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Accommodation of Oxygen Loss in WO_3 Equilibrated with $CO + CO_2$ Buffers

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Tungsten trioxide reduced at about 1270 K by means of controlled atmospheres ($P_{0_2} = 3.7 \cdot 10^{-8}$ to $1.7 \cdot 10^{-13}$ atm) was studied by high resolution transmission electron microscopy, electron diffraction, and X-ray powder diffraction. The accommodation of oxygen loss in the parent WO_3 lattice in the range WO_3 to $WO_{2.72}$ was clarified. The results indicate a solid state mechanism. Intergrowth has been found to take place between several of the structural types that occur in this composition range. The intergrowth features include directional changes in shear plane arrays ("swinging shear planes"). Details of the structural variation with the oxygen content are reported. Ordered shear planes on {102} directions were found to stabilize the orthorhombic WO_3 parent lattice at room temperature. $W_{24}O_{68}$ has been prepared in a fairly well-defined state.

Introduction

The WO_3–$W_{18}O_{49}$ portion of the tungsten–oxygen system has been the subject of many investigations, several comprehensive reviews of which have been published (*1–5*). According to accepted views, the parent WO_3 lattice accommodates oxygen loss by processes which may be regarded as more or less extensive rearrangements of the corner-sharing octahedra of WO_3.

The first distinct structural type is one characterized by crystallographic shear (CS) on {102} planes.[2] Structures with parallel, equidistant {102} CS planes correspond to Magnéli phases of the general formula W_nO_{3n-1}. The exact range of compositions over which this structural type exists in internal equilibrium is not known, "WO_3" or "α" being often used to describe any {102} CS material.

On further oxygen loss, {103} CS appears, corresponding in a similar way to a W_nO_{3n-2} homologous series, of which $W_{20}O_{58}$ is one well-characterized member. A careful study by Marucco *et al.* (*6*) has revealed that the equilibrium range of composition of this structural type is a narrow one close to the theoretical $WO_{2.90}$. On the other hand, the extreme slowness of the ordering processes makes it possible to prepare {103} CS material with compositions far outside this range (*7*).

At still lower oxygen contents, two more structural types appear, the $W_{24}O_{68}$ (*8, 9*) and the $W_{18}O_{49}$ (*10*), both characterized by tunnels and by pentagonal columns (a concept introduced by Lundberg (*11*)). Defects have been found in $W_{24}O_{68}$, but no equilibrium range of composition has been determined. $W_{18}O_{49}$ has repeatedly been re-

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[2] The indices are based on the idealized, cubic (ReO_3-type) structure.

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ported to be strictly stoichiometric or very nearly so.

Most of the experimental work on this system—as on other systems in which oxygen loss is associated with the formation of CS planes in a parent structure—has been carried out using samples prepared by annealing oxide or metal—oxide mixtures in closed, evacuated silica ampoules. While this method offers a convenient way to prepare samples of known compositions, it does have the drawback that there is no way to know the origin of a particular grain. Indeed, since vapor transport will often play a prominent role in this technique, one cannot even know whether it was produced by the transformation of an original grain or not. In a study of how the WO_3 lattice accommodates oxygen deficiency or transforms into other structures, this is a definite disadvantage. The above seems to apply to the great majority of papers published on this system. One exception is a study (*12*) in which large, recognizable WO_3 grains were reduced with tungsten metal. However, this method is rather unfavorable from a kinetic point of view unless positive steps are taken to provide a more efficient oxygen transport medium than a vacuum. For the same reason, the range of compositions that can be reached by heat treating WO_3 in a dynamic vacuum is quite limited (*13*).

This study is an attempt to explore the nature of reduced WO_3 using equilibration with gas atmospheres of controlled oxygen pressure as the preparative method and transmission electron microscopy as the main tool of observation.

Experimental

Preparative aspects. WO_3 crystals were grown from 99.9% pure WO_3 powder (Koch-Light Laboratories) by chemical transportation with water vapor in an oxygen atmosphere. The water content was about 20%, as obtained by passing oxygen through water maintained at 60°C. The flow rate was 5 to 10 ml/min in an 8-mm-i.d. reaction tube. The temperature gradient was 15 K/cm, the raw material being at 1323 K and the crystal growth at 1073–1173 K. The crystals were compact grains, the maximum size obtained being about 2 mm. Some prismatic and double-pyramidal shapes were observed, but most of the crystals were irregular, although with well-developed facets.

Yellow and yellowish crystals were selected under the optical microscope. These were then reduced by means of the double-buffer technique, i.e., by treating the sample with a gaseous buffer, the composition of which had previously been established by equilibration with a solid metal + metal oxide buffer. A detailed description of this technique and of the experimental setup is in preparation (*14*). In this case, $CO + CO_2$ at a total pressure of 1 atm was used as a buffer atmosphere. Water was removed by passing the circulating gaseous buffer through concentrated sulfuric acid. The solid buffers used were Ni + NiO prepared *in situ* by the decomposition of nickel oxalate in vacuum (samples 1–6), Co + CoO consisting of commercial high purity cobalt which had been slightly oxidized (samples 7–11), and "FeO" + FeO_4 prepared by heating an appropriate mixture of Fe and Fe_2O_3 (samples 12, 13 and Table II). The oxygen pressures were monitored by means of a stabilized zirconia oxygen concentration cell. The temperature measurements were carried out using calibrated Pt/PtRh (10%) thermocouples. The stability of the synthesis temperature during a run was of the order of ±1 degree. The oxygen pressures, temperatures, and reaction times for each preparation are presented in tabular form below.

Methods of sample examination. The samples were examined by optical microscopy, by X-ray powder diffraction using a Guinier–Hägg camera, and, in particular, by high resolution electron microscopy.

The electron microscope was a Siemens ELMISKOP 102. The electron microscopy procedures have been described previously (*9*). The acceleration potential was 125 kV. The plates were calibrated using the assumption that the intertunnel spacings along the CS plane are 8.5 and 12.0 Å in {102} and {103} CS planes, respectively. These values were derived using a structural model in which the WO_6 octahedra are undistorted. From the published structures of $W_{20}O_{58}$ (*15*) and $W_{25}O_{73}$ (*16*), {103} CS intertunnel spacings can be obtained; the values are 12.1 and 11.9 Å, respectively. Considering the accuracy of the experimental intertunnel distance measurements, the difference is negligible. These values are, in any case, of doubtful applicability when less ordered structures are considered.

Determination of the sample compositions. In compounds where CS constitutes the sole cause of nonstoichiometry, the composition is uniquely defined by the type and density of CS planes. For the specific case of parallel CS planes, the composition is determined by the average CS plane spacing in a way implicit in the structural type (*17*); formulas for this have been published (*7*, *18*).

As has been found in previous electron microscopy studies of reduced WO_3, even small fragments display a range of CS plane spacings rather than a single one. The average spacing in a region of parallel CS planes was determined by measuring the distance between two nonadjacent CS planes in the lattice image and counting the number in between (typically 10–15). The composition was then calculated. With average spacings accurate to about 2 parts in 100, x in WO_x had an error of less than 1 part in 1000, the experimental determination of the calibration factor being the main source of uncertainty.

The average composition of the CS domains present in a sample was then calculated (separately for {102} and {103} CS if both were present) as the mean of a number of such composition determinations based on data from a number of crystal fragments. Even in samples where only a single structural type was found, there was some variation between the compositions of the individual fragments, as reflected in the values of the standard deviation of the mean (see Table I).

No composition determination was carried out for samples that displayed nonparallel CS planes or for the $W_{24}O_{68}$ and $W_{18}O_{49}$ phases.

Results

A summary of the preparation of and observations on 13 samples is presented in Table I.

All the samples consisted of dark crystals, mostly of the size and shape characteristic of the original WO_3. In addition, a varying but small proportion of needles was found to grow on the surface of these crystals. No needles were ever found on the crucible walls or anywhere else in the preparation apparatus.

Under the electron microscope, the samples were found to fall (with some overlap) into the four major structural groups described in the Introduction. Only in one case (to be described below) did the needles differ structurally from their substrate. The presence of {102} CS, {103} CS, and $W_{18}O_{49}$ was in each case confirmed by comparing the X-ray powder patterns with previous data (*19*).

{102} CS

At low degrees of reduction (samples 1–3) the CS planes appeared to be randomly oriented on the four directions of this form. The rest of this group (samples 4–8) was characterized by domains of parallel CS planes, initially (sample 4) with a wide distribution of spacings but ordering with increasing reduction into arrays of closely

TABLE I

PREPARATION, STRUCTURAL, AND COMPOSITION DATA—DIFFERENT OXYGEN PRESSURES

Sample number	$-\log P_{O_2}$ (atm)	Temperature (K)	Time (hr)	Structural type	x in WO_x	Number of fragments examined
1	7.42	1270	48	{102}CS	(a)	15
2	8.79	1267	47	{102}CS	(a)	26
3	9.61	1273	46	{102}CS	(a)	13
4	10.11	1271	170	{102}CS	2.982 ± 0.007	18
5	10.45	1265	170	{102}CS	2.980 ± 0.012	13
6	10.56	1268	52	{102}CS	2.977 ± 0.010	20
7	11.19	1271	48	{102}CS	2.963 ± 0.020	27
				{103}CS	2.904 ± 0.014	16
8	11.21	1264	48	{102}CS	2.957 ± 0.018	7
				{103}CS	2.897 ± 0.011	4
9	11.38	1268	48	{103}CS	2.899 ± 0.008	24
10	11.96	1269	46	{103}CS	2.893 ± 0.006	48
11	12.36	1270	48	{103}CS	2.880 ± 0.009	18
				$W_{24}O_{68}$		29
12	12.54	1269	59	$W_{24}O_{68}$		21
				$W_{18}O_{49}$		13
13	12.78	1269	72	$W_{18}O_{49}$		32

[a] CS planes not parallel; no composition calculated.

and more regularly spaced CS planes. In addition, the X-ray diffraction patterns revealed that these samples containing parallel CS planes had a WO_3 parent lattice of the high-temperature orthorhombic type rather than the normal room-temperature monoclinic type of unreduced WO_3 and the first three, least reduced, samples. In samples 7 and 8, coexisting domains of {102} and {103} CS planes were found, including areas where an array of CS planes could actually be seen to change from one direction to the other one ("swinging shear planes", (*20*)). In these two samples, CS planes at spacings corresponding to $n = 12$ or slightly above were the predominant feature of the {102} CS domains; no lower n values were found.

{103} CS

The {103} CS plane spacings also became more regular with increasing degrees of reduction. The distribution of CS plane spacings narrowed from values corresponding to (predominantly) $n = 18$–22 (samples 7–9) to $n = 16$–18 (samples 10 and 11). The lowest n value found in a well-ordered array of {103} CS planes was 16. This is in agreement with the findings of Pickering and Tilley (*8*).

$W_{24}O_{68}$

This compound was not prepared in a pure state. The preparation data indicate that at this particular temperature, its range of thermodynamic stability in terms of oxygen pressure is quite narrow. However, its presence as a distinct phase was not in doubt. Sample 11 was the material used in the recent determination of the structure of this phase by Sundberg (*9*). Intergrowth was found with {103} CS in sample 11. Sample 12 consisted of $W_{18}O_{49}$ needles growing on a substrate that was at least predominantly $W_{24}O_{68}$. Despite an exten-

TABLE II

PREPARATION AND STRUCTURAL TYPE FREQUENCY DATA—DIFFERENT REACTION TIMES

$-\log P_{O_2}$ (atm)	Temperature (K)	Time (hr)	Number of fragments {102}CS	{103}CS	$W_{24}O_{68}$	$W_{18}O_{49}$
12.88	1270	7	10	6	1	—
12.91	1269	12	—	3	6	4
12.91	1269	16	—	—	8	14
12.82	1269	21	—	—	14	12
12.78	1269	72	—	—	—	32

sive search, no intergrowth between these two phases was found.

$W_{18}O_{49}$

This phase was observed in samples 12 and 13. As far as could be ascertained by the methods used in this study, $W_{18}O_{49}$ was the only structural type existing in sample 13. All the $W_{18}O_{49}$ fragments were perfectly well ordered except for a few that contained planar defects. Further studies on this matter are in progress.

The Time Factor

The present results give no indication of ordering beyond what takes place during the first 48 hr. However, the maximum reaction time was only about a week.

In order to elucidate the nature of the reduction process further, WO_3 samples were reduced for various shorter periods of time under similar conditions in the $W_{18}O_{49}$ stability range. The results are summarized in Table II. (The last sample is also included in Table I.) From a structural point of view, the reduction is obviously a stepwise one under these conditions.

Discussion

The question whether equilibrium has been attained in a system like this is a difficult one. In a previous study (6) in which this particular reduction was investigated by means of precision thermogravimetry, the reaction times varied from a few hours to many days. However, since the purpose of the present work was to clarify the structural changes that accompany the

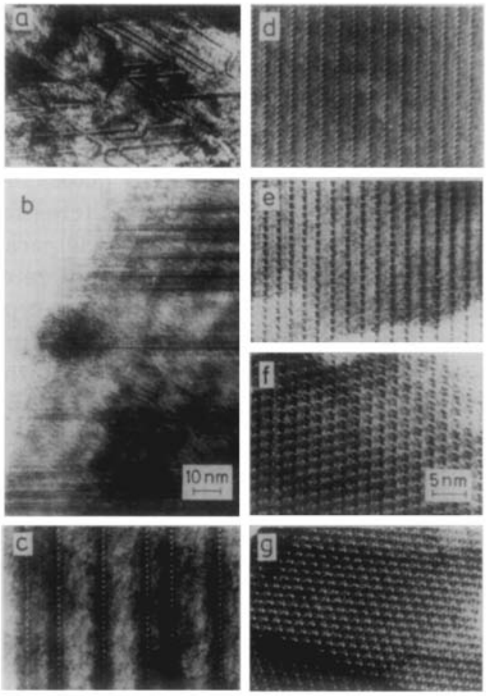

FIG. 1. Lattice images of WO_3 in various stages of reduction: (a) disordered {102} CS, sample 2, (b) parallel {102} CS, sample 4, (c) magnified portion of (b), (d) ordered {102} CS, sample 7, (e) ordered {103} CS, sample 10, (f) $W_{24}O_{68}$, sample 11, (g) $W_{18}O_{49}$, sample 13. Scale for (a) and (b) as indicated in (b), for (c)–(g) as in (f).

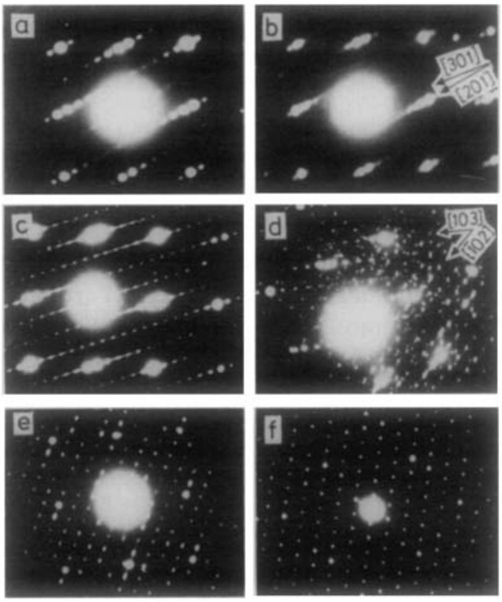

FIG. 2. Electron diffraction patterns of WO_3 in various stages of reduction: (a) ordered {102} CS, sample 7, (b) {102} + {103} CS coherent intergrowth, sample 7, (c) ordered {103} CS, sample 10, (d) {103} CS + $W_{24}O_{68}$ coherent intergrowth, sample 11, (e) $W_{24}O_{68}$, sample 11, (f) $W_{18}O_{49}$, sample 13.

reduction rather than to study the equilibrium thermodynamics, the requirements were somewhat less exacting. As is evident from Fig. 3, the composition–oxygen pressure data are consistent with earlier results.

The lattice image technique—as has been found both in this work and in all previous ones—always reveals more disorder in the CS structural types than can be reconciled with the existence of a series of discrete W_nO_{3n-1} or W_nO_{3n-2} phases separated by two-phase regions. Theoretical calculations (*21, 22*) nevertheless indicate that at least some such phases may be thermodynamically stable entities.

The present results clearly show that the reduction of WO_3 can be carried out coherently in the bulk all the way to $W_{24}O_{68}$ and that this reaction proceeds via the structural types previously observed in this system. (The structural details of the reduction process will be reported in a subsequent paper (*23*).) No other structural types were observed. In particular, since {103} CS and $W_{24}O_{68}$ have been found to intergrow under near-equilibrium conditions, it is unlikely that other types of CS (for example on {104} directions) exist at this temperature.

Although $W_{24}O_{68}$ and $W_{18}O_{49}$ undoubtedly exist in physical contact, no intergrowth regions could be located. This seems to indicate that $W_{18}O_{49}$ forms incoherently, with a highly distinct phase boundary even during the actual reduction process. On the other hand, the results show that $W_{18}O_{49}$ may form with no obvious change in the original WO_3 morphology. Thus, there seems to be no need to

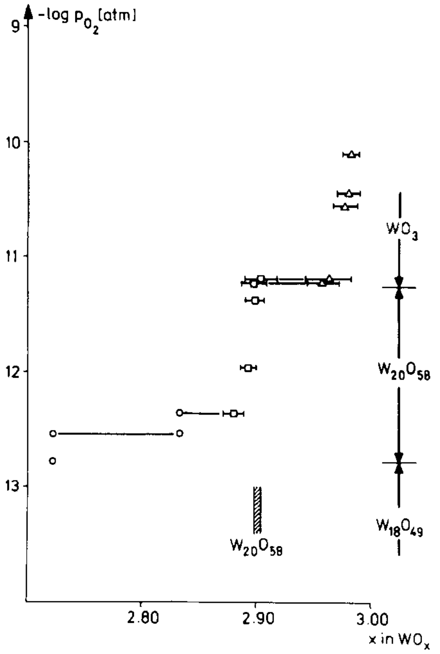

FIG. 3. The composition of reduced WO_3 (samples 4–13) as a function of the preparation oxygen pressure at 1270 K. △ {102} CS, □ {103} CS, ○ $W_{24}O_{68}$, and $W_{18}O_{49}$. The oxygen pressure stability ranges indicated along the right-hand edge of the diagram are those obtained by Rizzo *et al.* (*26*) by an emf technique; the composition range of $W_{20}O_{58}$ is from (*6*). Since no actual analysis of the $W_{18}O_{49}$ was performed, no range comparison can be made.

assume that vapor transport is a necessary step in this reaction. This is in conflict with a previous study of this subject by Sarin (*24*) in which the $W_{18}O_{49}$ was found exclusively in the form of whiskers. However, that preparation was carried out with hydrogen and under rather more drastic conditions, which may well have made a mechanistic shortcut possible. This assumption is supported by the fact that both Sarin and other authors (*6*) report the reaction to be quite fast under strongly reducing conditions, while it is very slow at near-equilibrium. Further studies on the morphology of $W_{18}O_{49}$ as a function of the conditions of preparation are needed.[3]

Some information has been obtained about the stoichiometry of the various WO_x phases. The coexistence of {102} CS (n = 12) with {103} CS (n = 22), and the simultaneous absence of lower and higher n values, respectively, seems to indicate that $W_{22}O_{64}$ ({103} CS) is marginally more stable than $W_{11}O_{32}$ ({102} CS), in agreement with the calculations of Iguchi and Tilley (*21*). Previous results (*6*) indicate that in the region $WO_{2.90-2.975}$, the oxygen equilibrium pressure varies very little with the composition and that a unique sample composition at a particular oxygen pressure cannot be attained even in a period of several weeks. The composition range of the {102} CS structural type may thus extend to, or almost to, that of the {103} type, but the lower part of this range would be preparatively almost inaccessible except in the form of microdomains.

The 740 K transformation of WO_3 from the orthorhombic to the monoclinic structure is suppressed by the presence of ordered {102} CS planes. This stabilization explains the presence of orthorhombic room-temperature WO_3 in samples prepared by other techniques (*25*).

There are no previous reports of $W_{24}O_{68}$ being found in samples prepared by gas reduction. Since its detection seems to require a high resolution both in defining the oxygen pressure and in the phase analysis, this is not surprising.

The role of the planar defects observed in $W_{18}O_{49}$ in the reported composition range of this compound ($WO_{2.7196-2.7224}$, (*6*)) and in the type of composition variation predicted by Pickering and Tilley (*8*) are problems that require further analysis.

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[3] More work along these lines is being reported elsewhere (*27*).

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