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Electrochemical preparation of precursor phases for obtaining alpha-alumina from aluminium scrap

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ABSTRACT

This work presents a study to obtain α-Al_2O_3 from thermal treatment of the precursor α-$Al(OH)_3$ (bayerite). The precursor was prepared from a cathodic electrosynthesis employing direct current (DC) and alternating current (AC) electrochemical techniques and using an aluminium solution prepared with scrap aluminium cans. Characterization techniques including X-ray diffraction (XDR), scanning electron microscopy (SEM) and thermogravimetric analysis (TG) were used to analyse the thermal behaviour, phase transformation, morphology and particle size of the products obtained. The range of potentials for electrodeposition was between −2.0 and 2.4 V with both DC and AC techniques. The presence of crystalline bayerite in the deposits obtained during all DC and AC experiments was observed, although a species of aluminium oxide ($Al_{2.427}O_{3.64}$) with AC was also identified. The surface morphology of the deposit with DC presented a compact uniform film, whereas with AC a granular form morphology with compact grains in the order of 1–3 μm was evident. In addition, the formation of an amorphous and low crystallinity bayerite precipitate was obtained from the solution, which presented a surface morphology of non-uniform fine grains and agglomerates. The thermal behaviour (TG) indicates three regions of change in the phase, which were verified via the thermal treatment; a transition of bayerite to η-Al_2O_3 in a temperature range between 290 and 300 °C and subsequently to α-Al_2O_3 at a temperature of 1100 °C was determined. The α-Al2O3 presents high purity, a surface morphology with fine grains and agglomerates in the order of 1–10 μm and an appreciable porosity.

1. Introduction

α-alumina is considered as an advanced ceramic material due to its wide field of applications in both the industrial and technological sectors. This material has various characteristics, such as high hardness, resistance to wear, thermodynamic stability and above all a high stability at high temperatures [1–4]. In addition, it is considered to be highly crystalline with large volumes of micropores and macropores in its preparation [3]. Among the different methods which have been reported in the literature for the preparation of alumina powders, thin films or nanoparticles entrapped, hydrothermal synthesis in acidic or alkaline conditions [5,6], synthesis by combustion (CS) [7], chemical deposition in vapor phase (CVD) [8], precipitation at low temperatures using the "seeding" technique [9], two-step hydrolysis and double cation-reverse anion hydrolysis [10,11], the Pechini process [12], alumina-coated multi-wall carbon nanotubes [13], sol–gel method and by in situ interfacial polymerization [14] stand out.

However, these methods also have some limitations such as the use of high temperatures, complex procedures with a wide variety of chemical reagents and in some cases relatively complex and expensive equipment; furthermore, the possibility of producing highly pure ceramic oxide deposits with controlled microstructures often becomes difficult. Electrochemical techniques can provide an alternative characterized by instrumental simplicity, moderate cost, and portability [15–17]; consequently, they also have introduced the some promising methods for the synthesis of metastable phases and α-alumina precursors with nanometric particle materials [16–18]. Literature reports reveal that there are two types of electrochemical deposition processes for the production of alumina precursor phases: anodic or cathodic [16–25]. The anodic process is based on the fact that a metal is oxidized at the anode by a fixed applied potential to form an insoluble metallic oxyhydroxide coating on the anode and subsequently apply a calcination [19]. On the other hand, the cathodic process involves the electrochemical reduction of water and the subsequent deposition of single

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or mixed oxyhydroxides at the cathode and its subsequent calcination to obtain films or ceramic oxide powders [16,20,23,24]. It also was reported the obtaining of alumina (α-Al_2O_3) from scrap aluminium cans [26,27]; however, the procedure is relatively complex, time and energy consuming, where in some cases the presence of remaining trace elements were obtained.

The intention within this study was to obtain precursor phases from a cathodic electrosynthesis employing direct current (DC) and alternating current (AC) electrochemical techniques, and using an aluminium solution prepared with scrap aluminium cans in the preparation of powders of α-Al_2O_3 with high purity. The deposits obtained were characterized by scanning electron microscopy (SEM-EDS) and X-ray diffraction (XDR); in addition, a thermogravimetric analysis (TG) and thermal treatment on products is presented to determine the phase transformation.

2. Material and methods

2.1. Preparation of the aluminium solution

To prepare the solution, scrap aluminium cans were cut and washed with soap and sandpaper to completely remove the paint or lacquer film on both sides of the sheet surface. The size of the sheet was reduced by cutting the pieces to an approximate size of 0.5 cm per side to ensure easy handling and subsequent dissolution. Subsequently, one gram of the cut sheet was weighed and 25 ml of a 2.8 M solution of NaOH was added with stirring. This is because the alkaline solutions or strong bases (containing OH^- ions) attack the layer of aluminium oxide which has formed on the surface naturally and consequently it is possible to attack the metal. Once the aluminium sheets were completely dissolved, the resulting solution was filtered and the insoluble fraction removed to eliminate some impurities. To this solution was added 25 ml 6 M of H_2SO_4 in order to form an insoluble white precipitate of $Al(OH)_3$ and neutralize the excess NaOH present in the solution. The soluble fraction was removed by decantation or centrifugation and the precipitate was rinsed with 25 ml of deionized water in order to remove the residues and some impurities. Following this, 25 ml of deionized water and 15 ml of a 6 M solution of H_2SO_4 was added to the perfectly washed precipitate before heating on an electric plate at 60 °C and stirring until these substances had completely dissolved. For the resulting solution, the chemical composition was determined by inductive couple plasma (ICP) to identify the metallic impurities and the aluminium concentration, its composition are given in Table 1. A high purity of the solution could be observed free of chemical elements such as Mg, Mn and Fe (although there were some traces of Cu) with an aluminium concentration of 0.97 g/L.

2.2. Electrochemical experiments

All of the experiments were carried out in a conventional electrochemical cell for three electrodes with a capacity of 100 ml. A Ru-coated titanium mesh was used as the counter electrode, a 99.9% pure aluminium sheet (1 × 1 cm) as the working electrode and a saturated calomel electrode (SCE) as the reference electrode. All potential values were reported with respect to the calomel electrode (SCE). The surfaces of the electrodes were polished before each experiment with sandpaper (1400 #) and cloth, and subsequently they were washed with acetone and deionized water. The, a pickling process was employed according to reference [28]. The solution prepared with scrap aluminium was adjusted to pH between 3.0 and 4.0 to be used as an electrolyte, since below pH 3.0 it can cause reversibility of the reaction due to interference caused by H^+ while above 5.0 due to hydrolysis of Al^{3+} [29]. Finally, electrochemical studies were performed using a PAR 263 A potentiostat/galvanostat controlled by the PowerSuit® software. All experiments were carried out with stirring.

Table 1
Chemical composition of aluminium solution (g/L).

Mn	Mg	Fe	Cu	Al
0.00	0.00	0.00	7×10^{-5}	0.9769

2.3. Characterization of deposits and precipitates

The thermal analysis of non-calcined deposits and precipitates was obtained by thermogravimetry (TG) behaviour; this was determined by heating the sample up to 1300 °C in air atmosphere at a ramp of 20 °C min^{-1} on a PerkinElmer TGA/SDTA 822^e. X-ray diffraction (XRD) was carried out on the deposits and precipitates obtained using an Equinox 2000 X-ray diffractometer (Inel), which uses a monochromatic CoKα radiation (λ = 1.789 Å), produced at 30 kV and 20 mA, to identify the aluminium species present. The surface morphological characterization of the deposits obtained on the electrodes was carried out using a JEOL scanning electron microscope (SEM) model 6300, equipped with an energy dispersive spectroscope (EDS).

3. Results and discussion

3.1. Electrochemical preparation

In order to identify the appropriate potentials for electrodeposition, cyclic voltammogram (CV) scans were performed during the application of a linear sweep voltage in the range of +1.2 V and −2.5 V. Fig. 1 shows the CV obtained in the anodic direction, which started and ended at the OCP (−0.3 V) at a sweep speed of 15 mV/s. The CV provides evidence of a reduction process C1 that appeared from −0.8 V versus SCE (see an inset), which could be due to both the reduction of an aluminium species and to the evolution of hydrogen. An indication that a species of aluminium was being deposited on the electrode was the appearance of an O1 oxidation peak, probably due to the oxidation of an aluminium species electrochemically reduced in the C1 process. However, the figure does not reveal the adequate voltage polarization where the deposit was located because the C1 process was very wide (between −0.8 V and −2.4 V vs. SCE) and was accompanied by the evolution of hydrogen, which increases to more cathodic potentials. It can be observed that the reduction current towards the cathodic direction was lower, between −1.5 V and −2.3 V, than after the inversion of the potential towards the anodic direction. This behaviour would probably be due to the fall in the ohmic potential through a deposited film of high resistance [24] to more cathodic potentials (above −2.3 V); a greater evolution of hydrogen detaches the deposit film, allowing the electrodeposition continue. Therefore, in order to identify the adequate voltage polarization where the electrodeposition

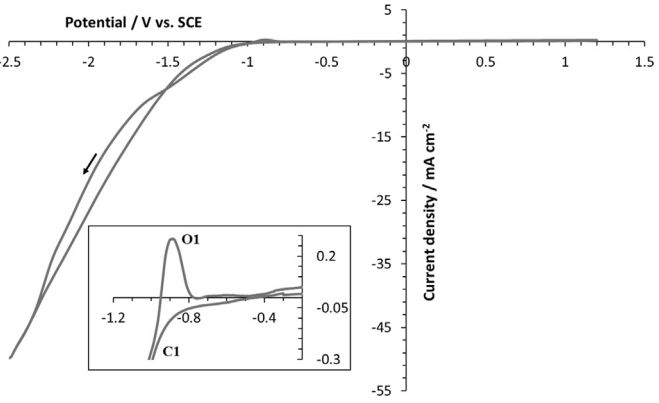

Fig. 1. Cyclic voltammogram obtained on aluminium electrode in solution prepared with scrap aluminium at pH 3.6.