SYNTHESIS AND CHARACTERIZATION OF TRANSITION ALUMINAS FROM RECYCLED SCRAP METAL

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ABSTRACT

This study was initiated in order to develop an alternative methodology for the synthesis of transition aluminas that could potentially be used as binder of monolithic refractories. The objective was established with the purpose to reduce ecological costs by using recycled metal scrap as raw material.

The synthesis technique employed yield a precursor comprised 55.4% of bayerite, 41.2% of boehmite and ammonium salt, according the characterization performed with X-ray diffraction and quantification by the Rietveld method. SEM evaluations showed the presence of agglomerates of particles between 50 and 300 μm. Bimodal grain sizes distribution was detected during laser granulometric test. Thermogravimetric analysis of the precursor indicated 40.6% total weight loss at 1000°C. The heat treatments at 350°C and 750°C of precipitates for 1, 2 and 4 hours, produced various transition aluminas (γ, η, θ), which might have potential use as binder in monolithic products, catalyst support or additive for puzzolanic materials, among others.

1. INTRODUCTION

The development of binding agents for monolithic refractories has always been an interesting challenge, among the most important topics for the new technologies of materials. A lot of work has been done because the binder is a relevant constituent for castables since it provides strength at green stage and at higher temperatures. Binding systems used in monolithic refractories started in the mid 1920's with the use of conventional cement bonded castables – a hydraulic mode of setting. Since then, several kinds of binders have been developed through the years with various mode of binding including: chemical binders, polymerization agents, materials with hydraulic plus coagulating setting, coagulating binders, carbon-bonded and nano-engineered binders, among others. Numerous papers and publications report the evolution and performance of several binding systems in monolithic ceramics[1-8].

For many years calcium aluminate cement (CAC) has been the most popular binder in the refractory castables. Nevertheless, the presence of associated CaO is detrimental because it forms gehlenite (C_2AS) and anorthite (CAS_2) which are low-melting phases and, also, reduces hot strength. Consequently, enhancement of the hot properties was an important target in castables technology and this was the motivation to prepare new materials with reduced CAC content, and later for the development of cement-free compositions[1-2]. Zero-cement castables comprises binders such as monoaluminum phosphate, sodium polyphosphates, sodium silicate, resins, hydratable alumina, silica sols, alumina sols, etc. Each of these binding systems has their own disadvantages and drawbacks. Over the last decade, a new generation of binders that are prepared through wet-chemistry route, have opened a new horizon for refractory technologists. Indeed, colloidal alumina and colloidal silica has received some attention in which is called "nanostructured" castables. Furthermore, nowadays, mullite and spinel sols have been reported as binding agents[3,4,6,7,8].Therefore, the actual tendency for binding systems in monolithic ceramics is the use of micro- and nano-binders which would allow a better control of the microstructure and final properties of the material.

On the other hand, there is an important drawback related to materials synthesized by wet-chemistry: they are usually obtained from analytical reagents and, consequently, they cost more than conventional materials which are obtained from natural compositions. Therefore, using recycled metal scrap to obtain a synthetic precursor will represent a milestone for the preparation of these kinds of materials. Nowadays, natural raw materials are recognized as valuable and limited resources that should be preserved. In this regard, recycling and reusing are considered as responsible steps for future developments in material science, in agreement with the refractory research roadmap till 2025[9], where the fields of “additives and binders” and “alternative material sources” are considered major research fields. Hence, both concepts could be conjugated to achieve eco-materials for a sustainable development.

In this context, the present study began with the purpose to generate a non-conventional procedure for the synthesis of transition aluminas from aluminum scrap that could potentially be used as binding system for monolithic refractories. Here preliminary work conducted as part of the research lines of The Research Group of Ceramic Materials at Universidad Simon Bolivar (UGEMACER-USB) is presented.

2. EXPERIMENTAL PROCEDURE

The experimental procedure included four steps: (1) synthesis of the precursor through precipitation in aqueous media at low temperature, (2) characterization of the precursor, (3) thermal treatment of the precursor in order to achieve transition aluminas and, finally, (4) characterization of the resulting products. Details of the experimental procedure and techniques used are shown in Fig. 1.

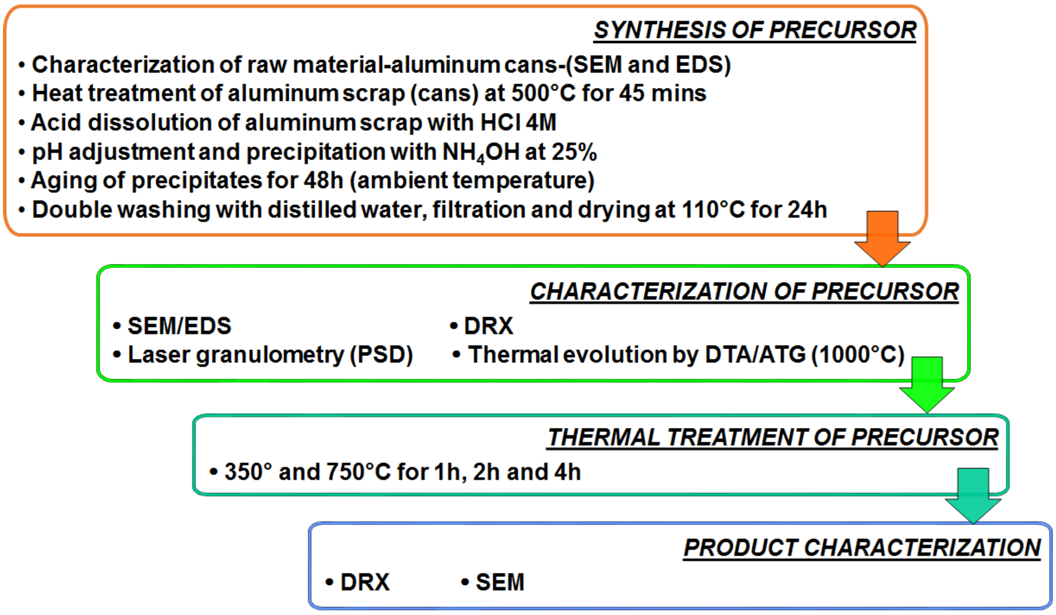

Fig. 1 Flowchart of experimental procedure

3. RESULTS AND DISCUSSION

Chemical composition analysis of raw material (aluminum cans), and the precursor (precipitated material), were performed by SEM/EDS and the results are shown in Table 1. Results were as expected in both materials. Chlorine (Cl) was detected in precipitated precursor due to acid media dissolution with HCl, and the presence of some reaction products as the following equation (1):

$$2Al_{(s)} + 6HCl_{(aq)} \rightarrow 2AlCl_{3(aq)} + 3H_{2(g)} \tag{1}$$

It is relevant to quote that precursor did not show any metallic element (like Fe or Mn) indicating that controlled precipitation process could allow the synthesis of materials free of contaminants.

Table 1. Chemical composition by SEM/EDS of aluminum scrap and precipitated precursor

Element (wt%)	RAW MATERIAL	PRECURSOR
Mg	2.33	-
Al	96.24	87.76
Mn	0.87	-
Fe	0.57	-
Cl	-	12.24

Results of characterization of precursor by XRD, particle size distribution (PSD) and morphological assessment with SEM are presented in Figs. 2, 3 and 4. Boehmite (γ-AlOOH) and bayerite (α-$Al(OH)_3$) were detected by X-ray diffraction. Both compounds are precursors phases of transition aluminas according to the sequences of phase transformations toward the stable α–phase reported by the literature[10].

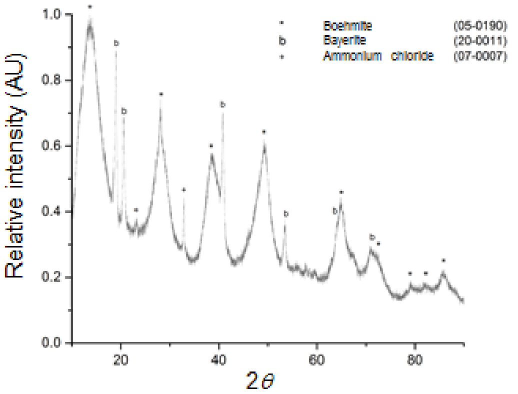

Fig. 2. XRD of precipitated precursor

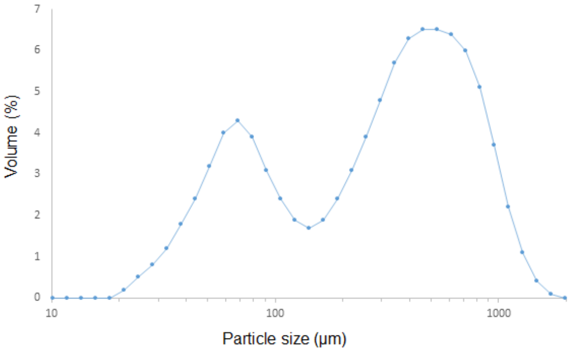

Fig. 3. PSD analysis of precursor

Percentages of detected phases were estimated with Rietveld technique and Pseudo-Voigt adjustment. The composition of the precipitated precursor was 55.4% of bayerite, 41.2% of boehmite and 3.4% of ammonium salt. Particle size distribution of precursor, shown in Fig. 3, indicates a bimodal distribution with two distinctive particle sizes, 68 y 500 µm, respectively. Scanning electron microscopy evaluation revealed agglomerates with particle size ranging from 50 to 300 µm which confirmed PSD performed with laser granulometer. Also, particles with sizes around 1 µm were observed.

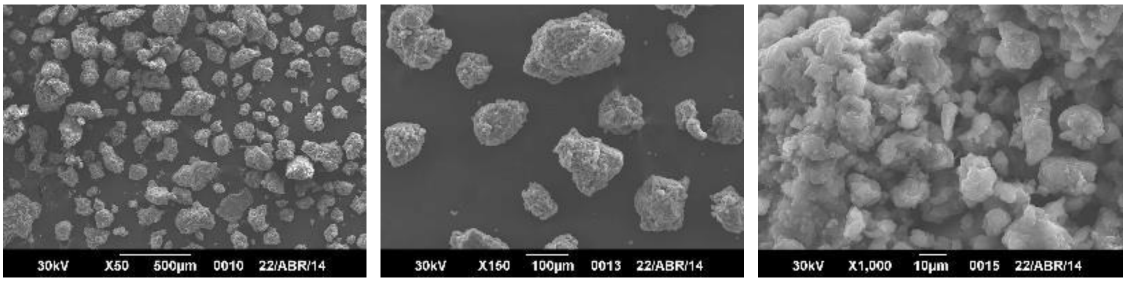

Fig. 4. SEM morphological evaluation of precursor

Thermal evolution of the precursor was studied through typical DTA/TGA methodologies and the results are presented in Fig. 5. The dehydration appears to start at 106°C indicated by the endotherm peak and continues till 145°C, probably because the small capillarity of the gelatinous precursor that slow down the water loss through the material. This step accounts for 8% of the mass loss. Sharp exothermic peak appears at 225°C which represents energy release during phase transformation from bayerite to η–alumina. Another step occurs between two endothermic peaks at 260° and 360°C, which may be attributed to two events: elimination of residual hydroxyls and ammonium chloride decomposition. The exotherm that appears at 490°C, corresponds to the transformation of boehmite into γ–alumina. Thermal evolution happenings between 190° and 750°C, approximately, account for 30% of mass loss.

Discrepancies between DTA and DTG curves may indicate that the change in enthalpy is not directly proportional to the rate of mass loss, which is, normally, encountered in complex reactions. However, in the present study, all the events observed during thermal evolution analysis were confirmed with the X-ray diffractograms at various temperatures of the precursor (see Fig. 6).

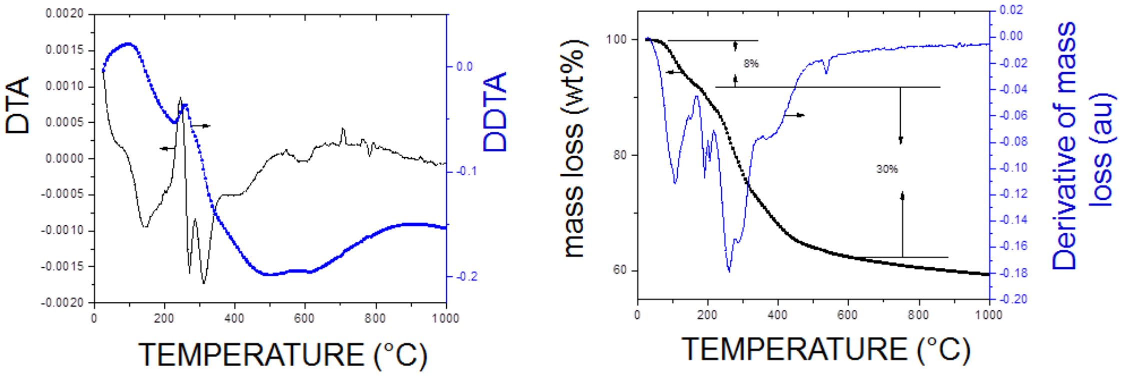

Fig. 5. Thermal evolution of precursor by DTA/TGA

Since transition aluminas could be prepared by calcining aluminum hydroxides, thermal treatment of the precursor was conducted at 350° and 750° at a rate of 10°C/min for 1h, 2h and 4h. The product obtained was characterized by XRD (see Fig. 7) and morphological studies by SEM (see Figs. 8-9).

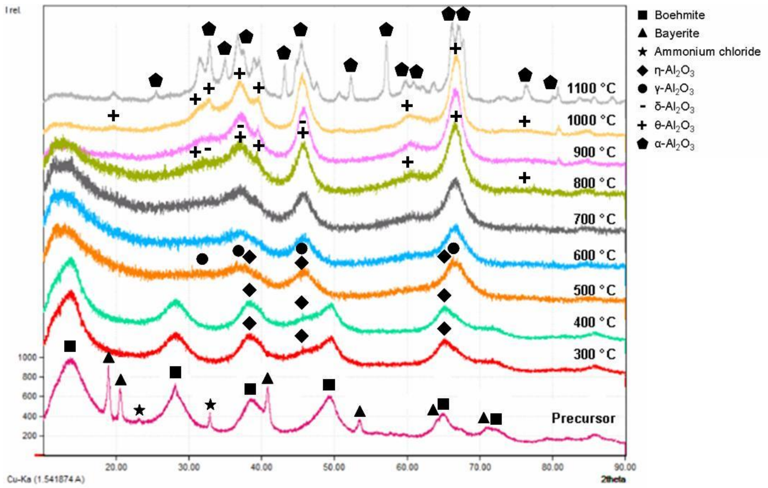

Fig.6. X-ray diffractograms of thermal evolution of the precursor

This later evaluation was conducted in order to detect possible hydraulic activity of the transition aluminas obtained. Thus, heat-treated samples of synthesized product (at 350° and 750°C) were subjected to hydration with distilled water for 168h. Then, the samples were washed with ethanol and prepared with gold for the observation in SEM model FEi Inspect F50. Figs. 8 to 10 display the results of this study.

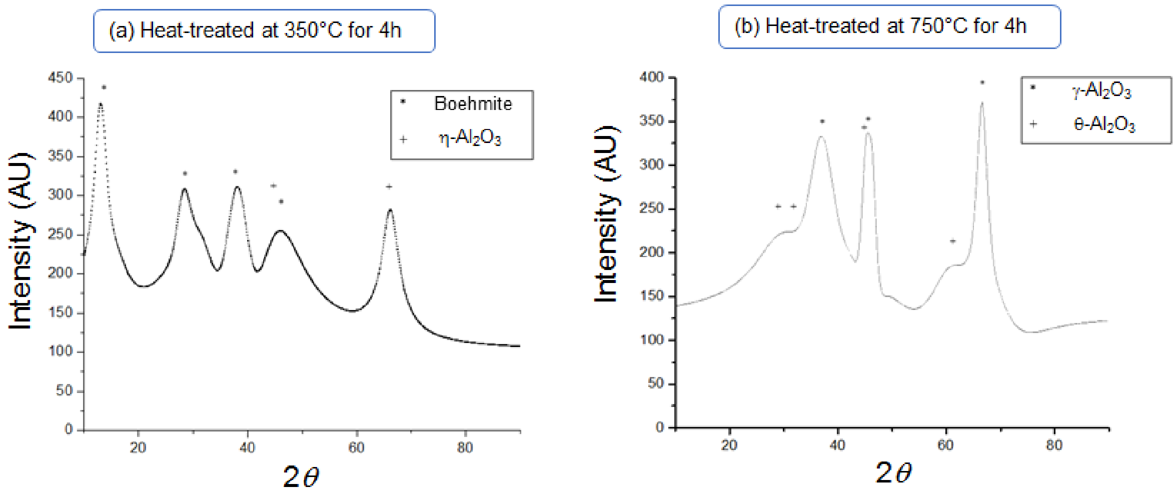

Fig. 7 X-ray diffractograms of synthesized transition aluminas

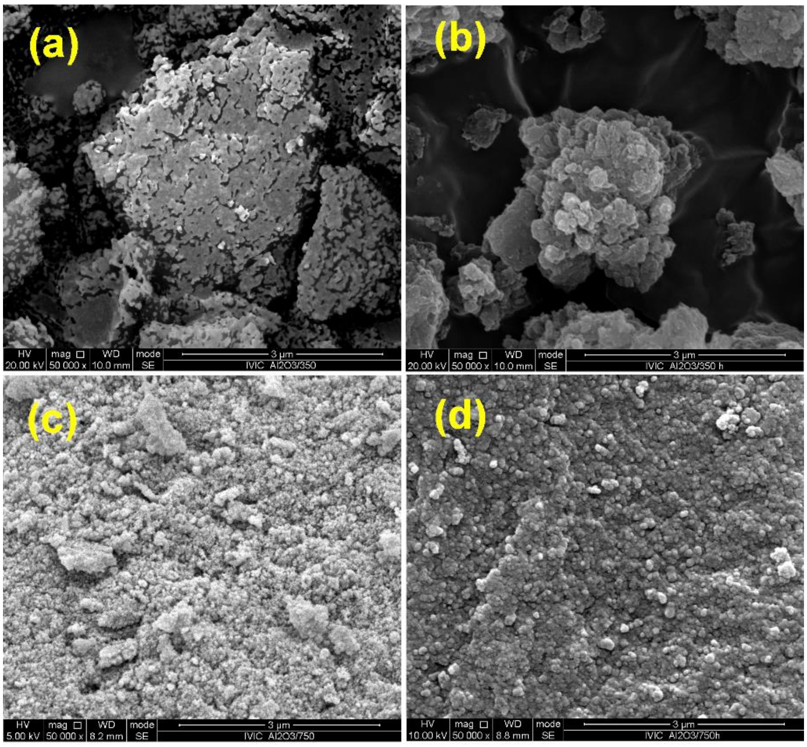

Fig. 8. Photomicrographs of transition aluminas at different conditions: (a) heat-treated at 350°C without hydration; (b). heat-treated at 350°C and hydrated for 168h; (c) heat-treated at 750°C without hydration; (d). heat-treated at 750°C and hydrated for 168h

Comparison of morphological features between Fig 8 (a) and (b) (heat-treated samples at 350°C) reveals morphological changes of the transition aluminas after hydration. This could be an indication of potential hydraulic activity due to the formation of new phases. In contrast, comparison of heat-treated samples at 750°C (8(c) and (d)), did not show any relevant difference in morphological features, thus, apparently this material do not present any hydraulic activity, at least under this conditions.

In Fig. 9, nanometric particles (<100 nm) were observed in the synthesized transition aluminas heat-treated at 350°C. This shows that the synthesis technique could yield micro- and nanometric alumina particles with potential conditions to be used in the binding systems of monolithic refractories. However, some parameters needs to be adjusted in future studies in order to improve the results of this preliminary work.

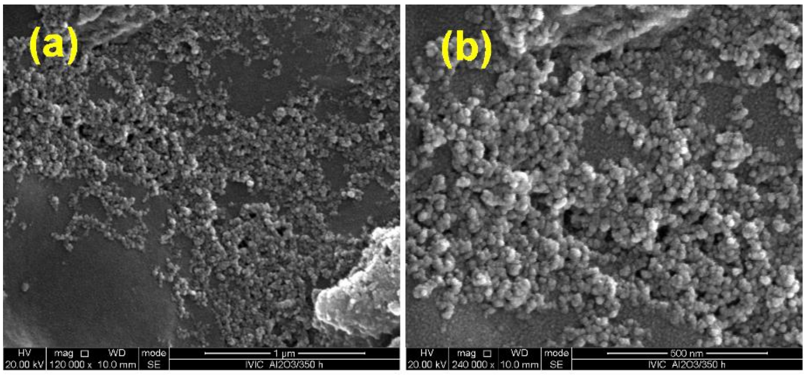

Fig. 9. Photomicrographs of transition aluminas heat-treated at 350°C and hydrated for 168h: (a) 120.000X and (b) 240.000X.

4. CONCLUSIONS

It is possible to synthesized transition aluminas (γ, η, θ) from aluminum scrap by using controlled conditions of a wet-chemical route. These materials could be potential candidates in the near future for binding systems in monolithic refractories. Further studies will be conducted to adjust variables in the methodology.

Agradecimiento: Trabajo enmarcado en la red HOREF (312RT0453) de CYTED

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