The Crystal Structure of the So-Called δ-Titanium Oxide and Its Structural Relation to the ω-Phases of Some Binary Alloy Systems of Titanium *

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The crystal structure of the so-called δ-titanium oxide has been determined using X-ray powder techniques. The structure may be described as a deficient interstitial solution of oxygen in a metal atom lattice of the type present in the ω-phases of binary alloy systems of titanium.

In 1953 it was reported by Bumps, Kessler and Hansen [1] that, when titanium oxide preparations of compositions ranging from $TiO_{0.66}$ to $TiO_{0.75}$ are annealed at temperatures below 900°C, a previously unknown phase (called δ-titanium oxide) is formed in addition to the solid solution of oxygen in α-titanium and titanium monoxide. Possible formulae suggested for the δ-oxide were Ti_3O_2 or Ti_4O_3. The powder pattern with the exception of one reflexion was said to be in conformity with a tetragonal unit cell with the dimensions $a = 5.333$ Å and $c = 6.645$ Å. Schofield and Bacon [2] confirmed the data given by Bumps *et al.*

Koncz and Koncz-Déri [3] observed the formation of δ-titanium oxide when oxidizing titanium metal at low oxygen pressures within the temperature region 570—820°C. They reported a different tetragonal unit cell ($a = 3.20$ Å and $c = 5.12$ Å) and suggested the composition Ti_3O_2.

EXPERIMENTAL

In the present investigation, samples of compositions ranging from $TiO_{0.5}$ to $TiO_{1.0}$ were kept in sealed, evacuated silica tubes at temperatures between 600° and 800°C for a month. (Details about the titanium oxide specimens employed in this investigation have been given in a previous report [4].) The identification of the samples was performed by means of the X-ray powder patterns obtained in a Guinier focusing camera of 80 mm

diameter using strictly monochromatized $CuK\alpha_1$ radiation and potassium chloride added to the specimens as an internal standard.

The intensities of the powder reflexions were measured by means of an X-ray diffractometer registering the pattern up to $2\Theta = 160°$ with $CuK\alpha$ radiation. The specimen was diluted with gum arabic in order to avoid orientation as far as possible. The positive effect obtained in this way was strikingly demonstrated when observing the intensities of the reflexions of the Ti_2O oxide which was always present in the sample *(v. infra)*. While the latter intensities were highly anomalous when using an undiluted specimen, the addition of gum arabic lead to values close to the ideal ones.

For studying the oxide at elevated temperatures, the diffractometer was provided with an electric vacuum furnace which allowed the specimen to be heated to 1 000°C.

DETERMINATION OF THE STRUCTURE

The results of the phase analysis of the composition region $TiO_{0.5}$-$TiO_{1.0}$ reported in a previous article [4] were confirmed by the additional experiments included in the present study. Thus the δ-oxide was never obtained pure but was mixed with considerable amounts of the Ti_2O phase in preparations $TiO_{\sim 0.55}$ and with Ti_2O and TiO (low-temperature form) in samples $TiO_{0.6-0.9}$. Evidently it has not been possible to obtain the δ-oxide under equilibrium conditions.

As it was not possible to prepare single crystals of the δ-oxide, the structure determination had to be based exclusively on powder data. The specimen found to be the most suitable for this purpose was $TiO_{0.55}$. After subtracting the Ti_2O lines from the pattern given by this sample, all the remaining reflexions, which should be those of the δ-oxide, could be indexed assuming a hexagonal unit cell with the dimensions

$$a = 4.991_5 \text{ Å}, \qquad c = 2.879_4 \text{ Å}, \qquad V = 62.13 \text{ Å}^3$$

The powder pattern is given in Table 1.

The positions of the lines of the δ-oxide were not perceptibly different in samples of other gross compositions which shows that the homogeneity range of this phase must be narrow.

Table 1. The Guinier powder pattern of δ-TiO_x. Dimensions of the hexagonal unit cell: $a = 4.991_5$ Å, $c = 2.879_4$ Å.

I	$\sin^2\Theta_{obs}$	hkl	$\sin^2\Theta_{calc}$
st	0.09526	110	0.09525
st	0.10332	101	0.10331
w	0.16678	111	0.16681
m	0.19856	201	0.19856
m	0.28590	300	0.28575
		002	0.28623
w	0.29385	211	0.29381
w	0.38136	220	0.38100
		112	0.38148

The following structure was derived from the powder diffractogram:
Unit cell content: 3 TiO$_x$
Space-group: $P6/mmm$ (No. 191)
1 Ti in 1(a): 0,0,0
2 Ti in 2(d): $\frac{1}{3},\frac{2}{3},\frac{1}{2}$; $\frac{2}{3},\frac{1}{3},\frac{1}{2}$
3xO in 3(f): $\frac{1}{2}$,0,0; 0,$\frac{1}{2}$,0; $\frac{1}{2}$,$\frac{1}{2}$,0

An attempt was made to estimate the oxygen content (x) of the δ-oxide by calculating the intensities corresponding to various values of x and comparing these data with the observed ones (*cf.* Table 2). This comparison was performed by means of an index of agreement

$$R = \frac{\Sigma \left| \sqrt{I_{obs}} - \sqrt{I_{calc}} \right|}{\Sigma \sqrt{I_{calc}}}$$

In this way the following values for R were obtained

composition	Ti	TiO$_{0.4}$	TiO$_{0.5}$	TiO$_{0.6}$	TiO
R	0.115	0.075	0.070	0.075	0.095

Table 2. Observed intensities and also calculated ones for different values of x in the formula δ-TiO$_x$. A temperature factor of $B = 1.2$ Å^2 was used.

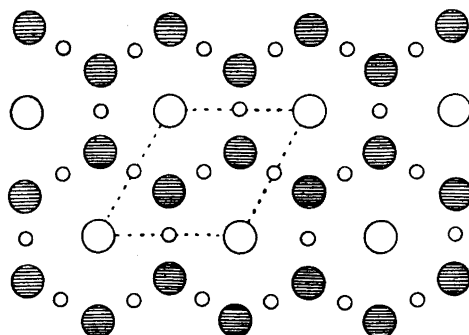| hkl	I_{obs}	I_{calc}(Ti)	I_{calc}(TiO$_{0.5}$)	I_{calc}(TiO)
100	—	0	2	10
001	—	0	0	0
110	100	130	118	103
101	86	94	82	67
200	—	0	3	12
111	24	12	19	25
201	53	36	58	86
210	—	0	0	1
300 002 }	40	30	31	32
211	31	38	33	29
102	—	0	0	0
301	—	3	1	1
220 112 }	30	30	33	35
310	—	0	0	0
202	—	0	0	1
221	—	2	1	0
311	—	11	10	9
400	—	0	0	0
212	—	0	0	0
302 401 }	11	12	13.5	14
320	—	0	0	0
003	—	0	0	0
410 222 }	18	12	14	14
321 103 }	8	8	7	6
312	—	0	0	0
411	—	1	1	1
113	—	0	0	1
203	—	2	2	3

Fig. 1. The crystal structure of δ-TiO$_x$. Projection after *c*-axis. Large and small circles represent titanium and oxygen atoms, respectively. Open circles have $z = 0$ and shaded ones $z = \frac{1}{2}$. The oxygen positions are partly vacant in a random distribution.

The best fit should thus correspond to the composition TiO$_{0.5}$. The experimental evidence given above suggests a higher content of oxygen but it may be that the actual composition is not very different from TiO$_{0.5}$.

The thermal expansion of the δ-oxide, which was obtained from the diffractometer data at elevated temperatures (20°—800°C), was found to be 10×10^{-6}/°C in the *a* direction and 9×10^{-6}/°C in the *c* direction.

DISCUSSION OF THE STRUCTURE

The structure thus derived is illustrated in Fig. 1 and the interatomic distances are given in Table 3. The metal atoms of the two atomic positions have rather different environments. The Ti atom in 1(*a*) has two close Ti neighbours at a distance equal to the *c* axis (2.88 Å) and twelve additional Ti atoms at a considerably longer distance (3.22 Å) forming a hexagonal prism. Six oxygen atom positions in the equator plane of this prism occur at a distance of 2.50 Å from the central Ti atom. Each of the Ti atoms in the position 2(*d*) is situated at the common center of a trigonal Ti bipyramid, a trigonal Ti prism and a trigonal O prism (randomly defective). The distances from the central Ti atom to the various atoms of these coordination polyhedra are 2.88, 3.22 and 2.04 Å respectively. The O atoms are surrounded by six Ti atoms, four forming a square and the other two completing an elongated Ti octahedron.

A structure analogous to the one thus derived for δ-titanium oxide but with all the non-metal positions filled is represented by the ε-TaN studied by Brauer [7,8] and Schönberg [9]. The δ-oxide may evidently be considered as having a non-metal deficient ε-TaN structure.

The structure can also be described as an interstitial solution of oxygen in the metal atom structure. This metal atom structure is actually present in the ω-phases occurring in the binary systems of titanium with vanadium [5] and chromium [6]. Thus it seems natural to describe δ-titanium oxide as an interstitial solution of oxygen in a titanium structure of ω-type (ω-TiO$_x$).

Table 3. Interatomic distances in δ-TiO$_x$.

Atom	Surrounding atoms	Interatomic distances, Å
Ti in 1(a)	2 Ti in 1(a) 12 Ti in 2(d) 6 O in 3(f)	2.879$_4$ 3.221$_4$ 2.495$_8$
Ti in 2(d)	2 Ti in 2(d) 3 Ti in 2(d) 6 Ti in 1(a) 6 O in 3(f)	2.879$_4$ 2.881$_8$ 3.221$_4$ 2.037$_6$
O in 3(f)	4 Ti in 2(d) 2 Ti in 1(a)	2.037$_6$ 2.495$_8$

Relationships between the structure of the δ-oxide and those of other phases occurring in various titanium systems will be discussed elsewhere.

The shorter Ti-Ti distances of δ-titanium oxide (2.88 Å) are similar in length to those observed for the ordered Ti$_2$O structure of *anti*-Cd(OH)$_2$ type (2.85 Å) [10]. In the δ-oxide, these close metal-metal contacts are present both parallel and normal to the c axis. In Ti$_2$O the short Ti-Ti distances are inclined to the c axis. The similarities between the coefficients of thermal expansion observed for the δ-phase (*v. supra*) and for Ti$_2$O ($\alpha_c = 10.3 \times 10^{-6}/°$C and $\alpha_a = 9.2 \times 10^{-6}/°$C within the temperature range 20°—500°C) are probably connected with the occurrence of these close metal-metal contacts.

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