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Electrical characterisation of cordierite bodies containing Al-rich anodising sludge

J.A. Labrincha [a,*], C.M. Albuquerque [a], J.M. Ferreira [a], M.J. Ribeiro [b]

[a] *Ceramics and Glass Engineering Department, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*
[b] *ESTG, Polytechnique Institute of Viana do Castelo, 4900 Viana do Castelo, Portugal*

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Abstract

Al-rich sludge produced from industrial anodising and surface treatment processes had been tested in the fabrication of cordierite-based materials, by using unidirectional dry pressing and extrusion as shaping techniques. Mixtures with commercial sand and magnesium-containing materials, like ball clay, and talc were prepared in order to achieve interesting final refractory and/or electrical insulating compositions. Microstructural changes upon sintering and crystalline phase evolution are detailed and their relationship with the electrical behaviour is now studied, by the use of impedance spectroscopy.
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Keywords: Cordierite; Electrical properties

1. Introduction

The recycling of Al-rich anodising sludge as a component of cordierite refractory bodies may represent a good environmental solution.[1–3] If properly treated (e.g., dried or calcined) and then correctly mixed with natural/commercial components and/or sub-products (ball clay, sand, talc or diatomite) suitable compositions might be obtained after sintering.[4] Refractoriness, low thermal expansion and electrical insulating characteristics of cordierite-based materials are well documented and several types of applications have been implemented.[5–9] However, such products are fully obtained from natural or chemically-prepared reagents, while the current approach assumes the major use of wastes and by-products.

In addition to preparation/shaping conditions, the sintering process is the most influential step in determining final desirable characteristics, since these are strongly dependent on microstructural details.[7] The sintering process is normally studied by the use of known techniques, such as dilatometry, SEM/EDS, etc., but recently new auxiliary tools have been tried for the same purpose. Electrical impedance spectroscopy (IS) is a good example, since contributions of grains, grain boundaries, pores and other morphological aspects might be discriminated.[7,10–12] Its use is referred for several situations: (i) characterisation of cordierite bodies in different crystal directions[7]; (ii) prediction of sintering process and relation with the properties of mullite-alumina ceramic bodies[10]; (iii) effects of cracks formation on different materials (e.g., TZP)[11,12]; (iv) corrosion effect caused by glass penetration in to YSZ-based oxygen sensors used in glass-making furnaces[13]; (v) curing process of cements[14]; (vi) characterisation of pressed clay products.[15]

In the current work, impedance spectroscopy is used for the electrical characterisation of new cordierite-based materials obtained from mixtures of Al-anodising sludge, talc and diatomite. The electrical response of sintered bodies was correlated with microstructural and crystalline phase evolution in order to evaluate the ability of impedance spectroscopy to predict relevant processing-sintering-related properties.

2. Experimental

The formulation prepared in the present work contains: 25 wt.% pre-calcined (at 1400 °C) Al-rich sludge derived

* Corresponding author. Tel.: +351 234370250; fax: +351 234425300.
E-mail address: jal@cv.ua.pt (J.A. Labrincha).

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Table 1
Average chemical composition (wt.%, by XRF) of the Al-sludge and diatomite, calcined at 1400 and 600 °C, respectively

Component	SiO_2	SO_3	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	Cr_2O_3
Al-sludge	4.54	0.79	87.16	0.72	1.37	–	5.06	0.36
Diatomite	92.30	–	1.40	1.80	1.80	2.70	–	–

from the wastewater treatment unit of an aluminium anodising or surface coating industrial plant (Extrusal S.A., Aveiro, PT) + 43 wt.% talc (Luzenac, FR) + 32 wt.% pre-calcined (600 °C) diatomite (Anglo-Portuguese Society of Diatomites, Óbidos, PT). Diatomite is a low-value sub-product of sand quarries, generated in high amounts in the central region of Portugal. The full characterization of Al-rich sludge and diatomite is given elsewhere.[1–3] Table 1 gives their average chemical composition, as used in actual conditions. The use of commercial talc as a source of magnesium was found necessary. Its average chemical composition (wt.%, determined by XRF) is: 62.2—SiO_2; 31.1—MgO; 1.0—CaO; 0.3—Fe_2O_3; 0.2—Al_2O_3.

Two different processing routes were used: (i) dry pressing, (ii) extrusion. Full details are given elsewhere.[3] Samples were sintered at different temperatures (1300–1380 °C) and microstructural changes were evaluated by SEM/EDS (Hitachi, S4100) after etching with a 5 (v/v) HF solution for 2–5 min. Stereological measurements[16] were conducted in order to evaluate the average grain size and the volumetric ratio between cordierite and glassy phase. Main mineralogical phases present were detected by XRD (Rigaku Denk Co.).

Sintered samples were electroded with Pt paste (Engelhard) and their electrical behaviour was studied by impedance spectroscopy. Measurements were conducted between 200–1300 °C in the experimental setup shown in Fig. 1, using an Hewlett Packard 4284A bridge and changing the frequency between 20 and 10^6 Hz. Fitting and interpretation of curves was done by using a specific routine program (NLLS mathematical tool).[17]

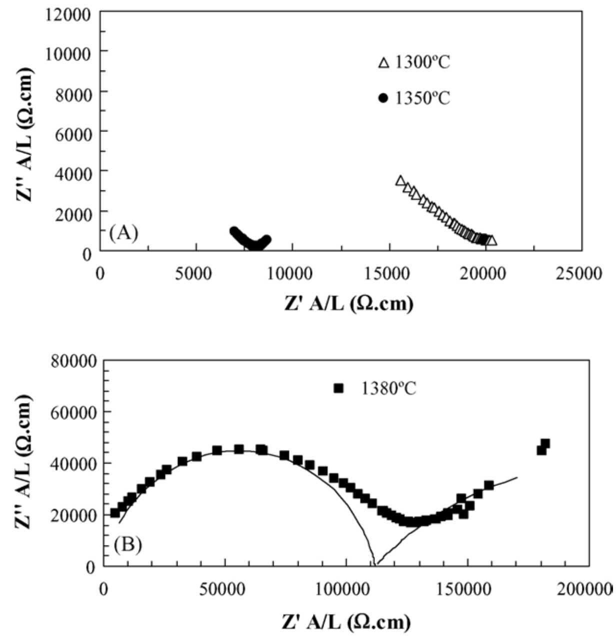

Fig. 2. Impedance spectra obtained at 800 °C for extruded bodies sintered at different temperatures: (A) 1300 and 1350 °C; (B) 1380 °C. Full lines correspond to fitted results.

3. Results and discussion

Fig. 2 shows the impedance spectra of extruded bodies sintered at different temperatures, recorded at 800 °C. The bulk response involves a low depressed ($0.886 < n < 0.900$) single arc that remains almost unchanged with the measuring temperature, apart the logical variation of its diameter magnitude. Pressed samples also respond in a similar way. This behaviour might correspond to that of a composite material, where the cordierite grains are completely embedded by a vitreous phase that is highly conductive.[10] In addition, isolated pores might also be present, as denoted by

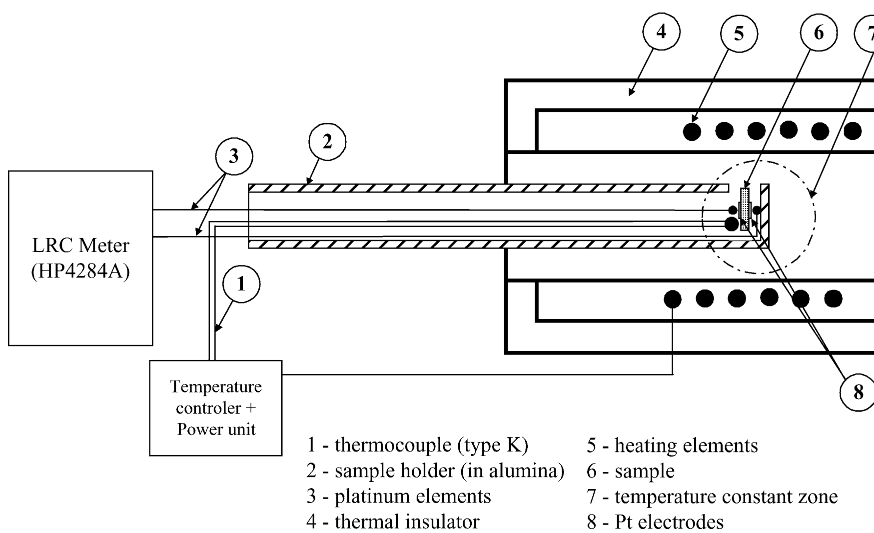

Fig. 1. Schematic view of impedance spectroscopy apparatus.

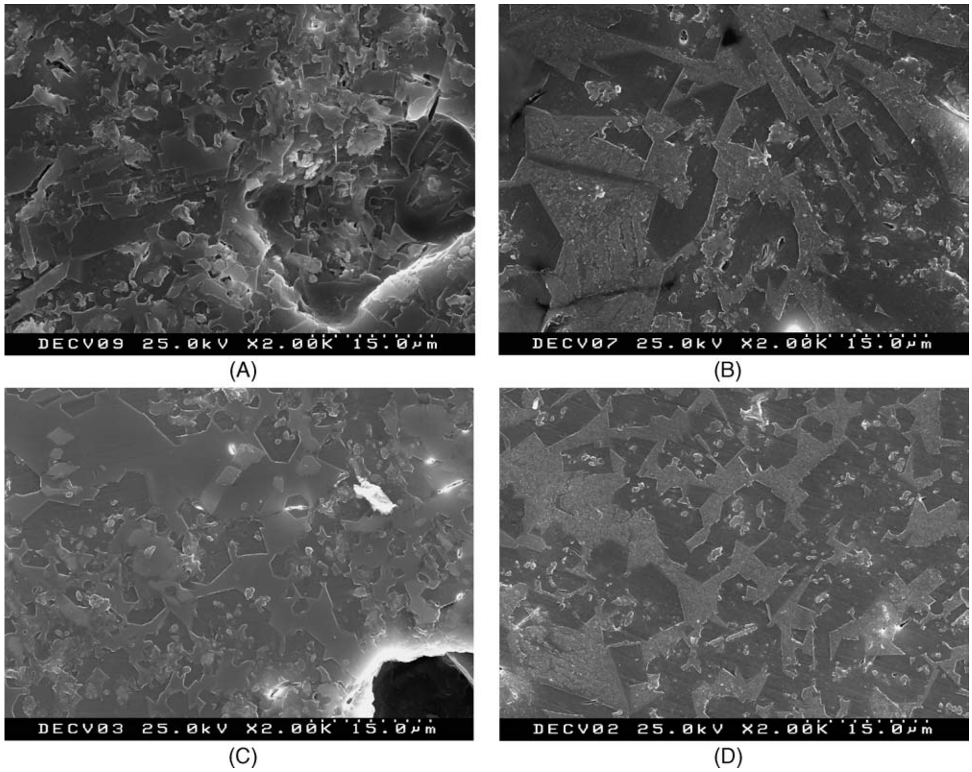

Fig. 3. Microstructural evolution of bodies sintered at different temperatures: (A) pressed—1300 °C; (B) pressed—1350 °C; (C) extruded—1300 °C; (D) extruded—1350 °C. The intergranular region is covered by the glassy phase, being mostly removed by chemical etching (HF).

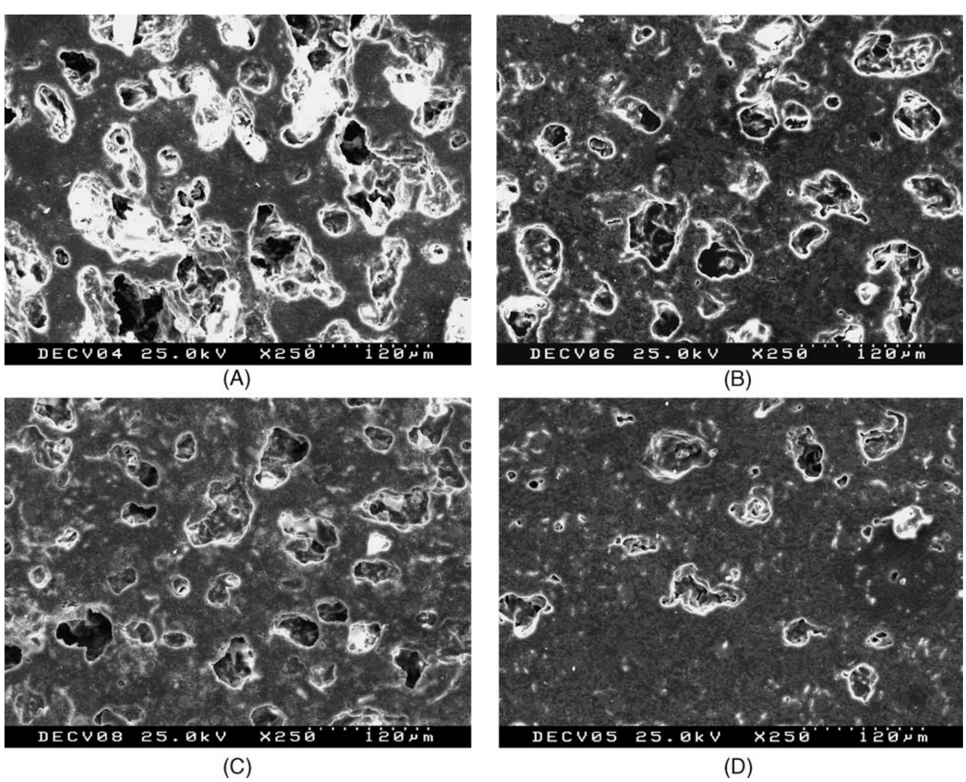

Fig. 4. Morphological views (SEM) of pressed and extruded samples sintered at different temperatures: (A) pressed—1300 °C; (B) pressed—1350 °C; (C) extruded—1300 °C; (D) extruded—1350 °C.

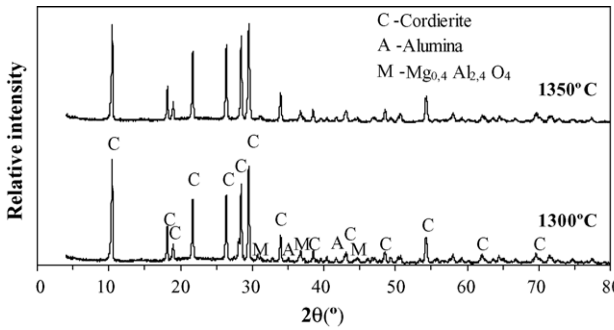

Fig. 5. XRD patterns of pressed samples, fired at different temperatures. At 1300 °C, peaks of the precursor phase (A—alumina) are still visible.

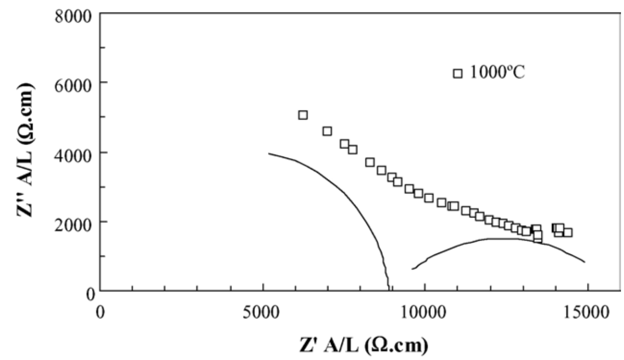

Fig. 7. Impedance spectra of extruded bodies sintered at 1380 °C and obtained at 1000 °C. Full lines correspond to fitted results.

the SEM views of Figs. 3 and 4. The strong jump in the resistivity from 1300 to 1350 °C (see Fig. 2A) is caused by the increasing formation of glassy phase and suppression of pores (the volume of open pores diminishes from 10 to 5%, as determined by water absorption tests), as expected to occur upon sintering. Moreover, the consumption of resistive precursor phases, such as alumina (see XRD of Fig. 5) also contributes to the increase of the electrical conductivity.

By further increasing the sintering temperature to 1380 °C, the conductivity tends now to decrease (see Fig. 2B) despite the expected continuous formation of glassy phase. Two morphological features might be responsible for the inversion in conductivity progression: (i) strong increase of the average size of relatively resistive cordierite grains up to a level where their contact becomes too effective and the interconection of the glassy phase is interrupted; (ii) formation of new and large pores due to an excess of temperature, in a typical process of overfiring.[10] The optical micrograph of Fig. 6 seems to suggest that feature (ii) is dominant, as the creation of porosity is the main relevant feature. The same suggestion is given by the impedance spectra of Fig. 2B and Fig. 7, since an additional contribution seems to appear in the intermediate frequency region. Although not resolvable, it is easy to observe the existence of a new and highly depressed arc in the right part of the IS of Fig. 7 (fr ≈ 8 KHz; $n = 0.853$). In Fig. 2B this contribution is seen in the midle of the bulk (high frequency) and electrode (low frequency) arcs. This extra contribution is normally ascribed to intergranular effects, such as that caused by pores formation.[10,13] If major changes are caused by grain size variations, no new contributions are expected and effects should be observed in the high frequency region.[14]

As previously mentioned, the general aspect of IS of samples processed by different techniques is similar. However, differences in the bulk conductivity are expected due to the differential degree of reactivity/sinterability of samples. Fig. 8 gives Arrhenius plots of all tested sintered samples and allows an easy comparison between them. By fixing the sintering temperature (e.g., 1350 °C) it is obvious that extruded samples are more conductive than pressed ones. This is in accordance with the expected higher sinterability of extruded samples, promoted by the increasing starting (post-processing or green) densification degree. As a reflex, the quantity of pores is lower (compare Fig. 4B and D), and the relative amount of glassy phase is higher in extruded bod-

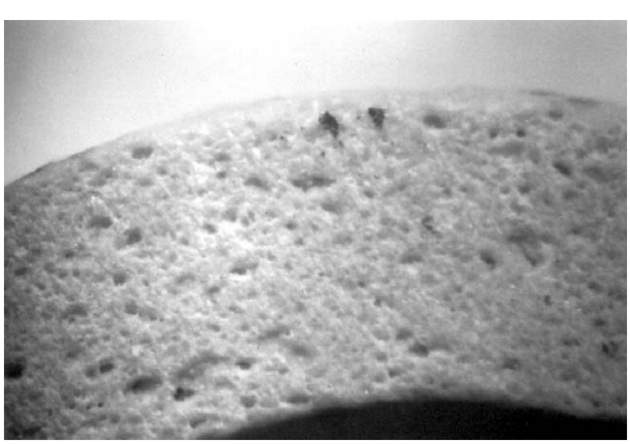

Fig. 6. Morphological aspect (×33 magnification) of extruded sample sintered at 1380 °C, denoting clear signs of overfiring.

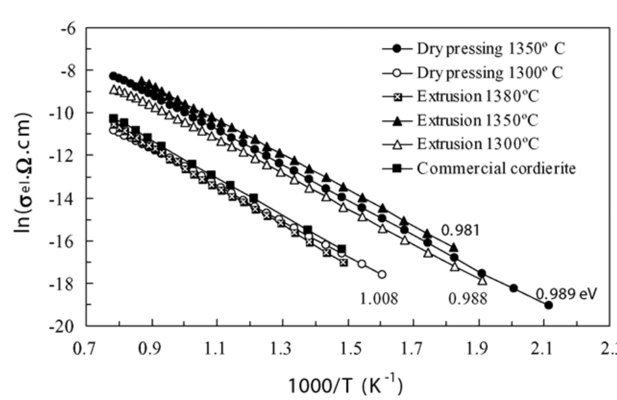

Fig. 8. Arrhenius-type plots of pressed and extruded bodies fired at different temperatures. For comparison, a commercial cordierite sample (from Annawerk) was evaluated. Numbers inserted correspond to the activation energy.

ies. Stereological measurements conducted on SEM pictures of samples sintered at 1350 °C (Fig. 3B and D), confirms these assumptions. Extruded samples show a relative amount of glassy phase of 57 vol% while pressed samples possess only 51 vol%. We should mention that this evaluation was conducted by avoiding the porosity of the samples, so considering only the relative fractions of grains and glassy phase. The comparison of the average size of cordierite grains of extruded (3.9 μm) and pressed (5.6 μm) samples sintered at 1350 °C might result in the single apparent microstructural discrepancy. If the starting size of grains in as-processed samples is similar, we should expect a greater increase upon sintering for extruded samples. However, their higher reactivity also means a higher dissolution rate of crystals in the higher abundant glassy phase.

For comparison purposes, a commercial cordierite sample was also tested, by simply cutting a piece of a furnace furniture plate previously pressed and sintered by the producer (Annawerk). Fig. 8 reflects the strong similarity of the electrical properties between this sample and our pressed body sintered at 1300 °C. Resistivity values measured at 850 and 1000 °C (1.10×10^5 and 5.12×10^4 Ω cm, respectively) are also similar to those reported in the literature.[7] This confirms the potential of the newly prepared partially recycled formulations and also suggests a working limit of about 1300–1320 °C. The equilibrium phase diagram of the system Al_2O_3–SiO_2–MgO[18] shows a eutectic at 1355 °C involving tridimite, protoenstatite and cordierite phases, justifying the sudden increase of glassy phase of samples sintered at 1350 °C. Moreover, the presence of impurities in the actual formulations, namely fluxing elements such as Na and K, might promote this reaction. The activation energy of the conductivity is almost constant for all tested samples, tending to slowly decrease with increasing sintering temperature and for extruded bodies (from 1.008 to 0.981 eV). This similarity confirms that no changes of the dominant conduction mechanism occurred and further gives confidence about the potential of the actual solution. The major drawback is the need of pre-calcination of the sludge at high temperature (above 1100 °C), and new efforts are currently in process to use dried material.

4. Conclusions

The production of cordierite-based materials based on Al-rich anodising sludge and diatomite processed both by dry pressing or extrusion was found to be possible and seems an interesting alternative for such kind of waste and sub-product re-use. As a source of magnesium, commercial talc was added in order to obtain desirable refractory and/or electrical insulating compositions. Microstructural changes and crystalline phase evolution were found very sensitive to variations of the sintering temperature, 1350 °C being considered the upper limit. The sintering process is promoted for extruded samples, when compared with dry-pressed ones.

The electrical behaviour was studied by impedance spectroscopy and major changes on the microstructure are clearly detected by this technique. The similarity of the electrical properties (resistivity level and activation energy) between the current samples and a commercial one confirms the potential of the new re-use alternative.

Acknowledgement

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