Melt Crystallization of Ammonium Dinitramide (ADN) Investigated by Means of X-ray Diffraction

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Ammonium dinitramide (ADN, NH₄N(NO₂)₂) is a promising oxidizing agent for solid rocket propellants. In situ XRD investigations of ADN and ADN suspensions have been performed in order to understand and refine the emulsion crystallization process for manufacturing spherical ADN particles (prills). The investigation revealed that the melt crystallization behavior depends on ADN quality, humidity, maximum temperature of temperature cycles, and suspension agents. Further investigations will focus on additives for controlling the mechanisms investigated, e.g., by seeding.

Keywords: Ammonium dinitramide, Emulsion crystallization, In-situ-investigation, XRD

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1 Introduction

Ammonium dinitramide (ADN, NH₄N(NO₂)₂) is a promising oxidizing agent for solid rocket propellants used in defense and space applications. The material melts about 93.5 °C and its decomposition may start with the melting [1]. Besides, early decomposition in applications with copper-based catalysts and the formation of eutectic mixtures with ammonium nitrate and/or water are reported [2–4]. In this context the influence of additives on the thermal stability of ADN were investigated in the last decades, and structure modification, such as prilling and coating, are applied in order to improve the stability, the processability, and in order to mitigate incompatibilities. For instance, an emulsion crystallization process for manufacturing spherical ADN particles (prills) was set up at the Fraunhofer ICT, where ADN suspensions are heated to 95 °C and emulsified molten ADN droplets are cooled and crystallized to ADN prills [5, 6]. However, there is little known about the interaction and stabilization mechanisms on the micro and crystal structure level. Therefore, systematic investigations of ADN were started by means of X-ray diffraction [7, 8] showing that the crystallization behavior of molten ADN droplets depend on product qualities and additives and that anisotropic crystal growth plays a key role in the stabilization [9]. In this context in situ investigations of the melt crystallization of ADN and ADN suspensions have been performed by means of temperature resolved X-ray diffraction.

2 Experimental and Evaluation

The sample portfolio included raw products of ADN, fine and coarse ADN prills sieved from same lot, coarse reference prills from the Swedish Defence Research Agency (FOI), Sweden, refined coarse prills (2.0) and suspensions of ADN and fumed silica in paraffin and ADN, tenside and fumed silica in decane, in concentrations applied in current prilling processes at the Fraunhofer ICT pilot plant. The investigations have been performed on a Bragg-Brentano diffractometer, D8 Advance from Bruker AXS, equipped with copper tube, Ni filter, two 2.5° Soller collimators, variable divergence slit (V6), temperature device from MRI with a copper sample holder, and silicon strip detector (LynxEye) with 3° 2θ detector opening. In order to simulate the prilling process, samples were cycled stepwise with the temperature program 20/Tₘₐₓ/90/80/70/60/50/40/30/20 °C with 95, 96, 97, or 98 °C maximum temperature (Tₘₐₓ), 12 K min⁻¹ nominal heating rate, 5 min relaxation time and about 12 min measuring time at each temperature step (Fig. 1). Diffraction patterns were monitored between 14 and 42 °2θ with 0.05 °2θ step width and 1 s counting time per step. In order to check the influence of humidity, samples were investigated in ambient air and under nitrogen flushing.

The temperature resolved X-ray diffraction patterns were monitored by means of waterfall plots, the crystallinities were evaluated at each temperature step using the program DIFFRAC.EVA V4.3 (Bruker AXS) and plotted versus temperature, and new phases were identified and quantified by means of Rietveld analysis using the program TOPAS (Bruker AXS).

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## Results

### 3.1 Temperature Cycles of ADN up to 95 °C

Fig. 2 shows the waterfall plot of a raw ADN sample. At room temperature (pattern at the bottom of the diagram) diffraction peaks indicate the presence of crystalline ADN before temperature cycling. The ADN melted completely when heated to 95 °C – the peaks disappeared and a halo emerged around 27 °C, but the sample did not recrystallize during cooling to 20 °C. Thus, a supercooled ADN melt was formed through the temperature cycling, and it was found to be stable at least over a couple of days. A different behavior was observed with coarse prills, which recrystallized spontaneously at about 80 °C during cooling, even when the prills were ground beforehand (Fig. 3) – in order to rule out a pure particle size effect, where residual micro-crystallites may survive melting to act as crystallization seeds.

The crystallinities of the ground and fine ADN samples during cycling to 95 °C in air and under nitrogen flushing are presented in Fig. 4. The plot provides an overview of the crystallization behavior, where coarse prills (triangles) and ground samples (x’s) equally melted in air at 95 °C and recrystallized during cooling between 80 and 70 °C, but the raw product (diamonds) and the fine prills (squares) once melted remained as supercooled melts or crystallized spontaneously only after hours. Under nitrogen flushing about 70 to 50 % of the fine and coarse ADN-prills did not melt during the cycling to 95 °C (stars and circles), most likely through the absence of atmospheric humidity. Hence, higher maximum temperatures or longer dwell times would be necessary for melting ADN under dry conditions. The residual crystallinities of a few percent, e.g., of the coarse prills measured in air at 95 and 90 °C, are considered to be artifacts of the evaluation tool, as no peaks were recognized in the related diffraction patterns.

### 3.2 Temperature Cycles of ADN up to 97 and 98 °C under Nitrogen Flushing

The degree of melting of ADN under nitrogen flushing in the XRD system was measured between 95 and 98 °C (Fig. 5). The melting started during heating to 95 °C, but 30 to 40 % ADN still survived in a crystalline state. Further ~10 % melted while heated to 96 °C until the samples were completely melted at 97 °C. However, sample quantities were found to be reduced after heating to 98 °C, indicating that sublimation or partial decomposition of ADN already took place.
The crystallinities of the temperature cycles up to 97 and 98 °C are depicted in Fig. 6. All samples were completely melted at maximum temperatures \(T_{\text{max}} = 97\) and 98 °C), but recrystallized quite differently. The reference sample from the Swedish Defence Research Agency (FOI) recrystallized immediately while being cooled from 97 to 90 °C (stars), but the ICT samples recrystallized at lower temperatures between 70 and 40 °C. It is interesting to note that the samples cycled to 98 °C recrystallized earlier than those cycled to 97 °C. An explanation may be that decomposition products act as crystallization seeds. The crystallization processes took place spontaneously and with high conversation rates. For instance, Fig. 7 shows a diffraction pattern section measured at 60 °C. At the crystallization point a broad halo of an amorphous structure on the left side of the pattern shortly switched to sharp peaks and low underground base line on the right side.

### 3.3 Temperature Cycles of ADN Suspensions up to 95, 96, and 97 °C under Nitrogen Flushing

The ADN suspensions were cycled up to 95, 96, and 97 °C and evaluated crystallinities were plotted versus temperature in Fig. 8. No cycles to 98 °C were measured in order to avoid decomposition or sublimation of ADN. The plot revealed quite different behavior of the ADN suspensions in decane and paraffin. At 95 °C ADN melted completely in paraffin, but only to 50 % in decane. While ADN in decane recrystallized during cooling to high crystallinities >80 %, amorphous structures with crystallinities below 20 % remained dominant in paraffin. It should be mentioned here, that the suspensions of course have lower crystallinities than pure raw ADN or prills, which reflects in lower starting values. An interesting detail was found during cycling ADN in decane up to 96 °C. 4 wt % ammonium nitrate phase II crystallized concomitantly with ADN at −60 °C (details will be reported elsewhere).

![Figure 3. Waterfall plot of ground coarse ADN prills measured during temperature cycling up to 95 °C.](image)

![Figure 4. Crystallinity of ADN samples during temperature cycling up to 95 °C in air and under nitrogen flushing.](image)
4 Summary and Discussions

The melt crystallization of ADN and ADN suspensions was investigated by means of temperature resolved X-ray diffraction. Samples were heated and cooled stepwise related to a pilot plant prilling process of the Fraunhofer ICT, and diffractions patterns were measured in situ and evaluated for phase analysis and crystallinity monitoring. However, it should be mentioned that sample stirring applied in the prilling process could not be realized in the XRD-measurements. The investigations revealed different melt and crystallization behavior of ADN qualities and influences of humidity, maximum temperature of temperature cycles, and suspension agents. In air ADN melted when heated to 95 °C, but in dry nitrogen complete melting was not reached below 96 till 97 °C. At such high temperatures decomposition and/or sublimation was already observed. Thus, a moderate humidity may be used to stimulate early melting and to avoid decomposition products, which may destabilize the ADN prills. Melting and recrystallization of ADN suspensions were realized most clearly in decane and the cycles up to 96 and 97 °C, but emerging decomposition products had to be taken into account in this system. For instance, a small amount ammonium nitrate was detected in an ADN/decane suspension, which most likely had been formed during heating to 96 °C, was immediately solved in a eutectic mixture with ADN, and crystallized concomitantly with ADN during the cooling process. Using paraffin as suspension agent, a maximum temperature of 95 °C would suffice to melt ADN, but mixtures tend to build supercooled melts, recrystallization take place partially and/or strongly postponed. Seeding may help in this system. Hence, further investigations will focus on additives for controlling the melt and recrystallization of ADN in various suspension agents in order to refine production and products for applications in rocket propellants.

Symbols used

\[ 2 \theta \] angle between incident and measured X-ray radiation
\[ \text{N}_2 \] symbol used for nitrogen flushing
\[ T_{\text{max}} \] maximum temperature of cycles

Abbreviations

ADN ammonium dinitramide
AXS Bruker AXS, Karlsruhe, Germany
FOI Swedish Defence Research Agency, Stockholm, Sweden
ICT Fraunhofer Institut für Chemische Technologie, Pfinztal, Germany
XRD X-ray diffraction
Figure 7. Magnified section of a diffraction pattern with spontaneous crystallization of molten ADN.

Figure 8. Crystallinity of ADN suspensions during cycling up to 95, 96, and 97°C under nitrogen flushing.

References

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Research Article: In situ X-ray diffraction experiments give insight into melt-crystallization mechanisms of ammonium dinitramide (ADN). The quality of the raw products, parameters of prilling processes, and, e.g., seeding additives shall be used for tailoring properties of ADN prills for applications in solid rocket propellants.