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Yttrium–Tungsten Oxides[1]

BY HANS J. BORCHARDT

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WO_3 and Y_2O_3 react to form five compounds whose stoichiometry can be represented by the formula $WO_3 \cdot x(YO_{1.5})$, where x has the values 2/3, 2, 15/4, 9/2, and 6. The pseudo-binary phase diagram of the system WO_3–Y_2O_3 has been determined in part. The system Y_2O_3–WO_2 has been investigated as well as the reactions of the several new phases with yttrium metal. This information, together with that resulting from studies of oxygen content, is used to arrive at the ternary composition diagram of the system W–Y–O. Some properties of the new phases are described.

In 1888 Duboin[2] reported the existence of yttrium tungstate, $Y_2O_3 \cdot 3WO_3$. No further work has been done with the system Y_2O_3–WO_3 since that time.

The present study was undertaken to contribute to the meager knowledge of the mixed oxide chemistry of rare earth type elements.

The System Y_2O_3–WO_3

Experimental

Y_2O_3 was obtained from Lindsay Chemical Division as 99.9% pure material. Analysis by emission spectrography revealed approximately 0.02% aluminum and trace quantities of Fe and Si.

Fisher "purified" WO_3 was utilized. It was found to contain Si, Fe, and Ba in the 100–500 p.p.m. range. Average particle sizes of Y_2O_3 and WO_3 were 2 and 8 μ, respectively, as determined on a Fisher sub-sieve sizer. Y_2O_3 and WO_3 were mixed on a Crescent "wig-l-bug," pressed into 0.5-in. diameter pellets with a paraffin binder, and fired in air in platinum lined boats. Samples containing less than 40 mole % $YO_{1.5}$ were heated 4 hr. at 1000° and those containing more than 40 mole % $YO_{1.5}$, 4 hr. at 1400°. X-Ray powder diffraction patterns of the products were obtained using CuKα radiation and a Ni filter.

Results and Discussion

Characterization.—X-Ray powder diffraction patterns of the products could be correlated by the assignment of phases shown in Table I. Phases I through V have the stoichiometric formulas $Y_2O_3 \cdot 3WO_3$, $Y_2O_3 \cdot WO_3$, $15Y_2O_3 \cdot 8WO_3$, $9Y_2O_3 \cdot 4WO_3$, and $3Y_2O_3 \cdot WO_3$. With the exception of $3Y_2O_3 \cdot WO_3$, the structures are not known. $3Y_2O_3 \cdot WO_3$ appears to be isostructural with $3Y_2O_3 \cdot UO_{2.9}$[3] as well as with Pr_7O_{12} and Tb_7O_{12}.[4] The structure of Tb_7O_{12}, a slight rhombohedral distortion of a fluorite type cell, is discussed in detail by Baenziger and co-workers.[5] Powder diffraction data on the several phases are given in Table II.

Low Temperature Behavior.—Phase I has been formed at temperatures as low as 750° by the methods described. No evidence was found for the formation of phase II below 1000° nor for the formation of phases III, IV, and V below 1100° when the corresponding oxide mixtures were heated for 1 week. At temperatures between 750 and 1000°, Y_2O_3-rich compositions react to form a sixth phase which has the approximate composition $3Y_2O_3 \cdot 2WO_3$. This phase persists indefinitely at temperatures below 1000°. It disappears on heating at 1100°. It does not reappear when any of the higher temperature phases are annealed at 1000°. This evidence, together with the fact that it has resisted efforts to form it free of any other phases, indicates that it is a metastable phase.

High Temperature Behavior.—$Y_2O_3 \cdot 3WO_3$ melts congruently at 1495°. It forms a eutectic with WO_3 at a composition of approximately 30 mole % $YO_{1.5}$ and a temperature of 1155°. $Y_2O_3 \cdot WO_3$ melts incongruently at 1700°. $Y_2O_3 \cdot 3WO_3$ and $Y_2O_3 \cdot WO_3$ form a eutectic at approximately 47 mole % $YO_{1.5}$ which melts at 1455°. $15Y_2O_3 \cdot 8WO_3$, $9Y_2O_3 \cdot 4WO_3$, and $3Y_2O_3 \cdot WO_3$ all melt above 2200°. X-Ray diffraction

TABLE I

COMPOSITION–PHASE DATA FOR THE SYSTEM WO_3–Y_2O_3

Mole % $YO_{1.5}$	Phases obsd.	Mole % $YO_{1.5}$	Phases obsd.
0	WO_3	78.3	II + III
0.1	WO_3	78.7	III
0.2	WO_3	78.9	III
1.0	WO_3	79.2	III + IV
2.2	WO_3	80.0	III + IV
3.2	WO_3	80.8	III + IV
4.8	WO_3 + I	81.5	III + IV
6.3	WO_3 + I	81.8	IV
7.7	WO_3 + I	82.1	IV
16.7	WO_3 + I	82.5	IV + V
20.0	WO_3 + I	82.8	IV + V
25.0	WO_3 + I	83.3	IV + V
33.3	WO_3 + I	83.6	IV + V
38.5	WO_3 + I	83.9	IV + V
40.0	I	84.4	IV + V
41.7	I + II	84.9	IV + V
50.0	I + II	85.3	IV + V
60.0	I + II	85.7	V
61.5	I + II	86.2	V
63.0	I + II	86.5	V + Y_2O_3
64.3	I + II	86.7	V + Y_2O_3
65.5	II + trace I	87.2	V + Y_2O_3
66.7	II	87.5	V + Y_2O_3
67.7	II + III	88.9	V + Y_2O_3
68.8	II + III	90.9	V + Y_2O_3
71.4	II + III	95.2	V + Y_2O_3
75.0	II + III	98.0	V + Y_2O_3
77.8	II + III	99.0	V + Y_2O_3

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[1] Presented in part at the XVIII International Congress of Pure and Applied Chemistry, Montreal, Canada, August, 1961.

[2] A. Duboin, *Ann. Ec. norm.*, (3) **5**, 436 (1888).

[3] E. J. Felten and S. F. Bartram, private communication.

[4] L. Eyring, private communication.

[5] N. C. Baenziger, H. A. Eick, H. S. Schuldt, and L. Eyring, *J. Am. Chem. Soc.*, **83**, 2219 (1961).

TABLE II

X-RAY DIFFRACTION DATA[a]

Line no.	I $Y_2O_3{\cdot}3WO_3$[b]		II $Y_2O_3{\cdot}WO_3$[c]		III $15Y_2O_3{\cdot}8WO_3$		IV $9Y_2O_3{\cdot}4WO_3$		V $3Y_2O_3{\cdot}WO_3$		X phase	
	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0
1	6.75	60	5.05	20	6.46	4	6.80	4	6.41	2	4.46	50
2	6.23	30	4.78	20	5.24	5	6.51	2	6.28	10	4.33	10
3	4.74	30	4.31	2	3.76	10	5.30	5	4.07	20	4.22	25
4	4.62	5	4.23	10	3.42	5	3.70	2	3.85	15	3.72	50
5	4.37	60	3.95	15	3.12	40	3.63	4	3.78	2	3.40	60
6	4.25	30	3.83	15	3.01	100	3.52	2	3.11	45	3.06	90
7	4.19	40	3.66	20	2.80	4	3.45	2	3.03	100	2.79	100
8	4.11	100	3.17	2	2.63	50	3.26	2	2.82	10	2.65	30
9	4.06	80	3.08	90	2.065	2	3.13	25	2.63	50	2.63	50
10	3.81	30	3.02	100	1.979	2	3.06	100	2.274	5	2.50	10
11	3.75	55	2.77	10	1.932	2	3.04	100	2.247	2	2.479	20
12	3.72	55	2.75	25	1.905	5	2.65	60	2.088	15	2.263	20
13	3.50	70	2.66	25	1.890	35	1.894	20	2.039	10	2.236	10
14	3.37	70	2.61	10	1.843	35	1.868	35	1.916	2	2.079	10
15	3.16	50	2.52	20	1.799	2	1.847	20	1.890	15	1.916	35
16	3.12	50	2.48	2	1.617	10	1.617	5	1.883	35	1.873	40
17	2.89	40	2.36	5	1.589	30	1.591	35	1.875	30	1.861	30
18	2.82	40	2.179	2	1.574	15	1.576	10	1.843	40	1.833	5
19	2.41	20	2.151	10	1.511	10	1.527	5	1.840	35	1.802	15
20	2.056	20	2.130	10			1.513	5	1.819	5	1.720	5
21	2.021	20	2.085	2			1.321	5	1.789	10	1.662	5
22			2.054	2					1.651	5	1.643	5
23			2.032	5					1.617	5	1.625	5
24			1.994	5					1.609	15	1.599	25
25			1.977	5					1.606	10	1.548	25
26			1.914	20					1.586	30		
27			1.888	15					1.581	20		
28			1.852	5					1.574	20		
29			1.833	40					1.571	15		
30			1.816	2								
31			1.779	10								
32			1.752	2								
33			1.734	10								
34			1.692	5								
35			1.682	5								

[a] CuKα radiation, Ni filter. [b] All lines weak and broad. [c] Lines 16–35 are doublets.

patterns of the quenched melts of $15Y_2O_3{\cdot}8WO_3$ and $9Y_2O_3{\cdot}4WO_3$ are the same as before melting. This indicates that they melt congruently. The X-ray pattern of $3Y_2O_3{\cdot}WO_3$ quenched from the melt has considerably fewer lines than phase V. These can be indexed on the basis of a face-centered cubic unit cell with a lattice parameter of 5.276 Å.

Since phase V has been prepared at temperatures as high as 1700°, a phase transformation must occur between 1700° and the melting point. It is likely that this phase transformation corresponds to the randomization of the oxygen vacancies in the fluorite type structure proposed by Baenziger, *et al.*[5]

The above results are summarized in part in Fig. 1 in the form of a pseudo-binary phase diagram of the system Y_2O_3–WO_3.

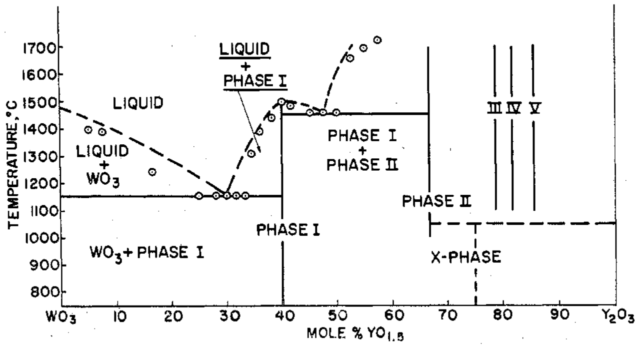

Fig. 1.—Pseudo-binary phase diagram of the system Y_2O_3–WO_3.

The System W–Y–O

Experimental

Reactions of Y_2O_3 with WO_2.—To prepare WO_2, WO_3 and elemental tungsten were heated in the appropriate ratio at 900° for 4 hr. in a sealed bomb. The product is a purple powder which was found to be a mixture by X-ray analysis. This product was heated for an additional 16 hr. at 1400° in argon, whereupon the typical brown color of WO_2 appeared. X-Ray diffraction identified this material as WO_2.

Y_2O_3–WO_2 mixtures were prepared as before except that no binder was utilized. They were heated in argon from room temperature to 1400°, held there for 4 hr., and cooled to room temperature before exposure to air.

Reactions of Y^0 with Yttrium–Tungsten Oxides and W^0.—Powdered yttrium metal was prepared by filing an yttrium metal ingot obtained from the Lindsay Chemical Division. The filings were mixed with each of the five phases, pressed into pellets, and heated at 1400° for 4 hr. in an argon atmosphere. Tungsten metal foil was used as container material.[6]

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(6) Yttrium metal was found to react with platinum to form compositions which melt below 1400°.

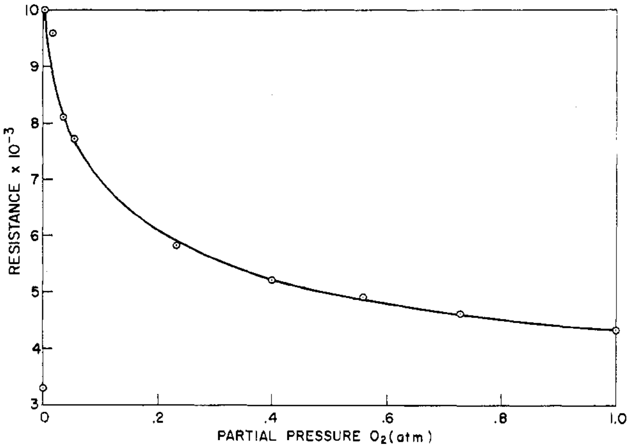

Fig. 2.—Resistivity of phase II at 1000° as a function of oxygen pressure.

Several attempts were made to alloy tungsten and yttrium without success. These include heating the metal powder mixtures just below and above the melting point of yttrium as well as arc melting tungsten onto a yttrium ingot. In the latter case, most of the yttrium was lost by vaporization, but that which remained was in the form of the free element. These results are consistent with the report by McGurty and Simmons[7] that tungsten is one of the best available container materials for molten yttrium.

Results and Discussion

X-Ray analysis of the products obtained by reaction of WO_2 with Y_2O_3 revealed that the same five phases which form in the system Y_2O_3–WO_3 form here also and that elemental tungsten was a product in each case (Table III). The stoichiometry of the reactions is equivalent to the disproportionation of WO_2 to yield WO_3 and W^0, the WO_3 reacting with Y_2O_3 in the same manner as before. A typical example is

$$9WO_2 + 2Y_2O_3 \rightarrow 2(Y_2O_3 \cdot 3WO_3) + 3W^0$$

The products obtained by reaction of Y^0 with the several new phases in each case were Y_2O_3, elemental tungsten, and yttrium, yttrium having been present in excess.

Oxygen Content of New Phases.—Preliminary measurements indicated that there were major deviations from stoichiometry with respect to oxygen in the several new yttrium tungsten oxides. Assuming yttrium to be entirely trivalent, average tungsten valences of +5.0 to +5.5 were found. Since the new compounds are white and since all known mixed valence oxides are deeply colored, a thorough study was made to clear up this anomaly. Methods utilized to determine oxygen content include: (1) total oxygen by the BrF_3 method, (2) reduction of ferric ion and back titration, (3) reduction with yttrium metal, (4) weight gain after decomposition (in nitric acid) and separation to Y_2O_3 and WO_3, and (5) weight loss during reaction on a thermobalance, as well as e.p.r. and magnetic susceptibility measurements. These experiments will not be discussed in detail. The final conclusion is that the preliminary measurements were in error and that, in fact, there are no *major* deviations from stoichiometry.

TABLE III

COMPOSITION–PHASE DATA FOR THE SYSTEM WO_2–Y_2O_3

Mole % $YO_{1.5}$	Phases present
10	Phase I + W^0 + WO_2
20	Phase I + W^0 + WO_2
30	Phase I + W^0 + trace WO_2
40	Phase I + phase II + W^0
50	Phase I + phase II + W^0
60	Phase II + W^0
70	Phase III + W^0
73.2	Phase III + phase IV + W^0
78.3	Phase IV + phase V + W^0
80	Phase V + W^0 + trace Y_2O_3
90	Phase V + W^0 + Y_2O_3

In view of the experimental error associated with the several measurements, it can only be said with certainty that any deviation must be less than that represented by the formula $WO_{2.95}$.

Evidence was obtained, however, for a *minor* variability in the oxygen content of $Y_2O_3 \cdot WO_3$ by measuring the electrical resistivity in various partial pressures of oxygen at 1000°. A pellet 1.266 cm. in diameter, 0.237 cm. thick, and weighing 1.280 g. was prepared by sintering at 1400°. The faces were coated with platinum paste (Hanovia No. 012). While the paste was still wet, platinum foil contacts were attached. Heating to1400° caused the contacts to adhere tightly to the pellet, presumably because of sintering of the fine platinum particles. Platinum lead wires were attached to the contacts and the pellet was inserted into a quartz tube in a tube furnace. Atmospheres were controlled by flowing argon–oxygen mixtures through the tube. Total pressure was nominally 1 atmosphere.

As seen in Fig. 2, resistance increases as the partial pressure of oxygen is lowered. In pure argon the resistance has again a low value (3.3 ohms). Thus, the resistance goes through a maximum at some very low partial pressure of oxygen.

This effect is fully reversible. Time for equilibration is considerably longer when going from oxygen to argon than *vice versa*, however. This is not unreasonable when considering the very low partial pressure of oxygen necessary to observe the reversal in resistance and the relatively slow rates of desorption of oxygen.

The above results can be interpreted to mean that the system is completely stoichiometric only at the very low oxygen partial pressure where the resistance is a maximum. Samples prepared in air would contain an oxygen excess, and those in argon, an oxygen deficiency. The donor and acceptor levels thus introduced result in lower resistivities. If this postulate is correct, the sign of the Seebeck coefficient should change as the resistivity passes through its maximum. By placing the sample in a temperature gradient and measuring the potential across the pellet while varying

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(7) J. A. McGurty and C. R. Simmons, "The Metal Yttrium," presented at the National Western Mining and Energy Conference, Denver, Colorado, April 23, 1960.

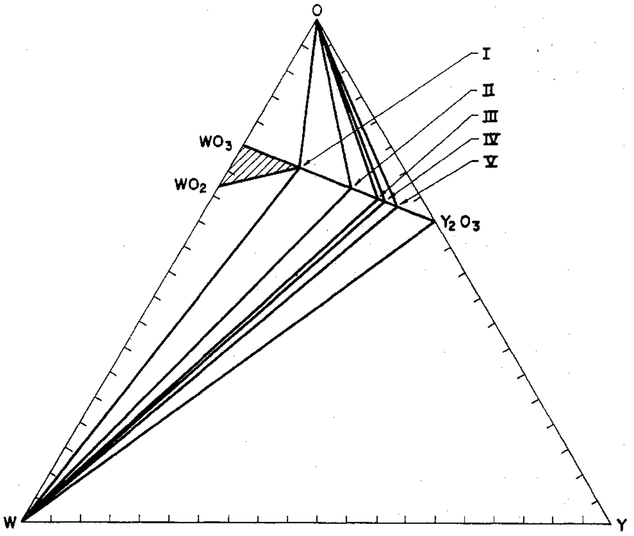

Fig. 3.—Ternary composition diagram of the system Y–W–O.

the atmosphere, it was observed that this, in fact, occurs.

It is concluded that in $Y_2O_3 \cdot WO_3$, the oxygen content is variable. The magnitude of this variation is too small to have any significance with respect to the phase diagram.

The Ternary Composition Diagram W–Y–O.—The data given above allow one to construct the ternary composition diagram of the system W–Y–O, Fig. 3. From this it is evident that no phases, other than the five reported, form from the elements tungsten, yttrium, and oxygen in the temperature range 1100–1400° at 1 atmosphere total pressure. Excluded from this conclusion are compositions in the range WO_3–WO_2–phase I, which were not investigated.

Properties of Tungsten–Yttrium Oxides.—Properties of the several tungsten–yttrium oxides are summarized in Table IV. It is interesting to note that whereas the normal tungstate ($Y_2O_3 \cdot 3WO_3$) has a much lower density than the weighted mean density of the constituent oxides, all the new phases have higher densities. $Y_2O_3 \cdot WO_3$ is a new photoluminescent material. It emits a bright blue-white light when excited with 2540 Å. ultraviolet light. Its emission spectrum is quite similar to that of the well known phosphor, $CaWO_4$, Fig. 4. More details on the luminescent properties of $Y_2O_3 \cdot WO_3$ will be published at a later date.

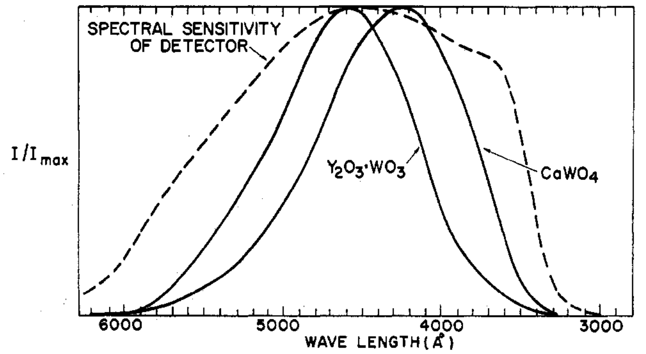

Fig. 4.—Spectral energy emission characteristics of $Y_2O_3 \cdot WO_3$ and $CaWO_4$. Mode of excitation: 2537 Å. ultraviolet light from a filtered low pressure Hg discharge. Detector: DuMont 6292 photomultiplier tube.

TABLE IV

SOME PROPERTIES OF NEW PHASES

Phase	Melting point	Color	Density, g./cc.	Weighted mean density of WO_3–Y_2O_3
I	1495 ± 5°, congruent	White	4.85	6.64
II	1700 ± 20°, incongruent	White	6.63	6.11
III	>2200°, congruent	White	6.08	5.78
IV	>2200°, congruent	White	5.95	5.70
V	>2200°, congruent, undergoes phase change	White	6.00	5.57

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The Preparation of Difluoroamino Sulfur Pentafluoride

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Difluoroamino sulfur pentafluoride (SF_5NF_2) has been synthesized by the ultraviolet irradiation of N_2F_4 and sulfur tetrafluoride or sulfur chloride pentafluoride, or by the thermal reaction of N_2F_4 with elemental sulfur. Similarly, trifluoromethyl difluoroamino sulfur tetrafluoride ($CF_3SF_4NF_2$) has been prepared by ultraviolet irradiation of N_2F_4 and trifluoromethyl sulfur trifluoride.

In contrast to the many compounds containing sulfur, fluorine, and nitrogen, *i.e.*, $S_4N_4F_4$, SN_2F_2, $F_3S{\equiv}N$, and $N{\equiv}S{-}F$, reported by Glemser and co-workers,[1–5] where the fluorine is exclusively bonded to the sulfur, there are no examples of compounds in the literature where sulfur is bonded directly to an NF_2 group. Roberts[6] recently has suggested $SF_5NF{-}CF_3$ as the probable structure for the product of the fluorination of methyl thiocyanate with elemental fluorine, although

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(1) O. Glemser, H. Schröder, and H. Haereler, *Z. anorg. allgem. Chem.*, **279**, 28 (1955).

(2) H. Schröder and O. Glemser, *ibid.*, **298**, 78 (1959).

(3) O. Glemser and H. Schröder, *ibid.*, **284**, 97 (1956).

(4) O. Glemser and H. Haereler, *ibid.*, **287**, 54 (1956).

(5) H. Rickert and O. Glemser, *Angew. Chem.*, **72**, 585 (1960).

(6) H. L. Roberts, *Quart. Rev.* (London), **15**, 55 (1961).