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Note

The Homogeneity Range in the System UP(O)

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A large number of samples of uranium monophosphide were prepared by direct reaction between uranium filings and red phosphorus, followed by homogenization in a high temperature furnace (Degussa) at 1200—1300 °C and a pressure of 10^{-4} Torr (1 Torr = 101.325/760 kPa). Samples were analyzed for uranium, phosphorus and nitrogen, assuming that the difference is oxygen. The oxygen content was found to vary from sample to sample, ranging from 0.54 (min.) up to 7.10 wt. % (max.). X-ray analysis did not indicate the presence of UO_2. The amount of oxygen or nitrogen was not controled in advance, but final results ensured the working hypothesis, since the analytical data were in acordance with the X-ray powder diagrams.

Uranium filings were first cleaned in the mixture of HNO_3 and ethanol (1 : 1) in order to remove surface layer of UO_2. Phosphorus and uranium were weighted in such proportions to have P/U atomic ratio ranging from 1.1—1.3, and sealed in evacuated silica capsules. They were placed in an electric furnace, and temperature slowly (3—4 days) increased to 900 °C and finally kept at this temperature during 2—3 weeks. UP and U_3P_4 were the only phases detected after such procedure.

The products were compacted into slabs ($5 \times 5 \times 15$ mm^3), placed in a tungsten crucible, and fired at 1200—1300 °C for 2 hours in vacuum (10^{-4} Torr). Under these conditions U_3P_4 decomposes forming more stable UP and elemental phosphorus[1,2,3]. After cooling, the samples were crushed to powder, and examined by chemical and X-ray analysis. Uranium was determined gravimetrically, phosphorus spectrophotometrically (phosphomolybdate method) and nitrogen by Dumas method. None of the samples showed the presence of nitrogen. Results for a representative set of samples are given in Table I. Oxygen content is obtained as a difference up to 100%.

TABLE I

Chemical analysis data for a representative set of samples

Sample	wt. % U	wt. % P	wt. % O	Chemical formula	Σ O + P
1.	86.67	6.23	7.10	$UP_{0.55}O_{1.18}$	1.73
2	87.91	7.38	4.71	$UP_{0.64}O_{0.80}$	1.44
3.	87.67	8.22	4.11	$UP_{0.70}O_{0.68}$	1.38
4.	88.12	8.73	3.15	$UP_{0.76}O_{0.53}$	1.29
5.	88.59	8.54	2.87	$UP_{0.74}O_{0.48}$	1.22
6.	88.85	8.51	2.64	$UP_{0.74}O_{0.44}$	1.18
7.	88.75	10.08	1.18	$UP_{0.87}O_{0.20}$	1.07
8.	88.14	11.32	0.54	$UP_{0.98}O_{0.09}$	1.07

Interaction between UP and UO_2 has been previously investigated[4], but no evidence for existence of an intermediate phase was found. All samples were of the two phase nature.

Under the experimental conditions described above all samples were single phase, as determined by X-ray powder diffraction method. This can be compared with low temperature oxidation behaviour of US[5]. Patterns were taken on Philips diffractometer using Ni-filtered CuK radiation. They exhibit sharp diffraction maxima corresponding to a FCC cell with the average lattice parameter $a = (5.589 \pm 0.005)$ Å. The lattice parameter virtually shows no variation from sample to sample, in spite of the different proportion of nonmetallic components. It is noticeable that oxygen content increases, when that of phosphorus drops down. The loss of phosphorus in the extreme case amounts 45% from that in UP. Samples with low oxygen content have atomic ratio P/U approaching unity.

In conclusion we may say that the prepared samples should be considered as homogenous phases being present in the system UP(O) with variable mutual ratio of nonmetallic components.

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IZVOD

Homogena područja u sistemu UP (O)

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Preparacijom uran-fosfida direktnom reakcijom strugotina urana i crvenog fosfora, u evakuiranoj i zataljenoj epruveti od kvarcnog stakla na 900 °C i uz atomski omjer P/U nešto veći od 1, dobivene su smjese faza UP i U_3P_4. Preparirani uzorci homogenizirani su 2 puta u peći tipa »Degussa« na 1200—1300 °C u vakuumu (10^{-4} Torr) Kemijska analiza homogeniziranih uzoraka pokazala je prisutnost veće količine kisika (0.54—7.10 tež. %). Rendgenografskom metodom praha utvrđeno je da kisik u uzorcima nije u obliku UO_2 i da homogenizirani uzorci pripadaju strukturnom tipu NaCl kao i čisti UP. Uočena je povezanost između promjenljivog sadržaja kisika i sadržaja fosfora u homogeniziranim uzorcima.

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