Thermal and X-ray diffraction analysis studies during the decomposition of ammonium uranyl nitrate

B. H. Kim · Y. B. Lee · M. A. Prelas · T. K. Ghosh

Received: 14 November 2011 / Published online: 3 January 2012 © The Author(s) 2011. This article is published with open access at Springerlink.com

Abstract Two types of ammonium uranyl nitrate (NH₄)₂UO₂(NO₃)₄·2H₂O and NH₄UO₂(NO₃)₃, were thermally decomposed and reduced in a TG-DTA unit in nitrogen, air, and hydrogen atmospheres. Various intermediate phases produced by the thermal decomposition and reduction process were investigated by an X-ray diffraction analysis and a TG/DTA analysis. Both (NH₄)₂UO₂(NO₃)₄·2H₂O and NH₄UO₂(NO₃)₃ decomposed to amorphous UO₃ regardless of the atmosphere used. The amorphous UO₃ from (NH₄)₂UO₂(NO₃)₄·2H₂O was crystallized to γ-UO₃ regardless of the atmosphere used without a change in weight. The amorphous UO₃ obtained from decomposition of NH₄UO₂(NO₃)₃ was crystallized to α-UO₃ under a nitrogen and air atmosphere, and to β-UO₃ under a hydrogen atmosphere without a change in weight. The amorphous UO₃ obtained from decomposition of NH₄UO₂(NO₃)₃ was crystallized to α-UO₃ under a nitrogen and air atmosphere, and to β-UO₃ under a hydrogen atmosphere without a change in weight. Under each atmosphere, the reaction paths of (NH₄)₂UO₂(NO₃)₄·2H₂O and NH₄UO₂(NO₃)₃ were as follows: under a nitrogen atmosphere: (NH₄)₂UO₂(NO₃)₄·2H₂O → (NH₄)₂UO₂(NO₃)₄·H₂O → (NH₄)₂UO₂(NO₃)₄ → NH₄UO₂(NO₃)₃ → A-UO₃ → γ-UO₃ → α-UO₃ → U₃O₈; NH₄UO₂(NO₃)₃ → A-UO₃ → α-UO₃ → U₃O₈; under an air atmosphere: (NH₄)₂UO₂(NO₃)₄·2H₂O → (NH₄)₂UO₂(NO₃)₄ → NH₄UO₂(NO₃)₃ → A-UO₃ → γ-UO₃ → α-UO₃ → U₃O₈; NH₄UO₂(NO₃)₃ → A-UO₃ → α-UO₃ → U₃O₈; and under a hydrogen atmosphere: (NH₄)₂UO₂(NO₃)₄·2H₂O → (NH₄)₂UO₂(NO₃)₄ → NH₄UO₂(NO₃)₃ → A-UO₃ → γ-UO₃ → α-UO₃ → U₃O₈.

Keywords Ammonium uranyl nitrate · Thermal decomposition · Modified direct denitration

Introduction

Ammonium uranyl nitrate (AUN) is an important intermediate product during conversion of uranyl nitrate [UO₂(NO₃)₂] solution to UO₂ powder for the fabrication of nuclear fuels, the so-called modified direct denitration (MDD) process. Many conversion processes have been developed, such as, ammonium uranyl carbonate (AUC), ammonium diuranate (ADU), and an integrated dry route (IDR). Each process has its merits and demerits. In comparison with other processes, the MDD process offers the greatest potential for cost reduction and good product quality for the production of UO₂ powder.

The modified direct denitration process involves the thermal decomposition of AUN double salts, which are prepared from a mixture consisting of a UO₂(NO₃)₂ solution and NH₄NO₃. The physical and chemical properties of an oxide powder depend upon its thermal treatment. Also, the sintering behavior of UO₂ powder can be related to its powder characteristics and processing parameters. It has been observed that the presence of NH₄NO₃ in a UO₂(NO₃)₂ feed solution prior to a thermal denitration greatly improved the sintering properties of UO₂ powder [1].

Three double salts are known for the UO₂(NO₃)₂-NH₄NO₃-H₂O system, but there have been only a few studies done on thermal decomposition of these salts. Laboratory scale denitration tests showed that NH₄UO₂(NO₃)₃ decomposes without melting, and thus does not form a dough stage.

B. H. Kim (✉) · Y. B. Lee
Department of Fast Reactor Technology Development, Korea Atomic Energy Research Institute, 150 Deokjin-dong, Daejeon 305-353, Korea
e-mail: bhkim1@kaeri.re.kr

M. A. Prelas · T. K. Ghosh
Nuclear Science and Engineering Institute, University of Missouri, Columbia, MO, USA
similar to that encountered during a denitration. Also, UO₂ produced from NH₄UO₂(NO₃)₃ in these tests appeared to be more active than a corresponding oxide produced from UO₂(NO₃)₂ solution. It was also reported that NH₄UO₂(NO₃)₃ decomposes without melting at 270–300 °C to give γ-UO₃ powder of an average size of approximately 3 μm, with good ceramic properties for its fabrication into UO₂ nuclear fuel pellets [2].

In the conversion of AUN to uranium oxides, the characteristic of the resulting powder particles depends upon the AUN preparation process and also upon the thermal decomposition procedures. ADU decomposes first and then leads to UO₃. Amorphous uranium trioxide (A-UO₃) is mainly formed in the absence of ammonium and nitrate ions, whereas deamination of the retained ammonia leads to β-UO₃ [3]. Meanwhile, AUC decomposes at around 190 °C, giving off CO₂, NH₃, and H₂O with the formation of an amorphous phase. In a N₂, Ar, or CO₂ atmosphere, the amorphous phase crystallizes to α-UO₃ before decomposing to U₃O₈ [4]. Various reports have been published on thermal analysis studies of the reactions occurring during a decomposition of AUC and ADU. However, few studies on the thermal decomposition of AUN can be found in the literature. Therefore, the objective of this study is to investigate the reaction pathways during a thermal decomposition and reduction of AUN to achieve a better knowledge of the influence of an AUN preparation process and thermal decomposition procedures on uranium oxides under a nitrogen, air, or hydrogen atmosphere.

Experimental

The UO₂(NO₃)₂·6H₂O and NH₄NO₃ solutions were prepared using various mole ratios of NH₄⁺/U. (NH₄)₂UO₂(NO₃)₂·2H₂O was resulted when the pH of the reaction solution was 2.58 and the mole ratio of NH₄⁺/U was 2.14. And NH₄UO₂NO₃ was resulted when the pH of the reaction solution was 2.01 and the mole ratio of NH₄⁺/U was 1.07. The volume of both UO₂(NO₃)₂·6H₂O and NH₄NO₃ solutions were 50 mL. The mixed reaction of these two solutions was performed in a heating mantle where the temperature could be automatically controlled. The reaction temperature was maintained at 90 °C. After the reaction had progressed to a point which a precipitate was generated, the heating was stopped and the precipitated solid was filtered. The precipitate remaining on the filter paper was then left at room temperature to dry. As a result, a primary sample was prepared. The primary sample contained unreacted UO₂(NO₃)₂·6H₂O and NH₄NO₃ as impurities. To eliminate these impurities, the primary sample was recrystallized. The recrystallization was performed by dissolving the primary sample in distilled water at 40 °C, and then cooling it down to room temperature. The crystals acquired through the recrystallization were referred to as the secondary sample. The pH of the mixed solution was controlled by adding UO₃ or concentrated nitric acid to the mixed solution. Next the synthesis of AUN was carried out. When the UO₃ was added to that, it was dissolved at a temperature of 30 °C. To eliminate any undissolved UO₃ from the reaction solution, it was filtered, and the filtrate was used as the reaction solution for AUN synthesis. The characterization of synthesized AUN was reported in previous studies [5].

To analyze the thermal decomposition and reduction pathways of each AUN, the respective thermal decomposition and reduction temperature must be determined beforehand to identify any intermediate phase produced from each reaction stage. For this purpose, a thermogravimetric (TG)/differential thermal analysis (DTA) experiment was carried out in various atmospheres, which were 100% nitrogen, air, and hydrogen gas. The flow rate for each gas was 50 mL/min, the heating rate was 5 °C/min, and the temperature was varied from room temperature to 800 °C. About 8 mg of sample was used in each run. Each reaction stage was identified on the basis of DTA results, and the temperature for the intermediate phase was determined. Samples used to acquire the intermediate phase were obtained by heating each AUN sample in the thermal analyzer up to the temperature as determined from the DTA results. About 40 mg of AUN was thermally decomposed and reduced in the thermal analyzer to produce the samples for use in the analyzer in order to identify the intermediate phases. The intermediate reaction phases were determined and identified by TG analysis and X-ray diffraction. The characteristic analyzes of the intermediate phases and sample preparations were performed by a TG-DTA unit (TA Instrument, Simultaneous SDT 2960). The X-ray diffraction analysis was performed at room temperature at a scan speed of 0.4°/min and by varying the value of 2θ from 10° to 70°. The target was Cu, and one slit was used for the divergence and scattering (Rigaku Max/3D).

Results and discussion

DTA analysis

The DTA results from the thermal decomposition of (NH₄)₂UO₂(NO₃)₃·2H₂O as manufactured under a nitrogen, air, and hydrogen atmosphere are shown in Fig. 1. The reaction under the nitrogen atmosphere started at around 50 °C with a dehydration of the hydrate, which is an endothermic reaction. Endothermic peaks, which seemed to be a phase change of NH₄NO₃, were due to the presence of extremely small amount of impurities. These peaks
appeared around 84, 130, and 155 °C. An endothermic peak as a result of the first thermal decomposition of (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·2H$_2$O into NH$_4$NO$_3$ appeared within a temperature range of 168 to 240 °C. A second endothermic that was due to the second thermal decomposition of NH$_4$NO$_3$ appeared in the temperature range of 268 to 307 °C. After the second endothermic peak continued, a weak exothermic reaction took place around 400 °C. This reaction continued for a while, and then ended as an endothermic reaction that took place at 579 °C.

The thermal decomposition under the air atmosphere showed a different trend. NH$_4$UO$_2$(NO$_3$)$_3$ was thermally decomposed to UO$_3$ at around 275 °C, which was about 7 °C higher than the corresponding temperature under the nitrogen atmosphere. An exothermic reaction was observed at a temperature slightly higher than 400 °C. However an endothermic reaction took place at around 599 °C. It is assumed that such a difference in the reaction temperature between an air and a nitrogen atmosphere was due to the different activation energy that was dependent on the atmospheric under which the decomposition was carried out. Also, it has been reported that if the composition of a compound is different or an impurity is present, the peak of the DTA curve moves toward a higher temperature [4].

Under a hydrogen atmosphere, the thermal decomposition was followed by a reduction reaction. First, the dehydration of (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·2H$_2$O occurred, and the thermal decomposition of NH$_4$NO$_3$ then took place, which had the same trend as that under nitrogen and air atmospheres. However, both the temperature at which the thermal decomposition took place and the maximum peak temperature shifted toward a lower temperature. Like the exothermic peak under the nitrogen and air atmospheres, the exothermic peak appeared at around 400 °C. However, the subsequent reactions were different from those under the nitrogen and air atmospheres due to the reduction by hydrogen, which caused the appearance of two different exothermic peaks. An exothermic reaction took place at 440 °C, then shortly after another exothermic reaction started at around 590 °C. Halldahl and Nygren [4] also observed a similar phenomenon, the DTA curves for decomposition of (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·2H$_2$O were dependent upon the atmospheric gas used during the decomposition. Halldahl also reported that the maximum peak temperature when AUC was thermally decomposed into UO$_3$ under a nitrogen, air, and hydrogen atmosphere was 195, 198, and 185 °C, respectively. The thermal decomposition temperature became lower in the following order: hydrogen < nitrogen < air. This result is similar to the result observed in the current study, where the maximum peak temperature appeared when (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·2H$_2$O was decomposed into UO$_3$.

The DTA results for the thermal decomposition and reduction of NH$_4$UO$_2$(NO$_3$)$_3$ when under different atmospheric gases are shown in Fig. 2. The results were found to be very similar to the DTA results of the thermal decomposition and reduction of (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·2H$_2$O. Plus, in the case of (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·2H$_2$O, the endothermic peaks appeared around 84, 130, and 155 °C due to a phase change of NH$_4$NO$_3$. It may be noted that in the case of NH$_4$UO$_2$(NO$_3$)$_3$, such peaks were very weak.

The endothermic peak resulting from the thermal decomposition of NH$_4$NO$_3$, which was the first reaction under a nitrogen atmosphere, appeared between 266 and 305 °C, and a weak exothermic reaction then took place at around 400 °C followed by an endothermic reaction at 578 °C. Also, in air, an endothermic reaction was observed at 277 °C, an exothermic reaction around 400 °C, and two endothermic reactions at around 598 °C. Under a hydrogen atmosphere, one endothermic reaction was observed at
270 °C, and three exothermic reactions were then observed at around 400, 441, and 590 °C.

Preparation of samples for analysis of intermediate phases

The temperatures at which the endothermic and exothermic reactions started and ended, as shown in the DTA curves, were used to determine intermediate phases during thermal decomposition of (NH₄)₂UO₂(NO₃)₄·2H₂O and NH₄UO₂(NO₃)₃ and during their reduction. These intermediate phases are shown in Table 1. The samples for acquiring the intermediate phases were prepared under the respective atmospheres by decomposing (NH₄)₂UO₂(NO₃)₄·2H₂O and NH₄UO₂(NO₃)₃ thermally at 390, 480, and 800 °C under nitrogen and air atmospheres, and at 390, 430, 480, and 600 °C under a hydrogen atmosphere. The samples were further reduced in a thermal analyzer and cooled down to room temperature. The X-ray diffraction analysis of each intermediate phase was performed to gain a better understanding of the intermediate phases.

X-ray diffraction analysis of intermediate phases obtained from AUN

Under a nitrogen atmosphere (NH₄)₂UO₂(NO₃)₄ and NH₄UO₂(NO₃)₃ were produced from (NH₄)₂UO₂(NO₃)₄·2H₂O, while NH₂NO₃ was thermally decomposed. A new intermediate phase was produced from NH₄UO₂(NO₃)₃ through an endothermic reaction. As shown in Fig. 3b, the structure of NH₄UO₂(NO₃)₃ disappeared completely at a thermal decomposition temperature of 390 °C, and amorphous UO₃, a new uranium oxide was formed. In addition, it was also found that in the intermediate phase, amorphous UO₃ was subsequently transformed into γ-UO₃ with a crystal structure at 480 °C (See Fig. 3c). The γ-UO₃ subsequently transformed into U₃O₈ by a phase change through a weak endothermic reaction at a temperature of 800 °C (See Fig. 3d).

The intermediate phase obtained after thermal treatment of (NH₄)₂UO₂(NO₃)₄·2H₂O under the air atmosphere appeared to be the same as that obtained under a nitrogen atmosphere. This is shown in Fig. 4. However, as identified in the DTA results, under an air atmosphere, the intermediate phase was produced at a higher temperature than that at a nitrogen atmosphere.

Under a hydrogen atmosphere (NH₄)₂UO₂(NO₃)₄·2H₂O produced a different intermediate phase through a thermal decomposition and reduction compared to the phase observed when decomposed under nitrogen and air atmospheres. The uranium oxide produced at a temperature of 390 °C under a hydrogen atmosphere was amorphous UO₃ as was the case under nitrogen and air atmospheres (See Fig. 5b), however, amorphous UO₃ was crystallized at 430 °C along with the phase change from UO₃ to γ-UO₃ (See Fig. 5c). Furthermore, γ-UO₃, which went through an exothermic reaction at 430 °C, was transformed into α-U₃O₈ by a phase change at 490 °C (See Fig. 5d), and α-U₃O₈ was finally reduced to UO₂ at 600 °C (See Fig. 5e).

The DTA results, as shown in Fig. 1 indicated that the temperature at which UO₃ was reduced to α-U₃O₈ under a hydrogen atmosphere was lower than the temperature at which UO₃ was reduced to U₃O₈ under an air atmosphere. When (NH₄)₂UO₂(NO₃)₄·2H₂O was thermally decomposed to UO₃, NH₄⁺, as a residual substance, was included in the UO₃ matrix. Therefore, as the temperature increased, the ammonia contained in the residual substance was released and further oxidized under an air atmosphere so that the

---

Table 1 Thermochemical conditions for the preparation of intermediates decomposed from (NH₄)₂UO₂(NO₃)₄·2H₂O and NH₄UO₂(NO₃)₃

| Atmosphere | Final temperature of thermal treatment for intermediates of (NH₄)₂UO₂(NO₃)₄·2H₂O and NH₄UO₂(NO₃)₃ (°C) |
|------------|-------------------------------------------------------------------------------------------------|
| N₂         | 390  480  800                                                                                     |
| Air        | 390  480  800                                                                                     |
| H₂         | 390  430  480  600                                                                                 |

---

Fig. 3 X-ray diffraction patterns of intermediates produced from (NH₄)₂UO₂(NO₃)₄·2H₂O in N₂ atmosphere
auto reduction from UO₃ to U₃O₈ was suppressed [6]. As such, it would appear that the production of U₃O₈ from UO₃ took place at a lower temperature under a hydrogen atmosphere. Generally, the reduction from UO₃ to U₃O₈ through an auto reduction is as follows:

\[3\text{UO}_3 \rightarrow \text{U}_3\text{O}_8 + 1/2\text{O}_2\]

It is hypothesized that in hydrogen atmosphere, hydrogen was adsorbed on to the matrix and reacted with oxygen ions and then diffused out of the UO₃ matrix to produce \(\text{H}_2\text{O}\). The produced \(\text{H}_2\text{O}\) desorbed from the UO₃ matrix surface, and at the same time, oxygen present in the UO₃ rapidly diffused onto the UO₃ matrix. This resulted in a fast reduction rate from UO₃ to U₃O₈. Meanwhile, in air atmosphere, the thermal decomposition rate of UO₃ to U₃O₈ was slow, because the oxygen present in the UO₃ was prevented from being diffused onto the UO₃ matrix.

As shown in Fig. 6, in the case of NH₄UO₂(NO₃)₄·2H₂O, amorphous UO₃ was produced at 390 °C. However, decomposition (NH₄)₂UO₂(NO₃)₄·2H₂O (See Fig. 6b) resulted in \(\alpha\)-UO₃ at 490 °C (See Fig. 6c). When comparing this phenomenon with the one in which (NH₄)₂UO₂(NO₃)₄·2H₂O produced \(\gamma\)-UO₃ at a temperature of 480 °C, it suggests that NH₄UO₂(NO₃)₃ was thermally decomposed through a different phase change route compared to (NH₄)₂UO₂(NO₃)₄·2H₂O decomposition route. Subsequently, the \(\alpha\)-UO₃ phase, which went through an endothermic reaction at 540 °C, changed into \(\alpha\)-U₃O₈ with a crystal structure at a temperature of 800 °C (See Fig. 6d). As shown in Fig. 7, the thermal decomposition process under an air atmosphere was found to be the same as that under a nitrogen atmosphere.

As can be seen from Fig. 8, the thermal decomposition and reduction of NH₄UO₂(NO₃)₃ under a hydrogen atmosphere resulted in a final product of UO₂ (See Fig. 8e) with a crystal structure through a series of phase changes to amorphous UO₃ (See Fig. 8b), \(\beta\)-UO₃ (See Fig. 8c), and U₃O₈ (See Fig. 8d). In the case of NH₄UO₂(NO₃)₃, when amorphous UO₃ crystallized, \(\beta\)-UO₃ was produced in the intermediate phase, whereas in the case of (NH₄)₂UO₂(NO₃)₄·2H₂O, \(\gamma\)-UO₃ was produced in the intermediate phase.

Table 2 shows a comparison of the above X-ray diffraction analysis results and thermal analysis results between ADU and AUC. Specifically, it is worth noting the phase change of UO₃ among the intermediate phases of the uranium oxide that are produced during thermal decomposition process of two AUNs. It may be noted that the sinterability of UO₂ powder is significantly related to the physical and chemical characteristics of the precursor and.
the reaction mechanism of the intermediate phases [7]. In the current study, it was found that $\gamma$-UO$_3$ was produced as an intermediate product when (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·2H$_2$O was thermally decomposed irrespective of the atmospheric gas used. However, when NH$_4$UO$_2$(NO$_3$)$_3$ was decomposed, different forms of UO$_3$ were produced depending on the atmosphere under which the decomposition was carried out. Under nitrogen and air atmospheres, $\alpha$-UO$_3$ was produced, whereas $\beta$-UO$_3$ was resulted while under a hydrogen atmosphere. It appears that starting substance, atmospheric gas, and reaction gas discharge affected the decomposition reaction. The thermal decomposition and reduction processes of AUN have not been studied adequately, and an understanding of various reaction processes of AUN is unavailable. However, various studies with different opinions have been reported in the literature on the reduction ADU and AUC. Woolfrey [8] explained that under a hydrogen atmosphere, ADU can be directly reduced to UO$_2$, under oxygen or nitrogen atmosphere, ADU is transformed into UO$_3$ and U$_3$O$_8$ through a calcination process, which can then be reduced to UO$_2$ under a hydrogen atmosphere. Cordfunke [9] reported that amorphous UO$_3$ and $\beta$-UO$_3$ exist in a crystal form during the process of thermal decomposition of ADU. Landspersky [10] and Rodriguez et al. [11] noted that the existence of two forms of UO$_3$ is due to the heating rate during thermal decomposition. Landspersky [10] reported that when the heating rate during thermal decomposition is slow (1 °C/min), amorphous UO$_3$ was produced, whereas when the heating rate increases (10 °C/min), $\beta$-UO$_3$ is produced. So far, it would seem that the forms of UO$_3$ produced during the process of a thermal decomposition of ADU are mostly amorphous UO$_3$ and $\beta$-UO$_3$, irrespective of the atmospheric gas used [7]. However, Kim [12] reported that in the case of thermal decomposition of AUC, under an air atmosphere, only amorphous UO$_3$ was produced, while under nitrogen and hydrogen atmospheres, amorphous UO$_3$ and $\beta$-UO$_3$ are produced. As shown in Table 2, the thermal decomposition and reduction process of AUC depend on the atmospheric gas or starting substance used. In particular, the reaction process differed depending on the two forms of AUN used in this study. In the case of AUN, the starting substance is produced by varying the mole ratio of NH$_4$?/U, and adding NH$_4$NO$_3$ as a reactant at a specified time. In the case of AUC, both NH$_3$ and CO$_2$ were used as reactants. In the case of ADU, both NH$_3$OH and NH$_3$ are used as reactants. These additives affected the thermal decomposition characteristics of final products.

An analysis of the intermediate phases and reaction characteristics has been discussed for each stage by using the data from DTA and X-ray diffraction analysis. By comparing these results with the TG analysis results, the
respective thermal decomposition and reduction characteristics of \((\text{NH}_4\text{)}_2\text{UO}_2(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}\) and \(\text{NH}_4\text{UO}_2(\text{NO}_3)_3\) were also reconfirmed. As already identified, \(\text{NH}_4\text{UO}_2(\text{NO}_3)_3\) is decomposed thermally according to the following reaction formula.

\[
\text{NH}_4\text{UO}_2(\text{NO}_3)_3 \rightarrow \text{UO}_3 + \text{N}_2\text{O} \uparrow + \text{N}_2\text{O}_5 \uparrow + 2\text{H}_2\text{O} \uparrow
\]

The TG curves corresponding to these reactions under different atmospheres are illustrated in Figs. 9 and 10. In the case of \((\text{NH}_4\text{)}_2\text{UO}_2(\text{NO}_3)_4 \cdot \text{C}_1\text{H}_2\text{O}\), thermal decomposition of \(\text{NH}_4\text{UO}_2(\text{NO}_3)_3\) into \(\text{UO}_3\) started at 268, 275 and 260 °C under a nitrogen, air, and hydrogen atmosphere, respectively, and ended at about 450 °C under nitrogen and air atmospheres, and at about 350 °C under a hydrogen atmosphere. The weight loss was 39.26, 39.16 and 39.05 wt% under a nitrogen, air, and hydrogen atmosphere, respectively, which was different from the theoretical value of 39.67 wt%. A difference was found for \(\text{NH}_4\text{UO}_2(\text{NO}_3)_3\) between the experimental value and the theoretical value. From the X-ray diffraction analysis, it was found that amorphous \(\text{UO}_3\) was produced at the respective reaction temperatures. The quantitative difference may be due to the existence of a residual substance in the amorphous \(\text{UO}_3\), mainly due to \(\text{NH}_4^+\) or \(\text{H}_2\text{O}\).

Sato et al. [13] reported that amorphous \(\text{UO}_3\) was produced due to such residual substances. Halldal and Sorensen [14] observed that the decomposition of AUC thermally under a...
hydrogen atmosphere up to 400 °C, resulted in the production of UO$_3$(H$_2$O)$_{0.15}$, which is amorphous hydrated urania. Govindan [16] reported that an amorphous UO$_3$(H$_2$O)$_x$ was produced due to the loss of ammonia and thermal disassembly of carbonate oxy-anion during the thermal decomposition of AUC. It was found in this study, through an X-ray diffraction analysis, that the amorphous UO$_3$ was crystallized into α-UO$_3$, β-UO$_3$ and γ-UO$_3$ at 480 °C under the nitrogen and air atmospheres, and at 430 °C under a hydrogen atmosphere, respectively, yet no weight loss took place as shown by the TG curve. Therefore, it appears that the crystallizing stage took place simply due to a phase change.

Conclusions

An intermediate phase, amorphous UO$_3$ was produced when (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$ and NH$_4$UO$_2$(NO$_3$)$_3$ were thermally decomposed under air, nitrogen, and hydrogen atmosphere, regardless of the atmosphere used. γ-UO$_3$ was produced as the intermediate product irrespective of the atmospheric gas used during the decomposition of (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·2H$_2$O. However, in the case of NH$_4$UO$_2$(NO$_3$)$_3$, when decomposed under the nitrogen and air atmospheres, α-UO$_3$ was produced, whereas β-UO$_3$ was produced under a hydrogen atmosphere.

The reaction paths of (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·2H$_2$O and NH$_4$UO$_2$(NO$_3$)$_3$ under each atmosphere were as follows:

- Under the nitrogen atmosphere
  - (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·2H$_2$O → (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·H$_2$O → (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$→ NH$_4$UO$_2$(NO$_3$)$_3$ → α-UO$_3$ → γ-UO$_3$ → U$_3$O$_8$
  - NH$_4$UO$_2$(NO$_3$)$_3$ → α-UO$_3$ → α-UO$_3$ → U$_3$O$_8$

- Under the air atmosphere
  - (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·2H$_2$O → (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·H$_2$O → (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$→ NH$_4$UO$_2$(NO$_3$)$_3$ → α-UO$_3$ → γ-UO$_3$ → U$_3$O$_8$
  - NH$_4$UO$_2$(NO$_3$)$_3$ → α-UO$_3$ → α-UO$_3$ → U$_3$O$_8$

- Under the hydrogen atmosphere
  - (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·2H$_2$O → (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·H$_2$O → (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$→ NH$_4$UO$_2$(NO$_3$)$_3$ → α-UO$_3$ → γ-UO$_3$ → α-U$_3$O$_8$ → UO$_2$

Fig. 9 TG curves of (NH$_4$)$_2$UO$_2$(NO$_3$)$_4$·2H$_2$O in a N$_2$, b air, and c H$_2$ atmosphere

Fig. 10 TG curves of NH$_4$UO$_2$(NO$_3$)$_3$ in a N$_2$, b air, and c H$_2$ atmosphere

Open Access This article is distributed under the terms of the Creative Commons Attribution Noncommercial License which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

References

1. Davis NC, Griffin CW (1982) PNL-4305 Pacific Northwest Laboratory
2. Notz KJ, Haas PA (1989) Conf-891206-1
3. El-Mamoon Yahia M, El-Fekey SA (1996) Radiochim Acta 72:205
4. Halldahl L, Nygren M (1986) J Nucl Mat 138:99
5. Kim BH, Hwang ST, Lee KY (2001) J Korean Ind Eng Chem 12:300
6. Ippolitova EA, Pechurova NI, Gribennik EN (1961) ANL Trans 33:114. Argone National Laboratory
7. Ainscough B, Oldfield BW (1962) J Appl Chem 12
8. Woolfrey JL (1974) AAEC/E-329. Australian Atomic Energy Commission
9. Cordfunke EH (1962) J Inorg Nucl Chem 24:303
10. Landspersky H (1963) International symposium on new nuclear fuel materials, vol 1. Prague, p 79
11. Rodriguez SA, Hernandez RR, Ma Garcia CR (1995) Vib Spectrosc 9:215
12. Kim EH (1995) Ph.D thesis, Seogang University, Seoul, Korea
13. Sato T, Osawa F, Shiota S (1985) Thermochim Acta 37:313
14. Halldahl L, Sorensen T (1979) Thermochim Acta 29:253
15. Price GH (1973) AAEC/E276. Australian Atomic Energy Commission
16. Govindan P (2002) J Radioanal Nucl Chem 254:65