

## Ternary Phases with the $\text{Mo}_5\text{O}_{14}$ Type of Structure

### II. A Study of the Molybdenum—Niobium—Oxygen and Molybdenum—Tantalum—Oxygen Systems

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The systems  $(\text{Mo}_{1-x}\text{T}_x)\text{O}_{2.80}$  with  $T$ =niobium or tantalum and  $0 < x \leq 0.40$  have been studied by differential thermal analysis and by means of X-ray powder diffraction photographs, at room temperature, of samples quenched from preparation temperatures within the interval 600–900°C.

Apparently stable ternary phases with the same type of structure as metastable binary  $\text{Mo}_5\text{O}_{14}$  (formation temperature around 500°C) have been found to form at temperatures exceeding 600°C for niobium contents of  $x \approx 0.09$  and  $x = 0.40$  and tantalum contents of  $x \approx 0.07$ . The ranges of formation, as well as unit cell dimensions are given.

The binary  $\theta$ -molybdenum oxide  $\text{Mo}_5\text{O}_{14}$ , first described by Kihlberg, has been found to form in a metastable state around 500°C.<sup>1,2</sup> By a partial substitution of vanadium, niobium or wolfram for molybdenum, Kihlberg<sup>3</sup> was able to prepare stable phases of the same metal-oxygen ratio and the same complicated crystal structure as  $\text{Mo}_5\text{O}_{14}$ . Ternary phases  $(\text{Mo}_{1-x}\text{T}_x)_5\text{O}_{14}$  where  $T$  stands for a transition metal have been called  $\theta(T)$ -oxides.

The results of an investigation of the  $\text{Mo}_5\text{O}_{14}$  type phase in the ternary molybdenum-wolfram-oxygen and molybdenum-vanadium-oxygen systems have been described in previous articles of this series.<sup>4,2</sup> The latter paper also gives some general remarks on the  $\text{Mo}_5\text{O}_{14}$  phase ( $\theta$ -phase) and on the structurally related phases  $\text{Mo}_{17}\text{O}_{47}$  ( $\alpha$ -phase) and  $\text{W}_{18}\text{O}_{49}$ . The present article is concerned with investigations of the formation of  $\theta$ -phases in the molybdenum-niobium-oxygen and molybdenum-tantalum-oxygen systems. Results obtained in a study of the molybdenum-titanium-oxygen system will shortly appear in this journal.<sup>5</sup>

#### EXPERIMENTAL

The starting materials used were niobium pentoxide (Kawecki 99.99 %), tantalum pentoxide (Koch-Light Lab. 99.9 %), molybdenum trioxide (Mallinckrodt, Anal. Reag., dried at 200°C), and molybdenum dioxide (prepared from the trioxide). The preparation technique of the samples has been described in a previous paper.<sup>2</sup>

The heating time varied depending on the temperature of preparation. The presence of several  $\theta(\text{Nb})$ -oxides with similar lattice parameters made the establishment of equilibrium in the preparations difficult. When no changes were observed in the X-ray powder patterns of some samples heated for periods of several weeks with intermittent regrinding, equilibrium was assumed to be reached. Thus, the molybdenum-niobium oxide samples prepared at 700°C and above were usually heated for a week, whereas those at 600°C had to be heated for two or more weeks, with repeated regrinding. The same conditions for preparation pertain also to the samples in the molybdenum-tantalum oxide system.

All the samples were investigated by recording their X-ray powder patterns at room temperature by a Guinier-Hägg focusing camera and most of them by DTA, as described in Ref. 2.

#### EXPERIMENTAL DATA OBTAINED IN THE (Mo<sub>1-x</sub>Nb<sub>x</sub>)O<sub>2.80</sub> SYSTEM

Three series of samples of gross composition (Mo<sub>1-x</sub>Nb<sub>x</sub>)O<sub>2.80</sub> with  $0.01 \leq x \leq 0.40$  were prepared by prolonged heat-treatment at 600°, 640°, and 750°C. Table 1 gives a survey of the phases found from the X-ray powder photographs. Some samples were also prepared in the temperature interval 760–900°C to establish the temperature ranges of stability for the  $\theta(\text{Nb})$ -oxides.

Within the region  $0.07 \leq x \leq 0.12$  the powder patterns from samples prepared at 750°C show only the lines of niobium substituted  $\theta$ -oxide, named  $\theta_1(\text{Nb})$ -oxide below. No significant variations in the lattice parameters of this phase could be observed (*cf.* Table 1), which suggests a rather narrow homogeneity range around the composition (Mo<sub>0.91</sub>Nb<sub>0.09</sub>)O<sub>2.80</sub>. In Table 2 the X-ray powder diffraction data for the  $\theta_1(\text{Nb})$ -oxide are given. The patterns obtained in this study for the  $\theta$ -phases are in concordance with those previously reported for Mo<sub>5</sub>O<sub>14</sub>.<sup>1</sup> The quality of the  $\theta(T)$  patterns as far as line sharpness and intensity are concerned is higher than that of the photographs of metastable Mo<sub>5</sub>O<sub>14</sub> samples. This is also manifested by the fact that several additional weak lines could be observed in the  $\theta(T)$ -phase photographs.

Another  $\theta(\text{Nb})$ -oxide was found at the composition (Mo<sub>0.60</sub>Nb<sub>0.40</sub>)O<sub>2.80</sub> which corresponds to the formula Nb<sub>2</sub>O<sub>5</sub>·3MoO<sub>3</sub> in the pseudo-binary Nb<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub> system.<sup>6,7</sup> The lattice parameters of this phase,  $\theta_2(\text{Nb})$ -oxide,  $a = 23.13$  Å and  $c = 4.000$  Å, are slightly different from those of the  $\theta_1(\text{Nb})$ -oxide,  $a = 22.87$  Å and  $c = 4.020$  Å. No indications of an extended homogeneity range were observed for the  $\theta_2(\text{Nb})$ -oxide. This phase was discovered by Trunov *et al.*<sup>7</sup> in their phase analysis of the Nb<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub> system; they reported the cell dimensions to be  $a = 23.12 \pm 1$  Å and  $c = 3.995 \pm 5$  Å.

In the compositional range  $0.15 \leq x \leq 0.35$  we found a two phase region between the two  $\theta(\text{Nb})$ -oxides. The patterns obtained were diffuse, and it was only possible to separate rather few lines because of the extensive overlap. No accurate unit cell dimensions could thus be derived for these samples. Within the limits of accuracy, however, they were in agreement with those of the  $\theta_1(\text{Nb})$ - and  $\theta_2(\text{Nb})$ -oxides.

Samples with  $0.03 \lesssim x \lesssim 0.10$  prepared at 600° and 640°C (but not at 750°C) contained indications of still another  $\theta$ -oxide,  $\theta_3(\text{Nb})$ -oxide, together with  $\theta_1(\text{Nb})$ -oxide. The lattice parameters of this additional phase ( $a = 23.0$  Å,  $c = 3.94$  Å) are of course of modest accuracy but close to those of binary Mo<sub>5</sub>O<sub>14</sub>. In spite of repeated powderings and a prolonged heating time (seven

Table 1. A survey of the data obtained from the X-ray powder photogram analysis of the system  $(\text{Mo}_{1-x}\text{Nb}_x)\text{O}_{2.80}$ . The brackets indicate traces of the phase concerned. The standard deviation given corresponds to the biggest  $\sigma$  observed in a single calculation.

$x =$ in $(\text{Mo}_{1-x}\text{Nb}_x)\text{O}_{2.80}$ Gross comp.	Temp. of prep. (°C)	Observed phases	Lattice parameters of the $\theta(\text{Nb})$ -oxides	
			$a \pm 0.005 \text{ \AA}$	$c \pm 0.002 \text{ \AA}$
0.01	640	$\text{Mo}_4\text{O}_{11}$ (o.r.h.), $\text{Mo}_{18}\text{O}_{52}$ , ( $\theta_1(\text{Nb})$ -oxide)		
	750	$\text{Mo}_4\text{O}_{11}$ (o.r.h.), $\text{Mo}_8\text{O}_{23}$ , ( $\theta_1(\text{Nb})$ -oxide)		
0.03	600	$\text{Mo}_4\text{O}_{11}$ (mon.), $\text{Mo}_{18}\text{O}_{52}$ , $\theta_1(\text{Nb})$ - oxide, ( $\theta_3(\text{Nb})$ -oxide)		
	640	$\text{Mo}_4\text{O}_{11}$ (o.r.h.), $\text{Mo}_{18}\text{O}_{52}$ , $\theta_1(\text{Nb})$ -oxide		
	750	$\text{Mo}_4\text{O}_{11}$ (o.r.h.), $\text{Mo}_8\text{O}_{23}$ , $\theta_1(\text{Nb})$ -oxide		
	600	$\text{Mo}_4\text{O}_{11}$ (mon.), ( $\text{Mo}_{18}\text{O}_{52}$ ), $\theta_1(\text{Nb})$ -oxide, ( $\theta_3(\text{Nb})$ -oxide)	22.874	4.013
0.04	640	$\text{Mo}_4\text{O}_{11}$ (o.r.h.), ( $\text{Mo}_{18}\text{O}_{52}$ ), $\theta_1(\text{Nb})$ -oxide, ( $\theta_3(\text{Nb})$ -oxide)	22.882	4.010
	750	$\text{Mo}_4\text{O}_{11}$ (o.r.h.), ( $\text{Mo}_8\text{O}_{23}$ ), $\theta_1(\text{Nb})$ -oxide	22.873	4.012
0.05	600	( $\text{Mo}_4\text{O}_{11}$ (mon.)), $\theta_1(\text{Nb})$ -oxide, ( $\theta_3(\text{Nb})$ -oxide)	22.875	4.010
	640	( $\text{Mo}_4\text{O}_{11}$ (o.r.h.)), $\theta_1(\text{Nb})$ -oxide, ( $\theta_3(\text{Nb})$ -oxide)	22.883	4.019
	750	( $\text{Mo}_4\text{O}_{11}$ (o.r.h.)), $\theta_1(\text{Nb})$ -oxide	22.885	4.014
	600	$\theta_1(\text{Nb})$ -oxide, ( $\theta_3(\text{Nb})$ -oxide)	22.862	4.015
0.07	640	» ( $\theta_3(\text{Nb})$ -oxide)	22.876	4.012
	750	»	22.864	4.021
	600	» ( $\theta_3(\text{Nb})$ -oxide)	22.878	4.012
0.10	640	» ( $\theta_3(\text{Nb})$ -oxide)	22.881	4.021
	750	»	22.865	4.025
0.12	600	»	22.868	4.025
	640	»	22.869	4.024
	750	»	22.886	4.023
0.15	600	» ( $\theta_2(\text{Nb})$ -oxide)		
	640	» »		
	750	» »		
0.20	600	» $\theta_2(\text{Nb})$ -oxide		
	640	» »		
	750	» »		
0.25	640	» »		
	750	» »		
0.30	640	» »		
	750	» »		
0.35	640	( $\theta_1(\text{Nb})$ -oxide), »		
	750	» »		
	640	$\theta_2(\text{Nb})$ -oxide	22.136	4.000

Table 2. X-Ray powder diffraction data for (Mo<sub>0.91</sub>Nb<sub>0.09</sub>)O<sub>2.80</sub>, CuK $\alpha$ <sub>1</sub> radiation.

<i>I</i>	<i>d</i> <sub>obs</sub>	sin <sup>2</sup> $\theta$ <sub>obs</sub> × 10 <sup>5</sup>	<i>hkl</i>	(sin <sup>2</sup> $\theta$ <sub>obs</sub> - sin <sup>2</sup> $\theta$ <sub>calc</sub> ) × 10 <sup>5</sup>
vw -	16.11	228	110	+1
m	11.44	453	200	0
m	10.22	567	210	0
w	7.219	1138	310	+3
vw	6.334	1478	320	+3
w	5.719	1814	400	-2
vw -	5.546	1928	410	0
w +	5.383	2046	330	+3
vw	5.113	2269	420	0
vw	4.476	2959	510	+7
vw	4.248	3288	520	-3
vw	4.035	3643	440	+11
vs	4.019	3673	001	-1
vw	3.920	3861	530	+1
m	3.812	4082	600	-4
w	3.758	4203	610	+4
w	3.615	4539	620	0
s	3.573	4646	540	-7
vw	3.508	4821	311	+10
w	3.409	5104	630	-2
vw	3.287	5492	401	0
w	3.231	5684	710	+8
vw	3.222	5715	331	-2
w	3.169	5908	640	+5
vw	3.140	6017	720	+1
vw	3.002	6582	730	0
vw -	2.928	6920	650	-4
vw	2.922	6949	521	-18
w	2.856	7271	800	+6
m	2.836	7375	810	-2
vw	2.770	7730	820	+11
w +	2.764	7767	601	+5
vw	2.746	7870	611	-4
vw	2.693	8178	660	+5
vw	2.688	8209	621	-6
m	2.671	8318	541	-10

weeks) traces of this phase remained in the preparations. According to Ref. 1 and our own experience (Ref. 2) Mo<sub>5</sub>O<sub>14</sub> is not formed either at 640° or 600°C. The conditions for formation and existence of the  $\theta_3$ (Nb)-oxide need further exploration.

DTA curves of the  $\theta_1$ (Nb)- and  $\theta_2$ (Nb)-oxides show peaks at 860° and 903°C, respectively. Samples prepared below and just above these temperatures gave clear evidence of the latter having been melted.

#### EXPERIMENTAL DATA OBTAINED IN THE (Mo<sub>1-x</sub>Ta<sub>x</sub>)O<sub>2.80</sub> SYSTEM

This system has been investigated in the temperature region 600–900°C and in the gross composition range  $0.01 \leq x \leq 0.40$  in (Mo<sub>1-x</sub>Ta<sub>x</sub>)O<sub>2.80</sub>. Two

Table 3. A survey of the data obtained from the X-ray powder photograph analysis of the system  $(\text{Mo}_{1-x}\text{Ta}_x)\text{O}_{2.80}$ . The lattice parameters given are averages of several preparations. The brackets indicate traces of the phase concerned. The standard deviation given for  $a$  and  $c$  corresponds to the biggest  $\sigma$  values observed in a single calculation.

For the monophasic samples the  $\sigma$  values have about half this magnitude.

$x$ in $(\text{Mo}_{1-x}\text{Ta}_x)\text{O}_{2.80}$ Gross. comp.	Temp. of preparation (°C)	Observed phases	Lattice parameters of the $\theta(\text{Ta})$ -oxide	
			$a \pm 0.005 \text{ \AA}$	$c \pm 0.002 \text{ \AA}$
0.01	640	$\text{Mo}_4\text{O}_{11}$ , $\text{Mo}_{18}\text{O}_{52}$ , $\theta(\text{Ta})$ -oxide		
	750	$\text{Mo}_4\text{O}_{11}$ , $\text{Mo}_8\text{O}_{23}$ , $\theta(\text{Ta})$ -oxide		
0.03	640	$\text{Mo}_4\text{O}_{11}$ , $(\text{Mo}_{18}\text{O}_{52})$ , $\theta(\text{Ta})$ -oxide	22.882	4.003
	750	$\text{Mo}_4\text{O}_{11}$ , $(\text{Mo}_8\text{O}_{23})$ , $\theta(\text{Ta})$ -oxide	22.870	4.004
0.05	640	$(\text{Mo}_4\text{O}_{11})$ , $\theta(\text{Ta})$ -oxide	22.884	4.001
	750	$(\text{Mo}_4\text{O}_{11})$ , $\theta(\text{Ta})$ -oxide	22.878	4.000
0.06	640	$\theta(\text{Ta})$ -oxide	22.887	4.002
	750	$\theta(\text{Ta})$ -oxide	22.881	4.001
0.07	640	$\theta(\text{Ta})$ -oxide	22.885	4.004
	750	$\theta(\text{Ta})$ -oxide	22.874	4.005
0.08	640	$\theta(\text{Ta})$ -oxide	22.883	4.002
	750	$\theta(\text{Ta})$ -oxide	22.877	4.004
0.10	640	$(\text{MoO}_3)$ , $(\text{Ta}_2\text{O}_5)$ , $\theta(\text{Ta})$ -oxide	22.889	4.004
	750	$(\sim \text{Ta}_2\text{O}_5 \cdot 3\text{MoO}_3)$ , $\theta(\text{Ta})$ -oxide	22.884	4.004
0.12	640	$\text{MoO}_3$ , $\text{Ta}_2\text{O}_5$ , $\theta(\text{Ta})$ -oxide	22.883	4.005
	750	$\sim \text{Ta}_2\text{O}_5 \cdot 3\text{MoO}_3$ , $\theta(\text{Ta})$ -oxide	22.889	4.003
0.15	640	$\text{MoO}_3$ , $\text{Ta}_2\text{O}_5$ , $\theta(\text{Ta})$ -oxide	22.879	4.002
	750	$\sim \text{Ta}_2\text{O}_5 \cdot 3\text{MoO}_3$ , $\theta(\text{Ta})$ -oxide	22.884	4.005
0.20	640	$\text{MoO}_3$ , $\text{Ta}_2\text{O}_5$ , $\theta(\text{Ta})$ -oxide	22.897	4.002
	750	$\sim \text{Ta}_2\text{O}_5 \cdot 3\text{MoO}_3$ , $\theta(\text{Ta})$ -oxide	22.890	3.998
0.30	640	$\text{MoO}_3$ , $\text{Ta}_2\text{O}_5$ , $\theta(\text{Ta})$ -oxide		
	750	$\sim \text{Ta}_2\text{O}_5 \cdot 3\text{MoO}_3$ , $\theta(\text{Ta})$ -oxide		
0.40	640	$\text{MoO}_3$ , $\text{Ta}_2\text{O}_5$ (no reaction)		
	750	$\sim \text{Ta}_2\text{O}_5 \cdot 3\text{MoO}_3$		

extensive series of samples were prepared by heat-treatment at the fixed temperatures 640° and 750°C (*cf.* Table 3).

In the powder patterns obtained from samples heated at 640° and 750°C no lines except those of a  $\theta(\text{Ta})$ -oxide could be observed for  $0.06 \leq x \leq 0.08$ , as well as no significant variations of the positions of the lines. A very narrow homogeneity range can thus be attributed to the  $\theta(\text{Ta})$ -oxide. The unit cell dimensions were found to be  $a = 22.88 \text{ \AA}$  and  $c = 4.003 \text{ \AA}$ .

A two phase region was observed for  $0.10 \leq x \leq 0.40$ . The second component was identified as  $\sim \text{Ta}_2\text{O}_5 \cdot 3\text{MoO}_3$ , a previously unknown phase in the pseudo-binary  $\text{Ta}_2\text{O}_5 - \text{MoO}_3$  system. This is not a  $\theta$ -phase in contrast to its counterpart in the  $\text{Nb}_2\text{O}_5 - \text{MoO}_3$  system. Further details about this phase and the  $\text{Ta}_2\text{O}_5 - \text{MoO}_3$  system have been reported previously.<sup>6</sup>

DTA curves for the  $\theta(\text{Ta})$ -oxide show a sharp peak at 848°C. Judging from the appearance of samples annealed at 830° and 855°C, this is the melting temperature, since the samples heated at the latter temperature gave clear evidence of having been melted and the powder patterns obtained did not contain the diffraction pattern characteristic for the  $\theta(\text{Ta})$ -oxide.

#### DISCUSSION

The Mo<sub>5</sub>O<sub>14</sub> type of structure can be remarkably stabilized by a partial substitution of vanadium,<sup>2</sup> niobium, and tantalum for molybdenum. Even after a heating period of about eight weeks at the formation temperatures of these  $\theta(T)$ -oxides, we observed no tendency for these phases to decompose into other oxides in the manner of Mo<sub>5</sub>O<sub>14</sub>, which forms in a metastable state and within a much more restricted and lower temperature range.

The  $\theta(T)$ -oxide preparations ( $T = \text{V}, \text{Nb}, \text{or Ta}$ ) except the  $\theta_2(\text{Nb})$ -oxide have shorter  $a$  axis and longer  $c$  axis than Mo<sub>5</sub>O<sub>14</sub> ( $a' = 23.00 \text{ \AA}$ ,  $c' = 3.937 \text{ \AA}^{-1}$ ) (*v. supra*). The superstructure of Mo<sub>5</sub>O<sub>14</sub> ( $a = 2a'$ ,  $c = 2c'$ ) found by Kihlberg is disregarded here as it can only be observed in single-crystal photographs<sup>1</sup> or by electron diffraction studies.<sup>8</sup> The unit cell volume of the vanadium-containing phase remains practically the same as that of Mo<sub>5</sub>O<sub>14</sub> ( $V = 2082 \text{ \AA}^3$ ),<sup>1,2</sup> whereas it is slightly larger for the  $\theta_1(\text{Nb})$ -oxide ( $V = 2103 \text{ \AA}^3$ ),  $\theta_2(\text{Nb})$ -oxide ( $V = 2140 \text{ \AA}^3$ ), and  $\theta(\text{Ta})$ -oxide ( $V = 2096 \text{ \AA}^3$ ).

It is striking that all three group V elements form a  $\theta(T)$ -oxide,  $(\text{Mo}_{1-x}\text{T}_x)_5\text{O}_{14}$ , at the approximate composition  $x = 0.08$ . However, in contrast to the niobium and tantalum substituted phases, which have a rather narrow homogeneity range, the vanadium phase exists within an extended range around this composition.

Niobium displays a different behavior, as substitution by this metal gives rise to more than one  $\theta$ -phase. Besides a probably metastable  $\theta(\text{Nb})$ -oxide, containing small amounts of niobium, one more stable phase exists at the composition  $(\text{Mo}_{0.60}\text{Nb})_{0.40}\text{O}_{2.80}$  or  $\text{Nb}_2\text{Mo}_3\text{O}_{14}$ . This phase belongs to the pseudo-binary system  $\text{Nb}_2\text{O}_5 - \text{MoO}_3$  and thus represents a state where the metal atoms have their highest oxidation numbers. It has a dark green colour in contrast to the other  $\theta(T)$ -oxides which are black.

All attempts to prepare a  $\kappa$ -phase (corresponding to Mo<sub>17</sub>O<sub>47</sub>) containing vanadium, niobium, or tantalum, at temperatures above 600°C were unsuccessful. However, a  $\kappa(\text{V})$ -phase seems to form as an intermediate in the decomposition of  $\theta(\text{V})$ -oxide.<sup>2</sup> This behavior has not been observed with niobium or tantalum, as these  $\theta$ -oxides melt before decomposition.

A study of the magnetic properties of the various  $\theta(T)$ -oxides is in progress.

*Acknowledgements.* The authors wish to thank Professor Arne Magnéli and Dr. Lars Kihlberg for many valuable discussions and for their never-failing interest in this work.

The present study has been performed within research programs supported by the Swedish Natural Science Research Council.

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Received September 15, 1971.