

Nonstoichiometric Phases in the Ti-W-O System

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Received December 4, 1989; in revised form April 3, 1990

The phases occurring in the Ti-W-O system close to WO_3 at 1273 and 1373 K were determined using X-ray diffraction and electron microscopy. In samples heated for up to 2 weeks an extended phase field of {001} crystallographic shear structures was found to exist between $MO_{2.88}$ and $MO_{2.99}$ along the Ti_xWO_3 line. These CS structures intergrew with {103} CS structures in the composition region between Ti_xWO_3 and the binary W-O line to form an operationally nonstoichiometric CS phase region. A disordered structure related to $W_{12}O_{34}$ with an extended homogeneity range was found for compositions $Ti_xW_{1-x}O_{2.83}$ with $0 < x < 0.04$. This phase was surrounded by a composition region in which disordered PC units were dispersed in the WO_3 -like matrix to form another nonstoichiometric phase region. Intergrowth between these PC structures and both CS phases and $W_{18}O_{49}$ were encountered. Heating for up to 2 months caused the ternary {001} CS and $(Ti_xW_{1-x})_{12}O_{34}$ phases to slowly decompose and their apparent phase ranges to narrow. © 1990 Academic Press, Inc.

Introduction

The complex and interesting structures which form when transition metal oxides are reduced have attracted considerable research efforts in recent years. In particular, the relationships that hold between crystallographic shear (CS), pentagonal column units (PC), hexagonal column units (HTB), and chemically twinned (CT) phases have been explored in detail and relationships extending as far as alloy structures have been discovered and clarified (1-4). As part of the body of experimental work relating to this area of study we have already presented the results of a preliminary phase analysis of the Ti_xWO_3 system when heated for short times at 1400 K (5). The results broadly indicated that as the x -value increased the corre-

sponding reduction in metal to oxygen ratio was accommodated by the introduction of CS planes into the parent WO_3 structure. At compositions close to WO_3 these were upon {102} planes, but as the degree of reduction increased toward $WO_{2.90}$ the orientation changed from {102} to {103} and finally to {001}. The samples, however, generally showed a range of different coexisting microstructures which appeared to indicate that equilibrium had not been reached. Because of this we have extended the study of the Ti-W-O system in the region of CS formation and in particular the times and temperatures of the preparations were varied over wider regimes. This has led to a clarification of the phase relations and the characterization of a new nonstoichiometric structure in the system in which PC units

are used to reduce the anion to cation ratio in the parent matrix. The results of this study are presented in this paper.

Experimental

The starting materials used for the sample preparations were H_2WO_4 (Matheson, Coleman and Bell) and TiO_2 (Baker Analyzed). WO_3 was prepared by heating H_2WO_4 in air at about 1100 K for several days, and WO_3 was prepared from the trioxide by reduction in a system of $\text{H}_2/\text{H}_2\text{O}$ at 1023 K. To obtain a suitable partial pressure of water vapor the hydrogen gas was allowed to bubble through water kept at a constant temperature of 358 K. The tungsten oxides were checked by X-ray powder diffraction, and the dioxide was also checked by careful weighing before and after reduction.

Appropriate amounts of the oxides were thoroughly mixed and sealed in evacuated silica tubes or in Pt ampoules and heated at temperatures in the range 1173 to 1673 K. The heating times extended from 6 hr to 8 weeks; the short times being used for the high temperature preparations as it was found that, at temperatures above 1500 K, heating times of 2 days caused the Pt tubes to recrystallize or to be attacked in such a way that most preparations had to be rejected.

The samples had gross compositions lying upon the Ti_xWO_3 , $\text{Ti}_x\text{W}_{1-x}\text{O}_{2.95}$, $\text{Ti}_x\text{W}_{1-x}\text{O}_{2.90}$, $\text{Ti}_x\text{W}_{1-x}\text{O}_{2.85}$, $\text{Ti}_x\text{W}_{1-x}\text{O}_{2.72}$, and $\text{TiO}_2\text{-WO}_3$ lines of the phase diagram, as shown in Fig. 1. After heat treatment the samples were quickly removed from the furnace and allowed to cool in air. No significant changes in the reaction products of quenched or air-cooled samples were found in control preparations.

All samples were investigated by recording their X-ray powder patterns at room temperature with a Hägg-Guinier focusing camera using strictly monochromatic $\text{CuK}\alpha_1$ radiation and KCl ($a_0 = 0.62930$ nm)

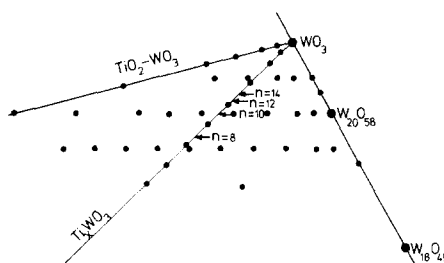


FIG. 1. Samples prepared in the Ti-W-O system at temperatures of 1273 and 1373 K; gross compositions, open circles. The arrows pointing at the Ti_xWO_3 line show the compositions at which the members of the ordered {001} CS homologous series of phases occur. The values shown correspond to the oxides $M_8\text{O}_{23}$ ($\text{MO}_{2.75}$), $M_{10}\text{O}_{29}$ ($\text{MO}_{2.90}$), $M_{12}\text{O}_{35}$ ($\text{MO}_{2.917}$), and $M_{14}\text{O}_{41}$ ($\text{MO}_{2.927}$) and to x -values of 0.095, 0.035, 0.028, and 0.027 respectively.

as an internal standard. In addition, the samples were examined optically using a Zeiss Ultraphot microscope, and selected samples were studied in a Jeol JEM 100B electron microscope operated at 100 kV and fitted with a goniometer stage. Electron microscope specimens were prepared by crushing selected material in an agate mortar under *n*-butanol and allowing a drop of the resultant suspension to dry on a net-like carbon film.

Results

In the results which follow, which were obtained by electron microscopy and X-ray diffraction, it was impossible to tell with confidence whether all the phases present contained Ti or whether they were strictly stoichiometric. Thus reference to a particular compound, say WO_3 , simply indicates that this type of structure was present, and does not indicate that the material did not contain Ti or that its composition was exactly $\text{WO}_{3.000}$. Additionally it is necessary to point out that the samples examined were invariably disordered and under these circumstances the X-ray powder patterns can-

TABLE I
X-RAY PHASE ANALYTICAL RESULTS: $Ti_xW_{1-x}O_{2.90}$

x	Phases observed ^a	
	1 week ^b	6 weeks ^b
0.005	{103}CS	{103}CS
0.01	{103}CS, {001}CS	{103}CS, ({001}CS)
0.02	{001}CS, {103}CS	{103}CS, {001}CS
0.03	{001}CS	{001}CS, {103}CS
0.04	{001}CS	{001}CS, {103}CS, (WO _{2.83})
0.05	{001}CS, (WO ₃)	{001}CS, WO ₃ , (TiO ₂)
0.06	{001}CS, WO ₃ , (TiO ₂)	WO ₃ , {001}CS, TiO ₂
0.08	WO ₃ , {001}CS, TiO ₂	WO ₃ , TiO ₂ , ({001}CS)

^a Brackets indicate trace amounts of a phase; the phase present in largest amounts is placed first.

^b Samples heated at 1373 K for 1 or 6 weeks.

not be interpreted exactly. Instead, the films show a characteristic fingerprint which is of use in gaining a broad picture of the phase relations being obtained. The characteristics of such patterns and their use in this way have been discussed previously (6-9).

The $Ti_xW_{1-x}O_{2.95}$ line. The most common phase observed by powder X-ray analysis in the samples heated at 1273 and 1373 K was WO₃. The occurrence of minor quantities of {103} CS structures could also be inferred from the X-ray patterns, especially in preparations with low Ti content close to the binary tungsten-oxygen line. In addition, {001} CS structures occurred in the materials heated for shorter times, with maximum amounts in preparations with $x = 0.02$, i.e., $Ti_{0.02}W_{0.98}O_{2.95}$, where it was present in about the same quantity as the WO₃. The diffraction lines from all of these structures were often diffuse, especially for samples heated for shorter times, signifying that the compounds were disordered. Extended heating times caused the relative amount of {001} CS structures to decrease and WO₃ to increase, while at the same time very small amounts of TiO₂ began to appear.

The electron microscope studies showed

that all samples contained crystal fragments of WO₃, which sometimes contained disordered {102} CS planes. The appearance of these crystals was similar to that found for slightly reduced WO₃ in the binary W-O system (6, 10). The other component in the samples depended upon the composition. In samples with $x = 0.005$, {103} CS planes were present. The microstructures of these crystal fragments also appeared to be identical to the microstructures previously observed in {103} CS phases found in the binary tungsten-oxygen system (6, 10). As the value of x tended toward 0.02, the CS type changed toward {001}. In this composition region crystal fragments containing intergrowths of {103} CS and {001} CS were often observed, the proportion of the {001} component increasing as x approached 0.02. This type of microstructure was illustrated in our initial report on this system (5).

The $Ti_xW_{1-x}O_{2.90}$ line. The results can be divided into two groups depending upon the heating time used, as detailed in Table I. The X-ray powder patterns of preparations which were heated for a week or less were complex and sometimes rather diffuse. A mixture of CS structures of the {001} and

{103} type were the only phases that could be identified in preparations with x -values below 0.03. When the compositions fell into the range 0.03 to 0.04 {001} CS structures predominated and only rarely were trace amounts of other phases detected. The nature of the X-ray powder patterns indicated that the crystals were generally disordered and it was not possible to determine the exact {001} homologs present. When x increased beyond 0.04, the amount of {001} CS structures present decreased. These phases were gradually replaced by WO_3 and TiO_2 until, on reaching the TiO_2 - WO_3 tie line, only these two phases were present. When heating times were increased to a month or more, one could clearly see that the amount of {001} CS structures decreased and WO_3 and very small amounts of TiO_2 could sometimes be seen.

Electron microscope examination revealed that in the samples with $x = 0.01$, the crystal fragments contained arrays of {103} CS planes similar in appearance to those found in the binary W-O system (6, 10). As x increased to 0.03 this changed to {001} CS, with many regions of wavy intergrowths between these two microstructures present. At one extreme the microstructure was almost completely {103} type with a few small incursions of {001} CS while at the other extreme the CS planes were almost exclusively of the {001} type with occasional inserts of {103} type present. This is identical to that reported previously (5).

The $\text{Ti}_x\text{W}_{1-x}\text{O}_{2.85}$ line. In these preparations X-ray diffraction revealed complex phase behavior for values of $x \leq 0.04$. For very short heating times, at most 2 days, the reaction products identified by X-ray diffraction were {001} CS phases, {103} CS phases, $\text{W}_{18}\text{O}_{49}$ and $\text{W}_{12}\text{O}_{34}$. Heating for a week showed that $\text{W}_{12}\text{O}_{34}$ was almost the only phase present over this composition range and only trace amounts of {103} CS or {001} CS structures could still be identified. In samples in which x fell in the range 0.05

to 0.09 the major structures found were {001} CS homologs. As x increased to 0.06 and beyond an increasing amount of TiO_2 could also be seen.

Prolonged heating caused the {001} CS structures to partly decompose into WO_3 and small amounts of TiO_2 . The $\text{W}_{12}\text{O}_{34}$ phase found in the Ti-rich samples in which x was greater than 0.01 also seemed to decompose slowly, as significant amounts of other oxides were identified in the samples. For the preparations made at lowest Ti-contents, however, heating for up to 8 weeks did not affect this phase.

The electron microscope analysis of these samples proved to be difficult, as the crystals were predominantly of a needle-like habit and tended to fracture perpendicular to their length to yield thin edges which provided no significant structural data. The crystal fragments which could be correctly aligned showed complex microstructures in which pairs of pentagonal columns were intergrown into the WO_3 -like matrix. The arrangement of these units was often similar to that in $\text{W}_{12}\text{O}_{34}$, but disorder was common in samples heated for shorter times. An example of this type of microstructure is shown in Fig. 2 which reveals rows of pentagonal columns identical to that in $\text{W}_{12}\text{O}_{34}$ but with variable spacings between the rows. As this spacing is often wider than in the parent phase, the composition of the crystal fragment must be richer in oxygen than $\text{WO}_{2.83}$. In other crystal fragments these pairs of pentagonal columns were found to coexist with disordered CS structures or with $\text{W}_{18}\text{O}_{49}$ as well as with areas of WO_3 -like matrix. This type of microstructure is shown in Fig. 3. The electron microscope findings thus show that pairs of pentagonal columns form the principle defect type in these samples.

The Ti_xWO_3 line. In the preparations heated for shorter times and with $x \leq 0.02$, WO_3 plus {001} CS structures were found. In the phase region $x = 0.03$ -0.05 only {001}

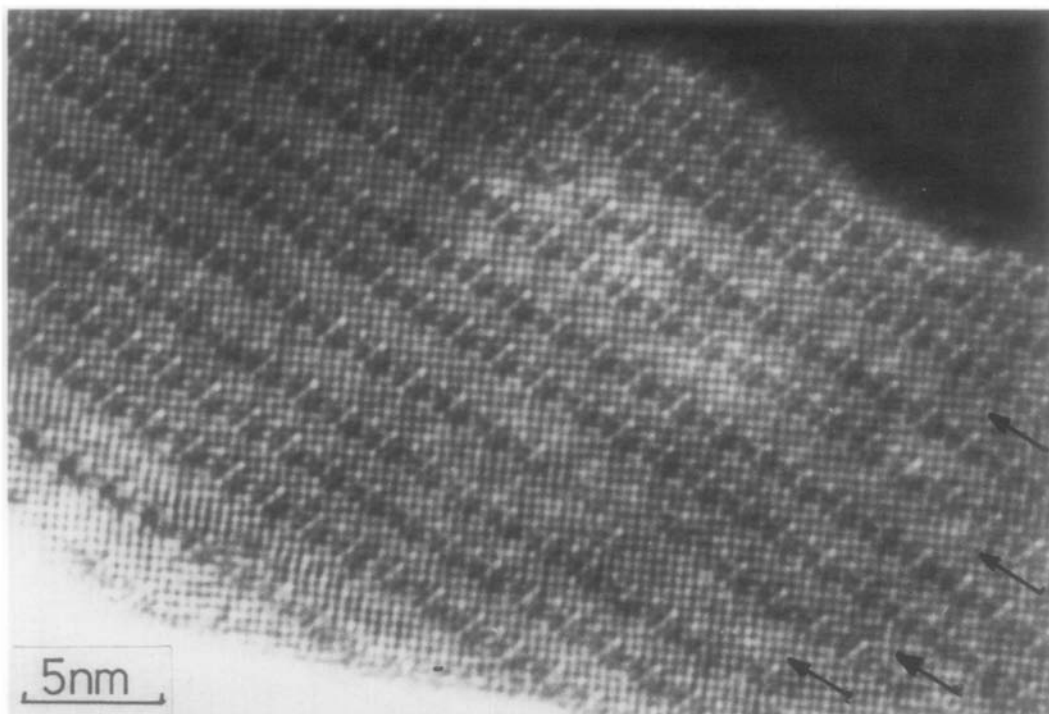


FIG. 2. Electron micrograph of a crystal containing disordered rows of pairs of PC units. The arrows mark rows with a wider separation than occur in the ordered phase $W_{12}O_{34}$.

CS was identified and for $x \geq 0.06$ very small amounts of TiO_2 and $W_{18}O_{49}$ or $W_{12}O_{34}$ could also be seen. By extending the heating time to 6 weeks at 1373 K the {001} CS oxides seemed to start to slowly decompose into TiO_2 and the appropriate tungsten oxide. However, significant amounts of the {001} structures still remained after 6 weeks heating in preparations with $x = 0.03$ – 0.05 as indicated in Table II.

To investigate the stability of the {001} CS phases a set of $Ti_xW_{3-x}O_3$ samples were heated at 1673 K for 2 days. The powder X-ray analysis showed clearly that the equilibrium was between TiO_2 and the appropriate binary tungsten oxide. In samples heated for 2 days at 1473 K {001} CS structures were observed to form. Samples heated for up to 8 weeks at the lower temperature of 1173 K produced X-ray powder patterns which,

although being quite complex and with diffuse lines, did not resemble the patterns from the {001} CS structures.

Electron microscope analysis revealed that in samples with compositions lying between $x = 0.03$ and 0.06 which had been heated for 3 days at 1373 K, {001} CS phases coexisted with slightly reduced WO_3 at the lower composition end and with disordered $W_{12}O_{34}$ at the higher composition end. The WO_3 crystals did not show typical low densities of {102} CS planes but a diffuse "chevron" contrast lying along {102} planes. This contrast has been interpreted as being due to CS plane precursor microstructures (6, 11). The values taken by n in the series formula for the {001} CS phases, $(Ti, W)_nO_{3n-1}$, were 7, 9, 10, and 11, corresponding to a composition range from $(Ti, W)O_{2.9091}$ to $(Ti, W)O_{2.8571}$.

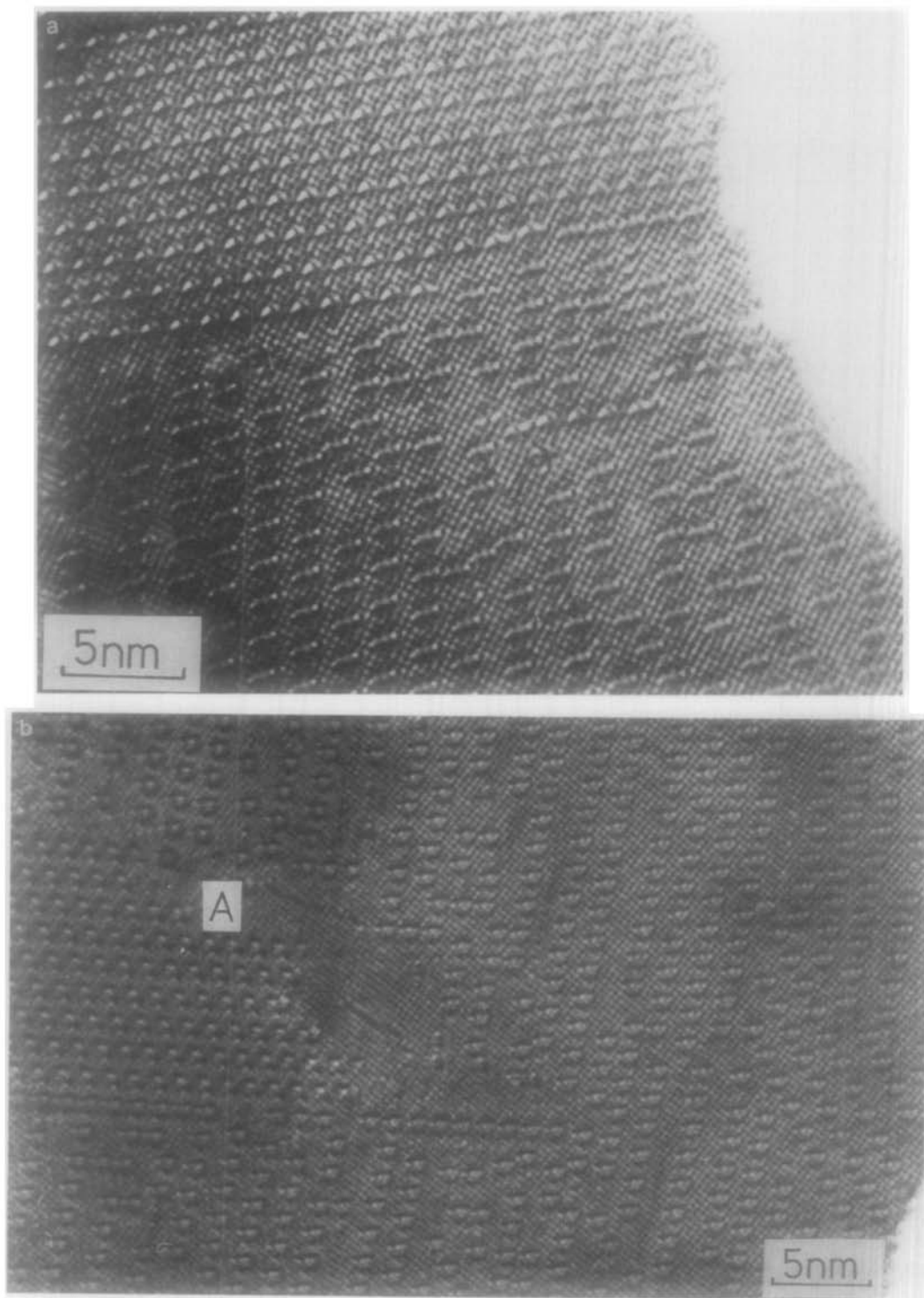


FIG. 3. Electron micrographs of crystals showing intergrowth between $W_{18}O_{49}$ and a WO_3 -like matrix containing disordered pairs of PC units. (a) The ordered $W_{18}O_{49}$ region is at the top. (b) The $W_{18}O_{49}$ region is at the left, marked A.

In samples heated for 10 days at 1373 K the diffuse chevron contrast was replaced by a low density of {102} CS planes. The {001} CS phases identified had n values of 8, 9, 10, and 11. No significance should be attached to the fact that $n = 7$ was not seen in these preparations, as an exhaustive search for all {001} type crystals was not made.

A series of samples with composition $Ti_{0.03}WO_3$ heated at 1373 K for increasing lengths of time showed that after short heating times WO_3 containing diffuse chevron type {102} contrast coexisted with {001} CS. At the longest times of heating used, 14 days, the reduced WO_3 contained a low density of {102} CS planes.

The TiO_2 - WO_3 line. A number of samples have been heated along this line at compositions close to WO_3 and at temperatures in the range 1273–1673 K. No reactions of TiO_2 with WO_3 or any CS formation was seen.

Discussion

The results obtained by X-ray diffraction and electron microscopy were in good agreement with each other and with those results reported previously (5) and allowed the phases occurring in the Ti-W-O system near WO_3 to be identified. The X-ray diffraction results showed that a phase field of {001} CS structures is centered along the Ti_xWO_3 line and bounded by the approximate composition limits $(Ti, W)_{11}O_{32}$, i.e., $MO_{2.9091}$ to $(Ti, W)_7O_{20}$, i.e., $MO_{2.8571}$. Additionally, a phase field with the $W_{12}O_{34}$ structure type exists at about $Ti_xW_{1-x}O_{2.83}$ for $0 \leq x \leq 0.04$. After prolonged heating some of these ternary structures seem to slowly decompose to produce small quantities of the appropriate binary oxides, but even after 6 to 8 weeks heating these phases still occur, indicating that the phase field of the ternary samples is narrowing rather than disappearing altogether. Considering the {001} CS phase field, the preparations made at 1173

K indicate that these compounds may not exist at this lower temperature, but this has not been studied here in any detail. Similarly, the preparations made at 1673 K again suggested that the {001} CS phases did not form. These two results indicate that the {001} CS structures might form in a restricted temperature range centered upon 1423 K.

The electron microscope results revealed that the microstructures found in the phase region covered in this study fall into two types, viz. CS structures and PC structures. In samples with compositions closest to WO_3 the microstructures seem to be identical to that found in the binary W-O system and consisted of low populations of disordered {102} CS planes or else the diffuse chevron-like contrast believed to be the precursor of {012} CS planes (6, 11). It is not possible to say whether any Ti has entered into the structure at this stage of the reaction.

At somewhat greater degrees of reduction the phase field consists of a WO_3 -like matrix consisting of {001}/{103} CS plane intergrowths. In the composition region near the binary W-O line the structures consist of {103} CS structures while near the Ti_xWO_3 line fairly well-ordered {001} CS phases are found. Between these composition limits an operationally nonstoichiometric phase region exists containing wavy intergrowths of {103} and {001} CS planes. These microstructures reveal that Ti is now entering the structure, as {001} CS does not occur in the binary system. The intergrowths between the {103} and {001} structures can be most reasonably associated with differing concentrations of Ti in the structure although there may not be a completely quantitative correlation as it has been shown that elastic strain energy influences the microstructures of CS phases appreciably, and so local concentrations of Ti-rich material may cause {001} CS to form even in adjacent Ti-poor regions of crystal.

TABLE II
X-RAY PHASE ANALYTICAL RESULTS: Ti_xWO_3

x	Observed phases ^a	
	1 week ^b	6 weeks ^b
0.005	WO ₃ , {001}CS	WO ₃ , ({001}CS)
0.01	{001}CS, WO ₃	WO ₃ , {001}CS
0.02	{001}CS, (WO ₃)	WO ₃ , {001}CS
0.03	{001}CS	{001}CS, WO ₃ , ({103}CS)
0.04	{001}CS	{001}CS, {103}CS, (MO _{2.83})
0.05	{001}CS	{001}CS, MO _{2.83}
0.06	{001}CS, (W ₁₈ O ₄₉)	MO _{2.83} , {001}CS, (TiO ₂)
0.07	{001}CS, W ₁₈ O ₄₉ , (TiO ₂)	MO _{2.83} , ({001}CS), (W ₁₈ O ₄₉)

^a Brackets indicate trace amounts of a phase; the phase present in largest amounts is placed first.

^b Samples heated at 1373 K for 1 or 6 weeks.

At increased amounts of reduction the nonstoichiometric phase region uses pairs of PC units in place of edge-shared octahedra to reduce the anion to cation ratio. In the binary W–O system Pickering and Tilley (12) were the first to report the existence of a compound with a composition close to WO_{2.82}, which was subsequently shown by Sundberg (13) to consist of an ordered arrangement of pairs of PC units in a WO₃-like matrix, giving a composition of W₁₂O₃₄. The present study has shown that the W₁₂O₃₄ structure type forms in the Ti–W–O system and there seems to be no doubt that titanium substitutes for tungsten and thereby speeds up the formation of this phase considerably compared to the rate in the binary system. The homogeneity range determined by X-ray diffraction is extended away from the binary tungsten oxide line but prolonged heating times causes this phase range to contract, although compositions close to tungsten oxide line are apparently unaffected. Thus the binary or pseudo-binary W₁₂O₃₄ oxide seems, once formed, to be stable.

The electron microscope study showed that for much of the composition range the structure is highly disordered. The defects

are pairs of PC units which are arranged in a variety of ways in the WO₃-like matrix. It is possible that the narrowing of the phase range observed by X-rays is simply due to ordering of these defects into the arrangement encountered in W₁₂O₃₄. When the overall composition of the sample was nearer to WO₃ the disordered PC structures intergrew with disordered CS structures. At lower compositions the PC units coexisted with regions of the W₁₈O₄₉ structure. As with the CS region, we thus have a nonstoichiometric phase region but which, in this case, relies upon a variable population of PC units to change the anion to cation ratio rather than edge-sharing octahedra.

The electron microscope study has revealed that the whole of the phase region studied consists of an operationally nonstoichiometric compound with WO₃ as the host structure. Near the exact WO₃ composition we find disordered {102} CS planes in a WO₃-like matrix. These defects give way to {103}/ {001} CS intergrowths and ultimately to PC units as the composition continues to fall toward W₁₈O₄₉. This latter phase has never been found in a significantly disordered state and seems to be a stoichiometric compound.

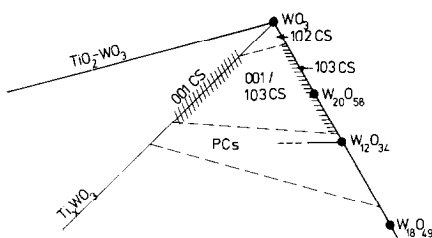


FIG. 4. A schematic representation of the phase regions occurring in the Ti-W-O system at a temperature of about 1373 K after 1-2 weeks heating. The phase regions are: a, WO_3 containing low populations of disordered $\{102\}$ CS planes; b, intergrowth between $\{103\}$ and $\{001\}$ CS planes; c, disordered pairs of PC units. The areas over which these structures occur is only approximately delineated as they depend both on the time and temperature at which the samples are heated.

Long heating times have not removed the disorder in the WO_3 -like matrix, but it appears that the phase ranges of the structures found are narrowing somewhat. This suggests that a slow ordering of the CS planes or PC units is taking place and that ultimately a succession of ordered structures might form. The driving force for this ordering will be small and the kinetics slow, but the trends observed suggest that the structures WO_3 , $\{001\}$ CS, $\{103\}$ CS, $\text{W}_{12}\text{O}_{34}$, and $\text{W}_{18}\text{O}_{49}$ will eventually emerge as the stable phases. The structure types encountered over the composition range studied are summarized in Fig. 4.

The size of the Ti^{4+} ion, which is comparable to that of W^{6+} , suggests that the Ti substitutes for W in these intergrowths. A number of transition elements which are similar in size and chemical behavior to tungsten have also been found to substitute for tungsten in ternary oxides (10, 14). Small amounts of Mo, Ta, and Nb produce a succession of CS and PC phases as the composition and temperature of preparation changes. However, the exact type of CS and PC structures encountered and the phase ranges over which they exist varies from one metal to another (10, 14). The most similar

system to that reported here is the Nb-W-O system, where the succession of CS phases also encompasses $\{001\}$ structures. It is known that within the early transition metals there is a diagonal and a horizontal relationship between the elements in the Periodic Table and the similarity between the Ti and Nb-W-O systems is not unexpected.

Despite the considerable amount of experimental data accumulating on the reduced binary and ternary W oxides an explanation of the composition ranges over which CS or PC phases occur is still not available. Because of this there is still continued interest in exploring from an experimental point of view, structures which form in related systems such as the closely allied ternary Nb oxides (15, 16). Notwithstanding such efforts, there is no obvious correlation with nominal ionic size, outer electron structure, ionization potential, or electronegativity compared to the neighboring atoms which do not form CS or PC phases. The temperature range over which CS is the favored mode of accommodating a change in the anion to cation ratio is narrow, as is the composition range over which the phases are found relative to the PC phases. This indicates that the forces controlling the structure are delicately balanced, a feature confirmed by the fact that elastic strain energy, which is a relatively small term in comparison to normal bonding energies, is able to have a large effect upon the structures formed (10). Hence further experiments are still needed before the factors which determine the structural mode in which these nonstoichiometric phases accommodate changes in anion to cation stoichiometry can be delineated.

Acknowledgments

Financial support for K.A.W. was provided by the SERC and ICI plc. The research has also been performed within a program supported by the Swedish Natural Science Research Council and T.E. is grateful to Professor A. Magnéli for the experimental facilities provided at this disposal.

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