Influence of additives on structure and thermal stability of ammonium nitrate
Influence of additives on structure and thermal stability of ammonium nitrate

Proefschrift

ter verkrijging van de graad van doctor aan de Technische Universiteit Delft, op gezag van de Rector Magnificus, prof.ir. K.F. Wakker, in het openbaar te verdedigen ten overstaan van een commissie aangewezen door het College van Dekanen op maandag 7 februari 1994 te 16.00 uur

door

Christoffel Adrianus van Driel

geboren te Rotterdam,
scheikundig ingenieur.

Druk: Judels en Brinkman B.V., Delft
Dit proefschrift is goedgekeurd door de promotor:
prof.dr.ir. G.M. van Rosmalen.
Contents

1. General introduction
   1.1 Ammonium nitrate
   1.2 Polymorphism of ammonium nitrate
   1.3 Production of ammonium nitrate
   1.4 Scope and outline

2. Growth of ammonium nitrate phase I and II dendrites
   2.1 Introduction
   2.2 Dendrite morphology
   2.3 Experimental procedure
   2.4 Results and discussion
   2.5 Conclusions

3. Morphology and growth of ammonium nitrate phase II dendrites in the presence of additives
   3.1 Introduction
   3.2 Morphology and growth of dendrites
   3.3 Experimental procedure
   3.4 Results and discussion
      3.4.1 Dendritic growth from a pure aqueous solution
      3.4.2 Dendritic growth from aqueous solutions containing additives

4. Isothermal coarsening of dendritic ammonium nitrate phase II: the influence of additives
   4.1 Introduction
   4.2 Coarsening
   4.3 Experimental procedure
   4.4 Results and discussion
   4.5 Conclusions
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.</td>
<td>The III-IV phase transition in ammonium nitrate: mechanisms</td>
<td>39</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>40</td>
</tr>
<tr>
<td>5.2</td>
<td>Previous observations</td>
<td>41</td>
</tr>
<tr>
<td>5.3</td>
<td>Experimental procedures</td>
<td>45</td>
</tr>
<tr>
<td>5.4</td>
<td>Results and discussion</td>
<td>46</td>
</tr>
<tr>
<td>5.5</td>
<td>Matching faces during the III-IV phase transition</td>
<td>48</td>
</tr>
<tr>
<td>5.5.1</td>
<td>Possible mechanisms of the III-IV phase transition</td>
<td>48</td>
</tr>
<tr>
<td>5.5.2</td>
<td>Determination of orientation relationships</td>
<td>49</td>
</tr>
<tr>
<td>5.5.3</td>
<td>Comparison of theoretical results with microscopic observations</td>
<td>54</td>
</tr>
<tr>
<td>5.5.4</td>
<td>Comparison of theoretical results with texture goniometry results</td>
<td>57</td>
</tr>
<tr>
<td>5.6</td>
<td>Conclusions</td>
<td>59</td>
</tr>
<tr>
<td>6.</td>
<td>Effect of the III-IV polymorphic phase transition on the texture and quality of ammonium nitrate products</td>
<td>61</td>
</tr>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>62</td>
</tr>
<tr>
<td>6.2</td>
<td>Experimental procedures</td>
<td>63</td>
</tr>
<tr>
<td>6.3</td>
<td>Results and discussion</td>
<td>64</td>
</tr>
<tr>
<td>6.3.1</td>
<td>Effects of the III-IV phase transition on the texture</td>
<td>64</td>
</tr>
<tr>
<td>6.3.2</td>
<td>Microscopy</td>
<td>67</td>
</tr>
<tr>
<td>6.4</td>
<td>Conclusions</td>
<td>70</td>
</tr>
<tr>
<td>7.</td>
<td>Thermal stability of ammonium nitrate: the influence of additives</td>
<td>73</td>
</tr>
<tr>
<td>7.1</td>
<td>Introduction</td>
<td>74</td>
</tr>
<tr>
<td>7.2</td>
<td>Production of high density ammonium nitrate</td>
<td>75</td>
</tr>
<tr>
<td>7.3</td>
<td>Experimental procedure</td>
<td>75</td>
</tr>
<tr>
<td>7.4</td>
<td>Results and discussion</td>
<td>76</td>
</tr>
<tr>
<td>7.4.1</td>
<td>Macrostructure and hardness of AN tablets</td>
<td>76</td>
</tr>
<tr>
<td>7.4.2</td>
<td>Final composition of additives in AN tablets</td>
<td>80</td>
</tr>
<tr>
<td>7.4.3</td>
<td>Thermal stability of AN tablets</td>
<td>82</td>
</tr>
<tr>
<td>7.5</td>
<td>Conclusions</td>
<td>86</td>
</tr>
</tbody>
</table>

Summary

Samenvatting

Dankwoord

List of publications

Curriculum vitae
Chapter 1

General introduction
1.1 Ammonium nitrate

Ammonium nitrate, NH₄NO₃ (AN), is a transparent, crystalline solid and has an extremely high solubility in water. As can be expected from the high solubility, AN is very hygroscopic and does not occur in nature.

AN was mainly applied as an ingredient of high explosives before World War II. Since that time AN became the most important nitrogen fertilizer in the world until in 1975 the world production of urea surpassed that of AN (5,400,000 versus 4,800,000 metric tons of nitrogen per year). In Western Europe AN is still the most important nitrogen fertilizer (3,900,000 metric tons of nitrogen per year in 1989/1990). Pure AN has the highest nitrogen content of all nitrogen fertilizers (35 wt%). For application as an explosive low density AN is used, while a high density AN product is required for use as a nitrogen fertilizer.

1.2 Polymorphism of ammonium nitrate

The quality of AN products may deteriorate during storage and transport. The main cause of this deterioration is one of the polymorphic phase transitions, occurring in AN. At least six polymorphic crystal phases have been reported in the literature. These are shown in the phase diagram [1] in fig. 1.1.

![Phase diagram of AN. Data from ref. [1].](image)
The transition temperatures at atmospheric pressure in pure ammonium nitrate are:

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>170 °C</td>
<td>125 °C</td>
<td>84 °C</td>
<td>32 °C</td>
<td>−18 °C</td>
<td>V*</td>
</tr>
<tr>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td>V</td>
<td>50 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>42 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>45 °C</td>
</tr>
</tbody>
</table>

 Besides the stable phase transitions II-III at 84 °C and III-IV at 32 °C the metastable phase transition II-IV can occur at a temperature of approximately 50 °C. This transition temperature is also found by extrapolation of the II-IV transition line in the phase diagram in fig. 1.1.

Some authors argue on the basis of several experimental results that other phases might exist as well, like phase VII and VIII. Phase VII is reported to be stable below −117 °C [2] and phase VIII would exist at a pressure of 30 kbar or higher [3].

In the sequence from phase I to phase V, which are stable at atmospheric pressure, the ammonium and nitrate ions have less freedom of movement and hydrogen bridges become more important. The crystal structures of these modifications revert to the CsCl-pattern of arrangement, except for phase III which has a completely different, 'loose' packing mode of molecules in the crystal lattice, and resembles the NiAs

<table>
<thead>
<tr>
<th>Table 1.1 Crystallographic data of the phases I to V of AN.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
</tr>
<tr>
<td>NH₄NO₃(I) [5]</td>
</tr>
<tr>
<td>NH₄NO₃(II) [6]</td>
</tr>
<tr>
<td>NH₄NO₃(III) [7]</td>
</tr>
<tr>
<td>NH₄NO₃(IV) [8]</td>
</tr>
<tr>
<td>ND₄NO₃(V) [9]</td>
</tr>
</tbody>
</table>

*a Cell parameters for AN(III) at room temperature containing 5 % KNO₃.*
Fig. 1.2 Projections of the crystal structures of AN(II) to AN(IV). The projection of phase I is rotated over 45° about one of its crystallographic axes and a monomolecular pseudocell is drawn in the $a_e$ projection of phase II (dashed line) to show the similarity between the structures of phase I, II and IV.

structure [4]. The crystallographic data of the phases I to V [5–9] are given in table 1.1. The structures of these phases are schematically drawn in fig. 1.2 which shows the structural similarity of the phases I, II, IV and V.

In fig. 1.2 the unit cell of phase I is rotated over 45° about one of its crystallographic axes which makes the similarity between the structures of phase I and II obvious. The transition from phase I into phase II involves partial ordering of both ions simultaneously with contraction of two of the $a_i$ axes to form the $a_{II}$ axes of the phase II pseudocell and expansion of the remaining $a_i$ axis to form the $c_{II}$ axis.

During the metastable phase transition II-IV the planes of the nitrate ions are
rotated over 45°, the ammonium ions are displaced and the lattice is further distorted from tetragonal to orthorhombic.

Phase V is again very similar to phase II and phase IV and can transform into phase IV with minor changes similar to those taking place during the II-IV transition. Phase V can transform even into phase II and vice versa via the metastable phase V*, existing between 42 and 45 °C [2,10].

The transitions I-II-IV-V as well as the metastable transitions II-IV and II-V occur with little distortion of the crystal lattice due to the relatively minor structure changes involved. The transitions of phase II and phase IV into phase III, however, involve much more drastic changes of the crystal lattices.

The projections of the unit cell of phase III, given in fig. 1.2, show that there are no obvious structural similarities to the other stable forms of AN. It is well known that the transition III-IV requires the presence of some moisture [5,11,12]. Several authors therefore suggest that these transitions take place by dissolution and recrystallization of the solid. Other authors, however, more or less contradict such a solvent mediated process by reporting that the orientation relations between the crystallographic axes in the II-III and III-IV transitions are not random although various rather complex relationships can develop [13,14].

Fig. 1.3 shows the molecular volume of AN (unit cell volume per molecule \( \text{ND}_4\text{NO}_3 \)) for the temperature range from 200 to 393 K according to data in ref. [15]. This figure shows that the molecular volume of phase IV is significantly smaller than those of the phases II and V, although these three phases are essentially identical in molecular packing (fig. 1.2). This is attributed to the fact that the nitrate ions in phase IV are stacked with their planes parallel to each other, while these ions are stacked perpendicular to each other in the phases II and V [15]. The large molecular

![Fig. 1.3 Molecular volume of \( \text{ND}_4\text{NO}_3 \) as a function of the temperature according to data from ref. [15]. The dashed line indicates the IV-II transition at 50 °C. The relative change in the molecular volume at each transition point is included in the graph.](image)
volume of phase III is related to the completely different, 'loose' packing mode of molecules in the unit cell of this phase.

The quality decrease due to the III-IV transition is often ascribed to the relatively large change of the molecular volume during this transition (fig. 1.3). This volume change of almost 4% induces an increase of the pore volume and simultaneously a breakdown of the product due to lattice strain. This phenomenon is described in the technical literature as disintegration. The resistance of AN granules to this disintegration is called thermal stability, and appears to be strongly affected by the water content, but also by the pretreatment of the product, and by the presence of specific additives [5,11,12].

1.3 Production of ammonium nitrate

AN products can be produced by various processes, like prilling, drum granulation, fluid bed granulation or by combinations of these. Most of the processes applied for the production of high density AN comprise layer wise crystallization of a highly saturated AN solution on recycled particles followed by a drying step. In some processes, like fluid drum and fluid bed granulation, the granulation and drying steps are integrated. The generalized granulation process for the production of high density AN is schematically shown in fig. 1.4.

AN is obtained by the reaction of ammonia with nitric acid:

\[ \text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3. \]

The AN solution, usually containing 10 to 30 wt% water, is evaporated to a water content of 1 to 5 wt%, depending on the production process concerned.

In various processes pure AN cannot be formed into well rounded granules. For that reason granulation aids are added, e.g. in the form of a clay. These additives somewhat lower the nitrogen content of the product but promote the conglomeration process in the granulator. Additives are also applied in order to stabilize the granules with respect to disintegration after the III-IV phase transition.

The concentrated AN solution which is fed to the granulator has a temperature of 160 - 180 °C. In most processes the amount of clay is not sufficient for the conglomeration process and, therefore, fine and grinded coarse particles, having a temperature of approximately 90 to 100 °C, are recycled to the granulator. The recycle ratio ranges from 50 to 200 % with respect to the on-size product depending on the granulation process. The residence time in the granulator is approximately 10 to 20 minutes.
Ammonia and nitric acid are neutralized, followed by vaporization. Additives are mixed, and the mixture undergoes granulation and drying. The resulting granules are sieved to separate fine and coarse fractions. Fine granules are cooled and coated, then stored. Coarse granules are ground before being sieved, cooled, coated, and stored.

Fig. 1.4 Simplified flow-sheet of AN granulation processes. In some processes the granulation and drying step are integrated.

In processes where the drying step is not integrated with the granulation the wet granules are dried at a temperature well above the II-III phase transition point.

On-size product is cooled to the required storage temperature after which it is coated to prevent moisture uptake and caking.

1.4 Scope and outline

This study focuses on the AN 33.5 product (96 wt% AN, at least 33.5 wt% nitrogen), since in particular this product gives rise to problems because of the high AN content, and, related to this, the little room for application of additives (less than 4 wt%). Although the III-IV phase transition in AN and its effects on the mechanical stability of AN products has been studied extensively, in many cases little attention has
been paid to the conditions under which the phase transition takes place (e.g. water content) and to the precise role of additives in this transition. The aim of this thesis is to gain a better insight in the effects of additives, which is of importance for the improvement of the AN product quality.

Stabilizing additives are added at an early stage of the production process, namely prior to crystallization in the granulation step (fig. 1.4). This means that they may affect various processes taking place during the formation history of the granules, which determine their final texture and structure, the way in which the III-IV transition proceeds, and, related to these points, the thermal stability of the granules.

The influences of granulation process conditions and additives on the solidification of AN are the subject of the next three chapters. Chapters 2 and 3 describe the influences of the water content and some additives on characteristic growth parameters and on the morphology of AN crystals which are formed in the earliest stages of the production process. Coarsening or ripening of the solidifying AN occurs during granulation and drying, and greatly influences the final structure of the product granules. This coarsening and the effect of additives on it are described in chapter 4.

The investigation of the III-IV transition mechanism is described in chapter 5. Some of the microscopic observations used in chapter 5 for the elucidation of the III-IV transition mechanism are described in chapter 6. In addition, chapter 6, and also chapter 7, finally, describe the effects of moisture and additives on the texture and structure of AN granules and on the thermal stability of AN.

References

Chapter 2

Growth of ammonium nitrate phase I and II dendrites *

Abstract

Ammonium nitrate (AN) phase I and phase II crystallize as dendrites from a melt containing respectively 0–4.5 and 4.5–12 wt% water. In situ microscopic measurements show that the, for dendrites, characteristic ratio $S/\rho$ (where $S$ = side branch spacing near the tip and $\rho$ = dendrite tip radius) varies between 2.3 and 5.1 for both AN(I) and AN(II). This agrees reasonably well with the theoretically derived value of 2.8 reported in literature. The water concentration has a strong influence on the relation between the side branch spacing near the tip, $S$, and the tip growth rate, $v$, of the dendrites. The findings satisfy at least qualitatively the theoretically expected relationship between $S$ and $v$.

2.1 Introduction

Ammonium nitrate (AN) is mainly used as a base chemical for the production of fertilizers and explosives. It develops in several polymorphic crystal phases. The transition temperatures at atmospheric pressure in pure ammonium nitrate are:

\[
\begin{align*}
\text{melt} & \quad 170 \degree C & \quad 125 \degree C & \quad 84 \degree C & \quad 32 \degree C & \quad -18 \degree C & \quad \text{V} \\
\text{I} & & \text{II} & \text{III} & \text{IV} & \text{V}
\end{align*}
\]

The crystal structures of all these modifications revert to the CsCl-pattern of arrangement, except phase III which resembles NiAs [1]. AN(I) has a cubic structure with \(a = 4.40 \ \text{Å} [1]\). AN(II) has a tetragonal space group \(P4_2/m\) with unit cell dimensions \(a = 5.7193 \ \text{Å} \) and \(c = 4.9326 \ \text{Å}, \ Z = 2 [2]\).

The crystallization temperature of an AN melt is decreased by the addition of water. A melt containing 0 to 4.5 wt\% water crystallizes as phase I at temperatures between 170 and 125 \degree C, respectively. At water concentrations of 4.5 to 12 wt\%, phase II crystallizes within the temperature range of 125 to 84 \degree C. In situ microscopic observations show that AN(I) as well as AN(II) grow as dendrites.

For fertilizer application, AN is often formed into granules. The texture of these AN granules, after cooling to room temperature, is expected to be influenced by the morphology of the intermediate AN(I) or AN(II) phases. Knowledge about this texture is of importance for the improvement of the mechanical quality of the granules, when subjected to temperature fluctuations around its III-IV transition point. The dendritic morphology of the intermediate phases can be quantified by the tip radius, the side branch spacing near the tip and the growth rate of the dendrite tips in relation to water content and undercooling, as will be demonstrated in this paper.

2.2 Dendrite morphology

A growing dendrite can be characterized by a dimensionless number \(\sigma\) [3] given by

\[
\sigma = \frac{2d_0D}{\rho^2 \nu}.
\]

Models which describe the dendrite tip as a parabola lead to relations between the tip radius, \(\rho\), and the tip growth rate, \(\nu\), on the one hand and \(\Delta T\) on the other (e.g. the modified Ivantsov model [4]). Combined with eq. (2.1) and the fact that \(\sigma\) takes a special value, \(\sigma^*\), determined by the microscopic solvability condition [5], these models
define the operating point \((\rho, \nu)\) of the dendrite tip at a given constant undercooling. Experimentally a value of \(\sigma^* = 0.02\) is found [6]. Anisotropy as well as the degree of undercooling and the impurity concentration may affect the value of \(\sigma^*\) [4,7,8].

Van der Eerden and Müller-Krumbhaar [7] have found theoretical values for \(S/\rho\) of \(2.8 \pm 0.4\) for three-dimensional and \(3.9 \pm 0.3\) for two-dimensional growth where \(S\) represents the side branch spacing near the tip of a dendrite. Anisotropy may be irrelevant for the ratio \(S/\rho\) [8,9]. For a constant \(S/\rho\) ratio, \(\rho\) can be eliminated from eq. (2.1), which can then be written as

\[
S = C \sqrt{1/\nu},
\]

where

\[
C = \left(\frac{S}{\rho}\right) \sqrt{\frac{2d_0D}{\sigma^*}}
\]

for \(\sigma = \sigma^*\). This model holds for dendritic growth from a pure melt, as well as for growth from a melt containing impurities such as water. In the former case the dendritic growth is thermally controlled; the transport of latent heat released by the solidification front governs the growth rate of the dendrite. In the latter case, chemical diffusion of impurities through the melt may override the thermal diffusion and the dendritic growth becomes more and more chemically controlled at higher impurity concentrations. \(D\) represents the thermal diffusivity or, respectively, the chemical diffusion coefficient of the impurity in the melt. The capillary length, \(d_0\), is in either case defined differently and can differ several orders of magnitude [4].

2.3 Experimental procedure

In situ microscopic measurements were performed using a hot stage as shown in fig. 2.1. The accuracy of the temperature control was better than 0.1 °C. Samples were prepared from 250 mg analytically pure AN which was ground and next well dried at 90 °C. 0 to 10 wt% doubly distilled water was added using a 5 or 10 µl micro-syringe (accuracy about 0.1 and 0.2 µl, respectively). The tip growth rate of primary dendrites, the distances between side branches near the tip and the tip radii were measured in the following way. After melting the sample until just one tiny crystal was left in the solution, the sample was equilibrated at a constant temperature for some minutes in order to eliminate temperature and concentration gradients. The temperature was then decreased by a value in the range of 0.2 to 2 °C. When the temperature became stable (within half a minute), the measurement was started using an optical microscope and
video equipment (total magnification 330×). This procedure was repeated for several undercoolings for each water concentration.

2.4 Results and discussion

The observations show that AN(I) and AN(II) dendrite tips are smooth and essentially parabolic.

Although a relatively large error (about 20 %) exists in the measurement of \( \rho \), due to the limited resolution of the microscope, the value of \( S/\rho \) has been found to vary significantly between 2.3 and 5.1 at various water concentrations (table 2.1). A relation between the ratio \( S/\rho \) and the water concentration could not be found for both AN(I) and AN(II) dendrites.

Table 2.1 Experimental and calculated data at various water concentrations. Values of \( d_0D \) and \( d_0 \) are calculated from the slopes in fig. 2.2 for \( a^* = 0.02 \).

<table>
<thead>
<tr>
<th>( H_2O ) [wt%]</th>
<th>( T_c ) [K]</th>
<th>( S/\rho ) [-]</th>
<th>slope ( \times 10^9 ) ( [m^{1.5}s^{-0.5}] )</th>
<th>( d_0D \times 10^{18} ) ( [m^3s^{-1}] )</th>
<th>( D \times 10^9 ) ( [m^2s^{-1}] )</th>
<th>( d_0 \times 10^{10} ) [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>442.8</td>
<td>2.7 ± 0.6</td>
<td>220 ± 44</td>
<td>66</td>
<td>87</td>
<td>8</td>
</tr>
<tr>
<td>0.5</td>
<td>439.1</td>
<td>4.1 ± 0.9</td>
<td>124 ± 25</td>
<td>9.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>435.0</td>
<td>2.3 ± 0.5</td>
<td>85 ± 17</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>417.3</td>
<td>2.7 ± 0.6</td>
<td>52 ± 12</td>
<td>3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>387.8</td>
<td>4.1 ± 0.9</td>
<td>33 ± 7</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>366.8</td>
<td>5.1 ± 1.1</td>
<td>29 ± 6</td>
<td>0.3</td>
<td>0.6</td>
<td>5</td>
</tr>
</tbody>
</table>
Fig. 2.2 Plot of the side branch spacing, $S$, versus square root of reciprocal growth rate, $\sqrt{(1/\nu)}$, of AN dendrites growing in water containing melt.

In fig. 2.2 the side branch spacing, $S$, is plotted versus $\sqrt{(1/\nu)}$ for dendrites grown from an AN melt containing various amounts of water. Because of the fact that the experimental points lie on straight lines, the conclusion follows that the relationship between $S$ and $\nu$ as given by eq. (2.2) holds at least qualitatively for the water concentration range considered here (0–10 wt%), and thus for both AN(I) and AN(II).

The slopes of the lines in fig. 2.2 change by a factor of about 10 at an increase of the water concentration from 0 to 10 wt%. For pure AN, a slope of $220 \cdot 10^{-9} \text{ m}^{1.5} \text{s}^{-0.5}$ is found which agrees well with the measurements of Derks ($218 \cdot 10^{-9} \text{ m}^{1.5} \text{s}^{-0.5}$) [10]. From the slopes, the values of $d_0 D$ have been calculated for $\sigma^* = 0.02$ by taking the corresponding values of $S/\rho$ from table 2.1 (see eq. (2.3)). The value of $d_0 D$ decreases by a factor of about $2 \cdot 10^2$ at increasing the water concentration up to 10 wt% (table 2.1).

Values for the thermal diffusivity and the chemical diffusion coefficient of a pure AN melt were not available from literature. The thermal diffusivity can be estimated from thermal conductivities of alkali nitrate melts [11]. The thermal conductivity of AN is assumed to be about the same as the thermal conductivity of RbNO$_3$ ($\kappa = 0.3$ W m$^{-1}$K$^{-1}$) because the sizes of the Rb$^+$ ion and the NH$_4^+$ ion are similar (1.48 Å). From the thermal conductivity the thermal diffusivity can be calculated as follows:

$$D(\text{AN}) = \frac{\kappa}{\rho_{\text{AN}} c_{\rho}} = \frac{0.3/1647 \times 2087}{8.7 \times 10^{-8}} \text{ m}^2\text{s}^{-1}.$$

Although this value may differ from the real value because of the higher molecular weight of RbNO$_3$ with respect to that of AN, the order of magnitude is assumed to be
correct. Using this value for the thermal diffusivity, the capillary length, $d_0$, of pure AN is found to be 8 Å.

The (chemical) diffusion coefficient of water in an AN melt is assumed to be of the same order of magnitude as the self-diffusion coefficient, $D_s$, of AN. This assumption might be in error because the water-water interaction might be underestimated.

The self-diffusion coefficient can be described by an Arrhenius type of equation [12]:

$$D_s = D_0 e^{-\Delta E/RT}.$$  \hfill (2.4)

The activation energy in diffusion, $\Delta E$, equals approximately $3.7 \times RT_m$ [12], and the pre-exponential factor, $D_0$, is estimated from the $D_0$ values of alkali nitrates to be about $5 \times 10^{-8}$ m$^2$s$^{-1}$. For pure AN this yields $D_s = 1.2 \times 10^{-9}$ m$^2$s$^{-1}$ at $T_m$(AN) = 442.8 K.

The dendritic growth is thermally determined in case of pure AN, while it becomes more and more chemically determined at increasing water concentrations. In principle, this causes a change in $d_0$ as well as in $D$. It is unknown at which water concentration the thermal diffusion is overruled by the chemical diffusion. This is assumed to be the case at least at 10 wt% water, the highest water concentration considered here. An AN melt containing 10 wt% water crystallizes at about 94 °C. At this temperature $D = D_s \approx 0.6 \times 10^{-9}$ and thus $d_0$ is found to be about 5 Å at a water concentration of 10 wt%, where $S/\rho = 5.1$.

The calculated values of the thermal diffusivity at 442.8 K and the chemical diffusion coefficient at 366.8 K differ by a factor of 150. The observed decrease of $d_0D$ by approximately two orders of magnitude at an increase of the water concentration from 0 to 10 wt% is thus mainly caused by a changing value of $D$, while $d_0$ does not differ significantly when growth becomes chemically determined.

It should be noted that the calculation of $d_0$ is sensitive to the value of $S/\rho$. For instance substituting the theoretically found ratio $S/\rho = 2.8$ leads to a value of $d_0$ of 18 Å in stead of 5 Å for 10 wt% water.

### 2.5 Conclusions

The ratio between the side branch spacing and the tip radius, $S/\rho$, of AN(I) and AN(II) dendrites has been found to vary significantly between 2.3 and 5.1. Taking into account effects of anisotropy and impurities these values correspond reasonably well with the theoretically derived value of $2.8 \pm 0.4$.

A relation between the side branch spacing, $S$, and the tip growth rate, $v$, exists in the case of AN(I) dendrites growing from a pure AN melt as well as in the case of
AN(I) and AN(II) dendrites growing from an AN melt containing 0–10 wt% water just as described by theory. The slope of the plot of $S$ versus $\sqrt{1/v}$ decreases by a factor of about 10 at an increase of the water concentrations (up to 10 wt.%). This slope is proportional to the square root of the product of the capillary length and the diffusion coefficient, $d_o D$. Theoretical estimates of $D$ in both the thermally and the chemically determined situations (0 and 10 wt% water) show that $D$ changes by a factor of about 150, leading to values of $d_o$ that remain almost constant under the assumption that $\alpha^*$ has a constant value of 0.02.

References

Chapter 3

Morphology and growth of ammonium nitrate phase II dendrites in the presence of additives

Abstract

Ammonium nitrate phase II crystals growing from an AN solution containing 5.7 wt% water develop as dendrites in the ab-plane and in the c-direction and are referred to as ab- and c-dendrites respectively. The compiled experimental data suggest that the growth form of the ab-dendrites growing in pure aqueous solutions results from the instability of the growth directions along the a- and b-axes.

If the growth rate of c-dendrites is sufficiently retarded by additives with respect to the growth rate of ab-dendrites, the ab-dendrite tips are stable, do not split, and grow along the a- and b-axes. If side branches growing in the c-direction are less retarded, the ab-dendrites show tip splitting, finally resulting in growth directions deviating from \textless 100\textgreater  and being approximately \textless 410\textgreater.

For both ab- and c-dendrites the tip growth rates as well as the side branch spacings were determined as a function of the undercooling. The experimental data satisfy basic relations between these growth parameters and the undercooling.

3.1 Introduction

Ammonium nitrate, \( \text{NH}_4\text{NO}_3 \) (AN), is a base chemical for the production of fertilizers and explosives. At atmospheric circumstances it develops in at least five polymorphic crystal phases:

\[
\begin{array}{cccccc}
170 \, ^\circ\text{C} & 125 \, ^\circ\text{C} & 84 \, ^\circ\text{C} & 32 \, ^\circ\text{C} & -18 \, ^\circ\text{C} \\
\text{melt} & \text{I} & \text{II} & \text{III} & \text{IV} & \text{V}
\end{array}
\]

Except for phase III, which resembles NiAs, the crystal structures of these phases revert to the CsCl pattern of arrangement [1]. AN(II) has a tetragonal space group \( \overline{P42_1m} \). The reflection conditions are \( h00: h = \text{even} \) and \( 0k0: k = \text{even} \). The unit cell dimensions are \( a = b = 5.7193 \, \text{Å} \) and \( c = 4.9326 \, \text{Å} \), \( Z = 2 \) [2].

For fertilizer application, solid AN is often produced from a highly concentrated aqueous solution (approximately 5 wt% water or less) by layer wise crystallization from this solution on seed particles. The addition of water to AN suppresses the crystallization temperature, \( T_c \). At water concentrations up to 4.5 wt% \( T_c \) decreases from 170 to 125 \( ^\circ\text{C} \) where AN(I) is stable. At water concentrations of 4.5 to 12 wt% AN(II) crystallizes at 125 \( ^\circ\text{C} \) > \( T_c \) > 84 \( ^\circ\text{C} \). Generally the temperature of the seed particles is approximately 100 \( ^\circ\text{C} \). This implies that on these AN(II) seeds AN(II) crystallizes, even if the water content is somewhat lower than 4.5 wt%.

After cooling to room temperature the mechanical quality of the final AN granules is affected by their internal macroscopic structure and their texture (i.e. the coherence and mutual orientations of the crystallites within in granules). Besides these, also specific additives affect the granule quality. Macrostructure and texture are determined by the solidification process. This process can be subdivided into dendritic crystallization and coarsening of the dendritic phase, both of which can be influenced by the additives.

This study describes the morphology of AN(II) dendrites, growing from an AN solution containing 5.7 wt% water. This water content is chosen to avoid the formation

<table>
<thead>
<tr>
<th>((hkl))</th>
<th>(d_{hkl})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>4.933</td>
</tr>
<tr>
<td>(110)</td>
<td>4.044</td>
</tr>
<tr>
<td>(101)</td>
<td>3.735</td>
</tr>
<tr>
<td>(011)</td>
<td>3.735</td>
</tr>
<tr>
<td>(200)</td>
<td>2.860</td>
</tr>
<tr>
<td>(020)</td>
<td>2.860</td>
</tr>
</tbody>
</table>
of AN(I) dendrites. Maximally 1.0 wt% of inorganic salts was added intentionally. These salts were selected for their known positive effect on the mechanical quality of AN products when subjected to the phase transition III-IV (chapter 7), as well as for their specific effects on the morphology of the AN(II) dendrites. The coarsening of the dendritic phase and the effects of additives on this process are described in chapter 4.

3.2 Morphology and growth of dendrites

In this study the morphology of the AN(II) dendrites is described by the crystallographic orientations of the main stems of the dendrites and those of their side branches. In cases that dendrites develop from originally faceted crystals the dendritic growth directions usually coincide with the directions of apices of three or more intersecting faces. In order to predict the growth directions of AN(II) dendrites the theoretical morphology of faceted AN(II) crystals is determined on the basis of the Donnay-Harker criterion. According to this criterion (hkl) faces will appear on faceted crystals which have large \( \Delta d_{hkl} \) values [3]. These faces are given in table 3.1 for AN(II). The predicted morphology of AN(II) is shown in fig. 3.1 which only shows \{001\} and prismatic faces.

The roughness of a crystal interface can be described by the surface entropy factor \( \alpha_{hkl} \), which was first defined by Jackson [4] for growth from the melt:

\[
\alpha_{hkl} = \xi_{hkl} \frac{\Delta H_f(T_m)}{R T_m},
\]

where \( \xi_{hkl} \) is the surface anisotropy factor, which equals the ratio of the total energy of the bonds per growth unit in a slice of the (hkl) face to the total crystallization energy per growth unit. \( \Delta H_f(T_m) \) is the heat of fusion at the melting temperature of the pure material, \( T_m \) (443 K), which equals 6.4 kJ mol\(^{-1}\) for AN, and \( R \) is the gas

![Fig. 3.1 Morphology of AN(II) crystals according to the Donnay-Harker criterion.](image)
constant. For values of $\alpha_{hkl} \leq 3$ growth of the $(hkl)$ face occurs roughened, while for $\alpha_{hkl} \geq 3$ a faceted face develops.

A more general approximation of $\alpha_{hkl}$ for growth from solution can be calculated from [5,6]

$$\alpha_{hkl} = \xi_{hkl} \left[ \frac{\Delta H_f(T_m)}{RT_m} - \ln x_{s,eq} \right], \quad (3.2)$$

in which $x_{s,eq}$ is the ratio of the number of solute particles per unit volume in the solution to the number of solid particles per unit volume in the solid phase.

The value of $\xi_{hkl}$ can be calculated easily for AN(II) if the ammonium and nitrate ions are assumed to rotate freely with a spherical symmetry. Because in that case all bond energies are equal, $\xi_{hkl}$ is simply the number of bonds within a $(hkl)$ slice divided by the total number of bonds per growth unit. The highest value of $\xi_{hkl}$ is then found to be 0.5. For a water content of 12 wt%, which is the highest water content at which AN crystallizes in the temperature region where phase II is stable, $x_{s,eq} = 0.84$. At this water content $\alpha_{hkl}$ is found to be maximally 1.0. The contribution of the term $-\ln x_{s,eq}$ to the value of $\alpha_{hkl}$ will be smaller at lower water contents, yielding an even lower value of $\alpha_{hkl}$ (e.g., $\alpha_{hkl} = 0.9$ at 4.5 wt% water). These low values of $\alpha_{hkl}$ indicate that AN(II) crystals are not faceted. In situ microscopic observations have shown that AN(II) grows dendritically (chapter 2).

Since AN(II) crystals grow dendritically the dendrites are expected to grow in crystallographic directions which contain chains of strong periodic bonds. Such directions generally coincide with the directions of apices where the predicted faces intersect. Other growth directions might appear due to anisotropy effects in the surface tension.

Dendritic growth from the melt has been studied extensively over the last decades [7–11]. Theories about dendritic growth provide various models describing the relationships between dendritic growth conditions like the undercooling, $\Delta T$, and growth parameters, such as the growth rate, $v$, the radius of curvature of the dendrite tip, $\rho$, and the distance between the side branches near the tip, $S$. Growing dendrites can be characterized by the universal relation $v \rho^2 = \text{constant}$. The ratio between $S$ and $\rho$ appears to be constant. The stability of the dendrite tip has been found to depend on the anisotropy of the surface tension. Tip splitting occurs if the surface tension is isotropic, and may result in a fractal structure.

Dendritic growth from solution is much more difficult to describe, because it involves not only heat transport, but also mass transport [12–15]. Simple relationships between dendrite growth parameters and growth conditions, however, still resemble those resulting from models developed for growth from the melt. The dependence of $v$ on $\Delta T$, for instance, can be described as
\[ v = C_1 \Delta T^n. \]  

(3.3)

Since \( S \propto \rho \) and \( \nu \rho^2 = \text{constant} \), a linear relationship exists between \( S \) and \( \sqrt{1/\nu} \). In chapter 2 it has been shown that this relationship holds for both AN(I) and AN(II) dendrites. Equation (3.3) can be rewritten with this linear relationship into

\[ S = C_2 \Delta T^{-n/2}. \]  

(3.4)

Literature data show that \( n \) equals values between 1.5 and 2.5 both for dendritic growth from the melt and from solution for various organic and inorganic materials [7–15].

### 3.3 Experimental procedure

In situ microscopic observations were performed using a hot stage and video equipment as described in chapter 2. The samples used for the experiments were prepared from a concentrated aqueous AN solution to which either 0, 0.05, or 1.0 wt% of the inorganic salts was added. After solidification and drying this mixture was ground and pressed into pellets in order to avoid air bubble formation during the experiment. 5.7 wt% water was added by using a micro-syringe upon inserting a pellet in the observation cell. The additives are given in table 3.2. All chemicals were p.a. grade.

The crystallization temperature of each sample was determined by dissolving the sample until just one tiny crystal remained in the solution which neither grew nor dissolved. The sample was then equilibrated for some minutes at a constant temperature in order to eliminate temperature and concentration gradients. The morphology of the dendrites, growing from the original tiny seed crystal by a decrease in temperature, were observed and recorded. From the recordings the relations between \( v, S, \) and \( \Delta T \) were determined.

### Table 3.2 Additives used for the experiments.

<table>
<thead>
<tr>
<th>amount</th>
<th>additive</th>
<th>composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 wt%</td>
<td>CuSO₄</td>
<td>58 wt% (NH₄)₂HPO₄</td>
</tr>
<tr>
<td>1.0 wt%</td>
<td>permalene</td>
<td>39 wt% H₃BO₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 wt% (NH₄)₂SO₄</td>
</tr>
<tr>
<td>0.05 wt%</td>
<td>Fe₂(SO₄)₃</td>
<td></td>
</tr>
</tbody>
</table>
3.4 Results and discussion

3.4.1 Dendritic growth from a pure aqueous solution

In samples containing no other additives than water, two distinct shapes of the AN(II) dendrites could be observed, depending on the accidental position of the original seed crystal. Both of these dendrite 'types', which grow in specific crystallographic directions, are shown in figs. 3.2a and b. The dendrites shown in fig. 3.2a have a fourfold symmetry. Since AN(II) has a fourfold rotation axis, parallel to the c-axis, this indicates that the stems of these dendrites grew in the ab-plane of the crystal. These dendrites are therefore referred to as 'ab-dendrites'. Microscopic observations have shown that perpendicular to these ab-dendrites other dendrites develop. Therefore, these must be oriented parallel to the c-axis. These dendrites are called 'c-dendrites' (see fig. 3.2b).

In order to observe the development of AN(II) dendrites from a spherical seed crystal an ab-dendrite was partially dissolved. This spherical seed crystal initially

Fig. 3.2 Photographs of an ab-dendrite (a, left) and a c-dendrite (b, right) growing from an AN solution containing 5.7 wt% water.
developed into a rounded octahedron which lower half could not grow out because the crystal was lying at the bottom of the observation cell as depicted in fig. 3.3. The top of this crystal grew in the c-direction, which is perpendicular to the observation plane in this case. The crystal was therefore observed as a square.

If it is assumed that at this initial stage of growth the seed crystal develops a shape which reflects the morphology that a crystal would obtain if it grew faceted, then this shape does not agree with the predicted morphology according to Donnay-Harker. In order to explain the observations, the morphology of AN phase IV can be used since this phase has a crystal structure which closely resembles the structure of AN(II). As a result of the structural similarity almost equal morphologies are predicted for AN(II) and AN(IV) according to the Donnay-Harker criterion [16]. For phase IV, which grows faceted from aqueous solutions, experimentally the \{111\} faces appear to be the most important, followed by the prismatic faces. The \{001\} face, which is predicted to be the most important, has a much lower morphological importance. Because of the resemblance between the AN(II) and the AN(IV) structures, it is not unlikely that the observed rounded octahedral AN(II) seed crystal is bounded by roughened \{111\} faces at the early stages of its growth. The morphology of an octahedral crystal which is bounded by \{111\} faces is given in fig. 3.4 and corresponds to the observed shape of the seed crystal. The corners of the seed crystal are therefore most likely oriented along the crystallographic axes.

**Fig. 3.3** Schematic drawings showing the development of the ab-dendrite out of the initially rounded seed crystal.

**Fig. 3.4** Predicted morphology of an AN(II) crystal which is bounded by \{111\} faces.
Morphology and growth of ammonium nitrate phase II dendrites

Fig. 3.5 Schematic drawing showing the growth directions of the \(ab\)-dendrite branches and the angles between them.

At further growth each of the corners in the \(ab\)-plane split into two protrusions which developed into separate \(ab\)-dendrites as shown in fig. 3.3. Side branches of the eight \(ab\)-dendrites evolved at short distances from the tip. During the growth of the \(ab\)-dendrites the growth directions of their side branches were restricted to those of the initial eight protrusions of the original seed crystals. The side branches in the \(ab\)-plane developed under angles of either \(26.8^\circ \pm 0.2^\circ\) or \(63.2^\circ \pm 0.2^\circ\) with the main stems as indicated in fig. 3.5. Besides side branches in the \(ab\)-plane also side branches were observed growing perpendicular to the \(ab\)-plane, hence in the \(c\)-direction.

Fig. 3.6 Growth rate, \(v\), (a) and side branch spacing, \(S\), (b) of \(ab\)- and \(c\)-dendrites growing from pure aqueous AN solution, plotted versus the undercooling, \(\Delta T\).
The \(<hkl>\) directions of the \(ab\)-dendrite branches are close to \(<410>\). These directions do not correspond to chains of strong periodic bonds. The growth directions of the dendrites in the \(ab\)-plane therefore result most likely from the instability of the dendrite tips which are originally oriented along the \(a\)- and \(b\)-axes.

The \(c\)-dendrites are characterized by their sharp tips and by the growth directions of their side branches, which are perpendicular to the main stem (fig. 3.2b). The side branches of these dendrites grow in the \(ab\)-plane and are in fact \(ab\)-dendrites. Secondary side branches were observed to grow in directions parallel to the main stem of the \(c\)-dendrites, hence also in the \(c\)-direction. The latter branches are similar to those which were observed on \(ab\)-dendrites and were growing perpendicular to the \(ab\)-plane.

Figs. 3.6a and b show the dependencies of \(v\) and \(S\) on \(\Delta T\) for \(ab\)- and \(c\)-dendrites. The slopes of both lines in fig. 3.6a, which are equal to \(n\) in eq. (3.3), are \(2.0 \pm 0.1\), which agrees fairly well with the values found for other materials [14,15]. The lines in fig. 3.6b have slopes of \(-1.1 \pm 0.2\) for \(ab\)-dendrites and \(-0.9 \pm 0.2\) for \(c\)-dendrites, showing the validity of eq. (3.4) for this system. These results demonstrate that the \(c\)-dendrites grow faster than the \(ab\)-dendrites. This might be caused by the anisotropy of AN(II), resulting in the different curvatures of the tips of the \(ab\)- and \(c\)-dendrites (causing a different diffusion field around the growing dendrite tips).

3.4.2 Dendritic growth from aqueous solutions containing additives

Dendrite morphology

AN(II) dendrites growing from an aqueous AN solution containing 1.0 wt% CuSO\(_4\) showed a morphology different from that of dendrites growing in the absence of additives. All of the observed dendrites had a fourfold symmetry if they were lying perpendicular to the view direction. This indicates that they were growing in the \(ab\)-plane. In this plane only four growth directions were observed which implies that tip splitting of \(ab\)-dendrites did not occur in the presence of CuSO\(_4\). The four growth directions are most likely parallel to the \(a\)- and \(b\)-axes. In contrast with the \(ab\)-dendrites growing in the absence of additives the side branches of these \(ab\)-dendrites grew perpendicular to the main stems (fig. 3.7). All dendrites appeared to be flat, having no side branches perpendicular to the \(ab\)-plane. This indicates that the growth in the \(c\)-direction was retarded considerably in these samples.

In samples containing 1.0 wt% of permalene, dendrites were observed at low undercooling (less than 0.5 °C) with a shape resembling that of dendrites grown in the presence of CuSO\(_4\), so with four growth directions oriented along the \(a\)- and \(b\)-axes. The side branches grew perpendicular to the main stems and the growth of dendrites in the \(c\)-direction appeared to be retarded. A typical example is shown in fig. 3.8a. At an increased undercooling the tips of the four \(<100>\) dendrites became unstable and
Fig. 3.7 a: Photograph of an ab-dendrite growing in the presence of CuSO₄. b: Schematic drawing showing the growth directions of the ab-dendrite branches in the presence of CuSO₄.

Fig. 3.8 Successive video prints of an ab-dendrite growing in the presence of permalene. a: Dendrite growing at low undercooling ($\Delta T \leq 0.5 \, ^\circ C$), just before tip splitting of the $<100>$ main stem occurs. b: Tip splitting occurs occasionally at increased undercooling ($\Delta T \geq 0.5 \, ^\circ C$). c: The left tip survives.

tip splitting occasionally occurred as shown in fig. 3.8b. After the tip had split only one of both new tips survived (the left one in figs. 3.8b,c) while the growth of the other was retarded. At further growth the surviving tip repeatedly split while the surviving tip was always positioned at the same side of the dendrite stem as the former one. This might be explained by the asymmetric shape of the diffusion profile around the asymmetrically developing dendrite tip which favours the growth of the dendrite that penetrates the solution the most. In this way a staircase-like profile of the main stem of the dendrite resulted (fig. 3.9). If the undercooling was increased further, tip splitting occurred more frequently and resulted in an apparent change of the net
dendrite growth directions at undercoolings of more than approximately 5 °C. The final growth directions of the dendrites growing at undercoolings of more than about 5 °C became similar to those of dendrites growing from pure aqueous solutions, i.e. oriented close to \(<410\>\).

Dendrites growing in samples containing Fe₂(SO₄)₃ showed a reversed trend concerning tip splitting and the growth direction of the dendrites with respect to undercooling. At low values of \(\Delta T (\leq 3 \, ^{\circ}\text{C})\) these dendrites have growth directions which are similar to those of dendrites growing in the absence of additives, so close to \(<410\>\). At higher undercoolings the growth directions of these dendrites changed to \(<100\>\) and the angle between the four main stems and their side branches became 90°.

**Dendrite growth**

The results of the measurements of \(v\) versus \(\Delta T\) in samples containing Fe₂(SO₄)₃ are plotted in fig. 3.10. Except for samples containing Fe₂(SO₄)₃ no freely growing \(c\)-dendrites could be observed. The trends of a decreasing \(S\) and an increasing \(v\) at increasing \(\Delta T\), expected theoretically, remain valid in all the samples containing additives. Fig. 3.10 shows that the \(ab\)-dendrites growing in the presence of Fe₂(SO₄)₃ experience a faster growth than the \(c\)-dendrites in these samples, which is opposite to
Fig. 3.10 Growth rate, $v$, of $ab$- and $c$-dendrites growing from an aqueous AN solution containing Fe$_2$(SO$_4$)$_3$, plotted versus the undercooling, $\Delta T$.

the growth of dendrites in samples without additives where the $ab$-dendrites grow slower than the $c$-dendrites. The slope of the line for the $c$-dendrites in fig. 3.10 seems to be somewhat lower than the one for $ab$-dendrites (1.84 ± 0.08 and 1.70 ± 0.23 respectively).

No tip splitting of the $ab$-dendrite tips was observed if the $c$-dendrites grow considerably slower than the $ab$-dendrites. This occurs in the case of CuSO$_4$, in the case of permalene at low $\Delta T$, and probably in the case of Fe$_2$(SO$_4$)$_3$ at high $\Delta T$, although it is questionable whether the difference between the slopes of the lines in fig. 3.10 is significant. Differences between the growth rates of $ab$-dendrites, $v_{ab}$, and of $c$-dendrites, $v_{c}$, lead to changes of the shape of $ab$-dendrite tips, which causes changes of the diffusion profile around these tips. It is not unlikely that small changes of the diffusion profile affect the stability of the $<100>$ growth directions since the stability of dendrite tips is highly sensitive to changes in the additive or solvent concentrations.

References

Chapter 4

Isothermal coarsening of dendritic ammonium nitrate phase II: the influence of additives *)

Abstract

Isothermal holding of dendritic ammonium nitrate phase II leads to a thickening of the dendrite branches via a mechanism which resembles Ostwald ripening. Water content and additives have no significant effect on the kinetic parameters of the isothermal coarsening process which can be described by an empirical power law. The effect of the volume fraction of solid on the kinetic parameters described in literature is not confirmed. In the absence of additives detachment of the dendrite side branches occurs which also happens in the presence of e.g. alkyl sulphonates. In the presence of additives like Al(NO₃)₃ or NaNO₃ coalescence of the dendrite branches occurs. In the case of isothermal coarsening of large dendrites this coalescence results in the formation of crystallites with a diameter up to several thousands of microns.

4.1 Introduction

Ammonium nitrate (AN) fertilizer products is generally granulated from highly concentrated aqueous AN solution (approximately 5 wt% or less water). At water concentrations up to 4.5 wt% the crystallization temperature, $T_{cr}$, of AN decreases from 170 °C (pure AN) to 125 °C. In this temperature region phase I of AN is stable. AN(II) is stable between 125 and 84 °C and crystallizes at water concentrations of 4.5 to 12 wt% respectively [1]. In situ microscopic observations show that both AN(I) and AN(II) crystallize dendritically (chapters 2 and 3).

Most of the granulation processes comprise layer wise crystallization from the aqueous solution on seed particles. Newly formed layers initially consist of dendritically crystallized AN while a saturated AN solution remains trapped between the dendrite branches. The water from this saturated solution is next evaporated in a drying step at approximately 90 °C. The crystallization and drying steps are repeated until the desired granule size is reached.

AN fertilizer has to meet quality requirements concerning detonation resistance after storage and transport. The mechanical quality of AN products may deteriorate due to the phase transition III-IV occurring at 32 °C which causes a volume change of approximately 4 %. In order to diminish the detrimental effects of this transition, additives are applied. These additives, like metal nitrates and sulphates as well as surface active agents, influence the solidification of AN phase I and II which determines the final phase IV structure of the granules. Additives also affect the kinetics of the III-IV transition.

The solidification of AN can be subdivided into nucleation, growth, and coarsening of AN phase I and II dendrites, which determine the final size, shape, and orientation of the crystal domains in the granules and thus their texture/structure which is of importance for the mechanical strength of the granules.

One of the most important phenomena for the development of the internal granule structure is dendritic coarsening or ripening, which results via thickening of the dendrite branches into either separate crystals or agglomerates. The coarsening occurs during and immediately after the dendritic growth has completed and before all the water is evaporated from the remaining interdendritic solution.

This study describes the effects of water concentration, undercooling, and various additives on the isothermal dendritic coarsening of AN phase II.

4.2 Coarsening

Isothermal coarsening is a micro-scale process taking place in finely divided solid-liquid systems, and comprises the disappearance of regions of the interface with a high
interfacial curvature in favour of those with a low interfacial curvature. Dendritic coarsening occurs in a wide variety of solidification processes and has been studied extensively [2–4].

Experimental observations have demonstrated that dendritic coarsening at low volume fractions of solid, $f_v$, proceeds by detachment of side branches from the dendrites followed by coarsening via an Ostwald ripening mechanism, which leads to the disappearance of smaller particles in favour of larger ones [2,5]. At higher values of $f_v$, the diffusion fields surrounding the particles overlap. This results in an increase of the average particle size by coalescence of the side branches.

Several authors have shown that dendritic coarsening of a variety of materials can be described by similar kinetic laws [5,6]. The average length scale, $\bar{R}$, such as the average particle radius or half of the branch thickness, correlates with the total time, $t$, during which liquid and solid co-exist according to the empirical power law

$$\bar{R} = At^n$$

(4.1)

where $0.25 < n < 0.4$ and $A \approx 10$ if $\bar{R}$ is expressed in micrometers and $t$ in seconds. Dann et al. [5] attributed $n = 0.25$ to Ostwald ripening (low $f_v$) and $n = 0.4$ to coalescence (high $f_v$).

In the classical theory of Ostwald ripening developed by Lifshitz, Slyozov, and Wagner (LSW) [4,7], $n$ equals $\frac{1}{2}$. This theory is derived in the limit of zero $f_v$, assuming that the coarsening is a purely diffusion controlled process. The coarsening kinetics depend on the temperature, $T$, the solute concentration, $C_s$, the surface tension, $\gamma$, and the diffusion coefficient. An extension of the LSW theory by Voorhees and Glicksman takes into account the effect of a non-zero $f_v$ on the Ostwald ripening kinetics [8].

Besides the effect of $f_v$ via the degree of undercooling also the influence of water and additives on the coarsening of AN(II) is investigated here. Water mainly determines the interdendritic solute concentration, $C_{AN}$. Additives, applied in amounts of 1 wt%, are expected to affect the surface tension and might therefore change the coarsening mechanism.

### 4.3 Experimental procedure

In situ measurements of coarsening in AN samples were performed by using a microscope connected to video equipment and an oil thermostated observation cell. The accuracy of the temperature control was better than 0.1 °C. The samples used for the experiments were prepared from a water containing AN melt in which either no or 1 wt% additive was dissolved. After solidification and drying this mixture was ground
and pressed into pellets in order to avoid air bubble formation during the coarsening experiment. Either 5.7 or 9.1 wt% water was added by using a micro-syringe upon inserting a pellet in the observation cell. All the chemicals were p.a. grade.

The crystallization temperature of each sample was determined by melting the sample until just one tiny crystal remained in the solution. The sample was then equilibrated for some minutes at a constant temperature in order to eliminate temperature and concentration gradients.

After determining $T_{cr}$ the sample was completely molten and subsequently cooled to either 10, 20 or 30 °C below its crystallization temperature and kept at that temperature. Video recordings were made at selected time intervals. After the measurement $\bar{R}$ was determined from the video recordings as a function of the isothermal holding time, being maximally 100 min. The coarsening measurements for each sample were performed in threefold.

4.4 Results and discussion

Composition of the samples and the results of the in situ measurements of isothermal coarsening in AN are given in table 4.1.

The microscopic observations showed no obvious changes in the coarsening mechanism in exps. 1 to 4 where no additives were applied. In these experiments a

<table>
<thead>
<tr>
<th>exp. no.</th>
<th>$H_2O$ [wt%]</th>
<th>additive$^a$</th>
<th>$T_{cr}$ [°C]</th>
<th>$\Delta T$ [°C]</th>
<th>$C_{AN}$ [wt%]</th>
<th>$f_v$ $^b$</th>
<th>$n$</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.7</td>
<td>-</td>
<td>116.9</td>
<td>10</td>
<td>92.6</td>
<td>0.22</td>
<td>0.29</td>
<td>3.3</td>
</tr>
<tr>
<td>2</td>
<td>5.7</td>
<td>-</td>
<td>116.9</td>
<td>20</td>
<td>90.6</td>
<td>0.38</td>
<td>0.23</td>
<td>4.7</td>
</tr>
<tr>
<td>3</td>
<td>5.7</td>
<td>-</td>
<td>116.9</td>
<td>30</td>
<td>88.4</td>
<td>0.49</td>
<td>0.22</td>
<td>4.8</td>
</tr>
<tr>
<td>4</td>
<td>9.1</td>
<td>-</td>
<td>97.8</td>
<td>10</td>
<td>88.6</td>
<td>0.19</td>
<td>0.25</td>
<td>3.1</td>
</tr>
<tr>
<td>5</td>
<td>5.7 Na$^+$RSO$_3$$^-$$^c$</td>
<td>113.8</td>
<td>20</td>
<td>0.38$^d$</td>
<td>0.25</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5.7 Pb(NO$_3$)$_2$</td>
<td>116.2</td>
<td>20</td>
<td>0.38$^d$</td>
<td>0.24</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5.7 NaNO$_3$</td>
<td>112.7</td>
<td>20</td>
<td>0.38$^d$</td>
<td>0.26</td>
<td>3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5.7 Mg(NO$_3$)$_2$$^-$$^d$6H$_2$O</td>
<td>114.0</td>
<td>20</td>
<td>0.38$^d$</td>
<td>0.20</td>
<td>7.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>5.7 Al(NO$_3$)$_3$$^-$$^d$9H$_2$O</td>
<td>118.7</td>
<td>20</td>
<td>0.38$^d$</td>
<td>0.23</td>
<td>5.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5.7 Al$_2$(SO$_4$)$_3$$^-$$^d$9H$_2$O</td>
<td>118.1</td>
<td>20</td>
<td>0.38$^d$</td>
<td>0.26</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The amount of additive (1 wt%) was calculated on the basis of the anhydrous form.
$^b$ Calculated from the solubility data of the AN-water system [1] assuming that water is not incorporated in the AN crystal lattice.
$^c$ $R$ = alkyl, exact composition unknown.
$^d$ The volume of the additive is negligible with respect to the volume of water and AN, and is supposed to change $f_v$ not considerably compared to cases where no additive is used.
thickening of the dendrite branches occurred within seconds via a mechanism which resembles Ostwald ripening, resulting in the formation of separate, more or less spherical particles. $\bar{R}$ equals the radius of these 'spheres'. The isothermal coarsening curve of exp. 2 is given in fig. 4.1 as a typical result.

The straight lines in the $\bar{R}-t$ plot indicate that the general power law, eq. (4.1), holds for the isothermal coarsening of AN(II) containing 5.7 to 9.1 wt% water. The slope of the lines in the $\bar{R}-t$ plot equals $n$ in eq. (4.1). From the fact that $n$ is always less than $\frac{3}{2}$ in the experiments described here it follows that the LSW theory does not hold for these experiments.

The coarsening mechanism, which determines the value of $n$, is supposed to be mainly influenced by $f_\nu$, $\gamma$, and $C_{AN}$. In literature most attention is paid to the influence of $f_\nu$ on the coarsening mechanism.

In exps. 1 to 3, where $f_\nu$ increases and $C_{AN}$ decreases with increasing $\Delta T$, the value of $n$ decreases. The change in $C_{AN}$ of only 4.5 % is too small for a reasonable change in $\gamma$. Therefore, these small variations in $C_{AN}$ and/or $\gamma$ are expected to be of minor influence on $n$. According to literature $n$ should increase with increasing $f_\nu$ [5]. Although the change in $n$ is hardly significant, taking into account the experimental error, it certainly does not increase with $f_\nu$. The results of exps. 3 and 4, where $f_\nu$ is the only significantly changing parameter, show the same trend.

Some of the additives contain crystal water. In these cases the net water content is increased to maximally 6.3 wt%. Besides, some additives reacted with AN and/or water during the experiments and formed other hydrates or double salts as could be determined by X-ray diffraction measurements at room temperature. Both facts resulted
in only minor changes of $C_{AN}$ and $f_w$. $\gamma$ might be affected to a greater extent by the additives, although this could not be quantified. The results of exps. 5 to 10 are therefore hard to explain quantitatively.

The coarsening mechanism is affected by some of the additives. For Pb(NO$_3$)$_2$ and Na$^+$RSO$_3^-$ the coarsening proceeded similar to coarsening in samples where no additives were applied, resulting in the formation of separate, more or less spherical particles (see fig. 4.2). In the case of NaNO$_3$, Mg(NO$_3$)$_2$, Al(NO$_3$)$_3$, and Al$_2$(SO$_4$)$_3$ the coarsening seemed to proceed via two mechanisms: parallel to the coarsening

**Fig. 4.2** Successive photographs of isothermal dendritic coarsening in a sample containing Na$^+$RSO$_3^-$ after 1, 5, 20, and 100 min, respectively. Coarsening results in the formation of separate, more or less spherical particles, which are finally partly fallen to the bottom of the observation cell. (Bar indicates 50 $\mu$m.)

**Fig. 4.3** Successive photographs of isothermal dendritic coarsening in a sample containing Al(NO$_3$)$_3$ after 1, 5, 20, and 100 min, respectively. Parallel to the coarsening via a mechanism resembling Ostwald ripening also coalescence of the branches occurred. (Bar indicates 50 $\mu$m.)
proceeding by a mechanism resembling Ostwald ripening also coalescence of the branches occurs. This leads, in the case of coarsening of large dendrites, to the formation of large grains (with a diameter of several thousands of microns) in which the individual 'branches' can still be recognized (Fig. 4.3). In these cases \( \bar{R} \) equals half of the average thickness of the 'branches'. The coalescence process is important for the final hardness of AN granules (Chapter 7).

### 4.5 Conclusions

- The kinetics of the isothermal coarsening of AN(II) dendrites in samples containing up to 9.1 wt% water, which can be described by an empirical power law, are not significantly influenced by the overall water content in the samples or by additives.
- The effect of the volume fraction of solid on the kinetic parameters described in literature is not confirmed.
- Some additives affect the coarsening mechanism. Besides coarsening proceeding via a mechanism which resembles Ostwald ripening also coalescence may occur depending on the additive applied.

### References

Chapter 5

The III-IV phase transition in ammonium nitrate: mechanisms *)

Abstract

The polymorphic phase transition III-IV in ammonium nitrate is well known to be catalyzed by water. Owing to this predominant role of water it has been suggested in literature that this transition proceeds via dissolution and crystallization occurring at a disordered phase boundary or even in a 'bulk' layer of solution.

A systematic study on the similarity between projections of specific \((hkl)_{III}\) and \((hkl)_{IV}\) faces predicts various orientation relationships between both phases. Several of these \((hkl)\) faces and orientation relationships are confirmed by microscopic observations of the III-IV and IV-III transitions, by texture goniometry results, as well as by microscopic observations reported in literature. The combined experimental and theoretical results substantiate the existence of a solid-solid transition mechanism especially for single crystals.

The breakage of hydrogen bonds required for the ammonium and nitrate ions to be rotated and displaced during the solid-solid phase transition, is facilitated by solvent molecules which are able to form hydrogen bridges. This suggests that, for the proposed solid-solid mechanism, such solvent molecules play a catalytic role.

5.1 Introduction

Ammonium nitrate, NH₄NO₃ (AN), is a base chemical for fertilizers and explosives. It develops in at least five polymorphic crystal phases at atmospheric pressure. The transition temperatures in pure AN are:

\[
\begin{align*}
\text{melt at } & 170 \, ^\circ\text{C} \\
& 125 \, ^\circ\text{C} \\
& 84 \, ^\circ\text{C} \\
& 32 \, ^\circ\text{C} \\
& -18 \, ^\circ\text{C} \\
\end{align*}
\]

Besides the (stable) phase transitions II-III and III-IV at 84 °C and 32 °C respectively, the metastable phase transition II-IV can occur at temperatures of 50–55 °C. In the sequence from phase I to phase V the ammonium and nitrate ions have less freedom of movement and hydrogen bridges become more important. The crystal structures of all these modifications revert to the CsCl-pattern of arrangement, except phase III which has a completely different, 'loose' packing mode of molecules in a crystal lattice that resembles NiAs [1]. The crystallographic data of the phases I to V [2–6] are given in table 5.1.

The stable phase transitions I-II and IV-V as well as the metastable II-IV transition require relatively little distortions of the crystal lattice. The transitions of phase II and phase IV into phase III, however, require more drastic changes of the crystal lattices.

The occurrence of the phase transitions II-III and III-IV strongly depends on conditions such as the presence of moisture, and the history of the crystals, as well as on the presence of impurities in the crystals [7–9]. In very dry AN the II-III and III-IV transitions do not occur, but instead the transition II-IV takes place.

Owing to the predominant role played by even trace amounts of water, Brown and McLaren [10] suggested in 1962 that the III-IV transition might proceed via dissolution and crystallization occurring at a disordered phase boundary. Recently

<table>
<thead>
<tr>
<th>Phase</th>
<th>Symmetry</th>
<th>space group</th>
<th>Z</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃(II) [2]</td>
<td>Cubic</td>
<td>Pm3m</td>
<td>1</td>
<td>4.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄NO₃(III) [3]</td>
<td>Tetragonal</td>
<td>P42₁m</td>
<td>2</td>
<td>5.7193</td>
<td>4.9326</td>
<td></td>
</tr>
<tr>
<td>NH₄NO₃(III) [4]</td>
<td>Orthorhombic</td>
<td>Pnma</td>
<td>4</td>
<td>7.6772</td>
<td>5.8208</td>
<td>7.1396</td>
</tr>
<tr>
<td>NH₄NO₃(IV) [5]</td>
<td>Orthorhombic</td>
<td>Pmnm</td>
<td>2</td>
<td>5.745</td>
<td>5.438</td>
<td>4.942</td>
</tr>
<tr>
<td>ND₄NO₃(V) [6]</td>
<td>Orthorhombic</td>
<td>Pccn</td>
<td>8</td>
<td>7.9804</td>
<td>8.0027</td>
<td>9.8099</td>
</tr>
</tbody>
</table>

*Cell parameters for AN(III) at room temperature containing 5 % KNO₃.*
Davey et al. [11,12] also concluded that the IV–III transition proceeds via this mechanism of dissolution and crystallisation in a 'bulk' layer of solution at the interface under circumstances where phase IV crystals transform while submerged in an aqueous AN solution. Other authors, however, more or less contradict such a solvent mediated process by reporting that the orientation relations between the crystallographic axes in the II–III and III–IV transitions are not random although various rather complex relationships can develop [13,14].

This study compiles previous in situ microscopic observations of both the III–IV and IV–III transitions, observed in single crystals and in pressed pellets under various circumstances. Supplementary in situ microscopic experiments were performed with samples having a history which resembles that of AN product granules more closely. The observations can be understood from the results of a study on the similarity between projections of specific phase III and phase IV crystal faces and are compared to the results from texture goniometry experiments in order to elucidate mechanisms of these phase transitions.

5.2 Previous observations

The IV–III transition in single crystals (chapter 6, [15])

In dry single crystals the phase transition IV–III occurred at temperatures between 32 and 45 °C upon the introduction of moistened air with a relative humidity of more than about 10 %. During this transition an irregular front composed of flat parts developed between the phases IV and III as is schematically drawn in fig. 5.1. The transition always started at the surface of the crystals. Seconds after passage of the transition front, cracks appeared in the transformed part of the crystal which then lost

![Fig. 5.1 Schematic drawing of a dry AN(IV) crystal transforming into phase III. The bright parts of the crystal are phase III. The thickness of the crystal is typically 1 – 2 mm.](image)
its mechanical strength. Upon cooling of the crystal below 32 °C the reverse transition III-IV occurred and more cracks appeared.

The time lapse before the IV-III transition started, shortened and the front propagation velocity during the transition increased with increasing relative humidity. When dry air was led over a transforming crystal, the transition stopped abruptly. When the air was moistened again, the transition continued immediately. The existence of a 'bulk' layer of saturated AN solution at the interphase therefore seems unlikely, because in that case such abrupt changes of the front propagation upon changes of the relative humidity are unlikely.

When AN(IV) single crystals were submerged in a solution which was saturated with respect to phase III at temperatures above 32 °C, the crystals started to dissolve due to the higher solubility of AN(IV). No phase III nuclei could develop at the dissolving surface of the phase IV crystals. The IV-III transition only started when a phase IV crystal was touched by a phase III crystal. In most cases the phase III crystal even grew together with the transforming crystal at their attachment point. The IV-III transition in these submerged AN(IV) single crystals proceeded by the propagation of one or more flat transition fronts.

The IV-III transition in dry pressed pellets [15]

During the phase transition IV-III in dry pellets which were pressed from AN

---

Fig. 5.2 Schematic drawings of AN needle crystals during the phase transition III-IV. a: A phase III crystal in a saturated solution which transforms from two sides on into phase IV, on the left side in a regular and on the right side in an irregular way. b: At further undercooling phase IV needles grew parallel to the transition front at an angle of 67° ± 5° with respect to the original phase III needle crystal. c: Observed orientations of the transition front during the III-IV transition in those cases where transparent phase IV crystals were formed. d: The newly formed phase III part often grew at an angle, θ, of a few degrees with respect to the original phase III needle crystal.
powder the transition front moved across the crystallites in the pellet, ignoring the boundaries of these crystallites. The domains of the new phase, formed by the transition appeared to be initially more or less rounded which means that the front propagation velocity in all directions is similar at constant temperature and relative humidity. Each newly formed domain has a specific crystallographic orientation depending on the orientation of the nucleus. Within these domains the boundaries of the original phase IV crystallites could still be recognized as vague ghost lines. The time lapse before the transition started and the front propagation velocity during the transition in these pellets depend similarly on the relative humidity as in the dry single crystals.

The III–IV transition in crystals submerged in solution (chapter 6)

The phase transition III–IV was observed in thin AN(III) needle crystals with a thickness of less than 300 μm submerged in a saturated solution. This transition always started at one or both ends of the needle or at a point where a transformed part of another crystal touched the needle. The interphase boundary in these thin crystals appeared to be a very flat front, which maintained its orientation during its propagation through the needle crystal.

The III–IV transition proceeded in two distinct ways as depicted in fig. 5.2a. In one case a transparent phase IV crystal with the same shape grew from a transparent phase III needle. In the other case the formed phase IV was fractured into thin, flat crystallites during the transition which were grown together. When from the phase III needle crystal a transparent phase IV crystal was formed, the transition was sometimes observed to be 'reversible': when the temperature was increased above 32 °C again a transparent phase III crystal was formed with the same shape. The orientation of the interface did not change when the direction of the transition inverted.

It has been observed several times that the phase III part separated from the phase IV part of the needle at the interface. In those cases the transition stopped. Davey et al. also observed this phenomenon during the IV–III transition [12].

At further cooling, needles grew into the solution from the newly formed phase IV crystal as depicted in fig. 5.2b. It was observed that the longitudinal axis of these phase IV needles was parallel to the interface during the phase transition.

Further study of the video recordings and photographs of the phase transition III–IV in AN(III) needle crystals gave rise to four additional results which were not reported in chapter 6.

The angle between the longitudinal axes of the newly formed phase IV needles and of the original phase III needle turned out to be 67° ± 5° as depicted in fig. 5.2b.

At least two transition front orientations were observed during the III–IV transition in those cases where transparent phase IV crystals were formed. These orientations are schematically drawn in fig. 5.2c.

In various cases it could be observed that the phase IV crystal formed by the
III-IV transition grew at an angle, $\Theta$, of a few degrees with respect to the phase III needle from which it grew, as depicted in fig. 5.2d. This angle was less than $5^\circ$.

Fig. 5.3 The phase transition III-IV occurring in phase III needle crystals. a (top): Video print of a typical transition front in a (hollow) needle crystal on which steps (indicated by arrows) can be observed. b (bottom): Schematic drawing which summarizes the possible orientations of the steps which were observed the most often on the interface during the transition. The indexing of the $(hkl)$ planes is explained in section 5.5.
In several cases straight steps oriented along specific directions were noticed on the interface during the III–IV transition. It could clearly be seen that the growth of phase IV at low front propagation velocities proceeded by the formation of new layers spreading across the interface as shown in figs. 5.3a and b.

5.3 Experimental procedures

In situ microscopy

Supplementary in situ microscopic observations were performed with samples prepared from pure AN crystals which were ground and well dried. The obtained dry powder was pressed into pellets in order to avoid air bubble formation at dissolving the sample. The pellets were approximately 0.3 mm thick. 5.7 wt% water was added with a micro-syringe just before inserting a pellet in an observation cell which is described in chapter 2. Evaporation of the water was prevented by sealing the observation cell. The sample was then dissolved by raising the temperature to approximately 120 °C, and subsequently cooled to 90 °C in order to crystallize AN(II). The obtained sample consisted of AN(II) dendrites with a fine structure, and a saturated AN solution, trapped between the dendrite branches. At holding the sample for 50 minutes at the same temperature, coarsening of the fine dendritic AN(II) occurred resulting in the formation of a coarse solid structure (chapter 4). The average thickness of the final branches was approximately 50 μm. This sample was then cooled to a temperature below 50 °C in order to observe the III–IV phase transitions.

Texture goniometry

Samples used for the texture goniometry experiments were prepared by pouring a highly concentrated aqueous AN solution (approximately 4.5 wt% water) in a mould which consisted of 5 mm deep and 8 mm wide holes. After solidification and drying at 90 °C to less then 0.25 wt% water, the obtained tablets were cooled to room temperature and conditioned under moistened air with a relative humidity of approximately 60%. The sample was then heated to 45 °C for approximately 1 hour and subsequently cooled to room temperature in order to obtain large phase IV domains in the sample. A small particle with a diameter of less than 1 mm was separated from a tablet and mounted in a random position with gummed tape on a piece of Mylar foil in the sample holder. This procedure insured effective isolation of the AN fragment from the ambient humidity, while still allowing X-ray transmission for diffraction.

The experimental conditions for the experiments were the following. Cu Kα radiation was generated using a STOE rotating anode generator. The setup was operated at 40 kV and low current of 25 mA, in order to reduce the risk of radiation damage
of the sample. The sample was placed in the texture cradle mounted on a Siemens D500 goniometer. The collimator was chosen such that the spot size of the X-ray beam was larger than the AN sample. The width of the receiving slit, which determines the width of the detected diffraction line, was 0.15°. The diffracted intensity was measured by a proportional counter. At a fixed diffraction angle continuous scans were made along circles of the pole figure. The distance of consecutive circles was 2.5°. The recording time for a single pole figure was approximately 1 hour, limited by the movements of the separators of the goniometer. Only reflection pole figures were measured, without the outer rings, which can only be detected in a transmission experiment.

After measuring of the \{001\}_{IV}, \{110\}_{IV}, and \{111\}_{IV} pole figures the enclosure containing the generator and the goniometer, was heated to approximately 45 °C in order to subject the sample to the phase transition IV–III. 45 minutes after raising the temperature above 32 °C the \{202\}_{III}, \{201\}_{III}, \{011\}_{III}, and \{111\}_{III} pole figures were determined while maintaining the temperature within the texture goniometer at 40–45 °C. After cooling to room temperature, again the \{001\}_{IV}, \{110\}_{IV}, and \{111\}_{IV} pole figures were measured. This type of experiment was performed three times using three separate samples. For one of these samples the temperature cycle and corresponding goniometry measurements were repeated a second time.

5.4 Results and discussion

In situ microscopy

In situ microscopic observations showed that in the samples, which were originally grown as dendritic AN(II), the IV–III transition proceeded with a rather rough and rounded interface which moved across crystallites of which the sample consisted, ignoring the boundaries between these crystallites. This is similar to the IV–III transition occurring in pressed pellets as described in section 5.2. Each newly formed phase III domain had its own orientation and could be millimetres wide.

The III–IV transition occurred by the development of needle-like phase IV domains as shown in fig. 5.4. The crystallographic orientation of these domains could not be determined. The propagation of the flat interfaces of these phase IV domains proceeded via macrosteps, in this way consuming layer wise the phase III domains. This thus resembled the growth of phase IV during the III–IV transition in phase III needles as shown in fig. 5.3.

Texture goniometry

Fig. 5.5 shows the pole figures obtained from the goniometry experiment during
which the temperature cycle was repeated a second time. The pole figures show that the original sample was polycrystalline, having approximately 10 different crystallographic orientations (fig. 5.5a). After subjecting the sample to the IV–III transition two main crystallographic directions were found, which were almost parallel (fig. 5.5b). This reduction in number of crystallographic directions is in line with the observation that the transition front during the IV–III transition in polycrystalline samples moved across crystallites of which the sample consisted, ignoring the grain boundaries.

When the sample was transformed back into phase IV by cooling to room temperature, the two main, almost parallel crystallographic orientations remained (fig. 5.5a). The poles measured during the second temperature cycle between room temperature and 45 °C practically coincided with those measured during the first cycle. Upon cooling the sample to room temperature after the second temperature cycle, again almost identical pole figures were measured as after the first cycle.

Since the sample was conditioned in a well moistened atmosphere it is assumed that the sample entirely transformed during all transitions. The fact that the crystallographic orientations during and after the first thermal cycle return during and after the second cycle can probably be attributed to the presence of 'nuclei' of the instable phase which remain in the sample after a transition into a stable phase [9,13].

The two other texture goniometry experiments also show that the number of crystallographic orientations in the initially polycrystalline samples was reduced to one or two after thermal cycling.
5.5 Matching faces during the III-IV phase transition

5.5.1 Possible mechanisms of the III-IV phase transition

The observations of the phase transitions III-IV in the various samples described above do not clearly exclude either one of the possible transition mechanisms: (a) dissolution and crystallization at a disordered phase boundary containing solvent molecules or in a solution layer, or (b) a solid-solid mechanism continuously catalyzed from the surface of the crystals by solvent molecules.
The observations of the IV-III transition in pressed pellets and in samples prepared from originally dendritic phase II show that during this transition the irregular interface between the phases moves across phase IV crystallites which are randomly oriented while each phase III domain, which stretches out over many of the former phase IV crystallites, has a single orientation. This suggests that in these samples this transition mainly proceeds via dissolution and crystallization. So, for these cases no specific orientation relationships are expected.

The fact that the interfaces during both the III-IV and IV-III transitions in single crystals are flat and that in some cases the transition is reversible, indicates either that the crystallization of the stable phase is the rate determining step during the dissolution-crystallization process [12] or that the transitions proceed via a solid-solid mechanism. For the latter case the development of cracks in thin transforming crystals with flat transition fronts can be better understood. The change of the molecular volume during the transition would not lead to lattice strain if the transition occurs via dissolution and crystallization in a solution layer because the crystal parts at both sides of the transition front can freely shift with respect to each other along this solution layer. In several cases, however, severe fracturing of the originally transparent phase into thin, flat crystallites was observed during the III-IV transition, which favours the idea of a solid-solid transition mechanism. The existence of specific orientation relationships between the crystallographic axes in the III-IV transition, occurring in single crystals, as reported in literature [13,14], also points at such a solid-solid mechanism.

If the III-IV transitions proceeds via such a solid-solid mechanism, one or more crystal faces of both phase III and phase IV should match. To investigate this possibility projections of various faces of both phase III and phase IV were generated using CHEM-X, a molecular modelling computer program*).

5.5.2 Determination of orientation relationships

If solid-solid transitions occur then, according to figs. 5.2c and 5.3b, different orientation relationships should be possible. Such relationships comprise the transition of phase III faces into phase IV faces, and can be described by transition matrices. These matrices are considered as rotation matrices \( R_{\text{III-IV}} \) which fix the (possible) orientation relations when transforming phase III into phase IV.

From the observation that the phase transition III-IV proceeds via flat fronts it is assumed that these transition fronts are represented by low index faces of phase III and phase IV. Low index faces are normally found on single crystals. Potential faces are therefore selected from the observations of the III-IV transition occurring in single crystals and the morphological crystal faces of AN(III) [16] and AN(IV) needle

*) Developed and distributed by Chemical Design Ltd, Oxford, UK.
Table 5.2 Morphological crystal faces of AN(III) needle crystals [16] and AN(IV) needle crystals [17].

<table>
<thead>
<tr>
<th>phase</th>
<th>prismatic faces</th>
<th>pyramidal faces</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN(III)</td>
<td>{101}, {200}, {002}</td>
<td>{111}, {011}</td>
</tr>
<tr>
<td>AN(IV)</td>
<td>{011}</td>
<td>{101}, {110}, {111}, {120}</td>
</tr>
</tbody>
</table>

crystals [17] given in table 5.2. The space groups of AN(III) and AN(IV) are *Pnma* and *Pmmn* respectively. Both space groups belong to the point group *mmm*. This implies that the \(hk\ell\) forms comprise all possible combinations of \(\pm h, \pm k,\) and \(\pm l\).

The following criteria for matching between faces of both phases are used. They will be explained with the help of figs. 5.6a-d. The boxes drawn in these figures represent repeating units. The orientation and length of their edges correspond to specific vectors as indicated in the figures.

1. The relative changes of the lengths of matching vectors in the corresponding faces should not exceed \(-10\%\), since otherwise lattice strain will be built up which would lead to cracking of the crystals. For phase transitions without cracking the maximum relative change is chosen to be of the order of magnitude of the maximum relative change occurring during the phase transition II-IV, which is 5% \((b_{IV}-a_{III})\) [9,10]. For instance, the relative change in length of the vector \([010]_{III}\) transforming into \([100]_{IV}\) equals 100% \(\times \frac{b_{III}-a_{IV}}{b_{III}} = -1.3\%\) (fig. 5.6a).

2. The deformation of the repeating units within the transforming faces (e.g. from parallelogram to rectangle) should not exceed 5°. This value is chosen arbitrarily. For example, the angle between the vectors \([100]_{III}\) and \([01\bar{1}]_{III}\) (fig. 5.6d) is equal to 90°. The corresponding angle in phase IV (between \([011]_{IV}\) and \([111]_{IV}\)) equals 85.7°. The transition of the \((022)_{III}\) face into \((21\bar{1})_{IV}\), drawn in fig. 5.6d, thus results in a deformation of 4.3°.

3. The side view projections drawn in figs. 5.6b and c show that the repeating units also deform in directions in which the repeating units are stacked. This deformation causes an oblique growth of the stable phase out of the instable one and results in a 'stacking angle'. For phase III (left in fig. 5.6b) the repeating units are stacked perpendicularly to the transforming \((200)_{III}\) face, the stacking angle thus equals 90°. For phase IV the stacking angle is equal to the angle between the transforming face \((011)_{IV}\) and the stacking direction \([011]_{IV}\) (84.5°). The difference between these two stacking angles yields an effective 'growth angle'. This growth angle is related to \(\Theta\) (see fig. 5.2d), for which values less than 5° were observed. Therefore, the growth angle found for possible matching faces should not be too large \((-10°)\).

4. The ions should not have to shuffle too far in directions parallel and perpendicular to the matching faces, i.e. the correspondence between the matching faces should not be too bad. The transition of \((200)_{III}\) into \((011)_{IV}\), for example, drawn in figs. 5.6a-c, requires, besides rotations of the ions, almost no translations: the ammonium ions and
half of the nitrate ions (those in the shaded halves of the boxes drawn in fig. 5.6b) translate over a short distance. The transition of \((022)_{III} \rightarrow (211)_{IV}\), shown in fig. 5.6d, requires much more reshuffling of the ions.

Pairs of faces which match well on the basis of criteria (1), (2) and (3) are given in table 5.3. Two in-plane vectors of phase III transforming into those of phase IV are given in this table as well. A third vector is added to this set for each phase by calculating the cross product of the other two vectors. The three vectors in each phase are (approximately) orthogonal. With the help of the normalized vectors a transition matrix is constructed for each transformation listed in table 5.3. This matrix can be considered as a rotation matrix \(R_{III-IV}\) if the angles between the vectors (assumed to be 90°) are preserved during the transition. The volume change of 3.8 % taking place

<table>
<thead>
<tr>
<th>trans. matrix</th>
<th>matching faces</th>
<th>matching vectors</th>
<th>relative length change(^a)</th>
<th>deformation angle</th>
<th>growth angle</th>
<th>correspondence</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (200)(<em>{III}) \rightarrow (101)(</em>{IV})</td>
<td>[010](<em>{III}) \rightarrow [0(\overline{1})0](</em>{IV}) [001](<em>{III}) \rightarrow [101](</em>{IV})</td>
<td>-6.5 %</td>
<td>0.0°</td>
<td>8.6°</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>B (200)(<em>{III}) \rightarrow (011)(</em>{IV})</td>
<td>[010](<em>{III}) \rightarrow [100](</em>{IV}) [001](<em>{III}) \rightarrow [011](</em>{IV})</td>
<td>-1.3 %</td>
<td>0.0°</td>
<td>5.5°</td>
<td>+ +</td>
<td></td>
</tr>
<tr>
<td>C (200)(<em>{III}) \rightarrow (111)(</em>{IV})</td>
<td>[020](<em>{III}) \rightarrow [112](</em>{IV}) [001](<em>{III}) \rightarrow [110](</em>{IV})</td>
<td>+8.7 %</td>
<td>2.0°</td>
<td>7.2°</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>D (002)(<em>{III}) \rightarrow (101)(</em>{IV})</td>
<td>[010](<em>{III}) \rightarrow [010](</em>{IV}) [100](<em>{III}) \rightarrow [101](</em>{IV})</td>
<td>-6.6 %</td>
<td>0.0°</td>
<td>3.1°</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>E (002)(<em>{III}) \rightarrow (011)(</em>{IV})</td>
<td>[100](<em>{III}) \rightarrow [01(\overline{1})](</em>{IV}) [010](<em>{III}) \rightarrow [100](</em>{IV})</td>
<td>-4.3 %</td>
<td>0.0°</td>
<td>5.5°</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>F (002)(<em>{III}) \rightarrow (111)(</em>{IV})</td>
<td>[100](<em>{III}) \rightarrow [110](</em>{IV}) [020](<em>{III}) \rightarrow [112](</em>{IV})</td>
<td>+3.0 %</td>
<td>2.0°</td>
<td>7.2°</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>G (202)(<em>{III}) \rightarrow (120)(</em>{IV})</td>
<td>[020](<em>{III}) \rightarrow [2(\overline{1})0](</em>{IV}) [101](<em>{III}) \rightarrow [002](</em>{IV})</td>
<td>+9.4 %</td>
<td>0.0°</td>
<td>4.9°</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>H (202)(<em>{III}) \rightarrow (120)(</em>{IV})</td>
<td>[11(\overline{1})](<em>{III}) \rightarrow [2(\overline{1})0](</em>{IV}) [13(\overline{1})](<em>{III}) \rightarrow [004](</em>{IV})</td>
<td>+6.0 %</td>
<td>2.0°</td>
<td>8.6°</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>I (202)(<em>{III}) \rightarrow (202)(</em>{IV})</td>
<td>[010(\overline{1})](<em>{III}) \rightarrow [10(\overline{1})](</em>{IV}) [1(\overline{0})1(\overline{1})](<em>{III}) \rightarrow [020](</em>{IV})</td>
<td>+30 %(^b)</td>
<td>0.0°</td>
<td>9.6°</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>J (011)(<em>{III}) \rightarrow (110)(</em>{IV})</td>
<td>[011(\overline{1})](<em>{III}) \rightarrow [002](</em>{IV}) [100](<em>{III}) \rightarrow [110](</em>{IV})</td>
<td>+7.3 %</td>
<td>0.0°</td>
<td>12.0°</td>
<td>+</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Based on the transition III-IV.
\(^b\) This transition does not satisfy criterion (1) but is in line with the observations described by Tang and Torrie [14], see text. For the reverse transition (IV-III), which was studied by them, relative length changes are found of -23 % and -3.7 %, respectively.
Fig. 5.6 Projections of some matching faces of phase III and phase IV illustrating the criteria (1) to (4) mentioned in section 5.5.2. a: matching faces (200)$_{III}$ and (011)$_{IV}$, drawn as mirror images; b: side view projections of the faces in a along [010]$_{III}$ and [100]$_{IV}$ respectively, drawn at both sides of the transition front; c: side view projections of the faces in a along [001]$_{III}$ and [011]$_{III}$ respectively, drawn at both sides of the transition front.
during the III-IV phase transition is assumed to be negligible and is therefore not accounted for in this approach. Due to these assumptions an error in the results obtained by describing the orientation relationships with rotation matrices is expected to be 10%.

The fact that, according to the experimental observations, more than one transition front occurs, suggests that more than one orientation relationship exist. This does not imply, however, that all of the orientation relationships given in table 5.3 — which are found by comparing the molecule arrangements in specific crystal faces — do occur in real III-IV transitions. Besides, other orientation relationships than those given in table 5.3 might exist as well, although these do not satisfy the criteria given above. A typical example of an orientation relationship which does not satisfy criterion (1) is described by transition matrix I, which will be discussed in the next section.

The rearrangement of ions in the corresponding faces during the transition requires the breakage of various hydrogen bonds. For matching faces with a good correspondence, indicated in table 5.3 by '++' (like (200)$_{\text{III}}$ - (011)$_{\text{IV}}$, fig. 5.6a), the reshuffling of the ions is restricted to only minor displacements and rotations. The conversion of faces which match less well (like (022)$_{\text{III}}$ - (211)$_{\text{IV}}$, fig. 5.6d) requires that ammonium and nitrate ions have to be displaced over much larger distances. For strictly solid-solid transitions it is questionable whether this is possible. The presence of water or other solvent molecules able to form hydrogen bridges, may, however, facilitate the rearrangements required. This is in line with the catalytic action of water in the III-IV transition. The transition front could then be formed by a disordered
boundary layer consisting of ammonium and nitrate ions and solvent molecules, as suggested by Brown and McLaren [10]. The presence of a bulk layer of solution, as assumed by Davey et al. [12], would be unlikely in view of the proposed solid-solid mechanism which implies a greater restriction than just a set of parallel faces, namely the requirement of matching of faces.

5.5.3 Comparison of theoretical results with microscopic observations

In situ microscopic observations have shown that during the III–IV transition sometimes needles grew into the solution from the newly formed phase IV, as depicted in fig. 5.2b. This suggests that the interface is formed by the \{011\}$_{IV}$ prismatic faces of the AN(IV) needle, although this could not be confirmed by the microscopic observation. Since the interface during the transition is observed to be not parallel to the longitudinal axis of the original AN(III) needle crystal (the b$_{III}$-axis), the interface cannot be either \{101\}$_{III}$, \{200\}$_{III}$ or \{002\}$_{III}$, which are the prismatic faces of the AN(III) needle. Other possibilities taken from table 5.2 would therefore be that the matching faces of phase III are \{111\}$_{III}$ or \{011\}$_{III}$, the pyramidal faces of the AN(III) needle. So \{011\}$_{IV}$ should correspond to \{111\}$_{III}$ and/or \{011\}$_{III}$ in this case. No correspondence, however, could be found between the projections of these faces.

The same observations show that the new phase IV needles (running out of the transforming phase III crystal) and the phase III needle subdivide at an angle of 67° ± 5°. By applying the inverse rotation matrices $R_{IV-II} = R_{III-IV}^{-1}$ to the [100]$_{IV}$ longitudinal axis of the phase IV needle, various phase III vectors result. The angles between these vectors and the [010]$_{III}$ needle axis of phase III can be compared with the observed angle of 67° ± 5°. According to this criterion, the transition matrices C, F and H are possible candidates, because these yield angles of 63°, 64° and 65° respectively.

Several other observations have shown the development of straight steps on the interface during the III–IV transition, which were oriented along specific directions, as depicted in fig. 5.3b. Since the longitudinal axis of phase III needles is oriented along [010]$_{III}$ and the prismatic faces of these needles are \{101\}$_{III}$ faces, two coordination systems are possible in this figure, the one with the a$_{III}$-axis and the other with the c$_{III}$-axis lying in the plane of the paper. The transition interface is estimated to be either \{220\}$_{III}$ or \{011\}$_{III}$ depending on which of the two coordination systems is chosen. \{220\}$_{III}$ has a lower morphological importance than \{011\}$_{III}$ and does not occur on the AN(III) needle [16]. \{011\}$_{III}$ is therefore more likely to form the interface and the coordination system for phase III in fig. 5.3b, with the a$_{III}$-axis lying in the plane of the paper, is chosen to illustrate the transformation.

Four main orientations of the steps were observed on this transition front. The orientation occurring the most often, was parallel to one of the diagonals of the
interface parallelogram, being $[01\bar{1}]_{\text{III}}$ in this system. Low index faces, other than $(011)_{\text{III}}$ containing this orientation are either $(200)_{\text{III}}$ or $(111)_{\text{III}}$. Two other step directions, $(10\bar{1})_{\text{III}}$ and $(10\bar{1})_{\text{III}}$, were observed parallel to the prismatic faces of the AN(III) needle crystal. The remaining step was found to be oriented along a direction between $[100]_{\text{III}}$ and $[\bar{1}1\bar{1}]_{\text{III}}$, most likely being $[2\bar{1}1]_{\text{III}}$, which lies in $(\bar{1}1\bar{1})_{\text{III}}$. Each of these five faces is found to transform into stable faces of phase IV via a transition described by matrix $B$ and are given in table 5.4. Other faces of phase III might match faces of phase IV as well although they were not observed in these experiments.

The conversion by matrix $B$ of the $(011)_{\text{III}}$ transition front results in the face $(2\bar{1}1)_{\text{IV}}$ (table 5.4). This face is morphologically not stable. Combined with the fact that the transition of the interface would require a lot of reshuffling of the ions, this explains why this transition proceeds via macrosteps, just like the growth of faceted crystals. The step sides oriented along faces which match best transform faster and occur relatively more often than those which match worse. The worst matching faces transform the slowest and become large (e.g. $(011)_{\text{III}}$).

If the transition front is formed by $(22\bar{0})_{\text{III}}$ instead of $(011)_{\text{III}}$ the other possible coordination system, with the $c_{\text{III}}$-axis in the plane of the paper, has to be chosen in fig. 5.3b. The step side which is indicated in this figure as $(200)_{\text{III}}$ is in that case $(00\bar{2})_{\text{III}}$ and the transition front transforms via matrix $B$ into $(2\bar{1}1)_{\text{IV}}$, which is also not a morphologically stable face (see table 5.4).

Because of the correspondence between matrices $B$ and $E$ an equivalent analysis of the compiled observations depicted in fig. 5.3b can be given, but now on the basis of matrix $E$. Matching faces described by this matrix are given in table 5.5. Also in this case two different settings of the coordination system are possible. On the basis of criteria (1)–(4) it can not be decided which of the two matrices $B$ and $E$ will be most likely.

Tang and Torrie [14] have found orientation relationships between the phases III and IV by polarization microscopy in single crystals which were subjected to the III-IV transition. They observed that $b_{\text{III}}$*) lies in the principal plane containing $a_{\text{IV}}$ and $c_{\text{IV}}$ and is inclined at an angle of $45^\circ \pm 5^\circ$ to the $c_{\text{IV}}$ axis. $a_{\text{III}}$ was found to meet $b_{\text{IV}}$ at an angle of $15^\circ$, $30^\circ$, $50^\circ$, or $75^\circ$ for different domains within the sample. This observation is in line with a solid-solid transition via the faces $\{2\bar{0}2\}_{\text{III}}$–$\{2\bar{0}2\}_{\text{IV}}$ (transition matrix I in table 5.3). According to this transition matrix the angle between $a_{\text{III}}$ and $b_{\text{IV}}$ should be $43^\circ$. In view of the errors in the results of Tang and Torrie as well as in the results presented here, the angle of $43^\circ$ matches the $50^\circ$ angle, reported by them, most closely. The other angles may correspond to other transition matrices which were not found in this study.

*) Note that in ref. [14] the crystallographic axes of phase III are interchanged with respect to those used here: $a_{\text{III}}$, $b_{\text{III}}$, and $c_{\text{III}}$ in ref. [14] are transposed to $c_{\text{III}}$, $a_{\text{III}}$, and $b_{\text{III}}$ respectively.
Table 5.4 Matching faces which can be described by transition matrix B.

<table>
<thead>
<tr>
<th>matching faces</th>
<th>matching vectors</th>
<th>relative length change</th>
<th>deformation</th>
<th>growth angle</th>
<th>correspondence</th>
</tr>
</thead>
<tbody>
<tr>
<td>(200)<em>{III} - (011)</em>{IV}</td>
<td>[010]<em>{III} - [100]</em>{IV}, [001]<em>{III} - [011]</em>{IV}</td>
<td>-1.3 %</td>
<td>0.0°</td>
<td>5.5°</td>
<td>++</td>
</tr>
<tr>
<td>(002)<em>{III} - (011)</em>{IV}</td>
<td>[100]<em>{III} - [011]</em>{IV}, [010]<em>{III} - [100]</em>{IV}</td>
<td>-4.3 %</td>
<td>0.0°</td>
<td>5.5°</td>
<td>-</td>
</tr>
<tr>
<td>(202)<em>{III} - (020)</em>{IV}</td>
<td>[101]<em>{III} - [002]</em>{IV}, [010]<em>{III} - [100]</em>{IV}</td>
<td>-5.7 %</td>
<td>0.0°</td>
<td>4.2°</td>
<td>+/-</td>
</tr>
<tr>
<td>(202)<em>{III} - (002)</em>{IV}</td>
<td>[101]<em>{III} - [020]</em>{IV}, [010]<em>{III} - [100]</em>{IV}</td>
<td>+3.8 %</td>
<td>0.0°</td>
<td>4.2°</td>
<td>+/-</td>
</tr>
<tr>
<td>(220)<em>{III} - (211)</em>{IV}</td>
<td>[001]<em>{III} - [011]</em>{IV}, [110]<em>{III} - [111]</em>{IV}</td>
<td>+2.9 %</td>
<td>4.3°</td>
<td>5.5°</td>
<td>-</td>
</tr>
<tr>
<td>(022)<em>{III} - (211)</em>{IV}</td>
<td>[100]<em>{III} - [011]</em>{IV}, [011]<em>{III} - [111]</em>{IV}</td>
<td>-4.3 %</td>
<td>4.3°</td>
<td>5.5°</td>
<td>-</td>
</tr>
<tr>
<td>(111)<em>{III} - (110)</em>{IV}</td>
<td>[121]<em>{III} - [220]</em>{IV}, [101]<em>{III} - [002]</em>{IV}</td>
<td>+1.3 %</td>
<td>2.8°</td>
<td>10.5°</td>
<td>-</td>
</tr>
<tr>
<td>(111)<em>{III} - (101)</em>{IV}</td>
<td>[121]<em>{III} - [202]</em>{IV}, [101]<em>{III} - [020]</em>{IV}</td>
<td>-3.3 %</td>
<td>2.8°</td>
<td>5.7°</td>
<td>-</td>
</tr>
</tbody>
</table>

*a Based on the transition III - IV.
*b Although these phase IV faces do not normally occur on AN(IV) needle crystals, and are therefore not included in table 5.2, they have been observed sometimes on crystals with shapes differing from needle shapes [17].

The transition described by matrix I requires relative changes in the lengths of the matching vectors of +30 and +3.8 % (see table 5.3), the former of which largely exceeds the maximum length change given by criterion (1). For a pure solid-solid transition such a change in length would give rise to severe lattice strain, probably leading to the formation of cracks in the crystal, which was observed by Tang and Torrie.

Several times severe fracturing of crystals as a result of the phase transition III - IV was observed in this study while the transition proceeded via a flat transition front. This also indicates that solid-solid transitions may occur causing relatively large changes of the lengths of matching vectors.

No experimental evidence was found for the orientation relationships described by the matrices A, G and J.
Table 5.5 Matching faces which can be described by transition matrix E.

<table>
<thead>
<tr>
<th>matching faces</th>
<th>matching vectors</th>
<th>relative length change&lt;sup&gt;a&lt;/sup&gt;</th>
<th>deformation</th>
<th>growth angle</th>
<th>correspondence</th>
</tr>
</thead>
<tbody>
<tr>
<td>(200)&lt;sub&gt;III&lt;/sub&gt;—(011)&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>[010]&lt;sub&gt;III&lt;/sub&gt;—[100]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>-1.3 %</td>
<td>0.0°</td>
<td>5.5°</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td>[001]&lt;sub&gt;III&lt;/sub&gt;—[011]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>+2.9 %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(002)&lt;sub&gt;III&lt;/sub&gt;—(011)&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>[100]&lt;sub&gt;III&lt;/sub&gt;—[011]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>-4.3 %</td>
<td>0.0°</td>
<td>5.5°</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>[010]&lt;sub&gt;III&lt;/sub&gt;—[100]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>-1.3 %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(202)&lt;sub&gt;III&lt;/sub&gt;—(002)&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>[101]&lt;sub&gt;III&lt;/sub&gt;—[020]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>+3.8 %</td>
<td>0.0°</td>
<td>4.2°</td>
<td>+/–</td>
</tr>
<tr>
<td></td>
<td>[010]&lt;sub&gt;III&lt;/sub&gt;—[100]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>-1.3 %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(202)&lt;sub&gt;III&lt;/sub&gt;—(020)&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>[101]&lt;sub&gt;III&lt;/sub&gt;—[002]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>-5.7 %</td>
<td>0.0°</td>
<td>4.2°</td>
<td>+/–</td>
</tr>
<tr>
<td></td>
<td>[010]&lt;sub&gt;III&lt;/sub&gt;—[100]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>-1.3 %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(220)&lt;sub&gt;III&lt;/sub&gt;—(211)&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>[001]&lt;sub&gt;III&lt;/sub&gt;—[011]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>+2.9 %</td>
<td>4.3°</td>
<td>5.5°</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>[110]&lt;sub&gt;III&lt;/sub&gt;—[111]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>-3.1 %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(022)&lt;sub&gt;III&lt;/sub&gt;—(211)&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>[100]&lt;sub&gt;III&lt;/sub&gt;—[011]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>-4.3 %</td>
<td>4.3°</td>
<td>5.5°</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>[011]&lt;sub&gt;III&lt;/sub&gt;—[111]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>+1.3 %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(111)&lt;sub&gt;III&lt;/sub&gt;—(101)&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>[121]&lt;sub&gt;III&lt;/sub&gt;—[202]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>-3.3 %</td>
<td>2.8°</td>
<td>10.5°</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>[101]&lt;sub&gt;III&lt;/sub&gt;—[020]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>+3.8 %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(111)&lt;sub&gt;III&lt;/sub&gt;—(110)&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>[121]&lt;sub&gt;III&lt;/sub&gt;—[220]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>+1.0 %</td>
<td>2.8°</td>
<td>5.7°</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>[101]&lt;sub&gt;III&lt;/sub&gt;—[002]&lt;sub&gt;IV&lt;/sub&gt;</td>
<td>-5.7 %</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Based on the transition III–IV.

<sup>b</sup> Although these phase IV faces do not normally occur on AN(IV) needle crystals, and are therefore not included in table 5.2, they have been observed sometimes on crystals with shapes differing from needle shapes [17].

5.5.4 Comparison of theoretical results with texture goniometry results

The crystallographic orientations of the sample which was used for the texture goniometry experiment can be deduced from those pole figures which were measured during and after the first and second temperature cycle (figs. 5.5a and b). Stereographic projections are constructed from these pole figures and are given in fig. 5.7. The measured poles are drawn as solid circles in these figures. The open circles represent reflections which could be deduced from the measured ones by plotting great circles through them.

The stereographic projections, given in fig. 5.7, show that the (200)<sub>III</sub> and (111)<sub>IV</sub> faces are almost parallel. The projections of these faces match if the transition can be described by transition matrix C (see table 5.3). Other faces which transform according to this matrix are for instance (111)<sub>III</sub>—(200)<sub>IV</sub>, (111)<sub>III</sub>—(111)<sub>IV</sub>, and (002)<sub>III</sub>—(110)<sub>IV</sub>. The last two sets of faces appear to be not completely parallel (fig. 5.7). This agrees
with the fact that according to transition matrix $C$ the transformations of these faces require relatively large length changes of the matching vectors in these faces or relatively large deformations. Also the calculated growth angle is considerable in these cases (16°). The theoretical possibility that these faces match does, however, not guarantee that the transition front is indeed formed by these faces. It is more likely that the transition proceeds via the best matching macrosteps, just as described before for the single crystals.

Relatively simple orientation relationships between the phases III and IV could be determined also from the remaining two texture goniometry measurements, as given in table 5.6. Because in these cases the length changes of the matching vectors are relatively large (up to 36 %) and the deformation of the matching faces is considerable these orientation relations do not satisfy criteria (1) and (2), mentioned in section 5.5.2. These sets of matching faces were therefore not found by comparing the projections of

<table>
<thead>
<tr>
<th>matching faces</th>
<th>matching vectors</th>
<th>relative length change$^a$</th>
<th>deformation</th>
<th>growth angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(020)<em>{III}$-$(002)</em>{IV}$</td>
<td>$(010)<em>{III}$-$(1\bar{1}0)</em>{IV}$</td>
<td>+36 %</td>
<td>3.1°</td>
<td>0.0°</td>
</tr>
<tr>
<td></td>
<td>$(001)<em>{III}$-$(110)</em>{IV}$</td>
<td>+10.8 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(002)<em>{III}$-$(020)</em>{IV}$</td>
<td>$(100)<em>{III}$-$(101)</em>{IV}$</td>
<td>−1.3 %</td>
<td>8.6°</td>
<td>0.0°</td>
</tr>
<tr>
<td></td>
<td>$(010)<em>{III}$-$(101)</em>{IV}$</td>
<td>+30 %</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Based on the transition III-IV.
(hkl)$_{\text{III}}$ and (hkl)$_{\text{IV}}$ faces. The simplicity of these orientation relationships, however, sustains the possibility of a solid-solid transition mechanism.

5.6 Conclusions

In situ microscopic observations, texture goniometry results and literature data confirm several of the orientation relationships between phase III and phase IV which were found from a systematic study on the similarity between projections of specific (hkl)$_{\text{III}}$ and (hkl)$_{\text{IV}}$ faces. The combined experimental and theoretical results substantiate the existence of a solid-solid transition mechanism especially in single crystals.

The breakage of hydrogen bonds required for the ammonium and nitrate ions to be rotated and displaced during the solid-solid phase transition, is facilitated by solvent molecules which are able to form hydrogen bridges. This suggests that, for the proposed solid-solid mechanism, such solvent molecules play a catalytic role.

References

Chapter 6

Effect of the III-IV polymorphic phase transition on the texture and quality of ammonium nitrate products *)

Abstract

Ammonium nitrate fertilizer granules may lose their mechanical strength due to the III-IV polymorphic phase transition in ammonium nitrate, occurring at 32 °C. In this study the causes of the quality decrease due to this recrystallization process under various conditions are described. It is demonstrated that water catalyses the nucleation as well as the growth of the new phase during the phase transition. Quantitative relations between the water content and the loss of mechanical strength has been observed. Specific additives have been proven to diminish the effects of the recrystallization process on the quality decrease but the mechanism of their performance is still not fully understood.

6.1 Introduction

Ammonium nitrate (NH₄NO₃, AN) is a base chemical for fertilizers and explosives. For application as an explosive low density AN is used, while a high density AN product is required for use as a nitrogen fertilizer.

AN fertilizer can be produced by granulation of AN melt, containing 4 wt% water, and clay. The product is dried to a water content below 0.25 wt%, sieved and partially recycled, all above 90 °C. After cooling the granules are coated to prevent caking during bulk storage.

AN occurs in at least six polymorphic phases [1]. Five modifications are stable at atmospheric pressure [2]:

\[
\begin{align*}
\text{melt} & \quad 170 \ ^\circ \text{C} \quad \text{I} \quad 125 \ ^\circ \text{C} \quad \text{II} \quad 84 \ ^\circ \text{C} \quad \text{III} \quad 32 \ ^\circ \text{C} \quad \text{IV} \quad -18 \ ^\circ \text{C} \quad \text{V}
\end{align*}
\]

The crystal structures of the phases II, IV and V differ slightly [3]. Phase III, however, has a completely different structure and the temperatures at which the II-III and III-IV phase transitions take place are highly dependent on several conditions, such as the presence of moisture, the history of the crystals and the heating or cooling rate [4–7]. Very dry AN does not show the II-III and III-IV transitions, but it transforms directly from phase IV into phase II or vice versa at about 50 °C.

High density AN has to meet quality requirements concerning the mechanical strength and detonation resistance after storage and transport. The main cause for the deterioration of the quality is the III-IV polymorphic phase transition which may occur by changes in temperature. The durability against these changes is called ‘thermal stability’. It is generally assumed that the volume increase of 4 % during the IV-III transition is the reason for the decrease of the mechanical strength of AN [8,9]. This volume change would cause a break down of the product due to lattice strain.

Much research has been done on this subject. In many cases, however, little attention has been paid to the conditions under which the phase transition takes place. In this study the effects of the III-IV phase transition on the texture and mechanical properties of AN products have been described, and the influence of various conditions on these effects have been investigated. Knowledge of these processes is of importance for the improvement of the quality of AN products.
6.2 Experimental procedures

Porosimetry and BET

The pore volume and the total surface area of two AN fertilizer products, produced with the aid of clay, has been determined by mercury porosimetry and BET adsorption of krypton. This has been done before and after thermal cycling between 20 and 50 °C with heating and cooling rates of 0.6 °C/min. Calorimetric measurements show that all samples entirely underwent the phase transitions IV–III–IV.

To determine the pore volume, the penetrometer with granules has been evacuated at room temperature and filled with mercury. Pores smaller then 0.1 μm cannot be measured reliably because of the large effect of the compression of AN.

The true density of the granules has been measured with helium.

To determine the BET surface area the granules have been evacuated at room temperature during 10 hours. The adsorption of krypton was measured at 78 K and 4 equilibrium pressures ($P/P_0 = 0.05, 0.10, 0.15$ and $0.20$).

Thermal stability test

A tablet test has been developed to investigate the disintegration of AN products. The tablets were produced by pouring out AN melt, containing 4 wt% water and sometimes additives, at a temperature of about 150 °C in a mould in which the melt crystallizes. The acquired tablets were dried at 90–100 °C. In this way the granulation process was simulated.

After drying to a desired water content the tablets were piled in a tube and subjected to thermal cycling between 20 and 50 °C with heating and cooling rates of 0.6 °C/min. The thermal stability of the tablets was measured by the increase of the height of the tablet pile, $Δh$, which is related to the thermal instability of the products.

Tablets made of pure AN and tablets with the same composition as the granules which are used for the porosimetry and BET measurements have been subjected to this tablet test. From calorimetric measurements it followed that the tablets in all cases entirely underwent the transitions VI–III–IV.

Microscopy

To study the III-IV phase transition in pure AN by optical microscopy crystals have been prepared by slow cooling a saturated solution from 30 °C to room temperature. These crystals were needle shaped and were several millimetres long and about one millimetre thick. The crystals used for observation did not contain included mother liquor. To control the temperature of the observed crystals a thermostated observation cell had been made. In this observation cell dry AN crystals and AN crystals in solution have been observed. To study the influence of the relative humidity
(RH) on the phase transition in dry crystals moistened air was led through the observation cell after measuring the RH with an electrical hygrometer. The applied humidities were between 0 and 60%. Above about 60% AN crystals were completely wetted by adsorbed water and they dissolved. The phase transition has been made visible by the use of polarizing filters which caused a change in colour of the crystals when the phase transition took place. The microscopic equipment is shown in fig. 6.1.

6.3 Results and discussion

6.3.1 Effects of the III-IV phase transition on the texture

The results of the porosity and BET measurements are summarized in table 6.1. In fig. 6.2 the cumulative intrusion volume of AN fertilizer product 2 before and after thermal cycling is shown as a function of the pore radius. This figure shows the appearance of pores with equivalent radii of 100 μm to 1 μm. There are hardly any pores with a radius of 1 to 0.1 μm.

From the pore volume distribution the pore surface area can be calculated
assuming the pores to be cylindrical shaped. The surface area derived from porosity measurements, given in table 6.1, applies only for pores with a radius above 0.1 μm. Pores with a radius smaller than 0.1 μm can have a large contribution to the total surface area of the particle. Therefore the surface area calculated from porosity measurements is smaller than the surface area determined by BET.

From the measurement of the He-density it follows that there are probably no or little blocked cavities between the crystallites before the transformation cycle. The development of micro and macro pores during phase transition would make originally blocked cavities accessible for helium causing an increase of the He-density. There is, however, no or little difference between the He-density before and after thermal cycling.

**Table 6.1** Results of mercury porosimetry and BET measurements on two AN fertilizer products before and after thermal cycling.

<table>
<thead>
<tr>
<th></th>
<th>before thermal cycling</th>
<th>after thermal cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>product 1</td>
<td>product 2</td>
</tr>
<tr>
<td><strong>Porosimetry</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>intrusion volume [ml kg⁻¹]</td>
<td>62.9</td>
<td>43.2</td>
</tr>
<tr>
<td>surface area [m² kg⁻¹]</td>
<td>47</td>
<td>28</td>
</tr>
<tr>
<td>He-density [10³ kg m⁻³]</td>
<td>1.68</td>
<td>1.68</td>
</tr>
<tr>
<td><strong>BET</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>surface area [10³ m² kg⁻¹]</td>
<td>0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>equiv. diam. crystal [μm]</td>
<td>29</td>
<td>32</td>
</tr>
</tbody>
</table>

![Fig. 6.2](image) Cumulative intrusion volume of product 2 as a function of the pore diameter (μm). ●: AN granules before thermal cycling, ○: AN granules after thermal cycling.
Fig. 6.3 Influence of water content on relative height increase of tablet pile ($\Delta h$) after five temperature cycles. ● = tablets of pure AN, ■ = tablets with composition of product 2.

After one temperature cycle the pore volume of the large pores determined by porosimetry and the BET surface area are increased. The increase of the BET surface area of product 1 is, however, clearly larger than the increase of the surface area caused by the large pores. This indicates the appearance of new pores with a radius smaller than 0.1 $\mu$m. These new pores are probably formed by breaking up of crystallites. The diameter of the crystallites is estimated from the BET surface area,
assuming that the crystallites are spherically shaped. Product 2 shows a much smaller increase of the BET surface area.

These examples demonstrate that the deterioration of the quality differs from product to product. Differences in quality decrease, however, are not the result of incomplete transitions: all samples entirely underwent the transitions IV–III–IV as mentioned before. Therefore it is concluded that the transition on its own is not determining for the quality decrease but in what way the transition proceed.

The stabilities of pure AN and AN with the composition of product 2 have been measured with the tablet test described above and are given in fig. 6.3 for various H₂O contents of the tablets. The instability of tablets which contain clay increases slower at higher water contents than the instability of tablets without clay. In both cases, however, there is a strong correlation between water content and instability.

6.3.2 Microscopy

Observation of the IV–III transition

For the observation of dry crystals relatively thick AN(IV) needles with a diameter of about 1 mm or more were used. At temperatures between 35 and 45 °C the IV–III phase transition occurred upon the introduction of moistened air with a RH of more then about 10 %. During this transition an uneven front was developed between the phases IV and III as is shown in fig. 6.4. The transition always started at the surface of the crystals. Seconds after the transition front passed, cracks appeared in the transformed crystal part which then loses its mechanical strength. When the crystal was next cooled below 32 °C the III–IV transition occured and more cracks appeared.

The propagation velocity of the front between the phases IV and III is strongly dependent on the RH. When dry air was led over a transforming crystal, the transition stopped. When the air was moistened again, the transition continued immediately. Fig. 6.5 shows the initiation time for the transition and the front velocity as a function of the RH at 38 °C.

From these observations it is concluded that the kinetics of the IV–III phase transition are not only determined by temperature: both initiation time and growth rate of the new phase are also dependent on the presence and the amount of adsorbed water.

The observed effect of water on the kinetics of the III-IV transition is probably related to the effect of the amount of water on the loss of quality of AN products.

Brown and McLaren [5], and recently Davey et al. [10], have suggested that during the III-IV transition water is present at the interface boundary between the two phases. It should form a 'bulk' layer of saturated water in which dissolution and recrystallisation occur. In their case the transforming crystals are surrounded by a
solution layer. If this hypothesis were correct for dry crystals in humid air, water has to be transported along the formed cracks and the interface boundary itself. When subsequently dry air is led over a transforming crystal, not all water present within the cracks and on the interface boundary will evaporate because of the large hygroscopicity of AN. The water within the already existing cracks and on the interface boundary will, however, be further spread over the newly formed cracks. In this way water will no longer be present on the moving interface boundary to catalyze the transition. When the air is moistened again, new water will be adsorbed and transported by capillary forces along the cracks and the interface boundary, and the transition process will be catalyzed again.

It has been observed, however, that the time gap between the moment that moistened air is passed over a dry crystal, where the transition front has formerly been stopped, and the moment the front starts to move further is very short (a few seconds). Sufficient diffusion of water along the cracks and the interface to form a new water layer along the front will most likely take more time. The transition in dry crystals seems to be continually initiated from the surface of the crystal by adsorbed water. The necessity of a continuous surface nucleation is not unlikely, because of the rigorous change of structure needed for the III-IV transition.

Observation of the III-IV transition

AN(III) crystals are easily grown by cooling crystallization, and are mostly needle shaped and very thin (smaller than 300 μm). The III-IV phase transition at cooling
below 32 °C has been observed in excess saturated solution. This transition always started at one or both ends of a needle or at a point where a transformed part of another crystal touched the needle. In almost all cases the interface boundary in these thin crystals is a very regular, flat front, which maintains its orientation during the transition.

The transition can proceed in two different ways. The texture of the crystal can remain the same: from a (transparent) phase III needle a transparent phase IV crystal growth with the same outward shape. Parallel to the interface ghost lines are formed. In the other case the formed phase IV is fractured into small, flat crystallites during the transition: the texture thus changes and the surface of the crystal becomes rough. A phase III crystal in which the phase transition started at both sides is shown in fig. 6.6. At one side a transparent phase IV crystal is formed, at the other side a rough crystal is formed consisting of small crystallites.

When from phase III a transparent crystal of phase IV was formed the transition appeared to be 'reversible': when the temperature was increased above 32 °C again a transparent phase III crystal was formed with the same outward shape. The orientation of the interface did not change when the direction of the transition inverted. The transition is called 'irreversible' when the crystal is fractured into small crystallites. In this case there is not a single crystal of phase III formed again at increasing the temperature above 32 °C. The reversibility seems to be related to the orientation of the interface during the transition (see fig. 6.6).
At further cooling needles are grown into the solution from the newly formed phase IV. It has been observed that the longitudinal axis of these needles lies parallel to the interface during the phase transition. So the interface between the phases III and IV during the transition is probably a morphological face of either one or both crystal structures.

In literature it has frequently been suggested that the cracks appearing in AN crystals during the III-IV transition are caused by a change in density during transition. Thin phase III crystals transforming into phase IV do not always break up as described above. The IV-III transition in rather thick phase IV needles generally proceeds via an irregular front, which means that several crystallographic orientations are developed in the newly formed crystal (see fig. 6.4). Because the expansion due to the change of the unit cell dimensions during the IV-III transition is different for the different crystallographic directions [7] the strain built up in the transformed needle depends on the mutual orientations of the crystallites. This strain causes cracking of the needle.

The mechanical stability of AN products after III-IV polymorphic phase transition thus depends on the crystallographic orientations of the nuclei which determine the interface between phase IV and phase III during the transition.

This explains why the loss of quality of AN products after thermal cycling differs from product to product as mentioned before.

6.4 Conclusions

- The deterioration of the mechanical quality of AN granules during the III-IV polymorphic phase transition is caused by a break up of crystallites. New micro and macro pores are formed and crystallites are pushed apart or crushed.
- The amount of disintegration differs from product to product although all samples entirely underwent the III-IV phase transition. The disintegration of AN products depends on the water content of the products during the transition.
- The way by which the III-IV phase transitions proceed, is determining for the loss of quality of AN products, and not the transitions on their own.
- The fact that several orientations can develop in different crystallites formed in a needle by the phase transition is probably the main cause of the deterioration of the quality of AN products. The mutual orientations of the crystallites is imposed by the crystallographic orientations of the nuclei.
- Water plays a role as a catalyst for the initiation and influences the growth rate during the III-IV transition.
- The III-IV phase transition in AN crystals in air is probably continually initiated from the surface of the crystal by water adsorbed from the air. The experimental
results do not sustain the existence of a 'bulk' layer of saturated solution at the interface between the phases during the transition in 'dry' AN crystals.

The interface between the phases IV and III during the phase transition in needle shaped crystals is probably formed by crystal faces of either one or both phases which correspond with the morphology of crystals when they are crystallized from solution.

References

Chapter 7

Thermal stability of ammonium nitrate: the influence of additives \(^1\)

Abstract

High density ammonium nitrate may lose its mechanical strength due to the polymorphic phase transition III-IV in ammonium nitrate, occurring by fluctuations in temperature around 32 °C. Additives which either form amorphous phases at the grain boundaries which block the III-IV phase transition front, or have a water binding capacity, or harden the granules, reduce the detrimental effects of the III-IV transition. The presence of heterogeneous nuclei during crystallization provided by some additives, in combination with the formation of amorphous phases, may also improve the thermal stability. The coarseness of the macrostructure of ammonium nitrate tablets is not related to their thermal stability.

7.1 Introduction

Ammonium nitrate, \( \text{NH}_4\text{NO}_3 \) (AN), is a base chemical for fertilizers and explosives. For application as an explosive low density AN is used, while a high density AN product is required for use as a nitrogen fertilizer.

AN develops in at least five polymorphic crystal phases at atmospheric pressure. The transition temperatures in pure ammonium nitrate are:

\[
\text{melt} \quad 170 \, ^\circ\text{C} \quad 125 \, ^\circ\text{C} \quad \text{II} \quad 84 \, ^\circ\text{C} \quad \text{III} \quad 32 \, ^\circ\text{C} \quad \text{IV} \quad -18 \, ^\circ\text{C} \quad \text{V} \\
50 \, ^\circ\text{C}
\]

Besides the stable phase transitions II-III at 84 °C and III-IV at 32 °C the metastable II-IV transition can occur at temperatures of 50—55 °C.

High density AN has to meet quality requirements concerning the mechanical strength and detonation resistance after storage and transport. The main cause for deterioration of the quality of high density AN products is the III-IV transition, which occurs in the presence of moisture. A change of the molecular volume of almost 4 % during this transition is generally assumed to cause the decrease of the mechanical strength of AN. This volume change induces an increase of the pore volume and simultaneously a breakdown of the product due to lattice strain. The loss of quality is strongly affected by the water content, but also by the pretreatment of the product, and by the presence of specific additives.

The III-IV transition in AN and its effect on the mechanical stability of AN products has been studied extensively [1—3]. In many cases, however, little attention has been paid to the conditions under which the phase transition takes place (e.g. water content) and to the precise role of additives in this transition. The III-IV transition requires the presence of some moisture, or more generally, a small amount of any solvent [2—5]. Several authors therefore suggest that this transition takes place by dissolution and recrystallization of the solid. Other authors, however, more or less contradict such a solvent mediated process by reporting that the orientation relations between the crystallographic axes in the II-III and III-IV transitions are not random although various rather complex relationships can develop [6,7]. A recent study shows on the basis of various experimental and molecular modelling results that the III-IV transition most likely proceeds via a solid-solid mechanism which is catalyzed by trace amounts of water (chapter 5). The main performance of additives is just ascribed to their ability to bind free water in the AN granules, thus avoiding the appearance of the III-IV transition. Other mechanisms might, however, play a role as well in the improvement of the product quality.

This study describes the structure of AN tablets which are produced in a way
which simulates the production process and the thermal stability of these tablets, i.e. their resistance against deterioration due to the III-IV transition. Also the effects of various additives on the thermal stability as a function of the water content are investigated.

7.2 Production of high density ammonium nitrate

AN is obtained by the reaction of ammonia with nitric acid. The AN solution is evaporated to a moisture content of 1 to 5 wt%, depending on the production process, e.g. prilling, drum granulation, fluid bed granulation or combinations. Granulation aids are sometimes required, depending on the type of granulation process. In order to improve the final mechanical product quality generally also specific additives are added to the AN solution.

Most of the granulation processes comprise layer-wise crystallization of the water containing AN melt on seed particles. Newly formed layers initially consist of dendritically crystallized AN(I) or AN(II) while a saturated AN solution remains trapped between the dendrite branches. The crystallographic texture and macrostructure of the granules are greatly influenced by the dendritic growth and the coarsening of the dendritic phase occurring in newly formed layers which contain interdendritic solution (chapters 2–4). The coarsening occurs during and immediately after the dendritic growth has completed and before all the water is evaporated from the remaining interdendritic solution. The evaporation of the water from this interdendritic solution takes place in a drying step at temperatures well above the II-III transition point. The granules are dried to water contents of less than 0.25 wt%. The crystallization and drying steps are repeated until the desired granule size is obtained. Finally, the granules are coated to prevent water uptake and caking during storage and transport.

7.3 Experimental procedure

Tablets were prepared in a way which simulates the granulation process. A concentrated aqueous AN solution was obtained by heating an AN-water solution until a boiling temperature of 170 °C was reached. At this temperature the solution has a water content of approximately 4.5 wt%. The obtained solution was poured in a rubber mould which was placed on a metal plate and thermostated at 90 °C (fig. 7.1). During 15 minutes the AN was crystallized and partly dried. The acquired tablets were then removed from the mould and dried further at 90 °C in a stove, which was equipped with in- and outlets for air which provided a natural air circulation through the stove. The residence time of air in the stove was determined to be less than 5 minutes.
Additives could be added to the water containing melt. The additives did not significantly influence the boiling temperature at a given water content. The additives used in the tablets are given in table 7.1. Although the additives may contain crystal water, they are referred to in their anhydrous form for reasons of simplicity.

Water contents were determined by Karl Fischer titrations. The composition of the obtained tablets was determined by Guinier X-ray diffraction after half an hour and/or after drying to a water content below 1 wt% which could take several days for various samples. Scanning electron microscopy (SEM) was applied to study the macrostructure of the tablets and the texture of the coprecipitated additives.

The water content of the tablets was measured as a function of the drying time. To decrease the error of these measurements two or three tablets were divided into four and from each tablet one part was used for a titration. By breaking the tablets a qualitative measure of the hardness of the tablets was obtained.

A tablet test has been developed to investigate the disintegration of AN products. The test is based on the net volume increase of AN after the transitions IV–III–IV. After drying to a water content between 0 and 4 wt%, 10 tablets were piled in a tube which was closed with a rubber stopper to prevent further drying. The tablet pile was then subjected to five temperature cycles between 18 and 50 °C, each cycle taking 3 hours. After finishing the tablet test the water content and the relative increase in height, Δh, which is a measure for the thermal stability of the sample, were determined. The test was performed for each sample at various water contents.

7.4 Results and discussion

7.4.1 Macrostructure and hardness of AN tablets

Fig. 7.2 shows low magnification SEM photographs (75×) of the internal structure of tablets to which either no additive, or BaSO₄, (NH₄)₂SO₄, or Mg(NO₃)₂ was
Table 7.1 Composition of the tablets. The amount of the crystalline phases found by X-ray diffraction is qualitatively indicated by dots with different sizes.

<table>
<thead>
<tr>
<th>substance(s) added</th>
<th>amount added (^a) [wt%]</th>
<th>crystalline phases found (besides AN(IV))</th>
<th>short drying period (0.5 hours)</th>
<th>long drying period (2 – 10 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(NO(_3))(_3)-9H(_2)O</td>
<td>2.0</td>
<td>nothing found</td>
<td>nothing found</td>
<td>(NH(_4))(_5)(NO(_3))(_3)SO(_4)</td>
</tr>
<tr>
<td>Al(_2)(SO(_4))(_3)-18H(_2)O</td>
<td>2.0</td>
<td>• Al(_2)(SO(_4))(_3)·14H(_2)O  +  • NH(_4)Al(SO(_4))(_2)·12H(_2)O</td>
<td>nothing found</td>
<td>AlPO(_4)</td>
</tr>
<tr>
<td>Al(NO(_3))(_3)-9H(_2)O + (NH(_4))(_2)HPO(_4)</td>
<td>2.0</td>
<td>nothing found</td>
<td>nothing found</td>
<td></td>
</tr>
<tr>
<td>Ba(NO(_3))(_2) + (NH(_4))(_2)SO(_4)</td>
<td>2.0</td>
<td>• BaSO(_4)</td>
<td>BaSO(_4)</td>
<td></td>
</tr>
<tr>
<td>Cu(NO(_3))(_2)-3H(_2)O</td>
<td>2.0</td>
<td>• Cu(_3)(OH(_3))NO(_3)</td>
<td>Cu(_3)(OH(_3))NO(_3)</td>
<td></td>
</tr>
<tr>
<td>CuSO(_4)-5H(_2)O</td>
<td>2.0</td>
<td>• (NH(_4))(_2)Cu(SO(_4))(_2)-6H(_2)O</td>
<td>(NH(_4))(_2)Cu(SO(_4))(_2)-(\frac{1}{2})H(_2)O</td>
<td></td>
</tr>
<tr>
<td>Fe(NO(_3))(_3)-9H(_2)O</td>
<td>2.0</td>
<td>nothing found</td>
<td>nothing found</td>
<td></td>
</tr>
<tr>
<td>FeSO(_4)</td>
<td>2.0</td>
<td>nothing found</td>
<td>NH(_4)Fe(_3)(SO(_4))(_2)(OH(_6)</td>
<td></td>
</tr>
<tr>
<td>Fe(_2)(SO(_4))(_3)-12H(_2)O</td>
<td>2.0</td>
<td>nothing found</td>
<td>nothing found</td>
<td></td>
</tr>
<tr>
<td>KNO(_3)</td>
<td>2.0</td>
<td>•</td>
<td>• AN(III) +</td>
<td></td>
</tr>
<tr>
<td>K(_2)SO(_4)</td>
<td>2.0</td>
<td>• AN(III) +</td>
<td>• AN(III) +</td>
<td></td>
</tr>
<tr>
<td>Mg(NO(_3))(_2)-6H(_2)O</td>
<td>2.0</td>
<td>• (NH(_4))(_5)(NO(_3))(_3)SO(_4)</td>
<td>(NH(_4))(_5)(NO(_3))(_3)SO(_4)</td>
<td></td>
</tr>
<tr>
<td>MgSO(_4)-7H(_2)O</td>
<td>2.0</td>
<td>• Mg(NO(_3))(_2)-6H(_2)O</td>
<td>Mg(NO(_3))(_2)-6H(_2)O</td>
<td></td>
</tr>
<tr>
<td>NaNO(_3)</td>
<td>2.0</td>
<td>•</td>
<td>• NaNO(_3)</td>
<td></td>
</tr>
<tr>
<td>(NH(_4))(_2)SO(_4)</td>
<td>2.0</td>
<td>• (NH(_4))(_2)Mg(_2)(SO(_4))(_3)</td>
<td>(NH(_4))(_2)Mg(_2)(SO(_4))(_3)</td>
<td></td>
</tr>
<tr>
<td>H(_3)BO(_3)</td>
<td>2.0</td>
<td>• H(_3)BO(_3) +</td>
<td>H(_3)BO(_3) +</td>
<td></td>
</tr>
<tr>
<td>(NH(_4))(_2)HPO(_4)</td>
<td>2.0</td>
<td>• NH(_4)(_2)HPO(_4)</td>
<td>NH(_4)(_2)HPO(_4)</td>
<td></td>
</tr>
<tr>
<td>H(_3)BO(_3) + (NH(_4))(_2)HPO(_4)</td>
<td>2.0</td>
<td>• NH(_4)(_2)HPO(_4)</td>
<td>NH(_4)(_2)HPO(_4) +</td>
<td></td>
</tr>
<tr>
<td>permalene (^d)</td>
<td>2.0</td>
<td>nothing found</td>
<td>nothing found</td>
<td></td>
</tr>
<tr>
<td>Na(^+)RSO(_3) (^{-}) (^e)</td>
<td>2.0</td>
<td>•</td>
<td>•</td>
<td></td>
</tr>
<tr>
<td>Na(^+)C(_6)H(_5)SO(_3) (^{-})</td>
<td>2.0</td>
<td>•</td>
<td>•</td>
<td></td>
</tr>
<tr>
<td>PSS (^f)</td>
<td>0.01</td>
<td>•</td>
<td>•</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Based on the anhydrous form of the additive.
\(^b\) The samples consisted for approximately one third of AN(III) as far as could be determined from the Guinier diffractograms.
\(^c\) Composition: 40 wt% H\(_3\)BO\(_3\) + 60 wt% (NH\(_4\))\(_2\)HPO\(_4\).
\(^d\) Composition: 39 wt% H\(_3\)BO\(_3\) + 58 wt% (NH\(_4\))\(_2\)HPO\(_4\) + 3 wt% (NH\(_4\))\(_2\)SO\(_4\).
\(^e\) R = alkyl, exact composition unknown.

\(^f\) Polystyrene sulphonate: + CH\(_2\)-HC(C\(_6\)H\(_5\)SO\(_3\)H) \(\dagger\), mean molecular weight 70000 g mol\(^{-1}\).

added during preparation. The macrostructure of the tablets containing no additive or BaSO\(_4\) is relatively fine, with a typical length scale of approximately 50 μm. Tablets to which (NH\(_4\))\(_2\)SO\(_4\) was added show a somewhat larger length scale (~ 100 μm).
Fig. 7.2 Low magnification SEM photographs (75 x) of tablets containing (a) no additives, (b) BaSO₄, (c) (NH₄)₂SO₄, and (d) Mg(NO₃)₂.

Tablets to which Mg(NO₃)₂ was added are even more coarse and show a typical length scale of approximately 150 μm.

The macrostructure of the tablets is mainly formed during crystallization and the coarsening of the dendritic AN(II). Since the tablets are not compacted, as occurs in granulation processes in industry, a porous structure is formed in which the original dendrite shapes can still be recognized after drying (fig. 7.2). The coarsening proceeds during crystallization and drying of the tablets as long as sufficient water is present in the tablets and is therefore expected to be related to the drying time of the tablets.

Drying curves of tablets to which BaSO₄, (NH₄)₂SO₄, and Fe₂(SO₄)₃ were added are shown in fig. 7.3 as typical examples of tablets which show a fast, an intermediate, or a slow drying process respectively. The drying curve of tablets containing BaSO₄ is almost similar to the curve for pure AN tablets, which also dry quickly. The slower decrease of the water content of tablets containing (NH₄)₂SO₄ is probably caused by an increase of the hygroscopicity of the tablets as mixtures of hygroscopic salts are
generally more hygroscopic than the individual salts. Tablets containing Mg(NO₃)₂ dry very slowly (comparable to e.g. Fe₂(SO₄)₃) because they are even more hygroscopic. BaSO₄, on the contrary, is not hygroscopic and has no effect on the drying time of the tablets.

The slower drying of tablets containing hygroscopic additives leads to a prolonged coarsening which explains the effect of these additives on the internal structure of the AN tablets. The SEM views in fig. 7.2 show a coarser macrostructure of tablets containing (NH₄)₂SO₄ and Mg(NO₃)₂ than those of tablets to which no additive or BaSO₄ were added. Within tablets to which Mg(NO₃)₂ was added, however, also an amorphous Mg(NO₃)₂·2·H₂O phase is present which has a strong water binding capacity, as will be discussed below. This amorphous phase has an extra retarding effect on the drying of these tablets and the water bound by it will probably not contribute to the coarsening process.

The hardness of the tablets varies depending on the applied additives. No relation could be found between the hardness and the coarseness of the macrostructure of the tablets. However, a relation between the hardness and the mechanism via which the coarsening proceeds exists. The coarsening proceeds via ripening of dendrite branches whether or not accompanied by coalescence of these branches, depending on the presence of specific additives (chapter 4). Coalescence of dendrite branches was not observed for e.g. pure AN tablets and tablets to which Na⁺RSO₃⁻ or were added, while addition of Al salts for instance favours the coalescence. The hardness of the AN tablets was increased for those tablets in which additives were applied which favour coalescence. The addition of Na⁺RSO₃⁻ for instance leads to extremely weak tablets, while additives containing Al salts were very hard.
7.4.2 Final composition of additives in AN tablets

As far as the additive compounds were crystalline their composition could be determined by Guinier X-ray diffraction, which is given in table 7.1. These results show that various additives form hydrates and/or double salts with AN. In these cases SEM views show tiny additive particles of 1 to 10 \( \mu \text{m} \) in diameter at the smooth AN pore surface.

Sjölin [3] observed that in AN prills containing \( \text{Mg(NO}_3\text{)}_2 \) crystallites also an amorphous \( \text{Mg(NO}_3\text{)}_2 \cdot 2\text{-4H}_2\text{O} \) phase existed, which developed as veins at the crystallite boundaries. Such veins were observed in tablets containing other additives as well. As an example a SEM photograph of a tablet to which \( \text{Cu(NO}_3\text{)}_2 \) was added is given in fig. 7.4. In tablets to which additives were supplied which form hydrates and/or double salts with AN mostly no or only very small amounts of crystalline coprecipitates could be detected by X-ray diffraction, although SEM photographs showed a few, mostly plate-like, particles. Since it is unlikely that the ions of these additives were incorporated in the AN lattice because of their different size and valence with respect to the \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) ions, these additives most likely formed amorphous compounds, just as \( \text{Mg(NO}_3\text{)}_2 \) and \( \text{Cu(NO}_3\text{)}_2 \).

Guinier X-ray diffraction shows that tablets to which \( \text{Al}_2(\text{SO}_4)_3 \), \( \text{CuSO}_4 \), or \( \text{MgSO}_4 \) were added, initially contained \( \text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} \) and \( \text{NH}_4\text{Al(}\text{SO}_4\text{)}_2 \cdot 12\text{H}_2\text{O} \),

Fig. 7.4 SEM photograph of the coprecipitates in tablets to which \( \text{Cu(NO}_3\text{)}_2 \) was added. A probably amorphous phase is present at the pore surface in the tablets as veins besides coprecipitated crystallites.
(NH₄)₂Cu(SO₄)₂·6H₂O, or (NH₄)₂Mg(SO₄)₂ respectively (see table 7.1). For stoichiometric reasons also other Al, Cu, and Mg compounds should have formed. Since these compounds were not detected by X-ray diffraction it is concluded that they are amorphous. This was proven by the fact that after prolonged drying of tablets to which MgSO₄ was added, besides the initially formed (NH₄)₂Mg(SO₄)₂ also Mg(NO₃)₂·6H₂O was formed, obviously from the amorphous phase.

X-ray diffraction patterns and SEM views show that more coprecipitates of AN with additives converted into other hydrates or other salts after prolonged drying. The most striking example is Al₂(SO₄)₃ which initially (after one day of drying) forms only plate-like crystallites as was observed by SEM. In these tablets Al₂(SO₄)₃·14H₂O and NH₄Al(SO₄)₂·12H₂O were determined by X-ray diffraction. Sjölin analyzed this coprecipitate as Al₂(SO₄)₃(NH₄)₂(OH)₂(H₂O)₆·10. The photograph of this additive in AN prills which Sjölin presented in his paper [3] shows similar plates as were observed here. After ten days of drying almost all plate-like crystals vanished while other rod-like crystals were formed (fig. 7.5). Guinier X-ray diffraction shows a pattern that exactly corresponds to that of (NH₄)₃(NO₃)₂SO₄. No other crystalline phase was detected by X-ray diffraction. During the long drying period the Al₂(SO₄)₃ additive apparently converted into (NH₄)₃(NO₃)₂SO₄ and an amorphous Al³⁺ containing compound.

Permalene is used in industrial products and stabilizes AN very well. It consists

Fig. 7.5 SEM photograph of the interior of a tablet to which Al₂(SO₄)₃ was added, after 10 days of drying at 90 °C. Almost all plate-like crystals (like in the middle of this photograph) disappeared while rod-like crystals had been formed.
of $\text{H}_3\text{BO}_3$ (39 wt%), $(\text{NH}_4)_2\text{HPO}_4$ (58 wt%), and $(\text{NH}_4)_2\text{SO}_4$ (3 wt%). As far as could be determined from the X-ray diffractograms $\text{H}_3\text{BO}_3$ formed only minor amounts of various crystalline hydrated double salts with AN (table 7.1) and it is expected that most of the additive is present as amorphous compounds with a strong water binding capacity. The extremely slow drying of these tablets confirms this.

Tablets to which a combination of $\text{H}_3\text{BO}_3$ and $(\text{NH}_4)_2\text{HPO}_4$ (ratio 2:3, similar as in permalene) was added, also dry very slowly. X-ray diffraction shows the presence of minor amounts of various hydrated ammonium borate double salts (table 7.1). The majority of the additive is expected to be present as an amorphous phase with a water binding capacity, and hence a slow drying. The small amount of $(\text{NH}_4)_2\text{SO}_4$ in permalene probably prevents the formation of crystalline coprecipitates since these were not detected in tablets containing permalene.

7.4.3 Thermal stability of AN tablets

**stability curves**

Fig. 7.6 shows the results of the stability tests. Tablets with a good durability against temperature cycles around 32 °C yield ‘flat’ stability curves if $\Delta h$ in % is plotted versus the water content of the tablets while tablets with a poor durability against thermal cycling have high $\Delta h$ values at low water contents. Pure AN tablets have a poor thermal stability as they have high $\Delta h$ values even below 1 wt% water content. The curve reaches a maximum of approximately 15 % at higher water contents.

It should be noted that the stability curves of tablets to which $\text{KNO}_3$ or $\text{K}_2\text{SO}_4$ was added during preparation suggest that these additives provide an improved thermal stability (fig. 7.6a). Guinier X-ray diffraction results, however, show that these tablets exist for approximately one third of AN(III) at room temperature. Tablets to which $\text{K}_2\text{SO}_4$ was added during preparation did not contain separate potassium salts (see table 7.1). $\text{KNO}_3$ and AN form solid solutions and small concentrations of $\text{KNO}_3$ (at least up to 5 wt%) may dissolve in AN at room temperature because of the similar size of the $\text{K}^+$ and $\text{NH}_4^+$ ions, causing the III-IV transition temperature to decrease below 32 °C. AN(III) becomes stable at room temperature if the concentration of $\text{KNO}_3$ is approximately 3 wt% or more [8]. Tablets to which 2 wt% of either $\text{KNO}_3$ or $\text{K}_2\text{SO}_4$ was added during preparation did not completely transform from phase III into phase IV during the stability test where the lowest temperature is approximately 18 °C. The obtained stability curves for tablets containing these additives are therefore lower than if the tablets would have been transformed entirely upon heating and cooling.

**influence of macrostructure and hardness**

Some typical results of the stability tests are given in table 7.2 in relation to the
Fig. 7.6 Stability curves of AN containing various additives.
Table 7.2. Drying, hardness, the presence of heterogeneous nuclei, the presence of amorphous phases and the thermal stability of AN tablets.

<table>
<thead>
<tr>
<th>substance(s) added</th>
<th>drying</th>
<th>hardness</th>
<th>amorphous additive</th>
<th>heterogeneous nuclei</th>
<th>thermal stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>no additive</td>
<td>fast</td>
<td>+/−</td>
<td>no</td>
<td>no</td>
<td>−</td>
</tr>
<tr>
<td>Al(NO₃)₂·9H₂O</td>
<td>slow</td>
<td>++</td>
<td>yes</td>
<td>no</td>
<td>++</td>
</tr>
<tr>
<td>Al₂(SO₄)₃·18H₂O</td>
<td>slow</td>
<td>++</td>
<td>yes</td>
<td>yes</td>
<td>++</td>
</tr>
<tr>
<td>Ba(NO₃)₂·2(NH₄)₂SO₄</td>
<td>fast</td>
<td>+/−</td>
<td>no</td>
<td>yes</td>
<td>−</td>
</tr>
<tr>
<td>Mg(NO₃)₂·6H₂O</td>
<td>slow</td>
<td>+/−</td>
<td>yes</td>
<td>no</td>
<td>++</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>slow</td>
<td>+</td>
<td>yes</td>
<td>yes</td>
<td>++</td>
</tr>
<tr>
<td>NaN₃</td>
<td>intermediate</td>
<td>+/−</td>
<td>no</td>
<td>no</td>
<td>−</td>
</tr>
<tr>
<td>permalene</td>
<td>slow</td>
<td>−</td>
<td>yes</td>
<td>?</td>
<td>++</td>
</tr>
<tr>
<td>Na⁺RSO₃⁻</td>
<td>fast</td>
<td>−</td>
<td>?</td>
<td>no</td>
<td>+</td>
</tr>
<tr>
<td>PSS</td>
<td>intermediate</td>
<td>++</td>
<td>?</td>
<td>no</td>
<td>+</td>
</tr>
</tbody>
</table>

influence of the additives on some other characteristics of the tablets. The results presented in table 7.2 show that tablets with an improved thermal stability often dry slowly. The related coarseness of the internal structure of the tablets, however, has no effect on the thermal stability. For instance, the thermal stability of tablets to which NaNO₃ or (NH₄)₂SO₄ was added is not improved with respect to that of pure AN tablets while these additives do cause a slower drying and hence a coarser internal tablet structure. The fact that tablets containing Al, Fe, or Mg salts show a highly improved stability is therefore not caused by the coarse structure of these tablets but probably by other factors, as will be discussed below.

Hard tablets, like those containing Al salts or PSS, often show an improved thermal stability (table 7.2). With respect to pure AN tablets the coherence between the crystallites in hard tablets is improved leading to a smaller increase of the pore volume during the III-IV phase transition and hence an improved thermal stability. This does not imply, however, that weak tablets, like those containing Na⁺RSO₃⁻ and Na⁺C₆H₅SO₃⁻, have a decreased thermal stability. The reason why these additives slightly improve the thermal stability may be attributed to the fact that they block the III-IV phase transition front, just like amorphous phases formed by various other additives.

influence of amorphous phases

The crystalline coprecipitates of various additives in the AN tablets contain crystal water which is often partly lost during drying in the stove as was determined by X-ray diffraction (see table 7.1). Most of these crystalline, hydrated compounds were present in only minor amounts. In these cases also amorphous phases were formed, as was mentioned above. Tablets in which such amorphous phases are present show an improved thermal stability (figs. 7.6b–d).

The amorphous phases are most likely formed at the grain boundaries in the
tablets during crystallization and drying. These phases probably block the transition front during the III-IV phase transition. In situ microscopic observations have shown that in samples containing no additives, the transition front moves across crystallites, ignoring the grain boundaries. This leads to the formation of large areas in the granules with the same crystallographic orientation. The presence of amorphous phases at the grain boundaries, which block the transition front, results in many small areas with different crystallographic orientations.

The fact that tablets containing amorphous phases dry relatively slowly, as is shown in fig. 7.3, indicates that these amorphous phases have a strong water binding capacity. This is also indicated by the fact that the additives producing amorphous phases often form various hydrated double salts with AN. The performance of these additives is therefore also partly due to the water binding capacity of the amorphous coprecipitates.

Both avoiding the formation of large areas with the same crystallographic orientation by the presence of amorphous coprecipitates at the grain boundaries and the ability of these coprecipitates to bind water result in a 'flattening' of the stability curve and a 'shift' of the curve towards higher water contents, and hence an improvement of the thermal stability of AN.

Influence of heterogeneous nuclei during tablet preparation; combined effects

The coprecipitates present in tablets to which \( \text{Al}_2(\text{SO}_4)_3 \), \( \text{MgSO}_4 \), \( \text{FeSO}_4 \), or \( \text{Fe}_2(\text{SO}_4)_3 \) was added during preparation are only slightly soluble in the AN solution from which the tablets were prepared. Optical microscopic observations have shown that the tiny additive crystals act as heterogeneous nuclei for the crystallization of AN(II) which is initially formed during tablet preparation. This leads to the formation of many small crystal domains in the tablets.

\( \text{BaSO}_4 \) was also expected to dissolve poorly in the AN melt. In order to obtain a \( \text{BaSO}_4 \) precipitate with a particle size which is comparable to that formed by the other additives, stoichiometric amounts of \( \text{Ba(NO}_3)_2 \) and \( (\text{NH}_4)_2\text{SO}_4 \) were added to the water containing AN melt. \( \text{BaSO}_4 \) indeed forms a finely divided precipitate in the AN melt which promotes heterogeneous nucleation, although to a lesser extent than the coprecipitate formed in an AN solution to which e.g. \( \text{Al}_2(\text{SO}_4)_3 \) was added. \( \text{BaSO}_4 \), however, hardly improves the thermal stability of the final AN tablets (fig. 7.6a). This implies that the presence of heterogeneous nuclei during preparation, and hence the initial formation of many small crystal domains in the tablets, has on its own no improving effect on the thermal stability of AN. In combination with the presence of amorphous phases formed at the grain boundaries which block the III-IV transition front in the small AN crystallites, however, an improved thermal stability is found. This is the case for e.g. \( \text{Al}_2(\text{SO}_4)_3 \). It cannot be excluded that other combinations of the influences of additives amplify the final effect on the thermal stability as well.
7.5 Conclusions

The thermal stability of AN granules, i.e. the resistance against deterioration of AN granules due to the polymorphic phase transition III-IV, is improved by additives which (1) form amorphous phases at the grain boundaries which block the transition front during the III-IV transition, (2) have a water binding capacity, and/or (3) harden the granules. The presence of heterogeneous nuclei during crystallization, provided by some additives, might also improve the thermal stability, but only combined with the formation of amorphous phases at the grain boundaries which block the III-IV transition front. The coarseness of the macrostructure of AN tablets is not related to their thermal stability.

References

Summary

Ammonium nitrate (AN), NH\textsubscript{4}NO\textsubscript{3}, is an important base chemical for the production of mainly fertilizers and explosives. AN exists in at least six polymorphic crystal phases, from which five are stable at atmospheric pressure. The transition between the phases III and IV, which occurs upon temperature fluctuations around 32 °C, causes a decrease of the mechanical quality of AN products, which may finally lead to pulverization. The resistance of AN granules to deterioration of the mechanical quality due to the III-IV phase transition is called thermal stability.

The thermal stability of AN products can be improved by the application of additives. For fertilizer products with a high nitrogen content (more than 94 wt% AN) often specific inorganic salts are applied, like Mg(NO\textsubscript{3})\textsubscript{2} or Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} or mixtures of such salts.

Most of the production processes comprise a layer wise crystallization from a highly concentrated aqueous AN solution (up to 5 wt% water) on already formed AN particles at temperatures well above 100 °C where phase I or phase II is stable. Stabilizing additives are added to the concentrated AN solution mostly prior to granulation. They can, therefore, affect various successive processes which occur during production, storage, and transport of AN granules, namely the crystallization of AN(I) and/or AN(II) and the subsequent ripening or coarsening process, the drying of the granules, which also affects the coarsening of the crystallized AN, and the phase transitions which occur during cooling of the granules and possibly during storage and transport due to temperature fluctuations.

All these processes, viz. the way in which crystallization, coarsening, and phase transitions occur, affect the macrostructure of the granules and their texture (i.e. the coherence and mutual orientations of the crystallites within the granules). The macrostructure and texture of the granules, as well as the applied additives themselves can affect the final mechanical properties and thermal stability of the granules. The aim of this thesis is to gain a better insight in the effects of additives on the structure and the thermal stability of AN granules, which is of importance for the improvement of their mechanical quality.

During the granulation process dendritic crystallization of AN(I) and/or AN(II) occurs. Dendrites can in general be characterized by a number of parameters, like the growth rate and the radius of the dendrite tip, and the distance between the side branches. Between these parameters relationships exist which, in general, hold for the
dendritic crystallization of non-facetted materials. The effects of the water concentration and the presence of additives on simple relationships between these parameters are established for AN dendrites. Further, the morphology of AN(II) dendrites has been studied. The growth directions of AN(II) dendrites appear not to correspond to predicted crystallographic directions. This may partially be caused by anisotropy in the surface tension of AN(II). In the presence of some additives other growth directions develop.

During and after the dendritic growth, ripening or coarsening of the dendritic phase occurs as long as sufficient interdendritic solution is present. This coarsening leads to a thickening of the dendrite branches via a mechanism which resembles Ostwald ripening. Water content and additives have no significant effect on the kinetic parameters of the isothermal coarsening process. In the absence of additives detachment of the dendrite side branches occurs which also happens in the presence of e.g. alkyl sulphonates. In the presence of additives like Al(NO$_3$)$_3$ or NaNO$_3$ coalescence of the dendrite branches occurs. In the case of isothermal coarsening of large dendrites this coalescence results in the formation of crystallites with a diameter up to several thousands of microns.

After drying and cooling of the granules the phase transition III-IV may occur as a result of temperature fluctuations. This transition is catalysed by trace amounts of water, which is well known form literature. If no water is present, the transition does not happen. Owing to the predominant role of water it is suggested in the literature that this transition proceeds via dissolution and crystallization in a disordered phase boundary or even in a 'bulk' layer of solution. A systematic study of the similarity between projections of specific crystal faces of phase III and phase IV leads to various orientation relationships between both phases. The existence of several of these crystal faces and orientation relationships is confirmed by results from experiments on samples which were subjected to different pretreatments and by literature data. The combined experimental and theoretical results substantiate the existence of a solid-solid transition mechanism in single crystals. Solvent molecules which are able to break hydrogen bridges facilitate the rotation and displacement of ammonium and nitrate ions during the solid-solid transition.

The III-IV phase transition leads to an increase of the pore volume and simultaneously to a decrease of the mechanical strength of AN granules. The thermal stability depends on the water content in the granules. At increasing water contents (up to a few percents) the deterioration of the quality of AN granules increases after thermal cycling around the III-IV transition point.

The thermal stability of AN is improved by specific additives via various mechanisms. Amorphous compounds formed in AN granules from additives like borate-phosphate mixtures or Mg(NO$_3$)$_2$, and solidified at the grain boundaries, block the III-IV phase transition front and thus avoid the formation of large areas with the same
crystallographic orientation during this transition. The prevention of the formation of such large areas during the III-IV transition leads to an improved thermal stability. Most of the amorphous compounds have a strong water binding capacity which also has an improving effect on the thermal stability since the III-IV transition is catalized by free water. The presence of heterogeneous nuclei during crystallization, provided by some additives, in combination with the formation of amorphous phases on the grain boundaries, may also improve the thermal stability. Finally, the thermal stability is increased by additives which harden the granules. The hardness of AN granules appears to be increased if additives are applied which favour coalescence during the dendritic coarsening, occurring in the crystallization and drying steps of the granulation process.
Samenvatting

Ammoniumnitraat (AN), NH₄NO₃, is een belangrijke grondstof voor de produktie van voornamelijk kunstmesten en explosieven. AN komt voor in ten minste zes polymorfe kristalfasen, waarvan er vijf stabiel zijn bij atmosferische druk. De overgang tussen de fasen III en IV, die optreedt bij temperatuurwisselingen rond 32 °C, veroorzaakt een afname van de mechanische kwaliteit van AN-produkten, die uiteindelijk kan leiden tot vergriizing. De weerstand van AN-korrels tegen verslechtering van de mechanische kwaliteit ten gevolge van de fasonovergang III-IV wordt thermische stabiliteit genoemd.

De thermische stabiliteit van AN-produkten kan verbeterd worden door de toepassing van additieven. Voor kunstmest toepassingen met een hoog stikstofgehalte (94 gew.% AN) worden vaak specifieke anorganische zouten toegepast, zoals Mg(NO₃)₂ of Al₂(SO₄)₃ of mengsels van zulke zouten.

De meeste produktieprocessen omvatten een laagsgewijze kristallisatie uit een sterk geconcentreerde waterige AN-oplossing (tot 5 gew.% water) op reeds gevormde AN-deeltjes bij temperaturen ruim boven de 100 °C waar fase I of fase II stabiel is. Stabiliserende additieven worden veelal vóór de granulatie aan de geconcentreerde AN-oplossing toegevoegd. Zij kunnen daardoor invloed hebben op verschillende op elkaar volgende processen die gedurende de produktie, opslag en transport van AN-korrels plaatsvinden, namelijk de kristallisatie van AN(I) en/of AN(II) en het daarop volgende rippings- of vergrotingsproces, de droging van de korrels, die eveneens invloed heeft op de vergroting van het gekristalliseerde AN, en de fasonovergangen die optreden tijdens het afkoelen van de korrels en eventueel tijdens opslag en transport ten gevolge van temperatuurwisselingen.

AI deze processen, te weten de wijze waarop kristallisatie, vergroving en fasonovergangen plaatsvinden, hebben invloed op de macrostructuur van de korrels en op hun textuur (d.i. de samenhang en onderlinge oriëntaties van kristallieten in de korrels). De macrostructuur en textuur van de korrels, als ook de toegepaste additieven zelf kunnen invloed hebben op de uiteindelijke mechanische eigenschappen en thermische stabiliteit van de korrels. Het doel van dit proefschrift is om een beter inzicht te krijgen in de effecten van additieven op de structuur en de thermische stabiliteit van AN-korrels, wat van belang is voor de verbetering van hun mechanische kwaliteit.

Tijdens het granulatieproces vindt dendritische kristallisatie plaats van AN(I) en/of AN(II). Dendrieten kunnen in het algemeen gekarakteriseerd worden met behulp van
een aantal parameters, zoals de groeisnelheid en de straal van de dendrietpunt, en de afstand tussen de zijtakjes. Tussen deze parameters bestaan relaties die algemeen gelden voor de dendritische kristallisatie van niet-gefacetteerde stoffen. De invloeden van de waterconcentratie en van de aanwezigheid van additieven op eenvoudige relaties tussen deze parameters zijn voor AN-dendrietjes bepaald. Verder is de morfologie van AN(II)-dendrietjes bestudeerd. De groeirichtingen van AN(II)-dendrietjes blijken niet overeen te komen met voorspelde kristallografische richtingen. Dit wordt waarschijnlijk ten dele veroorzaakt door anisotropie in de oppervlaktespanning van AN(II). In de aanwezigheid van sommige additieven blijken andere groeirichtingen op te treden.

Gedurende en na de dendrietgroei treedt rijping of vergroting van de dendritische fase op zolang er voldoende interdendritische oplossing aanwezig is. Deze vergroting leidt tot een verdikking van de dendrietarmen via een mechanisme dat lijkt op Ostwald-rijping. Watergehalte en additieven hebben geen significant effect op de kinetiekparameters van het vergrotingsproces. In de afwezigheid van additieven laten de dendrietarmen los wat ook gebeurt in de aanwezigheid van bijvoorbeeld alkylsulfonaten. In de aanwezigheid van additieven zoals Al(NO₃)₃ of NaNO₃ vindt er coalescecentie van de dendrietarmen plaats. In het geval van isotherme vergroting van grote dendrietjes resulteert deze coalescecentie in de vorming van kristallieten met een doorsnede tot enkele duizenden microns.

Na drogen en afkoelen van de korrels kan de fasenovergang III-IV optreden ten gevolge van temperatuurwisselingen. Deze overgang wordt door geringe hoeveelheden water gekatalyseerd, wat algemeen bekend is uit de literatuur. Als er geen water aanwezig is, vindt deze overgang niet plaats. Vanwege de dominante rol van water wordt er in de literatuur gesuggereerd dat deze overgang plaatsvindt via oplossing en kristallisatie in een verstoorde grenslaag of zelfs in een 'bulk' laagje oplossing. Een systematische studie naar de overeenkomst tussen projecties van specifieke kristalvlakken van fase III en fase IV leverde verschillende oriëntatierelaties tussen beide fasen op. Het vóórkomen van verschillende van deze kristalvlakken en oriëntatierelaties wordt bevestigd door resultaten van experimenten met monsters die verschillende voorbehandelingen hebben ondergaan en door literatuurgegevens. De gecombineerde experimentele en theoretische resultaten bevestigen het bestaan van een vast-vast overgangsmechanisme in eenkristallen. Oplosmiddelmoleculen die waterstofbruggen kunnen verbreken maken de rotatie en verplaatsing van ammonium- en nitratieen gedurende de vast-vast overgang mogelijk.

De fasenovergang III-IV leidt tot een toename van het porievolume en tegelijkertijd tot een vermindering van de mechanische sterkte van AN-korrels. De thermische stabiliteit hangt af van het watergehalte in de korrels. Bij stijgende watergehalten (tot een paar procenten) neemt de verslechtering van de kwaliteit van AN-korrels toe na het doorlopen van temperatuurcycli rond het punt waarbij de III-IV overgang plaatsvindt.

De thermische stabiliteit van AN wordt verbeterd door specifieke additieven via
verschillende mechanismen. Amorfe verbindingen die in AN-korrels gevormd worden door additieven zoals boraat-fosfaat mengsels of Mg(NO₃)₂ en die op de kristallietgrenzen neerslaan, blokkeren het front van de fasenovergang III-IV en voorkomen zo de vorming van grote gebieden met dezelfde kristalografische oriëntatie gedurende deze overgang. Het verhinderen van de vorming van zulke grote gebieden tijdens de overgang III-IV leidt tot een verbetering van de thermische stabilitéit. De meeste amorfe verbindingen hebben een sterke waterbindende capaciteit hetgeen eveneens een verbeterend effect heeft op de thermische stabilitéit aangezien de fasenovergang III-IV gekataliseerd wordt door vrij water. De aanwezigheid van heterogene kiemen gedurende de kristallisatie, waarin voorzien wordt door sommige additieven, zou, in combinatie met de vorming van amorfe fasen op de kristallietgrenzen, eveneens de thermische stabilitéit kunnen verbeteren. Ten slotte wordt de thermische stabilitéit verbeterd door additieven die de hardheid van de korrels doen toenemen. De hardheid van AN-korrels blijkt te worden vergroot indien additieven worden toegepast welke coalescentie bevorderen gedurende de dendritische vergroeiing die plaatsvindt in de kristallisatie- en droogstappen van het granulatieproces.
Dankwoord

Dit promotieonderzoek is verricht in de werkgroep Industriële Kristallisatie, onderdeel van de vakgroep Chemische Processtechnologie en de vakgroep Proces en Energie van respectievelijk de faculteit der Scheikundige Technologie en der Materiaalkunde en de faculteit der Werktuigbouwkunde en Maritieme Techniek. Graag wil ik mijn dank uiten aan hen die bijgedragen hebben aan de totstandkoming van dit proefschrift.

In de eerste plaats wil ik Gerda van Rosmalen, Antoine van der Heijden en Geert-Jan Witkamp bedanken voor hun stimulerende opmerkingen en discussies. Ook Rob Geertman, Piet Bennema, Wilbert Derks en Jan van der Eerden wil ik bedanken voor de met hen gevoerde gesprekken over met name het verschijnsel dendraigtgroei.

Dank ben ik ook verschuldigd aan DSM Research voor de financiële ondersteuning en begeleiding van het onderzoek. Met betrekking tot het laatste wil ik met name Tjien Tjoe en Steven de Boer noemen. Verder wil ik Sja Wagemans noemen die de voor dit proefschrift onontbeerlijke stabilitietstesten had ontwikkeld in het kader van reeds uitgevoerd experimenteel werk bij DSM Research.

Velen hebben bijgedragen aan het experimentele werk. Han van Lent en Nico van der Pers bedank ik voor hun hulp bij het maken en analyseren van de vele Röntgenopnamen. Paul Durville wil ik bedanken voor het maken van de SEM-foto’s en voor de uitvoering van de Karl Fischer waterbepalingen en de stabilitietstesten. Last but not least I would like to express my thanks to Jackie Egerton, Rachel Hawadi, Marcel de Haan, Marcel Oogink, Marc ten Have, Mark Westera, Maurice te Riele, Michel Lentelink, Michel Nijland, Wim Boeken, Tim Landsmeer, Ruud Gries, and Zhu Ling who collected many of the experimental data.
List of publications


Curriculum vitae

Christoffel Adrianus van Driel
geboren op 14 november 1964 te Rotterdam.


augustus 1985 Propaedeutische examen scheikundige technologie.

oktober 1989 Ingenieursexamen scheikundige technologie, afstudeerrichting chemische procestechnologie.