Synthesis of lanthanum beta alumina by the polymeric precursor technique

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Abstract: Lanthanum beta alumina powders were obtained by the polymeric precursor technique using lanthanum nitrate, aluminum nitrate, ethylene glycol and citric acid. The transformations that occur during thermal treatment of the precursor solution were evaluated by thermogravimetric and differential thermal analysis. Fourier Transform Infrared analysis for residual carbon qualitative detection and gas adsorption analysis for evaluating specific surface area, BET method, were carried out in powder specimens heat treated at different temperatures. High calcination temperature leads to the formation of hard agglomerates. The powders calcined at 800ºC for 4 h have high specific surface area, ~ 120 m^2/g. All processed powders and green pellets sintered at different temperatures were analyzed by X-ray diffraction for structural phase determination. Single phase LaAl$_{11}$O$_{18}$ pellets have application as solid electrolytes in disposable electrochemical devices for monitoring dissolved oxygen species in molten steel at very high temperatures, > 1500 ºC, during steel production.

Introduction

The most important ceramic solid electrolyte application is for to measuring the activity of dissolved oxygen in molten steel in steelmaking processes. In these processes it is considered important the control of oxygen at ppm levels by sensors that utilize ceramic solid electrolytes. In these cases the sensors are constituted by high melting point ceramic materials in order to support the high temperatures of liquid steels (1500 °C $\leq$ T $\leq$ 1700 °C) , to collect and amplify the response of the interaction of the ceramic with oxygen. However, at high temperatures most metals are corrosive so that only refractory ceramics can survive for a time long enough for detecting an electric response [1].

Zirconia-magnesia solid electrolytes, ZrO$_2$:8% mol MgO, are widely used in sensors to monitor oxygen concentration in liquid steels due to their high thermal shock resistance [2,3]. It is well known that zirconia-based solid electrolytes are not suitable for measuring ultra-low oxygen activity due to the electronic conductivity to the electrical conductivity at very low oxygen partial pressure [4]. Therefore, Ca-βAl$_2$O$_3$ oxygen sensors have been developed for determining ultra-low oxygen in molten steel. Laβ-Al$_2$O$_3$ is a promising candidate for substituting Ca-βAl$_2$O$_3$ due to its better ionic conductivity. The microstructure and electrical properties of lanthanum β-alumina can be improved by addition of MgO [5].

Laβ-Al$_2$O$_3$ was obtained by the polymeric precursor method (Pechini technique). Among other chemicals methods, the Pechini technique is a simple way to prepare ceramic

powders based on the capability of certain alpha-hydroxycarboxylic acids to form polybasic acid chelates with a large number of cations. After chelation between the complex cation and citric acid, the polyesterification of an excess of hydroxycarboxylic acid with glycol occurs by slightly heating the solution to form a viscous resin [6,7].

The purpose of this work is to obtain lanthanum β-alumina by the polymeric precursor method and to study structural phase evolution, powder morphology, sintering behavior and electrical properties by the impedance spectroscopy technique.

Experimental

$Al(NO_3)_3.9H_2O$ (Vetec), $La(NO_3)_3.6H_2O$ (Vetec) and MgO (Baker Analyzed) were used as purchased without further purification. The precursor solutions of aluminum, lanthanum and magnesium were prepared by adding the raw materials to ethylene glycol and citric acid with heating under stirring at 90 °C. Afterwards the precursor solutions were mixed in the molar ratios 1La:11Al:0.015Mg and heated at 120 °C to promote the polyesterification reaction. The polymeric solutions were heated at 350 ºC for 4 h and the resultant black powder was then calcined 800 ºC for 4 h. After calcination, the powder was ground in an attritor with zirconia milling medium and isopropylic alcohol at 1200 rpm during 1 h.

Furthermore, the polymeric solution was characterized by thermogravimetry (TG) and differential thermal analysis (DTA) aiming to determine the temperatures of decomposition and crystallization of $La\beta$- Al_2O_3 (TG/DTA-Netzch STA 409). The measurement was performed up to 1400 °C using α-Al_2O_3 as standard under synthetic air (50 cm^3/min).

The resulting powders were characterized by laser scattering (CILAS 1064), diffuse reflectance FTIR (Nicolet), BET surface area (Micromeritics - ASAP 2000) and scanning electron microscopy (Oxford - LEO 440I). After characterization the powders were pressed into cylinder form (10x4mm), first by uniaxial compaction (100 MPa) and then by isostatic compaction (200 MPa). The pellets were sintered in a tubular furnace with heating rate of 10 ºC/min from room temperature to 1200, 1300, 1400, 1500 and 1600 ºC for 2 h in air. The sintering process was performed in an alumina crucible with a powder bed of the same composition of the pellets to maintain the initial stoichiometry. The specimens were analyzed by X-ray diffraction (Bruker AXS D8 Advance) using Cu K_α radiation and by scanning electron microscopy.

The electrical properties were determined by impedance spectroscopy in the 10 Hz to 10 MHz frequency range at 1000 °C with a Hewlett Packard 4192A LF impedance analyzer connected to an HP 362 controller. An S-type thermocouple and platinum leads were used inside the resistive furnace. Platinum colloidal electrodes were applied to the specimens and cured at 800 ºC.

The whole experimental procedure is shown in the flowchart below (Fig. 1).
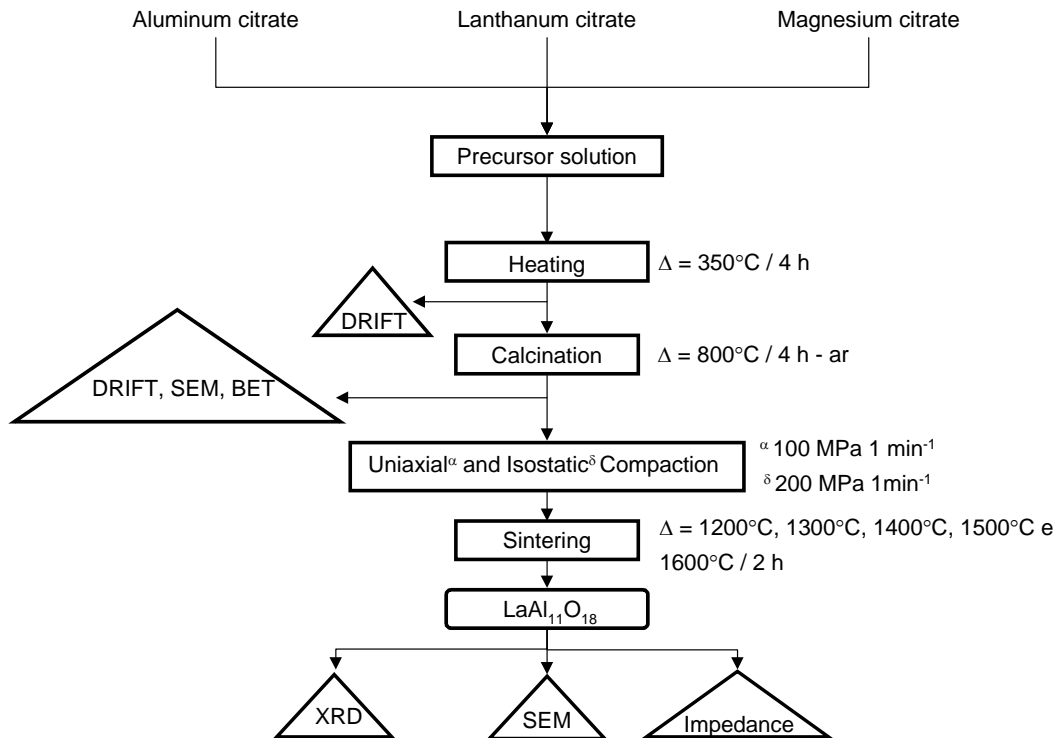
Fig. 1. Flowchart of the experimental procedure to obtain Laβ-Al$_2$O$_3$ by the polymeric precursor method.

Results and discussion

The thermal analysis shows that the decomposition of organic substances is complete by approximately 500 ºC and the Laβ-Al$_2$O$_3$ formation starts at 1160 ºC, first by the reaction La$_2$O$_3$+Al$_2$O$_3$→LaAlO$_3$, and then by the reaction LaAlO$_3$+5 Al$_2$O$_3$→LaAl$_{11}$O$_{18}$ [8].

Granulometric analysis shows that the calcined powder presents particle size values for 50 % population below 15.1 mµ and with an average particle size of 17.4 mµ. After 1 h of attrition milling, the powder agglomerates are significantly broken and the particle size for 50 % population dramatically decreases below 1.2 mµ with an average particle size of 3.3 mµ.

The SEM image of the calcined powder presents a similar aspect of sharp and irregularly shaped agglomerates. Powders analyzed by gas adsorption (BET method) show particles with high specific area (~ 121 m^2.g^{-1}) with equivalent spherical diameter 0.016 mµ. The formation of hard crystalline agglomerates is a problem for all the synthesis related to the Pechini technique [9].

The diffuse reflectance FTIR data provide evidence of the existence of C-O bonds mainly due to the presence of carbonate groups.

The X-ray data for the pellets sintered from 1200 to 1500 °C for 2 h are shown in Fig. 2. At 1200 °C the mains reflections corresponding to the intermediate α-Al$_2$O$_3$ and LaAlO$_3$ phases were observed, indicating that the solid-state reaction has started. All the reflections in the XRD pattern of pellets sintered at 1500 °C for 2h are in agreement with JCPDS file #33-0699, which means that the sample has fully turned into Laβ-Al$_2$O$_3$ phase.
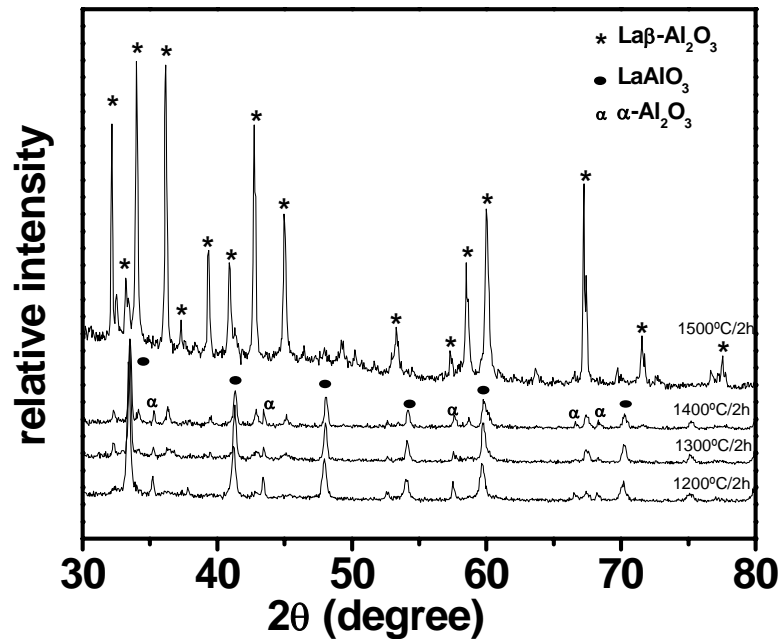
Fig. 2. X-ray diffraction patterns of Laβ-Al₂O₃ sintered under different conditions.

The microstructure of the pellets sintered at 1600 °C for 2 h obtained from powders before and after attrition milling was examined by SEM and illustrated in Fig. 3. Figs. 3b and 3d show that the specimens consist of a large number of platelet grains/agglomerates, with interconnected open and closed pores. The average dimensions of these grains are approximately 2 mµ. The formation of platelets retrains densification because platelet geometry does not favor efficient particle packing. The specimens obtained from powders before (Figs. 3a and 3b) and after attrition milling (Figs. 3c and 3d) do not present significance difference in porosity.

Fig. 4 shows the [-Z''(ω) x Z'(ω)] impedance diagrams of Laβ-Al₂O₃ measured at different temperatures. Usually the impedance diagrams of polycrystalline ceramics displays two semicircles [10]. These semicircles are usually attributed to the bulk and grain boundary contributions to the electrical resistivity at high and low frequencies, respectively. In the case of this work, the impedance diagrams are attributed to the total resistivity including grains and internal surfaces like grain boundaries and porosity. The electrical resistivity changes with porosity between wide limits. These limits can considered an idealized case of parallel slabs [11]. The total electrical resistivity of the specimens here reported increases with temperature because it is a thermally activated process that depends exponentially on the absolute temperature (Boltzmann factor).
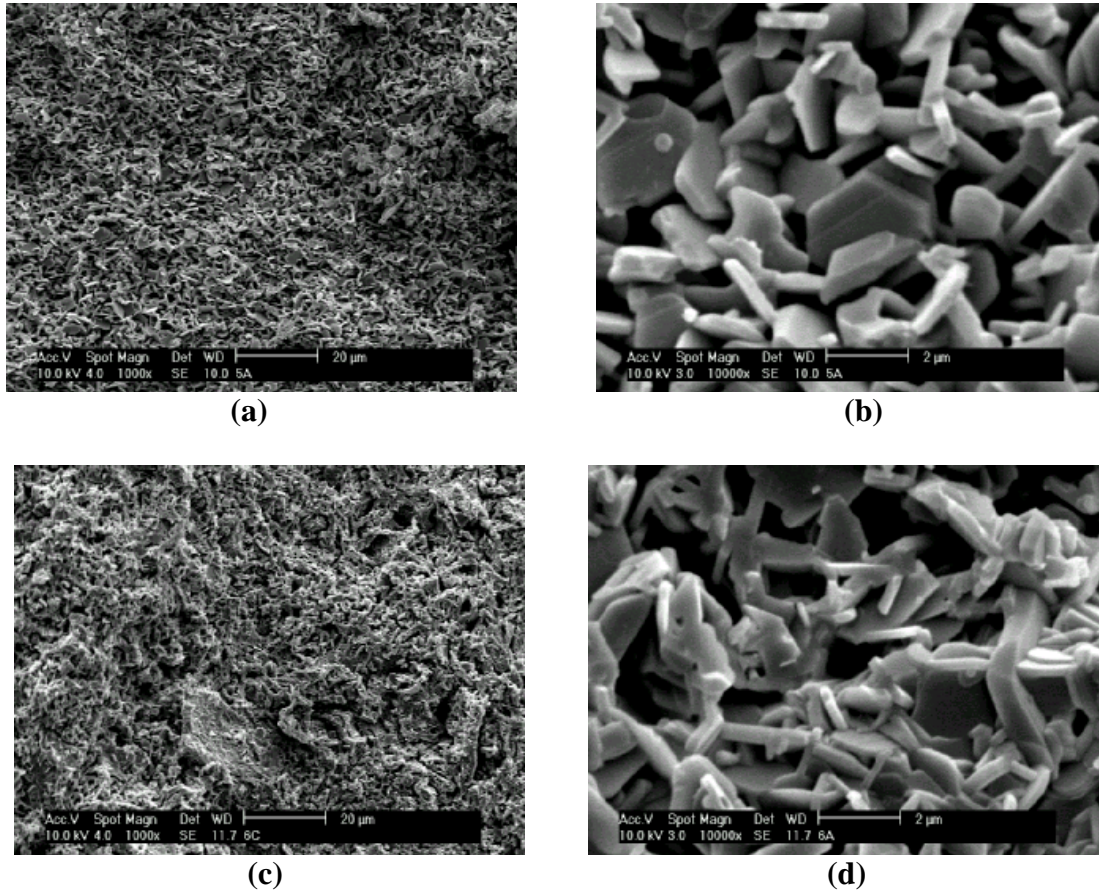
Fig. 3. Scanning electron microscopy micrographs of Laβ-Al₂O₃ pellets sintered at 1600 °C/2 h: before attrition (a) magnification 1000X and (b) magnification 10000X; after attrition (c) magnification 1000X and (d) magnification 10000X.
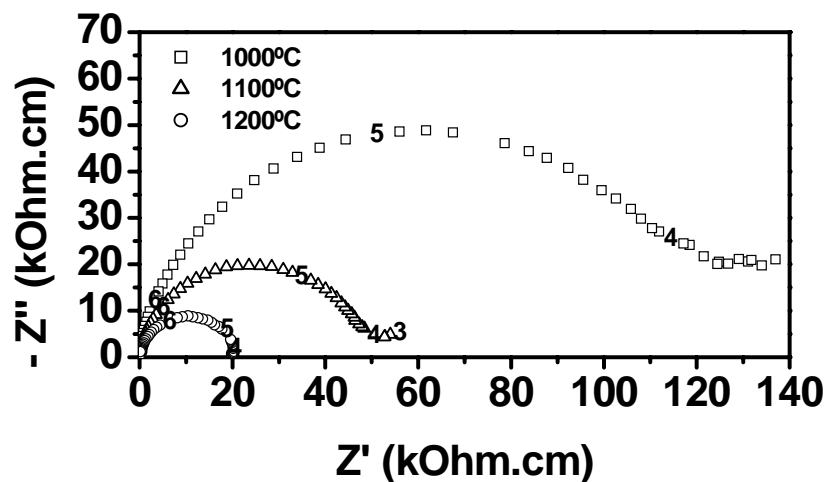

Fig. 4. Impedance diagrams of Laβ-Al₂O₃ sintered at 1600 ºC/ 2 h measured at different temperatures. The numbers stand for the logarithm of the frequency (Hz).

In Table 1 the electrical resistivity of the samples prepared from powders synthesized by the polymeric precursor technique is compared with the resistivity of the same material prepared by solid state reaction and also with the resistivity of the commercial solid electrolyte ZrO_2:8 % mol MgO. The highest value of the electrical resistivity is observed for

Laβ-Al$_2$O$_3$ prepared from powders synthesized by chemical route. This can be explained by the presence of pores that act as blocking regions for the charge transport.

Table 1. Values of the resistivity at 1600 °C for the Laβ-Al$_2$O$_3$ and ZrO$_2$:8 % mol MgO.

Material	$\rho_{1600\,°C}$ (Ω cm)
Laβ-Al$_2$O$_3$	7100
Laβ-Al$_2$O$_3$*	13
ZrO$_2$:8 % mol MgO*	2

* Laβ-Al$_2$O$_3$ [5] and ZrO$_2$:8 % mol MgO [12].

Conclusions

Single phase Laβ-Al$_2$O$_3$ powders were obtained by the polymeric precursor technique. Pellets sintered at 1500 °C for 2h are free from secondary phases, but sintering was restrained by the presence of pores and agglomerates. A compromise is still to be found between the chemical route, which produces homogeneous and high surface area powders, and the mixing of oxides route, which produces non-homogeneous powders but sintered compacts with higher electrical response to oxide ions.

Acknowledgements

References

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