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Disorder and Order in Solid Solutions of Oxygen in α-Titanium

BO HOLMBERG

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

The range of solid solubility of oxygen in α-titanium has been studied by means of X-ray powder and single-crystal techniques. Three phases have been observed, *viz.* a random solution (TiO_{0+x}) and two phases based on an *anti*-$Cd(OH)_2$ structure type. One of the latter (Ti_2O_{1-y}) has a broad range of homogeneity, the oxygen vacancies indicated in the formula being randomly distributed. The other, ($Ti_2O_{1-1/3}$), has one third of the oxygen positions of Ti_2O vacant in an ordered manner. The occurrence of the three phases was found to depend on both the oxygen content and the annealing temperature.

The hexagonal close-packed α-modifications of titanium, zirconium and hafnium are characterized by a remarkable ability to dissolve small nonmetal atoms to a large extent. This is especially so with oxygen which can enter into solid solution up to the compositions $TiO_{0.50}$ [1–4], $ZrO_{0.40}$ [5] and $HfO_{0.26}$ [6] in the three metals, respectively. The solubility mechanism has been thought to imply that the oxygen atoms occupy the major interstices of the metal structure, *i.e.* the octahedral holes, in a perfectly random way [7,8]. Studies recently carried out at this Institute have, however, demonstrated the existence of ordering at higher oxygen contents in the α-zirconium solid solutions [5] while a random arrangement is present in α-hafnium solid solutions [6].

According to previous investigators, the incorporation of oxygen atoms in the α-titanium and α-zirconium structures causes a considerable expansion of the *c* axes while the *a* axes are less affected by the oxygen content. It was, however, found by the present research group that the length of the *a* axes actually passes through a maximum value occurring at the composition $TiO_{0.33}$ [1] and $ZrO_{0.25}$ [5], respectively. At these contents of oxygen, there is also observed a marked acceleration of the rate of increase of the *c* axes.

The present investigation of the α-titanium-oxygen solid solutions has revealed that several preparations may give extra X-ray reflexions which are not compatible with the idea of random solutions of oxygen. The various samples employed in these studies were prepared in the way described in a

Table 1. Structural types identified in samples, $TiO_{0-0.50}$, quenched from the annealing temperature.

Annealing temperature	$TiO_{0.30}$	$TiO_{0.33}$	$TiO_{0.35}$	$TiO_{0.37}$	$TiO_{0.40}$	$TiO_{0.45}$	$TiO_{0.50}$
~ 1800°C	TiO_{0+x}	TiO_{0+x}	TiO_{0+x}	TiO_{0+x}	TiO_{0+x}	TiO_{0+x}	Ti_2O
800°C	»	»	»	»	»	Ti_2O_{1-y}	»
700°C	»	»	»	»	»	»	»
600°C	»	»	»	»	Ti_2O_{1-y}	»	»
500°C	»	»	Ti_2O_{1-y}	Ti_2O_{1-y}	»	»	»
400°C	»	$Ti_2O_{1-\frac{1}{3}}$	»	»			»

previous article [1] which also reports the X-ray techniques used in the phase analysis and the crystal structure determinations.

PHASE ANALYSIS

During the phase analysis of samples $TiO_{0-0.50}$, three types of phases were observed, viz.

(*i*) a phase characterized by the same size (approximately) of the unit cell as that of pure α-titanium metal but showing reflexions such as 003 which are not allowed by the structure of the metal. This phase is called Ti_2O_{1-y} for reasons developed below,

(*ii*) a phase showing the reflexions mentioned under *i* and additional ones corresponding to a unit cell six times the size of the metal unit cell ($Ti_2O_{1-1/4}$),

(*iii*) a phase giving powder patterns in full conformity with those of the metal (TiO_{0+x}).

The occurrence of the three phases depends on both the oxygen content and annealing temperature as shown in Table 1.

Detailed studies on the composition and region of temperature stability of the various phases and also of the characters of the phase transformations are in progress and will be reported at later date.

STRUCTURAL STUDIES

The various phases have been studied by means of single-crystal and powder techniques and the following results have been obtained:

The TiO_{0+x} region

The structure within this region (*cf. iii* above) is identical with the one suggested by Ehrlich [7] for the solid solution of oxygen in titanium *viz.*

Space-group: $P6_3/mmc$ (No. 194)
Unit cell dimensions of the sample $TiO_{0.325}$:
$a = 2.9700$ Å, $c = 4.7751$ Å
Unit cell content: 2 TiO_{0+x}
2 x O in 2(*a*): 0,0,0; 0,0,½ (random distribution)
2 Ti in 2(*c*): $\frac{1}{3},\frac{2}{3},\frac{1}{4}$; $\frac{2}{3},\frac{1}{3},\frac{3}{4}$

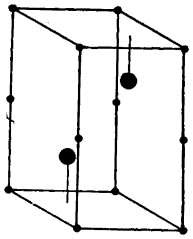

Fig. 1. The structure of α-Ti.

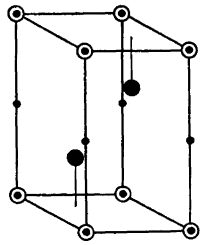

Fig. 2. The structure of Ti_2O.

The structure is illustrated in Fig. 1 which shows the metal atom positions in one unit cell and also the centers of the octahedral interstices in the metal arrangement. The holes are occupied by the oxygen atoms in a random way.

The formula TiO_{0-x} is used to indicate that the pure metal represents the limiting composition of the phase. The maximum content of oxygen (x) is, as mentioned above, dependent on the heat-treatment.

The Ti_2O structure and the Ti_2O_{1-y} region

Single-crystal studies on a sample analysed as $TiO_{0.50}$ were reported in a previous article [9] and gave the following atomic arrangement:

Space-group: $P\bar{3}m1$ (No. 164)
Unit cell dimenions: $a = 2.9593$ Å, $c = 4.8454$ Å.
Unit cell content: Ti_2O.
1 O in 1(*a*): 0,0,0
2 Ti in 2(*d*): $\frac{1}{3},\frac{2}{3},z$; $\frac{2}{3},\frac{1}{3},\bar{z}$; $z = 0.263$

The structure is illustrated in Fig. 2 which shows the atomic positions in one unit cell and also the centers of the octahedral interstices. The structure is of the *anti*-$Cd(OH)_2$ type, which implies that the oxygen atoms occupy the holes in every second layer of octahedral interstices extending parallel to the *ab*-planes. Thus all the holes of these planes are filled while those of the interleaving ones are empty. The metal atoms are not in the ideal positions of the hexagonal close-packed arrangement but somewhat displaced parallel to the *c* axis, away from the oxygen atoms.

For samples of this structure type with lower oxygen contents, a careful comparison of the powder patterns did not reveal any differences except those due to the variation of the unit cell size. This indicates that the structure is essentially unchanged over the entire region of composition. In particular, the intensities of the reflexions 001 and 003 were found to be constant, which shows that the z_{Ti} parameter is not affected by the oxygen content. Samples of the Ti_2O phase with a deficit in oxygen should thus contain vacancies in the oxygen arrangement in a random way. This phase is accordingly formulated Ti_2O_{1-y}.

Table 2. a Comparison of observed and calculated structure factors for Ti_3O. The measured intensities were corrected for absorption, the crystal being approximated to a cylinder of radius 0.020 mm.

hkl	$(hkl)Ti_2O_{1-y}$	$\|F\|_{obs}$	$\|F\|_{calc}$
002	001	—	10
004	002	150	150
006	003	52	53
008	004	141	123
0010	005	41	35
0012	006	71	71
300	110	139	151
302	111	—	2
304	112	121	110
306	113	39	39
308	114	95	103
3010	115	19	31

The Ti_3O structure

The following structure of the $TiO_{0.33}$ sample annealed at 400°C has been derived by applying trial and error techniques on single-crystal data.

Space-group: $P\bar{3}1c$ (No. 163)
Unit cell dimensions $a = 5.1411$ Å, $c = 9.5334$ Å
Unit cell content: 4 Ti_3O
2 O in 2(*a*): 0,0,1/4; 0,0,3/4
2 O in 2(*d*): 2/3,1/3,1/4, 1/3,1/3,1/4
12 Ti in 12(*i*): x,y,z; $\bar{y},x-y,z$; $y-x,\bar{x},z$;
$\bar{x},\bar{y},\bar{z}$; $y,y-x,\bar{z}$; $x-y,x,\bar{z}$;
$y,x,\frac{1}{2}+z$; $\bar{x},y-x,\frac{1}{2}+z$; $x-y,\bar{y},\frac{1}{2}+z$;
$\bar{y},\bar{x},\frac{1}{2}-z$; $x,x-y,\frac{1}{2}-z$; $y-x,y,\frac{1}{2}-z$.
$x = 1/3; y = 0; z = 0.118$

Table 2 a gives a comparison of observed and calculated structure factors for reflexions sensitive to the value of the z_{Ti} parameter. Table 2 b gives a comparison of observed and calculated intensities for reflexions sensitive to the distribution of the oxygen atoms.

Table 2 b. Comparison of observed and calculated Weissenberg intensities for reflexions depending only on the oxygen atom arrangement of the Ti_3O structure.

h k l	I_{obs}	I_{calc}
1 0 0	—	2
1 0 1	vw	5
1 0 2	—	1
1 0 3	—	2
1 0 4	—	0.5
1 0 5	—	0.9
2 0 0	—	0.6
2 0 1	—	2
2 0 2	—	0.4
2 0 3	—	1

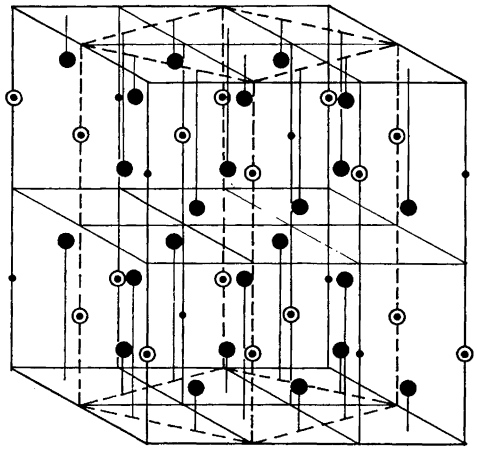

Fig. 3. The structure of Ti_3O.

The structure is a superstructure of the Ti_2O structure having the oxygen vacancies of the Ti_2O structure in an ordered distribution. One oxygen position out of three in every oxygen layer normal to the *c* axis is vacant. The vacant positions have a zigzag arrangement in the direction of the *c* axis. Fig. 3 shows a unit cell of Ti_3O and also the pattern of the basic Ti_2O units.

DISCUSSION

The structural analogy found to exist between the solid solutions of oxygen in α-titanium and α-zirconium does not, upon detailed inspection, exclude structural differences which are of considerable interest. Thus, the analogy is restricted to (*i*) a very high solubility of oxygen in both metals, (*ii*) a peculiar change in the lattice parameters with the oxygen content, and especially the occurrence of a maximum in the *a* parameter, (*iii*) the existence of random solutions of oxygen in the metal at lower oxygen contents and (*iv*) the existence of ordered solutions at higher proportions of oxygen.

The structural differences, on the other hand, manifest themselves in the dissimilar mechanisms of ordering of the oxygen atoms in the two metals. Thus, while in zirconium the oxygen atoms seem to assume an ordered arrangement as soon as a minimum oxygen content is reached, the ordering of the oxygen atoms in titanium is dependent not only on the concentration but also on the temperature. In this connection, it should also be noted that the anomalous change of the unit cell parameters and the process of ordering in the solid solutions are not associated phenomena since they do not occur at the same composition in the zirconium-oxygen system ($ZrO_{0.25}$ and $ZrO_{0.33}$ respectively).

There is a considerable difference in the ways in which the oxygen atoms are arranged in the ordered solid solutions of the two metals. Thus, in the ordered and partly ordered titanium phases, the interstitial atoms occur exclusively

in every second layer of octahedral holes extending normally to the *c* axis, which makes all these phases related to the *anti*-$Cd(OH)_2$ structure type. The metal atoms will thus be in a very asymmetric environment, the asymmetry being accentuated by the fact that the titanium atoms are slightly displaced from their ideal positions, away from the layers of oxygen atoms. In the ordered state of the zirconium-oxygen solid solution however, the oxygen atoms occur evenly distributed over ordered interstitial sites situated in all the layers of octahedral holes extending normally to the *c* axis. This arrangement is not associated with any principal changes in the atomic framework of the pure metal. Moreover, it does not imply large differences in interatomic distances like those found in the titanium-oxygen phases.

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