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The Study of the Interaction between Uranium Monosulphide and Nitrogen*

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The study of the process of interaction between nitrogen and nearly stoichiometric uranium monosulphide reveals at least three distinct stages. The first one (200—580⁰ C) is characterized by limited interstitial dissolution of nitrogen in the lattice. At approximately 580⁰ C, US starts to react with N_2 yielding uranium sulphonitride of the composition $U_2S_2N_y$. Above 1200⁰ C $U_2S_2N_y$ decomposes into US and $U_2S_{2-x}N_y$. The X-ray powder diffraction method was used in order to derive the most probable atomic positions in the crystal structure of U_2S_2N.

INTRODUCTION

Uranium monosulphide is considered to be a perspective nuclear fuel material[1]. However, its physical and chemical properties are not yet known to a degree which would warrant its practical use. Most of the fundamental studies in the system U-S were done by Picon and Flahaut[2,3]. Extensive studies of those properties of US which are relevant for its application in nuclear fuel technology, were carried out by Shalek[4,5]. He and his coworkers were the first to investigate the oxydation behaviour of US using X-ray diffraction and differential thermal analysis. In our recent paper[6] we described some unexpected results which were obtained if oxydation of US is carried out in a quasiisothermal manner. Instead of instantaneously igniting, oxygen slowly diffuses into the crystal structure and forms solid solutions. In the same paper we mentioned that a similar phenomenon occurs during the US-N_2 reaction. Because of the apparent disagreement between our results and those obtained by Dell[1], we decided to study this reaction in a more detailed way.

MATERIALS AND METHODS

The sample of US was obtained from the Nuclear Institute »Jožef Stefan«, Ljubljana, Yugoslavia. Extrapure nitrogen, containing 10 ppm O_2, (Dugi Rat, Yugoslavia) was purified by passing it through a set of columns filled with concentrated sulphuric acid, calcium chloride and molecular sieves (4 Å) held at liquid air temperature.

Experiments were carried out, both in static and flowing atmosphere of nitrogen. In the static atmosphere they were performed in an apparatus schematically drawn on Fig. 1.

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* A part of this work was presented at the III Conference of the Yugoslav Center for Crystallography, Belgrade, Yugoslavia, October 23—24, 1968.
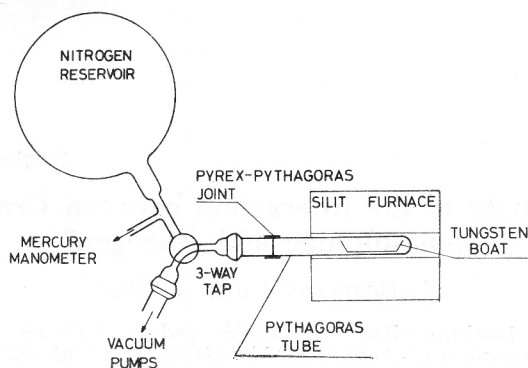
Fig. 1. The apparatus used for the experiments in the static atmosphere of nitrogen.

Prior to each experiment a flow of nitrogen was maintained through the columns during 24 hours. A two liter Pyrex flask (outgassed at 10^{-5} mm Hg) was filled with the pure gas. The sample of US (150 mesh) was placed in a tungsten boat and inserted in to the ceramic tube. The tube was then repeatedly pumped off and filled with nitrogen from the flask. When the temperature of the sample, in the evacuated tube, reached the desired level, nitrogen was admitted. Dynamic experiments were done in a Cahn thermobalance. The flow of nitrogen was kept at 1 ml/min. A typical heating rate was 4 deg./min. X-ray diffraction patterns were obtained on Philips PW 1010 and General Electric XRD-6 diffractometers employing Geiger and proportional counters, respectively. All patterns were taken using nickel filtered CuKα radiation. Each sample was chemically analized for all three components. Nitrogen was determined by the Dumas method, uranium gravimetrically with 8-oxychinoline and sulphur as sulphate.

RESULTS AND DISCUSSION

Between 200 and 400° C nitrogen enters and sulphur evolves to a certain extent from the sulphide. The amount of the absorbed nitrogen is mainly dependent on the initial stoichiometry of the sulphide. It is interesting to notice that hypostoichiometric samples pick up less nitrogen than those in which the sulphur content exceeds the ratio $U:S = 1$. Typical compositions, at 400° C, are $US_{1.04}N_{0.067}$ and $US_{0.99}N_{0.043}$.

According to the results of the chemical analyses, in the interval between 400 and 580° C, the content of nitrogen decreases. At approximately 580° C $US_{1\pm x}N_y$ starts to react with nitrogen and forms a compound to which Dell originally ascribed the chemical formula U_2N_2S. Such a compound would have a lower molecular weight than US, and therefore a weight loss should occur. By looking at the TGA curve (Fig. 2.) instead of the weight loss we see a continuous weight gain. This result indicates that the newly formed compound absorbs nitrogen but does not lose sulphur. This was later proved by chemical analyses of the samples equilibrated in the static atmosphere of nitrogen (Table I).

Up to 1000° C X-ray diffracton peaks sharpen but the lattice parameters remain almost unchanged. Above 1250° C the compound gradually loses sulphur. Arc melted samples of U_2S_2N and US in nitrogen atmosphere were found to consist of a mixture of US and $US_{2-x}N_y$ having the same structure.
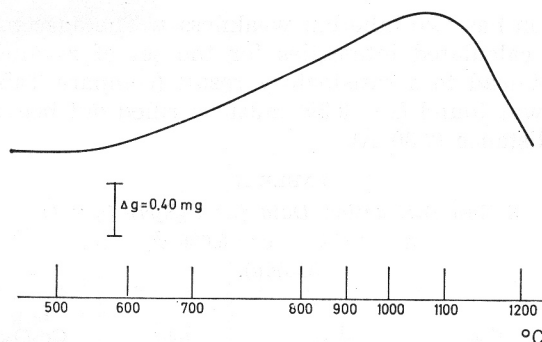
Fig. 2. The weight gain curve as obtained during the US-N_2 reaction (4 deg/min).

TABLE I

Composition of Equilibrated Samples at Different Temperatures

Temp. (°C)	Time (h)	Composition X_M			Phase composition	
		U	S	N		
750	20	2	1.84	0.43	$U_2S_2N_y$	$+$ US
800	24	2	2.18	0.83	$U_2S_2N_y$	
900	36	2	2.04	1.11	$U_2S_2N_y$	
1000	20	2	1.09	1.20	$U_2S_2N_y$	
1100	18	2	2	1.07	$U_2S_2N_y$	
1150	18	2	2.07	1.04	$U_2S_2N_y$	
1200	18	2	2.01	1.00	$U_2S_2N_y$	
Arc melted sample of US or U_2S_2N in nitrogen atmosphere					$US_{2-x}N_y$	$+$ US

Although the relative X-ray intensities are mostly determined by the positions of uranium atoms, we tried to derive the most probable atomic arrangement of all atoms in the structure of U_2S_2N. Sulphur atoms can be located because their scattering power is relatively significant in comparison with that of uranium. The positions of nitrogen atoms were derived on the basis of spacial considerations.

First, we assumed complete structural analogy with Ce_2O_2S (La_2O_2S, Pu_2O_2S)[7]. In this case, we would have the following atomic coordinates in the space group $P\bar{3}m1$:

$$2\,U \text{ in } \frac{1}{3}, \frac{2}{3}, z \qquad \frac{2}{3}, \frac{1}{3}, \bar{z}$$

$$2\,S \text{ in } \frac{1}{3}, \frac{2}{3}, y \qquad \frac{2}{3}, \frac{1}{3}, \bar{y}$$

$$N \text{ in } 0, 0, 0$$

where z = 0.29 and y = 0.63.

This assumption has two inherent weaknesses. The agreement between the observed and the calculated intensities for the set of z-values ranging from 0.23—0.29 does not lead to a satisfactory result (compare Table II.). The best agreement which was found (z = 0.29) must be ruled out because of the impossibly short U-S distance (2.30 Å).

TABLE II

X-Ray Diffraction Data for $U_2S_2N_y$ (y = 1)

a = 3.822   c = 6.650 Å

(CuKα)

H K L	$d_{obs.}$	$d_{calc.}$	$I_{obs.}$	$I_{calc.}$ Ce_2O_2S-type	$I_{calc.}$ »Th_2CH_2«-type
1 0 0 0 0 2	3.11	3.32	28*	57.2*	15*
1 0 1	2.950	2.948	78	124	77
1 0 2	2.330	2.318	22	24.2	22
0 0 3	2.220	2.222	3	8.6	2.9
1 1 0	1.913	1.921	25*	6.5*	4.6*
1 1 1 1 0 3	1.830	1.832	14	25.2	8
2 0 0 1 1 2 0 0 4	1.652	1.650	15	30.8	12
2 0 1	1.604	1.599	13	16.8	11
1 0 4 2 0 2	1.476	1.469	12	24.7	13.7
1 1 3	1.441	1.444	7	12.4	4.5
2 0 3 0 0 5	1.322	1.318	9	13	10
2 1 0 1 1 4	1.247	1.241	5	4	4.85
1 0 5 2 1 1	1.230	1.234	10	8.5	9.4

Sulphur atoms are expected to occupy larger (octahedral) and nitrogen atoms smaller (tetrahedral) voids in the structure. At this point it is worthwhile to mention that just the opposite situation was found by Zachariasen[7] in the crystal structure of Th_2N_2O ($R_N > R_O$).

A recent study of the crystal structure of Th_2CH_2[8] led us to conclusion that larger atoms (in our case S) can be put, besides the positions (0, 0, 0), also in (0, 0, 1/2), both being octahedraly coordinated. In this case much better agreement is obtained if we assume the following atomic coordinates:

2 U   in $\frac{1}{3}$, $\frac{2}{3}$, 0.29 $\frac{2}{3}$, $\frac{1}{3}$, 0.71

2 S   in 0, 0, 0   0, 0, $\frac{1}{2}$

N (statistically) in $\frac{1}{3}$, $\frac{2}{3}$, 0.62 $\frac{2}{3}$, $\frac{1}{3}$, 0.38

The intensities of some reflections (marked with the asterisk) are probably altered due to the preferential orientation of the crystallites[8]. The only interatomic distance, which seems to be somewhat short, is the S-S closest approach along the c-axis (3.32 Å), but it can be explained either by departure from sphericity of large atoms, or by the unknown valency state of all constituents in this particular structure, or by a strong S-S bond.

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IZVOD

Studij interakcije uran monosulfida i nitrogena

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Istraživanjem toka reakcije US-N_2 ustanovljeno je postojanje triju odvojenih faza toga procesa. U prvoj fazi dolazi do ograničene intersticijalne ugradnje nitrogena u rešetku US. U drugoj nastaje spoj $U_2S_2N_y$. Struktura ima trigonsku simetriju (P. G. P3ml) s parametrima ćelije a = 3,822 i c = 6,65 A. Rendgenografskom metodom praha utvrđen je najvjerojatniji raspored svih atoma u strukturi. Atomi urana čine gotovo kompaktnu heksagonsku slagalinu, atomi sulfura zauzimlju oktaedrijske, a atomi nitrogena tetraedrijske položaje.

Iznad 1200 ^{0}C dolazi do dekompozicije, pri čemu uz US vjerojatno nastaje i U_2N_2S.

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