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Ternary Phases with the Mo_5O_{14} Type of Structure

I. A Study of the Molybdenum—Vanadium—Oxygen System

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The system $(Mo_{1-x}V_x)O_{2.80}$ with $0 \leq x \leq 0.40$ has been studied by differential thermal analysis and by means of X-ray powder diffraction photographs, taken at room temperature, of specimens prepared within the temperature interval 600 – 800°C.

The binary molybdenum oxide Mo_5O_{14} ($MoO_{2.80}$) forms in a metastable state within a restricted range of temperature around 500°C, and decomposes upon prolonged heat-treatment into $Mo_{17}O_{47}$ and MoO_3. The apparently stable ternary phase $(Mo_{1-x}V_x)_5O_{14}$ of the same type of structure forms within the temperature region 600 – 760°C. Its maximum homogeneity range $0.02 \lesssim x \lesssim 0.11$ is observed at 600°C. No trace of decomposition into other oxides was observed even after a heating time of eight weeks. The composition and temperature ranges of formation as well as the variations in the unit cell dimensions of the vanadium substituted phase are given.

In a study of the binary system $MoO_2 - MoO_3$ Kihlborg observed two previously unknown phases at the compositions $MoO_{2.80}$ and $MoO_{2.77}$ which he called θ- and $\varkappa$-molybdenum oxide, respectively.[1] No indications of extended homogeneity ranges were observed. As a result of subsequent crystal structure determinations [2,3] their formulas were found to be Mo_5O_{14} and $Mo_{17}O_{47}$.

Phases of odd stoichiometrics are by no means rare in oxide systems of transition elements. However, it has often been demonstrated that such complex formulas may be logically derived from rather simple structural principles. This is the case with the large number of phases exhibiting crystallographic shear, which have been studied extensively at this institute and elsewhere. The two molybdenum oxides discussed here and an analogous compound in the wolfram-oxygen system, $W_{18}O_{49}$,[4] may not be described in such simple structural terms. The structures show complex patterns of metal-oxygen polyhedra – MO_6 octahedra and MO_7 pentagonal bipyramids – which are linked by sharing corners and edges. The arrangement present in Mo_5O_{14}

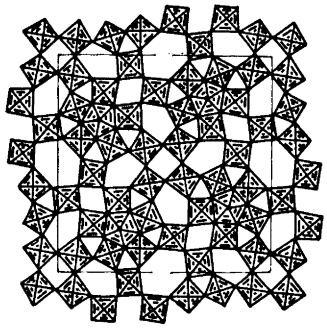

Fig. 1. The structure of Mo_5O_{14} viewed along [001], and depicted as a complex of linked MoO_6 octahedra and MoO_7 pentagonal bipyramids. The extension of the tetragonal subcell ($a' = \frac{1}{2}a$) is indicated. (The picture is a loan from Ref. 6, kindly permitted by Kihlborg ar d the editor).

is indicated in Fig. 1. As suggested by the formulas, the linking of the polyhedra in $Mo_{17}O_{47}$ and in $W_{18}O_{49}$ is different. Nevertheless, the three structures may be looked upon as markedly related to each other. The most obvious structural feature which they have in common is the presence of MO_7 bipyramids which have all their five equatorial edges in common with MO_6 octahedra. In $Mo_{17}O_{47}$ and $W_{18}O_{49}$, pairs of such aggregates of polyhedra are mutually linked by edgesharing between two MO_6 octahedra. The $M-M$ distances across the shared edges are very short, indicative of metal–metal bonds (Mo–Mo in $Mo_{17}O_{47} = 2.626$ Å [5] and W–W in $W_{18}O_{49} = 2.60$ Å [4]). The remarkable and complicated structures of these oxides have made it desirable to study their chemical and physical properties in order to make possible a more detailed and coherent understanding of the nature of these materials.

The present study was primarily initiated by the observation that binary Mo_5O_{14} appeared to be metastable [1] but could be stabilized by a partial substitution of transition metals such as vanadium, niobium, and wolfram for molybdenum.[6] This article will describe studies on the conditions of formation of stabilized Mo_5O_{14} in the molybdenum–vanadium–oxygen system. Results of investigations with niobium, tantalum, titanium, and wolfram as stabilizing metal atoms will be described elsewhere.[7–9]

EXPERIMENTAL

The starting materials used were vanadium pentoxide (UCB *p.a.*), molybdenum trioxide (Mallinckrodt, Anal. Reag., dried at 200°C) and molybdenum dioxide. The latter was prepared by reducing the trioxide in a stream of hydrogen gas at 500°C. The degree of reduction was checked by weighing and by inspection of the X-ray powder pattern. Appropriate amounts of the starting materials were thoroughly mixed and then sealed into evacuated silica tubes. The latter were put into borings in a heavy steel cylinder, because the high volatility of MoO_3 made it necessary to minimize any temperature gradient within the tubes, and the cylinder was placed in an electrically heated furnace. The accuracy of the heat-treatment temperatures of the samples given in the following is about ± 5°C.

The heating time varied depending on the temperature of preparation. The binary oxide Mo_5O_{14} was observed to form rather rapidly at 500°C. On the other hand, with vanadium present in the samples, $(Mo_{1-x}V_x)O_{2.80}$, these had not reached equilibrium after heat-treatment at 500°C for periods of several weeks with intermittent regrinding. The samples prepared at 700°C and above were usually heated for a week, whereas

those at 600°C had to be heated for two weeks with repeated regrinding. After the heat-treatment the samples were quenched to room temperature in cold water. All the samples were investigated by recording their X-ray powder patterns at room temperature, and most of them by differential thermal analysis.

The X-ray powder photographs were obtained with a Guinier-Hägg focusing camera. Cu$K\alpha_1$ radiation ($\lambda = 1.54051$ Å) was used and potassium chloride added to the samples as an internal standard ($a = 6.29228$ Å at 25°C [10]). The lattice parameters together with their standard deviations were calculated and refined by least squares techniques, using programs written for an IBM 1800 computer by Drs. A. G. Nord and P.-E. Werner of this institute.

As it was not possible to use inert atmosphere in the DTA apparatus, the samples were kept in sealed silica tubes (3 mm in diameter) filled with argon gas. Each silica tube, when investigated, was squeezed into a platinum tube (3.1 mm in diameter), the lower part of which was attached to the differential thermocouple. The reference thermocouple was in the same manner connected to an empty silica tube. The data collection was performed on a multichannel recorder; the ΔT signal fed to the recorder could be amplified up to 2000 times.

Test runs using the phase transitions in silver sulfate (412°C), α-quartz (573°C), potassium sulfate (583°C), and potassium chromate (665°C) as reference points [11] indicated that the silica tubes did not have any significant effect on the transition temperature readings. No peaks were present in blank runs.

Heating rates in the range 5 – 10°/min were used. The results presented below are those of the heating curves, as generally no reproducible data were obtained from the cooling runs.

SOME OBSERVATIONS ON THE BINARY Mo_5O_{14} PHASE

Within the present investigation the formation of the binary oxide Mo_5O_{14} was studied at temperatures above 470°C. It was observed to form relatively rapidly (1 week) within the temperature interval 470 to ~ 530°C, but decomposed slowly into $Mo_{17}O_{47}$ and MoO_3 upon prolonged heat-treatment (2 – 4 weeks). The conclusion that Mo_5O_{14} forms in a metastable state under these conditions is in concordance with the findings of Kihlborg.[1] Kihlborg found that single-crystal X-ray photographs of Mo_5O_{14} contain weak extra reflections, which show that the actual a axis of the tetragonal unit cell has twice the length reported here.[1,2] Recent electron diffraction studies have shown that the c axis is also doubled.[12] Since the presumably subtile nature of the superstructure is unknown and none of the extra reflections associated with it show up in powder photographs, all figures for θ-oxides in this article refer to the subcell. Calculations of the lattice parameters of the tetragonal subcell of Mo_5O_{14} gave as result $a = 22.989 \pm 2$ Å, $c = 3.938 \pm 1$ Å, which values are in excellent agreement with the previous data.[1]

THERMAL CHARACTERIZATION OF SEVERAL PHASES APPEARING IN THE DTA MEASUREMENTS

In order to be able to interpret the DTA curves of the vanadium substituted θ-oxide (see below) we found it necessary to register the thermal characteristics of major phases appearing in these studies, *viz.* MoO_3, $Mo_{18}O_{52}$(tricl.), Mo_8O_{23}, and Mo_4O_{11}(o-rh.). The results are comprehended in Fig. 2. The reproducibility was found to be ± 4°C.

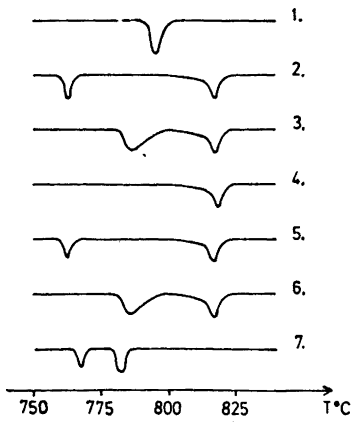

Fig. 2. A schematic presentation of the DTA curves observed for 1, MoO_3; 2, $Mo_{18}O_{52}$(tricl.); 3, Mo_8O_{23}; 4, Mo_4O_{11}(o-rh.); 5, $(Mo_{1-x}V_x)O_{2.80}$, $x = 0.02$ and 0.03, prepared at 640°C; 6, $(Mo_{1-x}V_x)O_{2.80}$, $x = 0.04$ and 0.05, prepared at 640°C; 7, $(Mo_{1-x}V_x)O_{2.80}$, $0.06 \leq x \leq 0.11$, prepared both at 640°C and 750°C.

The melting point of MoO_3 has been reported to be 795°C [13] compared to 793°C found in our experiment. The DTA curve of the orthorhombic modification of Mo_4O_{11} shows a peak at 815°C, with a slight deviation from the base line of the ΔT curve already around 800°C (*cf.* Fig. 2, curve 4). This is in fair agreement with the temperature interval 795 – 817°C given by Bousquet and Guillon,[14] whereas Rode and Lysanova report the interval to be 818 – 826°C.[15]

The phase transition of $Mo_{18}O_{52}$(tricl.) to Mo_9O_{26}(mon.) takes place at 760°C and the DTA curves show another peak at 816°C. The shape and temperature of this second peak indicate Mo_4O_{11} to be present (*cf.* Fig. 2 and curves 2 and 4). Kihlborg reports that the transition takes place at 760°C and that Mo_9O_{26} (mon.) decomposes into MoO_3 and Mo_4O_{11} when heat-treated at 785°C.[1] With a heating rate of 5 – 10°C/min one cannot, however, expect the DTA curve always to reflect slow equilibrium transitions such as reported in Ref. 1. The cooling curve of $Mo_{18}O_{52}$(tricl.) contained among others one peak at 760°C and the X-ray powder photographs of these samples showed $Mo_{18}O_{52}$, Mo_4O_{11}, and MoO_3 to be present. The peak at 760°C is the only one observed, except for the one at the melting point of pure MoO_3 (793°C), which appeared both on the heating and the cooling curves.

Our DTA curve of Mo_8O_{23} (*cf.* Fig. 2, curve 3) shows two peaks, one at 782°C and the other at 815°C which we primarily associate with the reactions $Mo_8O_{23} \rightarrow Mo_4O_{11} + 4MoO_3$ and $Mo_4O_{11} \rightarrow MoO_2 + 3MoO_3$, respectively. The former peak is broad, which can be explained by partial overlap with the peak caused by the melting of MoO_3. The X-ray powder patterns of the Mo_8O_{23} sample after the DTA measurements showed a mixture of MoO_3, $Mo_{18}O_{52}$, and Mo_4O_{11}. The presence in the cooling curve of a peak at 760°C is thought to indicate that Mo_9O_{26} exists in the sample above this temperature. The DTA curves reported by Rode and Lysanova [15] for a sample said to be Mo_9O_{26} suggest that this was actually a mixture of Mo_8O_{23} and $Mo_{18}O_{52}$. Kihlborg came to the same conclusion in his phase analysis of the system $MoO_2 - MoO_3$.[16]

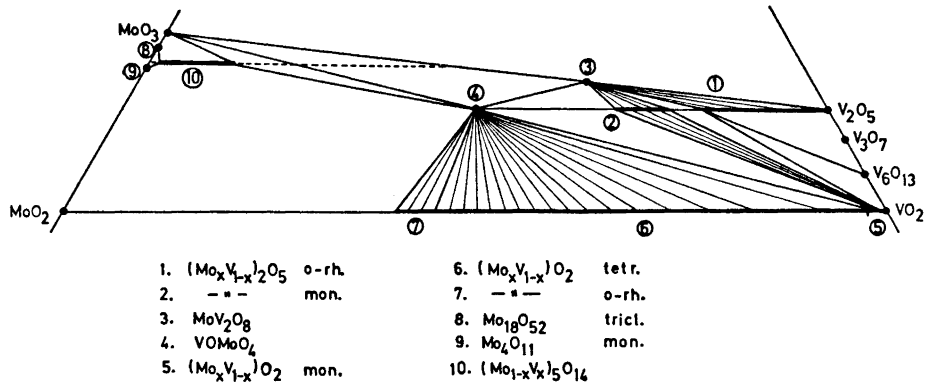

Fig. 3. Part of the phase diagram of the three component system Mo – V – O, obtained from samples quenched from 600°C. The heavily marked lines represent ranges of homogeneity and the dashed line corresponds to $(Mo_{1-x}V_x)O_{2.80}$, $0 \leq x \leq 0.40$, *i.e.* the compositional range of the samples prepared in this study. Most of the diagram is drawn according to Kihlborg in Ref. 17 and the extension of the θ(V)-oxide has been modified by the results of the present study. The length of the θ(V)-oxide line, *i.e.* the width of its homogeneity range, as a function of temperature, is represented in Fig. 5. The equilibria between V_3O_7 [18] and the surrounding phases are not known.

INTERPRETATION OF THE EXPERIMENTAL DATA OBTAINED FOR THE TERNARY SAMPLES

The part of the three component system Mo – V – O of interest for this study is schematically drawn for a temperature of 600°C in Fig. 3. With the data obtained in this study it is not possible to make a complete description of the relationships between the vanadium substituted θ-oxide, subsequently called θ(V)-oxide, and the surrounding phases. The dashed line indicates the range of the gross composition for the samples, which were prepared at temperatures within the 600 – 800°C interval. The oxygen to metal ratio was thus kept fixed at 2.80. At $x = 0.40$ in $(Mo_{1-x}V_x)O_{2.80}$ the dashed line in Fig. 3 intersects the two phase line $MoO_3 - MoV_2O_8$.

Two extensive series of samples were heat-treated at the fixed temperatures 640°C and 750°C. The results of the interpretation of the powder patterns are presented in Table 1, and the lattice parameters are plotted, in Fig. 4, as functions of the vanadium content. The extension of the homogeneity range of the θ(V)-oxide thus obtained is $0.02 \lesssim x \lesssim 0.11$ at 640°C and $0.05 \lesssim x \lesssim 0.11$ at 750°C.

The lattice parameters of the θ(V)-oxide shows a decrease in the a-axis and increase in the c-axis with increasing vanadium content, but the unit cell volume of the vanadium-containing phase remains practically the same as that of Mo_5O_{14}, the figures being 2078 – 2082 Å^3 and 2082 Å^3, respectively.

The samples prepared at 640°C and 750°C were used in the DTA studies. DTA curves for monophasic samples of θ(V)-oxide are given in Fig. 2. The congruent curves for $x = 0.02$ and 0.03 show peaks due to $Mo_{18}O_{52}$ and Mo_4O_{11}.

Table 1. A survey of the data obtained from the X-ray powder photograph analysis of the system $(Mo_{1-x}V_x)O_{2.80}$. The lattice parameters given for the tetragonal subcell of the θ(V)-oxide are averages of several preparations. The standard deviations given for a and c correspond to the biggest σ values observed in a single calculation. For the monophasic samples the σ values have about half this magnitude. The brackets indicate traces of the phase concerned.

x = in $(Mo_{1-x}V_x)O_{2.80}$ Gross comp.	Temp. of prep. (°C)	Observed phases	Lattice parameters of the θ(V)-oxide	
			$a \pm 0.005$ Å	$c \pm 0.002$ Å
0.01	640	$Mo_{18}O_{52}$, Mo_4O_{11}, θ(V)-oxide	22.919	3.957
	750	Mo_8O_{23}, Mo_4O_{11}, (θ(V)-oxide)	–	–
0.02	640	θ(V)-oxide	22.904	3.968
	750	Mo_8O_{23}, Mo_4O_{11}, θ(V)-oxide	22.862	3.985
0.03	640	θ(V)-oxide	22.882	3.975
	750	(Mo_8O_{23}), Mo_4O_{11}, θ(V)-oxide	22.862	3.986
0.04	640	θ(V)-oxide	22.872	3.978
	750	(Mo_8O_{23}), Mo_4O_{11}, θ(V)-oxide	22.850	3.986
0.05	640	θ(V)-oxide	22.852	3.987
	750	(Mo_4O_{11}), θ(V)-oxide	22.861	3.986
0.06	640	θ(V)-oxide	22.850	3.989
	750	θ(V)-oxide	22.851	3.990
0.07	640	θ(V)-oxide	22.845	3.992
	750	θ(V)-oxide	22.839	3.990
0.08	640	θ(V)-oxide	22.837	3.990
	750	θ(V)-oxide	22.842	3.992
0.10	640	θ(V)-oxide	22.831	3.991
	750	θ(V)-oxide	22.833	3.993
0.11	640	θ(V)-oxide	22.828	3.993
	750	θ(V)-oxide	22.829	3.995
0.12	640	(MoO_3), ($VOMoO_4$), θ(V)-oxide	22.825	3.990
	750	(MoO_3), ($VOMoO_4$), θ(V)-oxide	22.830	3.992
0.15	640	MoO_3, $VOMoO_4$, θ(V)-oxide	22.825	3.991
	750	MoO_3, $VOMoO_4$, θ(V)-oxide	22.825	3.992
0.17	640	MoO_3, $VOMoO_4$, (θ(V)-oxide)	–	–
	750	MoO_3, $VOMoO_4$, (θ(V)-oxide)	–	–
0.20	640	MoO_3, $VOMoO_4$		
	750	MoO_3, $VOMoO_4$		
0.25	640	MoO_3, $VOMoO_4$, (V_2MoO_8)		
	750	MoO_3, $VOMoO_4$, (V_2MoO_8)		
0.30	640	MoO_3, $VOMoO_4$, V_2MoO_8		
	750	MoO_3, $VOMoO_4$, V_2MoO_8		
0.35	640	MoO_3, ($VOMoO_4$), V_2MoO_8		
	750	MoO_3, ($VOMoO_4$), V_2MoO_8		
0.40	640	MoO_3, V_2MoO_8		
	750	MoO_3, V_2MoO_8		

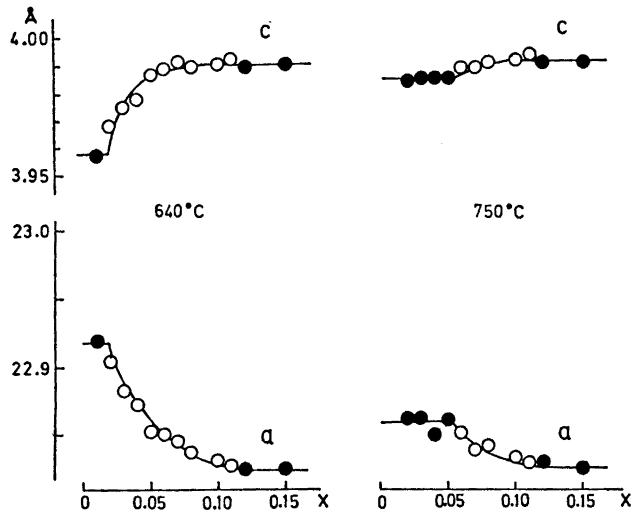

Fig. 4. The lattice parameters *versus* x in $(Mo_{1-x}V_x)O_{2.80}$. The open circles indicate monophasic samples, filled circles represent data obtained from samples containing other oxides besides the θ(V)-oxide.

As the peak characteristic of Mo_8O_{23} is not observed, the θ(V)-oxide seems to decompose below 650°C, the formation temperature of Mo_8O_{23} according to Ref. 1. No peaks were observed below 760°C that could be referred to the decomposition of the θ(V)-oxide. This was also the case for $x = 0.04$ and 0.05, but the presence of the peak characteristic of Mo_8O_{23} (*cf.* Fig. 2, curve 6) indicates the decomposition of the θ(V)-oxide to take place above 650°C.

In the region $0.06 \leq x \leq 0.11$ the DTA curves show two peaks, one at 765°C and the other at 785°C. The second peak can be ascribed to the passage of a liquidus line, in agreement with observations on samples prepared at 780°C and 790°C, the latter being melted. The peak at 765°C might be associated with the decomposition of the θ(V)-oxide. Preparations of samples around the

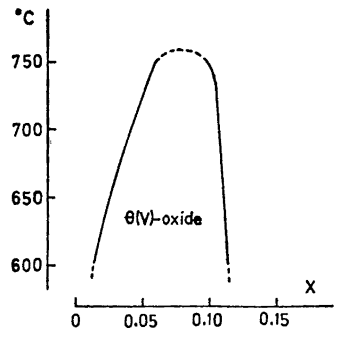

Fig. 5. The homogeneity range for the vanadium substituted θ-oxide (x in $(Mo_{1-x}V_x)O_{2.80}$) as function of the temperature.

temperature 760°C (see below) show, however, that this part of the phase diagram is fairly complicated, and the interpretation of the DTA curves in this temperature range is therefore rather difficult.

The results of the DTA study and the X-ray powder diffration investigation with respect to the extent of the homogeneity range of the θ(V)-oxide are presented in Fig. 5.

GENERAL REMARKS

Even after a heating period of eight weeks at the formation temperatures of the θ(V)-oxide, we observed no tendency for this phase to decompose into other oxides, in the way that Mo_5O_{14} does. Thus, the vanadium substituted θ-oxide appears to be quite stable at the temperatures of formation, in contrast to Mo_5O_{14} which forms in a metastable state and within a much more restricted temperature range.

Attempts to obtain a vanadium substituted phase corresponding to the $\varkappa$-molybdenum oxide $Mo_{17}O_{47}$ ($MoO_{2.765}$) at elevated temperatures have also been made. The binary oxide was observed to form at temperatures below about 560°C, and this result is in concordance with previous findings by Kihlborg.[1] Series of samples $(Mo_{1-x}V_x)O_{2.765}$ for $0.03 \leq x \leq 0.11$ were heat-treated at 725°, 750°, 760°, and 775°C. The results of the X-ray powder analysis showed only the θ(V)-oxide and Mo_4O_{11}(o-rh.) to be present in the heated samples, except those prepared at 775°C. The latter were partly melted for $x > 0.07$ and the powder patterns showed Mo_4O_{11} and (Mo, V)O_2 to be present. However, a $\varkappa$-phase containing vanadium seems to form as an intermediate in the decomposition of the θ(V)-oxide. Thus, when monophasic samples of θ(V)-oxide had been annealed for a week at 760°C, just in the vicinity of the decomposition temperature (*cf.* above), the powder patterns contained the lines of a $\varkappa$-oxide with the lattice parameters $a = 21.554 \pm 5$ Å, $b = 19.548 \pm 5$ Å and $c = 3.998 \pm 2$ Å. The corresponding values for $Mo_{17}O_{47}$ are significantly different being $\varkappa = 21.61_5$ Å, $b = 19.63_2$ Å and $c = 3.951_5$ Å.[1] The vanadium content in this $\varkappa$-oxide is not known, but the changes in the lattice parameters are similar to those found for θ(V)-oxide compared with the binary oxide, Mo_5O_{14}.

A study of the magnetic properties of the θ(V)-oxide is in progress.

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