An X-Ray Investigation of the Tantalum-Oxygen System

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The tantalum oxides TaO , Ta_2O_3 , TaO_2 , and Ta_2O_5 are described in literature. Among these compounds, however, the pentoxide is the only one whose existence has been firmly established. According to Zachariassen¹, the Ta_2O_5 phase is isostructural with the low temperature modification of Nb_2O_5 ². There exist two other modifications of the niobium pentoxide: $\beta\text{-Nb}_2\text{O}_5$ and $\gamma\text{-Nb}_2\text{O}_5$ ². In a recently published paper by Lagergren and Magnéli³, these authors point out that Ta_2O_5 irreversibly transforms into a high temperature tantalum pentoxide at a temperature of $1320^\circ \pm 20^\circ \text{C}$. The pronounced stability of Ta_2O_5 (low-temperature modification) was strikingly demonstrated by the negative result when attempts were made to reduce it in a stream of hydrogen at about 1250°C .

EXPERIMENTAL WORK

From the data given above it is obvious that the preparation of intermediate tantalum oxides involves experimental difficulties.

Tantalum metal powder (Fansteel), tantalum pentoxide (Kahlbaum, *pro analysi*) and tantalum hydride (Metal Hydrides Inc.) were used as starting materials.

The oxides were prepared by the following methods: *

A. Tantalum metal powder or tantalum hydride was oxidized with steam in the presence of hydrogen in great excess at temperatures varying between 600°C and 900°C , and for periods between one hour and about two days.

B. Tantalum carbides (TaC , Ta_2C) or tantalum nitrides (Ta_3N , Ta_2N) were oxidized with steam as in method A.

C. Tantalum carbide (TaC) was oxidized with steam in the presence of ammonia at 1100°C for periods varying between one and six hours.

D. Tantalum metal powder was oxidized by means of zinc oxide in evacuated and sealed silica tubes at about 700°C for two weeks, whereupon the zinc metal and remaining zinc oxide were separated from the sample by means of dilute hydrochloric acid.

E. Tantalum pentoxide was reduced with carbon (soot) in graphite or zirconia crucibles in a graphite tube vacuum resistance furnace⁴ or a high frequency vacuum induction furnace⁵ at about 1500°C for up to two hours.

* There certainly exist other more suitable methods for the preparation of intermediate oxides in the $\text{Ta}-\text{Ta}_2\text{O}_5$ interval, e.g. reduction of the pentoxide by means of potassium. Methods B, C, and E were originally used for the preparation of ternary $\text{Ta}-\text{N}-\text{O}$ and $\text{Ta}-\text{C}-\text{O}$ phases. This explains the use of these methods here, although they may not at first sight appear suitable for the preparation of oxides.

Some samples were homogenized, either in evacuated and sealed silica tubes at 800° C, or in zirconia crucibles in a vacuum induction furnace at 1400° C.

The phase analysis and structure determinations were made from powder photographs taken with $\text{CuK}\alpha$ radiation in a camera of the Guinier type, using a curved quartz monochromator. For measurements of the high-angle reflections, additional photographs were taken with focusing cameras of the Hägg-Phragmén type.

No single crystals of any of the new oxide phases could be obtained.

THE STRUCTURES AND COMPOSITIONS OF THE PHASES

Six phases were found to exist in the tantalum-oxygen system, *viz.* $\text{Ta}(\alpha)$, $\text{Ta}_4\text{O}(\beta)$, $\text{TaO}(\gamma)$, $\text{TaO}_2(\delta)$, TaO_x with $2 < x < 2.5$ (ϵ) and Ta_2O_5 (ζ). Several attempts were made to prepare the high temperature modification of the pentoxide reported by Lagergren and Magnéli³. The only result was a formation of small amounts of the ϵ phase, while the greater part of the tantalum pentoxide remained unaltered.

It was not possible to prepare the intermediate oxides in a pure state.

The results of the analysis of the powder photographs of the different specimens are given in Table 1.

α Phase: Ta

For pure tantalum the axial length was determined as $a = 3.311 \text{ \AA}$ ($V = 36.30 \text{ \AA}^3$), and this value was found to increase up to $a = 3.341 \text{ \AA}$ ($V = 37.29 \text{ \AA}^3$) for samples containing the α and β phases. It was not possible to determine the solubility of oxygen in the tantalum lattice, but the increase in volume makes a value of approximately 5 atom-% probable. This is practically equal to the solubility of oxygen in the niobium metal lattice².

β Phase: Ta_4O

The best samples of this bluish black, metallic oxide contained tantalum metal or tantalum pentoxide as impurity. The weight increase after oxidation to Ta_2O_5 , as well as the lattice configuration, makes the formula Ta_4O for the upper composition limit very probable.

The diffraction pattern indicated an orthorhombic unit cell closely related to the body-centered α phase lattice. The unit cell dimensions were found to

Table 1. Phases obtained from different methods of preparation.

Preparation method	Phases formed
A	$\alpha, \beta, (\zeta)$
B *	$\gamma, \delta, \epsilon, (\zeta)$
C *	$\delta, \epsilon, (\zeta)$
D	$\alpha, \beta, (\zeta)$
E *	$\delta, \epsilon, (\zeta)$

* Ternary Ta—N—O and Ta—C—O phases were also found to exist. A report of these phases will shortly appear elsewhere.

Table 2. Interatomic distances in the β phase (Ta_4O).

Atom	Surrounding atoms	Interatomic distance, Å
Ta in 1(a)	8 Ta in 2(d)	2.82
	4 Ta in 1(a)	3.21
Ta in 1(b)	8 Ta in 2(l)	3.04
	4 Ta in 1(b)	3.21
	4 O in 1(h)	2.29
Ta in 2(l)	4 Ta in 1(a)	2.82
	4 Ta in 1(b)	3.04
	4 Ta in 2(l)	3.21
	1 O in 1(h)	1.96
O in 1(h)	2 Ta in 2(l)	1.96
	4 Ta in 1(b)	2.29

vary between $a = 7.194$ Å, $b = 3.266$ Å, $c = 3.204$ Å ($V = 75.28$ Å³) and $a = 7.238$ Å, $b = 3.273$ Å, $c = 3.216$ Å ($V = 76.19$ Å³). The reflections with $h = 2n + 1$ were very weak, indicating a sublattice with the a axis half of the above value. This sublattice is body-centered, and its relation to the lattice of pure tantalum is shown by the mean axial ratio $a/2 : b : c : a_{\text{Ta}} = 1.09 : 0.99 : 0.97 : 1.00$. In spite of prolonged heat-treatment of the samples, it was not possible to obtain sharp reflections.

The most probable configuration is that corresponding to the following atomic positions in the space-group $D_{2h}^1\text{-Pmmm}$: 1Ta in 1(a) 0,0,0, 1Ta in 1(b) $\frac{1}{2}, 0, 0$ and 2Ta in 2(l) $x, \frac{1}{2}, \frac{1}{2}$; $x, \frac{1}{2}, \frac{1}{2}$, with x slightly different from $1/4$. Good agreement between calculated and observed intensities was obtained, when $x = 0.225$. If the atomic radius of tantalum is assumed to be greater than 1.3 Å, it is not possible to place more than one oxygen atom in the metal lattice of the unit cell, namely in the position 1(h) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ i. e. at the centre of a deformed metal atom octahedron. For this reason the most oxygen-rich composition for this phase is presumed to be Ta_4O . The variation of the unit cell dimensions indicate a comparatively broad homogeneity range.

The mean interatomic distances are listed in Table 2.

An oxide analogous to the β phase in the Ta—O system occurs in the V—O system, with the approximate homogeneity range $\text{VO}_{0.15-0.25}$ ⁶. The structure of this phase can be regarded as a tetragonally deformed version of the body-centered vanadium lattice. The present author considers it most likely that the oxygen atom is located at (or in the vicinity of) the centre of a deformed metal atom octahedron in a superlattice containing four metal atoms — in the same way as in the Ta_4O phase. This view is supported by the fact that the upper homogeneity limit of the vanadium suboxide corresponds to the composition V_4O .

γ Phase: TaO

It was only possible to prepare this phase in the presence of fairly great amounts of higher tantalum oxides, by the oxidation with steam of tantalum carbides or nitrides. Carbon and nitrogen analyses of the samples excluded the

presence of these non-metals. The lattice of the γ phase is of the NaCl type. The cube edge was found to vary between $a = 4.422 \text{ \AA}$ ($V = 86.45 \text{ \AA}^3$) and $a = 4.439 \text{ \AA}$ ($V = 87.45 \text{ \AA}^3$), indicating a narrow homogeneity range.

Each Ta atom in the lattice is surrounded by 12 Ta and 6 O atoms at distances of 3.13 $\text{\AA}$ and 2.22 $\text{\AA}$ respectively.

Because of the impurities it was not possible to determine the composition of the γ phase, but it is convenient to give it the ideal formula TaO by analogy with other metallic oxides of the NaCl type, viz. TiO, ZrO, HfO, ThO, VO, NbO (defective lattice), UO, NpO, PuO, and AmO.

δ Phase: TaO₂

From Table 1 it is evident that the δ phase could be identified in several samples prepared by oxidation as well as by reduction. A fairly pure product was obtained, when TaC was oxidized with steam in the presence of ammonia at 1100°C for two hours (ϵ phase occurring as impurity). The diffraction pattern of the black compound indicated the rutile structure (C4 type)⁷, making the formula TaO₂ most likely. No diffraction effects indicating a superlattice formation or a lower symmetry than tetragonal were visible in the powder photographs. This is in contrast to the vanadium oxide VO₂, for which Andersson⁸ reports a monoclinic structure, closely related to that of the tetragonal sublattice.

The unit cell dimensions were invariably found to be $a = 4.709 \text{ \AA}$, $c = 3.065 \text{ \AA}$, $c/a = 0.651$ ($V = 67.96 \text{ \AA}^3$).

The calculated density is 10.41. The observed value was 9.95.

The space-group is D_{4h}^{14} — $P4/mnm$. The tantalum ions are located in the two-fold position $2(a) 0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, and the oxygen ions in the four-fold position $4(f) \pm (x, x, 0; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2})$. As it is not possible to determine the value of the parameter x from X-ray data, this is calculated from the formula $8x = 2 + (c/a)^2$, which gives the best space distribution. This formula gives $x = 0.303$.

Interatomic distances are listed in Table 3.

The shortest O—O distance is 2.62 $\text{\AA}$, giving $r_{O2-} = 1.31 \text{ \AA}$. The Ta—O distances are 2.02 $\text{\AA}$, hence $r_{Ta4+} = 0.71 \text{ \AA}$. Goldschmidt's radius value for the Ta⁵⁺ ion is 0.68 $\text{\AA}$ (6-coordination). If the expression $r_z = (n B/A z^2)^{1/n-1}$ given by Pauling⁹ for the calculation of the radius r_z of an ion of valency z is used in this case, and the Born exponent⁹ taken to be $n \sim 9$, the value $r_{Ta4+} = 0.72 \text{ \AA}$ is obtained.

Table 3. Interatomic distances in the δ phase (TaO₂).

Atom	Surrounding atoms	Interatomic distance, $\text{\AA}$
Ta	2 Ta	3.07
	8 Ta	3.67
	6 O	2.02
O	1 O	2.62
	8 O	2.86
	3 Ta	2.02

It may be of interest to note that the tantalum ions in the TaO_2 phase can be replaced by titanium and vanadium ions. The metals (Ta, Ti, V) and metal oxides (Ta_2O_5 , TiO_2 , V_2O_5) were carefully mixed in the proportions corresponding to the gross compositions $(\text{Ta, Ti})\text{O}_2$ and $(\text{Ta, V})\text{O}_2$ respectively, moulded into small brickettes and heated in thoria crucibles in a vacuum induction furnace up to about 1800°C . The Ta/(Ti, V) ratio was varied in steps of 0.2, 0.4, 0.6, and 0.8. As indicated by the diffuse reflections in the powder photographs, it was not possible to reach equilibrium. Other oxides occurred as impurities.

The unit cell dimensions of the $(\text{Ta, Ti})\text{O}_2$ samples were found to vary continuously between those of TiO_2 (rutile): $a = 4.589 \text{ \AA}$, $c = 2.960 \text{ \AA}$, $c/a = 0.645$ ($V = 62.34 \text{ \AA}^3$) and those of TaO_2 : $a = 4.709 \text{ \AA}$, $c = 3.065 \text{ \AA}$, $c/a = 0.651$ ($V = 67.96 \text{ \AA}^3$). It is therefore very probable that a continuous solid solution series TiO_2 — TaO_2 exists.

The solubility of VO_2 in TaO_2 was found to be comparatively small, the unit cell dimensions of the $(\text{Ta, V})\text{O}_2$ phase varying between $a = 4.715 \text{ \AA}$, $c = 3.046 \text{ \AA}$, $c/a = 0.646$ ($V = 67.27 \text{ \AA}^3$) and those obtained for pure TaO_2 .

ϵ Phase

The powder photograph analysis showed that the black ϵ -phase exists as an intermediate oxide in the TaO_2 — Ta_2O_5 interval. The line distribution in the diffraction pattern indicates a complicated structure, neither related to that of TaO_2 nor to that of Ta_2O_5 .

ζ Phase: Ta_2O_5

According to Zachariassen¹, Ta_2O_5 is isomorphous with $\alpha\text{-Nb}_2\text{O}_5$ ⁵.

SUMMARY

Six phases have been found to exist in the tantalum-oxygen system.

The α phase (Ta) dissolves up to about 5 atom-% of oxygen in the body-centered metal lattice.

The β phase has a metal atom arrangement obtained by an orthorhombic deformation of the α -phase lattice. The upper phase limit corresponds to the formula Ta_4O . The metallic oxide has a bluish black colour.

The γ phase has the probable composition TaO , and is of the sodium chloride structure.

The black δ phase with the formula TaO_2 is isomorphous with rutile. It forms a complete series of solid solutions with TiO_2 (rutile).

The black ϵ phase exists as an intermediate oxide in the TaO_2 — Ta_2O_5 interval. The structure seems to be complicated.

No high temperature modification of the ζ phase (Ta_2O_5) has been found to exist.

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