

Effect of Oxide Additions on the Polymorphism of Tantalum Pentoxide (System Ta_2O_5 - TiO_2)

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The phase equilibrium relationships of the TiO_2 - Ta_2O_5 system were determined in air. An equimolar compound, $TiTa_2O_7$, was found to melt congruently at about 1662 °C and have a monoclinic unit cell $a=20.297$ Å, $b=3.804$ Å, $c=11.831$ Å, $\beta=120^\circ14'$, apparently isostructural with $TiNb_2O_7$. In addition, two other compounds are postulated to occur at about $TiO_2:49Ta_2O_5$ and $TiO_2:7Ta_2O_5$ and to dissociate at about 1230 and 1190 °C, respectively. TiO_2 apparently accepts a maximum of 9 mole percent Ta_2O_5 in solid solution at 1630 °C. Two eutectics occur in the system at 54 mole percent Ta_2O_5 and 1650 °C and 31 mole percent Ta_2O_5 and 1630 °C.

The high temperature form of Ta_2O_5 is apparently triclinic at room temperature with $a=3.801$ Å, $b=3.785$ Å, $c=35.74$ Å, $\alpha=90^\circ54.4'$, $\beta=90^\circ11.5'$, and $\gamma=89^\circ59.9'$. A metastable transition occurs at 320 °C to a monoclinic form which inverts to tetragonal at 920 °C with $a=3.81$ Å, $c=36.09$ Å. Several intermediate morphotropic phases are found with up to 9 mole percent TiO_2 in solid solution.

Key Words: Phase equilibria, polymorphism, tantalum pentoxide, titanium dioxide.

1. Introduction

The increased commercial importance of tantalum oxide together with the apparent ambiguity of its phase relationships have served as an impetus to investigate both the pure oxide and the interaction of Ta_2O_5 with other oxides. As part of a continuing program of phase equilibria studies, it was decided to investigate the effect of various impurities and environments on Ta_2O_5 . Titanium dioxide was selected to be studied in air because the cation has a radius similar in size to Ta^{+5} but differing in oxidation state. Investigations of other tantalate systems are in progress and the results will be reported subsequently.

No systematic attempt to study the phase equilibrium relationships in the system Ta_2O_5 - TiO_2 has been previously reported. However, some attempts to investigate the polymorphs of Ta_2O_5 have been described in the literature [1–12].¹ The exact relationships of the various polymorphs are still in doubt because of the lack of suitable single crystals needed to properly characterize the phases. However, it has been concluded by various workers [10, 11] that Ta_2O_5 has at least two structurally different polymorphs, with a reversible phase transition occurring at about 1360 ± 10 °C [11].

2. Materials

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

TiO_2 —Si present in amounts less than 0.01 percent, Cu present in amounts less than 0.001 percent, Ca present in amounts less than 0.0001 percent.

Ta_2O_5 —Al and Si present in amounts less than 1.0 percent; Cu and Mg present in amounts less than 0.1 percent; Ag, Ca, and Mn each present in amounts less than 0.0001 percent.

3. Specimen Preparation and Test Methods

Three-gram batches of various proportions of Ta_2O_5 and TiO_2 were weighed, mixed in a mechanical shaker for approximately 10 min, and pressed into disks at about 10^4 psi. The disks were placed on platinum setters and calcined in air at 1000 °C for 16 hr. Following this preliminary heat treatment portions of the ground specimen were placed in platinum alloy tubes and heated in the quenching furnace at various temperatures for different periods of time.

The tubes containing the specimens were quenched into ice water and examined by x-ray diffraction techniques. A high-angle recording Geiger counter-

¹ Figures in brackets indicate the literature references at the end of this paper.

diffractometer and Ni-filtered Cu radiation was used in the study. The Geiger counter traversed the specimen at 1/4 deg/min. and radiation was recorded on the chart at 1 deg-2 θ /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 a quenching furnace and an induction furnace. Because of the temperature limitation of the quenching furnace, melting points above 1800 °C were determined with an induction furnace. Some duplicate determinations below 1800 °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 consisted of an iridium crucible and cover which acted as the susceptor and specimen container. A small fragment of the calcined material was placed in the iridium crucible on an iridium setter or button and heated to the desired temperature for about 2 min to achieve thermal equilibrium. Apparent temperatures were measured with a calibrated, disappearing filament-type optical pyrometer which was sighted through a 45 deg 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 were calibrated frequently against the melting point of Au (1063 °C), Pd (1552 °C), and Pt (1769 °C). In addition, the measuring system of the induction furnace was calibrated against the melting point of Rh (1960 °C). Temperatures reported in the present study are considered accurate to within ± 10 °C below 1650 °C and to within ± 20 °C above. 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 container or iridium setter generally established the beginning of melting. In quenched specimens, complete melting was established by the formation of a meniscus. Similarly, the slumping or loss of shape of the inductively heated specimens established complete melting.

4. Results and Discussion

The phase diagram, figure 1, for the system Ta₂O₅-TiO₂ in air was constructed from data in table 1 (part A, B and C). Circles represent composition and temperature of experiments conducted in the quench-

ing furnace; triangles represent those conducted with a high temperature x-ray furnace. A triangle with an arc under the base represents experiments conducted in both types of furnaces at the same temperature and a square represents those conducted in an induction furnace. Heavy dashed lines delineate regions of the phase diagram where equilibrium could not be unequivocally established by the experimental methods employed in this study.

Alternate dotted and dashed lines represent metastable equilibrium relationships on the phase diagram.

Several melting points of Ta₂O₅ have been reported [11, 13] previously. The melting point of Ta₂O₅ determined in this investigation was 1887 \pm 20 °C which is in reasonable agreement with the previously reported value of Reisman et al., [11]. The numerous reported melting points of TiO₂ have been tabulated by Schneider [14]. A redetermination of the melting point of TiO₂ was not attempted because of the inherent problems associated with the determination.

4.1. L-Ta₂O₅ and Related Phases²

Brauer [1] reported a structural modification of Ta₂O₅ which was isostructural with the low temperature form of Nb₂O₅. Hahn [2] listed x-ray diffraction powder data for a similar form of Ta₂O₅.

The x-ray diffraction pattern of L-Ta₂O₅ is characterized by strong subcell lines and numerous weak superstructure lines. Lehovc [3] indicated that the major lines of the x-ray powder pattern for Ta₂O₅ could be accounted for on the basis of an orthorhombic subcell $a' = 6.20$ Å, $b' = 3.66$ Å, and $c' = 3.89$ Å. The powder pattern given in reference 4 failed to account for the superstructure lines on the basis of a similar size subcell. Zaslavskii [5] and Harvey and Wilman [6] on the basis of single crystal data, accounted for the superstructure lines in their respective patterns by increasing the b axis to $b = 44.02$ Å ($12b'$) and $b = 69.6$ Å ($19b'$), respectively. Frevel and Rinn [7] attempted to account for the superstructure lines of their powder pattern by selecting a monoclinic cell $a = 7.32$ Å ($2b'$), $b = 15.55$ Å ($4c'$), $c = 10.79$ Å, $\beta = 120^\circ 36'$. However, Terao [8] found that his powder pattern could be indexed only by utilizing approximately twice the previous monoclinic c axis ($c = 21.549$ Å).

The subcell of the low temperature form of Ta₂O₅ used for this study can be indexed on the basis of an orthorhombic cell $a' = 6.19$ Å, $b' = 3.67$ Å, $c' = 3.89$ Å. The various published unit cell constants [4-9], including those employed by the present authors as well as those derived by others from single crystal and electron diffraction data, failed to provide suitable hkl values to account for the superstructure reflections in the Ta₂O₅ used in this study. Therefore, no x-ray diffraction pattern for low Ta₂O₅ is given. Although the published d -spacings derived from the subcell of the various patterns of Ta₂O₅ agree with those found to occur in the present work, some reflections resulting from the superstructure have not been reported previously. The variance of superstructure reflections

² L-Ta₂O₅ represents the low temperature polymorph of Ta₂O₅.

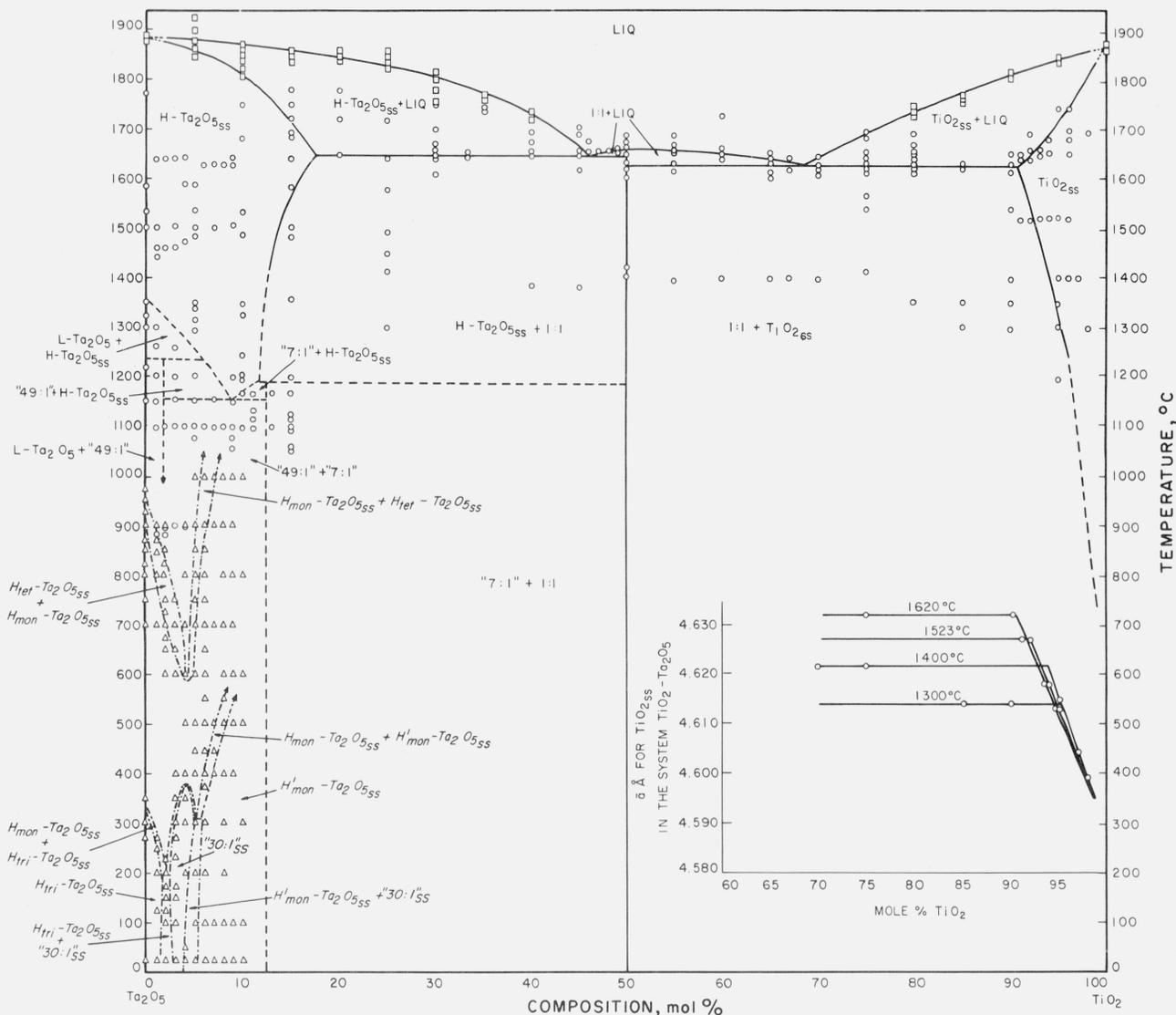


FIGURE 1. Phase equilibrium diagram for the system $\text{TiO}_2\text{-Ta}_2\text{O}_5$.

H-Ta₂O₅—High temperature form of Ta₂O₅.
H_{tet}-Ta₂O₅—Tetragonal form.
H_{mon}-Ta₂O₅—Monoclinic metastable form.
H_{tri}-Ta₂O₅—Triclinic metastable form.
"30:1"—A metastable monoclinic solid solution phase occurring at about 30Ta₂O₅:TiO₂.
H'_{mon}-Ta₂O₅—A morphotropic modification of H_{mon}-Ta₂O₅.
L-Ta₂O₅—Low temperature form of Ta₂O₅.
"49:1"—A L-Ta₂O₅ type compound postulated to occur at about 49Ta₂O₅:TiO₂.
"7:1"—A L-Ta₂O₅ type compound postulated to occur at about 7Ta₂O₅:TiO₂.
I—I-TiTa₂O₇.
Liq.—Liquid.
ss—Solid solution

○—Compositions and temperatures of experiments conducted in quench furnace.
△—Compositions and temperatures of experiments conducted in high temperature x-ray furnace.
□—Compositions and temperatures of experiments conducted in an iridium crucible induction furnace.
△—Compositions and temperatures of experiments conducted in both the quenching and high temperature x-ray furnaces.

For clarity not all experimental data appearing in table 1 are plotted on this diagram. Heavy dashed lines represent regions where equilibrium was not unequivocally established. Alternate dot-dash lines represent metastable equilibrium. Quotation marks around a composition indicate that the exact stoichiometry is not known.

may be due, among other things, to a nonequilibrium low-temperature poorly crystallized material lacking sufficient energy for proper ordering of the superstructure. Similarly the influence of anion and cation impurities on phase formation has essentially not been reported. In fact, most of the materials used for the previously reported Ta₂O₅ x-ray diffraction patterns apparently were not characterized by spectrographic analyses.

In the present work, TiO₂ additions were found to have a significant effect on the nature of the L-Ta₂O₅

type x-ray diffraction powder patterns. Specimens were prepared at close intervals, up to 13 mole percent TiO₂. Since equilibrium was difficult to achieve on heating, these specimens were equilibrated at 1500 °C and reheated at about 1100 °C in excess of 200 hr. A cursory examination of the x-ray data derived from these quenched specimens would suggest a solid solution between L-Ta₂O₅ and TiO₂ up to about 13 percent. However, these x-ray patterns show additional reflections derived from a superstructure. Moreover, the superstructure reflections shift significantly with the

TABLE 1. Experimental data for compositions in the system TiO_2 - Ta_2O_5
Part A. Quenching data

Composition		Heat treatments				Physical observation	Results
		Initial ^a		Final ^b			
TiO ₂	Ta ₂ O ₅	Temp	Time	Temp	Time		X-ray diffraction analyses ^c
Mole %	Mole %	°C	Hour	°C	Hour		
0	100			1220	264	Not melted.	L-Ta ₂ O ₅ .
				1306	16do.....	Do.
				1350	65do.....	H-Ta ₂ O ₅ + L-Ta ₂ O ₅ .
				1506	24do.....	H-Ta ₂ O ₅ .
				1535	4.5do.....	Do.
				1775	6do.....	Do.
				1329	336do.....	L-Ta ₂ O ₅ .
				1506	24do.....	Do.
				1204	72do.....	Do.
				1462	19do.....	H _{trt} -Ta ₂ O _{5ss} .
1	99			1506	24do.....	Do.
				1640	4.5do.....	Do.
				1641	16do.....	Do.
				1506	24do.....	L-Ta ₂ O ₅ phase(s).
				1100	432do.....	Do.
				1155	66do.....	H _{trt} -Ta ₂ O _{5ss} .
				1204	72do.....	L-Ta ₂ O ₅ phase(s) + H _{trt} -Ta ₂ O _{5ss} .
				1260	112do.....	Do.
				1299	90do.....	Do.
				1640	4.5do.....	H _{trt} -Ta ₂ O _{5ss} .
2	98			1461	19do.....	H _{trt} -Ta ₂ O _{5ss} + "30:1" _{ss} .
				1640	4.5do.....	Do.
				1641	19do.....	Do.
				887	65do.....	Do.
				1461	19do.....	Do.
				1640	4.5do.....	Do.
				1641	19do.....	Do.
				901	67do.....	Do.
				1100	432do.....	L-Ta ₂ O ₅ phase(s).
				1200	64do.....	"30:1" _{ss} .
3	97			1461	16do.....	Do.
				1506	24do.....	Do.
				1641	16do.....	Do.
				901	67do.....	Do.
				1100	432do.....	L-Ta ₂ O ₅ phase(s).
				1155	66do.....	"30:1" _{ss} + L-Ta ₂ O ₅ phase(s).
				1260	112do.....	Do.
				1471	16do.....	"30:1" _{ss} .
				1590	20do.....	Do.
				1641	16do.....	Do.
4	96			1471	16do.....	Do.
				901	67do.....	Do.
				1100	432do.....	L-Ta ₂ O ₅ phase(s).
				1297	20do.....	H _{mon} '-Ta ₂ O _{5ss} + L-Ta ₂ O ₅ phase(s).
				1316	65do.....	Do.
				1345	65do.....	Do.
				1486	16do.....	H _{mon} '-Ta ₂ O _{5ss} + "30:1" _{ss} .
				1506	72do.....	Do.
				1078	72do.....	Do.
				1104	65do.....	L-Ta ₂ O ₅ phase(s).
5	95			1150	16do.....	Do.
				1155	64do.....	H _{mon} '-Ta ₂ O _{5ss} + L-Ta ₂ O ₅ phase(s).
				1201	16do.....	L-Ta ₂ O ₅ phase(s) + H _{mon} '-Ta ₂ O _{5ss} .
				876	16do.....	H _{mon} '-Ta ₂ O _{5ss} .
				950	19do.....	H _{mon} '-Ta ₂ O _{5ss} + "30:1" _{ss} .
				1297	20do.....	Do.
				1351	2do.....	Do.
				800	2.5do.....	Do.
				1628	16do.....	Do.
				1097	336do.....	L-Ta ₂ O ₅ phase(s).
6	94			1506	72do.....	H _{mon} '-Ta ₂ O _{5ss} .
				1628	16do.....	Do.
				1506	72do.....	L-Ta ₂ O ₅ phase(s).
				1155	60do.....	H _{mon} '-Ta ₂ O _{5ss} + L-Ta ₂ O ₅ phase(s).
				1628	16do.....	H _{mon} '-Ta ₂ O _{5ss} .
				1097	336do.....	L-Ta ₂ O ₅ phase(s).
				1628	16do.....	H _{mon} '-Ta ₂ O _{5ss} .
				1643	24do.....	L-Ta ₂ O ₅ phase(s).
				1506	24do.....	H _{mon} '-Ta ₂ O _{5ss} .
				1055	112do.....	Do.
7	93			1078	72do.....	L-Ta ₂ O ₅ phase(s) + H _{mon} '-Ta ₂ O _{5ss} .
				1097	336do.....	Do.
				1104	72do.....	L-Ta ₂ O ₅ phase(s).
				1104	72do.....	L-Ta ₂ O ₅ phase(s) + H _{mon} '-Ta ₂ O _{5ss} .
				1150	16do.....	H _{mon} '-Ta ₂ O _{5ss} + L-Ta ₂ O ₅ phase(s).
				1155	64do.....	Do.
				1201	16do.....	H _{mon} '-Ta ₂ O _{5ss} .
				1345	65do.....	Do.
				1486	16do.....	Do.
				1504	24do.....	Do.
8	92			1535	4.5do.....	Do.
				1560	168do.....	Do.
				1580	2do.....	Do.
				1640	16do.....	Do.
				1684	16do.....	Do.
				1400	6do.....	Do.
				1486	16do.....	Do.
				924	89do.....	H _{mon} '-Ta ₂ O _{5ss} .
				1124	65do.....	Do.
				1247	48do.....	Do.
9	91			1400	6do.....	Do.
				1486	16do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.
10	90			1400	6do.....	Do.
				1486	16do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.
				1400	6do.....	Do.

See footnotes at end of table, p. 181.

TABLE 1. Experimental data for compositions in the system $TiO_2-Ta_2O_5$ —Continued
Part A. Quenching data

Composition		Heat treatments				Physical observation	Results
TiO ₂	Ta ₂ O ₅	Initial ^a		Final ^b			
		Temp	Time	Temp	Time		
Mole %	Mole %	°C	Hour	°C	Hour		X-ray diffraction analyses ^c
		1486	16		do.....	
		1535	4.5	1351	16do.....	H _{mon} -Ta ₂ O _{5ss} .
		1580	2	1097	192do.....	L-Ta ₂ O ₅ phase(s).
				1203	312do.....	H _{mon} -Ta ₂ O _{5ss} + L-Ta ₂ O ₅ phase(s).
11	89	1580	2	1097	192do.....	H _{mon} -Ta ₂ O _{5ss} .
		1580	2	1097	192do.....	L-Ta ₂ O ₅ phase(s).
				1132	64do.....	L-Ta ₂ O ₅ phase(s) + H _{mon} -Ta ₂ O _{5ss} .
				1167	168do.....	Do.
				1197	168do.....	L-Ta ₂ O ₅ phase(s).
13	89	1580	2	1097	168do.....	H _{mon} -Ta ₂ O _{5ss} .
				1167	168do.....	L-Ta ₂ O ₅ phase(s) + 1:1.
15	85	1400	6	1167	168do.....	L-Ta ₂ O ₅ phase(s) + H _{mon} -Ta ₂ O _{5ss} + 1:1.
				1358	7do.....	H _{mon} -Ta ₂ O _{5ss} .
				1470	16do.....	
				1480	16do.....	
				1486	16do.....	H _{mon} -Ta ₂ O _{5ss} + 1:1.
				1508	16do.....	Do.
				1580	16do.....	
				1640	16do.....	H _{mon} -Ta ₂ O _{5ss} .
				1687	16do.....	Do.
				1695	.5do.....	Do.
				1721	.16	Partially melted.	
				1750	.16do.....	H _{mon} -Ta ₂ O _{5ss} + Liq.
				1781	.16do.....	Do.
		1400	6			Not melted.	
		1470	16	1127	192do.....	H _{mon} -Ta ₂ O _{5ss} + L-Ta ₂ O ₅ phase(s) + 1:1.
		1406	6		do.....	
		1480	16	1167	168do.....	H _{mon} -Ta ₂ O _{5ss} + L-Ta ₂ O ₅ phase(s) + 1:1.
		1406	6		do.....	
		1486	16	924	89do.....	H _{mon} -Ta ₂ O _{5ss} + 1:1.
				1097	168do.....	L-Ta ₂ O ₅ phase(s) + 1:1.
		1406	6		do.....	
		1508	16	1055	112do.....	H _{mon} -Ta ₂ O _{5ss} + L-Ta ₂ O ₅ phase(s) + 1:1.
				1060	19do.....	Do.
				1091	120do.....	L-Ta ₂ O ₅ phase(s) + H _{mon} -Ta ₂ O _{5ss} + 1:1.
20	80	1406	6		do.....	
				1640	20do.....	H _{mon} -Ta ₂ O _{5ss} + 1:1.
				1651	.16	Partially melted.	H _{mon} -Ta ₂ O _{5ss} + 1:1 Liq.
				1687	.16do.....	
				1721	.16do.....	H _{mon} -Ta ₂ O _{5ss} + 1:1 Liq.
				1780	.16do.....	Do.
25	75	1406	6			Not melted.	
				1413	17do.....	H _{mon} -Ta ₂ O _{5ss} + 1:1.
				1450	3do.....	Do.
				1576	16do.....	Do.
				1646	16do.....	Do.
				1722	1	Partially melted.	Do.
		1400	6			Not melted.	
		1646	16	1300	16do.....	H _{mon} -Ta ₂ O _{5ss} + 1:1.
30	70	1400	6		do.....	
				1612	2do.....	H _{mon} -Ta ₂ O _{5ss} + 1:1.
				1642	0.16do.....	Do.
				1646	1do.....	Do.
				1652	1	Partially melted.	Do.
				1656	0.16do.....	
				1662	.16do.....	
				1671	.16do.....	
				1704	.33do.....	
				1726	.16do.....	
				1753	.16do.....	
				1759	.16do.....	
33.33	66.67	1400	6			Not melted.	
				1649	.16do.....	1:1 + H _{mon} -Ta ₂ O _{5ss} .
				1656	.16	Partially melted.	
35	65	1400	6			Not melted.	
				1735	.08	Partially melted.	
				1745	.08do.....	
40	60	1400	6			Not melted.	
				1388	113do.....	1:1 + H _{mon} -Ta ₂ O _{5ss} .
				1650	1do.....	Do.
				1660	0.08	Partially melted.	
				1679	.16do.....	1:1-Liq. + H _{mon} -Ta ₂ O _{5ss} .
				1698	.16do.....	Do.
				1722	.16do.....	
				1741	.16	Completely melted.	
45	55	1400	6			Not melted.	
				1388	113do.....	1:1 + H _{mon} -Ta ₂ O _{5ss} .
				1621	0.16do.....	
				1651	.16do.....	
				1653	.16	Partially melted.	
				1660	.16do.....	
				1666	.16do.....	
				1698	.16	Completely melted.	
				1708	.16do.....	
46	54	1400	6			Not melted.	
				1652	.16do.....	
				1662	.16	Partially melted.	
				1680	.16	Completely melted.	

See footnotes at end of table, p. 181.

TABLE 1. Experimental data for compositions in the system TiO₂-Ta₂O₅—Continued
Part A. Quenching data

Composition		Heat treatments				Physical observation	Results
		Initial ^a		Final ^b			
TiO ₂	Ta ₂ O ₅	Temp	Time	Temp	Time		X-ray diffraction analyses ^c
Mole %	Mole %	°C	Hour	°C	Hour		
47	53	1400	6	1662	.16	Not melted.	
48	52	1400	6	1662	.16	Completely melted.	
49	51	1400	6	1662	.16	Not melted.	
50 (1:1)	50	1406	6	1662	.16	Completely melted.	
				1669	.16	Not melted.	
				1402	18do.....	1:1 + TiO _{2SS} + H _{mon} -Ta ₂ O _{5SS} .
				1428	19do.....	1:1.
				1607	19do.....	Do.
				1626	16do.....	Do.
				1639	0.08do.....	Do.
				1656	.16do.....	Do.
				1663	19do.....	Do.
				1664	0.16	Completely melted.	1:1 + Liq.
				1678	1do.....	
				1690	3do.....	1:1 + Liq.
55	45	1400	22	1400	22	Not melted.	1:1 + TiO _{2SS} + H _{mon} -Ta ₂ O _{5SS} (nonequilibrium).
				1621	0.16	Partially melted ^d	1:1 + TiO _{2SS} .
				1636	.16	Partially melted.	1:1 + TiO _{2SS} .
				1653	.08do.....	Do.
				1661	.16do.....	
				1672	.16	Completely melted.	
60	40			1403	16do.....	
				1645	0.16	Partially melted.	
				1648	.16do.....	
				1654	.16	Completely melted.	
				1662	.16do.....	
				1730	.16do.....	
65	35			1403	16	Not melted.	1:1 + TiO _{2SS} .
				1606	0.16do.....	Do.
				1619	.16	Partially melted ^d	Do.
				1636	.16do.....	1:1 + Liq.
				1641	.16do.....	
				1647	.16	Completely melted.	
66.67	33.33			1656	.16do.....	
				1405	16	Not melted.	1:1 + TiO _{2SS} .
				1628	0.16	Partially melted. ^d	
				1645	.16	Completely melted.	
70	30			1405	16	Not melted.	1:1 + TiO _{2SS} .
				1611	0.16do.....	
				1620	.16	Partially melted. ^d	
				1624	.16do.....	
				1629	.16do.....	
				1631	.16	Completely melted.	
				1649	.16do.....	
75	25			1413	19	Not melted.	TiO _{2SS} + 1:1.
				1420	4do.....	
				1542	19do.....	TiO _{2SS} + 1:1.
				1569	2do.....	Do.
				1611	0.16do.....	
				1612	1do.....	TiO _{2SS} + 1:1.
				1619	0.16do.....	
				1625	1	Partially melted. ^d	TiO _{2SS} + 1:1.
				1626	0.16do.....	Do.
				1633	1	Partially melted.	
				1638	0.16do.....	TiO _{2SS} + Liq.
				1643	.16do.....	Do.
				1644	.16do.....	
80	20			1658	1do.....	
				1689	0.16do.....	
				1700	.16	Completely melted.	
				1357	16do.....	
				1617	0.25	Partially melted. ^d	
				1620	.25do.....	
				1623	.25do.....	
				1626	.25do.....	
				1627	.25do.....	
				1631	.25	Partially melted.	TiO _{2SS} + Liq.
				1642	.08do.....	Do.
				1649	.25do.....	
85	15			1674	.08do.....	
				1694	.16do.....	
				1725	.16do.....	
				1742	.08do.....	
				1303	16	Not melted.	TiO _{2SS} + 1:1.
				1357	16do.....	
				1627	0.16	Partially melted. ^d	TiO _{2SS} + 1:1.
				1630	.16	Partially melted.	TiO _{2SS} + Liq.
90	10			1303	16	Not melted.	TiO _{2SS} + 1:1.
				1357	16do.....	
				1406	16do.....	TiO _{2SS} + 1:1.
				1620	0.25do.....	Do.
				1624	1do.....	
				1628	0.16do.....	TiO _{2SS} + 1:1.
				1632	1	Partially melted.	TiO _{2SS} + Liq.
1542	19	1659	1do.....			
		900	19do.....	TiO _{2SS} + 1:1.		

See footnotes at end of table, p. 181.

TABLE 1. Experimental data for compositions in the system TiO₂-Ta₂O₅—Continued

Part A. Quenching data

Composition		Heat treatments				Results	
TiO ₂	Ta ₂ O ₅	Initial ^a		Final ^b		Physical observation	X-ray diffraction analyses ^c
		Temp	Time	Temp	Time		
Mole %	Mole %	°C	Hour	°C	Hour		
91	9			1523	19	Not melted.	Do.
				1637	1	Partially melted.	TiO _{2ss} + Liq.
				1643	0.25do.....	
				1653	.16do.....	
				1523	19	Not melted.	TiO _{2ss} + 1:1.
92	8			1647	0.16do.....	Do.
				1660	.16	Partially melted.	TiO _{2ss} + Liq.
93	7			1523	19	Not melted.	TiO _{2ss} .
				1651	19do.....	Do.
94	6			1666	19	Partially melted.	TiO _{2ss} + Liq.
				1396	1.5	Not melted.	
				1528	65do.....	TiO _{2ss} .
				1659	0.16do.....	
				1694	.16	Partially melted.	TiO _{2ss} + Liq.
95	5			1197	113	Not melted.	TiO _{2ss} + 1:1.
				1303	16do.....	TiO _{2ss} .
				1357	16do.....	Do.
				1406	16do.....	Do.
				1528	65do.....	Do.
				1623	2do.....	Do.
				1749	0.16	Partially melted.	TiO _{2ss} + Liq.
				1197	113	Not melted.	TiO _{2ss} + 1:1.
96	4	1357	16	1528	65do.....	TiO _{2ss} .
				1657	19do.....	Do.
				1659	0.16do.....	Do.
				1684	.16do.....	Do.
				1700	.16do.....	Do.
				1750	.16do.....	Do.
				1000	.16do.....	Do.
				1406	16do.....	Do.
97	3			1406	16do.....	Do.
				1303	16do.....	Do.

^a All specimens were initially calcined at 1000 °C for 10 hr with heating and cooling rates of approximately 4 °C/min. Small portions of this calcine were then reheated for the designated time of one or more designated higher temperatures and generally quenched in Pt tubes.

^b After the initial heat treatment(s) all specimens were reheated in Pt tubes to the indicated temperature.

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

H_{mon}-Ta₂O₅—Monoclinic metastable form.

H_{tri}-Ta₂O₅—Triclinic metastable form.

"30:1"—Metastable monoclinic solid solution phase occurring at about 30Ta₂O₅:TiO₂.

H_{mon}—A morphotropic modification of H_{mon}-Ta₂O₅.

L-Ta₂O₅ phase(s)—One or more phases with an x-ray powder diffraction pattern similar to low temp. form of Ta₂O₅.

1:1—TiTa₂O₇.

Liq.—Metastable phase which forms only from the quenched liquid and gives a characteristic but very poorly defined x-ray pattern.

ss—Solid solution.

"—"—Indicate that the exact stoichiometry is not known.

^d Specimens appeared partially melted below the solidus and were interpolated to provide the best approach to binary equilibrium.

TABLE 1.

Part B: Induction furnace data

Compo- sition ^a		Temp.	Observation	Compo- sition ^a		Temp.	Observation
TiO ₂	Ta ₂ O ₅			TiO ₂	Ta ₂ O ₅		
5	100	1872	Not melted.	30	70	1861	Completely melted.
		1882	Do.			1757	Not melted.
		1891	Melted.			1766	Do.
5	95	1850	Not melted.	35	65	1781	Do.
		1861	Partially melted.			1801	Do.
		1868	Do.			1810	Partially melted.
		1882	Completely melted.			1819	Completely melted.
		1903	Do.			1762	Partially melted.
10	90	1924	Do.	40	60	1776	Completely melted.
		1809	Not melted.			1726	Partially melted.
		1821	Partially melted.			1744	Completely melted.
		1840	Do.			1735	Partially melted.
15	85	1855	Do.	80	20	1742	Do.
		1865	Completely melted.			1757	Completely melted.
		1872	Do.			1762	Partially melted.
		1840	Partially melted.			1770	Do.
		1852	Do.			1778	Do.
20	80	1864	Completely melted.	90	10	1810	Do.
		1840	Partially melted.			1820	Completely melted.
		1850	Completely melted.			1840	Partially melted.
25	75	1860	Do.	95	5	1845	Completely melted.
		1829	Partially melted.			1860	Not melted.
		1840	Completely melted.			1875	Completely melted.

^a All specimens were initially calcined at 1000 °C for 10 hr with heating and cooling rates of approximately 4 °C/min.

TABLE 1.

Part C: High temperature x-ray diffraction experimental data for selected compositions in the system TiO₂-Ta₂O₅

Composition		Previous heat treatment		Temp.	Results ^a				
TiO ₂	Ta ₂ O ₅	Temp.	Time						
Mole %	Mole %	°C	hr	°C					
0	100	1000	10	1000	L-Ta ₂ O ₅ .				
		1220	264			25	Do.		
						500	Do.		
1	99	1000	10	1000	H _{tri} -Ta ₂ O ₅ .				
		1640	16			25	Do.		
1	99	1000	10	200	H _{mon} -Ta ₂ O ₅ .				
						1640	4.5	270	Do.
								300	Do.
								350	Do.
								700	Do.
								750	Do.
								800	Do.
								825	Do.
								850	Do.
								875	Do.
1	99	1000	10	200	H _{mon} -Ta ₂ O ₅ + H _{tri} -Ta ₂ O ₅ .				
						1640	4.5	900	Do.
								925	Do.
								950	Do.
		975	Do.						
		125	Do.						
		200	Do.						

See footnotes at end of table, p. 182.

TABLE 1.—Continued

Part C: High temperature x-ray diffraction experimental data for selected compositions in the system TiO₂-Ta₂O₅

Composition		Previous heat treatment		Temp.	Results ^a				
TiO ₂	Ta ₂ O ₅	Temp.	Time						
Mole %	Mole %	°C	hr	°C					
2	98	1000 1640	10 16	250	Do.				
				275	H _{mon} -Ta ₂ O _{5ss} .				
				700	Do.				
				800	Do.				
				825	Do.				
				850	H _{tet} -Ta ₂ O _{5ss} + H _{mon} -Ta ₂ O _{5ss} .				
				875	Do.				
				900	H _{tet} -Ta ₂ O _{5ss} .				
					H _{tri} -Ta ₂ O _{5ss} + "30:1" _{ss} .				
				25	Do.				
				100	Do.				
				125	Do.				
				150	Do.				
				175	Do.				
				200	H _{tri} -Ta ₂ O _{5ss} + H _{mon} -Ta ₂ O _{5ss} .				
				225	H _{mon} -Ta ₂ O _{5ss} .				
				600	Do.				
				650	Do.				
675	Do.								
700	Do.								
725	Do.								
750	H _{mon} -Ta ₂ O _{5ss} + H _{tet} -Ta ₂ O _{5ss} .								
775	Do.								
800	Do.								
825	Do.								
850	H _{tet} -Ta ₂ O _{5ss} .								
900	Do.								
3	97	1000 1640	10 40		"30:1" _{ss} .				
				25	Do.				
				150	Do.				
				175	Do.				
				200	Do.				
				235	Do.				
				275	Do.				
				300	Do.				
				350	H _{mon} -Ta ₂ O _{5ss} .				
				400	Do.				
				600	Do.				
				650	H _{mon} -Ta ₂ O _{5ss} + H _{tet} -Ta ₂ O _{5ss} .				
				700	H _{tet} -Ta ₂ O _{5ss} + H _{mon} -Ta ₂ O _{5ss} .				
				750	Do.				
				775	Do.				
				800	H _{tet} -Ta ₂ O _{5ss} .				
				4	96	1000 1590	10 20	25	"30:1" _{ss} + H _{mon} -Ta ₂ O _{5ss} .
								50	Do.
200	"30:1" _{ss} .								
300	Do.								
350	Do.								
400	H _{mon} -Ta ₂ O _{5ss} .								
500	Do.								
600	H _{mon} -Ta ₂ O _{5ss} + H _{tet} -Ta ₂ O _{5ss} .								
700	H _{tet} -Ta ₂ O _{5ss} .								
800	Do.								
900	Do.								
5	95	1000 1486	10 16						H _{mon} -Ta ₂ O _{5ss} + "30:1" _{ss} .
								25	Do.
								200	Do.
								100	Do.
								300	Do.
								400	H _{mon} -Ta ₂ O _{5ss} .
								450	Do.
				500	Do.				
				600	Do.				
				700	H _{tet} -Ta ₂ O _{5ss} + H _{mon} -Ta ₂ O _{5ss} .				
				750	Do.				
				800	H _{tet} -Ta ₂ O _{5ss} .				
				850	Do.				
				900	Do.				
				1000	Do.				
				6	94	1000 1628	10 16		H _{mon} -Ta ₂ O _{5ss} .
								25	Do.
								100	Do.
200	Do.								
300	Do.								
325	H _{mon} -Ta ₂ O _{5ss} + H _{mon} -Ta ₂ O _{5ss} .								
375	Do.								
400	Do.								
450	H _{mon} -Ta ₂ O _{5ss} .								
500	Do.								
550	Do.								
600	Do.								
650	Do.								
700	Do.								
750	Do.								
800	Do.								

TABLE 1.—Continued

Part C: High temperature x-ray diffraction experimental data for selected compositions in the system TiO₂-Ta₂O₅

Composition		Previous heat treatment		Temp.	Results ^a				
TiO ₂	Ta ₂ O ₅	Temp.	Time						
Mole %	Mole %	°C	hr	°C					
7	93	1000 1563	10 230	850	Do.				
				900	H _{mon} -Ta ₂ O _{5ss} + H _{tet} -Ta ₂ O _{5ss} .				
				930	Do.				
				1000	H _{tet} -Ta ₂ O _{5ss} .				
					H _{mon} -Ta ₂ O _{5ss} .				
				25	Do.				
				100	Do.				
				200	Do.				
				300	Do.				
				400	Do.				
				450	Ta ₂ O _{5ss} ^b .				
				500	Do.				
				700	Do.				
				900	Do.				
				1000	Do.				
				1100	H _{tet} -Ta ₂ O _{5ss} .				
				8	92	1000 1628	10 16		H _{mon} -Ta ₂ O _{5ss} .
								25	Do.
100	Do.								
200	Do.								
300	Do.								
400	Do.								
450	Ta ₂ O _{5ss} ^b .								
500	Do.								
700	Do.								
900	Do.								
1000	Do.								
1100	H _{tet} -Ta ₂ O _{5ss} .								
9	91	1000 1628	10 16						H _{mon} -Ta ₂ O _{5ss} .
								25	Do.
								100	Do.
								300	Do.
								400	Do.
								450	H _{mon} -Ta ₂ O _{5ss} ^b .
				500	H _{mon} -Ta ₂ O _{5ss} ^b .				
				550	Do.				
				600	H _{mon} -Ta ₂ O _{5ss} .				
				700	Do.				
				800	Do.				
				900	Do.				
				1000	Do.				
				1100	H _{tet} -Ta ₂ O _{5ss} .				
				10	90	1000 1560	10 168		H _{mon} -Ta ₂ O _{5ss} .
								25	Do.
								100	Do.
								300	Do.
400	Do.								
500	Do.								
600	H _{mon} -Ta ₂ O _{5ss} ^b .								
700	Do.								
800	Do.								
900	Do.								
1000	Do.								
1100	Do.								

^a L-Ta₂O₅ — low temperature stable form of Ta₂O₅.H_{tri}-Ta₂O₅ — a metastable triclinic form of Ta₂O₅ with *a* ≈ 3.8 Å, *b* ≈ 3.8 Å, and *c* ≈ 35 Å.H_{mon}-Ta₂O₅ — a metastable monoclinic form of Ta₂O₅ related to H_{tri}-Ta₂O₅ by *a* ≈ √2 × 3.8, *b* ≈ √2 × 3.8.H_{tet}-Ta₂O₅ — a high temperature tetragonal modification of Ta₂O₅.H_{mon}-Ta₂O_{5ss} — a monoclinic phase related to H_{tri}-Ta₂O₅ by having a significant smaller β angle than H_{mon}-Ta₂O₅."30:1" — a metastable monoclinic solid solution phase occurring at about 30Ta₂O₅:TiO₂.

ss — solid solution.

^b H_{mon}-Ta₂O_{5ss} could not be detected in the presence of H_{mon}-Ta₂O₅ because of β angle similarity.addition of TiO₂ whereas those derived from the sub-cell appear to have essentially the same spacings.

A typical example would be a diffraction line occurring at 26.53° 2θ in Ta₂O₅ which was found to occur at 26.24° with 10 percent TiO₂ addition. Conversely, a reflection positioned at 63.60° 2θ in Ta₂O₅ appeared to move less than 0.1° 2θ over the same compositional range. Some of the low angle x-ray diffraction lines, which, for a solid solution, should exhibit the least 2θ shift, actually shift more than many of the high angle lines.

The relative peak intensity of the x-ray powder patterns of specimens in this compositional range seem to show maximum intensity at 2 percent TiO₂, diminishing while becoming more diffuse with increasing TiO₂ and sharpen up with a maximum of intensity at about 12 mole percent TiO₂. These fine line differences, abnormal shifts in *d*-spacings, and intensity difference, are more characteristic of compounds than of solid solution phenomena. For these reasons, phases occurring at the approximate compositions 98Ta₂O₅:2TiO₂ ("49:1") and ³ 88Ta₂O₅:12TiO₂ ("7:1") are postulated in the system. Although the exact compositions of the postulated "nonstoichiometric" compounds cannot be established by x-ray powder diffraction this method is sufficient to indicate that the solid solution interpretation is unlikely. Since the stoichiometries of the compounds are not known exactly, the compounds are dashed on figure 1.

A similar phenomenon has been found to occur in other tantalate systems. For example, in the system Ta₂O₅-TaO₂F, Jahnberg and Andersson [15] obtained single crystal data on samples of different compositions within a field which might have been interpreted as a continuous solid solution series of the L-Ta₂O₅ type. From the single crystal data they concluded that a series of discrete compounds exist within this composition region.

Lehovec [3] described the structure of the tantalum oxide subcell with the tantalum atoms near positions (000), (1/2,1/2,0), two oxygen atoms at about (0,0,1/2) (1/2,1/2,1/2) and the other three oxygen atoms in the same plane as the tantalum atoms. He concluded that the loose packing of oxygen atoms in the plane *z*=1/2 could easily permit the diffusion of interstitial oxygen ions and/or the incorporation of interstitial cations and therefore the existence of oxides with cation/anion ratios differing from that of Ta₂O₅.

From x-ray powder diffraction data Moser [9] suggested that the low temperature form of Ta₂O₅ may occur in several states. On the basis of change in *d*-values of some weak powder lines, especially the one occurring between 3.6 and 3.3 Å, he arbitrarily divided low Ta₂O₅ into four "states" γ_1 , γ_2 , γ_3 , and γ_4 .

4.2. H-Ta₂O₅ and Related Metastable Phases⁴

Lagergren and Magneli [10] reported the existence of a high temperature polymorph occurring above 1320 °C and indexed the x-ray pattern on the basis of an orthorhombic unit cell with *a*=35.6 Å, *b*=3.79 Å, *c*=3.735 Å. Zaslavskii et al. [5], concluded from powder data that the high temperature form was tetragonal with *a*=3.801 Å, *c*=35.67 Å.

Reisman et al. [11], postulated from fine line splits in the x-ray powder diffraction pattern that the high temperature modification had a symmetry lower than orthorhombic. They further concluded that the phase transition occurred at 1360 °C, and was sluggish but completely reversible.

Laves and Petter [12] reported three polymorphic forms of high Ta₂O₅ from x-ray and optical data. At room temperature a monoclinic form (α'') was found to occur, with *a*=3.784 Å, *b*=3.802 Å, *c*=35.82 Å, and β =91.00°. This polymorph was reported to undergo a phase transition at 320 °C (to α') with *a*=*b*=5.365 Å, *c*=35.85 Å, β =91.00° at 400 °C. A tetragonal modification was apparently obtained with long time heating at 1450 °C which, when examined at 20 °C, was found to have *a*=3.795 Å, *c*=35.54 Å.

Franklin and Wu [16] have suggested that, from room temperature single crystal data, the high temperature form of Ta₂O₅ can be interpreted as triclinic with *a*=7.58 Å, *b*=7.59 Å, *c*=35.71 Å, α =90.23°, β =91.14°, and γ =90.12°.

4.2.1. H-Ta₂O₅

In the present investigation Ta₂O₅ was found to exhibit an enantiotropic phase transition at about 1360±10 °C. The addition of TiO₂ lowers the phase transition from about 1360 to about 1150 °C at 9 mole percent TiO₂. By extrapolation from high temperature x-ray data the high temperature form is postulated to be tetragonal in its stability field rather than the monoclinic or triclinic symmetry generally observed at room temperature. The symmetry of H-Ta₂O₅ cannot be proven conclusively since the phase transition temperature is above the upper temperature limitation of the high temperature x-ray furnace used for this study.

4.2.2. Metastable Phases of Ta₂O₅

From high temperature data, Ta₂O₅ can be shown to have a number of metastable phases occurring in the stability field of the low temperature polymorph. They are indicated on figure 1 as H_{tri}-Ta₂O₅,

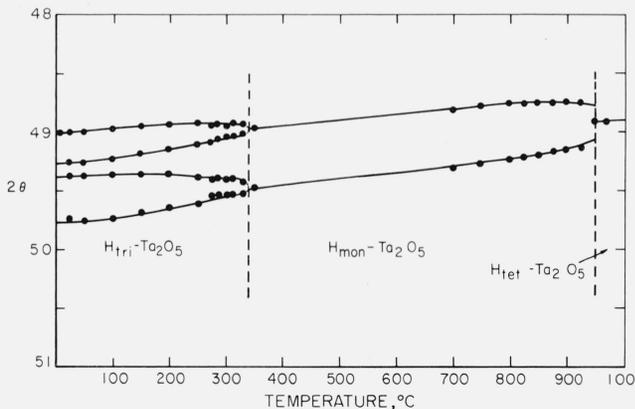


FIGURE 2. Metastable phase transitions in the high temperature form of Ta₂O₅ (from high temperature x-ray data) (CuK α).

H_{mon}-Ta₂O₅, and H_{tet}-Ta₂O₅. A plot of temperature versus 2 θ is shown in figure 2 for the family of peaks generated by symmetry changes for the tetragonal (1,0,17). The metastable phase assemblage of the high temperature form of Ta₂O₅ is significantly changed by the addition of TiO₂ and the existence of several solid solution phases was established. They are indicated on figure 1 as 30:1_{ss}, H_{mon}-Ta₂O_{5_{ss}}, and H'_{mon}-Ta₂O_{5_{ss}}.

³ Quotation marks around a compound indicate uncertainty in the exact composition.

⁴ H-Ta₂O₅ represents the high temperature polymorph of Ta₂O₅ and phases structurally related to it.

4.2.2.1. $H_{\text{tri}}\text{Ta}_2\text{O}_5$: Room Temperature Form

Ta_2O_5 when quenched from above the stable 1360 °C phase transition has undergone at least two metastable phase transitions (tetragonal \rightarrow monoclinic \rightarrow triclinic). "Single crystal" precession patterns show a multiplicity of crystallites partially ordered with respect to each other. If a quenched specimen is ground lightly in a mortar and pestle the x-ray powder diffraction pattern shows diffuse peaks. However, if the specimen is carefully prepared for diffraction, with a minimum of mechanical deformation, then the diffuse peaks are resolved into fine line splittings, as previously described by Reisman et al. [11]. This room temperature x-ray diffraction powder pattern (table 2)

TABLE 2. X-ray diffraction powder data for $H_{\text{tri}}\text{Ta}_2\text{O}_5$ ^a (CuK α radiation)

d_{obs}	d_{calc}	hkl ^b	I/I_0 ^c	d_{obs}	d_{calc}	hkl ^b	I/I_0 ^c
8.93	8.93	004	6				
4.47	4.47	008	7	2.485	2.485	0 $\bar{1}$ 11	12
3.776	3.781	101	58	2.474	2.474	1 $\bar{0}$ 11	17
3.773	3.778	101	70	2.466	2.465	1 $\bar{0}$ 11	26
3.768	3.770	011	55	2.457	2.458	$\bar{1}$ 16	64
3.759	3.758	011	51	2.454	2.453	116	73
	3.624	103		2.445	2.446	0,1,11	16
3.620			30	2.436	2.437	116	61
	3.624	0 $\bar{1}$ 3		2.433	2.433	116	58
3.617	3.617	103	30	2.239	2.241	0,1,13	4
3.590	3.591	013	3	2.232	2.234	0,0,16	12
3.363	3.367	015	68	2.230	2.231	1,0,13	9
3.357	3.360	105	77	2.224	2.224	1,0,13	8
3.354	3.351	105	68	2.207	2.208	0,1,13	4
3.321	3.323	015	20	2.031	2.031	0,1,15	7
3.060	3.064	017	25	2.022	2.022	1,0,15	7
3.052	3.054	107	26	2.015	2.016	1,0,15	7
3.044	3.044	107	25	1.8977	1.9004	200	27
3.015	3.018	017	16	1.8915	1.8924	020	27
2.979	2.978	0,0,12	100	1.8492	1.8502	0,1,17	8
2.763	2.762	019	3	1.8417	1.8422	1,0,17	14
2.751	2.750	109	3	1.8360	1.8369	1,0,17	15
2.739	2.741	109	5	1.8257	1.8255	0,1,17	9
2.717	2.718	019	5	1.7861	1.7869	0,0,20	3
	2.578	$\bar{1}$ 14			1.7525	028	
2.586	2.575	114	3	1.7517			1
	2.562	$\bar{1}$ 14			1.7508	$\bar{2}$ 08	
	2.559	114		1.7461	1.7466	208	1

^a Specimen of Ta_2O_5 heated to 1775 °C for 6 hr and quenched.

^b Relative intensity.

^c Based on triclinic cell $a = 3.801$ Å, $b = 3.785$ Å, $c = 35.74$ Å, $\alpha = 90^\circ 54.5'$, $\beta = 90^\circ 11.5'$, and $\gamma = 89^\circ 59.9'$. (The last decimal point of the angles is given for the purpose of recalculation.)

can be completely indexed on the basis of a triclinic cell with $a = 3.801$ Å, $b = 3.785$ Å, $c = 35.74$ Å, $\alpha = 90^\circ 54.4'$, $\beta = 90^\circ 11.5'$, $\gamma = 89^\circ 59.9'$. In this study, the triclinic form was found to undergo a phase transition on heating at about 320 °C to a monoclinic modification ($H_{\text{mon}}\text{Ta}_2\text{O}_5$).

4.2.2.2. $H_{\text{mon}}\text{Ta}_2\text{O}_5$

This modification is related to the triclinic form by $a_{\text{mon}} \approx \sqrt{2}a_{\text{tri}}$, $b_{\text{mon}} \approx \sqrt{2}b_{\text{tri}}$, $c_{\text{mon}} \approx c_{\text{tri}}$. This monoclinic polymorph is apparently the α' phase reported by Laves and Petter [12]. At about 950 °C on heating in the high temperature x-ray furnace, $H_{\text{mon}}\text{Ta}_2\text{O}_5$ inverts to a tetragonal modification ($H_{\text{tet}}\text{Ta}_2\text{O}_5$).

4.2.2.3. $H_{\text{tet}}\text{Ta}_2\text{O}_5$

This tetragonal modification of Ta_2O_5 may be related to the tetragonal phase (α) reported by Laves and Petter [12]. According to Laves and Petter [12] a tetragonal form was obtained at room temperature by heating Ta_2O_5 for extended periods of time at

1450 °C. The high temperature (950 °C) indexed powder pattern for the tetragonal modification of Ta_2O_5 is given in table 3. The pattern was indexed on the basis of a tetragonal cell $a = 3.81$ Å, $c = 36.09$ Å. In this study, pure Ta_2O_5 could not be stabilized to room temperature. However, the stabilization could be achieved by the addition of certain impurities [17].

TABLE 3. High temperature x-ray diffraction powder data for $H_{\text{tet}}\text{Ta}_2\text{O}_5$ ^a (CuK α radiation)

d_{obs}	d_{calc}	hkl ^b	I/I_0 ^c
4.55	4.51	008	7
3.80	3.79	101	93
3.65	3.64	103	37
3.37	3.37	105	80
3.07	3.07	107	54
3.02	3.01	0,0,12	80
2.76	2.76	109	10
2.491	2.487	1,0,11	53
2.461	2.461	116	100
2.256	2.256	0,0,16	10
2.247	2.245	1,0,13	17
2.039	2.035	105	7
1.907	1.907	200	43
1.900	1.897	202	47
1.855	1.855	1,0,17	37
1.702	1.704	211	23
	1.700	1,0,19	
1.687	1.690	213	7

^a X-ray taken at 950 °C.

^b Based on tetragonal cell $a = b = 3.81$ Å, $c = 36.09$ Å.

^c Relative intensity.

4.2.3. Metastable Solid Solutions

4.2.3.1. $H_{\text{mon}}\text{Ta}_2\text{O}_{5\text{SS}}$

The effect of TiO_2 additions was investigated by both high temperature x-ray and conventional quenching techniques. From high temperature x-ray data, Ta_2O_5 accepts in excess of 7 mole percent TiO_2 at 470 °C to form a metastable solid solution phase ($H_{\text{mon}}\text{Ta}_2\text{O}_{5\text{SS}}$, fig. 1).

The metastable tetragonal \rightleftharpoons monoclinic transition indicated in figure 1 as continuing to temperatures above 1000 °C may possibly be stable in the field labeled $H\text{-Ta}_2\text{O}_{5\text{SS}}$. An ultra-high temperature x-ray study would be needed to establish the equilibrium conditions in this region.

4.2.3.2. $H'_{\text{mon}}\text{Ta}_2\text{O}_{5\text{SS}}$

The $H_{\text{mon}}\text{Ta}_2\text{O}_{5\text{SS}}$ phase has an apparent morphotropic phase transition to another metastable monoclinic form ($H'_{\text{mon}}\text{Ta}_2\text{O}_{5\text{SS}}$, fig. 1). The monoclinic angle of $H'_{\text{mon}}\text{Ta}_2\text{O}_{5\text{SS}}$ apparently changes with composition and temperature, and grades into that of the other monoclinic form at about 550 °C and 9 mole percent TiO_2 . The x-ray diffraction pattern for $H'_{\text{mon}}\text{Ta}_2\text{O}_{5\text{SS}}$ from the 9:1 composition at room temperature is given in table 4. The specimen was indexed from powder data on the basis of a monoclinic cell with $a = 5.367$ Å, $b = 5.368$ Å, $c = 35.70$ Å, and

TABLE 4. X-ray diffraction powder data for the phase $H'_{\text{mon}}\text{-Ta}_2\text{O}_5$ ($10\text{TiO}_2\cdot 90\text{Ta}_2\text{O}_5$)^a (CuK α radiation)

d_{obs}	d_{calc}	hkl^b	I/I_0^c
4.469	4.461	008	8
3.771	3.781	111	100
	3.765	$\bar{1}11$	
3.638	3.637	113	38
3.596	3.593	$\bar{1}13$	8
3.380	3.379	$\bar{1}15$	65
3.321	3.322	$\bar{1}15$	50
3.076	3.075	117	20
3.014	3.014	$\bar{1}17$	25
2.973	2.973	0,0,12	95
2.714	2.713	$\bar{1}19$	15
2.492	2.492	1,1,11	28
2.472	2.472	206	38
2.444	2.441	$\bar{1},1,11$	63
2.418	2.418	206	43
2.247	2.247	1,1,13	3
2.232	2.231	0,0,16	8
2.203	2.202	$\bar{1},1,13$	5
2.036	2.035	1,1,15	5
1.897	1.897	220	63

^a Specimen heated to 1640 °C for 16 hr and quenched.

^b Based on monoclinic cell $a=5.367$ Å, $b=5.368$ Å, $c=35.707$ Å and $\beta=91^\circ42'$.

^c Relative intensity.

$\beta=91^\circ42'$. This phase is apparently related to $H_{\text{tri}}\text{-Ta}_2\text{O}_5$ in the following manner:

$$a_{\text{mon}} \approx \sqrt{2}a_{\text{tri}}, b_{\text{mon}} \approx \sqrt{2}b_{\text{tri}}, c_{\text{mon}} \approx c_{\text{tri}}.$$

4.2.3.3. "30:1_{ss}"

From high temperature x-ray data, another phase was found to occur from about 2.5 to 4.5 mole percent TiO_2 and to have a maximum dissociation temperature of about 375 °C. This metastable solid solution phase is apparently related to $H_{\text{tri}}\text{-Ta}_2\text{O}_5$ and can be indexed on the basis of a monoclinic cell $a=3.794$ Å, $b=3.807$ Å, $c=35.70$ Å, $\beta=90^\circ51'$. This phase corresponds closely to the α'' form of Laves and Petter [12]. The indexed x-ray powder pattern for the 3 mole percent TiO_2 specimen is given in table 5. It should be emphasized again that the high temperature tetragonal form of Ta_2O_5 is not quenched-in and that it is the various metastable phases which are detected when specimens are quenched from elevated temperatures and examined at room temperature by x-ray diffraction.

4.3. $\text{TiO}_2 \cdot \text{Ta}_2\text{O}_5$ (TiTa_2O_7)

The intermediate compound $\text{TiO}_2 \cdot \text{Ta}_2\text{O}_5$ was found to occur in the system and to melt congruently at about 1662 °C. From x-ray diffraction data, table 6, the compound can be indexed on a monoclinic basis $a=20.397$ Å, $b=3.804$ Å, $c=11.831$ Å, $\beta=120^\circ14'$ and is apparently isostructural to the compound TiNb_2O_7 reported previously by Roth and Coughanhour [18] and by Wadsley [19]. It is interesting to note that phases analogous to those compounds richer in Nb_2O_5

TABLE 5. X-ray diffraction powder data for the phase "30:1_{ss}" ($3\text{TiO}_2\cdot 97\text{Ta}_2\text{O}_5$)^a (CuK α radiation)

d_{obs}	d_{calc}	hkl^b	I/I_0^c
4.46	4.46	008	3
3.78	3.79	011	80
	3.78	$\bar{1}01$	
	3.78	101	
	3.63	$\bar{1}03$	
3.63	3.63	013	15
3.373	3.371	$\bar{1}05$	13
3.361	3.359	015	60
3.330	3.329	105	11
3.066	3.066	$\bar{1}07$	5
3.050	3.051	017	13
3.022	3.022	107	6
2.974	2.975	0,0,12	100
2.761	2.762	$\bar{1}09$	1
2.747	2.746	019	3
2.722	2.721	109	3
2.484	2.484	$\bar{1},0,11$	6
2.469	2.470	0,1,11	15
2.451	2.459	$\bar{1}16$	50
	2.448	1,0,11	
	2.439	$\bar{1}16$	
2.313	2.313	$\bar{1}18$	2
2.241	2.240	1,0,13	2
2.231	2.231	0,0,16	6
2.227	2.227	0,1,13	4
2.210	2.209	1,0,13	2
2.030	2.030	1,0,15	2
2.018	2.018	0,1,15	2
1.9034	1.9034	020	11
1.8964	1.8967	200	13
1.8926	1.8927	022	7
1.8885	1.8891	$\bar{2}02$	3
1.8486	1.8488	1,0,17	5
1.8394	1.8386	0,1,17	8
1.8257	1.8256	1,0,17	4
1.7846	1.7848	0,0,20	2

^a Specimen of $3\text{TiO}_2\cdot 97\text{Ta}_2\text{O}_5$ heated to 1640 °C for 40 hr and quenched.

^b Relative intensity.

^c Based on monoclinic cell $a=3.794$ Å, $b=3.307$ Å, $c=35.70$ Å, and $\beta=90^\circ51'$.

than TiNb_2O_7 [20, 21] were not found to occur in the $\text{TiO}_2\text{-Ta}_2\text{O}_5$ system under the conditions studied. Two eutectics were found to occur in the system (fig. 1) at approximately 54 mole percent Ta_2O_5 and 1650 °C and 31 mole percent Ta_2O_5 and 1630 °C, respectively. Some difficulty was encountered in establishing the solidus curve near the higher TiO_2 eutectic composition since the surface of specimens quenched in this compositional region appeared glazed or partially melted below the solidus. For this reason these data were interpolated to provide the best approach to binary equilibrium. This phenomena is probably due to partial reduction in the subsolidus near the melting point of the phase assemblage. The possible deviations in stoichiometry should be investigated at higher oxygen pressures and temperatures.

4.4. TiO_2 Solid Solutions

Titanium dioxide was found to exhibit maximum solubility of 10 mole percent Ta_2O_5 at 1625 °C. The

TABLE 6. X-ray diffraction powder data for $\text{TiO}_2 \cdot \text{Ta}_2\text{O}_5$ (TiTa_2O_7)^a
($\text{CuK}\alpha$ radiation)

d_{obs}	d_{calc}	hkl ^b	I/I_0 ^c
10.24	10.22	001	2
9.42	9.42	201	5
5.11	5.11	002	55
5.07	5.08	401	24
4.70	4.71	402	7
4.41	4.41	400	2
3.714	{ 3.718 3.689 }	{ 110 202 }	83
3.619	3.620	111	12
3.461	3.462	401	12
3.398	{ 3.407 3.388 3.381 }	{ 003 602 111 }	100
3.317	3.317	311	12
3.297	3.298	601	12
2.949	2.946	404	12
2.866	2.865	112	38
2.754	{ 2.760 2.753 }	{ 511 512 }	48
2.725	2.723	604	14
2.658	2.657	113	38
2.560	2.556	004	7
2.540	2.541	802	5
2.507	2.508	601	23
2.427	2.426	312	5
2.390	2.389	113	7
2.312	{ 2.312 2.310 }	{ 511 605 }	51
2.290	2.289	514	19
2.047	2.044	005	38
2.039	2.039	10,0,3	25
2.006	{ 2.006 2.004 }	{ 10,0,2 515 }	5
1.9019	1.9020	020	29
1.8797	{ 1.8822 1.8777 }	{ 806 115 }	7
1.8447	1.8440	404	5
1.8185	1.8177	603	5
1.7825	1.7825	022	7
1.7621	1.7623	10,0,0	7
1.7403	1.7410	910	7
1.7178	1.7162	115	14
1.7066	1.7064	712	8
1.6939	{ 1.6940 1.6938 }	{ 12,0,4 12,0,3 }	19
1.6653	1.6658	11,1,3	29
1.6620	1.6621	807	36

^a Specimen heated to 1620 °C for 16 hr and quenched.

^b Based on monoclinic cell $a=20.397$ Å, $b=3.804$ Å, $c=11.831$ Å and $\beta=120^\circ14'$.

^c Relative intensity.

amount of titanium dioxide solid solution ($\text{TiO}_{2\text{ss}}$, fig. 1) at the solidus of 1630 °C decreases with both increasing and decreasing temperatures. The extent of solid solution was delineated by both the disappearing phase

and parametric surface methods. The a parameters in Å for the various selected compositions used in the study are shown in figure 1.

Any discussion of the nature of the solid solution would be pure speculation; however, an investigation of the physical properties might prove enlightening in characterizing this solid solution.

5. Future Study

This study has established that although ions of a size similar to Ta^{+5} but with different valence apparently enter into solid solution with $\text{H-Ta}_2\text{O}_5$ they form discrete phases with $\text{L-Ta}_2\text{O}_5$. However, the reasons for this type of interaction cannot be determined without a knowledge of the crystal structures of both forms. The crystal structures cannot be determined without single crystals. *Single* crystals of pure Ta_2O_5 apparently cannot be grown in either of the two main polymorphic forms. We, therefore, propose that a study of other systems will be of help in determining proper compositions to be used in the growth of single crystals of phases having structures similar to the polymorphs of Ta_2O_5 . Such studies are in progress and will be reported at a future date.

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