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

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Abstract Two types of ammonium uranyl nitrate $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ and $NH_4UO_2(NO_3)_3$, 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 $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ and $NH_4UO_2(NO_3)_3$ decomposed to amorphous UO_3 regardless of the atmosphere used. The amorphous UO_3 from $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ was crystallized to γ-UO_3 regardless of the atmosphere used without a change in weight. The amorphous UO_3 obtained from decomposition of $NH_4UO_2(NO_3)_3$ was crystallized to α-UO_3 under a nitrogen and air atmosphere, and to β-UO_3 under a hydrogen atmosphere without a change in weight. Under each atmosphere, the reaction paths of $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ and $NH_4UO_2(NO_3)_3$ were as follows: under a nitrogen atmosphere: $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \cdot H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \rightarrow NH_4UO_2(NO_3)_3 \rightarrow$ A-$UO_3 \rightarrow \gamma$-$UO_3 \rightarrow U_3O_8$, $NH_4UO_2(NO_3)_3 \rightarrow$ A-$UO_3 \rightarrow \alpha$-$UO_3 \rightarrow U_3O_8$; under an air atmosphere: $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \cdot H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \rightarrow NH_4UO_2(NO_3)_3 \rightarrow$ A-$UO_3 \rightarrow \gamma$-$UO_3 \rightarrow U_3O_8$, $NH_4UO_2(NO_3)_3 \rightarrow$ A-$UO_3 \rightarrow \alpha$-$UO_3 \rightarrow U_3O_8$; and under a hydrogen atmosphere: $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \cdot H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \rightarrow NH_4UO_2(NO_3)_3 \rightarrow$ A-$UO_3 \rightarrow \gamma$-$UO_3 \rightarrow$ α-$U_3O_8 \rightarrow UO_2$, NH_4 $UO_2(NO_3)_3 \rightarrow$ A-$UO_3 \rightarrow \beta$-$UO_3 \rightarrow \alpha$-$U_3O_8 \rightarrow UO_2$.

Keywords Ammonium uranyl nitrate · Thermal decomposition · Modified direct denitration

Introduction

Ammonium uranyl nitrate (AUN) is an important intermediate product during conversion of uranyl nitrate $[UO_2(NO_3)_2]$ solution to UO_2 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 UO_2 powder.

The modified direct denitration process involves the thermal decomposition of AUN double salts, which are prepared from a mixture consisting of a $UO_2(NO_3)_2$ solution and NH_4NO_3. The physical and chemical properties of an oxide powder depend upon its thermal treatment. Also, the sintering behavior of UO_2 powder can be related to its powder characteristics and processing parameters. It has been observed that the presence of NH_4NO_3 in a $UO_2(NO_3)_2$ feed solution prior to a thermal denitration greatly improved the sintering properties of UO_2 powder [1].

Three double salts are known for the $UO_2(NO_3)_2$–NH_4NO_3–H_2O system, but there have been only a few studies done on thermal decomposition of these salts. Laboratory scale denitration tests showed that $NH_4UO_2(NO_3)_3$ decomposes without melting, and thus does not form a dough stage

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similar to that encountered during a denitration. Also, UO_2 produced from $NH_4UO_2(NO_3)_3$ in these tests appeared to be more active than a corresponding oxide produced from $UO_2(NO_3)_2$ solution. It was also reported that $NH_4UO_2(NO_3)_3$ decomposes without melting at 270–300 °C to give γ-UO_3 powder of an average size of approximately 3 μm, with good ceramic properties for its fabrication into UO_2 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 UO_3. Amorphous uranium trioxide (A-UO_3) is mainly formed in the absence of ammonium and nitrate ions, whereas deamination of the retained ammonia leads to β-UO_3 [3]. Meanwhile, AUC decomposes at around 190 °C, giving off CO_2, NH_3, and H_2O with the formation of an amorphous phase. In a N_2, Ar, or CO_2 atmosphere, the amorphous phase crystallizes to α-UO_3 before decomposing to U_3O_8 [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 $UO_2(NO_3)_2 \cdot 6H_2O$ and NH_4NO_3 solutions were prepared using various mole ratios of NH_4^+/U. $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ was resulted when the pH of the reaction solution was 2.58 and the mole ratio of NH_4^+/U was 2.14. And $NH_4UO_2NO_3$ was resulted when the pH of the reaction solution was 2.01 and the mole ratio of NH_4^+/U was 1.07. The volume of both $UO_2(NO_3)_2 \cdot 6H_2O$ and NH_4NO_3 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 $UO_2(NO_3)_2 \cdot 6H_2O$ and NH_4NO_3 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 UO_3 or concentrated nitric acid to the mixed solution. Next the synthesis of AUN was carried out. When the UO_3 was added to that, it was dissolved at a temperature of 30 °C. To eliminate any undissolved UO_3 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 atmospherics, 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 $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ 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 NH_4NO_3, were due to the presence of extremely small amount of impurities. These peaks
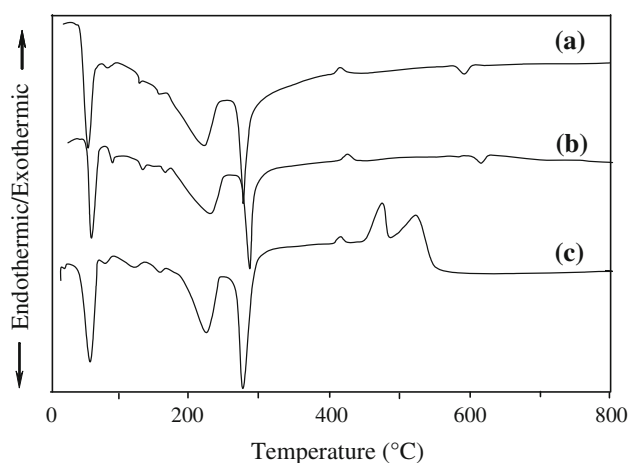
Fig. 1 DTA curves for $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ in **a** N_2, **b** Air, and **c** H_2 atmosphere

Fig. 2 DTA curves for $NH_4UO_2(NO_3)_3$ in **a** N_2, **b** air, and **c** H_2 atmosphere

appeared around 84, 130, and 155 °C. An endothermic peak as a result of the first thermal decomposition of $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ into NH_4NO_3 appeared within a temperature range of 168 to 240 °C. A second endothermic that was due to the second thermal decomposition of NH_4NO_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. $NH_4UO_2(NO_3)_3$ 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 $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ occurred, and the thermal decomposition of NH_4NO_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
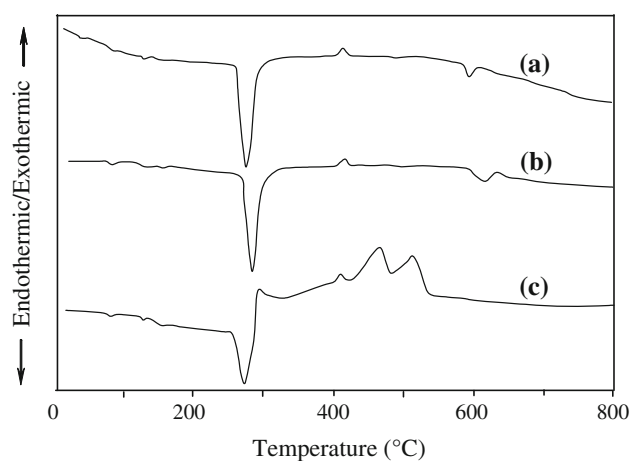
the nitrogen and air atmospheres due to the reduction by hydrogen, which caused the appearance of two different exothermic peaks. An exothermic reaction took place at 440 °C, then shortly after another exothermic reaction started at around 590 °C. Halldahl and Nygren [4] also observed a similar phenomenon, the DTA curves for decomposition of $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ 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 $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ was decomposed into UO_3.

The DTA results for the thermal decomposition and reduction of $NH_4UO_2(NO_3)_3$ 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 $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$. Plus, in the case of $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$, the endothermic peaks appeared around 84, 130, and 155 °C due to a phase change of NH_4NO_3. It may be noted that in the case of $NH_4UO_2(NO_3)_3$, such peaks were very weak.

The endothermic peak resulting from the thermal decomposition of NH_4NO_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

Table 1 Thermal treatment conditions for the preparation of intermediates decomposed from $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ and $NH_4UO_2(NO_3)_3$

Atmosphere	Final temperature of thermal treatment for intermediates of $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ and $NH_4UO_2(NO_3)_3$ (°C)			
N_2	390	480		800
Air	390	480		800
H_2	390	430	480	600

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 $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ and $NH_4UO_2(NO_3)_3$ 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 $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ and $NH_4UO_2(NO_3)_3$ thermally at 390, 480, and 800 °C, under the 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 $(NH_4)_2UO_2(NO_3)_4$ and $NH_4UO_2(NO_3)_3$ were produced from $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$, while NH_4NO_3 was thermally decomposed. A new intermediate phase was produced from $NH_4UO_2(NO_3)_3$ through an endothermic reaction. As shown in Fig. 3b, the structure of $NH_4UO_2(NO_3)_3$ disappeared completely at a thermal decomposition temperature of 390 °C, and amorphous UO_3, a new uranium oxide was formed. In addition, it was also found that in the intermediate phase, amorphous UO_3 was subsequently transformed into γ-UO_3 with a crystal structure at 480 °C (See Fig. 3c). The γ-UO_3 subsequently transformed into U_3O_8 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 $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ under the air atmosphere appeared to be the same as that obtained under a nitrogen
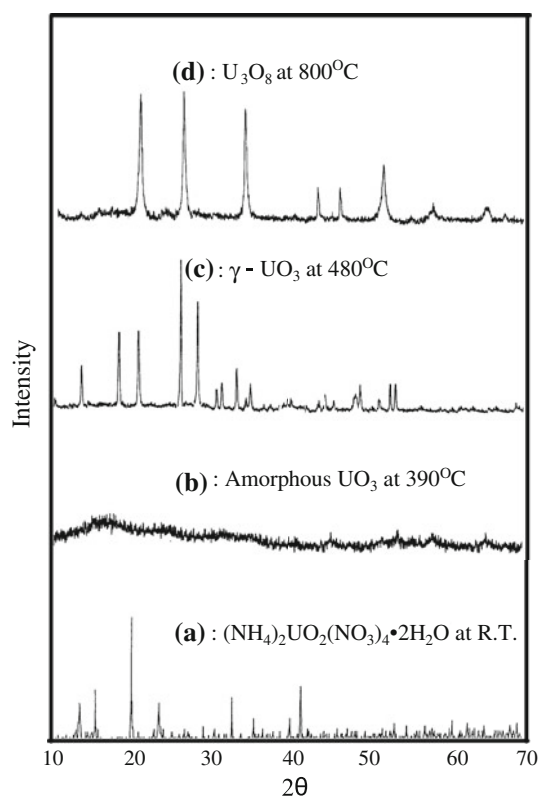
Fig. 3 X-ray diffraction patterns of intermediates produced from $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ in N_2 atmosphere

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 $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ 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 UO_3 as was the case under nitrogen and air atmospheres (See Fig. 5b), however, amorphous UO_3 was crystallized at 430 °C along with the phase change from UO_3 to γ-UO_3 (See Fig. 5c). Furthermore, γ-UO_3, which went through an exothermic reaction at 430 °C, was transformed into α-U_3O_8 by a phase change at 490 °C (See Fig. 5d), and α-U_3O_8 was finally reduced to UO_2 at 600 °C (See Fig. 5e).

The DTA results, as shown in Fig. 1 indicated that the temperature at which UO_3 was reduced to α-U_3O_8 under a hydrogen atmosphere was lower than the temperature at which UO_3 was reduced to U_3O_8 under an air atmosphere. When $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ was thermally decomposed to UO_3, NH_4^+, as a residual substance, was included in the UO_3 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
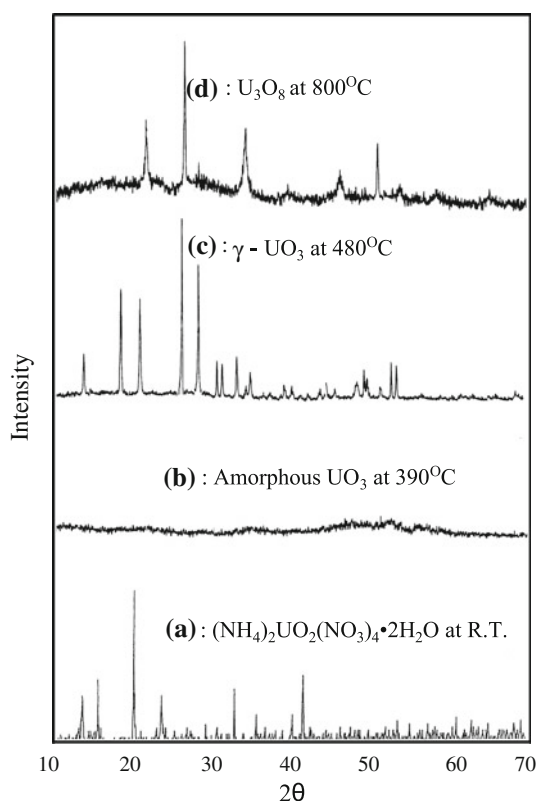
Fig. 4 X-ray diffraction patterns of intermediates from $(NH_4)_2UO_2$ $(NO_3)_4 \cdot 2H_2O$ in air atmosphere

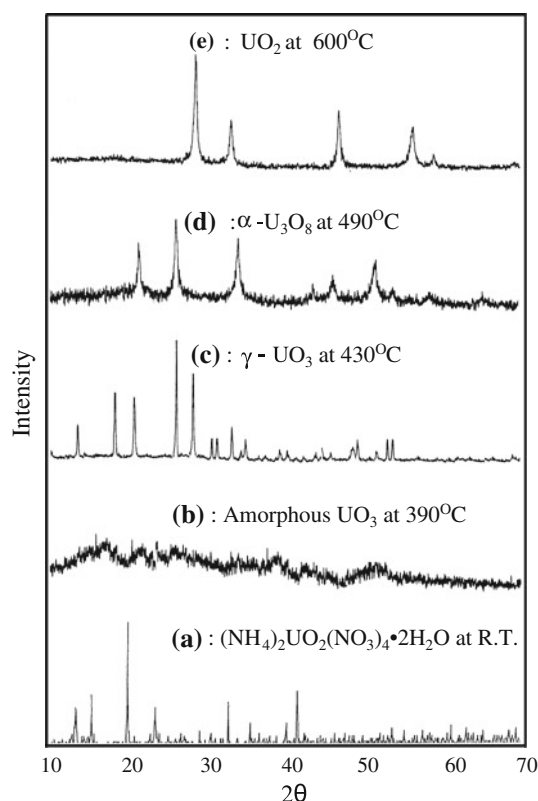**Fig. 5** X-ray diffraction patterns of intermediates produced from $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ in H_2 atmosphere

auto reduction from UO_3 to U_3O_8 was suppressed [6]. As such, it would appear that the production of U_3O_8 from UO_3 took place at a lower temperature under a hydrogen atmosphere. Generally, the reduction from UO_3 to U_3O_8 through an auto reduction is as follows;

$$3UO_3 \rightarrow U_3O_8 + 1/2O_2.$$
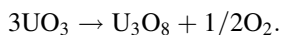
It is hypothesized that in hydrogen atmosphere, hydrogen was adsorbed on to the matrix and reacted with oxygen ions and then diffused out of the UO_3 matrix to produce H_2O. The produced H_2O desorbed from the UO_3 matrix surface, and at the same time, oxygen present in the UO_3 rapidly diffused onto the UO_3 matrix. This resulted in a fast reduction rate from UO_3 to U_3O_8. Meanwhile, in air atmosphere, the thermal decomposition rate of UO_3 to U_3O_8 was slow, because the oxygen present in the UO_3 was prevented from being diffused onto the UO_3 matrix.

As shown in Fig. 6, in the case of $NH_4UO_2(NO_3)_3$, under a nitrogen atmosphere, amorphous UO_3 was produced at 390 °C, However, decomposition $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ (See Fig. 6b) resulted in α-UO_3 at 480 °C (See Fig. 6c). When comparing this phenomenon with the one in which $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ produced γ-UO_3 at a temperature of 480 °C, it suggests that $NH_4UO_2(NO_3)_3$ was thermally decomposed through a different phase change route

compared to $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ decomposition route. Subsequently, the α-UO_3 phase, which went through an endothermic reaction at 540 °C, changed into α-U_3O_8 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 $NH_4UO_2(NO_3)_3$ under a hydrogen atmosphere resulted in a final product of UO_2 (See Fig. 8e) with a crystal structure through a series of phase changes to amorphous UO_3 (See Fig. 8b), β-UO_3 (See Fig. 8c), and U_3O_8 (See Fig. 8d). In the case of $NH_4UO_2(NO_3)_3$, when amorphous UO_3 crystallized, β-UO_3 was produced in the intermediate phase, whereas in the case of $(NH_4)_2UO_2$ $(NO_3)_4 \cdot 2H_2O$, γ-UO_3 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 UO_3 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 UO_2 powder is significantly related to the physical and chemical characteristics of the precursor and
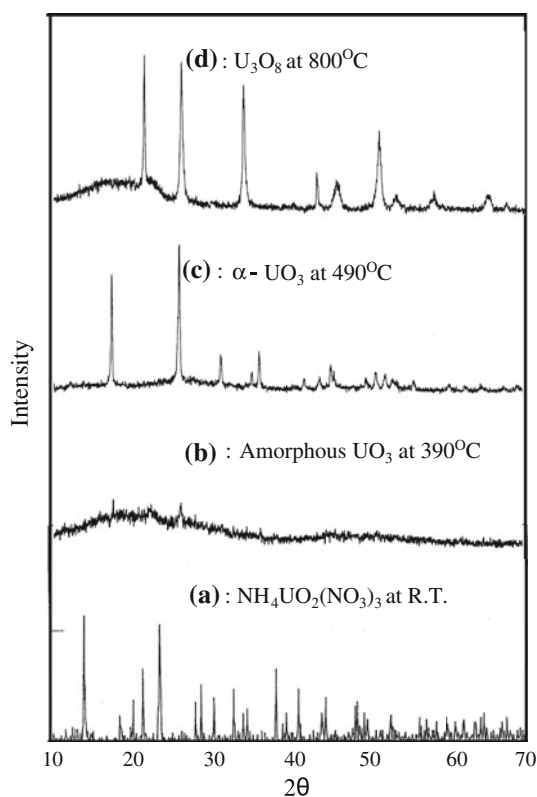
Fig. 6 X-ray diffraction patterns of intermediates produced from $(NH_4)UO_2(NO_3)_3$ in N_2 atmosphere

Fig. 7 X-ray diffraction patterns of intermediates produced from $(NH_4)UO_2(NO_3)_3$ in air atmosphere

the reaction mechanism of the intermediate phases [7]. In the current study, it was found that γ-UO_3 was produced as an intermediate product when $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ was thermally decomposed irrespective of the atmospheric gas used. However, when $NH_4UO_2(NO_3)_3$ 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, α-UO_3 was produced, where as β-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_3O_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 β-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
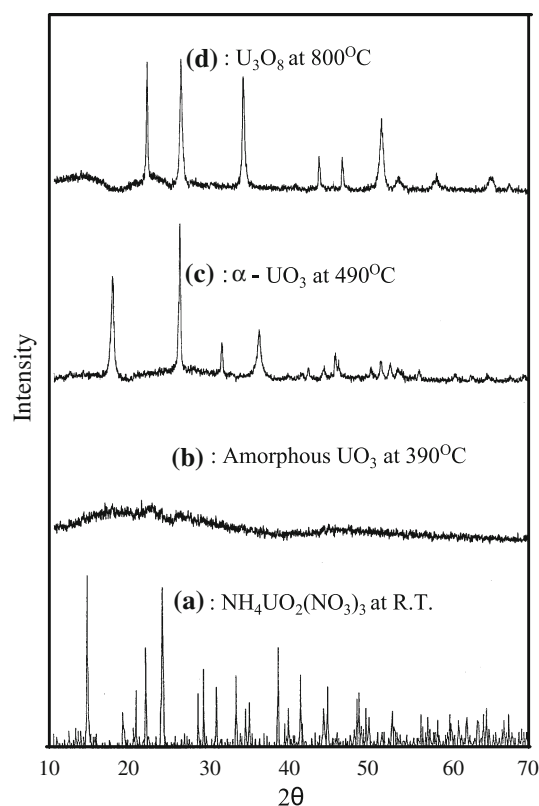
decomposition. Landspersky [10] reported that when the heating rate during thermal decomposition is slow (1 °C/min), amorphous UO_3 was produced, whereas when the heating rate increases (10 °C/min), β-UO_3 is produced. So far, it would seem that the forms of UO_3 produced during the process of a thermal decomposition of ADU are mostly amorphous UO_3 and β-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 β-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_4NO_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_4OH 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
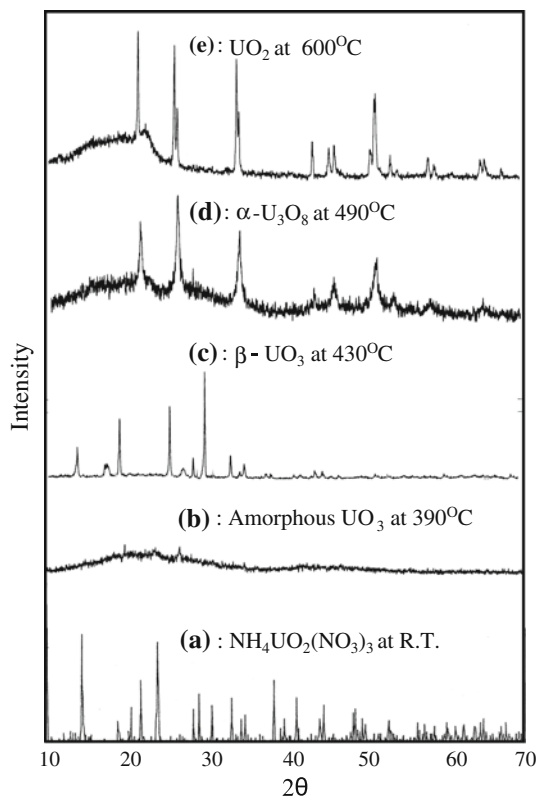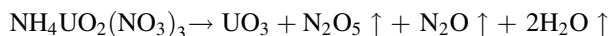
Fig. 8 X-ray diffraction patterns of intermediates produced from $(NH_4)UO_2(NO_3)_3$ in H_2 atmosphere

respective thermal decomposition and reduction characteristics of $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ and $NH_4UO_2(NO_3)_3$ were also reconfirmed. As already identified, NH_4UO_2 $(NO_3)_3$ is decomposed thermally according to the following reaction formula.

$$NH_4UO_2(NO_3)_3 \rightarrow UO_3 + N_2O_5 \uparrow + N_2O \uparrow + 2H_2O \uparrow$$

The TG curves corresponding to these reactions under different atmospheres are illustrated in Figs. 9 and 10. In the case of $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$, thermal decomposition of $NH_4UO_2(NO_3)_3$ into 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 $NH_4UO_2(NO_3)_3$ between the experimental value and the theoretical value. From the X-ray diffraction analysis, it was found that amorphous 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 UO_3, mainly due to NH_4^+ or H_2O. Sato et al. [13] reported that amorphous UO_3 was produced due to such residual substances. Halldal and Sorensen [14] observed that the decomposition of AUC thermally under a

Table 2 Comparison of the decomposition mechanisms of AU, AUC and AUN with previous results

Researchers	Decomposition mechanism of AU	Atmosphere
Woolfrey [8]	AU III/IV $\rightarrow$ AU II $\rightarrow$ AU I $\rightarrow$ β-UO_3 $\rightarrow$ A-UO_3 $\rightarrow$ U_3O_8/$UO_{2.9}$ $\rightarrow$ U_4O_9 $\rightarrow$ UO_{2+x}	H_2
Kim [12]	AU II/III $\rightarrow$ AU II/I $\rightarrow$ AU I $\rightarrow$ A-UO_3 $\rightarrow$ β-UO_3 $\rightarrow$ α-U_3O_8 $\rightarrow$ U_4O_9 $\rightarrow$ UO_2	H_2
	AUC $\rightarrow$ A-UO_3 $\rightarrow$ α-U_3O_8	Air
	AUC $\rightarrow$ A-UO_3 $\rightarrow$ α-UO_3 $\rightarrow$ α-U_3O_8	N_2
	AUC $\rightarrow$ A-UO_3 $\rightarrow$ α-UO_3 $\rightarrow$ α-U_3O_8 $\rightarrow$ UO_2	H_2
Sato [13]	AU $\rightarrow$ UO_3NH_3 $\rightarrow$ A-UO_3 $\rightarrow$ β-UO_3 $\rightarrow$ U_3O_8	Air
Price [15]	AU $\rightarrow$ UO_3xNH_3 $\rightarrow$ U_3O_8 $\rightarrow$ UO_2	H_2
Current study	$(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \cdot H_2O$ $\rightarrow (NH_4)_2UO_2(NO_3)_4 \rightarrow NH_4UO_2(NO_3)_3 \rightarrow$ A-UO_3 $\rightarrow \gamma$-$UO_3 \rightarrow U_3O_8$ $NH_4UO_2(NO_3)_3 \rightarrow$ A-$UO_3 \rightarrow \alpha$-$UO_3 \rightarrow U_3O_8$	N_2
	$(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \cdot H_2O$ $\rightarrow (NH_4)_2UO_2(NO_3)_4 \rightarrow NH_4UO_2(NO_3)_3 \rightarrow$ A-UO_3 $\rightarrow \gamma$-$UO_3 \rightarrow U_3O_8$ $NH_4UO_2(NO_3)_3 \rightarrow$ A-$UO_3 \rightarrow \alpha$-$UO_3 \rightarrow U_3O_8$	Air
	$(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \cdot H_2O$ $\rightarrow (NH_4)_2UO_2(NO_3)_4 \rightarrow NH_4UO_2(NO_3)_3 \rightarrow$ A-UO_3 $\rightarrow \gamma$-$UO_3 \rightarrow \alpha$-$U_3O_8 \rightarrow UO_2$ $NH_4UO_2(NO_3)_3 \rightarrow$ A-$UO_3 \rightarrow \beta$-$UO_3 \rightarrow \alpha$-$U_3O_8 \rightarrow UO_2$	H_2

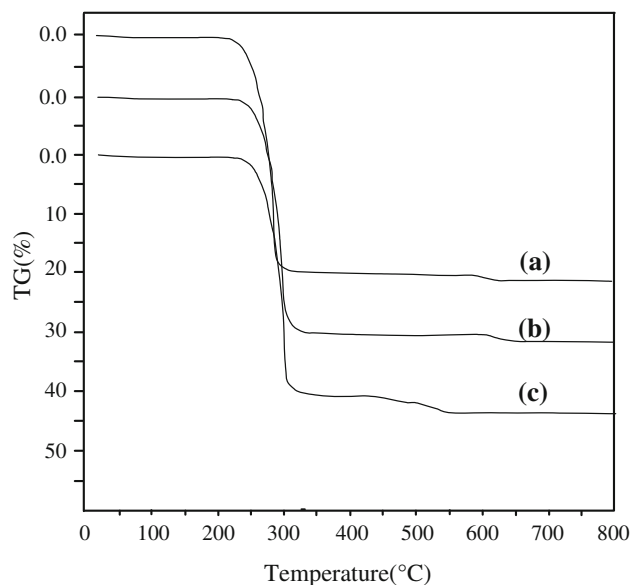**Fig. 9** TG curves of $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ in **a** N_2, **b** air, and **c** H_2 atmosphere

Fig. 10 TG curves of $NH_4UO_2(NO_3)_3$ in **a** N_2, **b** air, and **c** H_2 atmosphere

hydrogen atmosphere up to 400 °C, resulted in the production of $UO_3(H_2O)_{0.15}$, which is amorphous hydrated urania. Govindan [16] reported that an amorphous $UO_3(H_2O)_x$ 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 $(NH_4)_2UO_2(NO_3)_4$ and $NH_4UO_2(NO_3)_3$ 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 $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$. However, in the case of $NH_4UO_2(NO_3)_3$, 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 $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ and $NH_4UO_2(NO_3)_3$ under each atmosphere were as follows:

- Under the nitrogen atmosphere

  - $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \cdot H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \rightarrow NH_4UO_2(NO_3)_3 \rightarrow A\text{-}UO_3 \rightarrow \gamma\text{-}UO_3 \rightarrow U_3O_8$
  - $NH_4UO_2(NO_3)_3 \rightarrow A\text{-}UO_3 \rightarrow \alpha\text{-}UO_3 \rightarrow U_3O_8$

- Under the air atmosphere

  - $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \cdot H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \rightarrow NH_4UO_2(NO_3)_3 \rightarrow A\text{-}UO_3 \rightarrow \gamma\text{-}UO_3 \rightarrow U_3O_8$
  - $NH_4UO_2(NO_3)_3 \rightarrow A\text{-}UO_3 \rightarrow \alpha\text{-}UO_3 \rightarrow U_3O_8$

- Under the hydrogen atmosphere

  - $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \cdot H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 \rightarrow NH_4UO_2(NO_3)_3 \rightarrow A\text{-}UO_3 \rightarrow \gamma\text{-}UO_3 \rightarrow \alpha\text{-}U_3O_8 \rightarrow UO_2$
  - $NH_4UO_2(NO_3)_3 \rightarrow A\text{-}UO_3 \rightarrow \beta\text{-}UO_3 \rightarrow \alpha\text{-}U_3O_8 \rightarrow UO_2$

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