

Ternary Phases with the Mo_5O_{14} Type of Structure

III. A Phase Analysis of the Molybdenum—Titanium— Oxygen System

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The part $\text{MoO}_2 - \text{MoO}_3 - \text{TiO}_2$ of the ternary molybdenum-titanium-oxygen system has been studied by means of room-temperature X-ray powder patterns of series of samples quenched from preparation temperatures of 640°, 700°, and 775°C and by differential thermal analysis. Only one ternary phase was observed to form. It has a narrow range of homogeneity at $(\text{Mo}_{0.96}\text{Ti}_{0.04})\text{O}_{2.80}$ and the Mo_5O_{14} type of structure. It decomposes at about 765°C.

The present article belongs in a series of papers concerning the formation conditions of $\theta(T)$ -oxides, *i.e.* phases of the Mo_5O_{14} type of structure, stabilized by a partial substitution of transition metals (T) for molybdenum. The binary Mo_5O_{14} has been found to exist only in a metastable state.^{1,2} Results of a study of the effect of titanium as the stabilizing metal are presented below. Previous articles in the series have given a general background and data on the $\theta(V)$ -oxide,² and results on $\theta(W)$ -oxide,³ $\theta(\text{Nb})$ - and $\theta(\text{Ta})$ -oxides.⁴ Details on the experimental techniques employed in these studies have been given in a previous paper.² The starting materials used were titanium dioxide (Baker Analyzed), molybdenum trioxide (Mallinckrodt, Anal. Reag.) and molybdenum dioxide (prepared from the trioxide). Appropriate amounts of the starting materials were thoroughly mixed and heated in sealed evacuated silica tubes at the temperature of reaction for periods ranging from one to several weeks, with repeated regrinding. After the heat-treatment the silica tubes were quenched in cold water. All the samples were investigated by recording their X-ray powder patterns at room temperature in a Guinier-Hägg focusing camera. Some of them were also subjected to differential thermal analysis.

The phase conditions within the area $\text{MoO}_2 - \text{MoO}_3 - \text{TiO}_2$ were explored by means of the X-ray powder patterns of samples of the fixed oxygen/metal ratios 2.00, 2.25, 2.50, and 2.75, at each of the preparation temperatures 640°, 700°, and 775°C ($\pm 5^\circ\text{C}$). Further series of samples of gross composition

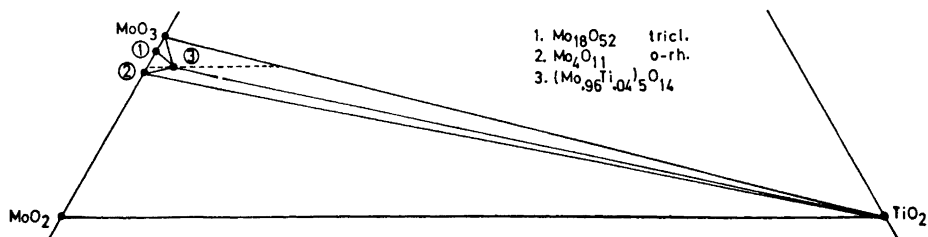


Fig. 1. A part of the phase diagram of the three component system Mo-Ti-O, obtained from samples quenched from 640°C. The dashed line corresponds to $(\text{Mo}_{1-x}\text{Ti}_x)\text{O}_{2.80}$, which at $x=0.20$ intersects the two phase line MoO_3 - TiO_2 .

$(\text{Mo}_{1-x}\text{Ti}_x)\text{O}_{2.80}$ with $x \leq 0.20$ were prepared by heat-treatment at 600°, 640°, 700°, and 750°C. The phase relationships at 640°C as observed in the present study are comprehended in Fig. 1. Table 1 gives a survey of the phases found from the X-ray powder analysis of the system $(\text{Mo}_{1-x}\text{Ti}_x)\text{O}_{2.80}$. The results obtained in the present study on the binary and pseudo-binary systems which are border-lines of the investigated area are in conformity with previous studies by others, but the ternary $\theta(\text{Ti})$ -oxide has not previously been reported.

In the binary MoO_2 - MoO_3 system all the phases observed in this study, with the exception of MoO_2 , exist in the rather narrow compositional range $\text{MoO}_{2.75}$ - MoO_3 , namely Mo_4O_{11} (mon.), Mo_4O_{11} (o-rh.), Mo_8O_{23} , $\text{Mo}_{18}\text{O}_{52}$ (tricl.), Mo_9O_{26} (mon.), and MoO_3 . It was not possible, with the reaction temperatures used to make a detailed analysis of the temperature ranges of formation for the phases. However, the results obtained are in conformity with the findings of Kihlberg¹ who has made an extensive study of the MoO_2 - MoO_3 system in the temperature interval 500°-800°C.

At the temperatures 640°, 700°, and 775°C, used in this study, MoO_2 and TiO_2 (rutile) did not react with each other. It is not known if the rutile-type phases $\text{Ti}_{0.75}\text{Mo}_{0.25}\text{O}_2$ and $\text{Ti}_{0.50}\text{Mo}_{0.50}\text{O}_2$ prepared by Marinder *et al.*⁵ at 1300°C are thermodynamically stable at these temperatures. Neither did MoO_3 and TiO_2 (rutile) form any intermediary phases in this study. This result is in agreement with the findings of Freundlich and Thoret⁶ on the TiO_2 - MoO_3 system in the temperature range 600°-900°C.

At the highest temperature of reaction employed (775°C), no ternary phase was observed to form within the area MoO_2 - MoO_3 - TiO_2 . The specimens prepared at 640° and 700°C showed, however, the existence of a ternary phase apparently isostructural with the binary Mo_5O_{14} ($\text{MoO}_{2.80}$) as evidenced by a comparison of the X-ray powder patterns.

In the powder patterns obtained from samples $(\text{Mo}_{1-x}\text{Ti}_x)\text{O}_{2.80}$ heated at 600°, 640°, 700°, and 750°C, no lines except those of the $\theta(\text{Ti})$ -oxide could be observed for $0.03 \leq x \leq 0.05$, as well as no significant variations in the unit cell dimensions of the $\theta(\text{Ti})$ -oxide (*cf.* Table 1). A very narrow homogeneity range around the composition $(\text{Mo}_{0.96}\text{Ti}_{0.04})\text{O}_{2.80}$ can thus be deduced. Visual inspection of the powder patterns of samples of somewhat different metal-to-oxygen ratios, $(\text{Mo}_{0.96}\text{Ti}_{0.04})\text{O}_{2.80} \pm 0.04$, indicated that no variation probably exists in the metal/oxygen ratio, since other oxides besides the $\theta(\text{Ti})$ -oxide were present,

Table 1. A survey of the data obtained from the X-ray powder analysis of the system (Mo_{1-x}Ti_x)O_{2.80} for 0.01 ≤ x ≤ 0.07. The brackets indicate traces of the phase concerned. 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.

x = in (Mo _{1-x} Ti _x)O _{2.80} Gross comp.	Temp. of prepara- tion (°C)	Observed phases	Lattice parameters of the θ(Ti)-oxide	
			a ± 0.005 Å	c ± 0.002 Å
0.01	600	θ(Ti)-oxide, Mo ₄ O ₁₁ (mon.), Mo ₁₈ O ₅₂	22.872	3.992
	640	θ(Ti)-oxide, Mo ₄ O ₁₁ (o.rh.), Mo ₁₈ O ₅₂	22.868	3.985
	700	θ(Ti)-oxide, Mo ₄ O ₁₁ (o.rh.), Mo ₈ O ₂₃	22.861	3.993
	750	θ(Ti)-oxide, Mo ₄ O ₁₁ (o.rh.), Mo ₈ O ₂₃	22.863	3.990
0.015	600	θ(Ti)-oxide, Mo ₄ O ₁₁ (mon.), (Mo ₁₈ O ₅₂)	22.851	3.992
	640	θ(Ti)-oxide, Mo ₄ O ₁₁ (o.rh.), (Mo ₁₈ O ₅₂)	22.844	3.987
	600	θ(Ti)-oxide, Mo ₄ O ₁₁ (o.rh.), (Mo ₈ O ₂₃)	22.836	3.996
	750	θ(Ti)-oxide, Mo ₄ O ₁₁ (o.rh.), (Mo ₈ O ₂₃)	22.835	4.000
0.02	600	θ(Ti)-oxide, (Mo ₄ O ₁₁ (mon.))	22.860	3.988
	640	θ(Ti)-oxide, (Mo ₄ O ₁₁ (o.rh.))	22.865	3.989
	700	θ(Ti)-oxide, (Mo ₄ O ₁₁ (o.rh.))	22.859	3.989
	750	θ(Ti)-oxide, (Mo ₄ O ₁₁ (o.rh.))	22.848	3.990
0.03	600	θ(Ti)-oxide, —	22.853	3.995
	640	θ(Ti)-oxide, —	22.861	3.988
	700	θ(Ti)-oxide, —	22.856	4.004
	750	θ(Ti)-oxide, —	22.841	3.994
0.04	600	θ(Ti)-oxide, —	22.863	3.994
	640	θ(Ti)-oxide, —	22.859	3.994
	700	θ(Ti)-oxide, —	22.854	3.991
	750	θ(Ti)-oxide, —	22.837	4.005
0.05	600	θ(Ti)-oxide, —	22.856	3.985
	640	θ(Ti)-oxide, —	22.860	3.994
	700	θ(Ti)-oxide, —	22.849	3.991
	750	θ(Ti)-oxide, —	22.848	3.995
0.06	600	θ(Ti)-oxide, (MoO ₃)	22.871	3.984
	640	θ(Ti)-oxide, (MoO ₃)	22.847	3.991
	700	θ(Ti)-oxide, (MoO ₃)	22.829	4.001
	750	θ(Ti)-oxide, (MoO ₃)	22.847	4.004
0.07	600	θ(Ti)-oxide, MoO ₃	22.861	3.983
	640	θ(Ti)-oxide, MoO ₃	22.855	3.991
	700	θ(Ti)-oxide, MoO ₃	22.836	4.003
	750	θ(Ti)-oxide, MoO ₃	22.850	3.995

and no significant variations of the positions of the lines for the θ -phase were observed.

Samples heat-treated at 760° and 770°C showed that decomposition of the θ (Ti)-oxide occurs within this temperature interval, without melting. X-Ray powder photographs of the 770° samples showed that the θ (Ti)-oxide decomposes into Mo_4O_{11} (o-rh.), MoO_3 , and TiO_2 (rutile). The observed temperature of decomposition is in agreement with the results from differential thermal analysis on monophasic θ (Ti)-oxide, for which a small and rather broad peak at about 770°C has been observed during heating (5–10°C/min). No reproducible data were obtained from the cooling runs.

The dimensions of the tetragonal unit cell of the θ (Ti)-oxide are $a = 22.85$ Å and $c = 3.991$ Å (cf. Table 1), significantly different from the corresponding values for the binary Mo_5O_{14} , $a' = 23.00$ Å and $c' = 3.937$ Å.¹ The unit cell volumes are very similar, however, being 2084 Å³ and 2082 Å³, respectively, as could be expected from the similarities in metal atom radii. It should be pointed out that the unit cell dimensions given here for Mo_5O_{14} refer to a subcell. The presence of a superstructure with $a = 2a'$ was apparent from the single crystal pattern.^{1,7} Recent electron diffraction studies have shown that the c axis is also doubled.⁸ It is not known whether the same superstructure exists in the θ (Ti)-oxide.

The binary phase Mo_5O_{14} is formed in a metastable state and within a restricted temperature range around 500°C.^{1,2} The partial substitution of a fixed titanium content for molybdenum in the θ (Ti)-oxide thus has a markedly stabilizing effect on the Mo_5O_{14} type of structure, as no tendency for the θ (Ti)-phase to decompose into other oxides, in the manner of Mo_5O_{14} , has been observed. As described in previous articles, a partial substitution of various transition metals for molybdenum has such stabilizing effect.^{9,2-4} In all cases, the temperature ranges of formation are considerably higher than for the binary oxide.

All attempts to prepare a similar θ (T)-oxide with the other two group IV elements, Zr and Hf, have been unsuccessful. This is presumably due to the fact that the metal atom radii of Zr and Hf differ much more from that of Mo than does the Ti radius.

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

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