ELSEVIER

Thermochimica Acta 290 (1996) 109–114

thermochimica acta

Oscillating processes during thermal decomposition of aluminiumhydroxide chloride gels

P. Brand, C. Günther *, G. Wolf

Fakultät für Chemie und Physik, TU Bergakademie Freiberg Leipziger Str. 29, D-09596 Freiberg, Germany

Received 17 April 1996; accepted 12 June 1996

Abstract

DTA-, DSC-, and DTG-diagrams of aluminiumhydroxide chloride gels show numerous sharp and often rather regular oscillations, caused by endothermal decomposition and exothermal crystallisation subprocesses in the temperature range between 550 and 600°C. In this range the formation of α-Al_2O_3, corundum, is observed. It is assumed, that the oscillations are produced by the periodic formation of dense layers of an intermediate phase, which act as diffusion barriers for the decomposition gas, and the crystallisation of these layers into corundum, connected with a reduction of transportation hindrance of the gas molecules. These processes are considered in their feedback with the decomposition reaction, by which the intermediate phase is formed.

Keywords: Aluminiumhydroxide chloride gels; Thermal oscillations; DTA; DSC; DTG

1. Introduction

Previous publications reported on the spontaneous crystallisation of corundum during thermal decomposition of gels from basic aluminium chlorides (aluminiumhydroxide chlorides) within the range of low temperatures (400 to 600°C) [1]. The preparation of the used gels having gross compositions of $Al_2O_3 \cdot xHCl \cdot yH_2O$ (x: 1 to 2; y: 4 to 7) has been carried out from partially thermally decomposed hexaquoaluminium chloride by dissolving in water to obtain a highly concentrated solution (sol) and the subsequent drying of the sol to a gel at low temperatures. During isothermal decomposition of these gels X-ray amorphous products occur below 400°C, from which α-Al_2O_3 (corundum) crystallises above 400°C. However, the sample cannot be completely transformed into corundum. At 550°C 50% of the precursor are transformed into corundum. At higher temperatures η-Al_2O_3 is formed increasingly. The amount of the formed corundum is strongly dependent on preparation conditions of the starting gel. Furthermore, the fast separation of the decomposition gases water vapour and hydrogen chloride from the solid is a decisive precondition. Electron microscopic investigations showed that the gels and their "amorphous" decomposition products are morphologically heterogeneous. By means of electron diffraction it has been proved that they contain aggregates consisting of fine platelet-like particles, which cause sharp interferences. The evaluation of electron diffraction diagrams lead to two lattices, which are related to those of the diaspore and corundum, resp., [2] and are characterised as struc-

---

* Corresponding author.

PII S0040-6031(96)03045-6

ture I and structure II. A considerable amount of the gel powders with compact particles showed no sharp interferences.

For corundum crystallisation a two-dimensional diffusion-controlled growth is discussed as kinetic model.
The mechanism

$$\begin{tikzcd}
\text{amorphous component} \arrow[r] & \eta\text{-Al}_2\text{O}_3 & \\
\text{structure I} \arrow[r] & \text{structure II} \arrow[u] \arrow[r] & \alpha\text{-Al}_2\text{O}_3
\end{tikzcd}$$

is assumed [3].

In the following sharp, frequently regular thermal oscillations are described, which after DTA- and DSC investigations of the gels first of all have been found casually [4] and could be observed only under certain recording conditions. An approximation for interpreting the phenomena is presented.

Oscillating processes during thermal decomposition reactions of solids are described by only a few authors. Freund et al. [5] report on periodical processes in the dehydroxylation of $Mg(OH)_2$, which are controlled by the crystallisation of a metastable solid decomposition product as intermediate state towards the thermodynamically stable periclase. In the dehydration of gypsum examined by means of thermogravimetry Heide et al. [6] observed oscillations of water removal from single crystals and distinct periodical fluctuations from polycrystalline compacts (36.1–50.5 mg) as TG samples. Strobel [7] presents a quantitative theoretical interpretation of these oscillating reactions. Patil et al. [8] obtained oscillations of the TG and DTA curves during the thermal decomposition of $[Co(NH_3)_6]Br_3$ and $CoBr_2 \cdot 2H_2O$ in the medium temperature range, if narrow and high crucibles are used. By extensive chemical investigations these authors are making efforts to explain the processes involved in the oscillations. As catalytically efficient substance the intermediate product CoOBr is discussed, and an interpretation on the basis of a branching mechanism and of a "population growth model" is undertaken.

2. Experimental

Aluminiumhydroxide chloride gels with an aluminium-/chlorine molar ratio of 1.2 to 1.5 were used as starting substance. The gel formation process by drying was performed at room temperature and below, resp., (0°C or freeze drying). The thermal decomposition of the gels connected with the formation of new phases has been dynamically recorded in a modified thermoanalysis apparatus from Setaram by means of DTA. Controlling investigations were carried out by means of the DSC 111 produced by the same firm.

The high temperature calorimeter (Setaram 1500) has been equipped with a new computer-aided data processing unit. The DTA and temperature signal were submitted via a multiplexer to a digital multimeter M2001 from Keithley, and within 3 s both voltages were measured ten times with an integration time of 20 ms each. The mean values of the voltages were stored immediately after each measuring loop as ASCII data on to the hard disc. Temperature calibration of the Pt-PtRh thermoelements was performed by the determination of the transformation or melting temperatures of K_2CrO_4, Au and Ni. The onset temperatures were determined by the use of the evaluation program Tawin from Linseis.

The temperature-voltage table of the thermoelement has been fitted by the three supporting values, such that the error of the onset temperatures is lower than 1 K. X-ray powder diffraction was used to prove the formation of corundum in the decomposition products of thermoanalysis.

3. Periodical phenomena

Figure 1 shows the diagram of an air-dried gel with a molar Al/Cl ratio of 1.24 (gel 1). Significant endothermal decomposition effects can be observed below 400°C, which are caused by dehydration, HCl formation and dehydroxylation and are connected with a removal of water and hydrogen chloride [3]. Above 550°C dampened oscillations occur as a consequence of endothermal and exothermal subprocesses. This is the temperature range, in which corundum formation takes place. The crystallisation of corundum is proved by diffractograms, which were taken with DTA samples within this temperature interval. The highly significant oscillations, as a rule, start with an endothermal response.

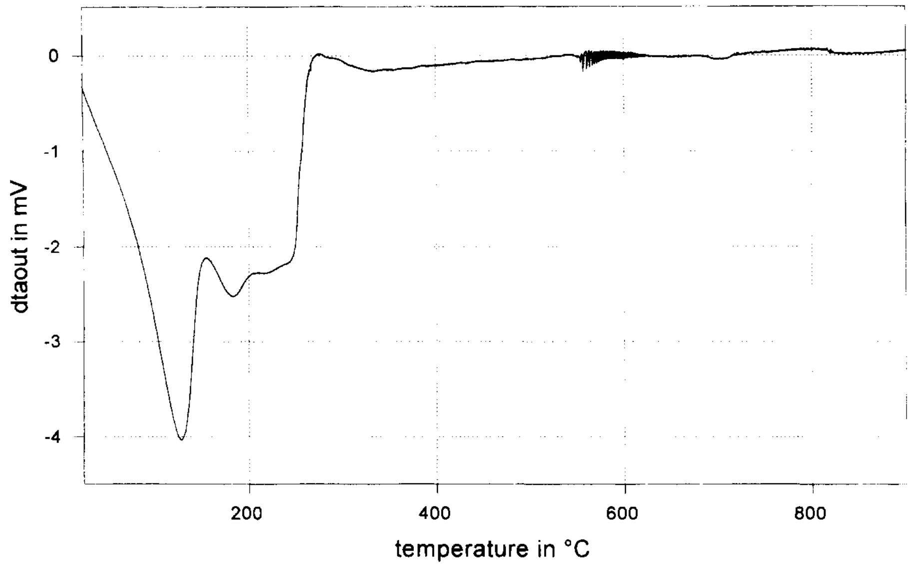

Fig. 1. DTA-curve of gel 1.

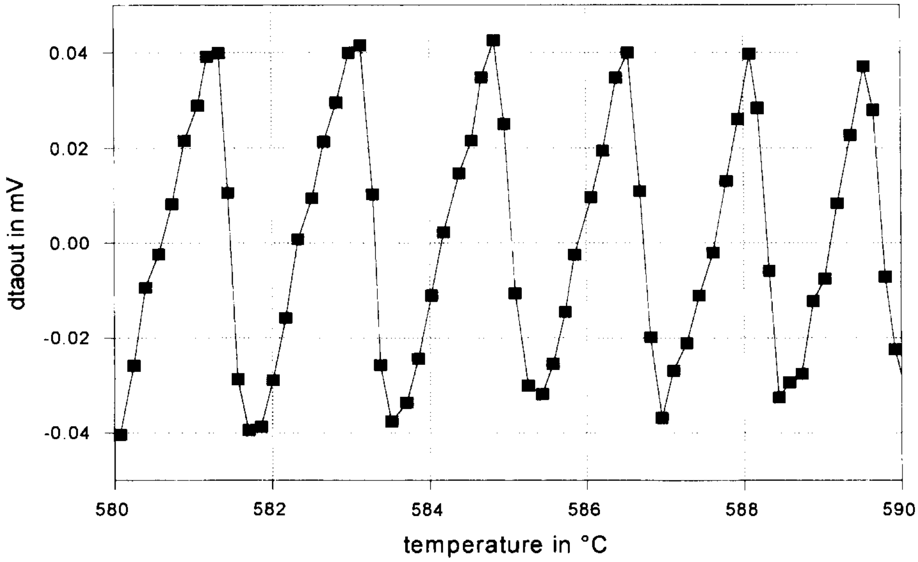

Fig. 2. Detail of DTA-curve with measured points.

At the beginning of oscillations the endothermal (negative) amplitudes are considerably higher than the exothermal ones; with increasing temperature both are matching each other and often the relations change. A magnified section shows this phenomenon much more distinctly (Figs. 1 and 2).

The occurrence of oscillations is strongly influenced by certain experimental conditions in DTA

Table 1
Measuring conditions: DTA and DSC/TG

sample weight:	5-80 mg
preparation:	ground gel powder, weekly compacted
crucible material:	high cylindrical platinum crucible, weight about 230 mg
purge:	air or argon, 1.2 l/h, 0.10 MPa
heating rate:	3 K/min
DTA-sensibility	0.8 mK/μV
reference material:	α-Al_2O_3

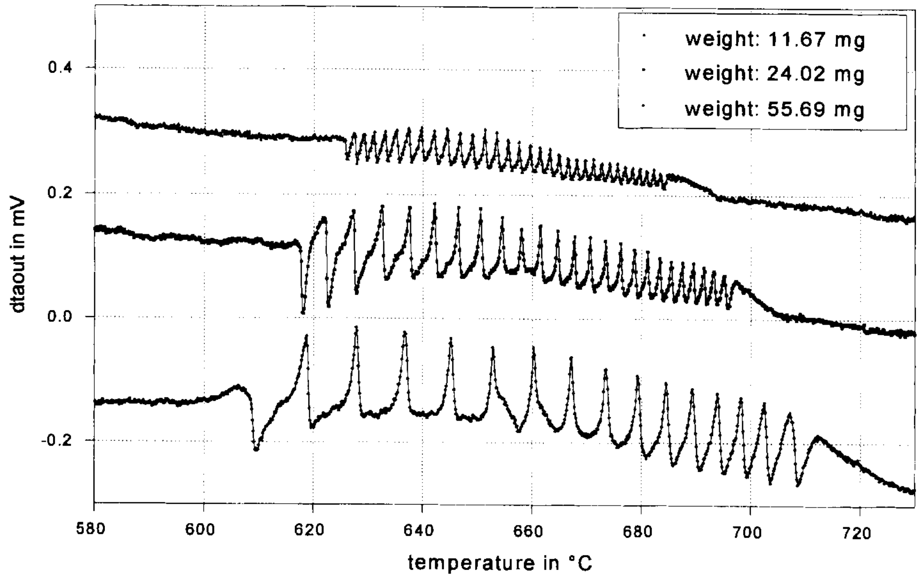

Fig. 3. DTA-oscillations of samples (gel 2) with different weights; The dtaout-scale is only valid for 55.69 mg, the other one's are moved + 0.2 mV or + 0.4 mV, respectively.

(see Table 1). The dependence on sample weight is obviously visible in Fig. 3. Experimental facts can nearly be excluded as cause for the observed oscillations, since in comparable investigations with DSC 111 oscillations are measured, too (Fig. 4).

The periodical effects are also observable as weight steps in the TG in spite of the still low amount of volatile components in the samples. A periodical change being synchronous with the temperature effects is shown by the weight changing rate (Fig. 4).

4. Discussion

Considering the mechanism extensively described above, the following subprocesses could cause the oscillations:

1) Thermal decomposition reaction

$$\text{structure I} \rightarrow \text{structure II} + x \cdot HCl(g) + y \cdot H2O(g)$$

short formula:

$$SI \rightarrow SII + g \qquad (1)$$

This reaction is endothermal. With hindered removal of decomposition gases from the reaction frontier also the reverse reaction must be considered.

$$SII + g \rightarrow SI \qquad (2)$$

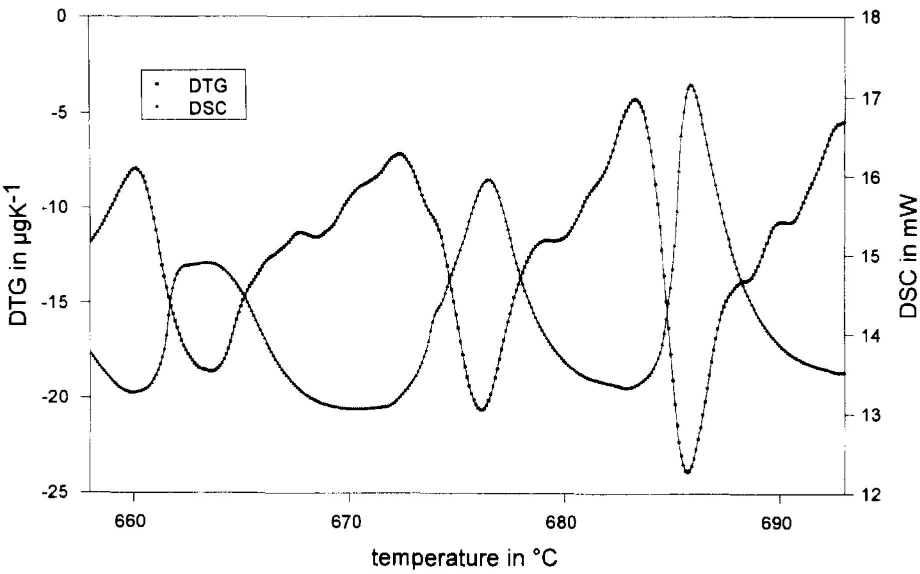

Fig. 4. Simultaneous DSC/DTG-curves of gel 1.

If reaction (1) proceeds from the surface to the internal part of the crystallite, then the solid reaction product (here SII) can form a dense layer around the small crystallites, through which the molecules of decomposition gas must penetrate. This growing transport barrier effects that the relationships at the reaction frontier approximate those of a closed system and the decomposition comes to a standstill.

2) Transport of the gases from the place of reaction Here the diffusion of gas molecules through the product layer is to be considered. The process may be symbolically described by

$$g_{inside} \rightarrow g_{outside} \qquad (3)$$

By reducing the partial pressures in the external atmosphere via an increase of circulation gas rate the difference of chemical potentials can be increased. The transported substance amount per unit cross section and unit time is essentially dependent on porosity of the layer, which is determined by the type and density of defects within the layer.

3) The crystallisation of structure II into thermodynamically stable α-Al_2O_3 modifi-cation (corundum)

$$SII \rightarrow \alpha\text{-}Al_2O_3 \qquad (4)$$

The activation energy of nucleation of corundum is relatively low due to the structural relationship with SII in comparison with its crystallisation from transition aluminium oxides. Corundum formation is exothermal. Corundum is the aluminium oxide of highest density (about 4 g/cm^3). Its formation by crystallisation from the reaction product of the subreaction (1), SII, is connected with an essential reduction of solid particle volume. This leads to the occurrence of pores and microcracks in the product layer, formed by reaction (1), after its transformation into α-Al_2O_3, whereby the gas permeability of the layer is essentially improved. An analogous step in the thermal decomposition of very fine-crystalline $Mg(OH)_2$ into MgO is considered by Freund et al. [5] as an essential process for periodical changes of gas formation rate during hydroxide heating. Crystallisation of stable periclase MgO from a formed metastable intermediate product only occurs, if the formed crust out of this intermediate product reaches a critical thickness. Similarly, the process of corundum crystallisation (3) only starts, if a certain amount of SII by (1) is formed. A critical reaction period of (1) and a critical layer thickness of the formed SII is the prerequisite for the onset of crystallisation (4). With the development of a permeable corundum layer diffusion (2) and decomposition reaction (1) starts again. These processes repeat periodically. The curve responses visible in Fig. 4 favour this constellation: maxima of the exothermal heat flux coincide with the minima of mass changing rate.

The discussion is related to the periodical course of reaction in a crystallite of SI at temperature increase. According to electron optical investigations these crystallites have the shape of platelets, some 10 nm in thickness and with lateral dimensions between 100 nm and 10 μm, frequently bent or buckled. The observed oscillations are the result of the almost synchronous progress of the described processes in many of the crystallites within an investigated sample. Synchronisation is reached by a very equal temperature distribution within the sample and by similar interaction ratios with atmosphere all over the sample. Such preconditions are met in a very small sample, preferentially.

The investigations are continued on gels of aluminiumhydroxide chlorides of another preparation type.

The performed research work has been supported by the German Fonds der Chemischen Industrie, whom we thank very much.

References

[1] P. Brand, R. Troschke and H. Weigelt, Cryst. Res. Technol., 24, (1989) 671.
[2] P. Brand and P. Dietzmann, Cryst. Res. Technol., 27, (1992) 529.
[3] P. Brand, G. Ziegenbalg and K. Köhnke, Cryst. Res. Technol., 29, (1994) 179.
[4] TH. Oberbach, C. Günther, G. Wolf, G. Werner and G. Tomandl, Thermochim., Acta 271, (1996) 155-162).
[5] F. Freund, R. Martens and N. Scheikh-el-Eslami, J. Therm. Anal., 8, (1975) 525.
[6] K. Heide, G. Kluge and W. Hlawatsch, Thermochim. Acta., 36, (1980) 151.
[7] H. Strobel, Thermochim. Acta., 102, (1986) 29.
[8] M. D. Patil, Gopal N. Natuand S. B. Kulkarni, Bull. Chem. Soc. Jpn., 65, (1992) 1026.