

TG/DTA and X ray Diffraction Studies on Ammonium Uranyl Nitrate

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1. Introduction

Ammonium uranyl nitrate (AUN) is an important intermediate product during conversion of a uranyl nitrate [$\text{UO}_2(\text{NO}_3)_2$] solution to UO_2 powder for the fabrication of nuclear fuels, the so-called modified direct denitration (MDD) process. The MDD process involves the thermal decomposition of AUN double salts, which are prepared from a mixture consisting of a $\text{UO}_2(\text{NO}_3)_2$ solution and NH_4NO_3 . The physical and chemical properties of an oxide powder depend upon its thermal treatment [1].

Three double salts are known for the $\text{UO}_2(\text{NO}_3)_2$ - NH_4NO_3 - H_2O system, but there have been only a few studies done on thermal decomposition of these salts.

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.

2. Experimental

The $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NH_4NO_3 solutions were prepared using various mole ratios of NH_4^+/U . $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ was resulted when the pH of the reaction solution was 2.58 and the mole ratio of NH_4^+/U was 2.14. And $\text{NH}_4\text{UO}_2\text{NO}_3$ was resulted when the pH of the reaction solution was 2.01 and the mole ratio of NH_4^+/U was 1.07.

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 TG (thermogravimetric)/DTA (differential thermal analysis) experiment was carried out in various atmospheres, which were 100% nitrogen, air, and hydrogen gas. 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.

The intermediate reaction phases were determined and identified by TG analysis and X-ray diffraction. The characteristic analyses of the intermediate phases and sample preparation were performed by a TG-DTA unit.

3. Results and Discussion

3.1 DTA Analysis

The DTA results for the thermal decomposition and reduction of $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$ under different atmospheric gases are shown in Fig. 1. The results were found to be very similar to the DTA results of the thermal decomposition and reduction of $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$. Plus, in the case of $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$, 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 $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$, such peaks were very weak.

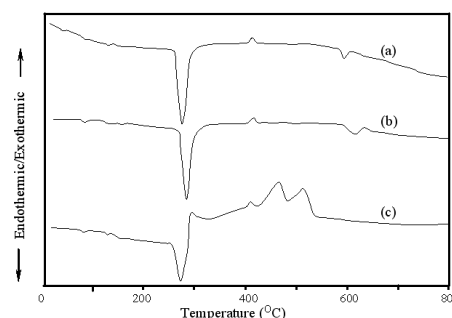


Fig. 1. DTA curves in (a) N_2 , (b) air, and H_2 atmosphere

3.2 X-ray Diffraction Analysis of Intermediate Phases obtained from AUN

Under a nitrogen atmosphere, $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4$ and $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$ were produced from $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$, while NH_4NO_3 thermally decomposed. A new intermediate phase was produced from $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$ through an endothermic reaction. As shown in Fig. 2(b), the structure of $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$ 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. 2(c)]. 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. 2(d)].

The intermediate phase obtained after the thermal treatment of $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ under an air atmosphere appeared to be the same as that obtained under a nitrogen atmosphere. However, as identified in the DTA results, under an air atmosphere, the intermediate phase was produced at a higher temperature than that in a nitrogen atmosphere.

produced from $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ in H_2 atmosphere

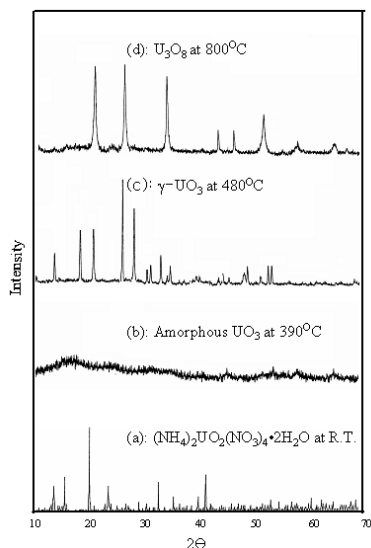


Fig. 2. X-ray diffraction patterns of intermediate produced from $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ in N_2 atmosphere

Under a hydrogen atmosphere, $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ 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. 3(b)], however, amorphous UO_3 was crystallized at 430°C along with the phase change from UO_3 to $\gamma\text{-UO}_3$ [See Fig.3(c)]. Furthermore, $\gamma\text{-UO}_3$, which went through an exothermic reaction at 430°C , was transformed into $\alpha\text{-U}_3\text{O}_8$ by a phase change at 480°C [See Fig. 3(d)], and then, $\alpha\text{-U}_3\text{O}_8$, which went through an exothermic reaction at 580°C , was finally reduced to UO_2 at 800°C .

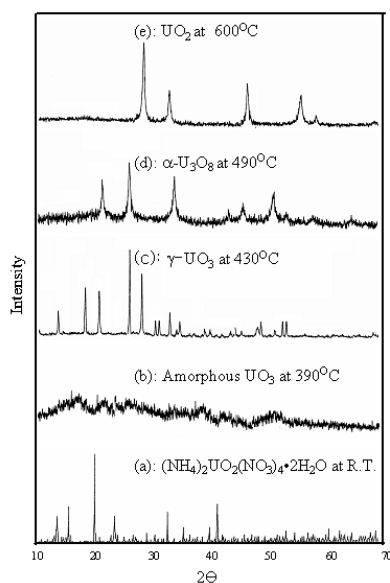


Fig. 3. X-ray diffraction patterns of intermediate produced from $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ in H_2 atmosphere

Woolfrey [2] explained that under a hydrogen atmosphere, ADU can be directly reduced to UO_2 , under an oxygen or nitrogen atmosphere, and 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 [3] reported that amorphous UO_3 and $\beta\text{-UO}_3$ exist in a crystal form during the process of thermal decomposition of ADU. Landspersky [4] and Rodriguez [5] noted that the existence of two forms of UO_3 is due to the heating rate during thermal decomposition.

It was found in this study, through an X-ray diffraction analysis, that the amorphous UO_3 was crystallized into $\alpha\text{-UO}_3$, $\beta\text{-UO}_3$ and $\gamma\text{-UO}_3$ at 480°C under 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.

4. Conclusions

An intermediate phase, amorphous UO_3 , was produced when $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4$ and $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$ were thermally decomposed under air, nitrogen, and hydrogen atmospheres, regardless of the atmosphere used. $\gamma\text{-UO}_3$ was produced as the intermediate product irrespective of the used atmospheric gas during the decomposition of $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$. However, in the case of $\text{NH}_4\text{UO}_2(\text{NO}_3)_3$, when decomposed under the nitrogen and air atmospheres, $\alpha\text{-UO}_3$ was produced, whereas $\beta\text{-UO}_3$ was produced under a hydrogen atmosphere.

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This study was performed under Nuclear Technology Development Program sponsored by Ministry of Education, Science and Technology of Korea