

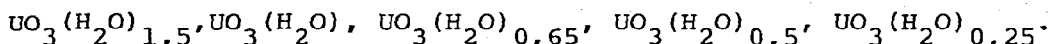
THERMAL ANALYSIS OF THE DECOMPOSITION OF AMMONIUM URANYL CARBONATE (AUC) IN DIFFERENT ATMOSPHERES

LARS HÄLLDAHL, ASEA-ATOM, Västerås, Sweden

O. TOFT SÖRENSEN, Risö National Laboratory, Roskilde, Denmark

ABSTRACT

The intermediate products formed during thermal decomposition of ammonium uranyl carbonate (AUC) in different atmospheres, (air, helium and hydrogen) have been determined by thermal analysis, (TG and DTA) and X-ray analysis. The endproducts observed are U_3O_8 and UO_2 in air/He and hydrogen, respectively. The following intermediate products were observed in all atmospheres:



X-ray diffraction analysis showed that these phases were amorphous.

INTRODUCTION

Ammonium uranyl carbonate (AUC) is an important starting material in the production of UO_2 -powders used in the fabrication of UO_2 -pellets for power reactor fuel elements. The processes taking place during the thermal decomposition of AUC and the subsequent reduction leading to the UO_2 -powders, which to a large extent determine the pressing and sintering properties of the produced powders, has, however, not yet been studied in details and the purpose of the present work is by thermal analysis (TG and DTA) to examine the nature of the intermediate products formed during these processes in different atmospheres.

EXPERIMENTAL

Equipment

The experiments in this work has mainly been carried out on the thermal analysis equipment of AEK, Risö. For TG and QIA we have used

Netsch STA 429, for DTA measurements we have used Netsch DTA 404 S, in air, helium and hydrogen, in the temperature range 25°C - 800°C. The X-ray diffraction analysis has been obtained on a Philips PW 1050 X-ray diffractometer.

Materials

The material used for this analysis is from one AUC charge, directly taken from a production line in ASEA-ATOMS Fuel Factory, with uranium content 45.82%. The only detectable impurity is fluoride at the level of 50 ppm. For more detailed information on AUC, see (ref. 1).

Experimental conditions

Thermogravimetric measurements were obtained in three different atmospheres, air, helium and hydrogen, by standard thermogravimetric analysis. The heating rate was in all three cases 10°C/min. Buoyancy corrections were made for the analysis in air, but were negligible both for helium and hydrogen. Quasi isothermal analysis was only made in hydrogen.

DTA analysis were also carried out in the three atmospheres. The gas flow was in all cases 5 l/h. Temperatures ranged from 25°C-800°C.

To measure the heat of reactions, standard compounds with known heat of reaction, (ref. 7), were used to calibrate the DTA equipment. Heating rate when analysing the standard compounds and AUC-samples for quantitative measurements was 20°C/min.

X-ray diffractometry

The samples used for X-ray diffractometry were taken from the DTA equipment. A sample was heated in the atmosphere of interest to a defined temperature, and was then cooled down to room temperature in an inert gas flow, before it was taken to the X-ray equipment. The diffractogrammes were taken with the X-rays from CuK_α , the angle 2θ ranging from 8 - 80°.

RESULTS

In (Fig. 1) TG curves are shown. The end product when treating AUC in air or helium is U_3O_8 , and when using hydrogen it is UO_2 .

In (Fig. 2) and (Fig. 3) are shown the results from QIA. These curves show the weight loss and corresponding reaction temperature as functions of time. Typical DTA-curves for the different atmos-

pheres are shown in (Fig. 4). In these curves are marked where the samples for X-ray diffraction have been taken.

Thermal decomposition of AUC

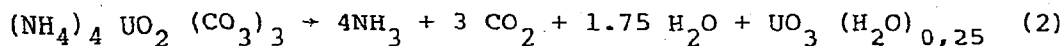
The first reaction which occurs is the thermal decomposition of AUC. It starts at the same temperature, 125°C, and is an endothermal reaction, regardless of what gas is present. The energy consumption for this endothermal reaction has been determined to be 516 cal/gU in helium and 396 cal/gU in hydrogen. The difference in energy consumption can be due to the reaction:



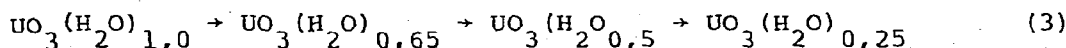
For this reaction, $\Delta G_{125^\circ\text{C}} = 1494 \text{ cal/mole}$, $k_p \approx 0.15$ (ref. 6). Ammonia, set free from the AUC, tries to reach equilibrium with nitrogen and hydrogen.

In hydrogen, however, the partial pressure of hydrogen is almost 1 atm, resulting in that the equilibrium for reaction 1 is far to the left, and nothing of the ammonia reacts. The energy consumption for the reaction in helium does consist of two parts; energy to decompose AUC, and a contribution from the endothermal reaction (1). In hydrogen this contribution is negligible.

From the thermogravimetric analysis, it seems that the composition at the end of the reactions is $\text{UO}_3 (\text{H}_2\text{O})_{0,25}$, (Fig. 1). When the reaction is carried out in hydrogen as QIA, and sufficient time is given each reaction step, it seems that there could exist some intermediate steps. The net reaction can be written;



From the QIA curves, (Fig. 2) and (Fig. 3), it can be seen that there are small changes in reaction rate, corresponding to new reactions taking place. The changing of the slope corresponds to that the reaction steps perhaps can be written;



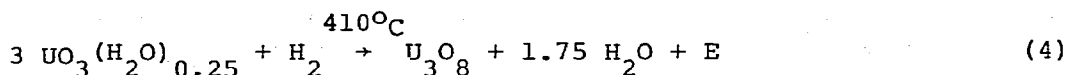
The weight loss curves, neither TG nor QIA, can resolve these reactions properly.

From (Fig. 1) it can be seen that the composition $\text{UO}_3 (\text{H}_2\text{O})_{0,25}$ (44.07% weight loss) exists at 380°C in all three atmospheres. From

X-ray diffraction analysis it was seen that $\text{UO}_3(\text{H}_2\text{O})_{0,25}$ from AUC reduced in hydrogen was amorphous. This has also been found by the authors of (ref. 8). The methods used have a "detection limit" of about 2000 Å (0.2 μ), which makes it possible that smaller crystallites can exist, although not a single reflexion was obtained. Some very brief data taken on electronmicroscopy, indicates that crystallites in the order of 10 - 20 Å could exist. This is subject to further investigations. From the literature (ref. 2), five crystalline and one amorphous are known. It is known that ADU forms crystalline $\text{UO}_3(\text{H}_2\text{O})_x$ compounds when reduced in inert gases, (ref. 3) and (ref. 4), air and hydrogen, (ref. 4).

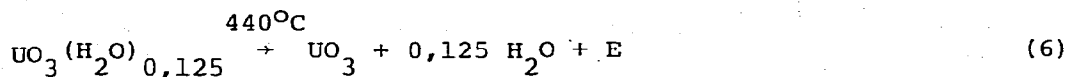
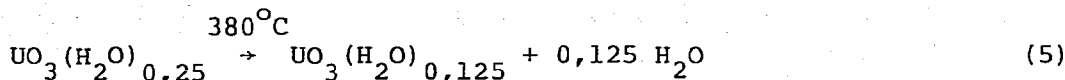
Formation of U_3O_8

From the TG curves, (Fig. 1), it can be seen that in hydrogen U_3O_8 is formed directly from $\text{UO}_3(\text{H}_2\text{O})_{0,25}$ without passing through UO_3 . This conclusion is confirmed by the QIA analysis. The DTA analysis shows that this reaction is exothermal, and starts at 410°C. The reaction formula can thus be written;



E has been measured to 25 cal/gU. The composition has been found to be U_3O_8 , from X-ray diffraction analysis, samples taken as indicated in (Fig. 4).

From TG and DTA curves, (Fig. 1) and (Fig. 4), it can be seen that the formation of U_3O_8 from $\text{UO}_3(\text{H}_2\text{O})_{0,25}$ in helium, starts with decomposition to $\text{UO}_3(\text{H}_2\text{O})_{0,125}$ at 380°C. When the temperature reaches approximately 440°C, anhydrous UO_3 starts to form. This corresponds to an exothermal peak on the DTA-curve. U_3O_8 starts to form at about 500°C. The reactions can be written in the following sequences;



E has been measured to 5,3 cal/gU.

Normally, reactions like (4), (5), (6) and (7) are endothermal. The exothermal contribution, which makes the net reactions exothermal, must be a crystallisation, either in UO_3 or U_3O_8 .

In (ref. 4), an exothermal reaction at 385°C is mentioned for reduction of ADU in air. This is interpreted as a recrystallization of UO_3 , due to a slow dehydration. The difference in released energy between reaction (4) and (6), could be explained from the difference in atmosphere. In hydrogen the oxygen set free reacts to water in an exothermal reaction.

From the TG-curve taken in air, (Fig. 1), there is no sign of an intermediate between $\text{UO}_3(\text{H}_2\text{O})_{0,25}$ and U_3O_8 . The U_3O_8 starts forming at about 560°C .

Formation of UO_2

Only in hydrogen, of course, the endproduct is UO_2 . From TG and DTA curves it can be seen that the reaction starts at about 460°C , and is an exothermal reaction. From the QIA analysis, where the resolution is much better, it seems that U_4O_9 eventually could exist as an intermediate product. The value for the heat of reaction E has been measured to 19 cal/gU.

The authors of ref. (5) have made reductions of UO_3 and U_3O_8 , derived from ADU, in hydrogen. They claim that UO_3 is reduced in two steps to UO_2 , passing U_3O_8 . This is what we have found here too, but it does not fit with ref. (4), as mentioned above.

ACKNOWLEDGEMENT

The authors wish to acknowledge the help received from Henning Jensen, Risö, and many stimulating discussions with Gunnar Jakobsen, ASEA-ATOM.

REFERENCES

- 1 R. Graziani, et. al. "Crystal Structure of Tetra Ammonium Uranyl Tricarbonate". J. Chem. Soc. Dalton Trans. 19 (1972) 2059-61.
- 2 Gmelin, Handbuch der Anorganischen Chemie, Band 55, Uran. Ergänzungsband, Teil C 1, Verbindungen.
- 3 M.C. Ball, et. al. "The Thermal Decomposition of Ammonium Diuranate". J. inorg. nucl. Chem. 36 (1974) 1527-1529.
- 4 P. Spacu, G.D. Cismaru, "Behaviour of Uranium Compounds on Heating. Thermal Decomposition of Ammonium Uranates". Rev. Roumaine Chim. 17

(1972) 947-952.

- 5 A.H. Le Page, A.G. Fane, "The Kinetics of Hydrogen Reduction of UO_3 and U_3O_8 . Derived from Ammonium Diuranate". J. inorg. nucl. Chem. 36 (1974) 87-92.
- 6 O. Kubaschewski, "Metallurgical Thermochemistry", London 1955.
- 7 J. Šesták, V. Satava, W.W. Wendlandt, "The Study of Heterogeneous processes by Thermal Analysis". Thermochimica Acta, 7 (1973) 333-556.
- 8 H-G. Bachmann, K. Seibold, H.Z. Dokuzoguz, H.M. Muller, "X-ray Powder Diffraction and some Thermodynamic Data for $(\text{NH}_4)_4[\text{UO}_2(\text{CO}_3)_3]$ ". J. inorg. nucl. Chem. 37 (1975) 735-737.

TG analysis of AUC in air, He, H_2

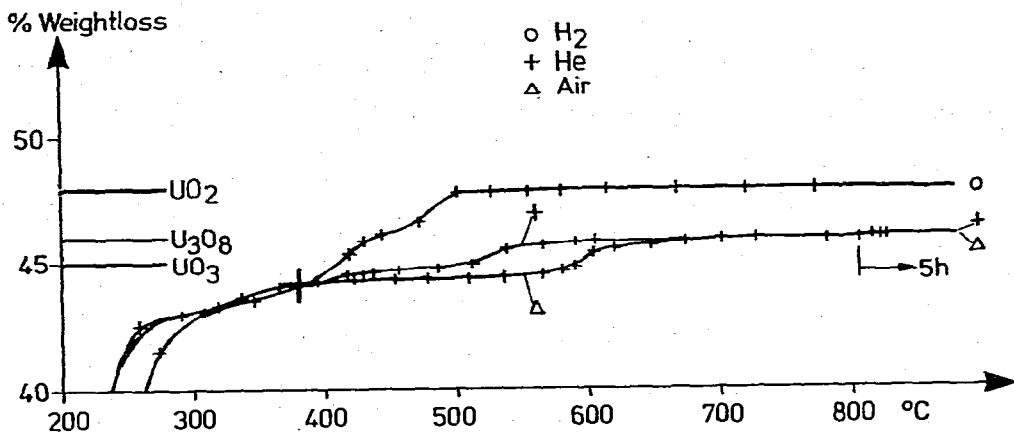


Figure 1

QIA-analysis of AUC in H_2
in the range 300–800 °C

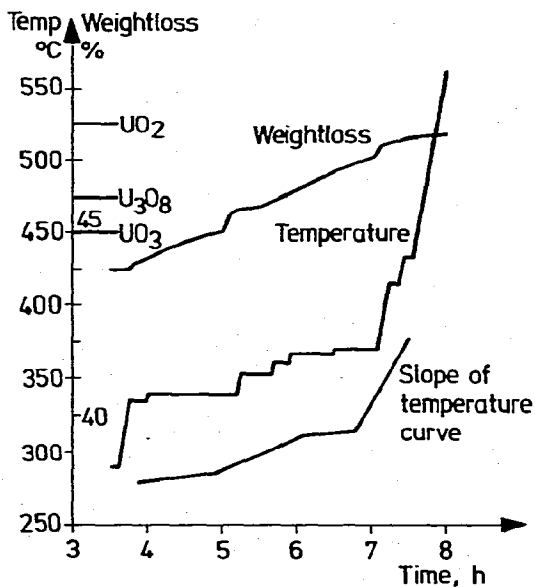


Figure 2

QIA-analysis of AUC in H_2
in the range 25–375 °C

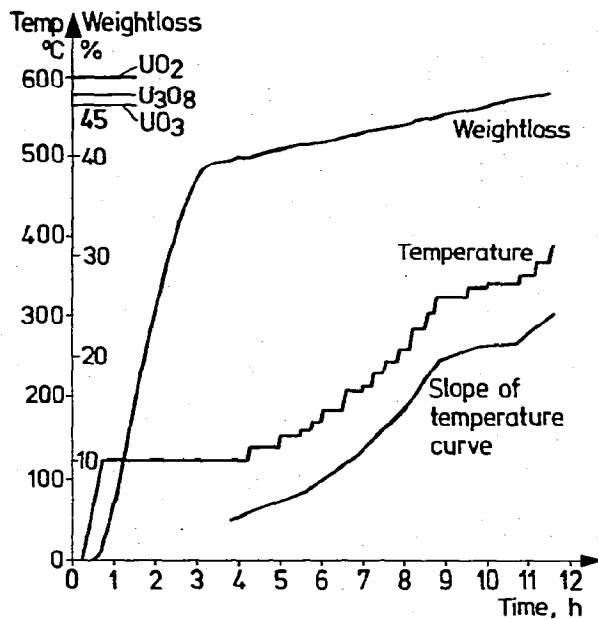
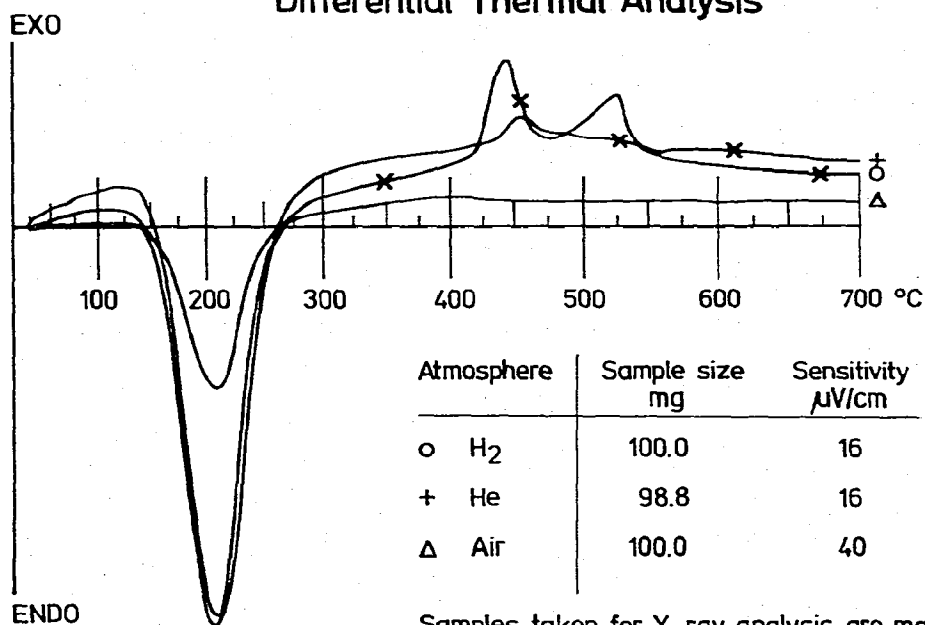


Figure 3

Differential Thermal Analysis



Samples taken for X-ray analysis are marked with x

Figure 4