

PHASE DIAGRAM OF THE V_2O_5 - MoO_3 - Ag_2O SYSTEM

II. Phase diagram of MoO_3 - Ag_2O system

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The phase diagram of the MoO_3 - Ag_2O system was constructed. A comparison of the phase diagram presented here with the phase diagram of MoO_3 - Ag_2MoO_4 system presented in [2] revealed some discrepancies.

It was found that phase equilibrium in MoO_3 - Ag_2O system could be reached only after cooling the previously melted mixtures of silver and molybdenum oxides.

In a previous paper [1] the V_2O_5 - Ag_2O phase diagram was described. As a continuation of the study of V_2O_5 - MoO_3 - Ag_2O triple system the present investigations is concerned with the MoO_3 - Ag_2O phase diagram. This diagram has been described by Kohmuller and Faurie [2] who investigated the composition range MoO_3 - Ag_2MoO_4 . When repeating their experiments with the use of differently prepared samples the present author could not confirm the incongruent melting of both latter compounds which was postulated by them. This was the reason why the reinvestigation of the MoO_3 - Ag_2O system was considered to be necessary.

Experimental

Four series of samples were prepared. The first one used for the introductory thermal analysis was obtained by heating the mixtures of MoO_3 and Ag_2O at 660° in open quartz tubes for 24 hours and slowly cooling to room temperature in the course of 24 hours. The chemical and phase composi-

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tions of the samples as well as the appropriate thermal data are given in Table 1.

In the range from 0 to ~ 15 mole % Ag_2O no melting of the samples took place. However, at higher Ag_2O content total or partial fusion occurred and in the case of samples with more than 50 mole % Ag_2O the segregation of metallic silver was observed.

Based on these results an additional series of samples containing 15-45 mole % Ag_2O was prepared by heating the mixtures of oxides at 470° - 500° in air for 24 hours and rapidly cooling to the liquid nitrogen temperature (Table 2). From the samples containing 40 and 45 mole % Ag_2O metallic silver segregated.

The third series of samples containing 20-80 mole % Ag_2O was prepared by heating the mixtures of oxides at 420° - 480° in air, keeping two or three days at these temperatures and slowly cooling down in the course of two days. The results are collected in Table 3.

Some discrepancies between the data obtained for the series 1, 2 and 3 were the reason for the preparation of the fourth series obtained by melting the mixtures of molybdenum and silver oxides in air and individually cooling down (Table 4).

The composition of all samples was checked analytically. The content of silver was determined by dissolving the samples in HNO_3 and subsequently in NaOH and titrating with NH_4SCN solution (Tables 1-4).

Differential thermal and thermogravimetric analyses were carried out using a Mettler TA-2 Thermoanalyzer. Al_2O_3 was used as reference material. The flow of air over the samples was 4 l/h and the heating rate 10 deg/min. The samples were heated from room temperature to 800° .

Owing to the sublimation of MoO_3 observed at high temperatures thermal analyses had to be carried out possibly rapidly. Under such conditions the check of the reversibility of thermal effects in the course of programmed cooling was impossible. The samples were characterized by x-ray powder diffractometry using a DRON-2 x-ray diffractometer ($\text{CuK}\alpha$ radiation). The interplanar distances of the samples were compared with the data from [2] and also Powder Diffraction File.

X-ray reflections characteristic of silver oxide as well as metallic silver were very much diffuse owing to the dispersion of the used radiation. The additional measurements using x-ray heating camera were performed for samples containing 20, 33 and 50 mole% Ag_2O . These were composition corresponding to the compounds: $\text{Ag}_2\text{Mo}_4\text{O}_{13}$, $\text{Ag}_2\text{Mo}_2\text{O}_7$ and $\beta\text{-Ag}_2\text{MoO}_4$ respectively. The aim of these experiments was the investigations of the phase transformations of the above compounds. The samples were prepared

Table 1 Data for samples heated at 660°C and slowly cooled down

No	Assumed composition, mole % Ag ₂ O	Chemical analysis, mole % Ag ₂ O	DTA peaks, °C (all endothermic)	Phases detected in the final product
1	1	1.0	510 790	
2	2	1.9	520 780	
3	5	4.6	515 760	MoO ₃ , Ag ₂ Mo ₄ O ₁₃ , Ag ₂ Mo ₂ O ₇
4	10	9.4	525 720	MoO ₃ , Ag ₂ Mo ₄ O ₁₃ , Ag ₂ Mo ₂ O ₇
5	15	14.4	530	MoO ₃ , Ag ₂ Mo ₄ O ₁₃
6	20	18.7	525	Ag ₂ Mo ₄ O ₁₃ , MoO ₃ , Ag ₂ Mo ₂ O ₇
7	20	18.9	497 527	Ag ₂ Mo ₄ O ₁₃ , MoO ₃ , Ag ₂ Mo ₂ O ₇
8	25	23.8	510 520	Ag ₂ Mo ₂ O ₇ , Ag ₂ Mo ₄ O ₁₃ , (MoO ₃)*
9	33		510	Ag ₂ Mo ₂ O ₇ , (Ag ₂ Mo ₄ O ₁₃), (MoO ₃)
10	40	38.5	490	Ag ₂ Mo ₂ O ₇
11	50	45.4	500 955	Ag ₂ Mo ₂ O ₇ , (Ag)

* () - means trace of compound

Table 2 Data for samples obtained by heating the mixtures of MoO₃ and Ag₂O at 470-500°C in air and rapidly cooled down

No	Assumed composition, mole % Ag ₂ O	Chemical analysis, mole % Ag ₂ O	DTA peaks, °C (all endothermic)	Phases detected in the final product
1	15	14.4	530 670	MoO ₃ , Ag ₂ Mo ₄ O ₁₃
2	17.5	16.8	532 623	Ag ₂ Mo ₄ O ₁₃ , MoO ₃ ,
3	20.0	17.4	509 534	Ag ₂ Mo ₄ O ₁₃ , MoO ₃ (Ag ₂ Mo ₂ O ₇)
4	22.5	21.8	506 533	Ag ₂ Mo ₄ O ₁₃ , Ag ₂ Mo ₂ O ₇
5	25.0	24.1	503 524	Ag ₂ Mo ₄ O ₁₃ , Ag ₂ Mo ₂ O ₇
6	27.5	24.4	492 516 530	Ag ₂ Mo ₄ O ₁₃ , Ag ₂ Mo ₂ O ₇
7	30.0	29.4	509	Ag ₂ Mo ₂ O ₇ , Ag ₂ Mo ₄ O ₁₃ ,
8	33.0	30.5	508	Ag ₂ Mo ₂ O ₇ , Ag ₂ Mo ₄ O ₁₃ ,
9	36.0	34.8	496 513	Ag ₂ Mo ₂ O ₇ , (Ag ₂ Mo ₄ O ₁₃)
10	40.0	36.1 ¹⁾	494 512 961	Ag ₂ Mo ₂ O ₇ , Ag, (Ag ₂ Mo ₄ O ₁₃)
		38.5	498	Ag ₂ Mo ₂ O ₇ , Ag
11	45.0	40.7 ²⁾	500	Ag ₂ Mo ₂ O ₇ , Ag
		78.0	506 960	Ag ₂ Mo ₂ O ₇ , Ag
12	100.0		440 961	Ag

1) and 2) - the samples composed of two phases. One of them remained on a sieve (38.5 mole % and 78 mole % Ag₂O)

*) () - means trace of compound

Table 3 Data for samples heated below their melting points and slowly cooled down

No	Assumed mole % Ag ₂ O	Chemical analysis, mole % Ag ₂ O	The way of preparation of the samples	DTA peaks, °C (all endothermic)	Phases detected in the final product
1	20	19.2	Heating during 340 h at 480°C	536	Ag ₂ Mo ₄ O ₁₃ , (MoO ₃)*
2	20	19.2	Additional heating during 288 h at 480°C	532	identical as above
3	21	20.6	48 h at 480° 72 h cooling down	532	Ag ₂ Mo ₄ O ₁₃ , (MoO ₃), (Ag ₂ Mo ₂ O ₇)
4	28	26.9	72 h at 480°C 120 h cooling down	518	
5	33	32.1	144 h at 480°C 48 h cooling down	516	Ag ₂ Mo ₂ O ₇ , (Ag ₂ Mo ₄ O ₁₃)
6	40	37.5	72 h at 420°C 48 h cooling down	504	Ag ₂ Mo ₂ O ₇

Table 3 continued

No	Assumed mole % Ag ₂ O	Chemical analysis, mole % Ag ₂ O	The way of preparation of the samples	DTA peaks, °C (all endothermic)	Phases detected in the final product
7	50		72 h at 420°C 96 h cooling down 386 h at 320°C 120 h at 320°	495 550 490 555 494 561	β -Ag ₂ MoO ₄ , Ag ₂ Mo ₂ O ₇ , Ag β -Ag ₂ MoO ₄ , (Ag ₂ Mo ₂ O ₇), (Ag) β -Ag ₂ MoO ₄ , (Ag ₂ Mo ₂ O ₇), (Ag)
8	55	54.6	76 h at 480°C 24 h cooling down	500 540	β -Ag ₂ MoO ₄ , Ag ₂ Mo ₂ O ₇ , Ag, (MoO ₃)
9	60	59.2	72 h at 450°C 3 h cooling down	500 562	Ag ₂ MoO ₄ , Ag ₂ Mo ₂ O ₇ , Ag
10	65	58.05	72 h at 480° 75 h cooling	494 550	β -Ag ₂ MoO ₄ , Ag ₂ Mo ₂ O ₇ , MoO ₃ , Ag
11	65	65.1	120 h at 480°C 96 h cooling	572	β -Ag ₂ MoO ₄ , Ag, (Ag ₂ Mo ₂ O ₇)
12	70	71.1	72 h at 460°C 48 h cooling down	494 526 554	Ag, β -Ag ₂ MoO ₄ , Ag ₂ Mo ₂ O ₇
13	80	83.1	168 h at 480°C	571	Ag, β -Ag ₂ MoO ₄ , Ag ₂ Mo ₂ O ₇

*) () - means trace of compound

Table 4 Data for samples melted and cooled down in various period of time

No	Assumed mole %	Chemical analysis, mole % Ag ₂ O	DTA peaks, °C (all endothermic)	Phases detected in the final product
1	17.5	17.4	502 538	
2	20	20.6	537	Ag ₂ Mo ₄ O ₁₃ , MoO ₃
3	25	23.7	506 528	
4	28	26.9	518	Ag ₂ Mo ₂ O ₇ , Ag ₂ Mo ₄ O ₁₃
5	30	29.4	511	Ag ₂ Mo ₂ O ₇ , Ag ₂ Mo ₄ O ₁₃
6	33	32.5	513	Ag ₂ Mo ₂ O ₇ , (MoO ₃)*
7	36	34.8	513	Ag ₂ Mo ₂ O ₇ , (Ag ₂ Mo ₄ O ₁₃)
8	40	36.1	498	Ag ₂ Mo ₂ O ₇ , β-Ag ₂ MoO ₄
9	40	38.0	500	Ag ₂ Mo ₂ O ₇ , β-Ag ₂ MoO ₄
10	45	41.9	497 534	β-Ag ₂ MoO ₄ , Ag ₂ Mo ₂ O ₇ , (Ag ₂ Mo ₄ O ₁₃)
11	45	43.0	500	β-Ag ₂ MoO ₄ , Ag ₂ Mo ₂ O ₇ ,
12	55	44.8	496 554	β-Ag ₂ MoO ₄ , Ag ₂ Mo ₂ O ₇ ,
13	60	59.2	494 572	β-Ag ₂ MoO ₄ , Ag ₂ Mo ₂ O ₇ ,
14	70	71.1	578	
15	80	83.7	572	β-Ag ₂ MoO ₄ , Ag, (Ag ₂ Mo ₂ O ₇), (Ag ₂ Mo ₄ O ₁₃) β-Ag ₂ MoO ₄ , Ag ₂ Mo ₂ O ₇ , (Ag)

* ()-means trace of compound

by sintering MoO_3 - Ag_2MoO_4 mixtures followed by grinding and repeated sintering. This procedure was repeated several times.

Results and discussion

On the basis of the data presented in Tables 1-5 the phase diagram of the MoO_3 - Ag_2O system shown in Fig. 1 was constructed.

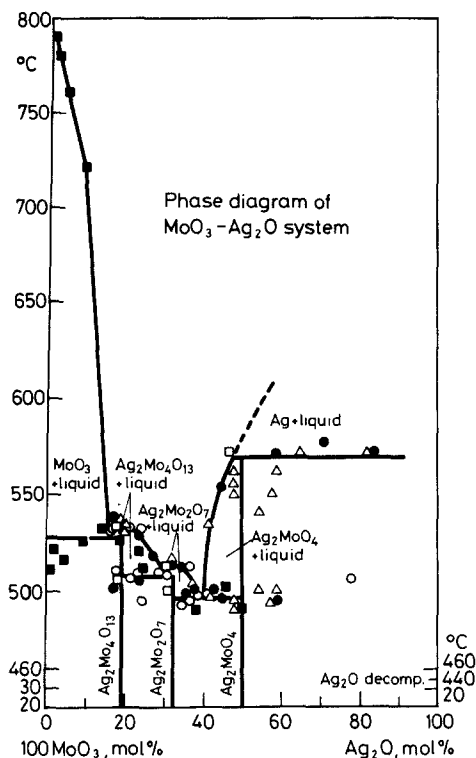


Fig. 1 Phase diagram of MoO_3 - Ag_2O system

The following phases were found: MoO_3 , $\text{Ag}_2\text{Mo}_4\text{O}_{13}$ (20 mole % Ag_2O), $\text{Ag}_2\text{Mo}_2\text{O}_7$ (33 mole % Ag_2O), β - Ag_2MoO_4 (50 mole % Ag_2O) and Ag_2O which decomposed at about 440° and above this temperature the metallic silver was observed in the system.

Phases: MoO_3 , $\text{Ag}_2\text{Mo}_4\text{O}_{13}$, $\text{Ag}_2\text{Mo}_2\text{O}_7$ and Ag melted congruently at 790° , 536° , 516° and 960° , respectively. β - Ag_2MoO_4 melts incongruently at 576° .

The mentioned phases form three simple eutectic systems:

1. $\text{MoO}_3\text{-Ag}_2\text{Mo}_4\text{O}_{13}$ mixture crystallizes at about 528° and for about 16 mole % Ag_2O the composition of the liquid is the same as that of the solid.

2. $\text{Ag}_2\text{Mo}_4\text{O}_{13} - \text{Ag}_2\text{Mo}_2\text{O}_7$, the composition of the eutectic corresponds to about 29 mole % Ag_2O and the eutectic temperature is about 508° .

3. $\text{Ag}_2\text{Mo}_2\text{O}_7 - \beta\text{-Ag}_2\text{MoO}_4$ system possesses eutectic point at about 40 mole % Ag_2O and melts at about 496° .

Table 5

No	The way of preparation of samples (according to [2])	DTA peaks, $^\circ\text{C}$ (all endothermic)	X-ray analysis
1	$\text{AgNO}_3 + \text{Na}_2\text{MoO}_4 = \text{Ag}_2\text{MoO}_4$ precipitation in the water solution	574	$\beta\text{-Ag}_2\text{MoO}_4$ ($\alpha\text{-Ag}_2\text{MoO}_4$)*
2	Ag_2MoO_4 after melting	578	$\beta\text{-Ag}_2\text{MoO}_4$ ($\text{Ag}_2\text{Mo}_4\text{O}_{13}$)
3	$\text{Ag}_2\text{MoO}_4 + \text{MoO}_3$ (450°C) $\text{Ag}_2\text{Mo}_2\text{O}_7$	492 513	$\text{Ag}_2\text{Mo}_2\text{O}_7$
4	$\text{Ag}_2\text{Mo}_2\text{O}_7$ after melting	511	$\text{Ag}_2\text{Mo}_2\text{O}_7$, (MoO_3)
5	$\text{Ag}_2\text{MoO}_4 + 2\text{MoO}_3$ (450°C) $\text{Ag}_2\text{Mo}_4\text{O}_{13}$	504 538	$\text{Ag}_2\text{Mo}_4\text{O}_{13}$, MoO_3
6	$\text{Ag}_2\text{Mo}_4\text{O}_{13}$ after melting	506 534 (606)	$\text{Ag}_2\text{Mo}_4\text{O}_{13}$ MoO_3

* () - means trace of compound

On the diagram results for the region above 580° and 50 mole % Ag_2O are lacking because in the course of experiments silver crept out of the crucible and formed an alloy with the platinum thermocouple.

Comparing the diagram of $\text{MoO}_3 - \text{Ag}_2\text{O}$ system presented here and the diagram of $\text{MoO}_3 - \text{Ag}_2\text{MoO}_4$ shown in paper [2] one can find similarities but also differences between the results. The diagram presented in [2] comprises the range of 0-50 mole % Ag_2O and the diagram shown in this work includes full range of 0-100 mole % Ag_2O .

In both investigations the same phases were observed. It was stated in (2) that $\text{Ag}_2\text{Mo}_4\text{O}_{13}$ and $\text{Ag}_2\text{Mo}_2\text{O}_7$ melted incongruently. Solution of the problem of the character of melting in the described system was by no means simple. The characteristic temperatures: 496° , 508° , 516° , 528° , 536° were very close. However, the course of liquidus and solidus curves and also the sharp shape of endothermic peaks of samples containing 20 mole % and 33

mole % Ag₂O indicated that Ag₂Mo₄O₁₃ and Ag₂Mo₂O₇ in our case melted congruently.

Based on their DTA analyses the authors of [2] suggested that Ag₂Mo₄O₁₃, Ag₂Mo₂O₇ and β-Ag₂MoO₄ undergo phase transitions at 490, 480 and 482° resp. In the present research the existence of such endothermic peaks in the case of Ag₂Mo₄O₁₃ and Ag₂Mo₂O₇ was not confirmed. On the other hand in the case of samples containing β-Ag₂MoO₄ (Tables 3 and 4) a weak endothermic DTA peak was observed between 492 and 500° corresponding to the 482° peak observed in [2]. However, no phase transformation about this temperature was observed in x-ray heating camera. The presence of small amounts of Ag₂Mo₂O₇ and metallic silver detected after heating Ag₂MoO₄ suggests that this effect might be due to the partial disproportionation:



Analogous experiments in the x-ray heating camera did not indicate any phase transformations neither in the Ag₂Mo₂O₇ nor in the Ag₂Mo₄O₁₃ phase.

The discrepancies between the results of both investigations may evidently be due to the differences in the way of the preparation of the samples. The role of experimental conditions should also be taken into account. If samples are obtained by the reaction occurring in the solid state (as it is in this case) such factors as dispersion of substrates and heating conditions may predominantly influence the kinetics of the process and thus the phase composition and generally the physico-chemical properties of the final product.

* * *

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Zusammenfassung — Es wurde das Phasendiagramm des Systemes $\text{MoO}_3\text{-Ag}_2\text{O}$ erstellt. Der Vergleich dieses Phasendiagrammes mit dem des in (2) beschriebenen Systemes $\text{MoO}_3\text{-Ag}_2\text{MoO}_4$, ergeben sich einige Unterschiede.

Man fand, daß ein Phasengleichgewicht im System $\text{MoO}_3\text{-Ag}_2\text{O}$ nur nach Abkühlen des zuvor geschmolzenen Gemisches aus Silber- und Molybdänoxides erreicht werden kann.