Phenomenology of corundum crystal formation in supercritical water fluid

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Abstract

This paper describes a solid phase transformation of aluminium hydroxide into oxyhydroxide (boehmite), and then into well formed fine crystals of corundum (α-Al_2O_3) in the medium of a supercritical water fluid at a temperature of $450\,°C$ and a pressure of 30 MPa. Using electron microscopy the development and processing of corundum crystal formation from incipient crystals to crystal growth and their perfecting is traced.

1. Introduction

The thermovaporous method of processing of hydroxides or amorphous oxides has been used to fabricate many substances, such as quartz, corundum, of aluminates, etc. For example, the scientific bases of synthesis methods of quartz and corundum have been reported elsewhere [1–5].

The present paper describes a solid-phase transformation of aluminium hydroxide into oxyhydroxide (boehmite) and then into the well-formed fine crystals of corundum (α-Al_2O_3). The formation of corundum proceeds in supercritical water fluid at temperatures of more than $380\,°C$. If the temperature is less than $380\,°C$, the process rate sharply drops and practically becomes negligible at $370\,°C$. The size and habitus of corundum crystals produced in this way depend on the parameters of the process. The advantage of this technology is the possibility of varying size and habitus of crystals. The corundum crystals can be obtained in an interval from 0.1 up to 400 μm by size. Other methods to produce the corundum crystals (for example, the air calcinations of aluminium hydroxides or oxides at temperatures above $1200\,°C$), do not allow control of their properties. It was found that structure transformations under thermovaporous conditions run with surprisingly low activation energy as compared with the high temperature recrystallization and crystallization processes in air environment. It is obvious that during the production of fine crystalline materials

one has to solve the problem of their properties: crystal size (in the range from tens of nanometres to hundreds of microns), morphology (isometric, lamellar, prismatic etc), chemical composition, aggregation degree and so on. To resolve these problems one needs to have knowledge of the peculiarities of oxide transformation from amorphous or crystalline oxides or hydroxides in other modifications. For example, the structure transformation of inorganic polymer amorphous silica goes through a number of stages: 1—coalescence of globules; 2—flocculation and formation of non-porous glass-like structure; 3—cristobalitization; 4—quartz nucleation and growth of crystalline quartz.

Changing the thermovaporous treatment regime and the use of micro-additives allows us to obtain fine crystalline powders with the desired properties.

However, there are not too many compounds in inorganic chemistry that have a internal polymer (net-like) organization and globule structure. Many important oxides and hydroxides are in crystalline form. For example, silicon usually does not form crystalline hydroxides, while aluminium and zirconium under various conditions form gels or crystalline hydroxides. And it is expected that in conditions of thermovaporous treatment another way of structure evolution of the latter substances is possible.

In this work a structural transformation of aluminium hydroxide (hydrargillite) under thermovaporous treatment has been studied. In these conditions the aluminium hydroxide passes into corundum, the thermodynamically stable phase, through intermediate—boehmite. Aluminium similarly to silicon can form more or less stable transition compounds or phases. The structure of boehmite and its formation have been investigated in detail [6–8]. However, there is little information on its transformation into the more stable phase, corundum, under thermovaporous conditions.

2. Experimental details

In this work we used commercial hydrargillite powder 'GD-00' (Pikalevo's PO 'Glinozem'). The precursor and prepared powders were characterized by XRD (diffractometer 'DRON-3M'), DTA (Derivatograph Q-1500 D), scanning electron microphotography (SEM) ('SCAN-48') and by specific surface measurements ('Gasometer GCh-1').

The laboratory autoclaves with a reaction volume of 0.015–5 l were used to carry out the thermovaporous treatment of the samples at a temperature of 450 °C and pressure of ∼10 MPa.

The starting material (hydrargillite powder) was put into stainless containers and placed in the autoclave containing a pre-calculated amount of water. For phase determinations of hydrargillite transformation, the samples of hydrargillite were treated in the autoclaves for 0.5–5 h. After that the samples were washed with distilled water and dried in air at 110 °C. The process temperature was measured directly from the surface of the autoclaves. The heating rate was ∼30 °C min^{-1}. The accuracy of the temperature maintained in the oven was better than 5 °C. As the experiments were performed under isothermal conditions the duration of heat treatments was considered to start after the desired temperature was obtained.

3. Results and discussion

SEMs of precursors are shown in figures 1(*a*)–(*c*). Hydrargillite powder consists of near-spherical aggregates with size 20–150 μm formed from fine 3–5 μm primary crystals (figure 1(*c*)). SEMs of the hydrargillite after the autoclave treatment at 450 °C for 30 min are shown in figure 2. The x-ray diffractograms of the samples indicated that under these conditions boehmite is formed as a single phase.

When heating such boehmite in air at temperatures higher than 500 °C its dehydration took place with the maximum of endothermic effect at 530–550 °C that corresponds to results
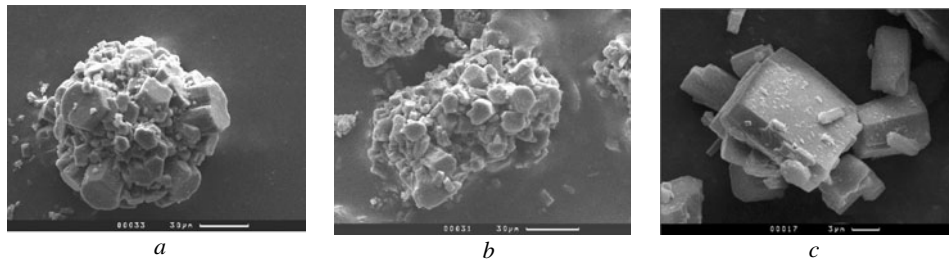
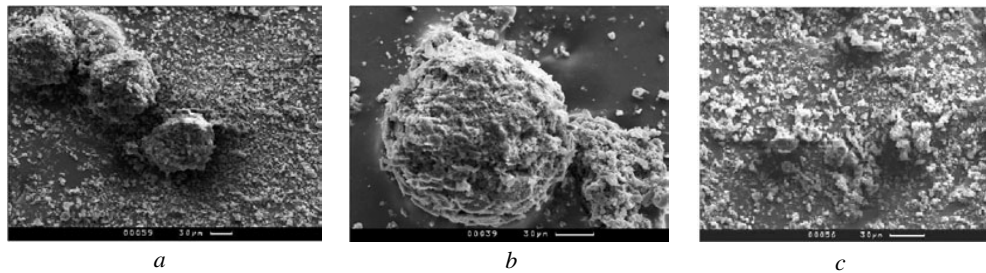**Figure 1.** SEMs of hydrargillite powder 'GD-00'.

Figure 2. Hydrargillite 'GD-00' treated in an autoclave at 450 °C for 30 min.
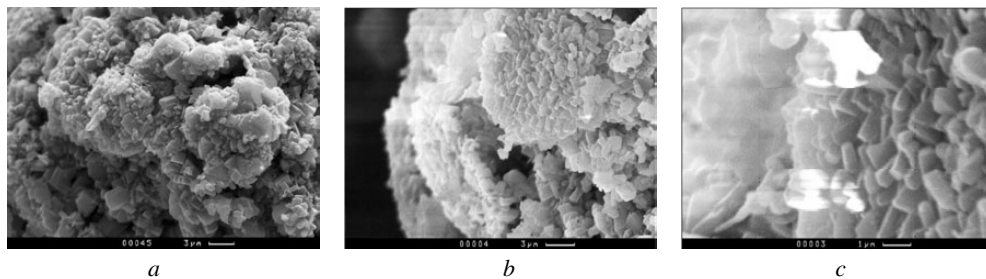

Figure 3. Structure of boehmite spherical aggregates formed from hydrargillite 'GD-00' after 30 min thermovaporous treatment at 450 °C.

presented in [9]. After 30 min treatment the samples consisted of finer spheres than the initial ones and some of them were well destructed (figure 2(c)). Transformation of hydrargillite into boehmite resulted in a noticeable change (by 26%–28%) in grain density. As a result, the spherical aggregates became soft and readily went to fine crystals form. The structure of the spherical aggregates is shown in the figure 3. The SEM showing the completely disordered structure of the aggregates at higher magnification also shows some well-packed boehmite grains.

It is obvious that the spheres of boehmite are inhomogeneous by density. They consist of particles with sizes up to 5–10 μm, which are formed by packed boehmite crystals of size <3 μm (figures 3(a), (b)). In some places the particles of the poorly packed boehmite crystals are seen.

After treatment for 1 h the samples contain a noticeable quantity of α-Al$_2$O$_3$ (corundum) in addition to boehmite. The spheres' size changed very little but they became less aggregated (figures 4(a), (b)). The transformation of boehmite into corundum is accompanied by an increase of 29–32% in density and by an decrease in the grain volume and by a change of grain shape.
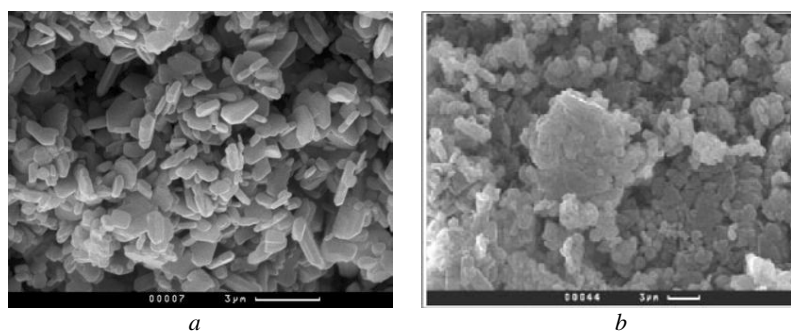
Figure 4. Structure of spheres obtained after 1 h thermovaporous treatment of hydrargillite 'GD-00' at 450 °C.
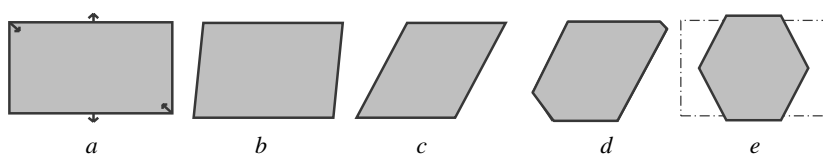

Figure 5. Evolution of the shape of grains during transformation from boehmite (*a*) to corundum (*e*) under thermovaporous conditions at 450 °C: initial orthogonal (*a*) and slightly distorted boehmite crystals; corundum (*c*)–(*e*). The faces (010) of boehmite and (0001) of corundum crystals are shown to coincide with the plane of the drawing.

Concurrent with the internal reorganization of the spheres, the primary orthogonal crystals of boehmite changed and gradually became hexagonal (figure 4). This is typical for corundum crystals [10].

The faces (010) of boehmite and (0001) of corundum crystals are shown to coincide with the plane of the drawing. SEMs at higher magnification show that well-formed boehmite powder consists of orthogonal and slightly distorted orthogonal fine crystals. The distortion can be seen as a progressive deviation from orthogonality of interfacial angles. The profile planes initially arranged at right angles after heating under thermovaporous conditions start rearranging to form two pairs of angles: 120° and 60°. Such angles correspond to trigonal corundum crystals. Usually, as the x-ray data show, the formation of the corundum phase finishes in respective development of near-rhombic crystals. Whereupon the new corundum faces start to form. It does not necessarily result in the complete formation of hexagonal regular polyhedrons. Usually the process substantially slows down with the formation of crystals having such shape as shown in figure 5(*d*). It seems that the complete formation is not necessary, because the formed crystals already have all the essential elements to start packing into the coarser corundum crystals (figure 4(*b*)). Other samples were exposed to treatment under thermovaporous conditions at 450 °C for 2.5 h. In these samples the partial orientation and ordering of fine crystals (mainly the corundum ones) became more noticeable. In this case the rather coarse aggregates consisted of oriented flat particles (figures 6(*a*), (*b*)). Moreover, one can find in the sample the relatively big corundum 'green' (or proto-) crystals (figure 6(*c*)).

Some characteristic features of the process of formation and growth of corundum crystals in autoclaves under thermovaporous conditions at 450 °C can be described as: (*a*) partial or complete disaggregation of hydrargillite spheres; (*b*) the changes of crystal volumes and habitus and, finally, the well-known fluctuations of the density. The fine crystals may find comfortable crystallographic positions and join like a chip into a connector assembly. Under
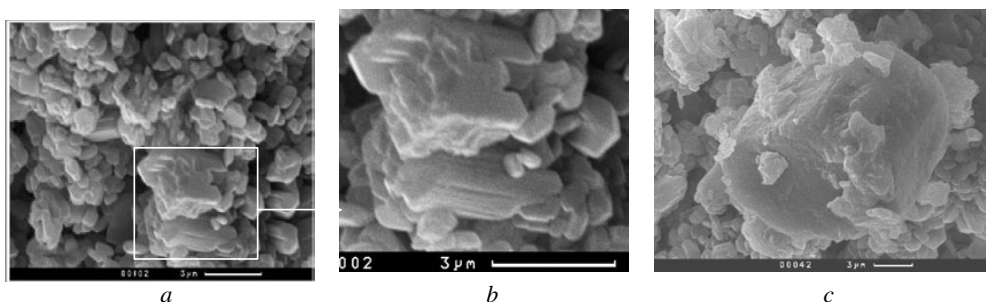
Figure 6. The aggregates formed after 2.5 h thermovaporous treatment of hydrargillite 'GD-00' at 450 °C.
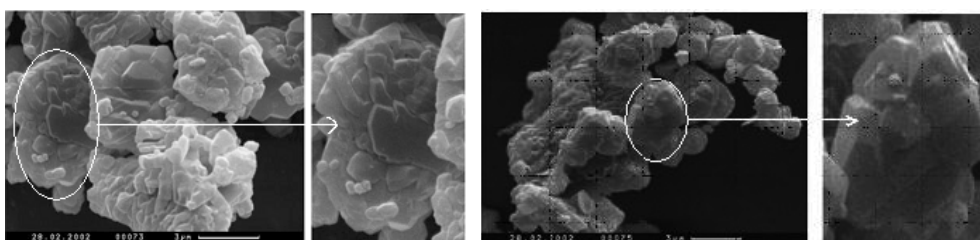
**Figure 7.** Evolution of spherical aggregates into coarse corundum crystals.
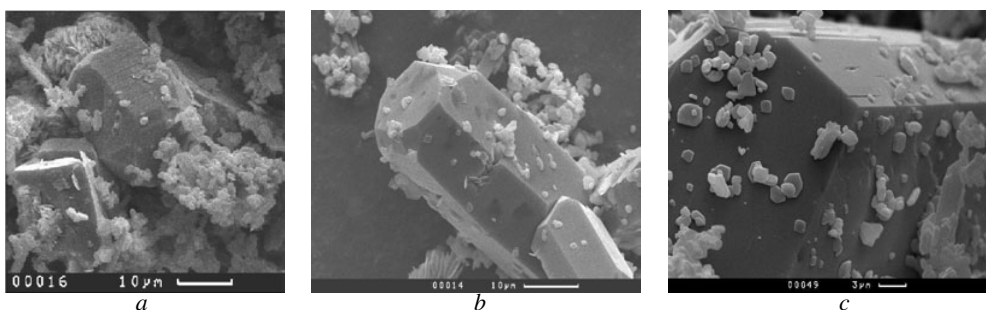
**Figure 8.** Corundum crystals at the end of crystallization.

favourable conditions (pressure, temperature, alkalinity of internal media) and after formation of the primary corundum crystals the further formation of crystals proceeds quickly. It results in the growth of crystals, both the associated and single ones (figures 7 and 8).

Figures 7 and 8 show that the flat particles adhere to the faces of crystals as if they have grown on them. This is typical in the formation of coarse-grained corundum. X-ray data show that if the process of the hydrargillite transformation into corundum is interrupted then the product consists of corundum and very fine boehmite crystals accompanied by an amorphous phase. In the beginning of the process in a volume filled with boehmite the formation of corundum is hindered, but on the faces of corundum crystals it occurs readily.

When boehmite liberates water and loses structure fragments, it becomes amorphous and very active on the faces of the bigger corundum crystals. During further thermovaporous treatment the motion of these fragments or atomic groups finishes the building of the structure of the block corundum crystals (figure 7). Thus a healing their surfaces (figures 8, 9) occurs. As a result, well-formed corundum crystals having smooth faces and straight edges are produced
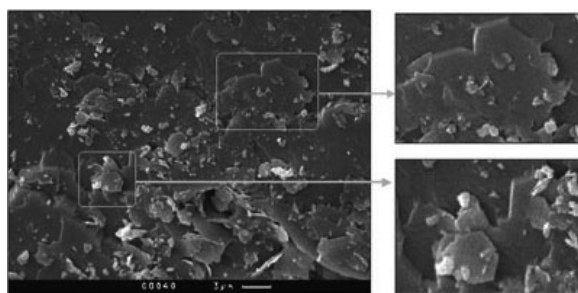
Figure 9. Growth and healing of faces of corundum crystals.
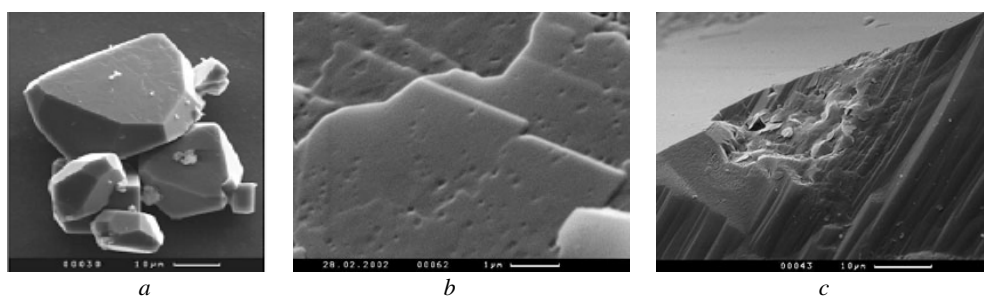
Figure 10. Corundum crystals grown under thermovaporous conditions (*a*)–(*c*), examples of surface defects (*b*), (*c*).

(figure 10(*a*)). In some cases the amorphous phase is so active that it builds into faces faster than diffusion occurs and the outer amorphous layers are not influenced by corundum and they crystallize and adhere to faces independently (figure 8(*c*)).

On the other hand, if crystallization proceeds fast enough, there is a lack of boehmite around the growing crystals for the healing of their faces and they can grow with a rather deep relief (figure 10). The vicinal forms of growth are shown in the figures 10(*b*), (*c*), and they are usual for corundum [10].

After 5 h the thermovaporous treatment of hydrargillite at 450 °C, the growth or formation of corundum crystals is substantially completed and further thermovaporous action usually results in the formation of hard druses or aggregates consisting of perfect corundum single crystals. Recrystallization or growth of big crystals from the finer crystals under thermovaporous conditions occurs at a very low rate.

4. Conclusion

The presented results establish the phenomenology of fine corundum crystal formation from hydrargillite in supercritical water fluid at a temperature of 450 °C and pressure of ∼10 MPa. The crystallization occurs readily and ends within 5 h. Under these conditions hydrargillite forms fine boehmite crystals, which then transform into hexahedral platelets. The formation of the amorphous phase based on boehmite decomposition was observed.

Fine corundum crystals are packed on suitable crystallographic planes, mainly (0001), and form the coarser block corundum crystals. Both the amorphous phase decomposing on the crystal surfaces and the finer corundum crystals thus produce a building of the interblock space and heal the surface defects. This complicated process results the in formation of a fine crystalline perfect corundum.

Acknowledgment

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