

Phase Analysis Studies on the Titanium-Oxygen System

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The titanium-oxygen system has been studied by means of X-ray powder photographs of preparations quenched after annealing at various temperatures. A number of phases not previously described has been observed, *viz.*

Ti₂O, TiO (low-temperature modification), Ti₄O₇, Ti₅O₉, Ti₆O₁₁, Ti₇O₁₃, Ti₈O₁₅, Ti₉O₁₇ and Ti₁₀O₁₉.

The extensions of the homogeneity ranges have been determined for the phases with variable composition.

The first phase analysis by means of X-ray methods on the titanium-oxygen system was carried out by Ehrlich^{1,2}, who reported the existence of three intermediary oxides and a high solubility of oxygen in the hexagonal titanium modification. Subsequent investigations by other authors have been numerous and comprise in addition to X-ray studies the employment of other techniques, *e.g.* microscopy and thermal measurements. These studies have contributed some modifications and added further details to the general conception of the titanium oxides established by Ehrlich but the results are not consistent throughout.

A phase diagram for the titanium-oxygen system constructed on the basis of data published up to 1954 has been given by De Vries and Roy³. The uncertainty in several respects was emphasized by these authors who actually characterized the diagram as a "not-impossible" phase diagram.

As there seemed to be reasons for considering the knowledge of the titanium-oxygen system as inadequate it was thought worth-while to undertake a comprehensive phase analysis. The results obtained so far will be reported in this article. X-Ray diffraction data for the various phases will be published separately⁴. Crystal structure studies on several of the oxides are in progress.

STARTING MATERIALS

Starting materials for the syntheses were titanium metal, titanium dioxide and intermediary titanium-oxide preparations of known compositions. The metal was "Matthey Titanium Sponge" (Johnson, Matthey & Co., Ltd), the principal impurities of which were stated by the manufacturer to be 0.01 % magnesium, 0.01 % iron and 0.003 % silicon. A determination according to Kjeldahl of the nitrogen content gave the result < 0.01 %. The titanium dioxide was of "Baker Analyzed" quality, the principal impurities being zinc (0.01 %), lead (0.006 %) and iron (0.008 %). The X-ray diffraction pattern showed that the sample consisted of the anatase modification.

The samples of intermediary titanium oxides used in the syntheses were prepared by melting mixtures of titanium metal and dioxide in an electric arc furnace. The products were analyzed in the way described below.

PREPARATION METHODS

The samples used in the present investigation were obtained by heat-treating appropriate mixtures of the starting materials. The heating was carried out in three different ways, *viz.* in an electric arc furnace under argon atmosphere, in an electric resistance furnace in a stream of argon and finally with the samples sealed in evacuated silica tubes. In order to accelerate the attainment of equilibrium, samples intended for heat-treatment at lower temperatures were generally premelted in the arc furnace.

The electric arc furnaces employed were of a design by Hägg and Kiessling⁵. The arc (DC) is formed between a negative wolfram electrode and the specimen in the form of a pressed tablet or pellet (positive electrode), which rests on a strongly water-cooled copper base. In this way no reaction occurs with the base, nor is there any transport of material from the wolfram electrode to the specimen. The cooling rate of the sample after disconnecting the arc is very high. The argon pressure within the furnace was for the actual preparations kept at about 0.5 at. When needed, the tablets were remelted once or twice in order to obtain a complete reaction. Due to segregation the samples prepared in the arc furnace were often not in a complete state of equilibrium — this was indicated by the relatively diffuse powder photographs given by these specimens.

For the syntheses in an argon stream, a horizontal electric resistance furnace (maximum temperature 1200°C) with a Pythagoras mass tube was used. The specimen tablets were kept in an alumina boat. For low contents of oxygen a superficial reaction was found to occur between the specimens and the boat. The reaction product, however, stuck to the boat and thus did not contaminate the titanium oxide samples. For high contents of oxygen no appreciable attack on the boat was observed. The argon was purified by passing it at about 770°C over finely divided uranium, obtained according to Kiessling⁶ by thermal decomposition of partially hydrogenated uranium chips. The titanium oxide samples were allowed to cool in the furnace under argon, the cooling rate thus being rather slow.

Most of the annealing operations were carried out with the specimen tablets sealed in evacuated silica tubes, which were heated in vertical, electric resistance furnaces. All the samples treated in this way were quickly quenched in water. For the lowest heating temperatures applied (400° and 600°C) no reaction was found to occur between the silica and the samples. Specimens low in oxygen only slightly affected the silica when heated for long periods of time at 800°C. At 1150°C preparations with oxygen contents below about $\text{TiO}_{1.5}$ attacked the tubes to an extent that made annealing under these conditions impracticable. Samples richer in oxygen did not react in a serious way with the silica at this temperature. In order to prevent a reaction with the silica tube at the beginning of the heating, it was found necessary to avoid as far as possible the use of titanium metal or low oxides as components in the sample.

CHEMICAL ANALYSIS

The oxygen contents of all samples prepared by arc-melting and by heating in an argon stream and of several of those heated in silica tubes were determined by the increase of weight when oxidized to titanium dioxide. Weighed samples of 0.3–0.5 g were heated in silica boats in an oxygen stream at 1000°C for periods ranging from one hour for specimens of high oxygen content to some ten hours for those low in oxygen. Following Ehrlich¹ the latter specimens were admixed with a known amount of titanium dioxide in order to avoid spitting. Only the rutile form (preheated at high temperatures) could be used for this purpose since anatase was found to cover the specimen grains with rigid shells of rutile, thus preventing complete oxidation. The reproducibility of the analyses was found to be good. The difference between starting composition and the analytically found composition after the various heat-treatments was small in most cases.

X-RAY METHODS

The phase analysis was performed by means of X-ray powder photographs taken in a Guinier focusing camera of 80 mm diameter with strictly monochromatized $\text{CuK}\alpha_1$ radiation. In order to depress the back-ground fogging caused by the fluorescence radiation from the titanium content of the samples, an aluminium filter foil of 35 μ thickness was placed in contact with the photographic film. The registration and evaluation of the patterns were carried out in the way described in a previous article⁷. Thus an internal standard (potassium chloride, British Drug Houses, Analar, $a = 6.2919 \text{ \AA}$ at 20°C⁸) was added to the powder specimens. Photographs of samples without admixture were used to reveal superpositions of lines. The effect of film shrinkage was overcome according to Hägg by printing a scale on the film prior to development⁹. Following Österlöf the measurement of the reflexions was made on the sharp, high-angle edge of the lines¹⁰. In this way it was generally possible to determine the line positions to within $\pm 0.01 \text{ mm}$.

The single-crystal photographs were taken in a Weissenberg camera using CuK radiation.

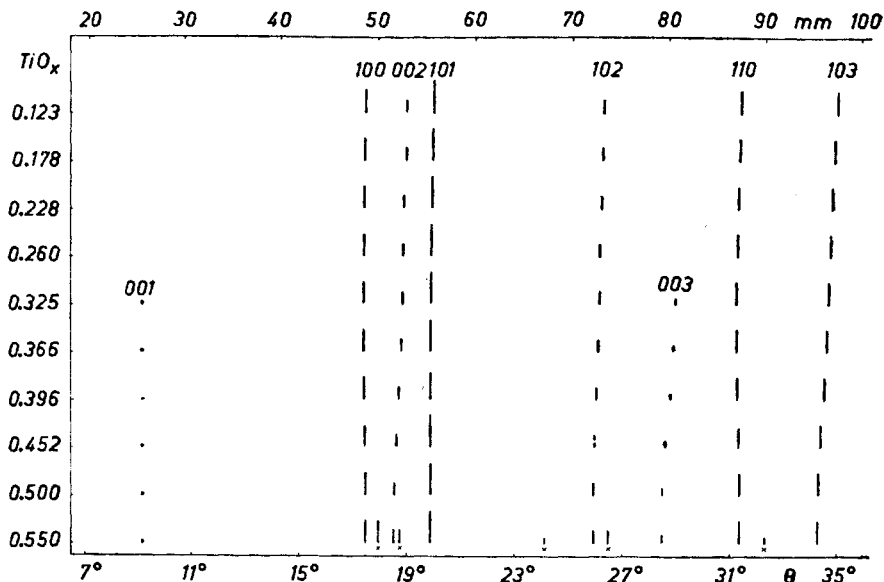


Fig. 1. Powder patterns of preparations $\text{TiO}_{0.12}$ - $\text{TiO}_{0.85}$ annealed at 400°C . The lines marked with an X in $\text{TiO}_{0.85}$ belong to the δ -oxide.

RESULTS OF THE PHASE ANALYSIS

On account of the experimental difficulties mentioned above the phase analysis studies have so far been restricted to a few temperature regions. Thus samples low in oxygen have been mostly studied after quenching from annealing temperatures of 800° , 600° and 400°C . The composition range $\text{TiO}_{0.5-1.5}$ has also been investigated by means of specimens quenched from the melting temperature (about 1800°C). For higher oxygen contents, samples heat-treated at 1150°C have been studied.

The results obtained for the various regions of composition will be discussed in the following.

The composition range $\text{TiO}_{0-0.5}$.

Data on the solubility of oxygen in α -titanium have been given by several authors¹¹. They all give values for the maximum oxygen content of this phase, corresponding to the approximate formula $\text{TiO}_{0.5}$, and the oxygen atoms are supposed to occur randomly distributed in the octahedral interstices of the hexagonally close-packed titanium lattice. The c-axis is said to increase over the whole composition range while the a axis, which is only slightly affected by the incorporation of the oxygen atoms, reaches a maximum value at about $\text{TiO}_{0.25}$ and then remains constant with increasing oxygen content.

The powder patterns of several samples within this composition range heat-treated at 400°C for 6 weeks are represented in Fig. 1. Photographs of samples annealed for several weeks at 600° and 800°C and of specimens quench-

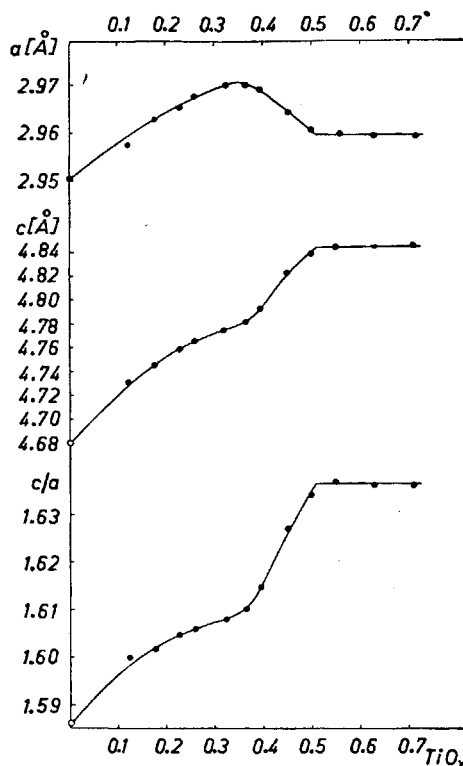


Fig. 2. Lattice parameters and axial ratios of the hexagonal specimens α -Ti- $TiO_{0.5}$.

ed in the arc furnace are all in full agreement with those shown in Fig. 1 except for the fact that the reflexions 001 and 003 are not always present (*v. infra*).

Fig. 2 shows the variation of the lattice parameters with the oxygen content. The dimensions for pure titanium are those given by Szántó¹², which, however, do not differ considerably from recent values reported by other authors¹¹. The maximum solubility of oxygen corresponds closely to $TiO_{0.50}$ and this value is evidently valid irrespective of the heat-treatment. The length of the a axis goes through a maximum at about $TiO_{0.35}$ and the steady increase of the c axis is suddenly accelerated at the same composition.

The lines 001 and 003, both of very low intensity, are incompatible with an hexagonal close-packed titanium structure containing randomly distributed oxygen atoms. The value of the axis ratio ($c/a = 1.637$) reached at the composition $TiO_{0.5}$ is evidently not connected with the presence of an almost perfect hexagonal close-packing of the atoms (ideal value of $c/a = 1.633$). For samples heat-treated at $400^\circ C$, the extra lines 001 and 003 occur in $TiO_{0.33}$ and specimens higher in oxygen. This is close to the composition where anomalous changes of the lattice parameters have been found to occur. For preparations annealed at 600° and $800^\circ C$ and quenched in the arc furnace, however,

the minimum compositions for the appearance of these two lines are about $\text{TiO}_{0.40}$, $\text{TiO}_{0.45}$ and $\text{TiO}_{0.50}$, respectively. In the patterns of the high-temperature samples the two lines are slightly diffuse.

The two extra lines may be accounted for if the oxygen atoms are assumed to be arranged in every second layer of octahedral interstices extending normally to the hexagonal axis of the titanium host lattice. Simultaneously the oxygen atoms force the adjacent titanium atom layers somewhat apart. The transition from the random TiO_{0+x} to the ordered $\text{Ti}_2\text{O}_{1-y}$ arrangement will be further studied. Details for the Ti_2O structure will appear elsewhere.

Ehrlich's observation² that samples $\text{TiO}_{\sim 0.2}$ are remarkably volatile has been confirmed by experiments in sealed, evacuated silica tubes and also in an argon stream at about 1 000°C. Further studies on this phenomenon are in progress.

The composition range $\text{TiO}_{0.5-1.4}$

According to Ehrlich¹ titanium monoxide is of the NaCl type with randomly distributed vacancies in both the titanium and oxygen lattices. The range of homogeneity extends from between $\text{TiO}_{0.58}$ and $\text{TiO}_{0.89}$ to between $\text{TiO}_{1.25}$ and $\text{TiO}_{1.33}$. All the titanium positions are occupied at the lower limit and all the oxygen sites are filled at the higher limit. At the composition $\text{TiO}_{1.00}$, 15 % of both atomic positions are vacant. Similar ranges of homogeneity have been reported by subsequent authors for samples prepared at high temperatures.¹¹

Naylor¹³ found, from heat capacity measurements, indications of a phase transition in TiO at 991°C. Jenkins¹⁴ reported that the powder photograph of $\text{TiO}_{1.00}$ heat-treated at 870°C is composed of the patterns of two distinct bodycentered cubic structures. Wang and Grant¹⁵ and also two of the present authors¹⁶ found that TiO (NaCl type) when annealed at 925° and 800°C transforms giving a phase of the stoichiometric composition TiO and a complicated powder pattern.

The existence of a phase of a composition close to Ti_3O_2 or Ti_4O_3 formed by annealing below 925°C was reported by Bumps, Kessler and Hansen¹⁷.

In the present investigation, arc-melted samples of compositions between $\text{TiO}_{0.64}$ and $\text{TiO}_{1.25}$ were found to give powder photographs showing exclusively the pattern of a NaCl-type phase. The lines were very sharp. No superstructure reflexions could be observed. Samples outside this composition region gave powder patterns showing an additional phase (α -Ti or Ti_2O_3). The homogeneity range of TiO (NaCl-type) derived from the observed unit cell dimensions extends from $\text{TiO}_{0.64}$ to $\text{TiO}_{1.26}$ (*cf.* Fig. 3). Table 1 lists the observed densities for the various TiO samples and the corresponding values for the occupancy of the atomic positions. The data confirm the results reported by Ehrlich¹.

Samples TiO_x ($0.5 < x < 1$) annealed at 900°C for 2 weeks gave powder photographs showing the pattern of Ti_2O and a great number of extra lines which appeared alone at the composition $\text{TiO}_{1.00}$. No reflexions of the NaCl-type oxide were present. The powder pattern of $\text{TiO}_{1.00}$ could not be accounted for by assuming the coexistence of two cubic phases as suggested by Jenkins¹⁴. Annealing at 800°C for two weeks was also performed for preparations with x values ranging from 0.55 to 1.40. For oxygen contents x below 1 the patterns were found to contain all those lines observed in the 900°C samples and in addition a considerable number of extra ones. The specimens annealed at

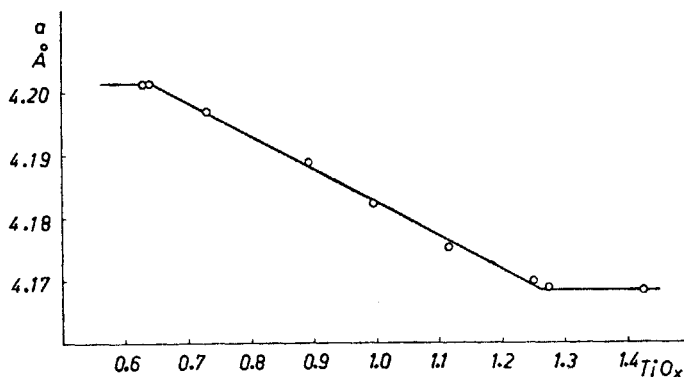


Fig. 3. Lattice parameter of TiO_x (NaCl type).

800°C were not in a state of equilibrium. The same three sets of X-ray reflexions were also found to occur in preparations heated for several weeks at 600°C.

Specimens TiO_x ($1 < x < 1.15$) annealed at 800°C gave powder patterns containing the lines found in the sample $\text{TiO}_{1.00}$ and those of TiO (NaCl-type). The latter pattern appeared alone in samples around $\text{TiO}_{1.20}$ and mixed with a corundum-type pattern (Ti_2O_3) at higher contents of oxygen. None of the systems of reflexions observed for the preparations heat-treated at 900–600°C showed any indication of line displacement with varying oxygen content.

The results may be accounted for in the following way. At 800°C there exist the phases Ti_2O , an oxide of the approximate composition $\text{TiO}_{0.65}$, not prepared in a pure state, TiO (low-temperature modification of stoichiometric composition), TiO (NaCl-type with a very narrow range of homogeneity and the approximate composition $\text{TiO}_{1.20}$) and Ti_2O_3 . The $\text{TiO}_{\sim 0.65}$ phase, the powder pattern of which is similar to that given by Bumps, Kessler and

Table 1. Occupancy of the atomic positions in TiO_x (defective NaCl-type)

x	a Å	Density		Occupancy	
		obs	calc for $4\text{TiO}_x/\text{cell}$	% Ti	% O
(0.637	4.201 ₆	5.00	5.20	96.2	61.3)
0.716	4.196 ₆	5.01	5.33	94.0	67.3
0.892	4.188 ₆	4.96	5.62	88.3	78.8
0.995	4.182 ₂	4.95	5.79	85.5	85.1
1.116	4.175 ₂	4.89	6.00	81.5	91.0
1.195	4.172 ₆	4.83	6.13	78.8	94.2
1.250	4.169 ₆	4.77	6.22	76.7	95.9
(1.275	4.168 ₆	4.80	6.26	76.7	97.8)

Hansen¹⁷ for the δ -phase, forms also at 600°C but not at 900°C. The low-temperature TiO is stable also at 900°C.

It has been pointed out^{15,16} that the densities of TiO (low-temperature form) and TiO_{1.00} (NaCl-type) are very nearly the same, *viz.* 4.91 and 4.95, respectively, and that there seems to be a pronounced relationship between the powder patterns of these two phases. This may indicate close structural kinship and it may be that the random atomic vacancies present in TiO (NaCl-type) occur in an ordered way in the low-temperature form.

The composition range TiO_{1.4-1.7}

The phases reported by previous authors within this range of composition are Ti₂O₃ and Ti₃O₅. The former, which according to Zachariasen¹⁸ has the corundum structure, was said by Ehrlich¹ to have an extended range of homogeneity, TiO_{1.48-1.58}. A compound said to be Ti₃O₅ has been studied by Rusakov and Zhdanov¹⁹ who found this substance to be isomorphous with pseudobrookite.

The phase conditions within this range of composition were studied by means of samples heat-treated at 1150°C for four days. A slight variation was found for the lattice parameters of Ti₂O₃ (corundum type), the limiting values being reached in the preparations TiO_{1.49} ($a = 5.160 \text{ \AA}$, $c = 13.60 \text{ \AA}$) and TiO_{1.51} ($a = 5.147 \text{ \AA}$, $c = 13.64 \text{ \AA}$). The range of homogeneity thus lies within the limits TiO_{1.49-1.51}.

The powder pattern of a phase appearing pure at the composition TiO_{1.67} (Ti₃O₅) is independent of the oxygen content. This pattern (*cf.* Fig. 4) is incompatible with the one reported by Rusakov and Zhdanov¹⁹ for Ti₃O₅. Single crystals have been obtained in the electric arc furnace and a structure determination using Weissenberg photographs is in progress. The single crystal data have made it possible to interpret the powder pattern and the following dimensions have been obtained for the monoclinic unit cell:

$$a = 9.757 \text{ \AA}, \quad b = 3.802 \text{ \AA}, \quad c = 9.452 \text{ \AA}, \quad \beta = 93.11^\circ$$

The observed density of 4.20 is in good agreement with the one calculated for a cell content of four formula units of Ti₃O₅ (4.24). The results of the structure determination will be published elsewhere²⁰.

It is of interest to note that studies on the system (Ti_{1-x}, Fe_x)₃O₅ have revealed the existence of a phase of pseudobrookite type for iron contents down to $x = 0.03$ ²¹. It may be that the crystal studied by Rusakov and Zhdanov, which was obtained from slag, contained impurities stabilizing the pseudobrookite structure.

The composition range TiO_{1.7-1.9}

Previous authors have reported the existence in this region of a phase with an extended homogeneity range, *viz.* TiO_{1.70-1.80} (Ehrlich¹) and TiO_{1.80-1.83} (Filonenko, Kudryavtsev and Lavrov²²).

The samples used in the present studies were with few exceptions annealed at 1150°C for three days. Specimens quenched in the arc furnace showed the same phases as those obtained at 1150°C, but were found less suitable

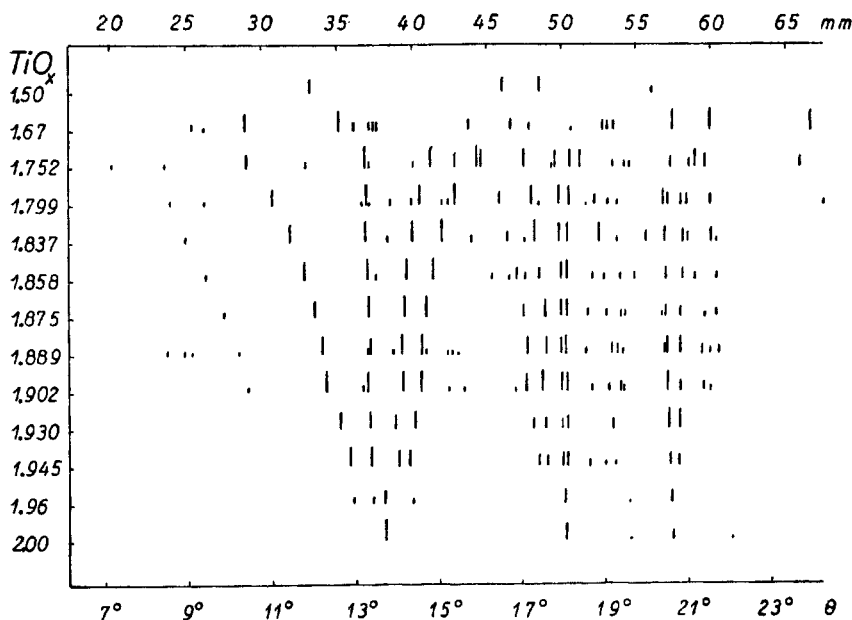


Fig. 4. Powder patterns of preparations $\text{TiO}_{1.50}\text{-TiO}_{2.00}$.

for X-ray studies because they gave less distinct powder lines. The reaction rate at $1\,000^\circ\text{C}$ was too low for equilibrium to be reached within a reasonable period of time.

Samples slightly higher in oxygen than $\text{TiO}_{1.70}$ still showed the presence of Ti_3O_5 but at about the composition $\text{TiO}_{1.75}$ the powder pattern showed only the reflexions of a new phase. With increasing oxygen content the pattern changed but was always of a similar general character (*cf.* Fig. 4). A detailed analysis, however, showed that this change was not a continuous one but that there was a periodic alternation of single-phase and two-phase regions of composition. This is demonstrated in Fig. 5 which shows the reflexions observed within a narrow range of θ . The reflexions at low θ angles provide the most sensitive test for the identification of these phases.

In order to find the compositions of the various phases, samples TiO_x were used with x values varied stepwise down to 0.002. Fairly large quantities were employed for the annealing in order to minimize the influence of the reaction with the silica. Chemical analyses performed on several of the samples confirmed that the compositions did not change during the heat-treatment.

The compositions of the phases thus derived are, within the limits of accuracy, in accordance with the general formula $\text{Ti}_n\text{O}_{2n-1}$ (*cf.* Table 2). Phases were thus identified with all values of n from 4 to 10. The formula Ti_5O_9 has been verified by means of the unit cell dimensions obtained from

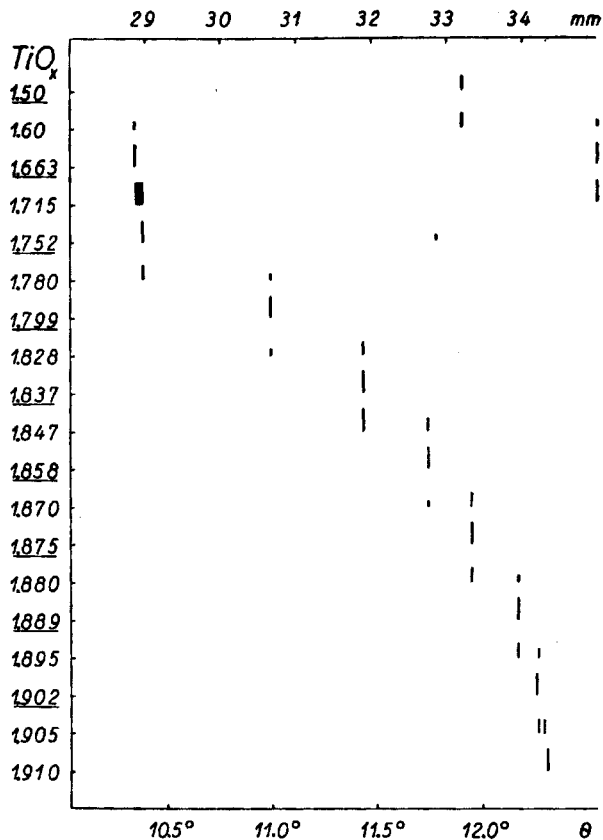


Fig. 5. Powder patterns within a narrow range of θ of preparations $TiO_{1.50}$ - $TiO_{1.91}$, demonstrating alternation of single-phase and two-phase regions of composition. Underlined x values correspond to single-phase photographs.

Table 2. Comparison between experimentally obtained compositions TiO_x and ideal compositions corresponding to a series Ti_nO_{2n-1} .

x_{obs}	n	$2n-1$	$x_{calc} = \frac{2n-1}{n}$	Ti_nO_{2n-1}
1.752	4	7	1.750	Ti_4O_7
1.799	5	9	1.800	Ti_5O_9
1.837	6	11	1.833	Ti_6O_{11}
1.858	7	13	1.857	Ti_7O_{13}
1.875	8	15	1.875	Ti_8O_{15}
1.889	9	17	1.889	Ti_9O_{17}
1.902	10	19	1.900	$Ti_{10}O_{19}$

single crystal data (triclinic symmetry) and density measurement. (The cell parameters were incorrectly given in a preliminary communication²³.)

$$\begin{array}{lll} a = 5.569 \text{ \AA} & b = 7.120 \text{ \AA} & c = 8.865 \text{ \AA} \\ \alpha = 97.55^\circ & \beta = 112.34^\circ & \gamma = 108.50^\circ \end{array}$$

The observed density is 4.29 in good agreement with the value 4.31 calculated for a cell content of two formula units of Ti_5O_9 .

The general appearance of the X-ray patterns suggests that the oxides $\text{Ti}_n\text{O}_{2n-1}$ form a homologous series of structurally interrelated compounds based on the rutile-type structure^{23,24}.

The composition range $\text{TiO}_{1.9-2}$

Several authors have reported on an extended homogeneity range of TiO_2 ¹¹. There are, however, no statements as to changes of the unit cell dimensions.

For higher oxygen contents than $\text{TiO}_{1.90}$ the powder patterns (samples annealed at 1 150°C) are still of the same type (*cf.* Fig. 4), which may suggest the existence of still higher members of the homologous series. It has, however, not been possible to prove the existence of two-phase regions above $\text{TiO}_{1.90}$. The difference between the powder patterns of consecutive homologues decreases with increasing n and it may be that the resolving power of the camera does not suffice to reveal the coexistence of two phases. Indications in favour of the supposition of distinct homologues above $\text{Ti}_{10}\text{O}_{19}$ are the considerable line displacements, which are not easily accounted for assuming a mechanism of solid solubility, and, especially, a periodical appearance of line broadenings with varying x . Anyhow, it is at present not possible to judge whether distinct phases $\text{Ti}_n\text{O}_{2n-1}$ exist up to the limit of the two-phase region towards rutile or whether the series ends with a phase of variable composition. It is worth mentioning that equilibrium conditions are not easily reached in this border region.

The first trace of TiO_2 (rutile) was observed at the composition $\text{TiO}_{1.95}$. The lattice parameters of TiO_2 in the two-phase region differ slightly but significantly from those of pure rutile. The data obtained for the latter

$$a = 4.593 \text{ \AA} \qquad c = 2.959 \text{ \AA}$$

are in good agreement with figures recently reported in the literature^{25,26}. For the lower oxygen limit (sample quenched from 1 150°C) the corresponding values obtained were:

$$a = 4.603 \text{ \AA} \qquad c = 2.960 \text{ \AA}$$

The data do not permit any accurate estimation of the width of the homogeneity range. The minimum content of oxygen is, however, higher than $\text{TiO}_{1.96}$.

When melted in the arc furnace, TiO_2 (rutile) was found to loose considerable amounts of oxygen. Thus, in one case, the composition of the sample after melting was found to be $\text{TiO}_{1.90}$. The powder photograph of this sample was diffuse. It showed no rutile lines but a pattern similar to that of the phases of the homologous series.

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REFERENCES

1. Ehrlich, P. Z. *Elektrochem.* **45** (1939) 362.
2. Ehrlich, P. Z. *anorg. Chem.* **247** (1941) 53.
3. De Vries, R. C. and Roy, R. *Am. Ceram. Soc. Bull.* **33** (1954) 370.
4. Andersson, S., Collén, B., Kruuse, G., Kuylenstierna, U., Magnéli, A., Pestmalis, H., and Åsbrink, S. *Acta Chem. Scand.* **11** (1957) 1653.
5. Hägg, G. and Kiessling, R. *IVA* **26** (1955) 105.
6. Kiessling, R. *Private communication*.
7. Westman, S. and Magnéli, A. *Acta Chem. Scand.* **11** (1957) 1587.
8. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
9. Hägg, G. *Rev. Sci. Instr.* **18** (1947) 371.
10. Österlöf, J. *To be published*.
11. McQuillan, A. D. and McQuillan, M. A. *Titanium*, London 1956, p. 250.
12. Szántó, I. *Acta Tech. Acad. Sci. Hung.* **13** (1955) 363.
13. Naylor, B. F. *J. Am. Chem. Soc.* **68** (1946) 1077.
14. Jenkins, A. E. (Discussion of Ref. ¹⁷). *Trans. Am. Soc. Metals* **45** (1953) 1025.
15. Wang, C. C. and Grant, N. J. *J. Metals & AIME Trans* **206** (1956) 184.
16. Kuylenstierna, U. and Magnéli, A. *Acta Chem. Scand.* **10** (1956) 1195.
17. Bumps, E. S., Kessler, H. D., and Hansen, M. *Trans. Am. Soc. Metals* **45** (1953) 1008.
18. Zachariasen, W. H. *Skrifter Norske Videnskaps-Akad. Oslo I. Mat. Naturv. Kl. Nr 4* (1928) 165S, S21.
19. Rusakov, A. A. and Zhdanov, G. S. *Doklady Akad. Nauk. SSSR* **77** (1951) 411.
20. Åsbrink, S. and Magnéli, A. *Acta Chem. Scand.* **11** (1957) 1606.
21. Åsbrink, S. *To be published*.
22. Filonenko, N. E., Kudryavtsev, V. I. and Lavrov, I. V. *Doklady Akad. Nauk. SSSR* **86** (1952) 561.
23. Andersson, S. and Magnéli, A. *Naturwiss.* **43** (1956) 495.
24. Andersson, S. *To be published*.
25. Legrand, C. U. J. and Delville, C. R. *Compt. rend.* **236** (1953) 944.
26. Baur, W. H. *Acta Cryst.* **9** (1956) 515.

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