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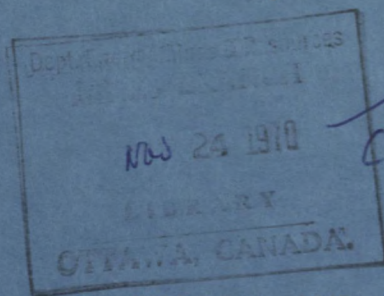
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MINES BRANCH

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THE STABILITY OF THE
POLYMORPHS OF TITANIUM MONOXIDE

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MINERAL SCIENCES DIVISION

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SUMMARY

A study has been made of the compositional and temperature stabilities of the high- and low-temperature modifications of titanium monoxide. The low-temperature form appears to exist as a single phase in the Ti–O system over only a narrow range of composition near $TiO_{0.84}$. It can be formed in equilibrium with the high-temperature form by prolonged annealing; the high-temperature form has the composition $TiO_{1.09\pm0.02}$ when the annealing is conducted at 900°C. The upper temperature limit of stability of the low-temperature form is somewhat in excess of 900°C, in agreement with earlier work. There is an indication that the high-TiO–Ti_2O_3 boundary should be placed at a higher oxygen content than has been given in earlier publications. Some consideration is given to the kinetic mechanism of the high–low transformation; it would appear to be diffusion-dependent.

INTRODUCTION

Titanium monoxide has been extensively studied from the viewpoint of the possibilities of non-stoichiometry that it exhibits[1-6]. The oxygen content of the non-stoichiometric titanium monoxide, which will be represented in this paper by the formula TiO_x, has been claimed to vary continuously from about $x=0.83$ to at least $x=1.20$. At high temperatures (above about 950°C), the oxide has the NaCl-type of cubic crystal-structure, but with up to about 15% vacancies in both the Ti and O lattice sites; this high-temperature form can easily be quenched down to room temperature. It can also be transformed by annealing, at temperatures at or below 900°C, to a low-temperature form whose crystal structure and composition have not yet been successfully and unequivocally defined. According to WAHLBECK[5(i)], the low-temperature modification can form solid solutions only over a narrow composition range around $x=1.0$, whereas SCHOFIELD AND BACON[8] claimed, in their phase diagram, that it forms solid solutions over a wide range of oxygen content, *viz.*, from $x=0.92$ to $x=1.27$.

Some anomalies in the behaviour of titanium monoxide, particularly in the

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region of the stoichiometric composition, $TiO_{1.0}$, were observed by one of the present authors several years ago[3]; it was hoped that the present study might throw some light on the unusual behaviour reported at that time. The apparent ex-solution behaviour observed in this earlier work is obviously closely related to a similar phenomenon reported by PEARSON[7]. Experiments in the present work were performed in order to find out, if possible, the true composition range of the low-temperature modification of titanium monoxide and to clarify the phase diagram of the Ti–O system in the vicinity of $x = 1.0$. Some consideration has also been given to the mechanism of the high–low transformation.

EXPERIMENTAL PROCEDURE

(a) Preparation of samples

The raw materials used were anatase (TiO_2) and α-titanium. The impurities contained in each of these materials are shown in Table I (a) and (b), respectively. The titanium was shown by neutron-activation analysis also to contain 1.33 wt.% of oxygen, and, by chemical analysis, to contain 0.17 wt.% of nitrogen. The two materials were blended thoroughly by grinding together in appropriate proportions and were

TABLE I

IMPURITIES IN RAW MATERIALS

Impurity	wt. %
(a) *Anatase*	
Water-soluble salts	0.04
As	0.00001
Fe	0.001
Pb	0.001
Zn	0.001

The above figures are the manufacturer's batch analysis.

(b) *α-Ti*	
Si	0.26
Al	0.05
Mn	0.05
Mg	0.13
Cr	0.17
Fe	0.30
Cu	0.03

The above determinations were spectrographic and are semiquantitative only.

then pressed without binder into disks 0.5 in. diam. by 0.5 in. height. Reaction to form the monoxide was achieved either by prolonged sintering in either a vacuum or an inert atmosphere, or, more frequently, by d.c.-arc fusion in an argon atmosphere. In preparing the Ti/TiO_2 mixtures, allowance was always made for the dissolved oxygen and nitrogen contents of the titanium.

(b) Determination of the composition of the titanium monoxide samples

The rapidly-cooled, solidified pellets were crushed to fine powders and were examined by X-ray diffraction procedures employing either a 114.6 mm Debye–Scherrer powder camera or, alternatively, a Guinier focussing camera. $CoK\alpha$ radiation

was used. Film-shrinkage corrections were applied and the lattice constants of the cubic phase(s) present determined as accurately as the films permitted, using the Nelson–Reilly extrapolation formula. The composition of the phases was then determined from the lattice constant by use of the lattice constant *vs.* composition relationship proposed by BUMPS, KESSLER AND HANSEN[1]. Occasionally, it was found desirable to check the gross composition of the product by oxidation to stoichiometric TiO_2 at 800°C in an oxygen atmosphere. Results in good agreement with those derived by X-ray means were obtained on these occasions.

EXPERIMENTAL RESULTS

The materials prepared by arc-fusion of Ti and TiO_2 mixtures were examined by X-ray diffraction. The photographs obtained showed very sharp diffraction lines corresponding to the NaCl-type, high-temperature form of TiO_x; the value of x was estimated from the lattice constant as indicated above. The relationship between the nominal composition, based upon the proportion of the raw materials used and the composition after fusion or sintering and quenching, but before annealing, as deduced from the lattice constant determination, is shown in Fig. 1. There was always a certain loss of oxygen content from the condensed phase during the arc-fusion process.
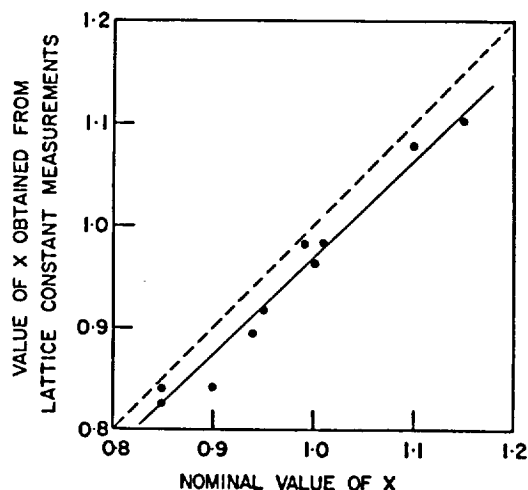

Fig. 1. Nominal composition *vs.* composition deduced from lattice constant measurements.

This may have occurred by reduction of the TiO_2 itself in the argon atmosphere at the high temperatures involved (probably >2000°C). The broken line in Fig. 1 would correspond to zero change in oxygen content between nominal and final composition; although the oxygen losses were small they were, nevertheless, always encountered.

Specimens thus prepared were then sealed into Vycor-glass tubes, either under vacuum or under an argon atmosphere, as desired, and were heated either at 950°C for 24 h, at 900°C for 77 h, at 850°C for 100 h, or at 800°C for 155 h. The samples were then rapidly cooled after these annealing treatments. In most instances, each composition studied was subjected to one or more of the four alternative annealing treatments. Debye–Scherrer powder diffraction patterns were obtained for all the annealed specimens using CoKα radiation and the phase(s) present determined from these patterns. With some annealed specimens, however, the patterns obtained were

too diffuse to determine the phase(s) present unequivocally. In these instances, the Guinier camera was used to provide more precise measurements of the diffraction lines.

An example of the improvement in resolution obtained by the use of the Guinier camera is as follows: in the case of certain samples, when one compared the *Debye–Scherrer* pattern of the as-prepared sample with that of the same material after annealing, it was observed that, after annealing, *seven* faint diffraction lines were visible in the low-angle of the pattern region that were not present in the pattern of the as-prepared sample and, in addition, each of the original lines had split into two. On the other hand, the *Guinier* camera photograph of the same annealed material showed *nine* low-angle, weak diffractions and the original (200) diffraction line of the high-temperature TiO_x was seen to have split into *three* lines instead of two. Two of these three lines were considered to belong to the low-temperature form, whereas the middle one of these three lines was considered to be associated with the presence of some residual high-temperature form, with, probably, an altered value of x.

Figure 2 shows the variation of the lattice constants corresponding to these three lines with composition, as represented by the cell-edge of the material before annealing at 850°C for the series of experiments. For convenience, each of these three lines has been indexed as (200).
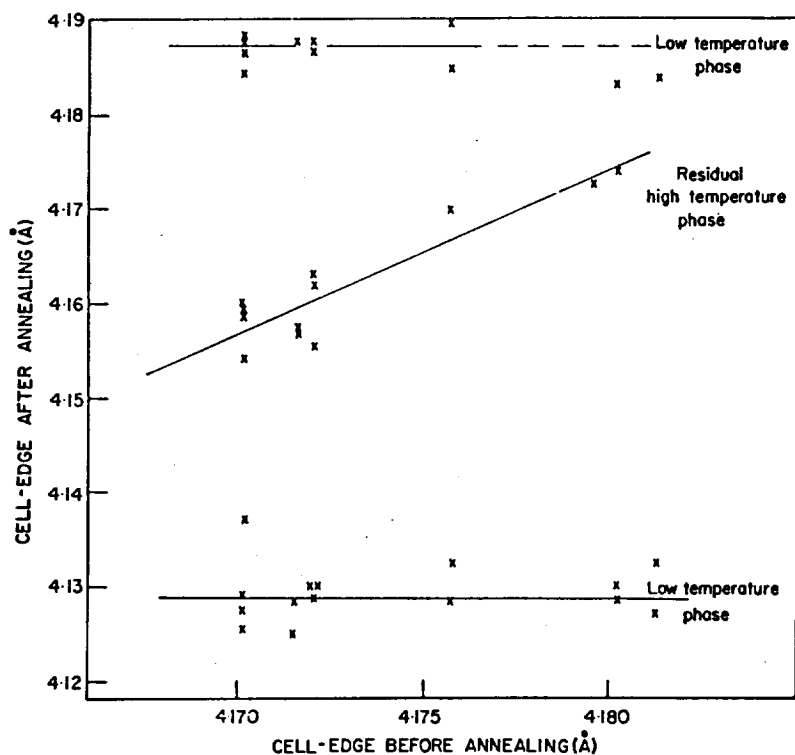

Fig. 2. Cell edges calculated from (200) lines of various TiO_x samples after annealing.

As stated earlier, the structure of the low-temperature form is not known for certain and, hence, it cannot be certain that two of these lines do, in fact, carry the indices 200, 020, or 002; however, for the purpose of comparison against the single line of the high-temperature form, which is unequivocally known to be (200), the other two lines have been considered as indicated. The two, low-temperature-form lines correspond to lattice constants of 4.128 Å and 4.188 Å, respectively, and do not change

TABLE II

PHASE ANALYSIS OF TYPICAL ANNEALED TiO_x SAMPLES

Sample no.	Nominal composition (x)	Lattice constant before annealing (Å)	Composition of high-temperature phase TiO_x before annealing (x)	Phase composition after annealing		
				Phases present	Lattice constant of residual H-phase (Å)	Composition of residual H-phase (x)
11	0.850	4.1812	0.830	H,X	4.1769	0.898
12	0.900	4.1802	0.845	L,H	4.1759	0.914
13	0.950	4.1757	0.917	L,H	4.1665	1.083
7–2	0.990	4.1720	0.980	L,H	4.1652	1.108
3–2	1.000	4.1716	0.987	L,H	4.1664	1.085
6–2	1.010	4.1701	1.014	L,H	4.1657	1.098
15	1.100	4.1663	1.086	H	4.1667	1.079
16	1.150	4.1646	1.120	H	4.1649	1.115

H = High-temperature TiO_x phase.
L = Low-temperature TiO_x phase.
X = Undetermined third phase.
Annealing conditions — 900°C in argon for 77 h.
The values of x were derived from the lattice constants using the results of BUMPS, KESSLER AND HANSEN[1].

their positions significantly, regardless of the starting composition. However, the single line lying between these two, that corresponds to the presence of residual high-temperature form, does change its position markedly with variation in starting material and in annealing time. Table II shows the results of the X-ray phase analysis of a group of typical annealed specimens. It will be seen from Table II that the composition of the specimens before annealing, as calculated from the X-ray measurements, corresponded, in general, to a lower value of x than the nominal composition, in accord with the results presented in Fig. 1. It will be seen also that, in the cases where the product after annealing was single-phase (samples No. 15 and 16), only slight changes in lattice constant occurred on annealing; on the other hand, when the annealed product was two-phase, significant changes in the lattice constant of the residual high-temperature form occurred as presented by the results in Fig. 2.

With the sample No. 11, which had an x value of 0.830, a phase that was neither high- nor low-temperature TiO_x was produced along with residual high-temperature TiO_x. The nature of this phase, which we will designate as the X-phase, was not specifically determined. It might have been the material referred to by some workers as Ti_2O or it might have been the δ-phase of BUMPS, KESSLER AND HANSEN[1]; in any case, it was present only as a minor constituent. Sample No. 12, on the other hand, which had an x value of 0.845, gave no sign of the X-phase on annealing but only of the high and low forms of TiO_x. It is considered that the X-phase may be metastable, in which case the result shown in Table II for sample No. 11 may not give any particular indication of the stability range of TiO_x (low) as a single phase. If equilibrium had been attained in this sample, and if the composition of sample No. 11 was below the value of x representing the lower limit of stability of TiO_x(low) as a single phase, then it would be expected that the assemblage found would have been either $(L+X)$ or $(L+$ some other phase such as $Ti_2O)$. The assemblage $(H+X)$ should not be found at equilibrium if the composition of L lies between those of the X and H phases, assuming that L itself is a stable phase; there is no indication that L is *not* a stable phase.

Table II, then, indicates that the upper limit of x for the L-phase as a single phase lies below 0.845 (the value for sample No. 12) at 900°C. The lower limit of stability of the H-phase as a single phase is seen to lie in the region of $x = 1.09 \pm 0.02$ at 900°C. Judging from the literature on the Ti–O system, the occurrence of metastable phase(s) in this region of the system is not unexpected. The width of the L-phase
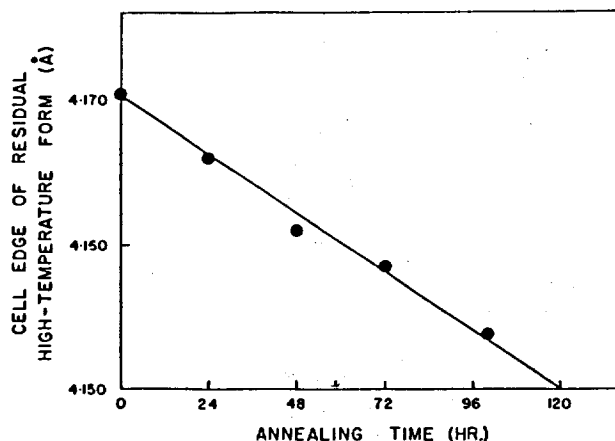

Fig. 3. Cell edges of residual high-temperature form *vs.* annealing time.

field (single-phase) is probably narrow and lies within the limits $x = 0.830$ and $x = 0.845$. For convenience, we will take $x = 0.835$ as representing the nominal composition of the L-phase.

Figure 3 shows the variation with time of annealing of the cell-edge of the residual high-temperature form, as calculated from the middle line of the three above-mentioned $(200)_o$ lines, when a specimen having an original value of $x = 1.008$ was annealed at 850°C for various times. It will be seen that the process of conversion of the high- to the low-temperature form is quite slow under these conditions and that the residual high-temperature form has a progressively lower lattice constant, corresponding to a progressively higher value of x, with increasing time of annealing.

DISCUSSION

(a) Rate of transformation of the high-temperature form of TiO_x to the low-temperature form

The variation of the composition of the residual high-temperature form with the annealing time was determined for the specimen mentioned above, having an original composition before annealing at 850°C of $x = 1.008$, using the data of BUMPS, KESSLER AND HANSEN[1]. This variation is plotted in Fig. 4 and is indicated thereon by the curve through the open circles (⊙). This will be seen to be a straight line within the range of annealing times studied in this work. It will also be seen from Fig. 4 that, under the conditions of the experiments reported here, the residual high-temperature form of TiO_x present in the sample after the longer times of annealing, and particularly after 100 h, has a composition in which the value of x is higher than is normally regarded as possible for a TiO_x cubic phase. There was an indication of

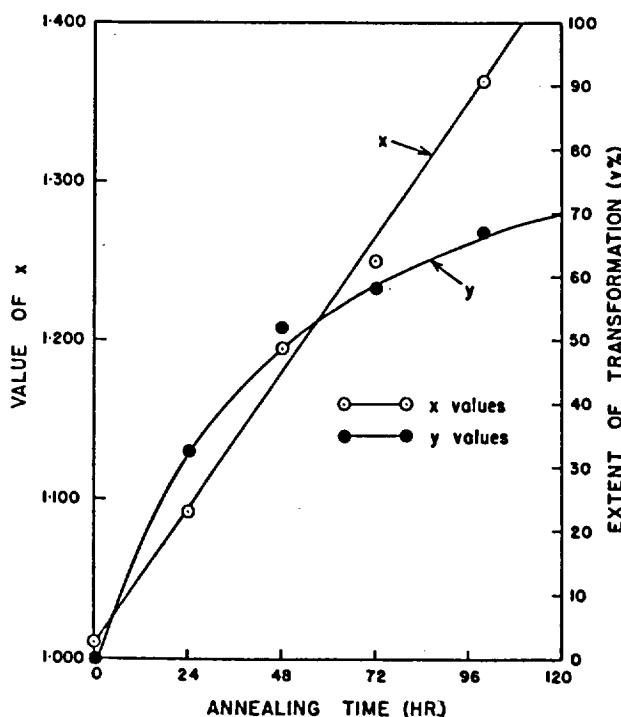Fig. 4. Variation of x and extent of transformation ($y\%$) with annealing time.

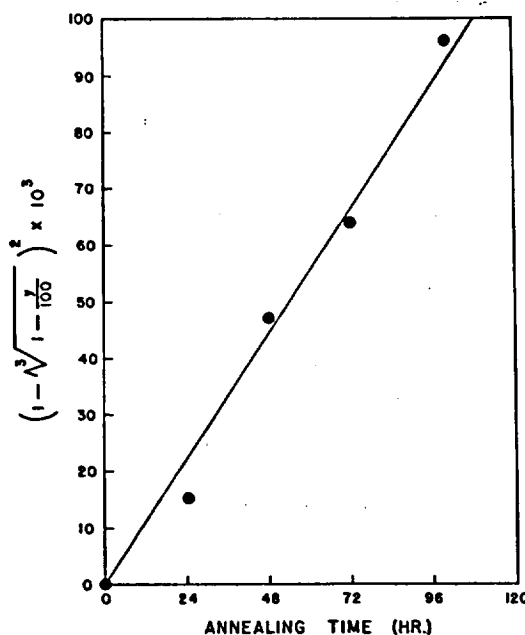Fig. 5. Variation of $[1 - (1 - y/100)^{\frac{1}{3}}]^2$ with annealing time.

a similar behaviour in the earlier work of one of us (see ref. 3, pp. 184–185). There was no evidence of the presence of any Ti_2O_3-type phase in any of these samples. It would, therefore, appear that some modification of the phase diagram of the Ti–TiO_2 system presented by WAHLBECK AND GILLES[5(1)] should be made insofar as it refers to the stability region of TiO(high) as a single phase at 850°C.

If the chemical formulae of the starting material, *i.e.*, before annealing, and of the final low-temperature phase are denoted by TiO_x and $TiO_{x'}$, respectively, then it is possible to estimate the extent of formation (y%) of the low-temperature form at any given annealing time from the results presented in Fig. 3. The difference (Δx) in the value of x of the high-temperature form between the materials before and after annealing can be shown to be

$$\Delta x = \frac{y\,(x-x')}{100-y} \tag{1}$$

The assumptions involved here are:

(a) a linear relationship between lattice constant and the value of x for cubic TiO_x, as per the work of BUMPS, KESSLER AND HANSEN[1]; and

(b) no over-all loss of oxygen occurring during the annealing process; this is supported by the results shown for Samples Nos. 15 and 16 in Table II.

The values of y were calculated from the results depicted in Fig. 3, using the above equation. It has been mentioned above that the value of x' probably lies near to $x'=0.835$ and this value will be assumed to apply. These values of y, as a function of annealing time, are plotted as filled circles(●) on Fig. 4. The value of y would appear to vary with the annealing time along a smooth curve of gradually decreasing gradient.

In the case of a solid-state reaction of the type:

Solid A → Solid B, $\tag{2}$
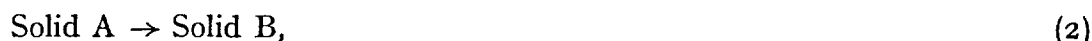
if the rate is controlled by the rate of diffusion of some species, then the well-known JANDER equation[9] will apply:

$$\left[1-\left(1-\frac{y}{100}\right)^{\frac{1}{3}}\right]^2 = \left(\frac{KD}{r^2}\right)t \tag{3}$$

where y is the percentage of the original material that has reacted to form the product, t, the time, K, a constant, D, the diffusion coefficient and r, the grain diameter.

Figure 5 shows the plot of

$$\left[1-\left(1-\frac{y}{100}\right)^{\frac{1}{3}}\right]^2$$

against t.

It is seen to be a straight line. In other words, the transformation reaction of the high-temperature form into the low-temperature form on annealing can be fully explained by postulating a diffusion-controlled mechanism. However, due to the lack of experimental data over a range of transformation temperatures, the activation energy of the diffusion process could not be estimated. It must be pointed out, however, that the determination of the rate of formation of the low-temperature form is not based on a direct observation on the amount of low-temperature form itself present, but on the change of composition of the residual high-temperature form as

inferred from the change in cell edge, and on the assumption of zero change in the gross overall composition on annealing. There is, therefore, a risk that the value of y obtained does not, in fact, show the real extent of formation of the low-temperature form, if the transformation should involve a rather longer time to accomplish the re-arrangement of the atoms than for them to assemble at the site of reaction. Rather, it shows the disappearance of the high-temperature form, neglecting the possibility of the presence of any disorganized material. In spite of these shortcomings, the technique does appear to yield a set of self-consistant results.

A solid-state reaction, in this case the precipitation of the low-temperature form of TiO_x from the high-temperature form, is usually controlled either by the rate of transport of materials to the reaction site or by the rate of reaction or re-arrangement of the atoms at the reaction site itself. In this instance, it is necessary to transport either Ti atoms (or ions) to, or O atoms (or ions) from the reaction site before the actual transformation of the high-temperature form to the low-temperature form can occur, because the oxygen content of the low-temperature form is, in general, lower than that of the high-temperature form. After the necessary concentrations of Ti and O have been attained by diffusion the re-orientation reaction between Ti and O occurs to produce the low-temperature form. The slower of these two processes will control the rate of the whole transition. Owing to the considerable difference between the ion sizes of titanium and oxygen, it is considered probable that the titanium ion may diffuse more rapidly to the reaction site than the oxygen ion would diffuse from it; then the re-orientation of the Ti and O species at the reaction site takes place to form the low-temperature modification. It is not possible at the present stage to determine the rate of formation of the low-temperature form directly; the only directly-observable quantity was the change in composition of the residual high-temperature form.

The rate of re-arrangement of the reacting species at the reaction site, the effect of vacancies in both the titanium and oxygen lattices of the cubic TiO_x on the rate of reaction, and the rate of nucleation of the low-temperature form should all be considered in determining the overall rate of transition, or the rate of change of composition of the residual high-temperature form, with annealing time; the composition of the starting material is also, of course, an operative factor. Unfortunately, no information was obtained in the present study relating to the rate of nucleation, nor to the rate of growth of individual nuclei. Hence, an *a priori* calculation of the rate of transition is not possible at present.

(b) Range of compositional stability of the low-temperature form of TiO_x

From the phase-analysis results presented in Table II, it appears that the compositional range of the unannealed material from which the low-temperature modification of TiO_x can be formed at 900°C lies approximately between $x = 0.84$ and $x = 1.05$. The stability limit of the L-form as a single phase on the high-oxygen side can be seen from Table II to lie at some value of x close to 0.84. As indicated earlier, the occurrence of the assemblage $(H + X)$ in the annealed sample No. 11 may not indicate anything significant about the stability range of TiO_x (low) owing the to possible metastability of the X-phase and the consequent non-equilibrium assemblage in this sample.

The change of composition of the high-temperature form after annealing at

$900°C$ for 77 h is shown in Fig. 6. This graph depicts the variation of the composition of the residual high-temperature form with that of the starting (un-annealed) material for these particular annealing conditions. The broken line corresponds to zero change of composition of the high-temperature phase on annealing; the experimental points are shown as open circles. This figure seems to indicate that, for the four samples having x-values before annealing of 0.917, 0.980, 0.987 and 1.014, respectively, the
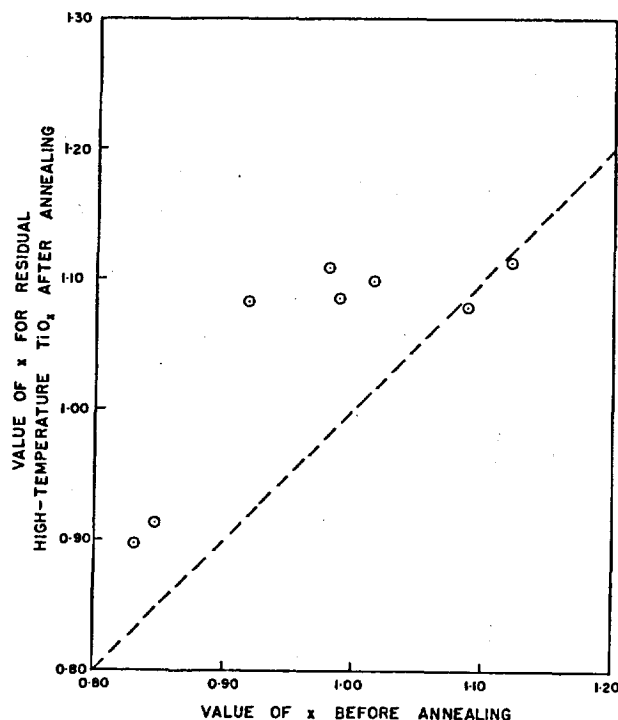

Fig. 6. Value of x before and after annealing.

reaction proceeded to equilibrium, giving the low-temperature phase plus the high-temperature phase having an x-value of 1.09 ± 0.02. The two samples having lower values of x before annealing, viz., 0.830 and 0.845, probably did not attain equilibrium, particularly in the case where $x = 0.830$ (before annealing), which yielded a mixture of the H- and X-phases. It is to be noted that the oxygen content of the residual high-temperature form always increased during the annealing process, irrespective of the annealing temperature or of the composition of the starting material, provided that the latter lay within the range that would yield a two-phased product on annealing. On the other hand, the positions of the diffraction lines belonging to the low-temperature form did not change significantly with starting composition (see Fig. 2). Therefore, it seems reasonable to consider that the composition of the low-temperature form that is in equilibrium with the high-temperature form represents the highest extreme of the compositional stability range of the low-temperature form as a single phase. Thus, at $900°C$, this low-temperature form (having $x \simeq 0.84$) appears to be in equilibrium with TiO_x (high), having $x = 1.09 \pm 0.02$. The two samples having low x-values before annealing would have a large change of composition to accomplish in order to yield residual high-TiO_x with $x = 1.09$ and, for this reason, probably, never reached an equilibrium assemblage on annealing within the period used in this work.

Although it is not unequivocally proved by the results reported herein, it is

considered very probable that the compositional range of the L-phase, as a single phase, is quite narrow. We would, thus, tend to agree with WAHLBECK[5(i)] that the low-temperature modification can form solid solutions only over a narrow range of values of x, if at all. However, we would set this value of x at 0.84 approximately, rather than at the 1.00 figure given by WAHLBECK. Thus, it is felt that, although the narrow single-phase TiO_x (low) field given by WAHLBECK AND GILLES[5(i)] is qualitatively correct, its position should be moved to lower oxygen contents to correspond to $x =$ 0.84. The remaining details of their phase diagram do not conflict with the findings in the present study, except possibly in the position of the TiO_x(high)–Ti_2O_3 boundary, where we encountered the TiO (high) phase with an x-value higher than that previously reported except for our own earlier work[3]. The reason for our quantitative disagreement with WAHLBECK AND GILLES is not immediately apparent; however, it is possible that the presence of a small proportion of the residual H-phase might have been missed when much L-phase was present if the resolution of the diagnostic lines was not as good as that given by the Guinier camera.

The range of stability for the low-temperature modification of TiO_x as a single phase found in this work is much narrower than that reported by SCHOFIELD AND BACON[8]. Insofar as the upper temperature limit of stability of the L-phase is concerned, it would appear from Table II that it must lie somewhat above 900°C. This is in accord with the results quoted by BUMPS, KESSLER AND HANSEN[1], SCHOFIELD AND BACON[8], and by PEARSON[7], all of whom indicated a temperature in the region of 950°C. The X-phase is considered to be metastable and no definite conclusion as to its temperature stability limit can be given.

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