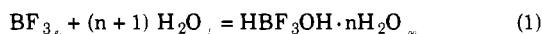


DISCUSSION

The heat of solution of boron trifluoride in water observed in this work is slightly lower than that obtained by Hammerl (1) and Laubengayer and Finlay (3). Their results adjusted to 25° C. are -25.7 and -25.1 kcal. mole⁻¹, respectively.

Wamser (6) and Ryss and his coworkers (4) have studied the hydrolysis equilibria of BF₃ solutions. Wamser reports the initial rapid reaction of BF₃ with water to be:



with further hydrolysis being much slower. Ryss and Elkenbard (4) have measured the heat of solution of KBF₃OH in water and aqueous NaOH. From these data, the heat of formation of BF₃OH⁻_(aq) has been derived as -363.1 kcal. mole⁻¹.

Assuming the solution reaction under the conditions of our study to be represented by Reaction 1, the heat of formation of BF₃OH⁻_(aq) may be derived as -363.1 kcal. mole⁻¹, using -270.1 kcal. mole⁻¹ for the heat of formation of BF₃ (7). The exact agreement with Ryss is undoubtedly fortuitous.

Our solution data in dilute HF indicate that, at low HF/BF₃ ratios (0.3-0.6), the heat of solution is unaffected by the presence of HF and the predominant species may still be assumed to be BF₃OH⁻.

Wamser (5) has shown that higher HF/BF₃ ratios (>3) drive the equilibrium toward formation of BF₄⁻ as the major species. We have measured a single heat of solution at an HF/BF₃ ratio of approximately 3. The observed heat of solution of -27.0 kcal. mole is in the direction one would expect, since the heat of formation of BF₄⁻_(aq) of -373.7, derived from the data of Ryss (4), gives a calculated heat for the reaction:



of -27.9 kcal. mole⁻¹.

The use of Equation 1 to represent the solution reaction in water is an oversimplification, since all of the possible acid species are present to some extent. This does not prevent, however, the discussion of the heat effects on solution as though they were produced only by the predominant species, HBF₃OH. Wamser (6) presents a more detailed hydrolysis scheme, but it is apparent from the results of the heat of solution measurements that the over-all heat balance of the complex equilibria is such that the measured heat is not significantly affected by minor changes in concentration of the various species.

ACKNOWLEDGMENT

We wish to thank W.E. Hazen for assistance in performing the analyses.

LITERATURE CITED

- (1) Hammerl, H., *Compt. rend.* **90**, 312 (1880).
- (2) Hubbard, W.N., Katz, C., Waddington, G., *J. Phys. Chem.* **58**, 142 (1954).
- (3) Laubengayer, A.W., Finlay, G.R., *J. Am. Chem. Soc.* **65**, 884 (1943).
- (4) Ryss, I.G., Slutskaya, M., *Compt. rend. acad. sci. URSS* **52**, 417 (1946). Ryss, I.G., Slutskaya, M., *Doklady Akad. Nauk SSSR* **57**, 689 (1947). Ryss, I.G., Elkenbard, A.G., *Ibid.* **91**, 865 (1953). Ryss, I.G., Slutskaya, M., Palevskaya, S.D., *Zhur. Fiz. Khim.* **22**, 1322 (1948).
- (5) Wamser, C.A., *J. Am. Chem. Soc.* **70**, 2109 (1948).
- (6) *Ibid.* **73**, 409 (1951).
- (7) Wise, S.S., Margrave, J.L., Feder, H.M., Hubbard, W.N., *J. Phys. Chem.* **65**, 2157 (1961).

RECEIVED for review November 7, 1963. Accepted March 12, 1964. This work was supported by the Air Force Office of Scientific Research under Contract AF-49(638)-1052.

Equilibrium Diagram of the System Nb₂O₅-WO₃

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An equilibrium diagram of the Nb₂O₅-WO₃ system has been presented. The existence of two new compounds, Nb₂O₅-WO₃ and Nb₂O₅·3WO₃, has been postulated. The work of Kovba and Trunov on Nb₂O₅·3WO₃ (a, b = 12.190A, c = 3.934A.) has been verified. Experimental procedures included room temperature x-ray diffraction of previously annealed samples, high temperature x-ray diffraction, and differential thermal analysis. Some work was also done on the low temperature transformation of WO₃ and WO₃-Nb₂O₅ compounds.

AS PART of a project concerning the oxides of the refractory metals, the phase equilibrium of the system Nb₂O₅-WO₃ was investigated. The one published report on this system was done by Goldschmidt (1). His results indicated that WO₃ was soluble in Nb₂O₅ to the extent of 60 mole % WO₃. He also postulated the existence of a compound existing at the 25% Nb₂O₅-75% WO₃ composition.

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EXPERIMENTAL

Sample Preparation. The oxide samples used in this investigation were prepared from materials obtained from A.D. Mackay and Co., Inc. The purities were 99.9+% for the Nb₂O₅ and 99.99% for the WO₃. Impurities detected spectroscopically in these materials were Si, Mg, Co, Zr, and Ni for Nb₂O₅ and Si, Al, and Mg for WO₃. Before mixing, the powders were pre-fired in air for 24 hours at 800° C. During this treatment and all subsequent annealing treatments, the samples were enclosed in platinum crucibles

to minimize contamination from Al₂O₃ and SiO₂ present in the furnace atmosphere.

Binary oxide samples were prepared by thoroughly mixing proper amounts of the pure oxides in a commercial vibrator, and pressing them in the form of round briquettes 3/4 inch in diameter, and three grams in weight.

Annealing. Isothermal annealing of the pressed samples was carried out in air for periods ranging from two to 45 days. The furnaces used for this purpose were wound with either Kanthal "A-1" or Pt-10% Rh wire on alumina cores. Temperatures were controlled to within ±5° of the temperature listed. To minimize WO₃ loss due to vaporization especially at the higher temperatures and also to minimize contamination, the samples were wrapped in Pt foil. After annealing for the prescribed time, the samples were quenched by removing them from the furnace while at temperature. Analyses of the samples after firing indicated that contaminants were just detectable by spectral analyses. Chemical analyses indicated a maximum deviation of 1 per cent from the nominal composition in most cases.

X-Ray Diffraction Measurements. To determine the phase distributions after annealing, a diffraction pattern of each fired sample was measured in a G.E. X-RD5 unit equipped with a spectrometer, a proportional counter, a copper anode, stabilized power source, and associated electronic circuitry. Film techniques were used in instances where it was necessary to detect very weak reflections.

High and Low Temperature Diffraction Measurements. A Norelco high-temperature diffractometer attachment using a Pt-40% Rh heating filament as the sample holder was used to determine the at-temperature phase distributions for the WO₃ rich samples. Samples for these high temperature diffraction studies were prepared from the same samples used for the room temperature measurements. In order to obtain even temperature distribution over the bulk of the samples very thin sections cut from repressed powders of the previously fired briquettes were used. Temperature was measured by a Pt-Pt/10% Rh thermocouple welded to the bottom of the heating filament and also with an optical pyrometer.

A low temperature attachment in which the heating element was replaced by a copper block was also used. This copper block was cooled by nitrogen gas which was first cooled by flowing through a Dewar flask containing a dry ice-acetone bath and then through a second Dewar flask containing liquid nitrogen. The desired temperature was maintained by controlling the flow rate of the nitrogen so that the temperature could be held to within ±5° quite easily.

D.T.A. A vertical furnace similar in construction to the one of Holtzberg and Reisman (3) was used for making differential thermal analysis determinations. Pt-Pt/10% Rh thermocouples were used for the differential and temperature measuring thermocouples. Al₂O₃ was used as the reference material. The sample and the Al₂O₃ were contained in platinum crucibles.

RESULTS AND DISCUSSION

Nb₂O₅ was found to undergo an irreversible transformation to the monoclinic form after a firing at or above 1100° C. as was first reported by Holtzberg and his co-workers (4). The WO₃ showed phase changes from monoclinic to orthorhombic at 300° C. and from orthorhombic to tetragonal at approximately 740° C. as reported by Perri, banks, and Post (7). The 300° C. transition was observed in the high-temperature x-ray measurements and the 740° transition by both high temperature x-ray and D.T.A. measurements.

The results of the diffraction and D.T.A. measurements were used to prepare a proposed diagram of the Nb₂O₅-WO₃ system (Figure 1). The liquidus region was postulated on the basis of being the most reasonable with the data available. Detailed results for each composition and firing temperature are listed in Table I. A discussion of the results and the significant features of the diagram follow.

Nb₂O₅ss: Note that Nb₂O₅ exhibits solid solubility for WO₃ to about 33% WO₃ content throughout the temperature range investigated whereas WO₃ exhibits very little, if any, solubility for Nb₂O₅. This is in contrast to Gold-

Table I. Heat Treatment Data for the Nb₂O₅-WO₃ System

T (° C.) Mole % Nb ₂ O ₅	N = α-Nb ₂ O ₅ ss W = WO ₃ ss		γ = Nb ₂ O ₅ ± 3WO ₃ δ = Nb ₂ O ₅ · WO ₃ ξ = 3Nb ₂ O ₅ · 2WO ₃			
	1200	1100	1000	900	800	700
100	α-Nb ₂ O ₅	α-Nb ₂ O ₅	α-Nb ₂ O ₅	α-Nb ₂ O ₅	α-Nb ₂ O ₅	α-Nb ₂ O ₅
95	N	N	N	N	N	N
95	N	N	N	N	N	N
85	N	N	N	N	N	N
80	N	N	N	N	N	N
75	N	N	N	N	N	N
70	N	N	N	N	N	N
65	N + ξ	N + δ	N + δ	N + δ	N + δ	N + δ
60	N + ξ	N + δ	N + δ	N + δ	N + δ	N + δ
55	ξ + γ	N + δ	N + δ	N + δ	N + δ	N + δ
50	ξ + γ	δ + γ	δ + γ	δ + γ	δ + γ	δ + γ
45	ξ + γ	δ + γ	δ + γ	δ + γ	δ + γ	δ + γ
40	ξ + γ	δ + γ	δ + γ	δ + γ	δ + γ	δ + γ
35	ξ + γ	δ + γ	δ + γ	δ + γ	δ + γ	δ + γ
30	ξ + γ	δ + γ	δ + γ	δ + γ	δ + γ	δ + γ
27	γ	γ	γ	γ	γ	γ
25	γ	γ	γ	γ	γ	γ
24	γ	γ	γ	γ	γ	γ
20	γ + α-W	γ + α-W	γ + α-W	γ + α-W	γ + α-W	γ + α-W
15	γ + α-W	γ + α-W	γ + α-W	γ + α-W	γ + α-W	γ + α-W
10	γ + α-W	γ + α-W	γ + α-W	γ + α-W	γ + α-W	γ + α-W
5	γ + α-W	γ + α-W	γ + α-W	γ + α-W	γ + α-W	γ + α-W
2	γ + α-W	γ + α-W	γ + α-W	γ + α-W	γ + α-W	γ + α-W
0	α-W	α-WO ₃	α-WO ₃	α-WO ₃	α-WO ₃	α-WO ₃

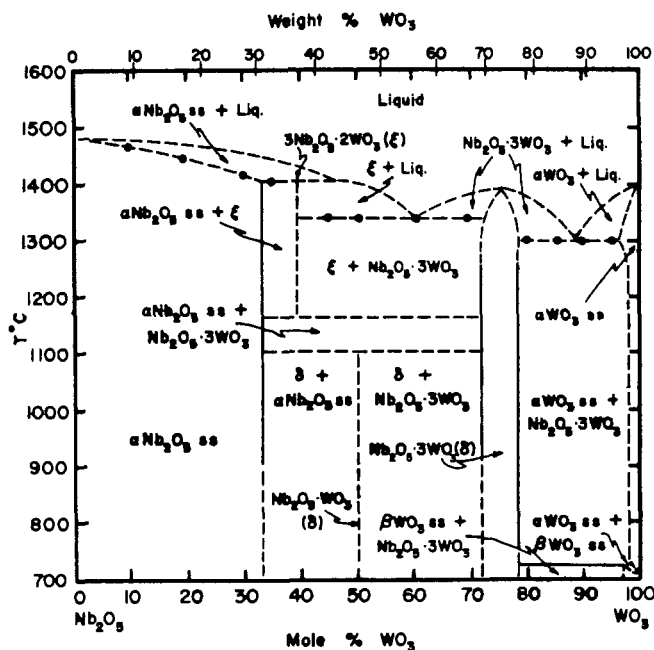


Figure 1. Equilibrium diagram of the Nb_2O_5 - WO_3 system

Schmidt's report of solid solubility of WO_3 in Nb_2O_5 to about 60% WO_3 content.

$\text{Nb}_2\text{O}_5 \cdot 3\text{WO}_3$ Compound. At the 25% Nb_2O_5 -75% WO_3 composition a pattern attributed to a new compound $\text{Nb}_2\text{O}_5 \cdot 3\text{WO}_3$ (the γ compound) was determined. The existence of this compound was first postulated by Goldschmidt (1) and later verified by Kovba and Trunov (5). These latter workers gave its unit cell as tetragonal with lattice constants $a = 12.190$ A. and $c = 3.934$ A. The x-ray results obtained for this compound in our laboratory agree with those reported by Kovba and Trunov. Investigation of solid solubility shows both Nb_2O_5 and WO_3 to be soluble in this compound to a very limited extent as indicated in the diagram.

1100° Isotherm and Below. To approximately 33 mole % WO_3 , α - Nb_2O_5 exhibits solid solubility for WO_3 . Beyond this composition extra peaks appear in the diffraction pattern which are tentatively attributed to a new phase designated in the diagram as δ . The extra lines are indicated in the d -spacing listing for the 60% Nb_2O_5 -40% WO_3 composition in Table II. These are present along with the Nb_2O_5 ss pattern up to approximately 50% WO_3 . Beyond this, in the region extending up to 75% WO_3 γ peaks appear along with the δ peaks. The phase is thus postulated to exist at 50% WO_3 (a 1:1 composition). In the patterns of samples from 35% WO_3 to 50% WO_3 it was noted that the intensities of these extra lines increased up to 50% WO_3 composition. As WO_3 content increased above 50%, the γ pattern appeared and the intensity of the pattern of the δ phase gradually decreased.

Samples fired at 1000° C. and 900° C. showed similar patterns and similar variations with composition as the 1200° C. samples. Samples fired at 600°, 700°, and 800° were found not to have reached equilibrium even after 30 days at the respective temperatures. Thus the low temperature limit to which the extra peaks persist could not be determined. In order to accelerate transformations, some samples were fired at 1200° C. for two days and then fired at these lower temperatures for one more day but the pattern observed at 1200° C. was retained in all cases. Clearly, the transformations at the low temperatures are very sluggish.

Two possibilities exist as to the structure of the δ -phase. Either it is a superstructure of Nb_2O_5 i.e., a highly ordered form of the Nb_2O_5 structure, or it corresponds to a new

compound with a distinct structure and a likely composition of $\text{Nb}_2\text{O}_5 \cdot \text{WO}_3$. The latter possibility appears more likely and has been adopted in drawing the proposed equilibrium diagram. However, a detailed comparison of the merits of these possibilities must be deferred until a crystallographic study of the δ -phase has been performed.

1200° C. Isotherm. The samples fired at this temperature indicated α - Nb_2O_5 ss up to approximately 33% WO_3 . Beyond this composition a new set of peaks, different from those observed between 900° and 1100° appeared in the diffraction pattern. These peaks coexist along with the α - Nb_2O_5 ss pattern until about 40% WO_3 , at which composition also their intensities reach a maximum. Beyond this composition, the Nb_2O_5 ss pattern is replaced by that corresponding to the compound $\text{Nb}_2\text{O}_5 \cdot 3\text{WO}_3$. Table II lists all the d -spacings observed for a 40% WO_3 sample indicating the extra lines.

These results can be interpreted to mean that a new phase exists at 40 mole % WO_3 corresponding to $3\text{Nb}_2\text{O}_5 \cdot 2\text{WO}_3$. This has been designated as ξ in the equilibrium diagram. In addition to the above observations, the D.T.A. results also substantiate the possibility of a new compound at this composition; however, the remarks made above in connection with the δ -phase apply here as well. From about 72% to about 78% WO_3 , $\text{Nb}_2\text{O}_5 \cdot 3\text{WO}_3$ has a slight region of solubility. At all the higher compositions for this isotherm there is a two-phase region consisting of WO_3 ss + $\text{Nb}_2\text{O}_5 \cdot 3\text{WO}_3$ extending at least up to the 98% WO_3 composition.

WO_3 ss. Without exception all samples consisting of 2% Nb_2O_5 -98% WO_3 showed the pattern of a two-phase region, WO_3 ss + $3\text{WO}_3 \cdot \text{Nb}_2\text{O}_5$. Thus, the WO_3 shows very little solubility for the Nb_2O_5 .

D.T.A. Results. Differential thermal analysis indicated a horizontal transition line between the two-phase regions β - WO_3 ss + γ and α - WO_3 ss + γ at a temperature of 720° C. The melting points observed by D.T.A. are indicated on the diagram by dots on the boundaries between the solidus and solidus plus liquidus regions. Whether $3\text{WO}_3 \cdot \text{Nb}_2\text{O}_5$ melts congruently could not be determined from the D.T.A. measurements. On the Nb_2O_5 -rich side of the diagram, the melting point remains above 1400° C. up to 40% WO_3 . At higher percentages of WO_3 the melting point drops to approximately 1360°.

High-Temperature X-Ray Diffraction Results. Because of the reversibility of the transformation of WO_3 samples containing 75% WO_3 or more were subjected to at-temperature measurements on the high temperature diffractometer attachment to obtain more information on the transformation between the β - WO_3 ss + γ and α - WO_3 ss + γ regions. That the indicated temperature of transformation declined to 680° C. to 80% WO_3 from about 710° C. at 98% WO_3 may be attributed to a possible hysteresis effect during the transformation since the D.T.A. results indicated the transformation temperature for this composition range was constant at 710°.

Low Temperature X-Ray Diffraction Results. Hirakawa (2) and Matthias and Wood (6) have reported observations of a low temperature transformation of WO_3 . These workers reported that this transformation occurs at approximately -75° C. Examination of pure WO_3 in a low temperature diffractometer attachment indicated that WO_3 does indeed undergo a transformation to a new structure at -75° C. on cooling. The transformation exhibits a large hysteresis effect in that on heating it does not revert back to the monoclinic structure, β - WO_3 , until -10° C. This is in agreement with the report on Hirakawa. Measurements on samples containing 2%, 5%, 10%, or 20% Nb_2O_5 , however, did not indicate any such transformation; the monoclinic structure was retained down to -160° C.

Summary. On the basis of x-ray diffraction and D.T.A. results a phase diagram for the Nb_2O_5 - WO_3 system has been proposed. Nb_2O_5 shows solubility for WO_3 up to

Table II. Powder Diffraction Data for α -Nb₂O₅ and 60% Nb₂O₅-40% WO₃ Samples

"d" Calculated in A. α -Nb ₂ O ₅ Holtzberg and Reisman		I/I ₁ ² -Holtzberg and Reisman	hkl	"d" Measured in A. Present Work	I/I ₁ ² -Present Work	"d" Measured in A. 60% Nb ₂ O ₅ -40% WO ₃ 1000° C. 30-day Firing	I/I ₁ ² -60% Nb ₂ O ₅ -40% WO ₃ 1000° C. 30-day Firing	"d" Measured in A. 60% Nb ₂ O ₅ -40% WO ₃ 1200° C. 30-day Firing	I/I ₁ ² -60% Nb ₂ O ₅ -40% WO ₃ 1200° C. 30-day Firing
1	2	3	4	5	6	7	8	9	
16.8	10	001	17.0	<10					
10.7	20	20 $\bar{1}$	10.6	<10	10.64	<10	10.64	<10	
9.7	10	10 $\bar{2}$							
9.2	<10	200	9.2	<10					
					8.93	<10			
8.4	<10	002	8.4	<10	8.39	10	8.3	<10	
					7.42	<10	7.36	<10	
							6.75	<10	
6.32	10	10 $\bar{3}$	6.32	<10					
							6.18	<10	
							5.82	<10	
5.60	<10	003	5.60	<10					
5.33	<10	40 $\bar{2}$	5.30	<10					
5.15	20	40 $\bar{1}$	5.13	20					
4.73	<10	103	4.74	<10	4.91	<10	4.91	<10	
4.64	20	104	4.63	17	4.70	<10	4.69	13	
							4.502	20	
					4.46	<10			
					4.39	<10			
					4.27	<10			
					4.19	<10			
					4.09	<10			
					3.97	100			
					3.90	<10			
3.82	<10	010	3.83	<10					
3.77	70	40 $\bar{5}$	3.76	75	3.77	80	3.77	80	
3.74	50	110	3.75	50			3.72	10	
							3.70	<10	
3.65	100	10 $\bar{5}$	3.65	100			3.68	100	
							3.66	60	
					3.61	85			
							3.59	90	
3.57	<10	111	3.55	<10					
3.55		11 $\bar{2}$	3.54	<10	3.54	<10	3.52	<10	
3.50	50	21 $\bar{2}$	3.50	70	3.46	90			
							3.45	<10	
3.44	<10	604							
3.38		402	3.39	<10			3.37	<10	
3.36	10	005	3.37	15					
3.32	<10	211	3.32	<10	3.32	<10			
3.28	<10	21 $\bar{3}$	3.26	<10					
3.27		11 $\bar{3}$			3.28	<10			
							3.25	<10	
					3.203	<10			
							3.18	<10	
3.16	<10	20 $\bar{6}$	3.16	<10	3.17	<10			
					3.11	50			
3.10	<10	41 $\bar{2}$	3.09	<10					
							3.08	<10	
							3.05	<10	
3.00	<10	10 $\bar{6}$	3.00	<10					
							2.98	<10	
					2.90	40			
							2.89	<10	
							2.89	<10	
2.84	10	51 $\bar{2}$	2.84	12					
2.83	10	70 $\bar{1}$	2.84	20	2.83	25	2.82	15	
							2.803	30	
2.78	20	51 $\bar{1}$	2.78	25	2.77	35			
					2.74	40	2.74	35	
					2.73	45			
2.71	20	21 $\bar{5}$	2.71	20					
2.681	<10	41 $\bar{5}$							
2.677		20 $\bar{7}$	2.676	<10					
					2.653	10			
2.637	<10	11 $\bar{5}$	2.634	<10					

(Continued on page 369)

Table II. Powder Diffraction Data for α -Nb₂O₅ and 60% Nb₂O₅-40% WO₃ Samples (Continued)

"d" Calculated in A. α -Nb ₂ O ₅ Reisman	I/I ₁ [°] -Holtzberg and Reisman	hkl	"d" Measured in A. Present Work	I/I ₁ [°] -Present Work	"d" Measured in A. 60% Nb ₂ O ₅ -40% WO ₃ 1000° C. 30-day Firing	I/I ₁ [°] -60% Nb ₂ O ₅ -40% WO ₃ 1000° C. 30-day Firing	"d" Measured in A. 60% Nb ₂ O ₅ -40% WO ₃ 1200° C. 30-day Firing	I/I ₁ [°] -60% Nb ₂ O ₅ -40% WO ₃ 1200° C. 30-day Firing
1	2	3	4	5	6	7	8	9
							2.616	< 10
					2.605	40	2.583	17
							2.565	33
2.552	10	10 $\bar{7}$	2.551	15	2.547	10		
2.544	< 10	503						
2.531		404						
2.531		412						
2.528	< 10	313	2.529	< 10				
2.504	10	80 $\bar{6}$	2.499	10				
2.482	< 10	511	2.486	< 10	2.486	< 10		
							2.479	< 10
2.459	< 10	61 $\bar{5}$	2.456	< 10				
2.453	< 10	80 $\bar{1}$						
					2.447	15		
					2.428	< 10	2.421	< 10
					2.403	< 10		
							2.374	< 10
							2.347	< 10
2.340	< 10	90 $\bar{3}$	2.336	< 10	2.336	10		
2.318	10	20 $\bar{8}$	2.318	15				
							2.321	< 10
							2.299	17
							2.290	13
					2.268	< 10		
					2.252	< 10		
							2.243	< 10
					2.225	< 10		
			2.209	< 10				
					2.199	< 10		
2.184	< 10	81 $\bar{4}$						
			2.164	< 10				
2.177		81 $\bar{3}$						
					2.154	< 10	2.159	< 10
2.116	< 10	513	2.113	< 10				
2.109		414						
							2.097	< 10
					2.092	< 10		
2.081	10	207	2.080	15	2.074	< 10		
							2.065	< 10
2.042	20	10-0- $\bar{7}$	2.041	15	2.043	< 10	2.043	< 10
2.039		80 $\bar{9}$					2.038	10
2.036	10	604						
					2.021	< 10	2.023	11
							2.019	15
			1.991	< 10				
					1.979	15		
					1.949	10		
1.932	< 10	117	1.933	< 10				

[°]I/I₁ = Relative peak intensity obtained by normalizing with respect to the strongest line.

about 33% WO₃. WO₃, on the other hand, shows only a very slight amount of solubility for Nb₂O₅. The existence of the Nb₂O₅·3WO₃ compound with a tetragonal unit cell is confirmed. In addition, the existence of two new compounds, 3Nb₂O₅·2WO₃ above 1100° C. and Nb₂O₅·WO₃ at 1100° C. and below, has been tentatively postulated.

ACKNOWLEDGMENT

The authors thank the U. S. Atomic Energy Commission for its partial financial support in this work, J. Peltier for assistance in the collection of x-ray data, and K. Easey for assistance in the experimental work.

LITERATURE CITED

- (1) Goldschmidt, H.J., *Metallurgia* **62**, 211, 241 (1960).
- (2) Hirakawa, K., *J. Phys. Soc. Japan* **7**, 331 (1952).
- (3) Holtzberg, F., Reisman, A., *J. Phys. Chem.* **65**, 1192 (1961).
- (4) Holtzberg, F., Reisman, A., Berry, M., Berkenblit, M., *J. Amer. Chem. Soc.* **79**, 2039 (1957).
- (5) Kovba, L.M., Trunov, V.K., *Dokl. Akad. Nauk. SSSR* **147**, 622 (1962).
- (6) Matthias, B.T., Wood, E.A., *Phys. Rev.* **84**, 1255 (1951).
- (7) Perri, J.A., Banks, E., Post, B., *J. App. Phys.* **28**, 1272 (1957).

RECEIVED for review October 31, 1963. Accepted January 20, 1964.