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The Dioxide–Trioxide Region of the Vanadium–Tungsten–Oxygen System

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The phases existing at 1373°K in the ternary vanadium–tungsten–oxygen system between the compounds WO_3, WO_2, VO_2, and V_2O_5 have been characterized by X-ray diffraction and electron microscopy. In the region close to WO_3, no evidence of substantial substitution of vanadium into the tungsten trioxide structure was found and extensive formation of ternary CS phases was not found. In samples heated for 14 days, the major ternary phase observed was a rutile phase $(V, W)O_2$, although some other less stable ternary compounds were also recorded in the V_2O_5 rich region of the phase field. Besides these, an orthorhombic modification of tungsten trioxide was found coexisting with the usual monoclinic form, disordered W_nO_{3n-1} (102) crystallographic shear phases and the binary oxide $W_{18}O_{49}$. These results are summarized in a phase diagram. Samples heated for short periods of time contained, in addition to the compounds listed above, another unidentified phase and disordered W_nO_{3n-2} (103) crystallographic shear phases. A comparison of both sets of results allows a possible mechanism to be put forward for the reaction between the original tungsten and vanadium oxides.

Introduction

Although electron microscopy has done much to clarify the structural nature of the crystallographic shear (*CS*) phases found in the tungsten–oxygen system, the chemical reasons for their formation are still obscure. One way to investigate the influence of chemically important parameters, such as outer electron structure, atomic size, and valence, in such compounds is to reduce tungsten trioxide with metals other than tungsten. Such experiments are now underway and reports of some results obtained in the systems Ti_xWO_3 (*1*) and Zr_xWO_3 (*2*) have already been given. While in both these systems reaction was appreciable, quite different behavior was found in the two cases. In the titanium tungsten oxides complex families of *CS* phases occur, whereas in the zirconium tungsten oxides bronzes related to the perovskite type are formed and no *CS* takes place.

This difference in chemical behavior suggests that other groups of elements in the periodic table should be investigated as substituents. Of these, one of the most interesting in the context of *CS* phase formation is the triad V, Nb, Ta, and indeed some studies that describe compounds existing in these ternary metal–tungsten–oxygen systems are already to be found in the literature. However, none of them covers the composition range close to tungsten trioxide and the M_xWO_3 line in detail, and they are not complete enough to allow a systematic comparison of the properties of the M_xWO_3 compounds with either the binary oxides or the titanium and zirconium results mentioned above. Because of this, a systematic study of these elements is also being undertaken. This

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report is largely concerned with results found in the vanadium tungsten oxides, although brief references will be made to the niobium and tantalum systems where necessary.

A number of ternary vanadium tungsten oxides are known, and some of these can be derived from a hypothetical parent possessing the ReO_3 (DO_9) structure by crystallographic shear. These are the oxides $V_3W_5O_{20}$ (*3*) which have a structure similar to V_2O_5 with *CS* planes on (001) of the parent and the block structures $(V_{0.65}W_{0.35})_2O_5$ (*4*) and $(V_{0.8}W_{0.2})_3O_7$ (*5*) in which the *CS* planes lie on (100) and (001) of the parent. Besides these, the only other ternary phase to be reported in the region of interest is the mixed dioxide $V_xW_{1-x}O_2$ with a structure closely related to that of rutile (*6*, *7*). Apart from these rutile compounds, the phases seem to be relatively unstable and have been reported to decompose at temperatures between 1073 and 1273°K (*6*, *8*, *9*). The only other study concerned with vanadium tungsten oxides close in composition to WO_3 was by Bursill and Hyde (*10*), who prepared several samples of bulk composition $V_{0.1}W_{0.9}O_{2.95}$. No long-period *CS* phases were found in this material; only WO_3 and an unidentified phase that appeared to be related to the V_2O_5 structure type were found.

As can be seen, none of these ternary compositions is close to the region of interest in our case, principally along the line WO_3–$V_{0.1}WO_3$, and the present research was undertaken to fill this gap. A temperature of 1373°K was chosen initially to concur with the titanium and zirconium studies. At this temperature, the binary tungsten oxides WO_3, W_nO_{3n-1} (containing {102} *CS* planes), W_nO_{3n-2} (containing {103} *CS* planes), $W_{18}O_{49}$ and WO_2 are stable. The vanadium oxides in the phase range of interest, V_2O_5, V_3O_7, V_4O_9, V_6O_{13}, and VO_2, are rather less stable and only the VO_2 phase is to be found in the solid state at 1373°K. The phase region of interest, therefore, is bounded by the compounds WO_3, WO_2, and VO_2. Initial results indicated that the whole of this region of the phase diagram needed to be understood before phase relations on the V_xWO_3 line could be clarified. Hence, the study was extended to cover the whole area lying between the dioxides and the higher oxide WO_3. These results are presented below.

Experimental

The starting materials used were tungstic acid (ex Matheson, Coleman and Bell, p.a.) and vanadium pentoxide (ex U.C.B. p.a.). Tungsten trioxide was prepared by heating the tungstic acid in air at about 1073°K for several days and tungsten dioxide was prepared by reduction of the trioxide in a stream of hydrogen–water gas mixture at 1023°K. To obtain a suitable partial pressure of water, the hydrogen gas was allowed to bubble through water kept at a temperature of 358°K. Vanadium sesquioxide was prepared from the pentoxide by reduction in flowing hydrogen gas at 1073°K. The degree of reduction of WO_2 and V_2O_3 were checked by careful weighing and by inspection of X-ray powder patterns.

Appropriate weighed mixtures of V_2O_3, V_2O_5, WO_2, and WO_3 were heated under vacuum in sealed ampoules. In general samples heated for 3 days at 1373°K were contained in silica while those heated for 14 days at 1373°K were contained in platinum tubes, which were themselves sealed inside evacuated silica ampoules. In samples rich in V_2O_5, unprotected silica tubes were often considerably attacked. If such attack was indicated in the present study, the results were rejected and the compositions were repeated in sealed platinum ampoules within the silica. Those compositions lying on the V_2O_5–WO_3 line were heated in tubes containing a reduced pressure of air (approximately $\frac{1}{4}$ atm at room temperature) to prevent reduction. A few samples were heated at temperatures up to 1573°K to clarify aspects of the lower temperature results. After the heat treatment, the samples were removed from the furnaces and allowed to cool to room temperature without special quenching techniques being employed.

All samples were investigated by recording their X-ray powder patterns at room temperature in a Guinier–Hägg focusing camera using $CuK\alpha_1$ radiation and KCl as an internal standard. Lattice parameters were refined by least-squares techniques (*11*). In addition, many samples were studied by optical and electron microscopy. Optical microscopy was carried out with a Zeiss Ultraphot optical microscope and electron microscopy with a JEM 100 B electron microscope operated at 100 kV or Siemens Elmiskop 102 operated at 125 kV. Both instruments were fitted with goniometer stages. Electron microscope specimens were prepared from chosen samples by crushing in an agate mortar and dispersing the resulting fragments in *n*-butanol. A drop of this suspension was allowed to dry upon a perforated carbon film resting on a conventional copper supporting grid. Crystal flakes over holes in the carbon film were chosen for study. High-resolution electron micrographs were taken following the procedures described by Iijima (*12*) and Allpress and Sanders (*13*).

Results

The bulk compositions prepared are shown on Fig. 1; portions of each composition were heated for either 3 or 14 days. In general, the results from the two heating times were similar although the samples heated for the longer period of time usually gave much sharper X-ray films. The results from the samples heated for 14 days were used to construct the phase diagram in Fig. 1. The detailed observations that lead to the phase diagram proposed are described in the following sections, and some aspects of it are considered further in the discussion.

Samples of composition V_xWO_3 were somewhat different from the majority in that the samples heated for 14 days were quite different in phase composition from those heated for only 3 days. In these cases, the 14-day samples are regarded as being nearer to equilibrium and were used in construction of the phase diagram shown in Fig. 1. As most emphasis in this study was placed upon the V_xWO_3 series and upon *CS* formation in this region of the ternary system, these particular results are discussed in greatest detail in the sections below.

V_xWO_3 *Samples Heated for 14 days*

In general, all samples were well crystalline and gave sharp X-ray powder photographs, which were, however, relatively complex and indicated that a variety of phases were usually present in each sample. Optical microscopy showed that they consisted predominantly of well-formed very dark green crystals which, with one exception, were of a uniform chunky habit, although often sintered together. These crystals were almost always twinned and seemed to be typical of WO_3. The exception was the $V_{0.005}WO_3$ sample where the crystals were frequently round, strongly suggesting that partial melting had taken place. In addition, the $V_{0.07}WO_3$ sample also contained a large number of blue-black crystals with a needle habit. Crushing the samples gave a green powder similar in color to crushed WO_3 again with the exception of the $V_{0.07}WO_3$ sample, which was rather more blue in color.

Electron microscopy revealed that the major component of the V_xWO_3 samples was very similar to slightly reduced WO_3 (*14*). Fracture fragments contained a low density of {102} *CS* planes, sometimes quite isolated and sometimes quasi-ordered in small regions of the crystal. The density of these *CS* planes did increase slightly as the degree of reduction

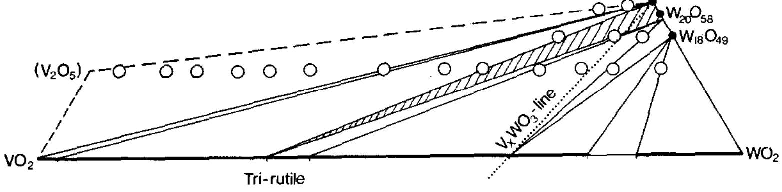

FIG. 1. Part of the phase diagram for the three component system V–W–O at 1373°K. The open circles indicate the gross compositions of the heat treated samples. Compositions on the V_xWO_3 line ($0.005, \leqslant x \leqslant 0.07$) have been omitted for clarity.

increased, but even in the lowest compositions no evidence for the extensive formation of well-ordered W_nO_{3n-1} homologous oxides was found, and many fragments contained very few *CS* planes. For example, in $V_{0.06}WO_3$ assuming the WO_3-like fragments are WO_{3-x} and all the reduction is taken up on {102} *CS* planes, local compositions of between $WO_{2.997}$ (with isolated *CS* planes) to $WO_{2.98}$ (with clusters of parallel *CS* planes) were found. An example of one fragment with such a range of composition is shown in Fig. 2. The sample $V_{0.07}WO_3$ contained, in addition some fragments of W_nO_{3n-2} oxides.

With this knowledge, WO_3-like lines were sought and eliminated from the X-ray films. In this way, many of the lines were accounted for, but the removal of almost all lines, necessary in the samples with low vanadium content, could be achieved only by assuming that in addition to the well-characterized monoclinic variety of WO_3, a quite high percentage of an orthorhombic modification was also present. Such a modification occurs in WO_3 between the temperatures of 593–993°K (*15*) and has been observed in samples at room temperature when doped with small amounts of other metals, sodium (*16*), or Nb_2O_5 (*17*), for example, and also in slightly reduced samples of tungsten trioxide prepared under vacuum (*18*). In the present study, the lattice parameters of the monoclinic and orthorhombic forms of WO_3 were, within normal experimental scatter, identical to those for the pure binary oxide; the observed values were: for monoclinic WO_3, $a = 7.31$ (±1) Å, $b = 7.54$ (±1) Å, $c = 7.69$ (±1) Å, and $\beta = 90.9$ (±1)°; and for orthorhombic WO_3, $a = 7.38$ (±1) Å, $b = 7.54$ (±1) Å, and $c = 7.73$ (±1) Å. This result is taken as indicating that essentially no vanadium entered the WO_3 matrix. Complete elimination of both the monoclinic and orthorhombic "WO_3" lines still left a few lines remaining. These were interpreted as being due to a phase with the rutile structure after consideration of samples on the $MO_{2.72}$ and $MO_{2.50}$ lines of the phase diagram. Even in the $V_{0.005}WO_3$ samples, one or two very weak rutile reflections could be detected, substantiating the inference that no significant amount of vanadium had entered the WO_3 lattice. Thus, the conclusion to be drawn is that under the sample preparation conditions employed in the present study V_xWO_3 compositions with x lying between 0.005 and 0.06 yield a rutile-like $(V,W)O_2$

FIG. 2. Electron micrograph of a crystal fragment from a sample of gross composition $V_{0.06}WO_3$ heated for 14 days at 1373°K. The parallel straight lines are {102} *CS* planes in a WO_3 matrix. The compositions of the two regions are $WO_{2.980}$ (left) and $WO_{2.997}$ (right).

compound and a slightly reduced tungsten oxide WO_{3-x}, which can have either orthothombic or monoclinic symmetry.

In an attempt to investigate the orthorhombic WO_3 more fully, a number of small well-formed WO_3 crystals (from a $V_{0.02}WO_3$ sample) were studied by the Weissenberg technique. These were usually found to be twinned, but one apparently untwinned crystal was investigated further. It was found that the reflections were split, sometimes diffuse, and often irregular in shape. Comparison with a film from monoclinic WO_3 showed the same basic structure in both cases. The differences in the two films could be explained satisfactorily if the crystal from the $V_{0.02}WO_3$ preparation consisted of an intergrowth of orthorhombic and monoclinic WO_3 with the *b*-axis of both parallel.

The approximate composition of the rutile phase found in the V_xWO_3 preparations was estimated by comparing the observed lattice parameters with those of Israelsson and Kihlborg (*6*). No significant change was observed on passing from $V_{0.02}WO_3$ to $V_{0.07}WO_3$ and the rutile phase was accorded a composition of $V_{0.69}W_{0.31}O_2$. This composition is close to or within the trirutile region of the phase diagram, but the characteristic trirutile lines were not recorded regularly on the X-ray films. This can be attributed to the preparation conditions employed, as the trirutile phase was only obtained in the experiments of Israelsson and Kihlborg when samples were quenched extremely rapidly (*6*). Hence, reaction at 1373°K was assumed to yield an oxide of composition close to V_2WO_6, which sometimes possessed an ordered trirutile structure.

Compositions on the $V_xW_{1-x}O_{2.72}$ Line

These samples gave results analogous with those above. The cell parameters of the $W_{18}O_{49}$ phase observed at room temperature were $a = 18.32$ (±1) Å, $b = 3.784$ (±2) Å, $c = 14.03$ (±1) Å, and $\beta = 115.2$ (±1)°. These show no significant shifts compared to the literature values (*19*) and suggest that no substitution of tungsten by vanadium takes place. In addition, the samples were never monophasic and even at the composition of $V_{0.05}W_{0.95}O_{2.722}$, rutile lines were already present, again providing an indication that effective substitution of vanadium in the tungsten compound was not taking place.

Compositions in the V_2O_5–WO_3 Line

The results from the samples on the V_2O_5–WO_3 line are similar to those above. The WO_3 lattice parameters are unchanged, indicating negligible vanadium substitution. It was significant that in these fully oxidized samples only the monoclinic form of WO_3 was found.

Compositions on the $V_xW_{1-x}O_{2.5}$ Line

The series of samples on the $V_xW_{1-x}O_{2.5}$ line can be divided into two groups. Those with low vanadium content are straightforward and the results obtained are indicated by the phase fields in Fig. 1, although in this region sharp rutile lines were not always obtained, presumably due to the lack of any special precautions during reaction and quenching (*6*). In compositions richer in vanadium, and particularly those with $x \geqslant 0.63$ all samples were complex and often contained four phases. For samples with $x = 0.50$, 0.63, 0.70, and 0.75, a $W_3V_5O_{20}$ phase was present in varying amounts. This phase has been reported to decompose at approximately 1273°K (*8*) and its presence in these samples may be due to rapid formation as the samples cooled. A few samples heated at 1573°K showed that the $W_3V_5O_{20}$ phase was present in the same amounts as in the lower temperature preparations. In samples with $x =$ 0.82, 0.87, and 0.95, no WO_3 phase was observed, suggesting that the tungsten is being incorporated into a V_2O_5-like phase. In the sample $V_{0.95}W_{0.05}O_{2.5}$ the "V_2O_5" lines were clearly divided into two sets on the X-ray photographs, indicating a coexistence of V_2O_5 with a$(V_{1-x}W_x)_2O_5$ modification, which may be the V_2O_5 related phase observed by Bursill and Hyde (*10*). These results for the phases formed in samples with $x \geqslant 0.65$ must, however, be regarded as incomplete. The oxygen pressures over the samples are uncertain, as is the behavior of any volatile vanadium–oxygen species, and a more complete and careful study may reveal the presence of still other unknown phases.

V_xWO_3 Samples Heated for 3 Days

This series of samples was different from the samples heated for 14 days in a number of respects. Those with smallest vanadium content, in which $x = 0.005$ and 0.01, were rather similar to their 14-day counterparts, but in the 3-day specimens the melted appearance was greatly enhanced and the $V_{0.005}WO_3$ sample in particular contained an appreciable number of apparently quite round globules. The compositions $V_{0.02}WO_3$ and $V_{0.03}WO_3$ were clearly multiphasic and contained large well-formed needle-shaped crystals, and also chunky WO_3-like crystals. All the other samples seemed to consist solely of needles, which were very small and sintered together in aggregates.

The X-ray analysis confirmed that different products were present in the majority of these specimens compared to the 14-day ones, the exceptions being the samples with $x = 0.005$ and 0.01, which were almost identical to those heated for the longer time and contained both orthorhombic and monoclinic WO_3. The relative amounts of these modifications present were similar to the proportions observed in the 14-day samples. X-ray films of the specimens containing needle-shaped crystals showed line broadening and diffuseness of a sort usually associated with disordered {103} *CS* phases and suggested that much greater degrees of reduction of the WO_3 had taken place. The rutile phase was also observed to be present in small amounts in these specimens and the photographs showed that there was no significant difference between its composition in these samples and those heated for 14 days. The results were found to be $V_{0.68}W_{0.32}O_2$ present in $V_{0.02}WO_3$, $V_{0.69}W_{0.31}O_2$ present in $V_{0.04}WO_3$ and $V_{0.61}W_{0.39}O_2$ present in $V_{0.06}WO_3$.

Electron microscopy showed that the samples with lowest vanadium content. $V_{0.005}WO_3$ and $V_{0.01}WO_3$, were composed of slightly reduced WO_3 containing disordered *CS* planes. Similar fragments were also observed in the $V_{0.02}WO_3$ and $V_{0.03}WO_3$ materials, but less often. In these, {103} *CS* phases were also quite frequently observed and can be considered to be fragments from the needle-shaped crystals, which are frequently characteristic of W_nO_{3n-2} oxides.

In addition to the {103} *CS* phases, another phase was present, always severely twinned. The twin lamellae were always disordered and often extremely thin, down to unit cell thicknesses. This gave rise to extensive streaking on the diffraction patterns from these flakes. These features are illustrated in Fig. 3, which shows a typical fragment and the corresponding diffraction pattern. This material was extremely sensitive to electron irradiation, and it decomposed to an amorphous product while being observed. This precluded a great deal of study, particularly at high magnifications. However, parallel studies on the Nb_xWO_3 and Ta_xWO_3 systems revealed the same phase in a somewhat more stable form. Careful tilting of crystals from suitable Nb_xWO_3 samples allowed a probable unit cell to be constructed despite the fact that all fragments examined were heavily twinned. The results of such experiments indicated a unit cell of cubic symmetry within the discrimination of the electron microscope, and of edge about 7.6 Å. On this basis, the twin axis was [111] and the twin plane was (111). X-ray lines from such a cell would be masked on powder photographs by the lines of the W_nO_{3n-2} tungsten oxides and not readily observed. However, from the electron diffraction information, favorable X-ray photographs were able to yield a value for the unit cell size in the V_xWO_3 system. The parameters obtained were $a = 7.64$ Å, $b = 7.57$ Å, and $c = 7.65$ Å and the phase was of orthorhombic symmetry.

The identity of this compound is unknown as yet. Maximum amounts were found in the preparations $V_{0.05}WO_3$ and $V_{0.06}WO_3$, where it was present in fairly substantial amounts. The inference to be drawn from this fact is that the material is a ternary oxide rather than a metastable binary vanadium oxide. Thus, it presents some analogies with the "*X* phase" of Gadó and Magnéli (*20*) and the unidentified phases reported by Trunov, Kovba, and their co-workers (*21–23*). All these authors use relatively small monoclinic cells to index their powder patterns. The orthorhombic cell given above also can be assumed to be a

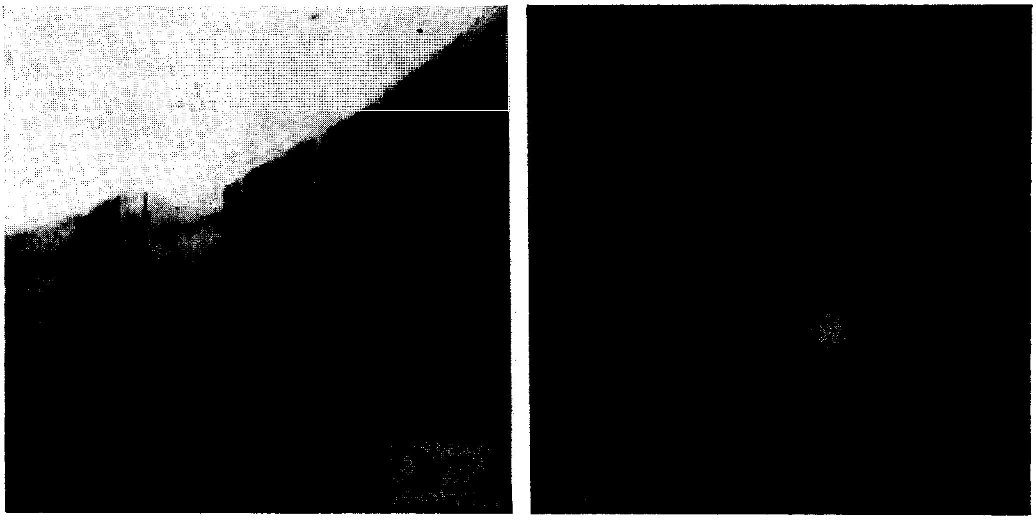

FIG. 3. (a) Electron micrograph of the unstable pseudo-cubic phase found in a sample of gross composition $V_{0.06}WO_3$ heated for 3 days at 1373°K. The fragment is heavily twinned, revealed by the alternate dark and light parallel bands of contrast. (b) Diffraction pattern of a fragment of twinned material indexed on the basis of a cubic unit cell of 7.6 Å edge. The streaking is normal to the twin planes (111) and is due to the disorder and thinness of the twin lamellae. (a) and (b) are correctly oriented with respect to each other.

superstructure of a four times smaller monoclinic cell, although the electron diffraction evidence suggested that the orthorhombic cell was to be preferred. The study of the Nb_2O_5–WO_3 system by Roth and Waring (*17*) also revealed polymorphs of WO_3 with cell parameters similar to this new orthorhombic phase, but the associated electron microscope investigation by Allpress (*24*) did not reveal any compound at all similar to the present one. The reason for this is likely to lie in the different preparation conditions employed by Roth and Waring, particularly in the higher temperatures that they used.

Discussion

Some indications in the results suggest that complete equilibrium may not have been achieved in all samples; those in the rutile and $W_3V_5O_{20}$ regions of the phase diagram being obvious examples. However, as the primary object of the investigation was to determine if ternary *CS* phases formed in significant quantities at 1373°K, this was considered to be of secondary importance. Annealing for longer times at 1373°K would certainly be necessary if a true equilibrium phase diagram was desired.

From the present results, it is clear that at 1373°K no appreciable amounts of vanadium are entering the tungsten trioxide lattice. This conclusion is based mainly upon the X-ray results and it must be considered in this light. Nevertheless, the precision of phase analysis by Guiner–Hägg camera, using lattice parameter variation as well as the detection of other phases by the appearance of diffracted lines, is very high, and is corroborated in this instance by the electron microscope observations. Thus, the substitution of vanadium into the tungsten trioxide lattice can be ignored in further discussions.

Following from this result, it is apparent that, at least in the tungsten-rich part of the phase diagram, reaction leads to a ternary rutile phase, (V, W)O_2 and a binary tungsten oxide. The compounds WO_2 and $W_{18}O_{49}$ give rise to traditional two- or three-phase areas on the phase diagram as they have no appreciable metal to oxygen composition ranges. However, in the phase range between WO_3

and approximately $WO_{2.84}$ any binary WO_x composition is allowed. In the composition range between WO_3 and $WO_{2.93}$ any metal to oxygen ratio is accommodated by disordered or ordered {102} *CS* planes, while below that it is accommodated by quasi-ordered {103} *CS* planes (*25*). Thus, the rutile phase $W_{1/3}V_{2/3}O_2$ will exist in equilibrium with an oxide $WO_{3-\delta}$ if δ lies between 0 and 0.16 and only two phases will be present. Below the approximate composition of $WO_{2.84}$ a three-phase area will again be found, between a rutile oxide, an oxide of composition close to $W_{16}O_{46}$ and $W_{18}O_{49}$. The region on the phase diagram over which these *CS* phases exist and any binary tungsten oxide composition is allowed has been indicated on the phase diagram in Fig. 1 by a shaded area. The point $WO_{2.90}$ ($W_{20}O_{58}$) has been included to indicate the {103} *CS* phase field.

Because of the negligible degree of substitution of vanadium into WO_3, the presence of an orthorhombic form of WO_3 seems unlikely to stem from an impurity effect. The absence of this orthorhombic form in the fully oxidized samples on the V_2O_5–WO_3 line of the phase diagram is in accord with this and further suggests that it is associated with some degree of reduction of the WO_3 structure. Both of these observations are in agreement with unpublished results on the binary tungsten–oxygen system in which an orthorhombic modification of WO_3 also has been obtained in room-temperature samples of oxides with bulk compositions lying between WO_3 and $WO_{2.90}$ (*18*).

Reduction in these crystals is almost certainly associated with the presence of varying numbers of {102} *CS* planes in the matrix (*14*), and hence, one is drawn to the conclusion that these faults are able to prevent the small atomic movements required to transform the high temperature high symmetry form of WO_3 into the monoclinic room temperature form. Moreover, a certain minimum concentration of *CS* planes would be expected to be critical in this respect. The present samples were widely inhomogeneous in the *CS* plane densities found (cf. Fig. 2), and hence, if the presence of a critical concentration of *CS* planes is instrumental in stabilizing the orthorhombic form to room-temperature "single crystals" should be composed of a complex of monoclinic and orthorhombic domains. This sort of structure was possessed by all of the "single crystals" examined, and hence, is in accord with the present speculations. To verify these suggestions, more careful experiments should be carried out, including annealing for much longer periods of time than 14 days to throw light on the true equilibrium stability of the mixed crystals. As such a program of research is at present underway and will be reported in detail in the future (*18*), the topic was not pursued further in this study.

The fact that the vanadium does not substitute for tungsten extensively in the oxides WO_3, W_nO_{3n-1}, W_nO_{3n-2}, and $W_{18}O_{49}$ is not altogether surprising. Chemically, V^{5+} prefers a rather distorted environment, and in the oxide V_2O_5 this is of pentagonal pyramid form rather than octahedral (*26*, *27*). The situation in the oxides rich in V_2O_5 is more complex. Recently published papers containing lists of ternary vanadium oxides $M_aV_bO_c$ in which the ratio of M to V is closer to unity than in the V_xWO_3 compositions of interest here show that V^{5+} can take a variety of coordinations, 4, 5, or 6 (*28*, *29*). Shannon, Chenevas, and Joubert (*30*) have, in fact, rationalized much of this aspect of the structural behavior of V^{5+} by considering both the sizes of the atoms involved in bonding to the vanadium and the strengths of such bonds formed. However, these authors point out that their considerations would not be expected to apply so well to situations, where one can consider vanadium atoms to be doped into an oxide in a few atom percent rather than at much higher concentrations, where normal valence compounds occur. As none of these mixed oxides was of importance in this study, further discussion is unnecessary, but the papers cited above can be consulted for more information on this aspect of the structural chemistry of V^{5+} ions.

In contrast, both V^{4+} and V^{3+} ions appear to prefer octahedral coordination and the extensive mixed rutile phase $(W_xV_{1-x})O_2$ is understandable. Although an ionic model is not entirely suitable for a description of these phases in view of their often metallic behavior, the V_2WO_6 composition found in the V_xWO_3 samples is of interest as it has a formal ionic distribution of V_2^{3+} $W^{6+}O_6$. This would indicate that the reduction of V^{5+} to V^{3+} is energetically more favorable than a reduction of V^{5+} to V^{4+} and W^{6+} to W^{4+}. One would therefore anticipate that the formation of M_2WO_6 would take place in other M_xWO_3 preparations if the metal atom enjoys a fairly stable M^{3+} formal valence. In such cases then, binary tungsten oxides WO_{3-x} may coexist with the appropriate M_2WO_6 phase in preference to forming a bronze or ternary *CS* phase.

A consideration of the 14-day samples alone would lead one to expect that the reaction between the initial components was directly to the rutile phase. This appears not to be so, especially in the region of V_xWO_3 samples with x lying near to 0.05. In these, the presence of quite large amounts of a heavily twinned pseudo-cubic phase in samples heated for only 3 days proves that the reaction mechanism is more complex. For a complete analysis of the course of reaction, a large number of samples should be studied, employing heating times from several hours to months. In such a set of experiments, more than the one phase reported here may well be formed, at least in a transitory fashion.

Within the rather limited experimental evidence obtained so far, it would seem that the pseudo-cubic phase forms and partially decomposes within the 3-day time scale of the shorter experiments. Indeed, as mentioned above, none was found in the samples with $x < 0.03$ by X-ray analysis, although it was observed in the $V_{0.02}WO_3$ sample by electron microscopy. This suggests that an initial reaction takes place.

$$V_2O_5 + WO_3 + WO_2 \rightarrow \text{pseudo-cubic phase} + W_nO_{3n-2}$$

followed by

$$\text{pseudo-cubic phase} + W_nO_{3n-2} \rightarrow W_{1/3}V_{2/3}O_2 + WO_{3-\delta}.$$

In the case of the low vanadium content preparations only a small amount of the pseudo-cubic phase would have formed, and almost all of this is assumed to have decomposed by the time the samples were examined. In the 0.05 and 0.06 samples, however, the pseudo-cubic phase forms in larger quantities, and it would still be present after 3 days. In the 0.07 sample, the pseudo-cubic phase seems to form less readily, probably as $W_{18}O_{49}$ is becoming a favored species. Such a reaction scheme suggests that the composition of the material is close to $V_{0.05}WO_3$, i.e., $MO_{2.82}$.

More complex reaction schemes can be envisaged. For example, it could be supposed that the reactions that take place vary with vanadium pentoxide concentration and no pseudo-cubic material forms in the low vanadium content preparations. Also, alternative products could form which themselves have not been detected clearly in our experiments. These considerations are fruitless in view of the lack of knowledge at present available concerning the composition of this phase and will be postponed until this information is available.

In conclusion, it is possible to say that reaction between vanadium and tungsten oxides in the phase region covered in this study yields a mixed rutile dioxide $(V, W)O_2$ and the appropriate binary tungsten oxide. Oxide bronzes do not appear to form and neither do *CS* phases, which involve vanadium substitution into the WO_3 matrix. The products observed in any experiment are somewhat dependent upon heating times and sample cooling times. Therefore, it may well be that at higher temperatures oxide bronze or *CS* phase formation may take place, conceivably even from a reaction between a binary tungsten oxide and the rutile phase. Further experimental work to check this is planned. Finally, an unidentified ternary phase also has been found in this system. It is unstable and further studies of its composition and structure are being carried out on analogous phases in the Nb_xWO_3 and Ta_xWO_3 systems, where it appears to be rather more stable.

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References

1. T. Ekström and R. J. D. Tilley, *Mater Res. Bull.* **9**, 705 (1974).
2. T. Ekström and R. J. D. Tilley, *Mater Res. Bull.* **9**, 999 (1974).
3. M. Israelsson and L. Kihlborg, *J. Solid State Chem.* **1**, 469 (1970).
4. M. Israelsson and L. Kihlborg, *Arkiv Kemi* **30**, 129 (1968).
5. J. Darriet and J. Galy, *J. Solid State Chem.* **4**, 357 (1972).
6. M. Israelsson and L. Kihlborg, *Mater Res. Bull.* **5**, 19 (1970).
7. W. Rüdorff and H. Kornelson, *Rev. Chim. Min.* **6**, 137 (1969).
8. W. Freundlich, *Comp. Rend.* **260**, 3077 (1965).
9. S. Launay-Mondet, *Rev. Chim. Min.* **8**, 391 (1971)
10. L. A. Bursill and B. G. Hyde, *J. Solid State Chem.* **4**, 430 (1972).
11. B. G. Brandt and A. G. Nord, *Chem. Commun. Univ. Stockholm*, No. V (1970).
12. S. Iijima, *Acta Crystallogr.* **A29**, 18 (1973).
13. J. G. Allpress and J. V. Sanders, *J. App. Crystallogr.* **6**, 165 (1973).
14. J. G. Allpress, R. J. D. Tilley, and M. J. Sienko, *J. Solid State Chem.* **3**, 440 (1971).
15. R. J. Ackermann and C. A. Sorrell, *High Temp. Sci.* **2**, 119 (1970).
16. A. Magnéli, *Acta Chem. Scand.* **5**, 670 (1951).
17. R. S. Roth and J. L. Waring, *J. Res. Nat. Bur. Stand.* **70A**, 281 (1966).
18. M. Sundberg, private communication.
19. A. Magnéli, *Arkiv Kemi* **1**, 223 (1949).
20. P. Gadó and A. Magnéli, *Mater. Res. Bull.* **1**, 33 (1966).
21. L. M. Kovba, V. K. Trunov, and Yu. P. Simonov, *Zh. Neorg. Khim.* **9**, 1930 (1966).
22. V. K. Trunov, L. M. Kovba, and E. J. Sirotkina, *Dokl. Akad. Nauk SSR* **153**, 1085 (1963).
23. L. M. Kovba and V. K. Trunov, *Zh. Strukt. Khim.* **6**, 244 (1965).
24. J. G. Allpress, *J. Solid State Chem.* **4**, 173 (1973).
25. M. Sundberg and R. J. D. Tilley, *J. Solid State Chem.* **11**, 150 (1974).
26. H. G. Bachmann, F. R. Ahmed, and W. H. Barnes, *Z. Krist.* **115**, 110 (1961).
27. H. G. Bachmann and W. H. Barnes, *Z. Krist.* **115**, 215 (1961).
28. M. Gondrand, A. Collomb, J. C. Joubert, and R. D. Shannon, *J. Solid State Chem.* **11**, 1 (1974).
29. K. Waltersson, B. Forslund, K.-A. Wilhelmi, S. Andersson, and J. Galy, *Acta Crystallogr.* **B30**, 2644 (1974).
30. R. D. Shannon, J. Chenevas, and J. C. Joubert, *J. Solid State Chem.* **12**, 16 (1975).