samples at 1350 and 1650 °C for C and M formulations, respectively, and are plotted in Fig. 7. Average thermal expansion coefficients (TEC) estimated between 20 and 800 °C are similar to values of corresponding commercial materials [12,15]: M ~ $5.62 \times 10^{-6}\,K^{-1}$ (~$5 \times 10^{-6}\,K^{-1}$ for mullite); C ~ $1.92 \times 10^{-6}\,K^{-1}$ K^{-1} ($\leq 2 \times 10^{-6}\,K^{-1}$ for cordierite). As it may be seen in Fig. 7, curves for C and commercial cordierite are almost parallel. The higher TEC of the C formulation might be caused by the presence of fluxing impurities (e.g. alkalis) in the formed glassy phase.

Test sample refractoriness was evaluated by measuring the bending of bars under a known load and at elevated temperature (Table 4). The high temperature deformation is strongly dependent on microstructural parameters, such as the grain size and shape, the relative volume of solid and vitreous phases, and the viscosity of the vitreous phase, porosity, etc.; in addition to the effect of the overall composition. Using pct deformation as a criteria, composition C is less refractory than M because of the higher amount of vitreous phase (51 and 22 vol.% in C/1350 °C and M/1650 °C compositions, respectively, estimated

Table 4
High temperature deformation (%) under charge of M and C pressed bodies

Composition	Testing temperature (°C)	Load (MPa)	Bending (%)
M	1200	0.5	0
		1.5	0
	1280	0.5	0
		1.5	0
C	1200	0.5	0
		1.5	24.7
	1280	0.5	29.4
		1.5	38.7

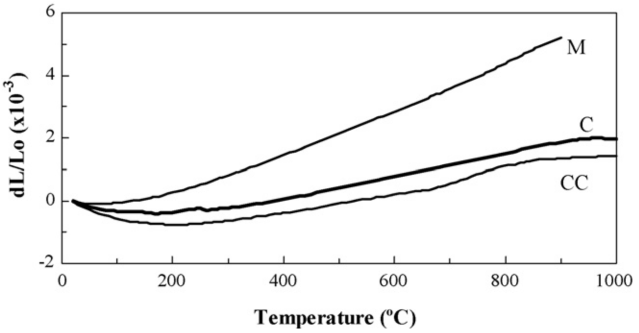


Fig. 7. Thermal expansion behaviour of M and C samples fired at the corresponding maximum sintering temperatures (1650 and 1350 °C, respectively). For comparison, commercial cordierite (CC) (cut piece of a 1350 °C sintered Annawerk plate) was also evaluated.

from stereological measurements). In fact, an acceptable performance in the C composition was obtained at 1200 °C only at the low load. In all other conditions, data indicated poor performance in the C samples. By contrast, M samples showed very good performances at all test conditions. The lower amount of glassy phase and the typical prismatic shape of mullite grains are the relevant features responsible for this behaviour.

4. Conclusions

The production of mullite and cordierite-based pressed bodies containing Al-rich anodising sludge and diatomite as the main constituents was evaluated. The two compositions produced had properties that indicated potential for recycling the anodising sludge as a component of low grade refractory and/or electrical insulating bodies.

Microstructural changes and crystalline phases evolution were found to be sensitive to variations in the sintering temperature of the C and M compositions evaluated, with optimal firing temperatures of 1350 for the C and 1650 °C for the M compositions. The indirect evaluation of refractoriness by testing the high temperature deformation at high temperature indicated that the cordierite-based material could not be safely used above 1200 °C. The mullite-based recycled material shows high refractoriness in the tested conditions.

Acknowledgement

The work was supported by Portuguese Science Foundation (FCT-Project CTA/42448/2001).

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