Phase Relations in the Ternary W–Mo–O System

THOMMY EKSTRÖM

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

AND E. SALJE* AND R. J. D. TILLEY

School of Materials Science, University of Bradford, Bradford BD7 1DP, West Yorkshire, United Kingdom

The phases in the ternary W–Mo–O system have been determined using X-ray diffraction and electron microscopy. Series of mixed crystals occur for the fully oxidized compounds $W_xMo_{1-x}O_3$. Slightly reduced crystalline samples consist of *CS* phases containing $\{102\}$ *CS* planes which are ordered when the Mo content is high. These latter have overall compositions $(W_xMo_{1-x})_nO_{3n-1}$ with n increasing with increasing W content from 9 to 16. More substantially reduced crystals show less tendency to form mixed crystals. In samples of overall composition near $MO_{2.90}$ phase separation occurs into $\{102\}$ containing *CS* phases which are molybdenum rich and $\{103\}$ *CS* phases which are tungsten rich. The tungsten oxides $WO_{2.82}$ and $W_{18}O_{49}$ seem to contain little or no Mo. These results are summarized on a phase diagram.

Introduction

The structural chemistry of the higher tungsten and molybdenum oxides is quite well known. In the tungsten oxides initial reduction leads to the introduction of $\{102\}$ crystallographic shear (*CS*) planes into the WO_3 matrix (*1*). Reduction to compositions of the order of $WO_{2.93}$ produces oxides containing $\{103\}$ *CS* planes, which persist to compositions of approximately $WO_{2.85}$ (*2*). These are succeeded by two other phases, one of composition close to $WO_{2.82}$ and the other of composition $W_{18}O_{49}$ ($WO_{2.72}$), which are not *CS* structures (*2–4*). Below this composition only the dioxide, WO_2, forms.

Reduction of MoO_3 also leads to *CS* phases. Some of these are based upon the MoO_3 structure (*5, 6*) but two *CS* phases, Mo_8O_{23} and Mo_9O_{26}, have structures similar to WO_3 and contain ordered $\{102\}$ *CS* planes (*6*). In addition, two other phases occur at low temperatures, $Mo_{17}O_{47}$ and Mo_5O_{14} (*6*). Structurally these are somewhat similar to the tungsten oxide phases $WO_{2.82}$ and $W_{18}O_{49}$ and contain pentagonal columns (*PC*s) as a structural building unit (*4, 7*). Further reduction leads to the dioxide, MoO_2.

In the light of the structural relationships in the two binary systems the corresponding area of the ternary system is of obvious interest. In the ternary system, the fully oxidized compounds $W_xMo_{1-x}O_3$ have recently been synthesized and their structural chemistry examined (*8*). It was found that a structure based on an MoO_3-like octahedral

* Permanent address: Mineralogisches Institut, University of Hannover, Welfengarten 1, D3 Hannover, West Germany.

network is only found for compositions near to MoO_3. All other compounds possess structures closely related to the WO_3-type. Here the metal–oxygen octahedra are distorted and this leads to phase transitions due to changes in the distortion parameters near to compositions $x = 0.5$ and $x = 0.78$. Phase analytical investigations have also shown that a complete solid solution exists for the rutile-related dioxide phases $W_xMo_{1-x}O_2$ (9, 10) with no intermediate phase formation.

In the composition region between the dioxide and trioxide lines on the phase diagram the situation is less clear. It is known, though, that a series of CS oxides of general formula $(W_xMo_{1-x})_nO_{3n-1}$ with n equal to 9, 10, 11, 12, and 14 form (11, 12). These contain ordered {102} CS planes and are structurally of the same CS family as the binary oxides Mo_8O_{23} and Mo_9O_{26}. Bursill and Hyde also studied these CS phases briefly (13) and found that the composition $(Mo_{0.5}W_{0.5})O_{2.90}$ contained only {102} CS phases. More recently Viswanathan and Salje (14) have determined the crystal structure of $(W_{12.64}Mo_{1.36})O_{41}$ and showed that it contained ordered {102} CS planes and corresponds to the $n = 14$ member of the homologous series. In this material the metal–oxygen octahedra are appreciably distorted and from a consideration of the distortions it was suggested that oxides in the homologous series with n taking values of 8, 9, 10, 12, 14, and 16 should occur more frequently than those with other n values, in line with other results to this effect (11, 12, 15).

Apart from these CS phases, other studies by Ekström, mainly along the composition lines $Mo_{1-x}W_xO_{2.765}$ and $Mo_{1-x}W_xO_{2.80}$, for x less than 0.4 showed that ternary oxides having the Mo_5O_{14} and $Mo_{17}O_{47}$ structures form (16). However, an Mo_5O_{14} oxide does not form in the ternary system when only small percentages of Mo are present (17).

These results suggest that in some areas of the ternary system extensive replacement of tungsten by molybdenum and vice versa can occur while in other regions it is prohibited. The aim of the present study was to clarify the situation and to systematically map out the structure types to be found. The results obtained are reported in this paper and discussed in terms of the known crystal chemistry of the binary oxides.

Experimental

Synthesis of the substoichiometric ternary compounds was performed by two different approaches: the growth of crystals from appropriate mixtures of oxides and the direct reduction of the fully oxidized mixed crystals with the help of tungsten metal.

The starting materials for the first method used were molybdenum trioxide (Mallinckrodt, Analytic Reagent) and tungstic acid (Matheson, Coleman, and Bell, p.a.). Tungsten trioxide was prepared by heating the tungstic acid in air at about 1073 K for several days. The dioxides of molybdenum and tungsten were prepared by reduction of the corresponding trioxides in a stream of hydrogen/water gas mixture. The oxides were thoroughly mixed and heated in sealed evacuated silica tubes in the temperature range 873–1048 K for samples close to the binary molybdenum oxide line and up to 1373 K for tungsten richer samples. The mixtures were heated for periods of time ranging from a few days to several months. After heat treatment the samples were quenched to room temperature.

For reduction of the fully oxidized $W_xMo_{1-x}O_3$ crystals, material identical to those of former investigations (8), was heated together with tungsten metal in sealed evacuated silica tubes at 750 K for 3 days. No decomposition of the mixed crystals is expected from the phase diagram (8).

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 ($a = 0.6292$ nm). The lattice constants were refined using least-squares techniques. Selected samples were examined with a JEM 100B electron microscope fitted with a goniometer stage and operated at 100 kV. Electron microscope samples were prepared by grinding the crystals in an agate mortar under n-butanol and allowing a drop of the resulting suspension to dry on a net-like carbon support film.

Results

In general it was found that equilibrium was not always easy to achieve. In the preparations of samples with very low tungsten content reaction took place fairly rapidly and equilibrium was apparently reached after a couple of weeks. With increasing tungsten content or at the lower temperatures in this range the reaction speed dropped drastically. For tungsten contents higher than about 40 at.% equilibrium seemed not to be reached in every case although heating times of several months together with intermittent grinding was used. A similar trend was noted during reduction of the fully oxidized $(Mo,W)O_3$ compounds. For the molybdenum-rich materials reduction was fast at temperatures of the order of 750 K while the tungsten rich compositions reduced much more slowly and the pure WO_3 did not show signs of substantial reduction even after two weeks of heating.

The results of the investigation are summarized on the phase diagram shown in Fig. 1. Because of the slow approach to equilibrium in some composition regions, it should be noted that the diagram may not represent the true equilibrium phase diagram for the system. However, it does give
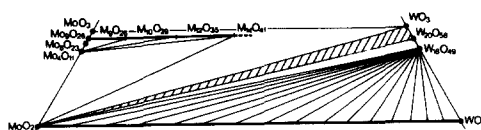

FIG. 1. Schematic representation of the phases found in the dioxide–trioxide region of the Mo–W–O system at 1043 K, tentatively drawn from the phase analytical data found in this study and reported by others (see text). Phase relations between the $(Mo,W)_nO_{3n-1}$ oxides and the structures found on the MoO_3–WO_3 line were not investigated here and data for this region have been omitted.

an accurate indication of the phases to be found after heating periods of several weeks. Further aspects of the diagram are explained in the following sections.

X-Ray Analysis

In the tungsten-rich part of the ternary phase diagram three series of samples were prepared along the lines Mo_xWO_3, $Mo_xW_{1-x}O_{2.80}$ and $Mo_xW_{1-x}O_{2.722}$ with $0 < x < 0.2$. The temperatures used for the heat-treatment were within the range 1023 – 1373 K. Samples along the Mo_xWO_3 lines contained CS phases for $x < 0.1$. That is, close to WO_3 disordered $\{102\}$ CS oxides were found while at somewhat higher x-values disordered or quasi-ordered $\{103\}$ CS oxides were present. At x-values around 0.1 a three-phase area of $\{103\}$ CS oxides, $W_{18}O_{49}$ and MoO_2 could be seen. Samples along the $Mo_xW_{1-x}O_{2.80}$ line showed that no mixed oxide with the Mo_5O_{14} structure formed close to the binary W–O line in the phase diagram and did not indicate the presence of a large phase field for the binary oxide of approximate composition $WO_{2.82}$.

No indications that Mo would replace W in the $W_{18}O_{49}$ phase was seen along the $Mo_xW_{1-x}O_{2.722}$ line as other oxide phases were clearly present in the preparations with $x \geq 0.05$. In addition, no significant variations were observed in the lattice pa-

rameters of the $W_{18}O_{49}$ oxide, which were a = 1.832 ± 1 nm, b = 0.3784 ± 1 nm, c = 1.403 ± 1 nm and, β = 115.2 ± 1° for a sample with x = 0.05. The corresponding parameters for the monoclinic cell of the binary $W_{18}O_{49}$ oxide are a = 1.8334 ± 3 nm, b = 0.3786 ± 1 nm, c = 1.4044 ± 2 nm and β = 115.20 ± 2° (4).

The samples prepared in the molybdenum-rich part of the ternary system were heated at temperatures within the range 873–1048 K because of the higher volatility and lower stability temperatures of the binary molybdenum oxides. Samples were prepared along the compositional lines $Mo_{1-x}W_xO_y$ for y = 2.90, 2.85, 2.80, 2.765, and 2.70, mainly concentrating on the region with x < 0.40.

At temperatures above 983 K the only ternary phases observed to form in this area were of general formula M_nO_{3n-1} where n = 9, 10, 12, and 14. From the powder patterns these ternary phases could be identified as being identical to those reported by Magnéli *et al.* (12). The exact extensions of the tungsten : molybdenum homogeneity ranges were difficult to obtain, as the samples often contained a mixture of two phases. The homogeneity ranges estimated were, however, in fair agreement with those previously reported, being approximately x = 0.1, 0.25 and 0.45 for the shifts between n = 9 to 10, 10 to 12, and 12 to 14 respectively at a temperature of 1048 K.

At temperatures below 983 K the results were somewhat different from those obtained above. In a series of samples prepared on the $Mo_{1-x}W_xO_{2.90}$ line at 913 K, the M_9O_{26} phase formed readily, the $M_{10}O_{29}$ phase formed slowly and the reaction between the starting materials then tended to be as slow as for higher tungsten contents. It was not certain that any significant amounts of the higher homologs formed within the experimental conditions used. In more reduced samples two new ternary phases were found to form. These occurred

along the $Mo_{1-x}W_xO_{2.80}$ and $Mo_{1-x}W_xO_{2.765}$ lines of the phase diagram and were isostructural with the binary Mo_5O_{14} and $Mo_{17}O_{47}$ oxides, respectively. Both phases have extended homogeneity ranges that vary with temperature as reported in a previous publication (16). At the lowest temperature studied, 873 K, up to about 30 at.% of tungsten could be substituted for molybdenum. It was found that the (Mo, W)$_5O_{14}$ oxide formed relatively rapidly, but that prolonged heating over extended times made this phase decompose, as shown in Table I.

One of the decomposition products of the $(Mo,W)_{17}O_{47}$ phase was the $(Mo,W)_{17}O_{47}$ phase, that formed along the $(Mo,W)O_{2.765}$ line of the phase diagram. The $(Mo,W)_5O_{14}$ oxide always seemed to form first for any gross composition close to its formation range along the $(Mo,W)O_{2.80}$ line. No evidence could be found to suggest that the $(Mo,W)_{17}O_{47}$ oxide formed in metastable state, as heating times of several months at its formation temperature did not lead to decomposition. The X-ray powder pattern of this oxide is given in Table II.

Electron Microscope Studies

Samples on the fully oxidized WO_3–MoO_3 line of the phase diagram were examined initially to confirm that they were free of *CS* planes. This was found to be so. The other electron microscope studies were confined to those reduced samples which were expected to contain *CS* structures.

From a phase analysis viewpoint the most significant samples were those heated for 775°C for 1 month, and which we hoped would represent a situation fairly close to equilibrium. In these samples, {102} *CS* planes were the major structural feature observed. The most interesting result is that in these samples no diffraction patterns corresponding to odd n values were found at all in over 100 crystal flakes examined.

TABLE I

Powder X-Ray Data for $Mo_{1-x}W_xO_{2.80}$ Preparations[a]

x	Temp. of prepar. (°K)	Phases[b] observed after heat-treatment for		
		1 week	3 weeks	2 months
0.01	873	I, III	I, II, (III)	(I), II, (IV)
	923	I, III	I, (III), (IV)	I, IV
0.03	873	I, III, Θ	I, (II), V, (Θ)	I, II, V
	923	I, V	I, (V), (IV)	I, IV
0.05	873	Θ	Θ, (κ), (I)	κ, (Θ), II, (I), (V)
	923	Θ, I	Θ, κ, I, (V)	κ, I, V
	973	I, V	I, V	I, V
0.10	873	Θ	Θ	Θ, κ, (V)
	923	Θ, (I)	Θ, (I), (κ)	(Θ), κ, (I), (V)
	973	I, V	I, (κ), VI	I, (κ), VI
0.15	873	Θ, (κ), (IX)	Θ, (κ)	Θ, κ
	923	Θ, (IX)	Θ, κ	(Θ), κ, (V), (VI)
	973	(Θ), I, V, VI	(κ), I, V, VI	(κ), I, (V), VI, (VII)
0.20	873	Θ, (IX)	Θ, (IX)	Θ, (κ)
	923	Θ, (IX)	Θ, κ, (VI)	(Θ), κ, (VI)
	973	Θ, (κ), (I)	Θ, κ, (I), (VI)	(Θ), κ, (VI), (VII)
0.25	873	Θ, IX, (I)	Θ, IX, (κ)	Θ, (IX), (κ)
	923	Θ, (IX), (I)	Θ, (IX), (κ)	Θ, κ, (VI)
	973	Θ, κ, I, (VI), (VII)	(Θ), κ, (I), (VI), (VII)	κ, (VII)
0.30	873	Θ, IX, (VIII)	Θ, IX, (κ)	(Θ), κ, (IX)
	923	Θ, (IX)	Θ, (IX), (κ)	κ, (IX), (VII)
	973	Θ, (IX), (κ)	Θ, κ, (VII)	Θ, κ, VII
0.35	923	Θ, IX, (κ)	Θ, (IX), κ	Θ, κ, (VII)
	973	Θ, (IX), (κ), (VII)	Θ, κ, (VII)	(Θ), κ, VII

[a] Typical data from the phase analysis by powder X-ray diffraction of the $Mo_{1-x}W_xO_{2.80}$ line to show the formation and decomposition of the $(Mo,W)_5O_{14}$ oxide which has been denoted with Θ in the table and similarly the $(Mo,W)_{17}O_{47}$ oxide is denoted with κ. Brackets indicate trace amounts of a phase.

[b] The following Roman figures have been used to denote other oxide phases present: I = Mo_4O_{11} (o-rh.); II = Mo_4O_{11} (mon.); III = $Mo_{18}O_{52}$ (tricl.); IV = Mo_8O_{23} or $(Mo,W)_8O_{23}$; V = $(Mo,W)_9O_{26}$; VI = $(Mo,W)_{10}O_{29}$; VII = $(Mo,W)_{12}O_{35}$; VIII = MoO_2; IX = WO_3.

There was also a change in the degree of order present in the crystals. At the molybdenum-rich side the CS planes were fairly well ordered and most crystal fragments could be considered to belong to the homologous series $(W,Mo)_nO_{3n-1}$, with n values close to 10. As the tungsten content increased the n values tended toward 16, and the number of crystal fragments which gave disordered diffraction patterns increased enormously. Examination of electron micrographs of such crystals showed that there was noticeable variation in the spacings between the CS planes, so that, strictly speaking, the fragments no longer represented single crystals of the $(W,Mo)_nO_{3n-1}$ series, but rather disordered coherent intergrowth of several members of the series. As

TABLE II

The X-Ray Powder Pattern of a Monophasic $(Mo,W)_{17}O_{47}$ Oxide of Gross Composition $Mo_{0.30}W_{0.70}O_{2.765}$

d_{obs} (nm)	I_{obs}	$\sin^2 \theta_{obs} \times 10^5$	hkl	Δ^a
1.469	m	275	110	−2
1.086	w	503	200	0
0.9878	m	608	020	−1
0.9510	m	656	210	0
0.8997	m	733	120	−2
0.7314	w	1109	220	−4
0.6803	w	1282	310	−2
0.5628	w	1873	230	−3
0.5437	vw	2007	400	−6
0.4870	w	2502	330	−3
0.4810	vw	2564	140	−1
0.4491	w	2941	240	−2
0.4241	m	3299	510	1
0.4076	w	3571	340	−1
0.3910	vs	3880	001	−7
0.3773	vw	4167	111	0
0.3651	s	4450	440	−3
0.3581	vw	4627	121	3
0.3560	w	4682	610	0
0.3463	vw	4946	350	0
0.3397	w	5142	620	2
0.3285	w	5497	060	5
0.3258	m	5588	540	2
0.3208	w	5764	231	0
0.3172	m	5896	630	−4
0.3063	m	6323	041	4
0.3033	w	6450	141	−3
0.2996	w	6611	360	−13
0.2949	vw	6823	241	−8
0.2921	w	6955	550	−3
0.2873	w	7188	511	2
0.2819	w	7464	341	3
0.2812	w	7504	460	−1
0.2794	m	7599	170	−1
0.2753	vw	7829	151	1
0.2727	m	7980	270	1

^{a} A refinement of the orthorhombic cell parameters by least-squares technique gave $a = 2.1714 \pm 3$ nm, $b = 1.9720 \pm 3$ nm and $c = 0.3906 \pm 1$ nm. In the table $\Delta = 10^5 \times (\sin^2 \theta_{obs} - \sin^2 \theta_{calc})$.

such defect structures have been illustrated frequently in the past (1, 2) they will not be shown here.

In samples with more tungsten than approximately $(W_{0.6}Mo_{0.4})O_{2.95}$ the CS planes, although remaining on {102} became disordered and fewer in number, approaching the microstructures to be found in slightly reduced WO_3. The results indicate that a tie line joins Mo_9O_{26} to WO_3 and along this line a succession of ordered and disordered {102} CS structures are found.

In the samples Mo_xWO_3 in which x is up to 0.03 the samples were needle-like and contained {103} CS phases as well as {102} CS phases. In $Mo_{0.02}WO_3$, the {103} CS phases were found to correspond to oxides close in composition to $M_{25}O_{73}$, which is near to the top of the {103} CS phase range as found in the binary W–O system. This composition region therefore corresponds to a "two-phase" region in which {102} and {103} CS structures coexist. This suggests that the amount of substitution of Mo into what are essentially binary {103} CS oxides is small. Our electron microscope results, though, do not rule out some degree of substitution in these latter phases.

Similar results to those just described were found for samples heated for shorter periods of time, except that greater degrees of disorder were found. There were, though, more differences when the microstructures of the reduced (Mo,W)O_3 crystals were examined. The most notable feature was the presence of diffraction patterns corresponding to members of the $(W,Mo)_nO_{3n-1}$ series with n taking the odd values of 11, 13, and 15. Most diffraction patterns were heavily streaked and disordered, but nevertheless, fairly well-ordered examples of these did occur, which is a surprisingly different result to that found for the equilibrium samples. In $Mo_{0.15}W_{0.85}O_3$ crystals reduced to compositions of the order of $MO_{2.95}$ {103} CS phases were found as well as {102} CS phases, in agreement with the equilibrium situation.

Another defect structure was also found in reduced (Mo,W)O_3 crystals, and this is illustrated in Fig. 2. It is seen that dark blobs of contrast appear in the micrograph,
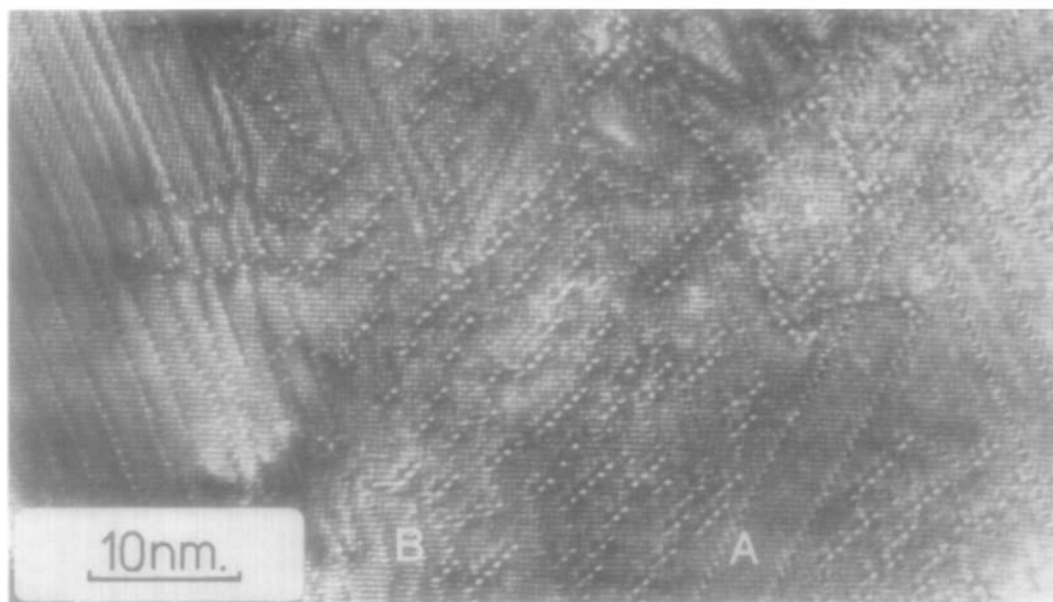
FIG. 2. Electron micrograph of a crystal of approximate composition $Mo_{0.5}W_{0.5}O_{3.0}$ which has been reduced at 750 K for 3 days. The crystal shows {102} CS planes (A) and short rows of PC features (B). In thicker parts of the crystal CS planes are more prevalent, but the image contrast is degraded in this region.

as well as CS planes. A comparison of this contrast with similar features found in the Nb_2O_5–WO_3 and Ta_2O_5–WO_3 tetragonal tungsten bronze structure region suggests that these are likely to be filled pentagonal tunnels. As pentagonal tunnel phases are stable in the Mo–O system at temperatures of the order of the temperature of reduction employed here, 750 K, this explanation is also reasonable chemically. A further study of these defects and the reduction of $(Mo,W)O_3$ crystals at lower temperatures will form the subject of a subsequent paper.

Discussion

From the results of the X-ray and electron microscope studies and the literature cited the tentative phase diagram of Fig. 1 was drawn. Before a discussion of the features of this diagram, though, it should be pointed out that it does not necessarily represent a true equilibrium phase diagram.

The reason for this is that the molybdenum component has a high vapor pressure due to volatile molybdenum–oxygen species. Therefore in order to specify the system completely we should include either oxygen isobars or alternatively some means of showing the equilibrium pressures of metal–oxygen species in contact with the oxides. As this has not been done, and as samples in the slightly reduced region have been prepared at rather low temperatures to prevent excessive loss of molybdenum by sublimation the diagram is best regarded as a guide to the structure types found in sealed-tube experiments. Despite this proviso, there are three features of the results which merit some consideration: the substitution of tungsten for molybdenum and vice versa in these oxides, the stability of the {102} CS phases compared to {103} CS phases in the mixed oxides and the preferential formation of n-even homologs in the $(Mo,W)_nO_{3n-1}$ oxides.

The general pattern to emerge from the present studies is that tungsten is able to substitute into the molybdenum oxides but molybdenum does not substitute into the tungsten oxides. As an example of this we can cite the large $\{102\}$ CS phase field, especially the $(Mo,W)_nO_{3n-1}$ oxides with n lying in the range of 9 to approximately 16. In this case mixed oxides with a $\{102\}$ CS structure seem to form over a large area of the composition range, even along the $MO_{2.90}$ line, and compositions close to the binary W–O line must be approached before phase separation takes place into $\{102\}$ and $\{103\}$ components. The results in other parts of the phase diagram parallel this behaviour. Substitution of tungsten into the molybdenum oxides Mo_5O_{14} and $Mo_{17}O_{49}$ is possible (16), while virtually no substitution of molybdenum into the oxides $WO_{2.82}$ and $W_{18}O_{49}$ seems to take place. Although it should be remembered that this result is largely derived from Guinier–Hägg X-ray data, and as such the substitution of a little molybdenum into these structures cannot be completely ruled out, what is certain is that appreciable homogeneity ranges do not occur for these tungsten oxides.

The reasons for this behavior may rest in the volatility of the molybdenum–oxygen species. The literature shows that a series of mixed oxides forms along the fully oxidized MO_3 line of the phase diagram (8). In these compounds, molybdenum seems able to substitute into the WO_3 structure and the WO_3 structure type, or minor variants of it, is maintained across much of the phase range. However, these phases only form if a substantial partial pressure of molybdenum–oxygen species is present over the crystals, and if this is not the case the molybdenum is lost from the crystals and a phase separation into the almost pure end members, WO_3 and MoO_3 occurs. In fact heating mixed $(Mo,W)O_3$ crystals in air at about 1073 K leads to total removal of the molybdenum by way of volatile Mo–O species, and results in a sublimate of MoO_3 (8).

A similar situation may exist in the case of the reduced oxides which lie in the composition field between $(Mo,W)O_3$ and approximately $(Mo,W)O_{2.72}$. Clearly in the molybdenum rich part of phase diagram the partial pressure of the molybdenum–oxygen species will be high, and, as in the case of the fully oxidized line, mixed CS phase crystals form. In the tungsten-rich samples the overall vapour pressure of the molybdenum component would be lower, and mixed crystals would be less likely to form. Arguing in a parallel fashion to the case of the fully oxidized compounds, it may well be that complete mixed series of CS phases may form if sufficiently high partial pressures of molybdenum could be maintained over the whole of the phase region. Such experiments would be of great interest, especially along the $MO_{2.90}$ line of the phase diagram, where a swinging CS plane region between $\{102\}$ and $\{103\}$ CS planes may form. Similarly it may be that an increase in the molybdenum substitution range would be obtained if a higher pressure of molybdenum species could be achieved in the other tungsten-rich composition regions, and that substitution into the binary tungsten oxides $WO_{2.82}$ and $WO_{2.72}$ could also take place under these circumstances.

The second interesting feature of the phase diagram is the broadness of the $\{102\}$ phase field. In the binary W–O system reduction of samples to compositions below about $WO_{2.98}$ results in "two-phase" mixtures of slightly reduced WO_3 containing random $\{102\}$ CS planes and more reduced materials of composition near to $WO_{2.93}$ containing reasonably well ordered arrays of $\{103\}$ CS planes. In order to obtain high densities of $\{102\}$ CS planes in fairly well-ordered arrays it is necessary to reduce fairly large WO_3 crystals at rather low temperatures (18). It would seem,

therefore, that the incorporation of Mo into the system tends to stabilize $\{102\}$ CS geometry over $\{103\}$ CS geometry.

Calculations on the stability and formation energy of CS planes in WO_3-like structures have been made by Iguchi and Tilley (15, 19). These have shown that an important factor in determining the stability of one particular CS plane geometry over another is the elastic strain in the crystal. This elastic strain energy is composed of two parts, the elastic strain in the matrix between the CS planes and the relaxation energy of the atoms in the CS planes themselves and it was found that the elastic strain field in CS phases arises in the groups of edge-sharing octahedra that compose the CS planes themselves. The recent study of Viswanathan and Salje (4) shows that Mo ions are preferentially located in these edge-sharing groups. Now although the Mo^{6+} and W^{6+} ions have the same nominal ionic radius and charge, it is highly likely that the elastic strain contribution from the $4d$ ion, Mo, will be smaller than that of the $5d$ ion, W. This will mean that the $\{102\}CS$ series will be stable to lower oxygen; metal ratios than in the binary W–O system, as the elastic strain energy of each $(Mo,W)_nO_{3n-1}$, oxide will be lower than its hypothetical W_nO_{3n-1}, analog.

The preferential localization of Mo in the CS planes has another effect which may be important here. It has been suggested that the mobile charge carriers in these reduced oxides are polarons of small or medium size (20). The polaron density between the CS planes also contributes an unfavorable energy term to CS plane stability, which becomes more important as the polaron density increases. In the (Mo,W) oxides, the charges are trapped on Mo ions in the CS plane, and so the polaron density between the CS planes is lower than in the case of the binary tungsten oxides, for comparable degrees of reduction. This effect will also

tend to stabilise the $\{102\}$ CS series for the mixed oxides as compared to the undoped tungsten oxides.

The elastic strain energy calculations referred to above (15, 19) have also been of some value in explaining the third feature of our results, namely, the preferential formation of $\{102\}$ CS phases with n even rather than n odd values. The agreement between observation and theory was found to be good, and in particular it was shown that n even homologs of the M_nO_{3n-1} series were more stable than n odd oxides. The calculations, however, suffered in that they were made for the idealized structures only, as the real structures of most of these phases was unknown at the time.

The relaxation and strain effects are often manifested in crystals by the movement of cations away from the centres of their nearest neighbour coordination polyhedra into off-center environments. This type of distortion is well known in both the tungsten and molybdenum oxides, and Magnéli and co-workers have referred to this as "puckering" of the metal atom planes, and expressed the opinion that the puckering influenced the stability of CS phases (21).

These concepts of elastic strain and puckering have been brought closer by the recent determination of the crystal structure of $W_{12.64}MO_{1.36}O_{41}$ by Viswanathan and Salje (14). They have shown that structural deformations of the metal-oxygen octahedra appear which do not occur in the fully oxidized material. The typical "tilts" of octahedra of the $W_xMo_{1-x}O_3$ structures were not found in the CS phase, and hence, from a structural point of view, the linkage of the WO_3-octahedra between the CS planes is far from being similar to that of WO_3. The Mo positions are highly segregated into the CS planes (4), and only in the case of Mo-rich compounds is a substantial amount of Mo to be expected between the CS planes. The geometrical distortions of

the crystal structures can be classified as following:

(a) oxygen–oxygen repulsion in the M_4O_{11} blocks due to the insufficient shielding by the metal positions,

(b) off-centering of the metal positions in the direction of the monoclinic b axis in the form of zig-zag chains which are linked together in the CS planes,

(c) off-centering of the metal positions in the a–c plane. Three types of octahedra-layers could be distinguished, with different degrees of deformation. As a rule, the highest degree of deformation was found close to the CS planes, the lowest in the middle between two CS planes.

Starting from these typical geometrical distortions, the hypothetical crystal structures of all the $\{102\}$ CS phases could be theoretically constructed and mutually compared with respect to their different strain energies. As a result, Viswanathan and Salje (4) found that phases with n-values 8, 9, 10, 12, 14 and 16 are more stable than those with $n = 1$–7, 11, 13, 15, 17. This result is in good agreement with our present observations.

In conclusion, we can say that considerations of the relative volatilities of the molybdenum and tungsten oxides, and the relative strain energies of these two ions in oxide matrices seem to have explained some of the previously puzzling features of the phase relations in the Mo–W–O system. Further experiments at high molybdenum–oxygen pressures would be of interest to test these ideas.

Acknowledgments

References

1. R. J. D. TILLEY, Chem. Scripta 14, 147 (1978–79).
2. R. PICKERING AND R. J. D. TILLEY, J. Solid State Chem. 16, 247 (1976).
3. M. SUNDBERG, Chem. Scripta 14, 161 (1978–79).
4. K. VISWANATHAN, K. BRANDT, AND E. SALJE, J. Solid State Chem. in press.
5. L. A. BURSILL, Proc. Roy. Soc. A 311, 267 (1969); Acta Crystallogr. Sect. A 28, 187 (1972).
6. L. KIHLBORG, Ark. Kemi 21, 471 (1963).
7. T. EKSTRÖM, Chem. Commun. Univ. Stockholm, No. 7 (1975).
8. E. SALJE, R. GEHLIG, AND K. VISWANATHAN, J. Solid State Chem., in press.
9. B. O. MARINDER AND A. MAGNÉLI, Acta Chem. Scand. 12, 1345 (1958).
10. H. KORNELSON, Thesis, Universität Tubingen (1968).
11. B. BLOMBERG, L. KIHLBORG, AND A. MAGNÉLI, Ark. Kemi 6, 133 (1953).
12. A. MAGNÉLI, B. BLOMBERG-HANSSON, L. KIHLBORG, G. SUNDKVIST, Acta Chem. Scand. 9, 1382 (1955).
13. L. A. BURSILL AND B. G. HYDE, J. Solid State Chem. 4, 430 (1972).
14. K. VISWANATHAN AND E. SALJE, Acta Crystallogr. in press.
15. E. IGUCHI AND R. J. D. TILLEY, Phil. Trans. Roy. Soc. A 286, 55 (1977).
16. T. EKSTRÖM, Mater. Res. Bull. 7, 19 (1972).
17. T. EKSTRÖM AND R. J. D. TILLEY, J. Solid State Chem. 19, 125 (1976).
18. M. SUNDBERG AND R. J. D. TILLEY, J. Solid State Chem. 11, 150 (1974).
19. E. IGUCHI AND R. J. D. TILLEY, J. Solid State Chem. 37 112 (1981).
20. E. IGUCHI, E. SALJE, AND R. J. D. TILLEY, J. Solid State Chem., in press.
21. A. MAGNÉLI, in "The Chemistry of Extended Defects in Non-Metallic Solids" (L. Eyring and M. O'Keeffe, Eds.), p. 148. North-Holland, Amsterdam, (1970).