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Imperfections within the Phase Ti_2O_3 and its Structure Found by the Lattice Parameter and Density Method

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By interpolating the lattice parameters of 7 samples of the Ti_2O_3 phase containing from 32·16 to 34·45% b.w. oxygen, the a and c constants of pure Ti_2O_3 (hexagonal-rhombohedral) were found at 25 °C. (corrected for refraction): $a = 5{\cdot}148 \pm 0{\cdot}002$ and $c = 13{\cdot}636 \pm 0{\cdot}002$ Å, with $c/a = 2{\cdot}649_3$; or the rhombohedral constants $a_{\text{rh}} = 5{\cdot}431 \pm 0{\cdot}001$ Å and $\alpha_{\text{rh}} = 56{\cdot}58 \pm 0{\cdot}002$ ang. degrees. The other data obtained are: $v_{\text{hex}} = 313{\cdot}0 \pm 0{\cdot}3$ Å^3; the linear thermal expansion coefficients between 10 and 60 °C. along the a and c axes: $\alpha_a = -5{\cdot}8 \times 10^{-6}$ and $\alpha_c = 2{\cdot}6 \times 10^{-5}$ deg.$^{-1}$; the experimental density: $d_{25} = 4{\cdot}5868 \pm 0{\cdot}0005$ g.cm.$^{-3}$. The phase at the composition of Ti_2O_3 is sound (within the limits of error) with $n' = 6{\cdot}008 \pm 0{\cdot}015$ molec. per unit cell.

Going from the left Ti^0 rich border to the right oxygen rich border of the phase, the a parameter of the samples increases and simultaneously the c constant deminishes; the experimental density and the actual number of molecules per unit cell n' decreases. The element in excess of Ti_2O_3 (Ti^0 on the left side and O^0 or O^{2-} on the right side of the phase) is partially located in interstitial positions and partially on regular respective positions. The latter condition causes, because of electroneutrality, formation of vacant sites among the opposite positions (e.g. Ti^0 atoms on cationic regular positions cause vacant sites among the anionic positions). The concentration of defects on the left border is: Ti^0 interstitials—$0{\cdot}96 \times 10^{21}$, anionic vacancies $1{\cdot}75 \times 10^{21}$; on the right border—oxygen interstitials $1{\cdot}53 \times 10^{21}$, cationic vacancies $0{\cdot}83 \times 10^{21}$ per cm.^{3}. The X-ray density agrees with the experimental only at the point of exact Ti_2O_3 composition. The extent of the phase is determined by its capability to absorb imperfections (created by the excess of one of the elements) in its structure.

Introduction

Intermediate homogeneous phases within alloy systems have a certain width, which may be very narrow or wide depending upon the nature of the components. An intermediate phase crystallizes in a certain structure type, and the question which arises is: what happens to this lattice and its properties if the composition of the homogeneous alloy is changed within the boundaries of the phase? The literature concerning this question is extensive if only composition and lattice parameter measurements are considered (Barrett, 1952). If, in addition, density determinations are taken into account to disclose imperfections of the structures, then only a few such articles can be found (Bradley & Taylor, 1937; Ellwood, 1951; Hume-Rothery & Raynor, 1956; see also Straumanis, 1949*a*, 1953*a*, 1960*a*). There are no references at all in the literature concerning changes in concentration of imperfections in intermediate phases with the change of temperature.

In the present article the attempt was made to study not only some physical properties (lattice parameters, expansion coefficients, densities) of Ti–Ti_2O_3 homogenous solid solutions, but also to give an explanation for the appearance of imperfections (interstitials and vacancies) within the range of the phase.

The phase Ti_2O_3, being a part of the system Ti–O, was first described by Ehrlich (1939) as extending from 32·5 to 34·5 wt.% oxygen with the exact composition of Ti_2O_3 (33·38% oxygen) nearly in the middle of the phase. Other investigators came to similar results (Bumps *et al.*, 1953; Schofield & Bacon, 1955). Ti_2O_3 is a dark violet compound which crystallizes in the hexagonal-rhombohedral system, and has a corundum structure (Bragg, 1922). The parameters of the hexagonal unit cell, containing six molecules of Ti_2O_3 and those of the rhombohedral cell (with two molecules in it) are listed in Tables 4 and 5.

In order to explore the perfection of the Ti_2O_3 lattice (of stoichiometric composition) and the phase on both sides of it, the lattice parameters and also the expansion coefficients of the compound Ti_2O_3 have to be known. As it turned out to be very difficult to prepare samples of the exact Ti_2O_3 composition (Ehrlich, 1939; Lunde, 1927; Zachariasen, 1928) because of easy deviation to both sides of theoretical composition, another method of attack was chosen.

The method

Seven samples within the homogeneity range of the phase Ti_2O_3, containing increasing amounts of oxygen

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[*] Extract from a thesis of T. Ejima submitted in partial fulfillment of the requirements for the Doctor's degree to the Graduate School of the University of Missouri.

Table 1. *Composition of* Ti^0–Ti_2O_3 *and* Ti_2O_3–O^0 *solid solutions*

x-Values and the mean molecular weights *M*

Sample	Total Ti at.%	Total Ti % b.w.	Free Ti^0 at.%	Excess O at.%.	*x* in Ti_2O_x	*M* Chem.
I	41·34*	67·84	2·235	—	2·8379†	141·21‡
II	40·52	67·15	0·876	—	2·9358	142·77
III	40·30	66·90	0·482	—	2·9628	143·20
Ti_2O_3	40·00	66·62	0·00	0·00	3·0000	143·80
IV	39·59	66·24	—	1·02	3·0518	144·63
V	39·15	65·83	—	2·12	3·1086	145·54
VI	39·07	65·75	—	2·33	3·1190	145·70
VII	38·86	65·55	—	2·86	3·1467	146·15

* The X-ray pattern did not display TiO lines, although the oxygen content was less than 32·5% b.w., the apparent left limit of the phase.

† Standard deviation $s = \pm 0{\cdot}0005$ (systematic errors not included).

‡ Standard deviation $s = \pm 0{\cdot}02$.

were prepared. Then the lattice parameters of the samples were determined at constant temperatures (±0·05 between 10 and 60 °C.), and plotted against the composition of the preparations. The exact parameters of Ti_2O_3 of the theoretical composition were then obtained by interpolation. In the same manner the experimental density and the coefficients of thermal expansion were found.

For the determination of perfection or of soundness of the crystals of all the preparations it appeared advantageous to calculate n', the number of molecules per unit cell, from the equation (Straumanis, 1949, 1953*a*, 1953*b*, 1954, 1960*b*)

$$n' = dvN_0/M\ , \tag{1}$$

where N_0 is the Avogadro's Number ($6{\cdot}02403 \times 10^{23}$ g.mol.$^{-1}$, chemical scale), v is the volume of the unit cell in Å^3, d the experimental density in g.cm.$^{-3}$ and M the mean chemical molecular weight calculated from the Ti_2O_x, as derived from the analyses of the solid solutions. Comparing the n' with $n = 6.0000$ (for the ideal Ti_2O_3 structure) one can immediately find the kind of defect structure, and the changes associated with the increase of oxygen concentration in the samples. Furthermore, $n' - n$ permits one to calculate the concentration of defects in sites per unit cell.

Materials and measurements

The samples were prepared by heating pellets made of a mixture of dry titanium powder (+65 mesh, 98·27% purity, supplied by the Belmont Smelting and Refining Works) with calculated amounts of titanium dioxide (99·9% purity) in alundum or zirconia crucibles in a vacuum furnace at 1400 °C. for four and more hours. The charges, usually sintered to one piece, were crushed, ground, and stored in a desiccator. If the samples, when examined by X-ray methods and by the microscope, were not homogeneous, they were powdered and reheated again. All the samples were slowly cooled together with the furnace. They were quite pure, because the metal used contained mainly oxygen, and the dioxide some water as admixture.

In determining the composition of the samples two cases have to be distinguished: the preparations within the left side of the phase (the Ti^0–Ti_2O_3 solid solutions) which contain an excess of metallic or free titanium (Ti^0), and those of the right side (the Ti_2O_3–O^0 solid solutions) containing an excess of oxygen. Accordingly the free Ti^0 and the oxygen of the first preparations was determined by the hydrogen evolution method, dissolving the samples in hydrofluoric acid (Straumanis, Cheng & Schlechten, 1956*a*, *b*). In the latter ones the total amount of titanium was determined volumetrically (Rahm, 1952) and the oxygen content from the balance. The composition of the 7 samples and their molecular weights are given in Table 1.

The X-ray powder patterns obtained with these analysed samples were sharp, and using cobalt radiation, $\lambda_{\alpha_1} = 1{\cdot}78529$ kX., displayed two distinct doublets 1,3,10 and 3,0,12 in the back reflection region with θ angles of about 77·6 and 82·3 respectively. The exact angles were computed, after measuring the positions of the lines on the asymmetric films, by a method already described (Klug & Alexander, 1954; Azároff & Buerger, 1958). From these two Bragg angles, by solving two equations, the constants a and c of the *hexagonal cell* were calculated. The parameter determinations were made at constant temperatures in 10·0° increments in a precision camera 64 mm. in diameter (Straumanis, 1949*b*, 1953). The powder mounts had a thickness of about 0·18 mm. so that the absorption correction could be disregarded (Straumanis & Weng, 1956). The refraction correction was added to the final results (Straumanis, 1955, also 1959, 1960*a*).

The volume of the hexagonal cell (v_t) was calculated (Buerger, 1942) from

$$v_t = a_t^2 c_t \sqrt{3}/2 \tag{2}$$

in which the subscript t indicates the temperature (in °C.) of the samples.

The linear thermal expansion coefficients of the hexagonal cell α_a and α_c were determined in the direction of the two main axes a and c. For the calculation of α the equation

$$\alpha = \Delta p/(p\Delta t) \tag{3}$$

was used, where p is the respective lattice parameter and Δp and Δt are the differentials of parameters and temperatures.

The thermal volume expansion coefficient β was found from

$$\beta = 2\alpha_a + \alpha_c\,. \tag{4}$$

The density determinations were made by an improved Baker & Martin (1943) method, weighing the sample (about 430 to 620 mg.) in purest benzene (300 to 400 cm.^{3}) and in air. To reduce the errors of such determinations as much as possible, the material was ground to the finest size (325 mesh), the benzene and powder mixture outgassed while stirring at a reduced air pressure; the temperature of the air and of the benzene while the sample was weighed in it was kept constant within ±0·1 °C., and then the benzene was slowly and completely evaporated from the 10 cm.^{3} cup containing the sample, to make the second weighing in air.

The coefficients of the straight line equations were determined by the method of least squares and the errors listed are the standard deviations s. An attempt was also made to estimate the limits of the systematic errors and to find the final error due to error propagation (Straumanis, 1953*a*).

The results

The lattice parameters of the samples and of pure Ti_2O_3

The lattice parameters of the 7 analysed samples were calculated from films obtained at 3 to 6 different constant temperatures, and the straight line relationship between the parameter and the temperature was determined for each sample. Table 2 shows the constants obtained of sample I and reduced to 25 °C. as an example.

Table 2. *Lattice parameters a and c of sample I (see Table* 1) *at the temperatures given, and reduced, using the expansion coefficients of Table* 4, *to* 25 °C.

Temp. (°C.)	a_t (kX.)	a_{25} (kX.)	c_t (kX.)	c_{25} (kX.)
10·0	5·1311	5·1304	13·6260	13·6316
20·0	297	295	290	07
30·0	292	294	350	31
40·0	275	282	384	28
50·0	295	307	397	04
60·0	283	299	450	19
	Average	5·1297	Average	13·6318
		$s = \pm 0{\cdot}0006$		$s = \pm 0{\cdot}0007$

The a and c parameters of the 7 samples were corrected for refraction by adding 0·00013 to the a constant and +0·00017 kX. to the c constant; finally the parameters were converted into Å by multiplying them with 1·00202. The results are summarized in Table 3.

Thus, Table 3 shows that the a-axis expands when the titanium content is decreased, while the c-axis contracts under the same conditions. The interpolation of these lattice parameters to the Ti^0-content equal to zero leads to the parameters of the pure Ti_2O_3 (see Fig. 1). Using these interpolated values, other physical constants of the lattice of pure Ti_2O_3 were found and compared with the data of other investigators in Table 4.

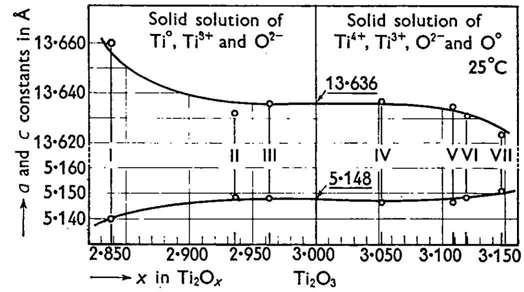

Fig. 1. Interpolated lattice constants (in Å) of pure Ti_2O_3 at 25 °C. Samples I to VII.

Actually Ti_2O_3 crystallizes in the rhombohedral system. The volume of the unit cell of this compound, if described by the rhombohedral lattice parameters, is 3 times as small as that given by the hexagonal

Table 3. *Hexagonal lattice parameters, linear* (α) *and volume* (β) *expansion coefficients, c/a and volumes v of the unit cells of* 7 *preparations within the* Ti_2O_3*-phase at* 25 °C.

Decreasing Ti^0 content (see Table 1)

Sample	a_{25} (Å)	$\alpha_a \times 10^6$ (deg.$^{-1}$)	c_{25} (Å)	$\alpha_c \times 10^5$ (deg.$^{-1}$)	c/a	v (Å^3)	$\beta \times 10^5$ (deg.$^{-1}$)
I	5·1402	−9·1	13·660	2·7	2·657	312·65	0·9
II	5·1486	−4·4	13·632	2·4	2·648	312·95	1·5
III	5·1482	+0·2	13·636	2·3	2·644	312·99	2·4
IV	5·1469	−13·6	13·637	3·1	2·650	312·86	0·4
V	5·1470	−7·3	13·635	2·6	2·649	312·82	1·1
VI	5·1488	−9·7	13·631	2·9	2·648	312·95	1·0
VII	5·1511	+3·7	13·624	1·8	2·645	313·06	2·6

s for the a-constant: between ±0·0001 and ±0·0006; for the c-constant: between ±0·0002 and ±0·0007 Å.
s for c/a ±0·0008; for the volume between ±0·02 and ±0·09 Å^3.

Table 4. *Interpolated lattice constants, c/a, volume of the unit cell, linear and volume expansion coefficients of pure* Ti_2O_3 *at* 25 °C.

Comparison with data of other investigators

Author	a (Å)	c (Å)	c/a	v (Å³)	α_a* deg.$^{-1}$ × 10^6	α_c* deg.$^{-1}$ × 10^5	β* deg.$^{-1}$ × 10^5
Zachariasen (1928)	5·15	13·56	2·633	311·4	—	—	—
Ehrlich (1939)	5·141	13·61	2·647	311·5	—	—	—
Magnéli (1957)							
$TiO_{1·49}$	5·160	13·60	2·636	313·6	—	—	—
$TiO_{1·51}$	5·147	13·64	2·650	312·9	—	—	—
Present inv.	5·148 ±0·002	13·636 ±0·002	$2·649_3$	313·0 ± 0·3	−5·8	+2·6	+1·4

* Since there was no definite relation between the expansion coefficients and the composition of the samples (see Table 3), the average of the coefficients found was taken for pure Ti_2O_3.

Table 5. *Rhombohedral lattice parameters; linear* ($\alpha_{a_{\mathrm{rh}}}$) *and angular* ($\alpha_{\alpha_{\mathrm{rh}}}$) *thermal expansion coefficients*

Volumes of the unit cells of preparations within the phase Ti_2O_3 and of pure Ti_2O_3– at 25 °C.

Sample	a_{rh} (Å)	$\alpha_{a_{\mathrm{rh}}} \times 10^5$ (deg.$^{-1}$) (C)	α_{rh} (ang.deg.)	$\alpha_{\alpha_{\mathrm{rh}}} \times 10^5$ (deg.$^{-1}$)	v (Å³)
I	5·4349	1·7	56·442	−2·8	104·18
II	5·4299	1·5	56·601	−2·2	104·32
III	5·4310	1·6	56·586	−1·8	104·34
Ti_2O_3*	5·431 ± 0·001	1·6	56·58 ± 0·02	−2·4	104·32 ± 0·08
IV	5·4308	1·8	56·570	−3·4	104·29
V	5·4303	1·6	56·577	−2·5	104·27
VI	5·4298	1·8	56·604	−2·9	104·32
VII	5·4284	1·4	56·647	−1·1	104·35

* Interpolated and average values.

s for a_{rh} is between ±0·0001 and 0·0004 Å; for α_{rh} between ±0·01 and 0·09 ang.degr.; for the cell volume between ±0·01 and ±0·02 Å³.

constants. For the transformation of the latter ones (a and c) into rhombohedral constants (a_{rh} and α_{rh}) the equations as follows are used (Buerger, 1942):

$$a_{\mathrm{rh}} = (3a^2+c^2)^{\frac{1}{2}}/3 \qquad (6)$$

and

$$\sin(\alpha_{\mathrm{rh}}/2) = 3a/2(3a^2+c^2)^{\frac{1}{2}}, \qquad (7)$$

where α_{rh} is the interaxial angle. The data for the Ti_2O_3-phase, considering a rhombohedral unit cell, are shown in Table 5.

The most recent measurements made with Ti_2O_3 by other authors (Newnham & de Haan, 1960), a_{rh} = 5·433 Å and α_{rh} = 56·566°, agree well with the respective data of Table 5.

Experimental densities

Of each of the 7 samples four to five density determinations were made at slightly different temperatures and all the densities were reduced to 25·0 °C. For instance, for the sample II the following densities, reduced to 25 °C., were obtained: 4·6056, 4·6076, 4·6055, 4·6073 and 4·6039 with an average of 4·6060 ± 0·0011.

The densities decreased clearly with increasing excess oxygen content x as shown in Fig. 2.

At the composition of stoichiometric Ti_2O_3(x = 3), the density of the compound is then d_{25} = 4·5868 g.cm.$^{-3}$ which again compares favorably with 4·6014 (Zachariasen, 1928), and 4·601 (Friedel & Guérin, 1876) or 4·56 (Shomate, 1947) of the literature for somewhat pure Ti_2O_3.

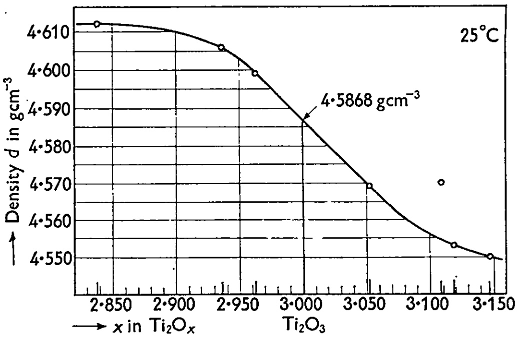

Fig. 2. Variation of density within the phase Ti_2O_3 with composition (25 °C.).

Actual number n′ of molecules

This number per unit cell was calculated from equation (1) substituting the experimentally determined values for v, d and M (see Tables 1 and 3 and Fig. 2). If n' is plotted against the composition, a straight line is obtained; n' at the composition Ti_2O_3 is very close to 6 (see Table 6), within the limits of error (±0·015 mol./unit cell). The latter value was calculated from the equation for error propagation used previously. Thus, the experimental and X-ray densities agree exactly *only at the stoichiometric composition* of Ti_2O_3 of the phase.

However, a closer insight into the structure of the phase can only be obtained by calculation of the number of constituents (atoms and ions, or shortly of ions per unit cell) compiling the phase at any composition.

Number of ions per unit cell

This number (as well as the number of separate Ti^0, Ti^{3+} and O) can easily be calculated from n' and the composition of the samples, assuming that the formula of the phase is Ti_2O_x (x varies from 2·838 to 3·147). The data obtained are summarized in Table 6, and they show that with decreasing n' the number of ions augments with the increasing oxygen concentration of the phase. Of course, the composition of the phase can also be expressed in terms of Ti_yO_3. In such a case n' increases with decreasing Ti-content of the phase, the Ti_2O_3-vertical is crossed at the same point as in the first case, but the number of ions per unit cell calculated *is exactly* the *same* as that calculated from Ti_2O_x.

Table 6. *Number of ions per unit cell of 7 preparations within the* Ti_2O_3*-phase*

Sample no.	n' molec./u.c.	Ions per u.c.	$2n'$ Ti-ions/u.c.	xn' O-ions/u.c.
I	6·151	29·76	12·30	17·46
II	6·082	30·02	12·16	17·86
III	6·055	30·05	12·11	17·94
Ti_2O_3 (interp.)	6·008	30·04	12·02	18·02
IV	5·954	30·08	11·91	18·17
V	5·917	30·23	11·83	18·40
VI	5·891	30·16	11·79	18·37
VII	5·871	30·22	11·74	18·48
		±0·05*		

* 50% confidence limits.

Knowing the actual number $2n'$ of Ti and xn' of O-ions, the number of interstitials ($2n'-12$ for Ti and $xn'-18$ for O) and of vacant sites per unit cell can be found. A positive difference designates excess ions or atoms; a negative difference indicates vacant sites of the respective constituent. The change of concentration of these imperfections depending on composition within the phase Ti_2O_3 is pictured in Fig. 3.

Structure of the phase and conclusions

Fig. 3 shows that on the left side of the phase there is an excess of titanium. This titanium may be in form of lower valency ions or even in form of metallic, Ti^0, atoms. Because of reasons given in a previous article on the TiO-phase (Straumanis and Li), the authors favour the latter possibility. In a layer type hexagonal structure, to which the Ti_2O_3 belongs, the oxygen and titanium layers alternate, and there are octahedral and tetrahedral holes in the arrangement. The excess Ti^0 may intrude in the form of interstitials into the layer's octahedral holes, which are closer to the Ti-layers and cause the expansion of the lattice along the c-axis (see Fig. 1). Simultaneously the O^{2-} missing in the oxygen layers (Fig. 3) cause the contraction of the lattice along the a-axis (Fig. 1). Similar observations were also made previously (Faivre & Michel, 1938; Wagner, 1951). Thus, such interstitials and vacancies coexist and cannot be 'annealed out' ('constitutional imperfections'). There is still a question why there are oxygen empty sites on the left and titanium vacancies on the right side of the phase (Fig. 3). This relation follows directly from the composition of the phase and the n'.

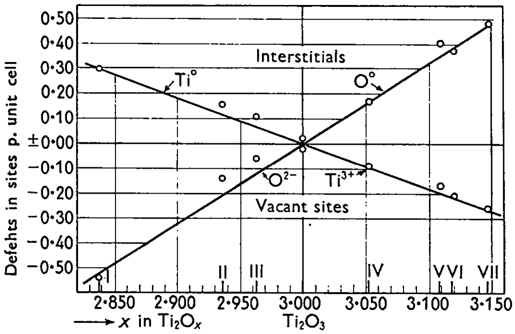

Fig. 3. Titanium interstitials and vacant sites within the range of the phase Ti_2O_3.

The general formula of the phase, as derived from chemical analyses is

$$Ti^0_{2-2x/3}Ti_{2x/3}O_3O^0_{x-3}\,. \tag{8}$$

If $x=3$, Ti_2O_3 is obtained, as Ti^0 and O^0 drop from the formula; if $x<3$, Ti^0 is present in the phase, but no O^0, and the formula becomes $Ti^0_{2-2x/3}Ti_{2x/3}O_x$ (left, Ti-rich side of the phase); if $x>3$, no Ti^0 is present but an excess of O^0 (right side of the phase): $Ti_2O_3O^0_{x-3}$.

The number of interstitial Ti^0 atoms on the left side, as it follows from Table 6 and Fig. 3, is: $2n'-12$ per unit cell. However, the amount of free metallic Ti^0, found by direct chemical analysis (see Table 1) is $n'(2-2x/3)$ atoms per unit cell, which is larger than $2n'-12$. Therefore, one part of Ti^0 atoms is located on regular cationic positions: $n'(2-2x/3)-(2n'-12)=12-2n'x/3$. Because of electroneutrality this amount of Ti^0 atoms knocks out the corresponding amount of O^{2-}, leaving their sites empty. The number of them is $-(12-2n'x/3)\times 1{\cdot}5=n'x-18$, which explains the simultaneous appearance of interstitials and vacancies on the left side of the phase.

Table 7. *Concentration i of various constituents per unit cell of the* Ti_2O_3 *phase*

(For x and n' values see Tables 1 and 6)

Constituents	Ti-rich side		O-rich side	
Interstitials	Ti^0	$2n'-12$	O^0	$n'x-18$
Total concentr.	Ti^0	$n'(2-2x/3)$	O^0	$n'(x-3)$
On regular pos.	Ti^0	$12-2n'x/3$	O^0	$18-3n'$
Vacancies	O^{2-}	$n'x-18$	Ti^{3+}	$2n'-12$

The same considerations can be used for the right part of the phase ($x>3$); only it has to be assumed that at least partially the excess of oxygen is in form of atoms O^0 (not charged).

The number of various constituents i per unit cell at any composition within the Ti_2O_3-phase is listed in Table 7.

Of course, the number of O^{2-} vacancies, as well as that of Ti^{3+} vacant sites agrees with the number as calculated from the directly determined excess of Ti^0 or excess of O (see Table 1). Furthermore, it follows from Table 7 that the concentration of vacancies and interstitials, if plotted against the composition of the phase, should lay on two straight lines crossing at the composition Ti_2O_3 (Fig. 3).

Fig. 3 also shows that on the left side of the phase there are more vacant anionic sites than there are Ti^0 interstitials. As the size of both constituents is nearly equal ($r=1{\cdot}40$ and $1{\cdot}46$ Å respectively), at least one part of the interstitials (or lower valency Ti-ions) can be located on the missing O^{2-} sites (Buerger, 1960). Interstitial oxygen atoms on the right part of the phase because of their smaller size ($r=0{\cdot}6$ Å) can easily be squeezed into the structure, or they may, at least partially, be located on the empty cationic sites. However, the excess oxygen may also be in form of O^{2-}, the equivalent amount of Ti^{3+} being converted into Ti^{4+}. Thus, at a certain composition and temperature of the alloy there seems to be an equilibrium between all the constituents of the phase, including interstitials and vacant sites (Wagner, 1930, 1952). The minimum of imperfections occurs at the exact composition Ti_2O_3, where the X-ray density is equal to the experimental.

The number of imperfections I per cm.³ can also be calculated from the data of Fig. 3, as $I=i/v$, where i is the number of imperfections per unit cell and v is the volume of the cell in cm.³ (see Table 3). Thus $I=3{\cdot}2i\times10^{21}$ sites per cm.³, which gives $0{\cdot}96\times10^{21}$ Ti^0 interstitials and $1{\cdot}75\times10^{21}$ anionic vacancies at the left border of the phase and $1{\cdot}53\times10^{21}$ O^0 interstitials and $0{\cdot}83\times10^{21}$ cationic vacant sites per cm.³ at the right border of the phase. Evidently, a still larger increase of imperfections by adding or subtracting Ti^0 is impossible and results in the formation of new phases (TiO and Ti_3O_5). The extent of the phase is determined by its capability to absorb imperfections (created by the excess of one of the elements) in its structure.

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