BOLETIN DE LA SOCIEDAD ESPAÑOLA DE
Cerámica y Vidrio
ARTICULO

Impedance spectroscopy evolution upon sintering of Al-rich anodising sludge-based extruded bodies

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Alumina based ceramic materials, containing Al-rich sludge as the major component, were processed by extrusion. The sludge derived from the wastewater treatment of aluminium anodising industrial process. Long rods were produced using a vacuum screw extruder, by a careful control of all relevant processing parameters. Then, thick discs were obtained by cutting dried selected rods, to be tested as probes for sintering-dependent electrical properties.
The sintering process was followed by performing common dilatometric/thermal analyses but the evolution of electrical conductivity, estimated by impedance spectroscopy (IS), was also used for this purpose.
Results show that sintering-dependent morphological evolution up to 1300ºC strongly affects the electrical behaviour of samples, and as a consequence IS seems to be a useful technique to follow the firing process.

Keywords: alumina waste-based materials; impedance spectroscopy; sintering; microstructural development

Evolución de la espectroscopia de impedancia sobre cuerpos extruidos basados en barros de anodizado ricos en Al.

Los materiales cerámicos basados en alúmina, conteniendo barros ricos en Al como componente mayoritario fueron procesados por extrusión. Los barros empleados provienen de tratamientos de lavado de residuos de un proceso industrial de anodizado de aluminio. Se produjeron varillas empleando un extrusor de tornillo en vacío con control de todos los parámetros relevantes del proceso. A partir de varillas seleccionadas, se obtuvieron por corte en seco discos cerámicos para evaluar la dependencia de la sinterización y las propiedades eléctricas. El proceso de sinterización se siguió mediante ensayos dilatométricos y análisis térmicos, junto con la evolución de la conductividad eléctrica mediante espectroscopia de impedancia. Los resultados mostraron la evolución de la sinterización y la dependencia morfológica hasta 1300ºC, que afecta fuertemente a la respuesta eléctrica y como consecuencia la espectroscopia de impedancia parece ser una técnica útil en el seguimiento de los procesos de cocción.

Palabras clave: Materiales basados en residuos de alúmina, espectroscopia de impedancia, sinterización, desarrollo microestructural.

1. INTRODUCTION

The monitoring of ceramic sintering process is extremely important for understanding the sintering mechanisms and improving the efficiency of ceramic production. Impedance spectroscopy (IS) is a relatively mature, cheap, and simple technique for non-destructive testing, which has been used to characterise the electrical properties of the material and relate them with changes in the microstructure (1). Examples of the use of IS to characterise the microstructural evolution include sintering of ceramics (2-4), and hydration and hardening of cements (5-7). These works demonstrated the potential of IS to discriminate the partial contribution of grains, grain boundaries, pores and other morphological details, in the final properties of the materials.

In other hand, the recycling of an Al-rich anodising sludge as a major component of different ceramic compositions has been tested (8-10). Full characterization and specification of pre-treatment needs of the Al-sludge, and its mixture with natural components, such as kaolin and clays has been studied and related before (8,9). The main goal was to prove that this waste can be regarded as a useful raw material for other industries, such as ceramic, thus reducing the negative environmental impact associated with landfill and preserving non-renewable nature resources. The processing of alumina, mullite, and cordierite-based formulations are described in those works.

Ceramic formulations can be very complex and then, their behaviour upon firing might be very diverse as well (1). Normally the formation of liquid phase controls the sintering process of the common ceramic formulations. The relative amount and composition of such phase is crucial in determining the sintering kinetics and then all the related properties of the fired material, such as the densification, mechanical strength, etc (1). Dilatometry is the common technique used to follow this process. In general, the liquid phase tends to concentrate the highest diffusing species (Na^+, K^+, etc) and behave as an ionic conductor. By contrast, grains in the matrix are much less conductive. Since the microstructural development upon sintering involves dramatic changes of the relative volumetric amount of grains, grain boundary phases (and their average compositions) and pores, strong changes are expected on the electrical response of the system.

The purpose of this work is the use of IS measurements as a non-destructive tool for monitoring the sintering evolution of a mullite-based recycled formulation and then to control the firing process.

2. EXPERIMENTAL PROCEDURE

The mullite-based recycled formulation used in the present work include an Al-rich sludge as the main component, derived from the wastewater treatment unit of an aluminium anodising industrial plant, 42% (Extrusal S.A., Aveiro, PT); 15% of a plastic ball clay (BM-8, Barracão-Leiria, PT); 15% of a kaolin (Mibal-B, Barqueiros, PT); and 28% of a pre-calcined (600ºC) diatomite (Sociedade Anglo-Portuguesa de Diatomites, Óbidos, PT). The as-received Al-sludge is mostly constituted by aluminium hydroxide and water (about 85 wt. %), but aluminium, calcium and sodium sulphates are also present as minor constituents. In the present work the Al-rich sludge was used after calcination (1400ºC - 2 h). The full characterization of the others raw materials is given elsewhere (8,9).

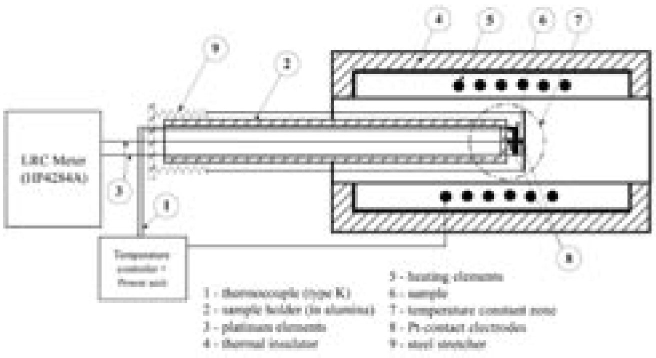

Fig. 1- Schematic view of impedance spectroscopy apparatus.

Extruded rods were obtained in a pilot-scale screw extruder with two single screws in series separated by a vacuum chamber. After drying (110ºC, 24 hours) the samples were cut (∅ ≈ 10mm and with 2-3mm of thickness) assuring that contact surfaces are parallel. Pt-foil contact electrodes (∅ = 2.2mm) were used. The electrical behaviour upon firing was studied by impedance spectroscopy. Measurements were conducted between 500-1300ºC in the experimental setup represented in Figure 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 (12).

The microstructural evolution was evaluated by SEM/EDS (Hitachi, SA100) after polishing and the crystalline phases were detected by XRD (Rigaku Denk Co.).

3. RESULTS

To anticipate decompositions and other reactions during the sintering evolution process, which can make some influence in the electrical response, DTA/TGA analyses of mullite-based recycled composition were performed (figure 2). The TGA and DTA curve shows two regions of strong weight loss. The first one between room temperature and 200ºC is due to the removal of free water (≈ 4 % of weight loss), while the second (500-600ºC) corresponds to the characteristic clay-mineral decomposition: Both reactions are endothermic, as revealed by the DTA curve. Another slight weight loss occurs at higher temperature (≈ 1100ºC), ascribed to sulphates decomposition (Na and/or Ca). DTA analysis denotes the occurrence of an exothermic reaction at ≈ 980ºC, attributed to the formation of primary mullite ($Al_2O_3.SiO_2$).

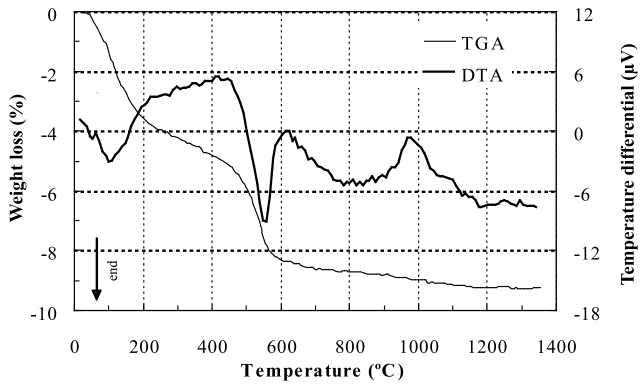

Fig. 2- TGA and DTA curves of the mullite-based recycled composition.

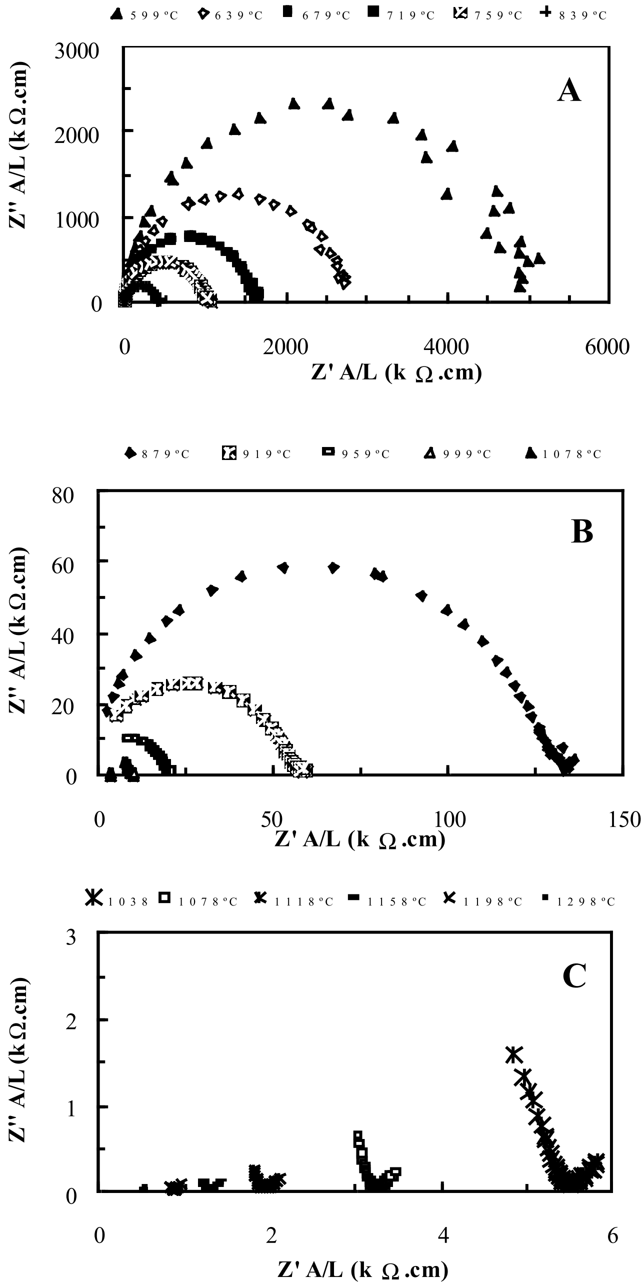

Fig. 3- Impedance spectroscopy evolution with the sintering temperature of extruded and dried mullite-based recycled samples.

Figure 3 shows typical impedance spectra of extruded and dried samples, with a single-arc response very slightly depressed (n > 0.98, while a centred semicircle shows n = 1) usually attributed to dominant contribution of intragranular or bulk response. Normally the impedance spectra of a polycrystalline ceramic material are expected to have two semicircular arcs, one attributed from the grain and another from the grain boundary (1). However, at relative low temperature there was only one semicircle corresponding to the bulk effect according to the impedance spectra results observed by Wang and Xiao (1). The results also show that by increasing the sintering temperature the electrical resistivity tends to decrease and above ≈ 900ºC only a part of the complete arc response can be observed (figure 3C).

The Arrhenius plot shown in figure 4, representing the conductivity properly corrected by knowing the thickness variation during firing, exhibits slope changes. The low temperature conductivity is thermally activated as usually observed in ionic-type conductors. No changes were observed in regions where decomposition reactions were detected by DTA/TGA (e.g., 500-600ºC or 1.30-1.12 K^{-1}), despite gas phase liberation is expected to occur. At about 859ºC (≈ 0.883 K^{-1}, as indicated by a vertical line) the slope of the curve clearly changes, suggesting a change in the controlling conduction process or the appearance of a new contribution to the electrical conductivity. In the highest temperature range of figure 4, the observed slope is quite similar to that observed in the pre-sintered sample (at 1350ºC during 1 hour) which indicates a comparable sintering maturation in both samples.

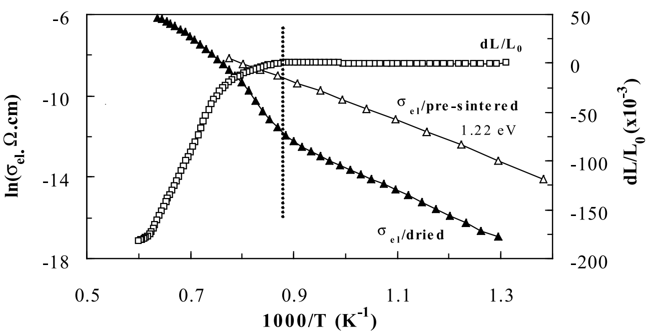

Fig. 4- Dilatometric curve (dL/L_0) of dried mullite-based recycled sample and Arrhenius-type plot (σ_{el}, estimated by IS) of the same composition dried and pre-sintered at 1350ºC.

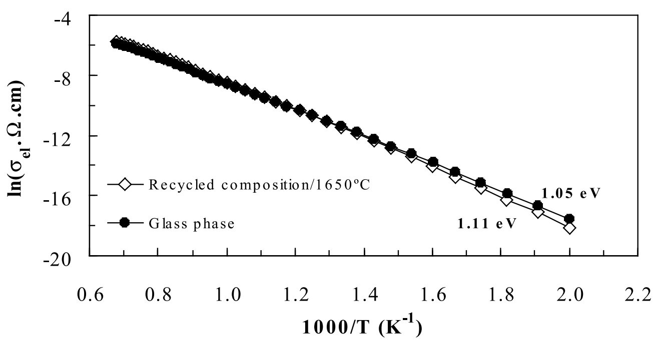

Fig. 5- Arrhenius-type plots of the mullite-based recycled sample, pre-sintered at 1650ºC, and of the synthetic glass having the same chemical composition (estimated by EDS) of the intergranular glassy phase present in the recycled bodies.

The comparison with the dilatometric curve (dL/L_0), shows a clear correspondence, namely in the temperature region where the shrinkage tends to be intensified, corresponding to the beginning of the sintering process (also marked by a vertical line in the graphic).

In common ceramic formulations, the sintering process is controlled by the presence/formation of liquid phase. The presence of glassy phase led to a significant change in the total electrical conductivity since it tends to concentrate the highest mobile ionic species, as been demonstrated in a previous work with similar formulations but on sintered samples (11). According to some authors (1), the electrical conductivity change is a consequence of the creation of a continuous conductive pathway by the glassy phase. We proved that the conductivity evolution is easily interpreted by models used for composite materials, considering the relative volume fractions of glassy and less conductive granular phases, estimated from stereological measurements (13).

The Arrhenius plot shown in figure 5 compares the electrical response of (a) the mullite-based recycled composition, pre-sintered at 1650ºC, and (b) the synthetic glass (made of pure oxides) that simulates the chemical composition (estimated by

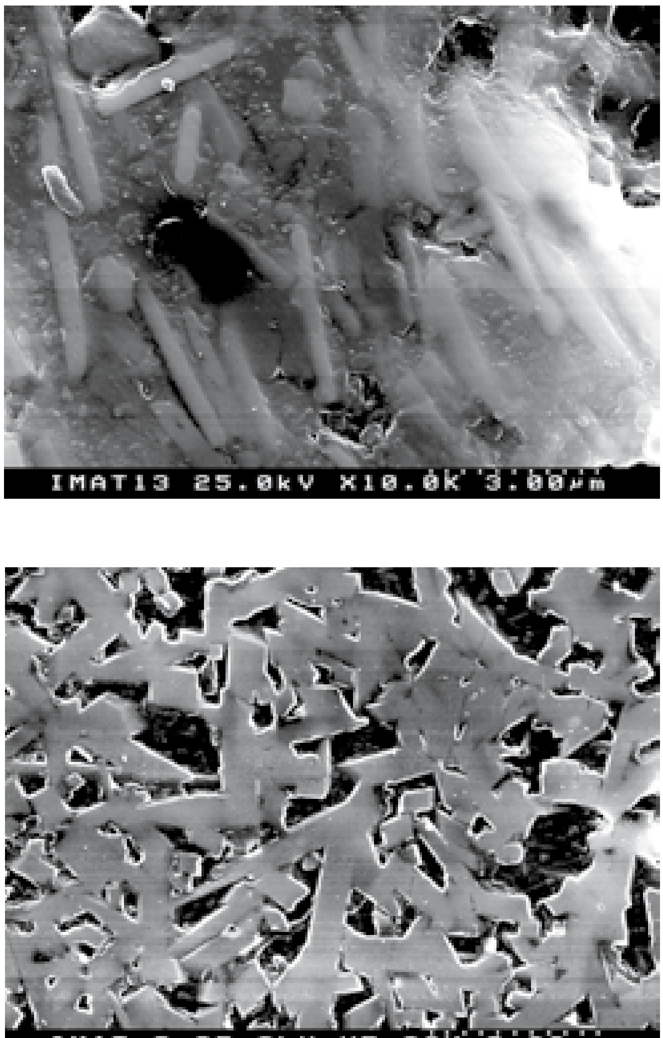

Fig. 6- Typical microstructures of mullite-based recycled samples: (a) sintered at 1250ºC; (b) sintered at 1650°C. In this sample the intergranular region was covered by the glassy phase, being mostly removed by chemical etching.

EDS) of the intergranular glassy phase present in the ceramic samples. The similarity of the results, both in terms of the conductivity values and also concerning the activation energy (1.11eV and 1.05 eV, respectively), confirms the relevant role of the glassy phase in determining the electrical conductivity of these samples.

Figure 6 shows a representative view of the microstructure of the mullite-based recycled extruded bodies fired at 1250ºC. At this temperature, a reasonable amount of large pores still persist but crystals of diverse shapes are visible as well (needles and primatic grains, corresponding to mullite and quartz and/or cristobalite, respectively). A large amount of glass phase is also detected, involving the grains. The SEM observations were confirmed by XRD analyses (figure 7). At 1250°C, mullite has already been formed, being one of the main crystalline phases, co-existing with alumina, and small amounts of cristobalite and α-quartz. With temperature rising, the intensity of mullite peaks increases while those of the others (precursor) phases tend to disappear. Accordingly, although all of these crystalline phases are still present at 1350ºC and only mullite crystals exist in the sample fired at 1450ºC. Between 1450ºC and the maximum sintering temperature (1650ºC) mullite is the single crystalline phase detected. Grains tend to grow in size (figure 6b) and might create barriers to the continuous diffusion of ionic species through the matrix, being possibly responsible for the slight decrease in the slope of conductivity in the Arrhenius plot of figure 4, observed for temperatures larger than 1200ºC. Despite not proved alkaline cations are expectably the conductive species. Since their abundance is relatively high in the current waste-based (less pure) formulations, values of the electrical resistivity are lower than those obtained for pure mullite ($1.4x10^2 – 4.6x10^3$ Ω.cm and 10^6 Ω.cm (14), respectively). Moreover, the expectable amount of glassy (conductive) phase is also higher in less pure materials.

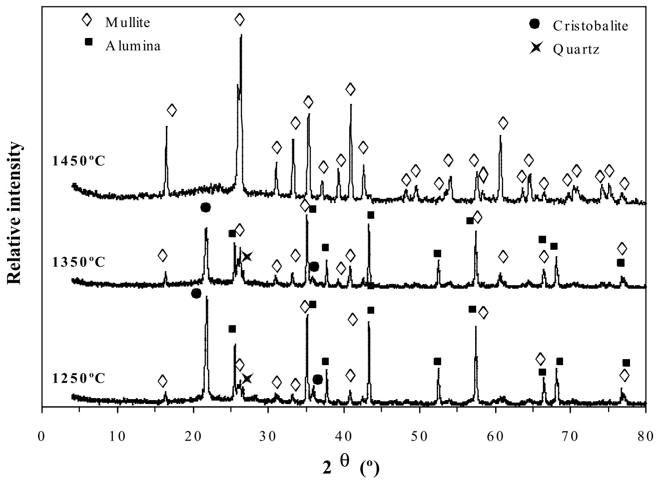

Fig. 7- XRD patterns of powdered samples sintered at three different temperatures for 1 hour.

4. CONCLUSION

Impedance measurements of mullite-based recycled composition proved to be a useful technique to study the sintering evolution and able to understand the relationships between electrical behaviour and some microstructural parameters. The variation of electrical conductivity gives a precise indication of the beginning of the liquid phase formation, showing a good agreement with common predictions get from dilatometric measurements. Values of the electrical resistivity of the waste-based formulation are lower than those obtained for pure mullite, but still very high to permit its use for less severe insulating purposes.

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Recibido: 29.11.05
Aceptado: 04.04.06

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