

Effect of Oxide Additions on the Polymorphism of Tantalum Pentoxide.

IV. The System Ta_2O_5 - Ta_2WO_8

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The low-temperature form of pure Ta_2O_5 has been found to exist in two slightly different modifications. The lowest temperature form has a b axis multiplicity of 14 whereas the highest temperature form (about 1350°C) has a multiplicity of 11. At intermediate temperatures an "infinite" number of at least partially ordered sequences of these two modifications exist in equilibrium.

The addition of WO_3 to Ta_2O_5 causes the "stabilization" of an "infinite" number of phases similar in structure to the low temperature form of Ta_2O_5 . From just less than 10 mol % WO_3 to the last compound in the series at 26 $\frac{2}{3}$ mol % WO_3 these phases are in equilibrium with liquid, and the high temperature structure type of pure Ta_2O_5 is eliminated from the phase diagram. One compound, $15Ta_2O_5 \cdot 2WO_3$ with a multiplicity of 8, was found to melt congruently at about 1815°C and the last phase, $11Ta_2O_5 \cdot 4WO_3$ with a multiplicity of 13, melts incongruently at about 1605°C.

1. Introduction

Tantalum pentoxide is known to occur in at least two structurally distinct polymorphs. However, because of the complex nature of their X-ray diffraction patterns neither of these forms has previously been adequately studied. No large single crystals of pure Ta_2O_5 can be grown by present day techniques. In Part I of the present study (1) it was shown that the high-temperature polymorph (H - Ta_2O_5) actually undergoes several phase transitions on quenching and although it is triclinic at room temperature the symmetry is apparently tetragonal at the temperature at which H - Ta_2O_5 is stable. In Part II (2) it was demonstrated that several other oxides when added to Ta_2O_5 in small amounts can be used to "stabilize" the high-temperature polymorph in its apparently tetragonal symmetry. Large single crystals of this polymorph were obtained by pulling from a melt containing 4 mol % Sc_2O_3 . These single crystals have been used to determine the crystal structure of the high-temperature polymorph (3).

In Part III (4) it was also shown that certain other oxides can be used to "stabilize" phases very similar to the low-temperature polymorph of Ta_2O_5 (L - Ta_2O_5). In general this second group of oxides has cations with a smaller radius than those which "stabilize" the

high-temperature form. In the system Ta_2O_5 - WO_3 it was found that phases with subcells similar to L - Ta_2O_5 exist from pure Ta_2O_5 to at least 25 mol % WO_3 and that these phases are stable at solidus temperatures over a large portion of this system. It should therefore be possible to grow single crystals sufficiently large for crystal structure determination, under solid-plus liquid *equilibrium* conditions. For this reason the subsystem Ta_2O_5 - Ta_2WO_8 has been studied in detail. A preliminary discussion of the chemical and structural investigations in this system was published earlier (5). Crystal structure determinations of several of the phases found in this study as well as pure L - Ta_2O_5 have also been completed and are reported elsewhere (6). The results of the complete phase equilibria study are reported in the present paper.

2. Materials

The starting materials used in this study were found by general spectrochemical analyses to have the following impurities:

WO_3 -Si present in amounts less than 0.1 %; B, Ca, Cr, and Mg present in amounts less than 0.001 %; Cu present in amounts less than 0.0001 %; Pb only questionably present.

Ta₂O₅—Al and Si present in amounts less than 1.0 %; Cu and Mg present in amounts less than 0.1 %; Ag, Ca, and Mn each present in amounts less than 0.0001 %.

In addition to these starting materials a few compositions were prepared with a Ta₂O₅ of much higher purity showing only Si present in about 2 ppm and Mg present in amounts less than 1 ppm. There were no apparent differences in the phase equilibria experiments except that equilibrium was

attained more slowly when the high purity Ta₂O₅ was used.

3. Specimen Preparation and Test Methods

One gram batches of various proportions of Ta₂O₅ and WO₃ were weighed, mixed in a mechanical shaker for approximately 10 min and pressed into disks at about 10⁴ psi. The disks were placed on platinum setters and calcined in air, generally at 700°C. After this preliminary heat treatment the

TABLE I

INDEXED X-RAY DIFFRACTION POWDER PATTERN OF PURE *L*-Ta₂O₅ WITH *m* = 11 (CuK α RADIATION)^a

<i>hkl</i> ^b	<i>d</i> _{obsd}	2 <i>θ</i> _{obsd}	2 <i>θ</i> _{calcd}	<i>I</i> ^c
140	5.282	16.77	16.78	6
080	5.038	17.59	17.60	3
001	3.885	22.87	22.85	210
1,10,0	3.377	26.37	26.36	12
1,11,0	3.152	28.29	28.28	240
141	3.131	28.48	28.49	10
200	3.098	28.79	28.79	95
210	3.090	28.87	28.87	10
081	3.077	28.99	28.99	5
1,12,0	2.9511	30.26	30.25	4
0,14,0	2.8760	31.07	31.05	4
270	2.7274	32.81	32.80	8
280	2.6391	33.94	33.94	8
1,10,1	2.5489	35.18	35.16	10
1,11,1	2.4490	36.69	36.66	180
201	2.4231	37.07	37.07	88
211	2.4187	37.14	37.14	10
1,12,1	2.3517	38.24	38.25	6
271	2.2345	40.33	40.35	5
281	2.1827	41.33	41.31	4
1,18,0	2.1054	42.92	42.92	8
330	2.0421	44.32	44.33	5
2,15,0	2.0304	44.59	44.61	11

TABLE I (continued)

340	2.0244	44.73	44.74	14
1,19,0	2.0073	45.13	45.15	10
350	2.0019	45.26	45.28	7
002	1.9442	46.68	46.68	60
1,18,1	1.8514	49.17	49.17	8
3,10,0	1.8378	49.56	49.55	12
0,22,0	1.8319	49.73	49.75	42
142	1.8243	49.95	49.95	7
331	1.8071	50.46	50.44	9
3,11,0	1.7994	50.69	50.69	44
341	1.7958	50.80	50.82	10
1,19,1	1.7837	51.17	51.19	7
351	1.7801	51.28	51.30	6
3,12,0	1.7600	51.91	51.92	8
1,10,2	1.6846	54.42	54.41	3
3,10,1	1.6612	55.25	55.23	17
0,22,1	1.6562	55.43	55.41	65
1,11,2	1.6549	55.48	55.48	78
202	1.6470	55.77	55.78	35
212	1.6456	55.82	55.83	22
3,11,1	1.6332	56.28	56.29	30
2,21,0	1.6316	56.34	56.36	20
1,12,2	1.6237	56.64	56.64	4
3,12,1	1.6022	57.47	57.44	6
2,22,0	1.5764	58.50	58.49	21
400	1.5495	59.62	59.62	10

TABLE I (continued)

410	1.5485	59.66	59.67	10
420	1.5447	59.82	59.82	7
2,21,1	1.5043	61.60	61.60	6
480	1.4810	62.68	62.68	7
3,19,0	1.4797	62.74	62.74	7
490	1.4638	63.50	63.48	5
2,22,1	1.4609	63.64	63.63	24
3,17,1	1.4455	64.40	64.39	3
401	1.4395	64.70	64.71	8
411	1.4381	64.77	64.76	7
421	1.4355	64.90	64.89	3
332	1.4081	66.33	66.33	3
342	1.4019	66.66	66.65	8
471	1.3965	66.95	66.96	5
481 } 3,19,1 }	1.3832	67.68	67.64	8
			67.69	
3,10,2	1.3355	70.45	70.44	8
0,22,2	1.3330	70.60	70.60	15
3,11,2	1.3205	71.37	71.37	17
3,12,2	1.3048	72.36	72.38	7
003	1.2962	72.92	72.93	9
0,30,1	1.2694	74.72	74.72	4

^a Specimen heated to 1327°C for 312 hr and quenched.

^b Indexed on the basis of an orthorhombic unit cell $a = 6.198 \text{ \AA}$, $b = 40.29 \text{ \AA}$, $c = 3.888 \text{ \AA}$ with the aid of intensities observed from single-crystal diffractometer data.

^c Observed intensity, peak heights.

specimens were generally ground and given a second higher temperature calcine in a sealed Pt tube at 1450°C. After calcining they were usually heated in air at 900°C for a few minutes in order to assure complete oxidation of the tungsten ions. Following these heat treatments portions of the ground specimen were placed in sealed platinum tubes and heated in the quenching furnace at various temperatures for different periods of time.

The sealed tubes containing the specimens were

quenched into ice water and the specimen examined by X-ray diffraction techniques. A high-angle recording Geiger counter diffractometer and Ni-filtered Cu radiation was used in the study. The Geiger counter traversed the specimen at $\frac{1}{2}^\circ/\text{min}$ and the diffraction pattern was recorded on the chart at $1^\circ-2\theta/\text{in}$. The unit cell dimensions reported can be considered accurate to about ± 2 in the last decimal place listed. Equilibrium was considered to have been achieved when X-ray patterns showed no

change after successive heat treatments of a specimen or when the data were consistent with the results from a previous set of experiments. Solidus and liquidus temperatures were obtained by using both quenching and induction furnaces. Because of the temperature limitation of the quenching furnace, melting points above 1700°C were determined with an induction furnace. Some duplicate determinations below 1700°C were made using both furnace types.

The quenching furnace consisted of two concentric ceramic tubes wound with platinum-rhodium alloy wire. The inner tube served as the primary winding and the outer one as the booster. Separate power sources were used with each winding.

The power for the outer winding (booster) was supplied from a variable autotransformer. An a.c. bridge type controller in which the furnace winding was one arm of the bridge was used to control the temperature of the inner winding.

The induction furnace was contained in a stabilized-ZrO₂ crucible 3 in. high × 1½ in. diameter with a 0.2-in. wall thickness. Inside this crucible, imbedded in coarse grain stabilized-ZrO₂ was an iridium cylinder 1¾ × ¾ in. with ~0.1-in. wall thickness acting as the susceptor. An Al₂O₃ crucible

0.8 × 0.3 in. resting on a ¼-in. high iridium ring inside the susceptor contained a sealed 80%Pt-20%Rh tube. This sealed tube, which contained the specimen, was necessary to eliminate loss of WO₃ by vaporization. A very small hole in the covers of both the Al₂O₃ crucible and the Ir susceptor enabled the temperature to be monitored under near blackbody conditions. Determinations of the melting points of the specimen inside the sealed platinum alloy tubes could then be made by the same methods as those used in the quenching experiments.

Apparent temperatures were measured with a calibrated, disappearing filament-type optical pyrometer which was sighted through a 45° calibrated prism into a viewing hole at the center of the crucible cover. The temperature measuring system of both the quenching furnace and the induction furnace was calibrated frequently against the melting point of Au (1063°C), Pd (1552°C), and Pt (1769°C). Temperatures reported in the present study are considered accurate to within ±10°C. The measurements were reproducible to within ±5°C, or better. The degree of melting was determined by the physical appearance of quenched or cooled specimens. The first adherence of the specimen to the platinum

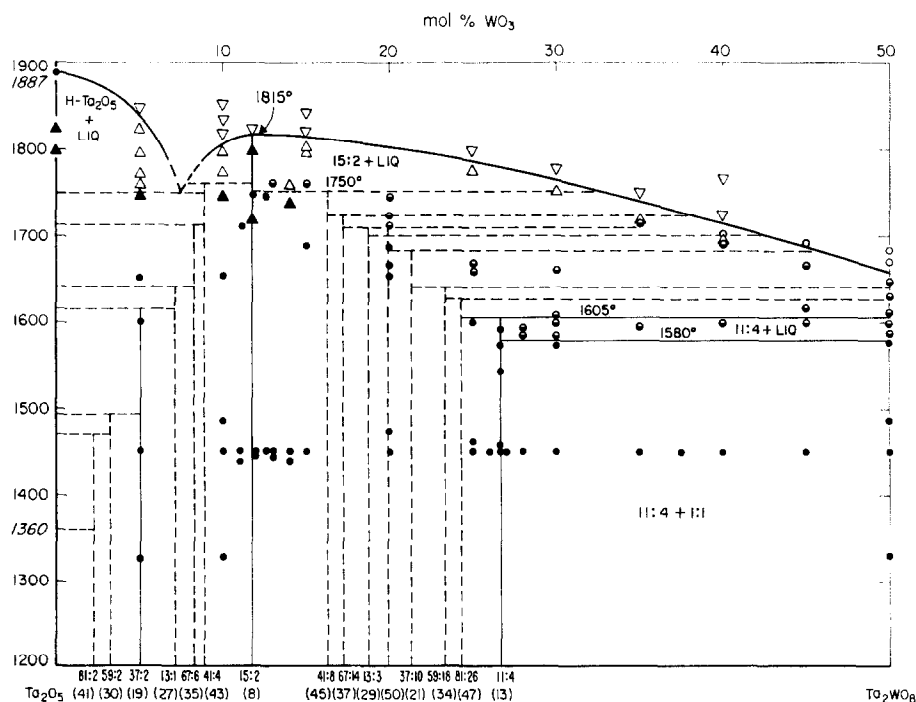


FIG. 1. Proposed phase equilibrium diagram for the system Ta₂O₅-Ta₂WO₈. Circles indicate experimental data points from quench furnace: ●—not melted; ◐—partially melted; ○—completely melted. Triangles indicate experimental data points from induction furnace: ▲—not melted; △—partially melted; ▽—completely melted. Numbers with colons indicate mole ratios of the proposed phases. Numbers in brackets indicate the multiplicity of the *b* axis of the proposed phases.

container generally established the beginning of melting. Complete melting was established by the formation of a meniscus.

4. Results and Discussion

4.1. The Low-Temperature Form of Ta₂O₅

The proper method of indexing the powder pattern of the low-temperature form of Ta₂O₅

(L-Ta₂O₅) has puzzled crystallographers for a long period of time. All agree that the more intense diffraction lines can be indexed on the basis of an orthorhombic subcell with $a' = 6.20 \text{ \AA}$, $b' = 3.66 \text{ \AA}$, and $c' = 3.89 \text{ \AA}$. However, numerous weak lines which also appear in the pattern have never been interpreted unambiguously. The major reason for this ambiguity is that the position of these "superstructure" lines is strongly dependent upon both

TABLE II
EXPERIMENTAL DATA OBTAINED BY THE QUENCHING TECHNIQUE FOR THE SYSTEM Ta₂O₅-Ta₂WO₈

Composition		Heat Treatment				X-Ray Diffraction Analyses ^{c/}	C-line	m
Ta ₂ O ₅ mol %	WO ₃ mol %	Initial ^{d/}		Final ^{b/}				
		Temp °C	Time hr	Temp °C	Time hr			
95	5	1000	10	1326	19	L-Ta ₂ O ₅ phase(s)	26.17	
				1453	16	do	26.15	
				1652	4	L-Ta ₂ O ₅ phase(s) + H-Ta ₂ O ₅ (tr)	25.98	
		700	10					
		1450 ^{d/}	60					
		900	0.25			L-Ta ₂ O ₅ phase(s)	26.25	
		1540 ^{d/}	60					
		900	0.25			L-Ta ₂ O ₅ phase(s)	26.18	
				1603	100	do	26.05	19
		90	10	500	64			
1000	60							
				1327	19	L-Ta ₂ O ₅ phase(s)		
				1449	19	do	25.85	
				1486	2.5	do	25.85	
				1649	4	do	do	
				1651	5	do	do	
				1652	4	do	do	
89	11	1450 ^{d/}	60				25.90	
		700	10	1439	16	L-Ta ₂ O ₅ phase(s)	25.85	
		1450 ^{d/}	60			do	25.90	
88.89 (8:1)	11.11	700	10					
		1450 ^{d/}	60					
		900	0.25			L-Ta ₂ O ₅ phase(s)	25.90	
		1540 ^{d/}	60					
88.24 (15:2)	11.76	900	0.25	1710	4	L-Ta ₂ O ₅ phase(s)	25.78	
		700	10					
		1225 ^{d/}	336			L-Ta ₂ O ₅ phase(s)	26.05	
		1450 ^{d/}	60			do	25.98	
88	12			1748	3	do	25.74	8
		700	10					
		1450 ^{d/}	60	1443	16	L-Ta ₂ O ₅ phase(s)	25.80	
						do	25.88	

TABLE 2 (continued)

87.5 (7:1)	12.5	700	10						
		1450 ^{d/}	60						
		900	0.25			L-Ta ₂ O ₅ phase(s)	25.86		
		1540 ^{d/}	60						
		900	0.25						
				1747 ^{e/}	4	L-Ta ₂ O ₅ phase(s)	25.70		
87	13	700	10						
		1450 ^{d/}	60	1442	16	L-Ta ₂ O ₅ phase(s)	25.74	8	
							25.85		
				1760 ^{e/}	1	L-Ta ₂ O ₅ phase(s)	25.74	8	
86	14	700	10						
		1450 ^{d/}	60	1439	18	L-Ta ₂ O ₅ phase(s)	25.68		
							25.75		
85	15	700	10						
				1445	19	L-Ta ₂ O ₅ phase(s)	25.72		
				1687	4	do	25.55		
		1450 ^{d/}	60			do	25.69		
		900	0.25						
80	20	700	10						
				1761 ^{e/}	0.5				
				1100	168	L-Ta ₂ O ₅ phase(s)	25.50		
				1472	20	L-Ta ₂ O ₅ phase(s)	25.45		
		1450 ^{d/}	60			do	25.45		
		900	0.25						
				1654	16				
				1668	64				
				1687	1				
				1711 ^{e/}	1				
				1723 ^{e/}	1	L-Ta ₂ O ₅ phase(s)	25.60		
				1743 ^{e/}	0.75	do	25.70		
				1749 ^{e/}	1	L-Ta ₂ O ₅ phase(s) + Q-Liq			
75	25	700	10						
				1100	672	L-Ta ₂ O ₅ phase(s) + Ta ₂ WO ₈	25.55		
				1463	64	L-Ta ₂ O ₅ phase(s)	25.24		
				1659 ^{e/}	4	L-Ta ₂ O ₅ phase(s) + Q-Liq	25.42		
		1450 ^{d/}	60			L-Ta ₂ O ₅ phase(s)	25.25		
				1669	1	L-Ta ₂ O ₅ phase(s) + Q-Liq	25.40		
		900	0.25						
		1540 ^{d/}	60						
900	0.25								

TABLE 2 (continued)

				1600	22	L-Ta ₂ O ₅ phase(s)	25.26	
				1640	24			
74	26	700	10					
		1450 ^{d/}	60			L-Ta ₂ O ₅ phase(s)	25.20	
73.33	26.67	700	10					
(11:4)		1450 ^{d/}	60			L-Ta ₂ O ₅ phase(s)	25.18	13
		900	0.25					
				1456	144	L-Ta ₂ O ₅ phase(s)	25.18	13
				1541	168	do	25.18	13
				1544	18	do	25.18	13
				1574	68	do	25.18	13
				1593	3	do	25.18	13
73	27	700	10					
		1450 ^{d/}	60					
		900	0.25			L-Ta ₂ O ₅ phase(s) + Ta ₂ WO ₈	25.18	13
72	28	700	10					
		1450 ^{d/}	60					
		900	0.25					
				1586 ^{e/}		L-Ta ₂ O ₅ phase(s) + Q-Liq	25.18	13
				1593 ^{e/}		do	25.18	13
70	30	700	10					
				1100	672	Ta ₂ WO ₈ + L-Ta ₂ O ₅ phase(s)		
				1452	21	L-Ta ₂ O ₅ phase(s) + Ta ₂ WO ₈	25.18	13
		1450 ^{d/}	60					
				1603 ^{e/}	4	L-Ta ₂ O ₅ phase(s) + Ta ₂ WO ₈ + Q-Liq		
				1661 ^{e/}	1			
		900	0.25					
				1574	16	L-Ta ₂ O ₅ phase(s) + Ta ₂ WO ₈		
				1583 ^{e/}	3	L-Ta ₂ O ₅ phase(s) + Q-Liq	25.18	13
				1601	4	do	25.18	13
				1609	4	do	25.48	
65	35	700	10					
		1450 ^{d/}	60					
		900	0.25					
				1595	1	L-Ta ₂ O ₅ phase(s) + Q-Liq	25.18	13
				1717 ^{e/}	1			
62.5	37.5	700	10					
		1225 ^{d/}	336					
		1450 ^{d/}	60			L-Ta ₂ O ₅ phase(s) + Ta ₂ WO ₈		
60	40	700	10					
				1100	672	Ta ₂ WO ₈ + L-Ta ₂ O ₅ phase(s)		

TABLE 2 (continued)

		1450 ^{d/}	60				Ta ₂ WO ₈ + L-Ta ₂ O ₅ phase(s)		
		900	0.25						
				1598 ^{e/}	1		L-Ta ₂ O ₅ phase(s) + Q-Liq	25.18	13
				1690 ^{e/}	1.5				
				1700 ^{e/}	1				
55	45	700	10						
		1450 ^{d/}	60				Ta ₂ WO ₈ + L-Ta ₂ O ₅ phase(s)		
		900	10						
				1598 ^{e/}	1		L-Ta ₂ O ₅ phase(s) + Q-Liq + Ta ₂ WO ₈	25.18	13
				1616 ^{e/}	1		L-Ta ₂ O ₅ phase(s) + Q-Liq		
				1667 ^{e/}	1		do		
				1692 ^{f/}	1				
50	50	700	10						
				1166	64		Ta ₂ WO ₈ + "bronze" (tr)		
				1330	20		do		
				1486	2.5		do		
				1684 ^{f/}	2		L-Ta ₂ O ₅ phase(s) + Q-Liq		
		1450 ^{d/}	60						
		900	0.25						
				1576	1.0		Ta ₂ WO ₈		
				1586 ^{e/}	1.0				
				1586 ^{e/}	6.5		L-Ta ₂ O ₅ phase(s) + Q-Liq	25.18	13
				1599 ^{e/}	1.0				
				1610 ^{e/}	0.75				
				1632 ^{e/}	1.0				
				1646 ^{e/}	1.0				
				1667 ^{f/}	1.0				

^{a/} All specimens were calcined as pressed disks on Pt foil at the indicated heat treatment with heating and cooling rates of approximately 4°C/min, unless otherwise specified.

^{b/} All specimens were quenched in sealed Pt tubes from the indicated temperature, unless otherwise specified.

^{c/} The phases identified are given in order of amount present at room temperature (greatest amount first). The phases are not necessarily those present at the temperature to which the specimen was heated.

^{d/} Heated in a sealed Pt tube to minimize loss of WO₃ due to volatilization.

^{e/} Specimen was partially melted, above solidus temperature.

^{f/} Specimen was completely melted, above liquidus temperature.

the nature of the heat treatment and the amount of cation and anion impurities (4).

Zaslavski (7) grew small single crystals by vapor transport (with chlorine as a transport medium) and reported that the unit cell of *this* material had the *b'* axis increased by 12 times. Harvey and Wilman (8) examined fine grained material by selected area electron diffraction and interpreted the results obtained on *their* material (heated at about 750°C) as having the *b'* axis multiplied by 19. Frevel and Rinn (9) attempted to account for the superstructure

lines of *their* powder pattern by selecting a large monoclinic cell with $a = 7.32 \text{ \AA}$ ($2b'$), $b = 15.55 \text{ \AA}$ ($4c'$), $c = 10.79 \text{ \AA}$, $\beta = 120^\circ 36'$. However, Terao (10) reported that *his* pattern could be indexed only by utilizing approximately twice the previous monoclinic *c* axis ($c = 21.549 \text{ \AA}$).

Lapitzkiy, Simanov, et al. (11) and Simanov, Lapitzkiy, et al. (12) were the first to suggest a polymorphic behavior of Ta₂O₅ below 1200°C. Moser (13) attempted to define four different conditions ("Zustanden") occurring in the low-temperature

form of Ta_2O_5 based on the position of one characteristic line labelled the "C"-line, occurring between about 25° and $27^\circ 2\theta$ ($CuK\alpha$ radiation).

Roth and Waring (4) have shown that the low-temperature form of Ta_2O_5 can be completely equilibrated into a structure with a b axis multiplicity (m) of 11 times the subcell at temperatures of about $1350^\circ C$. The crystal structure of this polymorph of Ta_2O_5 has been reported by Stephenson and Roth (6). The X-ray powder diffraction pattern of $L-Ta_2O_5$ with $m = 11$ is given in Table I. This

pattern has been indexed on the basis of an orthorhombic unit cell with $a = 6.198 \text{ \AA}$, $b = 40.29 \text{ \AA}$, $c = 3.888 \text{ \AA}$, with the aid of the intensities observed from single crystal diffractometer data.

Electron microscope lattice images of the material used for the X-ray powder pattern were prepared by Dr. J. Allpress (CSIRO; Melbourne, Australia). They show sharp and clear lattice image fringes of 40 \AA corresponding to the b axis of the $m = 11$ type unit cell. Selected area single-crystal electron diffraction patterns show no extinctions, unlike

TABLE III
EXPERIMENTAL DATA OBTAINED BY INDUCTION HEATING FOR THE SYSTEM Ta_2O_5 - Ta_2WO_8

Composition		Heat Treatment			Physical Observation and X-Ray Diffraction Analyses					
Ta_2O_5 mol %	WO_3 mol %	Initial ^{a/}		Final ^{b/}						
		Temp	Time	Temp						
95	5	700	10							
						1450 ^{c/}	60		1748	No melting - Pt standard not melted
									1758	Just begun to melt - Pt standard not melted
		900	0.25		1771	Partially melted - Pt standard melted Contains $L-Ta_2O_5$ phase(s) + $H-Ta_2O_5$				
					1797	do				
					1820	do - Contains $H-Ta_2O_5$ + $L-Ta_2O_5$ phase(s)				
					1822	do				
					1849	Completely melted				
		90	10	700	10					
								1450 ^{c/}	60	
1772	Just begun to melt - $L-Ta_2O_5$ phase ($m = 8$)									
900	0.25				1795	Partially melted				
					1799	Partially melted - $L-Ta_2O_5$ phase ($m = 8$)				
					1818	Completely melted				
					1834	do				
					1849	do				
88.24 (15:2)	11.76			700	10					
								1225 ^{c/}	336	
		1450 ^{c/}	60							
								1718 ^{c/}	2	
		1000	0.25							
			1820	Completely melted						
86	14	700	10							
						1450 ^{c/}	60			
			1759	Partially melted						

TABLE 3 (continued)

85	15	700	10		
		1450 ^{a/}	60		
		900	0.25		
				1797	Partially melted; L-Ta ₂ O ₅ phase(s)
				1801	do
				1816	Completely melted
				1819	do
				1841	do
75	25	700	10		
		1450 ^{a/}	60		
		900	0.25		
				1776	Partially melted
				1797	Completely melted
70	30	700	10		
		1450 ^{a/}	60		
		900	0.25		
				1750	Partially melted
				1778	Completely melted
65	35	700	10		
		1450 ^{a/}	60		
		900	0.25		
				1721	Partially melted
				1750	Completely melted
60	40	700	10		
		1450 ^{a/}	60		
		900	0.25		
				1694	Partially melted
				1724	Completely melted
				1725	do
				1769	do

a/ Specimens were initially calcined as pressed disks on Pt foil at the indicated temperature with heating and cooling rates of approximately 4°C/min.

b/ Specimens were heated in sealed 80%Pt/20%Rh tubes for five minutes at the indicated temperature in the special inductively heated furnace described in text.

c/ Heated in sealed Pt tubes to minimize loss of WO₃ due to volatilization.

X-ray diffraction where many nonsystematic extinctions occur. A neutron powder diffraction pattern of the same material however, shows only the same diffraction effects as are found with X-rays.

At temperatures below 1350°C the "C-line" of the X-ray diffraction powder pattern gradually shifts to lower *d* values when the specimen approaches equilibrium, regardless of whether the specimen was previously heated to higher temperatures or not. In order to obtain the equilibrium values, the specimen *must* be quenched from the temperature under study, as slow cooling tends to shift the

peaks in the diffraction pattern towards those values which would occur at lower temperature equilibrium. At some low temperature, Ta₂O₅ apparently has a structure with a multiplicity of the *b* axis equal to 14. At all intermediate temperatures, L-Ta₂O₅ has a structure which is apparently an ordered (or partially ordered) intermediate between the *m* = 14 and the *m* = 11 polymorphs.

4.2. The System Ta₂O₅-WO₃

The phase equilibrium diagram for the system Ta₂O₅-Ta₂WO₈ is shown in Fig. 1. The data from

which this diagram was interpreted are listed in Tables II and III.

As WO_3 is added to Ta_2O_5 , a series of phases is formed that involve ordered mixtures of the $m = 11$ structure with another structure in which $m = 8$. It has been found in the present study that the composition at which $m = 8$ occurs at the ratio $15\text{Ta}_2\text{O}_5 \cdot 2\text{WO}_3$. This is the smallest unit cell which has been found for the $L\text{-Ta}_2\text{O}_5$ -type phases. This composition is also the most stable, having a congruent melting point of about 1815°C . The crystal structure of this compound has been reported by Stephenson and Roth (6) and the X-ray diffraction powder pattern is listed in Table IV, indexed on the basis of an orthorhombic unit cell with $a = 6.175 \text{ \AA}$,

$b = 29.29 \text{ \AA}$, $c = 3.874 \text{ \AA}$, with the aid of intensities observed from single crystal diffractometer data.

The smallest multiplicity that can occur between Ta_2O_5 ($m = 11$) and $\text{Ta}_{30}\text{W}_2\text{O}_{81}$ would be $m = 11 + 8 = 19$ at a composition of $37\text{Ta}_2\text{O}_5 \cdot 2\text{WO}_3$. The crystal structure of this phase has also been reported by Stephenson and Roth (6).

The next small structure which should occur in the system with the addition of more WO_3 would be $m = 5$ ($\text{M}_{10}\text{O}_{26}$) at a ratio of $4\text{Ta}_2\text{O}_5 : 2\text{WO}_3$. However, this phase does *not* occur in this system. Instead the last compound to form (the one with the maximum WO_3 content) has $m = 8 + 5 = 13$ at a ratio of $11\text{Ta}_2\text{O}_5 : 4\text{WO}_3$ ($\text{Ta}_{22}\text{W}_4\text{O}_{67}$). The crystal structure of this compound has been reported

TABLE IV

INDEXED X-RAY DIFFRACTION POWDER PATTERN OF THE COMPOUND $15\text{Ta}_2\text{O}_5 \cdot 2\text{WO}_3$ ($m = 8$) ($\text{CuK}\alpha$ RADIATION)^a

hkl^b	d_{obsd}	$2\theta_{\text{obsd}}$	$2\theta_{\text{calcd}}$	I^c
130	5.226	16.95	16.97	14
060	4.886	18.14	18.16	5
001	3.877	22.92	22.94	200
170	3.460	25.73	25.70	13
180	3.149	28.32	28.32	280
131	3.110	28.68	28.67	15
200	3.088	28.89	28.90	85
210	3.071	29.05	29.06	20
061	3.033	29.42	29.41	7
190	2.8787	31.04	31.04	8
250	2.7298	32.78	32.76	11
260	2.6093	34.34	34.34	8
171	2.5809	34.73	34.71	10
181	2.4435	36.75	36.75	180
201	2.4144	37.21	37.21	80
211	2.4062	37.34	37.34	20
191	2.3121	38.92	38.94	5
241	2.2940	39.24	39.26	3
2,10,0	2.1243	42.52	42.51	7
1,13,0	2.1167	42.68	42.68	10

TABLE IV (continued)

320	2.0378	44.42	44.41	8
2,11,0	2.0158	44.93	44.92	18
330	2.0136	44.98	44.97	12
1,14,0 } 340 }	1.9820	45.74	{ 45.75 45.75	16
002	1.9372	46.86	46.86	75
1,13,1	1.8575	49.00	49.00	8
370	1.8465	49.31	49.30	17
0,16,0	1.8305	49.77	49.77	38
132	1.8162	50.19	50.20	5
321	1.8034	50.57	50.56	10
062	1.7998	50.68	50.66	12
380	1.7941	50.85	50.85	53
331	1.7873	51.06	51.07	18
1,14,1 } 341 }	1.7647	51.76	{ 51.78 51.78	8
390	1.7400	52.55	52.57	10
172	1.6903	54.22	54.21	4
371	1.6668	55.05	55.04	12
0,16,1	1.6549	55.48	55.47	52
182	1.6502	55.65	55.66	140
202	1.6413	55.98	56.00	40
381	1.6282	56.47	56.48	48
391	1.5876	58.05	58.08	13
252	1.5799	58.36	58.35	7

TABLE IV (continued)

2,16,0	1.5742	58.59	58.58	35
400	1.5441	59.85	59.87	10
410	1.5413	59.97	59.96	9
3,13,0	1.5194	60.92	60.92	6
2,16,1	1.4583	63.77	63.75	38
401	1.4340	64.98	64.98	11
411	1.4318	65.09	65.07	10
3,13,1	1.4145	65.99	65.98	8
322	1.4039	66.55	66.54	5
332	1.3961	66.97	66.97	10
451	1.3928	67.15	67.15	12
461	1.3761	68.0	68.09	5
3,14,1	1.3723	68.25	68.30	8
372	1.3366	70.38	70.38	8
0,16,2	1.3307	70.74	70.75	18
382	1.3163	71.63	71.63	28
392	1.2942	73.05	73.05	5
003	1.2913	73.24	73.24	12

^a Specimen heated to 1442°C for 16 hr in a sealed Pt tube and quenched.

^b Indexed on the basis of an orthorhombic unit cell $a = 6.175 \text{ \AA}$, $b = 29.29 \text{ \AA}$, $c = 3.874 \text{ \AA}$, with the aid of intensities observed from single crystal diffractometer data.

^c Observed intensity, peak heights.

by Stephenson and Roth (6) and the X-ray diffraction powder pattern is listed in Table V, indexed on the basis of a C-centered orthorhombic unit cell with $a = 6.138 \text{ \AA}$, $b = 47.56 \text{ \AA}$, $c = 3.857 \text{ \AA}$ with the aid of intensities observed from single crystal diffraction data. This compound has been found to melt incongruently at about 1605°C.

From this last compound $\text{Ta}_{22}\text{W}_4\text{O}_{67}$, to the 1:1 compound Ta_2WO_8 a two-phase region is found. The compound Ta_2WO_8 is apparently isostructural with $\text{LiNb}_6\text{O}_{15}\text{F}$ (14) with $a = 16.70 \text{ \AA}$, $b = 8.864 \text{ \AA}$, $c = 3.877 \text{ \AA}$ (15). It has been found to melt incongruently to $\text{Ta}_{22}\text{W}_4\text{O}_{67}$ plus liquid at about 1580°C.

In the region of the $L\text{-Ta}_2\text{O}_5$ type phases, theoret-

ically every composition should represent another compound. Thus, a two phase region is never found. The phase diagram (Fig. 1) shows only those phases which would have a multiplicity of the b axis ≤ 50 . This series cannot be drawn as a solid solution because of the completely discontinuous shift of the b axis with composition. In a true solid solution *all* extensive properties must be continuous. Apparently, adjacent specimens with very large multiplicities all melt experimentally at approximately the same temperature to the nearest small multiplicity phase. Thus, the solidus appears to be a series of steps rather than the continuous line required by a solid solution series.

TABLE V

INDEXED X-RAY DIFFRACTION POWDER PATTERN OF THE COMPOUND $11\text{Ta}_2\text{O}_5 \cdot 4\text{WO}_3$ ($m = 13$) ($\text{CuK}\alpha$ RADIATION)^a

hkl^b	d_{obsd}	$2\theta_{\text{obsd}}$	$2\theta_{\text{calcd}}$	I^c
150	5.160	17.17	17.18	14
0,10,0	4.756	18.64	18.64	5
001	3.852	23.07	23.04	130
1,11,0	3.534	25.18	25.17	12
1,13,0	3.142	28.38	28.38	148
151	3.087	28.90	28.88	23
200	3.068	29.08	29.07	100
220	3.044	29.32	29.32	28
0,16,0	2.9742	30.02	30.04	5
1,15,0	2.8177	31.73	31.74	10
280	2.7274	32.81	32.81	6
1,11,1	2.6063	34.38	34.39	4
2,10,0	2.5773	34.78	34.76	6
1,13,1	2.4358	36.87	36.86	95
201	2.4025	37.40	37.42	53
221	2.3908	37.59	37.61	33
1,15,1	2.2756	39.57	39.58	3
281	2.2265	40.48	40.48	7
2,10,1	2.1436	42.12	42.12	5
1,21,0	2.1243	42.52	42.51	5

TABLE V (continued)

330	2.0287	44.63	44.62	4
2,18,0	2.0015	45.27	45.25	7
350	1.9989	45.33	45.30	4
1,23,0 } 370 }	1.9592	46.30	{46.29 46.30	6
002	1.9283	47.09	47.09	50
390	1.9077	47.63	47.62	3
1,21,1	1.8603	48.92	48.90	8
3,11,0	1.8493	49.23	49.23	30
0,26,0	1.8295	49.80	49.81	42
3,13,0	1.7863	51.09	51.11	25
351	1.7756	51.42	51.42	13
1,23,1	1.7471	52.32	52.32	10
3,15,0	1.7194	53.23	53.24	21
3,11,1	1.6679	55.01	55.02	8
2,24,0	1.6643	55.14	55.12	6
0,26,1	1.6530	55.55	55.56	90
1,13,2	1.6442	55.87	55.89	33
202	1.6327	56.30	56.30	18
222	1.6287	56.45	56.44	14
3,13,1	1.6206	56.76	56.76	55
3,19,0	1.5838	58.20	58.19	5
282	1.5749	58.56	58.58	11
2,26,0	1.5713	58.71	58.71	31
400	1.5345	60.26	60.26	8

TABLE V (continued)

420	1.5313	60.40	60.40	6
2,24,1	1.5286	60.52	60.52	6
3,21,0 } 3,17,1 }	1.5181	60.98	{ 60.98 60.98	6
460	1.5068	61.49	61.50	5
1,31,0	1.4885	62.33	62.33	5
480	1.4859	62.45	62.45	5
3,19,1	1.4652	63.43	63.43	5
2,26,1	1.4550	63.93	63.92	58
2,16,2	1.4311	65.13	65.13	6
401	1.4262	65.38	65.40	17
421	1.4231	65.54	65.53	10
3,21,1	1.4130	66.07	66.08	6
352	1.3883	67.40	67.40	7
372	1.3743	68.18	68.18	6
4,10,1	1.3658	68.66	68.67	6
3,11,2	1.3345	70.51	70.49	4
0,26,2	1.3268	70.98	70.96	23
3,13,2	1.3102	72.02	72.02	10
003	1.2854	73.63	73.62	7

^a Specimen heated to 1574°C for 68 hr in a sealed Pt tube and quenched.

^b Indexed on the basis of a C-centered orthorhombic unit cell $a = 6.138 \text{ \AA}$, $b = 47.56 \text{ \AA}$, $c = 3.857 \text{ \AA}$ with the aid of intensities observed from single-crystal diffractometer data.

^c Observed intensity, peak heights.

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