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A STUDY OF THE COMPOSITION OF THE AMORPHOUS PHASE FORMED DURING DECOMPOSITION OF AMMONIUM URANYL CARBONATE IN VARIOUS ATMOSPHERES

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ABSTRACT

When ammonium uranyl carbonate is decomposed, CO_2, NH_3 and H_2O are evolved. Chemical analysis of the amorphous UO_3 matix thus formed have shown that it contained besides UO_3 also carbon, nitrogen and H_2O. The amounts of these compounds varied with the atmosphere used during the reaction (H_2, O_2, CO_2 and N_2) and with the annealing time and temperature.

INTRODUCTION

In the so called AUC process to convert UF_6 to UO_2 powder for the fabrication of nuclear fuels, one step is a reduction of the intermediate compound ammonium uranyl carbonate (AUC) in a mixture of water vapour and hydrogen at a temperature of 520°C. Previous investigations have shown that parameters such as heating rate and oxygen partial pressure strongly influence the characteristics of the UO_2 powder produced (1, 2, 3, 4, 5). In this investigation the reduction of AUC has been carried out in different atmospheres, ranging from a strongly reducing atmosphere, hydrogen, via mixtures of hydrogen and carbon dioxide, to an oxidizing atmosphere, oxygen. Special interest has been devoted to the first endothermal decomposition of AUC, and to the chemical composition of the intermediate amorphous phase formed during the reaction. When AUC is decomposed, CO_2, NH_3 and H_2O are evolved. TG measurements and chemical analysis have shown that these species are partly absorbed by the amorphous UO_3 matrix.

EXPERIMENTAL

The AUC was taken directly from the production lines at ASEA-ATOM's fuel factory. It is a very pure material; except for small remainders of moisture and ammonium carbonate, it contains about 25 ppm fluoride as the only detectable impurity.

The TG and DTA analyses were carried out simultanously in the temperature range 20-300 °C in a Mettler 1200C apparatus with a heating rate of 10°C/min. The atmospheres used were pure H_2, a mixture of 90% H_2-10% CO_2, a mixture of CO_2 and 43 ppm H_2, and, finally, the pure gases CO_2, N_2 and O_2.

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Samples for analysis of composition at different annealing temperatures were prepared by treatment of 10 g of AUC at the temperature of interest for 30 minutes in each of the four atmospheres H_2, N_2, CO_2 or O_2. After heat treatment each sample was cooled down to room temperature in the respective atmosphere.

The analysis of nitrogen was performed by the conventional Kjeldahl titration method, and the analysis of carbon was done by combustion in oxygen, followed by absorption in $BaClO_4$-solution and coulometric titration.

The specific surface area was measured by the BET-method.

RESULTS

AUC starts to decompose around 120 °C, according to the formula:

$$(NH_4)_4UO_2(CO_3)_3 \rightarrow UO_3(H_2O)_x + 4NH_3 + 3CO_2 + (2-x)H_2O - E$$

This formula is only approximative since the amorphous UO_3 matrix has been found to contain not only UO_3 and H_2O but also minor amounts of carbon and nitrogen (see below).

The reaction is endothermal and the Δ H-values and DTA peak temperatures varied with the atmosphere used. The peak maximum temperature of the DTA-curves and the weight losses at 300°C in the various atmospheres used are given in Table 1.

TABLE 1

Weight loss data and peak maximum temperature for the decomposition of AUC in various atmospheres.

Atmosphere	Number of measurements	Peak maximum (°C)	% weight loss
H_2	4	185 ± 1	42.52
H_2 + 10% CO_2	2	190 ± 1	42.15
N_2	1	195 ± 1	42.20
O_2	11	198 ± 1	41.83
CO_2	4	200 ± 1	41.20

This variation of peak maximum temperature with the atmosphere used, was verified in a second experimental series, comprising more than 20 samples. In these experiments a heating rate of 5 °C/min was used. The lower heating rate caused a shift in the peak temperatures towards lower values but the order between temperatures in different atmospheres did not change.

The weight loss at 300°C also varied with the heating rate used. With 5 °C/min a weight loss of 42.52 % ± 0.6 % was found, independently of the atmosphere used. The corresponding data for the 10 °C/min series are different, as can be seen in Table 1. In this connection it should be noted that a complete transformation of AUC to pure UO_3 corresponds to a weight loss of 45.21 %. The variation of ΔH with the atmosphere used is discussed in Ref (3).

The chemical analyzes of carbon and nitrogen remaining in the samples after heat treatment for 30 minutes at various temperature in the different atmospheres used are given in Table 2.

TABLE 2
Carbon and nitrogen (% by weight) in the samples after heating for 30 min at the given temperatures.

Atmosphere	Temperature °C	Carbon weight %	Nitrogen weight %	weight ratio C/N
N_2	300	0.36	0.58	0.62
N_2	430	0.15	-	-
N_2	550	-	-	-
CO_2	300	0.57	2.20	0.26
CO_2	500	-	0.05	-
CO_2	630	-	0.03	-
O_2	300	0.45	1.40	0.32
O_2	550	-	-	-
H_2	200	0.44	0.55	0.80
H_2	300	0.31	0.30	1.03
H_2	400	-	-	-

Some samples were also analyzed after 60 minutes heat treatments (see Table 3)

TABLE 3

Carbon and nitrogen in samples heated for 60 min at 300 °C in various atmospheres.

Atmosphere	Carbon weight %	Nitrogen weight %	weight ratio C/N
CO_2	0.31	0.70	0.44
O_2	0.31	0.80	0.39
H_2	0.30	0.40	0.75

With the analytical procedures used, the detection limits for carbon and nitrogen are about 0.05 weight percent and 0.01 weight percent, respectively. The amounts of remaining carbon and nitrogen are expressed as weight percent of the elements.

The carbon is most probably present as carbonate and the nitrogen as adsorbed NH_3 or ammonium (see below). In stoichiometric AUC, one would find a C/N ratio of 0.64 and in $(NH_4)_2CO_3$ the C/N ratio is 0.43.

Samples treated for 30 minutes at 300°C were also analyzed for specific surface area, which was found to be 46.0 m^2/g for AUC treated in CO_2, 49.9 m^2/g in O_2 and 51.2 m^2/g in H_2.

X-ray and electron diffraction studies have shown that all samples heat-treated at 300 °C in these atmospheres are amorphous (3).

DISCUSSION

Amorphous UO_3 was found, by Vlasov et al. (6), to absorb moisture to an amount of $28 \cdot 10^{-6}$ mol/m^2 at 300°C. For the specific surface areas measured in this investigation, this corresponds to about 0.025 g H_2O/g UO_3. The same authors also gave absorption isobars for H_2, N_2, NH_3 and CO_2, from room temperature up to 150°C. For H_2 the absorption increases with temperature and partial pressure of H_2. At 150°C, 300 Torr it equals $0.125 \cdot 10^{-6}$ mol/m^2 UO_3. Extrapolation to 300°C gives an estimated amount of $15 \cdot 10^{-6}$ g H_2/g UO_3, corresponding to only 0.0015 weight percent. Calculating the amounts of ammonia and carbon dioxide in the same way gives expected amounts of 0.4 % NH_3 and 0.01-0.02 % CO_2 at 300°C. The absorption of N_2 is strongly decreasing with raising temperature, and can be neglected over 150°C. In this connection it thus seems that NH_3 is the only gas species which is absorbed in significant amounts at 300°C.

As can be seen from Table 1, the decomposition temperature is dependent on the atmosphere used. In H_2 this temperature is lowest, and the remainders are the least (see Table 2 and 3). Since H_2 absorption can be neglected, the difference between the weight expected for pure UO_3 and the sample weight found, is made up by remainders of carbon, nitrogen and H_2O. Assuming that carbon and nitrogen occurs as carbonate and ammonium, the amorphous material also contains ~ 1 weight percent water at 300 °C. This finding agrees with previous observations (1, 3).

The addition of 10 % CO_2 to the H_2 atmosphere raises the peak maximum temperature about 2 °C. Some experiments were also carried out with an addition of 43 ppm H_2 to CO_2, and this small amount lowered the peak maximum temperature about 0.5 °C.

In nitrogen atmosphere the peak maximum temperature is intermediate between those of the reducing and the oxidizing atmospheres. As discussed above, absorption of N_2 is not expected. The ratio of the analyzed amounts C to N corresponds to the ratio expected for AUC. However, according to the discussion above, one would expect absorbed NH_3 to be present at 300°C, implying that carbon (as carbonate) and H_2O might also occur as remainders.

The decomposition temperature in oxygen atmosphere lies in between the decomposition temperatures observed in hydrogen - and carbon dioxide - atmospheres. O_2 lacks the reducing capacity of H_2, and unlike CO_2 it is not one of the species given off. The large amounts of carbon and nitrogen found in this case account for the difference in weight loss between UO_3 with no remaining impurities (45.21 %) and the experimentally found value (41.83 %). Thus no water seems to be present in the material.

The reaction temperature is highest in a CO_2 atmosphere. Evolution of CO_2 from the material is delayed and the remainders of carbon and nitrogen are the highest. As shown above, NH_3 is absorbed strongly by the amorphous material, and traces of nitrogen can be found as high as at 630 °C (see Table 2). The large amounts of carbon and nitrogen indicate again that the amount of absorbed water is small. This is also in agreement with the findings in Ref (3), that the TG curve in a CO_2 atmosphere above 300°C does not exhibit any plateau with a constant amount of water .

After a prolonged heating at 300°C, the amount of remainder decreases, as is shown in Table 3.

It can also be noted that the specific surface area varies with the gas used. There seems, however, to be a correlation between the size of specific surface area and the amount of remainder. Thus materials exposed to H_2 exhibit the largest specific surface area and contain the lowest amount of remainder, while for CO_2 the lowest specific surface area and largest amount of remainder is observed. This can however be explained by the fact that the specific surface area determination is based on absorption of N_2 at low temperatures. If thus part of the available absorption sites already are occupied by species of the remainder, one would expect less specific surface area for samples with reminders than for samples without.

In conclusion, the amount of carbon, nitrogen and H_2O, adsorbed by the amorphous UO_3 matrix varies not only with the atmosphere used but also with the annealing time and temperature. As the amount of carbon and nitrogen decreases substantially with increasing time and temperature, independently of the atmosphere used, H_2O must be the main impurity at elevated temperatures. This point is further discussed in Ref (3), where also the thermal behaviour of this amorphous material upon further heating is described.

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REFERENCES

1. L. Hälldahl and O. Toft Sørensen Thermochimica Acta 29 (1979) 253-259
2. L. Hälldahl and M. Nygren Thermochimica Acta 72 (1984) 213-218
3. L. Hälldahl and M. Nygren. To be published.
4. L. Hälldahl. J. Nucl. Mater 126 (1984) 170-176
5. L. Hälldahl. Dissertation, Chem. Commun 2 (1985) Stockholm
6. V.G. Vlasov, V.M. Zhukovskii, A.G Lebedev and V.N. Shelaginov J. Appl. Chem. USSR 37 (1964) 2147/51