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Abstract

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ON DOUBLE OXIDES

IN THE URANIUM–TUNGSTEN–OXYGEN SYSTEM

The study of double oxides of uranium and tungsten has not hitherto been carried out. In the literature there are only indications of the preparation of aqueous uranyl tungstates and polytungstates ($^{1-3}$).

We have studied the oxides formed in the interaction of various oxides of uranium and tungsten, and also in the thermal decomposition and reduction with hydrogen of uranyl tungstate. Tungstic acid and uranyl nitrate of chemically pure grade were used as starting preparations; the other preparations used $(WO_2, W, UO_2, U_3O_8, UO_3)$ were obtained from the above-mentioned compounds. The corresponding procedures are well known. The investigation was carried out by the method of X-ray phase analysis (RKD-57 cameras, Cu K_α radiation, Ni filter). A number of samples were recorded in Cu K_α radiation monochromatized by reflection from a flat single crystal of germanium (this gives better resolution of lines for cameras of the given diameter) (^{4}). To obtain samples in the system UO_3—WO_3, aqueous suspensions of H_2WO_4 and $UO_2(OH)_2$ were boiled for a long time, then evaporated to dryness and calcined at 900° for 45 hr. X-ray—

Table 1

Results of X-ray phase analysis

Composition of the starting preparation	Method of treatment	Observed phases
$UO_3 : WO_3 = 1 : 1$	Calcination, 900°	UO_2WO_4
$UO_3 : WO_3 = 1 : 2;\ 1 : 3$	Calcination, 900°	$UO_2WO_4 + WO_3$
$UO_3 : WO_3 = 3 : 1$	Calcination, 450°	$UO_{3-x} + WO_3$
UO_2WO_4	$H_2,\ 300°$	UO_2WO_4
Same	$H_2,\ 400°$	Same
» »	$H_2,\ 500°$	$WO_2,\ UO_2,\ UWO_{5+x}$
» »	$H_2,\ 600°$	$W,\ UO_2,\ WO_2$
» »	$H_2,\ 700°$	$W,\ UO_2$
$UO_2 : WO_2 = 1 : 1;\ 2 : 1;\ 1 : 2$	Calcination, 1250°	$WO_2,\ UO_2$

Composition of the starting preparation	Method of treatment	Observed phases
$UO_2WO_4 : W = 1 : 1$	Calcination, 1250°	$WO_2,\ UO_2$
$U_3O_8 : W = 1 : 1$	Calcination, 1250°	Same
$U_3O_8 : WO_2 = 1 : 1$	Calcination, 1250°	$UO_2,\ (U, W)O_{3-x}$
$U_3O_8 : WO_3 = 1 : 1$	Calcination, 1250°	$U_3O_8,\ (U, W)O_{3-x}$
$UO_2 : WO_3 = 1 : 1;\ 1 : 10$	Calcination, 900°	$(U, W)O_{2+y},\ (U, W)O_{3-x}$
$UO_2 : WO_3 = 1 : 25;\ 1 : 50$	Calcination, 900°	$(U, W)O_{3-x}$
UO_2WO_4	Decomposition in vacuum, 800°	$UWO_{5.5}$
UO_2WO_4	Decomposition in vacuum, 900°	$UWO_{5.01}$
$U_3O_8 + UO_2 + 2WO_2 + 2WO_3$	Calcination, 900°	$(U, W)O_{3-x},\ (U, W)O_{2+y}$
$UWO_{5.01}$	Calcination, 1250°	$(U, W)O_{5+x},\ UO_2,\ (U, W)O_{3-x}$

phase analysis of the samples obtained showed that in the system UO_3—WO_3 only one compound is formed–UO_2WO_4 (see Table 1). For comparison, uranium chromate and molybdate were synthesized. Uranium chromate was obtained by dehydration of $UO_2CrO_4 \cdot 5.5H_2O$ at 400°, and the molybdate by sintering U_3O_8 in air with an excess of MoO_3 at 750°.

The X-ray patterns of all three substances are very close to one another (Fig. 1), which indicates their isostructural character.

Oxides of uranium and tungsten of lower valence were obtained by thermal decomposition of UO_2WO_4 in vacuum at 600—900°, reduction of uranium tungstate with hydrogen at temperatures of 300—800°, and sintering of various oxides of uranium and tungsten in evacuated ampoules at 1250° and 900°. The results of phase analysis of the reaction products are given in Table 1, from which it is evident that in the case of uranium and tungsten oxides of lower valences, two new phases appear. One of these phases is structurally close to U_3O_8 (Fig. 2). The composition of the phase structurally close to U_3O_8 corresponds to the formula UWO_{5+x}. An analogous phase is formed upon decomposition of UO_2MoO_4. The X-ray pattern of this phase proved to be identical with the X-ray pattern of the UWO_{5+x} phase. In the purest form, the UWO_{5+x} phase was obtained by thermal decomposition of UO_2WO_4 in vacuum at temperatures of 800 and 900°. The gross composition of this phase corresponds to the formula $UWO_{5.5}$ for the sample obtained at 800°, and to the formula $UWO_{5.01}$ for the sample obtained at 900°. The Debye pattern of the other phase is indexed in cubic symmetry with the parameter of the primitive unit cell

$$a = 3.805 \pm 0.001 \text{ kX}.$$

Fig. 1. Schemes of Debye patterns of UO_2WC_4 (1), UO_2MoO_4 (2) and UO_2CrO_4 (3)

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Fig. 2. Schemes of Debye patterns of U_3O_8 (3), phases UWO_{5+x} (1), $UMoO_{5+x}$ (2)

Figure 2: Fig. 2. Schemes of Debye patterns of U_3O_8 (3), phases UWO_{5+x} (1), $UMoO_{5+x}$ (2)

Fig. 2. Schemes of Debye patterns of U_3O_8 (3), phases UWO_{5+x} (1), $UMoO_{5+x}$ (2)

The compound with the cubic unit cell was synthesized by sintering UO_2 and WO_3 in ratios of $1 : 1$ and $1 : 10$. At compositions $UO_2 : WO_3 = 1 : 25$ and $1 : 50$, a tetragonal distortion of the cubic primitive cell was observed. At the same time, when WO_3 and WO_2 were sintered in ratios of $15 : 1$, $25 : 1$, and $50 : 1$, and also WO_3 and ThO_2 in a ratio of $10 : 1$, the cubic phase is not formed, and a rhombic distortion of the elementary cubic cell occurs, as in the case of WO_3. Thus, the cubic phase is formed only in the presence of uranium; structurally it is close to WO_3 and, apparently, contains a smaller amount of oxygen, i.e., its composition is expressed by the formula $(W, U)O_{3-x}$. In the sample $UO_2 + 10WO_3$, a phase of the UO_2 type is present, probably containing some amount of tungsten, since the lattice parameter of this phase ($a = 5.461 \pm 0.001$ kX) differs from the periods of the lattices of the UO_{2+x} phases, although only slightly. In the sample $UO_2 + 25WO_3$, the cubic phase is not yet formed. From this it may be concluded that the ratio between U and W in the cubic phase is close to $1 : 15$—20, and x is about $1/15$—$1/20$.

Thus, the UWO_5 samples have different phase compositions depending on the method of preparation: in the products of reduction and thermal decomposition of uranium tungstate, the UWO_{5+x} phase was detected, whereas upon sintering the oxides a mixture of the phases $(U, W)O_{3-x}$ and UO_2 or $(U, W)O_{2+y}$ is formed. After annealing UWO_{5+x} at 1250°, 3 phases were found in the sample: the initial oxide UWO_{5+x}, UO_{2+x} or $(U, W)O_{2+y}$, and $(U, W)O_{3-x}$, i.e., at a higher temperature the UWO_{5+x} phase disproportionates.

No interaction between UO_2 and WO_2 was detected up to 1250°. The lattice parameters of the initial phases do not change upon sintering; i.e., solid solutions apparently are not formed.

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Note: Figure translations are in progress. See original paper for figures.

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