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TG, DSC, X-ray and Electron Diffraction Studies of Intermediate Phases in the Reduction of Ammonium Uranyl Carbonate to UO_2.

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ABSTRACT

It is well known that several intermediate phases are formed when Ammoniumuranylcarbonate (AUC) is reduced to UO_2. One of these phases has been found to be amorphus. It can be obtained by heat treatment of AUC in N_2 atmosphere at 575 K.

DSC and electron diffraction studies indicate that at room temperature and with time a partial crystallization takes place in this material. The crystallization of this amorphus phase has been monitored by the DSC experiments and the phases formed with time and/or after various heat treatments have been identified by means of their X-ray and electron diffraction patterns.

1.

INTRODUCTION

Ammonium Uranyl Carbonate (AUC) is an intermediate compound in a process to convert UF_6 to UO_2 for fabrication of nuclear fuels, the so-called AUC-process (1). The conditions during the reduction of AUC to UO_2 are important for the powder characteristics. Previous investigations (2, 3) have shown there exists an amorphous phase in the reaction path from crystalline AUC to crystalline UO_2. The aim of this paper is to report on a study of some of the properties of this amorphous phase, and the crystallization process.

2.

EXPERIMENTAL

2.1.

Material and experimental procedure.

AUC samples were taken from the production lines at ASEA-ATOMs fuel factory. The material is very pure, the only detectable impurity is fluorid at the level 30 ppm. About 10 grams of AUC was heated in a furnace in N_2 for 30 minutes at 575K, and then cooled to room temperature. The amorphous material thus formed was then used as starting material for the present investigation. The freshly prepared material and material stored for 3, 35 and 105 days at room temperature have been investigated by means of X-ray and

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electron diffraction techniques, DSC and TG. For each analysis a sample of the starting material was taken directly to the electron microscope for an analysis of its cristallinity. Samples heattreated in the DSC apparatus at three different temperatures, 650K, 700K and 775K, were also analyzed.

2.2.

Equipment

The TG-analyses in an N_2 atmosphere were carried out with a Perkin-Elmer TGS-2 apparatus. A heating rate of 20 K/min was used for a sample weight of about 10 mg. The DSC-analyses were also run in an atmosphere of N_2, and were carried out by means of a Perkin-Elmer DSC-2c with TADS. The sample size ranged from 5 to 10 mg, and of a linear heating rate of 20 K/minute was used. The samples were quenched from the end temperature to room temperature.

The material for EM studies was crushed in an agate mortar, suspended in butanol and applicated on a perforated carbon film supported on a copper grid. (The butanol was left to evaporate to dryness at room temperature). The microscope used was a Siemens ELMISKOP102, operated at 125 KV. The search for suitable fragments was carried out at a magnification of 40000X.

The X-ray powder diffractograms were obtained in a Guiner-Hägg camera, using Cu K α1 radiation with Si as internal standard. Elemental carbon was analyzed for by a conventional coulometric method, and hydrogen was detected by changes in heat conductivity in the gas evolved by a fused sample. Both analyses yielded an accuracy of $\pm$ 0.02 weight percent.

3.

RESULTS AND DISCUSSIONS.

The material stored for 105 days was found to contain 76,12 wt % uranium, 0,70% H and 0,41% C. The TG graph of this sample is shown in fig. 1. The total weight loss corresponds to 9,6% from room temperature to 975 K. The X-ray powder pattern of the residue shows it to be U_3O_8. If the assumptions are made that all hydrogen is in the form of water, and the carbon leaves the sample as CO_2 while the uranium oxide is reduced to U_3O_8, the resulting weight loss would be 9,9%. From room temperature to 725K, the sample gives off its water content. The observed weight loss is thus 6,60%, while the hydrogen content according to the analysis corresponds to 6,3% water. At this temperature, the weight curve reaches a plateau, which is stable for about 100K. The X-ray diffractogram of a sample heat treated at 725K for 15 minutes revealed it to be α-UO_3 with a = 3,930 Å and c = 4,146 Å. The final weight loss between 825K - 975K would then correspond to a reduction of α-UO_3 to U_3O_8, and to carbon dioxide being evolved.

The second curve in fig. 1 shows the weight loss for freshly prepared material, kept only for 30 minutes in ambient atmosphere during which a weight increase of 5% due to uptake of moisture was recorded. At 725K, all of this water has been lost and the decomposition of the residue starts almost immediately. No plateau can be observed in this case. It can be noted that the weight loss in the temperature range 725K - 975K is the same for both samples.

Typical DSC-curves are shown in fig 2, obtained from materials that have been stored for different time intervals. Ageing of the material seems to affect the shape of the DSC-curves in the temperature region 450K - 700K; the endothermal shift of the base line might be associated with the loss of water. According to the EM studies (see below) freshly prepared material starts to crystallize already at 650K, and so does, to a less extent however, also the three-days-old preparation, while almost no effect of the heat treatment could be observed in the other samples. This exothermal crystallisation process counteracts the endothermal effect of giving off water.

Just above 700K, all DSC traces exhibit an exothermal peak (see fig 3) which represents the crystallisation of the larger part of the sample. The amount of energy released by freshly prepared samples is 5,5 cal/g U, which fits very well with data from (2). The increase in the peak area with ageing also reflects the observation that freshly prepared materials start to crystallize even before 725K.

Freshly prepared starting material that is taken directly to the microscope is very unstable and sensitive to the experimental conditions, i.e. high vaccum and an impinging electron beam, which heats the sample. Thus, the complete reaction path in the reduction of AUC to UO_2 has been studied in situ in the microscope, (4). In this case amorphous fragments have also often been seen to crystallise directly into UO_2.

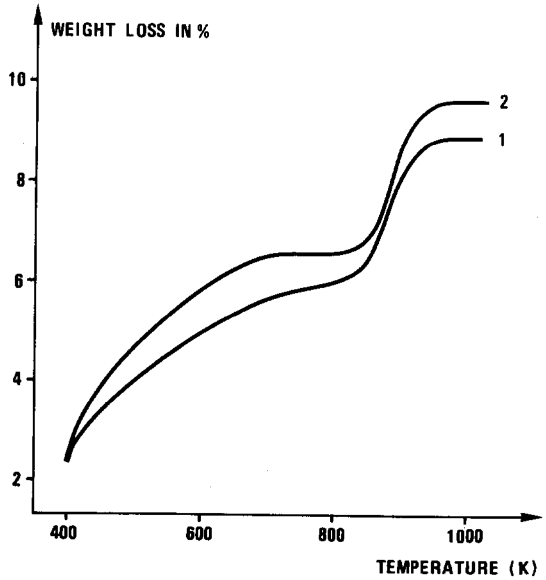
After three days or longer storage, the amorphous material is stable, and thus not effected by the electron beam. Upon longer storage, 1-3 months, some traces of a spontaneous crystallisation have been found. The electron diffraction patterns (DP's) thus obtained show that U_3O_8 and α-UO_3 have been formed. A DP of α-UO_3 is shown in fig 4. Traces of an uranium oxide hydrate have also been seen. All these samples were X-ray amorphous. Samples from DSC-runs, interrupted at 650 K, show an increased fraction of crystalline fragments, mostly α-UO_3, but also traces of U_3O_8.

In the freshly prepared samples this fraction is substantially larger than in aged materials. Thus the fraction of crystalline fragments in the 105-days-old preparation is almost the same before and after the heat treatment at 650K. It can also be noted that all samples heat-treated to 650K showed tendencies to be unstable in the electron beam. All samples were found to be X-ray amorphous.

The EM studies of the samples heated to 700K in the DSC apparatus showed that these samples were very similar to those obtained at 650K. However, the X-ray diffraction patterns of freshly prepared samples, quenched from 700K, exhibit a few weak and diffuse lines, which seems to indicate the presence of crystallites of α-UO_3. All other samples from 700K were found to be X-ray amorphous.

Samples obtained after passing the exothermal peak were, according to X-ray and EM studies, all completely crystalline. The only phase found was α-UO_3, which, however, could be reduced to U_3O_8 or UO_2 in the electron microscope beam. UO_2 was formed more frequently in freshly prepared material than in aged material.

Fig. 1. TG curves in the starting material kept at ambient atmosphere for 30 min. (1) and 105 days (2).



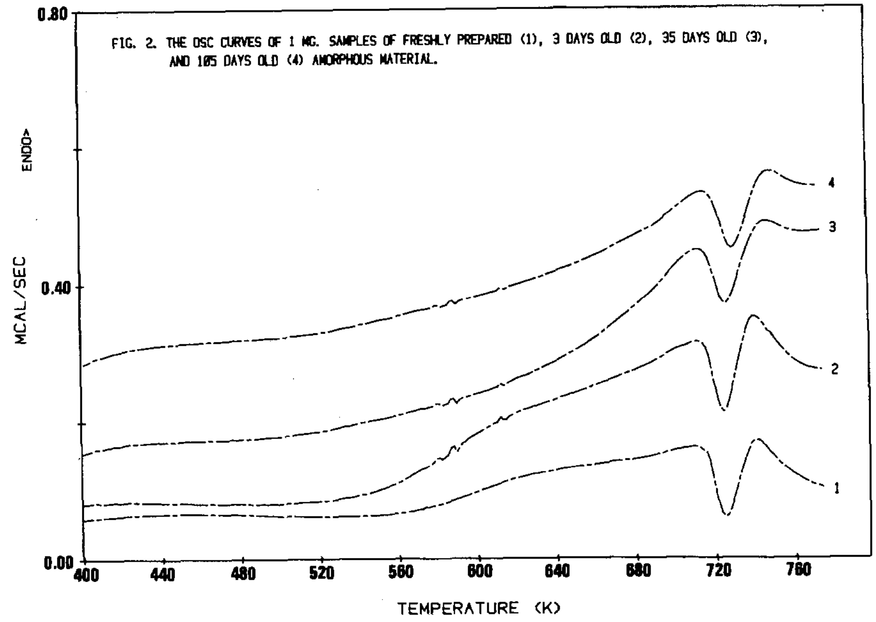


FIG. 2. THE DSC CURVES OF 1 MG. SAMPLES OF FRESHLY PREPARED (1), 3 DAYS OLD (2), 35 DAYS OLD (3), AND 105 DAYS OLD (4) AMORPHOUS MATERIAL.

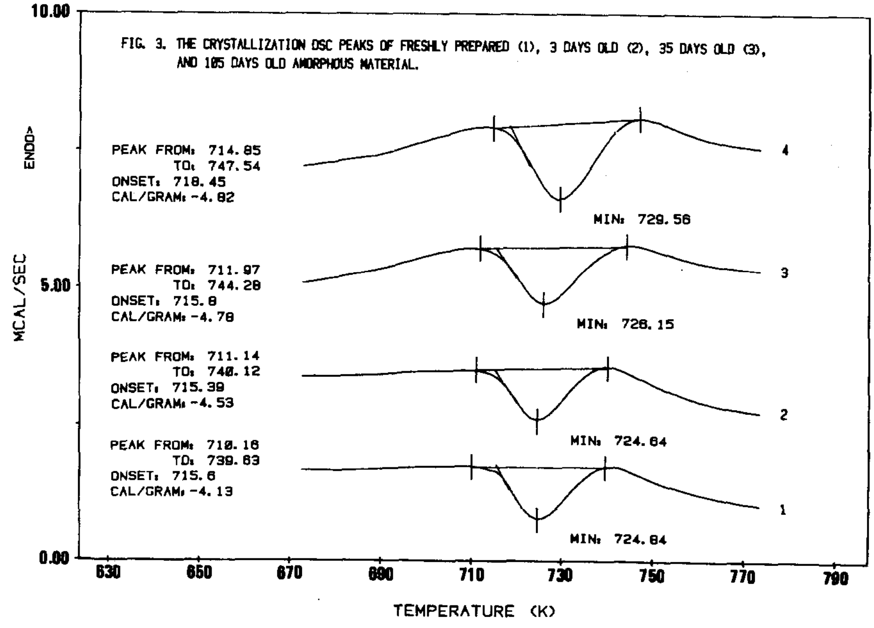


FIG. 3. THE CRYSTALLIZATION DSC PEAKS OF FRESHLY PREPARED (1), 3 DAYS OLD (2), 35 DAYS OLD (3), AND 105 DAYS OLD AMORPHOUS MATERIAL.

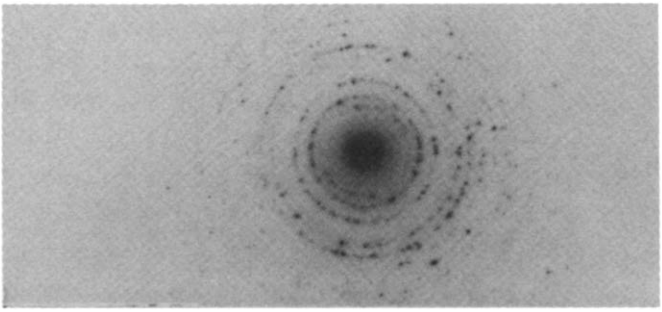


Fig. 4. Diffraction pattern from $\alpha - UO_3$

4.
CONCLUSIONS

AUC heat treated at 575K in an N_2 atmosphere gives an amorphous material which adsorbs moisture when exposed to ambient atmosphere. The analysis of this amorphous material has shown it to be essentially a moisten hexavalent uranium oxide but also to contain carbon, probably as carbonate. The moisture is continuously lost on heating to 725K in N_2, whereupon the crystallisation takes place, and α-UO_3 is formed. Upon further heating α-UO_3 is reduced to U_3O_8 in the temperature interval 825K - 975K. Freshly prepared amorphous materials have been shown to be more unstable in the EM electron beam and in various heat treatments below the crystallisation temperature, than amorphous material stored in the ambient atmosphere for longer periods.

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