JOURNAL OF SOLID STATE CHEMISTRY **18**, 123–131 (1976)

Structural Relations in the Nb–W–O and Ta–W–O Systems for the Phase Region near WO_3

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Received February 2, 1976

Phase relationships in the two systems Nb–W–O and Ta–W–O have been determined for metal to oxygen ratios between $MO_{3.0}$ and $MO_{2.72}$ at a temperature of 1373°K, using a combination of X-ray diffraction, electron microscopy, and optical microscopy. The two systems are found to be very similar. An extensive series of crystallographic shear (*CS*) phases existing over a wide phase field did not form and all *CS* structures found had compositions close to the binary W–O line. These *CS* phases were based upon {102} and {103} *CS* planes and no evidence for *CS* upon any other planes was found. Within the phase region examined the majority of the niobium or tantalum combines to form ternary tungsten oxides of the tetragonal tungsten bronze type which are often disordered and which coexist either with the *CS* phases or with $W_{18}O_{49}$. In addition, the high-temperature forms of WO_3 were often found to be stabilized to room temperature in slightly reduced samples. The results are summarized in phase diagrams.

Introduction

Since the oxides known as crystallographic shear (*CS*) phases or Magnéli phases were first discovered there has been interest in understanding both why they form and the nature of the interactions between the *CS* planes which can lead to ordering over considerable distances in the solid. One reason why the problem still remains unsolved is because the body of experimental evidence defining *CS* phase formation with respect to chemical and physical parameters is still largely incomplete. In an attempt to try to explain *CS* occurrence and formation in both the binary tungsten–oxygen system and in related ternary *M*–W–O systems we have been systematically mapping phase relations for ternary systems of interest in the region close to WO_3. To date accounts have been published relating to Ti (*1*), Zr (*2*), V (*3*), and Cr (*4*) at temperatures in the region of 1400°K. It has been found that in these systems only the ternary Ti–W oxides support *CS* phase formation. Of the others Zr forms a perovskite related bronze, and V and Cr form rutile-related phases which do not possess any significant degrees of cation to anion nonstoichiometry.

In order to complete this low-temperature survey of the early transition metals, we are reporting here some results obtained for the Nb–W–O and Ta–W–O systems. The amount of previous work on these systems close to WO_3 is not large and all of it concerns fully oxidized M_2O_5–WO_3 samples. The Nb_2O_5–WO_3 system has been studied in depth by Roth and Waring (*5*) and they indicated that a *CS* phase region existed at temperatures above about 1540°K. Prior to this study, Trunov, Kovba, and co-workers published some data on phases formed by Nb_2O_5–WO_3 and Ta_2O_5–WO_3 (*6–8*), Gruehn (*9*) published the results of an X-ray study of the Nb_2O_5–WO_3

and Ta_2O_5–WO_3 systems with most emphasis upon the M_2O_5-rich region of the phase diagram, and Sleight and Magnéli (*10*) and Sleight (*11*) considered tetragonal tungsten bronze related phases in the Nb_2O_5–WO_3 and Ta_2O_5–WO_3 systems. In a series of experiments to determine the structural effects of the addition of small amounts of Nb_2O_5 or Ta_2O_5 to WO_3 Gadó and Magnéli reported the existence of a *CS* phase $Ta_4W_{35}O_{115}$ (*12*, *13*) and a phase very closely related to WO_3 with an unknown structure, which they called the "X-phase" (*13*). More recently, Stephenson (*14*) and Craig and Stephenson (*15*) have refined the structures of several tetragonal tungsten bronze related phases formed by Nb_2O_5 and WO_3.

In addition, a number of electron microscope studies have been carried out both on the *CS* phases (*16*, *17*) and on the tetragonal bronze related tunnel compounds (*18*) that occur in the Nb_2O_5–WO_3 system. These have considerably clarified the nature of the real microstructures in samples which are rich in WO_3 and which were complex and only poorly understood in terms of X-ray studies. In the first of these, Allpress (*16*) showed that at temperatures higher than 1540°K Nb_2O_5 reacts with WO_3 to form an extensive series of *CS* phases with *CS* planes lying on {102} planes for ~6 mole% Nb_2O_5 and gradually changing to {001} planes for ~10 mole% Nb_2O_5. This result was confirmed by Bursill and Hyde (*17*), who also briefly studied the equivalent Ta_2O_5–WO_3 preparations where only {103} *CS* planes were observed. Iijima and Allpress (*18*) studied samples within the tungsten trioxide-rich region of the Nb_2O_5–WO_3 system which had been prepared at temperatures below 1540°K and showed that in them *CS* planes were not present, but that tetragonal tungsten bronze microstructures were formed, sometimes quite well ordered and at other times poorly ordered and coherently intergrown with the parent WO_3 host matrix.

In all of these studies the fully oxidized M_2O_5–WO_3 line on the phase diagram has been followed. However, it is known that the formation of *CS* phases is often associated with loss of oxygen from the WO_3 matrix and the question of whether the *CS* phase fields reported or suggested by the accounts referred to above also exist away from the fully oxidised M_2O_5–WO_3 line is unknown. In addition, the extent to which the tetragonal tungsten bronze structures occur in samples which are effectively oxygen-deficient or the extent to which Nb or Ta can substitute into the known WO_{3-x} *CS* phases has yet to be determined.

It is in order to answer these questions that the study reported here was undertaken. We have paid particular attention to the M_xWO_3 line of the phase diagram, but have also studied relationships in the whole of the oxygen-rich region between the phases WO_3, $W_{18}O_{49}$, and $M_8W_9O_{47}$, where M is either Nb or Ta. The present study has been divided into two parts. Firstly, a study of the phase relations below 1470°K was undertaken to concur with those of Ti, Zr, V, and Cr already referred to, to check whether the high-temperature *CS* phase field reported in the Nb_2O_5–WO_3 line of the ternary Nb–W–O system extended to lower temperatures on increasing the degree of reduction, and to ascertain if a similar situation existed in the Ta–W–O system. It is these results that are reported here. The second part of the study concerning the phase relations at temperatures higher than 1470°K and the interrelation between the high- and low-temperature phases will be presented in a further communication.

Experimental

The starting materials used were tungstic acid (ex Matheson, Coleman and Bell, p.a.), Nb_2O_5 (ex Kawecki, 99.99%), and Ta_2O_5 (ex Koch–Light, 99.99%). Tungsten trioxide was prepared by heating the tungstic acid in air at about 1073°K for several days and tungsten dioxide 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. The degree of reduction of WO_2 was checked by careful weighing and by inspection of X-ray powder patterns.

Appropriate weighed mixtures of Ta_2O_5 or Nb_2O_5, WO_2, and WO_3 were heated under vacuum in sealed ampoules usually for between 3 and 14 days. 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. If the unprotected silica tubes were observed to be attacked 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 M_2O_5–WO_3 line were heated in tubes containing a low pressure of air (approximately $\frac{1}{4}$ atm at room temperature) to prevent excessive reduction of the samples. 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 Cu$K\alpha_1$ radiation and KCl ($a =$ 0.629228 nm) as an internal standard. Lattice parameters were refined by least-squares techniques (*19*).

In addition, samples were examined by optical microscopy using normal and polarized light with a Zeiss Ultraphot microscope. Selected samples were also investigated by electron microscopy using a JEM 100B electron microscope fitted with a goniometer stage and operated at 100 kV or a Siemens Elmiskop 102 fitted with a goniometer stage and operated at 125 kV. All electron microscope specimens were prepared by crushing the materials in an agate mortar under *n*-butanol and allowing a drop of the resultant suspension to dry on a net-like carbon support film. High-resolution micrographs of suitably oriented crystal fragments were taken following the techniques described by Allpress and Sanders (*20*) and Iijima (*21*).

Results

The phase analysis in these systems presented some difficulty as, in general, reaction to give well-crystalline and well-ordered phases requires temperatures in excess of those used in the present study (*5*). Thus, many of the materials produced had disordered structures and the X-ray powder diagrams revealed only the underlying WO_3-like host matrix. The disordered tetragonal tungsten bronze tunnel compounds and the disordered *CS* phases came into this group. Secondly, although the amount of reaction which had taken place was substantial, even for samples heated for only 3 days, judged both from X-ray diffraction and electron microscopy, crystallite size was small, and the predominant crystal habit was needle-like. This resulted in the electron microscope analysis being slow and incomplete as the number of crystal fragments which were suitably oriented to allow a correct analysis of their structure type to be made was small. However, these two techniques, when supplemented by careful optical microscopy, were able to clarify phase relations in these systems. This was because the crystal habits of the phases present were characteristic enough to allow them to be distinguished readily by optical means which in turn allowed analysis of the X-ray and electron microscope results to be made with a greater degree of confidence.

The major structural constituent in many samples was of the tetragonal tungsten bronze structure type. Such material took the form of extremely small needle-like crystals which appeared as tiny grains of dust under usual optical observation. Rarely the cristallites were larger, so that at magnifications of 500× using polarized light the needle shape could be discerned. Thus the presence or absence of this dust-like material in the samples was a great help in allowing the general nature of the phase diagram to be sketched out. The other phases present were also tentatively characterized as follows. Black cristallites were regarded as reduced phases. If the crystal habit was similar to WO_3, that is, rather chunky, the material was considered to contain {102} *CS* planes. If the habit was needle-like, the material was considered to contain {103} *CS* planes or else to be $W_{18}O_{49}$. Unreduced WO_3 was readily recognised by its color and rather chunky habit.

Finally we should mention that cristobalite was present in many samples, often intimately intergrown with the ternary and binary tungsten oxides. It was also found in this form in samples which were contained in platinum tubes which had not been completely sealed by melting. This latter fact initially led us to believe that it was a ternary oxide, particularly as a pseudocubic cell of dimensions similar to WO_3 was deduced from electron diffraction patterns (*3*). As a full report on this phase is at present being prepared it will not be discussed further here.

Preliminary experiments showed that the two systems Nb–W–O and Ta–W–O had very similar phase behavior, and preparations with a particular composition in the Nb–W–O system were almost identical to preparations with the same composition in the Ta–W–O system. Because of this the majority of initial preparations were carried out in the Nb–W–O system, allowing the phase diagram to be completely understood. Far fewer preparations were then needed to clarify the situation in the Ta–W–O case. It was also found that the samples heated for 3 days were quite similar to those heated for 14 days and no phases were found in the 14-day preparations that were not encountered in the 3-day experiments. The major difference between them was that the amount of {103} *CS* phases or of $W_{18}O_{49}$ in the 14-day preparations was less than in the 3-day preparations, suggesting that these oxides are formed rapidly in the initial reaction and then they are partially reoxidized or else react further to form other products as the heating time increases. The results obtained by the three different methods, X-ray diffraction and optical and electron microscopy, were all in accord with each other and are summarized in the phase diagrams in Figs. 1 and 2. The form of these diagrams and a more detailed account of some results of particular importance are given below.

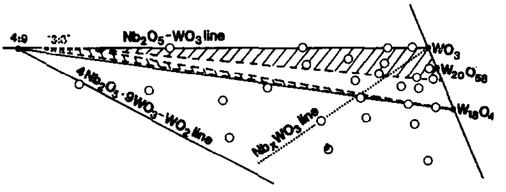

FIG. 1. Part of the phase diagram for the three-component system Nb–W–O at 1373°K. The open circles indicate the gross compositions of the heat treated samples. Compositions on the Nb_xWO_3 line ($0.005 \leqslant x \leqslant 0.07$) have been omitted for clarity.

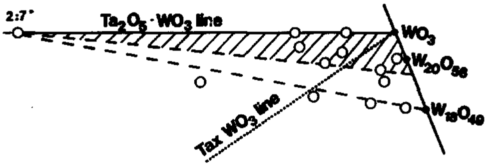

FIG. 2. Part of the phase diagram for the three-component system Ta–W–O at 1373°K. The open circles indicate the gross compositions of the heat treated samples. Compositions on the Ta_xWO_3 line ($0.005 \leqslant x \leqslant 0.07$) have been omitted for clarity.

The Nb–W–O System

The results of preparations on the WO_3–Nb_2O_5 line are in agreement with those of Roth and Waring (*5*) and compositions close to WO_3 show only WO_3 and the tetragonal tungsten bronze substructure. Within the region marked with a heavily dashed line at about the $3Nb_2O_5:8WO_3$ (3:8) composition only the tetragonal tungsten bronze substructure was seen. However, we do not believe that this indicates that the "3:8" phase has an extended homogeneity range. Instead, we feel that in this region disordered or only partly ordered intergrowths between the various phases of the tetragonal tungsten bronze type occur. Such disorder has been shown to occur by Iijima and Allpress (*18*). The small cristallite sizes in our samples made it unprofitable to confirm this ourselves in our particular preparations. The unit cell size of the disordered 3:8 tetragonal tungsten bronze phase obtained in a preparation of composition $3Nb_2O_5:8WO$ was

$$a = 12.19\ (\pm 1)\ \text{Å}, \quad c = 3.950\ (\pm 3)\ \text{Å}$$

in accord with the findings of Roth and Waring (*5*) and Sleight (*11*).

Below the 3:8 phase, the 4:9 phase, i.e., $4Nb_2O_5:9WO_3$, was found to form quite well at 1100°C in preparations heated for 14 days. The unit cell size,

$$a = 12.14\ (\pm 1)\ \text{Å}, \quad b = 36.72\ (\pm 1)\ \text{Å},$$
$$c = 3.942\ (\pm 3)\ \text{Å}$$

is in agreement with previous findings (*5*, *10*, *11*, *14*). Finally on the Nb_2O_5–WO_3 line the 1:1 phase, Nb_2WO_8, was also prepared. This formed rather slowly, and samples heated for 4 days still contained a small amount of a tetragonal tungsten bronze phase, but reheating for a further 7 days resulted in a monophasic sample. The unit cell dimensions found were

$$a = 3.953\ (\pm 3)\ \text{Å},\quad b = 17.62\ (\pm 1)\ \text{Å},\quad \text{and } c = 16.62\ (\pm 1)\ \text{Å}$$

in agreement with the data of Roth and Waring (*5*) and Lundberg (*22*).

The reduced samples fall into several groups, depending upon their composition. Those lying in the upper part of the phase diagram indicated by a hatched area in Fig. 1, that is, samples Nb_xWO_3 with x up to about 0.006, and samples $(Nb_xW_{1-x})O_y$ with y up to about 2.85 consisted of disordered tetragonal tungsten bronze and a *CS* phase. The *CS* phases were of disordered {102} type for compositions close to WO_3 (for example, $Nb_{0.005}WO_3$ and $Nb_{0.01}WO_3$) and quasi-ordered {103} type for samples nearer to $MO_{2.85}$, (i.e., $Nb_{0.05}WO_3$). As usual, samples of most compositions contained fragments exhibiting {102} *CS* planes and fragments of {103} *CS* plane type, indicating that final equilibrium might not have been achieved. Compositions within this hatched area are therefore resolved into the tetragonal tungsten bronze phase and a *CS* phase which for practical purposes can be considered to have a continuously variable composition between the limits WO_3 and approximately $WO_{2.85}$. At present we have no direct evidence either for or against the possible substitution of Nb in these *CS* phases, but in view of results on samples prepared at higher temperatures (*5*, *16*, *17*) it would seem that this may be happening. However, the amount must be rather small at the temperatures considered here as no *CS* plane indices other than {102} or {103} were found, and it has been shown that when the niobium content of samples $(Nb,W)O_{3-x}$ reaches $(Nb_{0.1}W_{0.9})O_{2.95}$ (on the Nb_2O_5–WO_3 line) the *CS* plane indices start to change from (103) to (104) and higher (*16*, *17*).

In samples with compositions below $MO_{2.85}$, the phase $W_{18}O_{49}$ was often found. A series of samples prepared on the $MO_{2.72}$ line always contained other phases in addition to $W_{18}O_{49}$. The unit cell parameters of the $W_{18}O_{49}$ phase in a sample of composition $(Nb_{0.02}W_{0.98})O_{2.72}$ were found to be

$$a = 18.33\ (\pm 1)\ \text{Å},\quad b = 3.786\ (\pm 3)\ \text{Å},\quad c = 14.03\ (\pm 1)\ \text{Å and}\quad \beta = 115.2\ (\pm 1)^\circ$$

which are not significantly different from those of the pure binary oxide (*23*). These observations suggest that no niobium is substituting for tungsten in this structure.

Between the $MO_{2.72}$ and $MO_{2.80}$ lines on the phase diagram shown in Fig. 1 another hatched area is shown. Samples within this region consisted of $W_{18}O_{49}$ and a disordered 3:8 type of tetragonal tungsten bronze which is continuously variable in composition for practical purposes.

Below the $MO_{2.72}$ line, several samples were prepared, as shown in Fig. 1. These showed clearly the existence of the three-phase area between $4Nb_2O_5{:}9WO_3$, $W_{18}O_{49}$, and WO_2.

The Ta–W–O System

Samples prepared on the fully oxidized Ta_2O_5–WO_3 line were rather similar to those on the Nb_2O_5–WO_3 line. Near to WO_3, samples contained WO_3 of monoclinic or sometimes higher symmetry and a tetragonal tungsten bronze phase which showed no superstructure lines on the X-ray powder photographs. The composition of this material was close to $2Ta_2O_5{:}7WO_3$ and the unit cell dimensions of a sample of this composition were

$$a = 12.20\ (\pm 1)\ \text{Å},\quad c = 3.860\ (\pm 3)\ \text{Å}.$$

This width of the apparent 2:7 phase was not investigated in this study, but it appears to have some extension along the Ta_2O_5–WO_3 line. It would thus appear to be analogous in behavior to the phase $3Nb_2O_5{:}8WO_3$ in the Nb–W–O system. A similar conclusion was arrived at by Sleight (*11*). Because of the uncertainty in the limits of the $2Ta_2O_5{:}7WO_3$ compound the phase boundary lines in Fig. 2

joining it to other parts of the diagram are shown dashed.

At the Ta_2O_5-rich side of the 2:7 composition two other preparations were made. Firstly, an ordered tetragonal tungsten bronze phase of composition $4Ta_2O_5:9WO_3$ was readily prepared at 1373°K. The unit cell parameters are

$$a = 12.24\ (\pm 1)\ \text{Å},\quad b = 36.60\ (\pm 1)\ \text{Å},\quad c = 3.877\ (\pm 3)\ \text{Å}$$

in agreement with previous reports (*10*, *11*). Secondly, a sample of composition $Ta_2O_5:WO_3$ did not yield an oxide isostructural with the Nb_2WO_8 analog at this temperature. Instead the ordered 4:9 phase was found to coexist with a lower oxide. Kovba and Trunov (*8*) have, however, reported that an isostructural oxide exists but gave no data about the reaction temperature. Therefore it might be possible that this oxide only forms at temperatures lower than those employed here. However, as the main interest in the present study was in the WO_3-related structures, this topic was not pursued further.

In the reduced phases the pattern found was very similar to that found in the Nb–W–O system. *CS* phases were obtained only in samples with a gross composition close to the binary W–O line and these contained either {102} or {103} *CS* planes, no other *CS* plane indices being observed. In addition $W_{18}O_{49}$ was observed in the samples on the $MO_{2.80}$ and $MO_{2.72}$ lines. Also, in all but the compositions closest to WO_3, i.e., $Ta_{0.005}WO_3$ and $Ta_{0.01}WO_3$, the small needles of the tetragonal tungsten bronze phase were found. Occasionally a fragment would yield an electron diffraction pattern which showed diffuse scattering as well as the sharp tetragonal tungsten bronze host structure spots, indicating some measure of short-range ordering in the structure. Such fragments also showed disorder when examined electron microscopically at high resolution and magnification.

As in the niobium case, there was no direct evidence to indicate that tantalum was entering the *CS* phases. However, in samples of gross compositions $Ta_{0.03}WO_3$ and $Ta_{0.04}WO_3$ quite-well ordered M_nO_{3n-2} {103} *CS* phases were found with $n \approx 30$. Although many samples of pure binary tungsten oxides containing {103} *CS* planes have been examined by electron microscopy (*24*), relatively well-ordered *n* values higher than 25 have not been found, although isolated spacings equivalent to *n* values higher than 30 have been observed in disordered crystal fragments. This suggests that small amounts of tantalum may be entering the structure and stabilizing the {103} *CS* planes to compositions nearer to WO_3 than is usual in the binary system. This finding is in agreement with earlier reports by Gadó, Holmberg, and Magnéli (*12*) and Bursill and Hyde (*17*). It is noteworthy that similarly large *n* values were not found in the equivalent Nb–W–O preparations.

Samples prepared on the $MO_{2.72}$ line give indications that tantalum is not entering the $W_{18}O_{49}$ structure. All samples prepared contained oxides in addition to a $W_{18}O_{49}$ phase, and the lattice parameters of this former phase were not found to be significantly different from those of the pure binary oxide. The values of $W_{18}O_{49}$ in a preparation of gross composition $Ta_{0.02}W_{0.98}O_{2.72}$ were

$$a = 18.33\ (\pm 1)\ \text{Å},\quad b = 3.787\ (\pm 3)\ \text{Å},\quad c = 14.03\ (\pm 1)\ \text{Å and}\quad \beta = 115.2\ (\pm 1)^\circ$$

This is in agreement with the results obtained in the Nb–W–O preparations.

The symmetry of WO_3 and $WO_{3-\delta}$

A careful examination of the X-ray films from samples containing substantial amounts of WO_3 showed that it frequently existed in modifications with a higher symmetry than the usual monoclinic one. Similar findings were reported by Roth and Waring (*5*) for samples on the Nb_2O_5–WO_3 line, and by the present authors for samples in the systems Cr–W–O (*4*) and V–W–O (*3*). In the present study, these higher symmetry modifications were found in both reduced samples and compositions on the M_2O_5–WO_3 line, although these latter samples were prepared in tubes containing some air. In all cases, electron microscope examination revealed the presence of disordered {102} *CS* planes in these crystal fragments, indicating that a small degree of reduction was present even for the M_2O_5–WO_3 preparations.

Discussion

The present experiments have shown that the behavior of the Nb–W–O and Ta–W–O systems in the neighborhood of WO_3 is very similar. Both react quite rapidly (within 3 days at 1373°K) to produce a range of structures based upon corner- and edge-sharing of metal–oxygen polyhedra. Three structures are formed, the tetragonal tungsten bronze types, *CS* structures containing {102} and {103} *CS* planes, and $W_{18}O_{49}$. In addition, the WO_3 structure itself is also found to be present in one or other of its modifications in samples with gross compositions near to MO_3.

It is of interest to note that although the whole of the composition range studied could have been accommodated by *CS* structures built up from corner and edge sharing octahedra alone, *CS* phases were only found for gross compositions lying close to the binary W–O line in the phase diagram. In the majority of compositions prepared, the formation of tunnel structures containing pentagonal bipyramids as structural elements seems to have been favored. The tunnel structures formed, which were of the tetragonal tungsten bronze type, did not appear to be oxygen deficient when prepared in strongly reduced samples such as $M_{0.04}WO_3$ as they seemed to be identical to those found on the fully oxidized M_2O_5–WO_3 line of the phase diagram. It therefore appears that the majority of the M_2O_5 starting material reacts to form fully oxidized tetragonal tungsten bronze structures at the temperatures employed in the present studies. The oxygen balance appears to be taken up by the formation of the appropriate binary tungsten oxide, either a {102} *CS* phase, a {103} *CS* phase, or $W_{18}O_{49}$.

This behavior is rather similar to the reactions involving Cr (*4*) and V (*3*) previously reported, except that in these latter two cases ternary rutile structures form rather than the pentagonal bipyramid containing bronze structures. The crystal chemical reasons for this difference in behavior and why Nb and Ta have an apparent preference for pentagonal tunnel structures is not yet clear. For additional information concerning the crystal chemistry of compounds containing pentagonal tunnels and a discussion of factors which may be pertinent to this question of preferred geometry the recent review by Ekström (*25*) may be consulted.

Similarly, the reason why *CS* phases appear to be virtually restricted to the binary tungsten oxides has not been clarified by the present study. However, as mentioned earlier, there is some slight evidence, particularly in the Ta–W–O system that some M^{5+} ions are able to substitute for tungsten in the {103} *CS* phases. The high-temperature results of Roth and Waring (*5*) and Allpress (*16*) on the Nb_2O_5–WO_3 oxides and our own experiments at temperatures above 1373°K (*24*) suggest that this substitution may become much more extensive at higher temperatures. In this case, anion to cation stoichiometry may well be accommodated by wider *CS* phase fields in the Nb–W–O and Ta–W–O systems at high temperatures and by analogy a similar situation may also hold in the Cr and V systems.

The crystal habit of the tetragonal tungsten bronze phase, very small but well-formed needles, suggests that they may have been produced by a partial vapor phase reaction as their form is quite different from that of the starting products. It is possible to suggest, for example that the bronze phase results from the interaction of the more volatile vapor phase tungsten-oxygen species with the less volatile and probably solid M_2O_5 oxides resulting in the bronze structures and a "residue" of binary tungsten oxide to balance the overall oxygen to metal stoichiometry, in accord with our findings. The substitution of M^{5+} ions into the *CS* phases may then come about by a slower reaction of the bronze structures with the *CS* phases. Thus, the products observed in our experiments may not be the ultimate equilibrium products to be found in these systems at this temperature. Further experiments involving higher temperature studies are under way at present and these may clarify this suggestion.

In our present studies we found no new structural type that we could equate to the

"*X*"-phase of Gadó and Magnéli (*13*) or the $M_2O_5:nWO_3$ phases reported by Trunov, Kovba et al. (*6–8*). However, we do commonly find that higher symmetry forms of WO_3 are present on the M_2O_5–WO_3 line when sealed tubes are used for the preparation and it is only by using a free air atmosphere that the normal monoclinic form of WO_3 is found in isolation. An identical result is reported by Roth and Waring (*5*). Moreover we have shown that these higher symmetry forms of WO_3 are quite possibly stabilized in slightly reducing atmospheres by the presence of a low concentration of disordered {102} *CS* planes (*3, 4*). A consideration of the work of Gadó and Magnéli shows that their samples were prepared in sealed silica tubes, as were the samples prepared by Trunov and Kovba et al. This suggests that the "*X*-phase" and the $M_2O_5:nWO_3$ phases could be high symmetry

TABLE I

A COMPARISON BETWEEN THE X-RAY POWDER PATTERNS OF THE MONOCLINIC ROOM-TEMPERATURE FORM OF WO_3, THE TWO HIGH-TEMPERATURE FORMS OF WO_3 STABILIZED TO ROOM-TEMPERATURE IN THE $Nb_2O_5WO_3$ SYSTEM AND THE $M_2O_5:nWO_3$ PHASES

WO_3(mon) (*24*)		WO_3(o-rh) (*5*)		WO_3(tetr) (*5*)		$Nb_2O_5:nWO_3$ (*6*)		$Ta_2O_5:nWO_3$ (*8*)	
I	*d* value, Å	*I*	*d* value, Å	*I*	*d* value, Å	*I*	*d* value, Å	*I*	*d* value, Å
s	3.85	248	3.84	280	3.85	8	3.82	6	3.82
s	3.77	156	3.75						
s	3.66	232	3.69	252	3.72	10	3.69	10	3.70
vw	3.41	5	3.63						
m	3.35	18	3.35						
						1	3.24		
m	3.12	60	3.10	58	3.11			1	3.13
m	3.09					3	3.07	2	3.08
								½	3.06
								¼	2.96
m+	2.69								
m	2.67	85	2.69	116	2.67	6	2.68	4	2.68
		80	2.66						
s	2.62	126	2.63	96	2.64	7	2.63	5	2.63
w	2.53	10	2.53						
w+	2.52								
								¼	2.45
								¼	2.35
								½	2.28
								¼	2.23
m	2.18					1	2.19	1	2.20
m	2.16	42	2.17	40	2.17	4	2.14	4	2.14
vw	2.10	5	2.10						
w	2.05	5	2.05						
w	2.03	20	2.02	25	2.01	1	2.02	½	2.03
w	2.02								
w	2.00	14	2.00					¼	1.99
w	1.97					2	1.97	2	1.98
m	1.92	48	1.92	45	1.93	4	1.91	3	1.91
m	1.88	33	1.88						
m+	1.83	46	1.85	48	1.86	6	1.83	4	1.85

forms of WO_3 which have been stabilized to room temperature by the presence of a small number of CS planes. In Table I the powder patterns of the high-symmetry WO_3 phases reported by Roth and Waring (*5*) are compared with the $M_2O_5:nWO_3$ phases of the Russian authors. (The "*X*-phase" of Gadó and Magnéli was said to have an X-ray powder pattern nearly identical to those of the $M_2O_5:nWO_3$ phases). The table shows that the unknown phases bear a marked resemblance to the tetragonal form of WO_3. The faint lines are almost totally accounted for by assuming the presence of some of the other modifications of WO_3. The conclusion that all phases are essentially different modifications of WO_3 is strengthened by observing that Gadó and Magnéli concluded from single crystal Weissenberg data that their "*X*-phase" was basically a WO_3-like structure with no ordered defects at all but containing some kind of disordered structure undetected by X rays. Disordered *CS* planes would fit this description completely.

In conclusion, we have shown that in the Nb–W–O and Ta–W–O systems at 1370°K equilibrium lies between slightly reduced WO_3 or WO_3-related *CS* phases and *M*–W–O tetragonal tungsten bronze tunnel compounds at compositions above about $MO_{2.85}$ and between $W_{18}O_{49}$ and the same tetragonal tungsten bronze tunnel compounds at compositions near to $MO_{2.72}$. The structures formed are largely disordered and thus often appear over appreciable stoichiometry ranges. There was no evidence to suggest that Nb or Ta enters the WO_3 structure in large amounts and extensive series of *M*–W–O *CS* phases do not appear to be formed at the temperatures of our studies. In addition, in the slightly reducing conditions found in sealed tubes, the high-temperature forms of WO_3 can be preserved to room temperature. As it is known that more extensive series of *CS* phases form in the Nb_2O_5–WO_3 system at higher temperatures, the present series of studies are in the course of being extended to this region in an attempt to clarify the factors which influence which of the two structural types, *CS* phases or tunnel compounds, are favored.

Acknowledgments

R.J.D.T. is indebted to the Science Research Council (London) for an equipment grant, and would also like to acknowledge the fact that part of this study was carried out in the University of Stockholm. The Swedish Natural Science Research Council has provided travel and subsistence funds. The research was also performed within a program supported by the Swedish Natural Science Research Council (T.E.).

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