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THE THERMAL DECOMPOSITION OF AMMONIUM URANATES PRECIPITATED FROM SULPHATE AND NITRATE MEDIA BY UREA

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ABSTRACT

Ammonium uranates are precipitated from nuclear-pure uranyl nitrate and sulphate solutions using urea. The thermal decomposition of the obtained uranates in air has been studied using DTA, DTG and TG. The effect of sulphate and nitrate impurities and calcination at different temperatures is discussed, making use of additional information obtained from X-ray analysis. The kinetics of the thermal decomposition of UO_3 to U_3O_8 are studied using Kissinger's shape index method.

INTRODUCTION

The fabrication of nuclear fuel generally involves the preparation of intermediate uranium oxides (UO_3 and U_3O_8) which can be processed either to ceramic or metallic nuclear fuel [1]. Both UO_3 and U_3O_8 are prepared either by the direct thermal decomposition of uranyl nitrate [2,3] or by the calcination of ammonium uranate [4,5]. Ammonium uranates (AU) are precipitated by the reaction of uranyl solution with ammonia [4–6] or a donor compound containing ammonia such as urea [6–8], ammonium carbonate [9], and ammonium sulphate [10].

In order to produce a material reactive enough to be processed satisfactorily in subsequent steps to both UO_2 and UF_4, either enough H_2SO_4 is added to the uranyl feed to assure a sulphur concentration in the finished product of 1500–2000 ppm on a uranium basis [1,11], or the obtained UO_3 is soaked in uranyl nitrate [12] or ammonium nitrate [13] solutions before subsequent treatment. However, it is known that Eldorado Mining and Refining Ltd. [14], who produced UO_2, and UKAEA Atomic Weapons Research Establisment [15], who produced UO_2 and mixed Pu–U oxides, both wash their precipitates before further processing, but their reasons for doing so are not known [16].

The aim of the present investigation was to study both the influence of washing on the thermal decomposition of ammonium uranates precipitated from nitrate and sulphate solutions, and the kinetics of the thermal decomposition of UO_3 to U_3O_8.

EXPERIMENTAL

Preparation of samples

Ammonia solution was added to nuclear-pure uranyl nitrate or sulphate solutions to achieve a pH of 2.8. The solutions were stirred vigorously and heated to 95°C. The uranate was precipitated by adding 1 volume of urea solution (500 g l^{-1}) to 2 volumes of uranyl solution (145 g uranium l^{-1}). The temperature was kept at 95°C during the process. Precipitation was allowed to continue until pH reached 6. Classification of the samples is shown in Table 1.

Thermal analysis

Thermal analysis was carried out using the derivatograph which measures simultaneously the temperature of the sample (T), the temperature difference between the sample and the thermally inert material (DTA), the change in mass of the sample (TG), and the rate of change in mass (DTG) of the sample. The sample weight was varied between 0.5 and 1 g for sample A and was equal to 1 g for samples B–E; the rate of heating was 10°C min^{-1} up to 900°C, and α-Al_2O_3 was used as reference material.

X-Ray analysis

A Siemens D-500 instrument was used for X-ray diffraction analysis. The

TABLE 1

Classification of samples

Sample	Mode of preparation
A	The uranate was precipitated from uranyl nitrate solution containing 0.05 M free nitric acid, filtered off immediately, washed with water and alcohol, then air-dried.
B	The uranate was precipitated from uranyl sulphate solution containing 1.0 M free sulphuric acid, filtered without washing, and air-dried.
C	The uranate was precipitated from uranyl nitrate solution containing 1.0 M free nitric acid, filtered without washing, and air-dried.
D	α-UO_3 was prepared as described by Cornman [17].
E	γ-UO_3 was prepared as described by Cornman [17].

diagrams were taken using a copper target, nickel filter, $K_\alpha = 1.54$ Å, 40 kV, 20 mA, 2×10^3 pulse s^{-1} and speed = 2° min^{-1}.

Calculation of some kinetic parameters

The orders of reactions were calculated from DTA curves using Kissinger's shape index method [18]. According to Kissinger, the order of reaction (n) is given by the relation

$$n = 1.26\,(a/b)^{1/2}$$

RESULTS AND DISCUSSION

The effect of the thickness of the AU powder layer on thermal analysis

The DTA and TG curves obtained for sample A are shown in Fig. 1. To elucidate the effect of thickness of the powder layer on the thermal curve, weights of 500, 750 and 1000 mg of uranate corresponding to layer thicknesses of 6, 8 and 10 mm respectively, were heated in the derivatograph up to 800–C.

In the DTA curves, it is evident that the thinner the layer the smaller is the area obtained for both endothermic and exothermic peaks. This observation is expected since the heat effects are directly proportional to the mass used.

With thinner layers, the reactions are shifted to lower temperatures and at the same temperature, the percentage loss in weight is higher, ensuring that in the case of thin layers, the temperature gradient is low and the mass exists at a relatively higher temperature.

Woolfrey [19] summarised the previous work on the thermal analysis of ammonium uranates and showed that the results are contradictory. The difference between the present results and those published earlier [19] is that a double endothermic peak is observed in the range 40–200°C due to the dehydration and evaporation of H_2O molecules. Below 100°C dehydration produces water in the liquid state and above 100°C the free water evaporates, giving the second peak. This is in conformity with Stuart [20] where the release of water took place in two stages at 80 and 160°C.

Ippolitova et al. [21] found that the dehydration of ammonium uranate starts at 20°C and proceeds up to 200°C. Szabo [22] observed it to proceed up to 220°C. The latter temperature was adopted as the initial reading for deducing the percentage weight decrease of the samples, as also applied in our previous work [23,24]. TG curves (Fig. 1) indicate that the percentage loss in weight in thick calcined layers is generally greater than in thin calcined ones in the temperature range 220–400°C. The same degradation

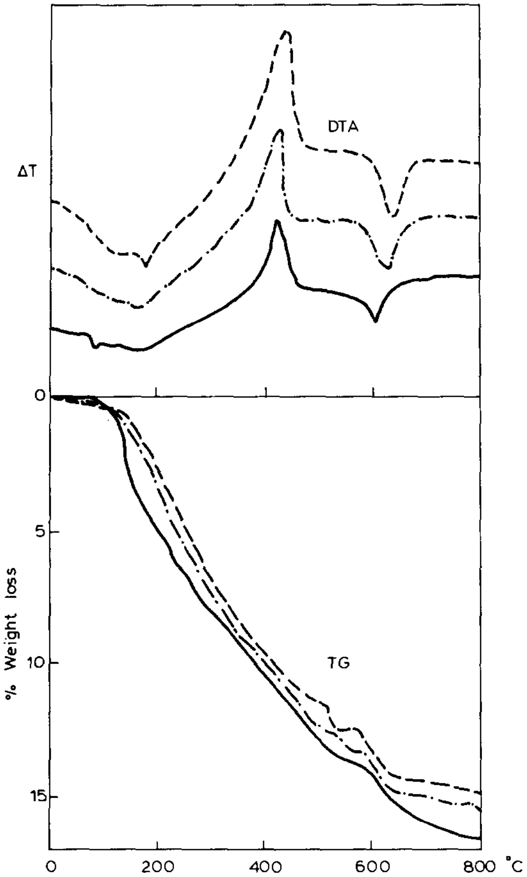

Fig. 1. Relation between layer thickness and thermal analysis for sample A. ———, 0.6 cm; ·—·—·, 0.8 cm; - - - - - -, 1.0 cm.

was also observed in the temperature ranges 220–500°C and 220–600°C. Chemical analysis [6] also indicated that the amount of reduced uranium in thick calcined layers is generally greater than in thin ones because in thin calcined layers ammonia reacts with atmospheric oxygen before auto-reduction, i.e. before reaction of the retained ammonia with UO_3.

Figure 1 also indicates that the percentage loss in weight due to oxygen departure above 600°C is generally greater in thin calcined layers than in thick calcined ones, presumably the oxygen is retarded from evolution within the thicker layer. The loss in weight due to oxygen departure increased with the increase of temperature as it is known that the U_3O_8 phase is non-stoichiometric and is significantly oxygen-deficient at higher temperatures [6].

The X-ray diffraction data obtained for uranium oxides, formed after heating sample A at temperatures varying between 300 and 500°C, are in complete agreement with similar data for β-UO_3 obtained after heating washed ammonium uranate, precipitated by ammonia gas, in the same temperature range [25,26].

The kinetics of the thermal decomposition of β-UO_3 to U_3O_8, calculated from the last endothermic peak for the three curves, are found to be typically those of a first-order reaction (the average value of the three samples is equal to 1.073). This is in fair agreement with that of Dharwadkar and Markhanavala [27] where the order of reaction, calculated by this method, was found to be 0.889, i.e. approximately unity.

The effect of the presence of sulphate ions on the thermal decomposition of AU

The presence of sulphate impurities can be explained by the fact that AU precipitated from uranyl sulphate solution contains residual sulphate as a

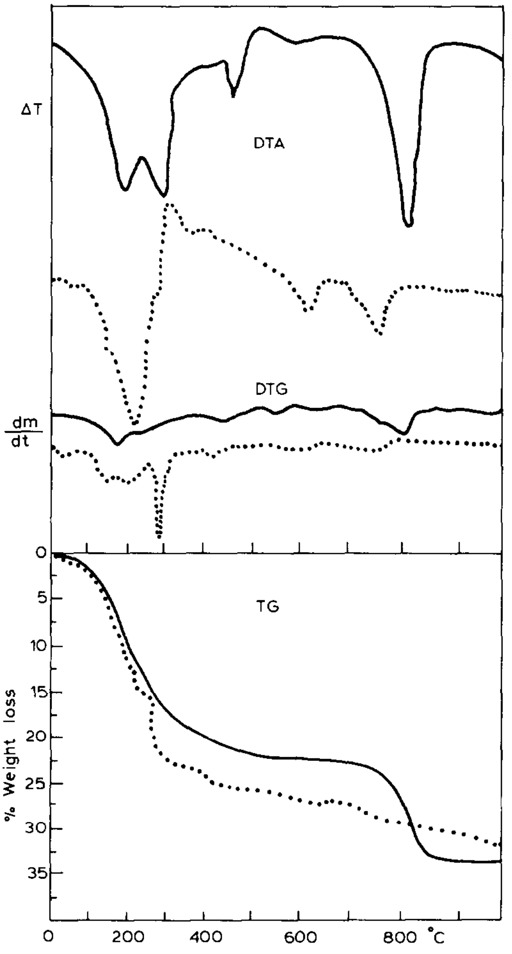

Fig. 2. Effect of sulphate and nitrate impurities. ———, Sample B; - - - - - -, Sample C.

major impurity. The majority of these ions can be removed by washing with water.

The DTA and TG curves for sample B are shown in Fig. 2. The DTA curve shows six endothermic peaks: three large peaks at 180, 280 and 800°C; a broad peak at 360°C; a medium peak at 450°C; and a small peak at 615°C. The curve does not show any exothermic peaks.

The DTA exothermic peak for sample A (Fig. 1) corresponds mainly to the removal of nitrate impurities and some retained ammonia, as reported in our previous work [25] for ammonium uranates precipitated by ammonia gas. The disappearance of this exotherm for sample B (nitrate-free uranate) confirms that this peak is associated with nitrate removal.

The first two large endothermic peaks at 180 and 280°C can be attributed to the removal of water with a small amount of ammonia. Stuart [20] observed a peak at 275°C corresponding to the removal of NH_3, besides

TABLE 2

X-ray diffraction patterns of sample B calcined at 350 and 500°C

Sample B calcined at 350°C				Sample B calcined at 500°C	
d (Å)	I/I_0	*d* (Å)	I/I_0	*d* (Å)	I/I_0
7.32	23	2.536	25	6.563	11
6.90	47	2.44	7	6.18	11
6.08	57	2.39	7	4.99	55
5.567	41	2.33	14	4.81	30
5.303	21	2.24	13	4.7	30
5.103	100	2.238	17	4.37	64
4.92	25	2.14	25	4.205	68
4.80	30	2.08	13	4.125	100
4.39	39	2.065	11	3.90	20
4.166	20	2.016	10	3.275	51
4.001	70	1.99	12	3.099	38
3.708	10	1.966	18	3.04	13
3.586	12	1.91	10	2.87	20
3.502	35	1.857	7	2.80	20
3.469	68	1.81	13	2.744	45
3.339	75	1.79	13	2.665	32
3.23	15	1.74	18	2.59	22
3.13	22	1.73	20	2.52	25
3.068	20	1.68	12	2.07	22
3.025	14	1.59	10	1.95	17
2.845	13	1.56	7	1.915	21
2.80	30			1.89	19
2.71	12			1.825	20
2.685	12			1.76	20
2.611	16			1.71	22
2.596	16			1.56	15

those at 60 and 180°C for the removal of H_2O. It is known that the dehydration of ammonium uranates starts at 20°C [21] and proceeds up to 220°C [22] and is associated with the first endothermic deflection [19], and it is also known that the removal of ammonia starts before the termination of the removal of water [25].

The broad endothermic peak at 400°C is mainly associated with the melting of ammonium sulphate impurity, which then reacts with part of the UO_3 formed to produce uranyl sulphate, leading to the medium peak at 470°C.

The X-ray diffraction data of powders obtained after calcining sample B at 350 and 500°C are shown in Table 2. The characteristic *d*-lines of β-UO_3 [25] besides those of uranyl sulphate, quoted in ASTM cards 8–191 and 9–167, are evident for sample B calcined at 350°C. At 500°C, the characteristic *d*-lines of $UO_{2.9}$ [α-$UO_3(O)$] as given by Cornman [17] and Nicolas-Jarleton [28] are found, besides those of uranyl sulphate [29] and γ-UO_3 [17].

The endothermic peak at 615°C represents the decomposition of α-$UO_3(O)$ to U_3O_8, while the final peak at 800°C represents the decomposition of γ-UO_3, besides the formed uranyl sulphate to U_3O_8. It is known that the anhydrous uranyl sulphate is stable to about 600°C, then decomposes to U_3O_8 at about 800°C, leading to a large endothermic peak [29].

The conversion of UO_3 to U_3O_8 in two steps can be explained as follows. Two types of UO_3, amorphous UO_3 (A) and β-UO_3, have been reported in the literature [30–32) as being formed during the decomposition of Au. Landspersky et al. [31] found that the rate of heating had an effect on the type of UO_3: slow heating (1°C min^{-1}) gave A-UO_3 while rapid heating (10°C to 100°C min^{-1}) gave a mixture of β-UO_3 and A-UO_3.

In a moist atmosphere the initial mixture of A-UO_3 + β-UO_3 may become hydrated to form $UO_3 \cdot 0.8\ H_2O$ [31]. On further heating, this compound is converted to a mixture of α-UO_3 and γ-UO_3 [17]. The decomposition of this mixture to U_3O_8 gives two endothermic peaks. The first peak at 615°C is due to the conversion of α-$UO_3(O)$ to U_3O_8, and the second is due to the conversion of γ-UO_3 to U_3O_8 [17].

The TG curve for sample B (Fig. 2) indicates that the total weight loss between room temperature and 900°C is 32.5%. This decrease in weight cumulates mainly the multistep departure of water, ammonia, oxides of sulphur, and oxygen.

The effect of the presence of nitrate ions on the thermal decomposition of AU

The presence of nitrate impurities can be explained as described previously for sulphate impurities. The DTA curve for sample C (Fig. 2) shows three endothermic peaks at 80, 160 and 275°C due to dehydration and removal of coordinated H_2O molecules. This result is in good agreement with that of Stuart [20] who found that when the rate of H_2O release is plotted as a function of temperature, three maxima at 80, 160, and 275°C are obtained during decomposition in inert gas. The large endothermic peak at 210°C represents mainly the boiling point (210°C) of ammonium nitrate.

The exothermic peaks at 320 and 340°C correspond mainly to the removal of nitrate impurities and ammonia to form UO_3, as also reported previously [19,25]. The presence of excess nitrate impurities leads to the oxidation of the ammoniates and prevents self-reduction [6], i.e. before self-reduction can take place the oxides of nitrogen from NH_4NO_3 oxidise the ammoniate formed, leading to the exothermic peak at 400°C. This exothermic peak is therefore due to the reaction of ammoniate H_3N^{-} with oxides of nitrogen.

The two endothermic peaks at 615 and 750°C correspond to the conversion of UO_3 to U_3O_8 in two steps owing to the formation of α- and γ-UO_3 produced on heating in moist atmosphere. The DTG curve indicates that the two endothermic peaks are due to decomposition and not phase transition. For confirmation, samples D (α-UO_3) and E (γ-UO_3) were prepared as recommended by Cornman [17]. The X-ray diffraction data for samples D and E, besides those obtained after calcining sample C at 350 and 500°C, are

TABLE 3

X-Ray diffraction patterns of samples C, D and E

Sample C calcined at				Sample D (α-UO_3)		Sample E (γ-UO_3)	
350°C		500°C					
d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
7.146	25	7.146	29	7.368	31	6.51	15
5.106	85	5.095	7	4.139	92	5.12	12
4.818	5	4.79	5	3.423	100	4.99	47
		4.14	7	2.637	69	4.77	6
3.703	4	3.703	13	2.073	20	4.378	57
3.583	20	3.583	100	1.980	19	3.448	100
3.415	100	3.41	40	1.779	41	3.255	61
3.108	5	3.065	50	1.716	8	3.044	41
2.855	50	3.025	65	1.583	10	2.798	69
2.626	3	2.629	5	1.434	10	2.746	18
2.465	50	2.467	70	1.385	5	2.626	17
2.139	20	2.25	5	1.322	6	2.188	12
2.05	20	2.068	5	1.285	10	2.129	13
1.991	35	1.99	10	1.237	6	2.106	16
1.978	30	1.949	25	1.136	6	2.02	14
		1.912	20	1.100	6	1.991	18
1.816	10	1.882	10			1.839	20
1.785	25	1.79	15			1.741	28
1.741	20	1.715	10			1.722	27
1.712	20	1.67	10			1.54	14
						1.373	12

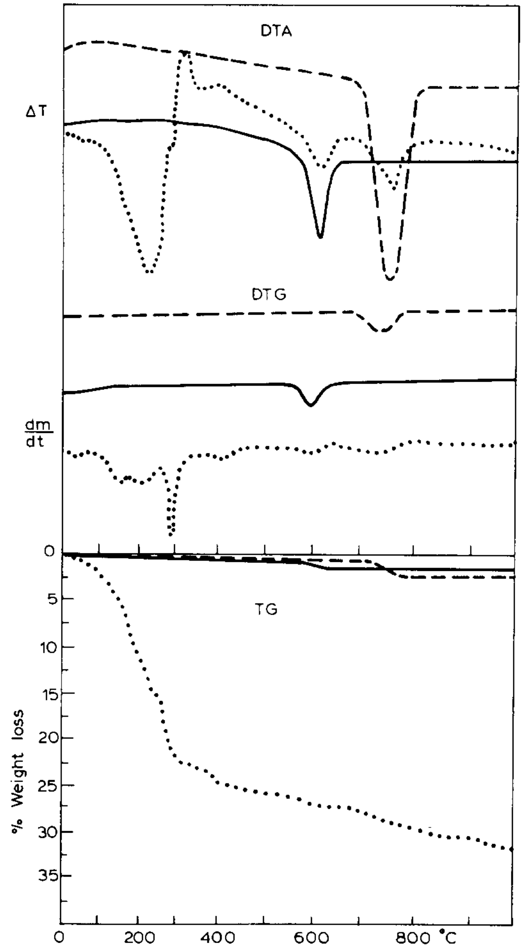

Fig. 3. Thermal analysis curves of samples C–E. ------, Sample C; ——, sample D; - - - - - -, sample E.

shown in Table 3. This table indicates the formation of β-UO_3 after calcining, in open air, at 350°C for 18 h; for the same duration at 500°C, the X-ray data (Table 3) indicate the formation of a mixture of β-UO_3 and $UO_{2.9}$ [α-$UO_3(O)$] whereas the thermal analysis curves (Fig. 3) indicate the formation of a mixture of α- and γ-UO_3 during heating in a covered crucible on the derivatograph, presumably due to formation of $UO_3 \cdot 0.8\ H_2O$ during heating.

The DTA, DTG and TG curves for samples C, D and E shown in Fig. 3 also confirm this concept. Therefore in order to prevent the formation of γ-UO_3 besides α-UO_3, it is recommended to heat in a dry atmosphere. Heating of unwashed AU, precipitated by ammonia gas, in a dry atmosphere leads to the formation of a mixture of A- and β-UO_3 at 350°C and a mixture of β-UO_3 and $UO_{2.9}$ [α-$UO_3(O)$] at 500°C [26].

The kinetics of the thermal decomposition of UO_3 to U_3O_8 calculated from the last two endothermic peaks are found to be those of a first-order reaction, the average value being equal to 0.991, i.e. approximately unity.

The DTA curve for sample C (Fig. 2) indicates that the total loss in weight between room temperature and 900°C is 30%. This decrease in weight cumulates mainly the multistep departure of water, ammonia, oxides of nitrogen and oxygen.

REFERENCES

1 C.D. Harrington and A.E. Ruchle (Eds.), Uranium Production Technology, Van Nostrand, Princeton, NJ, 1959.
2 A. Rodrigo Otero, Proc. Int. Symp. Fluidisation, Madrid, 1967.
3 A. Rodrigo Otero, Publicado en An. R. Soc. Esp. Fis. Quim. Ser. B, 4 (1970) 399.
4 M.Y. Farah and S.A. EL-Fekey, Recent Adv. Sci. Technol. Mater., 3 (1974) 343.
5 M.Y. Farah, S.A. EL-Fekey, F.H. Hammad and A.F. Bishay, in J. Lehouliar and M. Mantega (Eds.), The European Nuclear Conference on Nuclear Energy Maturity, Paris, 1975. Societé Française de L'Energie Nucléaire, Clamart, France, 1975, p. 112.
6 S.A. EL-Fekey, M.Y. Farah and N.H. Rofail, Anal. Chim. Acta, 89 (1977) 413.
7 M.A. Khilla, S.A. EL-Fekey and M. EL-Mamoon Yahia, Radiochim. Acta, 28 (1981) 115.
8 M.E.A. Hermans and T. Markestein, J. Inorg. Nucl. Chem., 25 (1963) 461.
9 J.C. Clayton and S. Aronson, J. Chem. Eng. Data, 6 (1961) 43.
10 N.I. Pechurova, L.M. Kovba and E.A. Ippolitova, Zh. Neorg. Khim., 10 (1965) 918.
11 E.W. Mautz, Rep. NLCO-1068 (1970).
12 S.N. Robinson and J.E. Todd, Rep. MCW-1509 (1966).
13 Eldorado Nuclear Ltd. Fr. Demande 2,302,967 (1976); Can. Appl. 221,214 (1975).
14 R.M. Berry, Can. Nucl. Technol., 6,2 (1967) 30.
15 S.E. Smith, J.S. Broadley, P. Brown and W.C.L. Kent, Proc. 3rd. Int. Conf. Peaceful Uses At. Energy, Geneva, Vol. 10, 1964, p. 161.
16 J. Janov, P.G. Alfredson and U.K. Vilkaitis, U.S.A.E.C. Rep. E220, 1971.
17 W.R. Cornman, Rep. DP-749 (1962).
18 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
19 J.L. Woolfrey, U.S.A.E.C. Rep. TM-476, 1969.
20 W.I. Stuart, J. Inorg. Nucl. Chem., 38 (1976) 1378.
21 E.A. Ippolitova, N.I. Pechurova and E.N. Gribennik, ANL Trans., 33 (1961) 114.
22 E. Szabo, 3rd Int. Conf. Peaceful Uses At. Energy, Geneva, Vol. 10, 1964, p. 450.
23 M.Y. Farah, M.R. Zaki and S.A. EL-Fekey, Thermal Analysis, Vol. 2, Academic Press, New York, 1969.
24 M.Y. Farah and S.A. EL-Fekey, Arab J. Nucl. Sci. Appl., 10 (1977) 1.
25 S.A. EL-Fekey, M.A. Khilla, M.N.A. EL-Hakim and N.H. Rofail, Thermochim. Acta, 54 (1982) 327.
26 S.A. EL-Fekey, M.A. Khilla and N.H. Rofail, Acta Crystallogr., in press.
27 S.R. Dharwadkar and M.D. Markhanavala, J. Indian Chem. Soc., 6 (1968) 45.
28 J. Nicolas-Jarleton, Ph.D. Thesis, Faculty of Science, University of Paris, 1970.
29 J. Karl and Notz, Jr., U.S.A.E.C. Res. Dev. Rep., NLCO-814, 1960.
30 H. Landspersky, I. Imrisova, L. Sedlakova and Z. Urbanec, Int. Symp. New Nucl. Fuel Mater., Prague, Vol. 1, 1961, p. 79.
31 H. Landspersky, L. Sedlakova and D. Jakes, J. Appl. Chem., 14 (1964) 559.
32 E.H.P. Cordfunke and A.A. Van der Giessen, 5th International Symposium on the Reactivity of Solids, Munich, 1965, p. 456.