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DILATOMETRY AS A TOOL TO STUDY A NEW SYNTHESIS FOR CALCIUM HEXALUMINATE

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Abstract

By using a wet chemical route, pure calcium hexaluminate (CA_6) was yielded, significantly lowering the reaction temperature and shortening the synthesis time if compared to usual industrial procedures.

However, dilatometric studies performed on compacts made of the as-prepared powder, just after pre-heating at 450°C, has shown a superposition between sintering shrinkage and expansion related to CA_2 formation, an intermediate phase formed during calcination and phase evolution to CA_6.

Coupling of such opposite phenomena led to microcracking of the material, mainly if the heating rates (10°C min^{-1}) were high. However, lower heating rates (1–5°C min^{-1}) could quite avoid microcracking but also limit densification.

Keywords: calcium hexaluminate, dilatometry, sintering, sol-gel synthesis

Introduction

Calcium hexaluminate ($CaO{\cdot}6Al_2O_3$) is a promising refractory material in iron and steel industries, due to its stability in reducing atmospheres, its low solubility in iron melts and its improved thermal shock behaviour respect to alumina [1].

Studies [2–4] concerning such applications of CA_6 mention a reaction sintering preparation method, starting from alumina and calcium carbonate powders, as the more common preparation route.

However, reaction sintering temperatures are necessarily high (>1450°C) and dwelling times are long (up to 12 h) so that this way is rather expensive, also considering the commercial applications of such material.

On the other hand, all the parameters (chemical composition, particle size distribution, forming procedure…) are not always well controlled and the quality of the final product may suffer.

Finally, the process is complex due to the appearance of many intermediate reaction steps. In fact, during such a synthesis, calcium carbonate firstly decomposes into calcium oxide at about 890°C which in turn reacts with alumina to form first

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$CaO{\cdot}Al_2O_3$ (CA) in the temperature range 990–1090°C. Then $CaO{\cdot}2Al_2O_3$ (CA_2) is yielded between 1170–1230°C, accompanied by a linear expansion of about 1% [5], and finally $CaO{\cdot}6Al_2O_3$ (CA_6) at 1460–1560°C.

This paper deals with a new sol gel route for the synthesis of pure calcium hexaluminate, starting from calcium hydroxide and aluminium chloride hexahydrate, in order to overcome the above-mentioned drawbacks of the reaction-sintering method.

Materials and methods

Powders were prepared by precipitation of aluminium hydroxide, starting from an aqueous solution of $Ca(OH)_2$ (1 mol L^{-1}, Riedel-de Haën, extra pure) by adding a solution of $AlCl_3{\cdot}6H_2O$ (0.5 mol L^{-1}, Fluka, ≥99%) as a Ca source.

Two syntheses were performed with different starting precipitation pH. Synthesis A was carried out by adding the basic solution the aluminium chloride aqueous one, which was strongly acid thanks to the hydrolysis of the salt. Once the two solutions were mixed, the pH reached a value of about 2.6, which was then adjusted to 9.0, by means of a solution of NH_4OH (4 M). On the contrary, synthesis B was performed by adding $AlCl_3$ aqueous solution to the ammonium and calcium hydroxide one, at a pH of about 12.4. At the end of the mixing, pH went down to about 8.8 and was then corrected to 9.0, by limited NH_4OH (4 M) additions. These two procedures were investigated for obtaining different transition alumina types and consequently possible differences in reactivity and synthesis steps could be expected.

Precipitates were then dried overnight in oven without any preliminary washing for avoiding calcium ions depletion and calcined at various temperatures. After drying, powders were ball milled in a planetary mill, for half an hour in an agate jar with agate balls.

Specific surface area measurements were performed by BET analysis (Carlo Erba Sorptomatic 1800 series) whereas the different intermediate products and synthesis steps were put in evidence by coupling simultaneous DTA-TG (Netzsch STA 409) on samples dried at 105°C and X-ray diffraction analyses (XRD, Philips 1710 diffractometer). The agglomerate size was determined by laser granulometry (Malvern particle sizer 3600D type), after 10 min ultrasonification in an ultrasonic bath, to break soft agglomerates.

Dimensional changes related to the above synthesis steps and to densification were investigated by dilatometry performed on bars uniaxially pressed at 200 MPa (Netzsch 402 E absolute dilatometer with a pushing rod in alumina), obtained by compacting powders pre-treated at 450°C for 1 h.

Results and discussion

Synthesis A yielded a gelly-like product, whereas route B gave a suspension of a very fine precipitate.

After drying at 105°C in oven, the only crystalline phases detected by XRD were boehmite (AlOOH) in the product A and bayerite ($Al(OH)_3$) in B; both precipitates were obviously polluted by NH_4Cl. This result was expected, being well known in literature that different aluminium hydroxides can be obtained as a function of precipitation pH [6].

Both powders presented a mean particle size of their agglomerates of about 4 μm. After calcination at 450°C for 30 min, for removal of volatile by-products, the agglomerate size grew to 6.2 and 4.6 μm, for product A and B, respectively, whereas high specific surface areas were still present (273 $m^2 g^{-1}$ for powder A and 204 $m^2 g^{-1}$ for the B one).

TG-DTA measurements, on about 50 mg of each powder in a platinum crucible, were recorded at 10°C min^{-1} and are reported in Figs 1a and b.

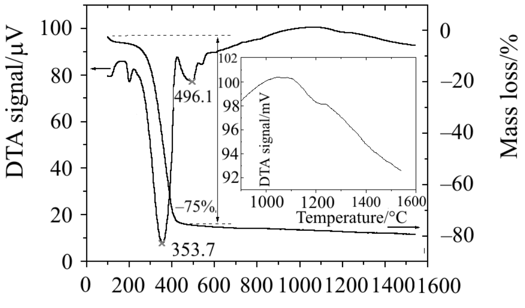

Fig. 1a Dynamic DTA at 10°C min^{-1} on powder A

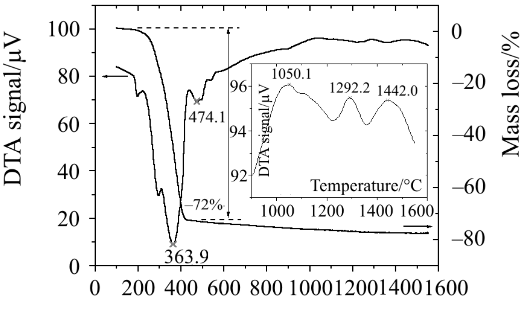

Fig. 1b Dynamic DTA at 10°C min^{-1} on powder B

The two curves differed in the low temperature range (from ambient to 350°C) due to decomposition of the different aluminium hydroxides yielded: A large endothermic peak at about 360°C is present in both curves associated to NH_4Cl decomposition and loss of OH^- groups from transition aluminas. A last endothermic peak between 470–500°C was attributed to γ-Al_2O_3 crystallisation from boehmite, which also appeared in powder A, after decomposition of bayerite, according to literature [7].

In the case of powder A, any DTA signal was recorded in the medium-high temperature range, whereas powder B showed two weak exothermic peaks at 1024 and 1278°C which have been imputed to the appearance of CA_2 and CA_6, respectively, as confirmed on the ground of XRD data and literature [5]. Finally an exothermic signal at about 1400°C was associated to α-alumina crystallisation. Also in powder A crystallisation of CA_2 and CA_6 was clearly detected by XRD, respectively starting from 1050 and 1200°C, but any thermal effect associated to it was observed on the DTA-TG curve.

Therefore, in both cases, probably thanks to the higher reactivity of such powders, both CA_2 and CA_6 were yielded at temperatures about 150–200°C lower than those reported in the case of reaction sintering between α-alumina and calcium carbonate [5].

On the contrary, the temperature at which residual transition aluminas converted into α-alumina were quite higher than the expected ones, due to the presence of calcium ions, which are well-known stabilizers of transition aluminas [8].

Dilatometric curves were recorded at different heating rates: 1, 2, 5, 10 and 20°C min^{-1} and significant differences were observed as a function of the synthesis route and of the heating rate (Figs 2a and b). In the case of powder B, dilatometric analyses put clearly in evidence the superposition between two opposite phenomena,

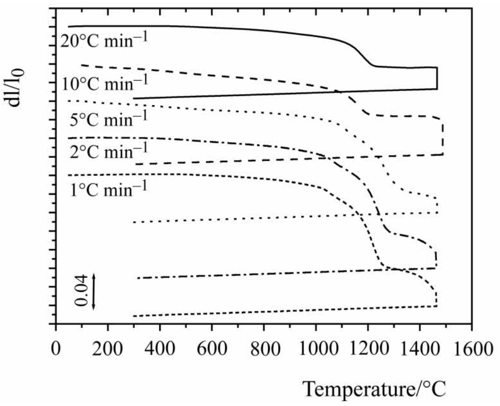

Fig. 2a Dilatometric curves at various heating rates, isothermal for 4 h at 1500°C, on uniaxially pressed bars from powder A

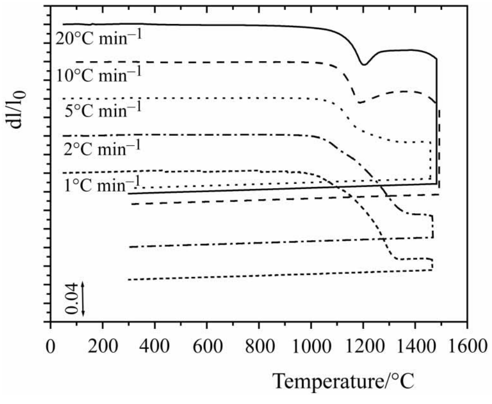

Fig. 2b Dilatometric curves at various heating rates, isothermal for 4 h at 1500°C, on uniaxially pressed bars from powder B

a shrinkage associated to sintering starting from 1100°C, and an expansion due to CA_2 appearance below 1200°C (Fig. 2b, 10 and 20°C min^{-1}). The latter effect became more and more important with increasing the heating rate and led to a diffuse microcracking of the sintered bars. Lowering the heating rates, a balance between expansion and contraction effects could be progressively reached and crack formation was quite completely avoided; however, densification was also delayed and the higher residual porosity probably aided in damping the opposite effects. The calculus of the derivative curve at 10°C min^{-1} showed that at 1160 and up to 1200°C the expansion due to CA_2 crystallisation was predominant over sintering shrinkage. Thus a very slow heating rate of 1°C/3 min, limited to this temperature range (keeping a ramp of 10°C min^{-1} outside this domain), avoided such strong competition between CA_2 expansion and sintering shrinkage, thus leading in a sample free of cracks. In this case, the final shrinkage was equivalent to the sample continuously heated at 10°C min^{-1} up to isothermal step, and reached about 15 linear %.

In the case of powder A, such contrast between opposite phenomena was less evident and never reached the condition in which expansion prevailed on shrinkage (Fig. 2a).

The different behaviour of the two powders could be reasonably imputed to a different reactivity through CA_2 formation, as also strengthened by DTA effects. A faster kinetics of CA_2 formation could be reasonably ascribed to powder B, at which is associated a measurable exothermic peak on DTA curve and a significant expansion compressed in a narrow temperature range in dilatometric curve.

An indirect demonstration of the difference in reactivity between powders A and B comes also from XRD data. Using the procedure set up by Cinibulk [9], from intensities ratios of major peaks of each crystalline products, namely (104) peak of α-Al_2O_3, (11-2) peak of CA_2 and (10-17) peak of CA_6, the percentage of CA_6 yielded in the temperature range from 1350 to 1600°C was evaluated. Also in this case the higher reactivity of powder B was confirmed (about 90 mol% of the powder was converted in CA_6 at 1600°C, without soaking time), since such samples always contained higher amounts of CA_6 than the A ones. Being CA_2 an obligatory, intermediate product through CA_6 formation [2–4], it could be reasonable to suppose that the higher amount of yielded CA_6 in sample B must be related to higher amount of available CA_2, and therefore to a faster kinetics of its formation.

In both cases the microstructure of the final product (after sintering at 1600°C for 60 min and thermal etching at 1500°C for 12 min) was made of quite homogeneous grains, many of them regular in shape and submicronic (Fig. 3); also the

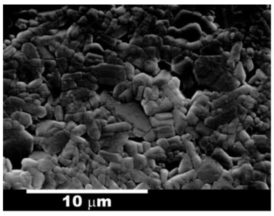

Fig. 3 SEM image of a powder B pellet sintered at 1600°C for 1 h

amount of residual porosity was limited. In general, such samples presented a more homogeneous microstructure than that obtained by reaction sintering, after 5 h at 1750°C [2].

As a consequence, it was necessary to increase the final sintering temperature to obtain an almost fully dense CA_6, therefore loosing the main advantage related to the chemical wet synthesis.

Conclusions

In this paper calcium hexaluminate was synthetized by a chemical wet route and compared to the product of a conventional reaction sintering between α-alumina and calcium carbonate.

Two syntheses having a different starting pH of aluminium hydroxides precipitation were proposed and this led to different α-Al_2O_3 precursors, which in turn gave a different reactivity and kinetics of CA_2 and CA_6 formation, even if synthesis steps were similar. However, CA_2 and CA_6 temperatures of formation were about 150–200°C lower respect to traditional synthesis and contrarily to conventional reaction-sintering route, CA formation was, in our case, avoided.

The proposed synthesis could be strongly improved by substituting aluminium chloride hexahydrate with an industrial γ-Al_2O_3, avoiding NH_4Cl elimination steps. Even if, B route, leading to a fine particle suspension, could be easier to handle in view of an industrial production.

A compromise between the above described opposite mechanisms (CA_2 appearance and sintering) has to be found, especially for B route, and dilatometry was a very useful tool to determine the limited critical range where heating temperature has to be reduced, without limiting final sintering shrinkage, as for very slow continuous heating ramps up to isothermal stage.

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