

PHASE RELATIONS IN THE SUBSOLIDUS AREA OF THE CoV_2O_6 – CoMoO_4 – CoO SUBSYSTEM INCLUDED BY THE TERNARY CoO – V_2O_5 – MoO_3 SYSTEM

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Abstract

The phase diagram of CoV_2O_6 – CoMoO_4 – CoO system in subsolidus area was investigated by DTA and XRD methods. It was shown that this area consisted of five subsidiary systems in which there existed three solid phases. The melting temperatures of these systems were also determined.

Keywords: cobalt(II) vanadato-molybdate, DTA, phase diagram, XRD

Introduction

The hitherto published studies on the reactivity of $\text{Co}_3\text{V}_2\text{O}_8$ towards CoMoO_4 in the solid state have shown that the system components react with each other to form a previously unknown phase of $\text{Co}_{2.5}\text{VMoO}_8$ that is isostructural with $\text{Mg}_{2.5}\text{VMoO}_8$ [1, 2]. The phase relations occurring in the $\text{Co}_3\text{V}_2\text{O}_8$ – CoMoO_4 system are already known [2]. This system is an actual section of the ternary CoO – V_2O_5 – MoO_3 system. Phase equilibria within the V_2O_5 – MoO_3 , CoO – V_2O_5 and CoO – MoO_3 external walls as well as the properties and structure of compounds existing in these binary systems are extensively described in literature [3–7]. Thus, the phase diagram of the CoO – MoO_3 system is known [3, 4]. In this system only one compound is formed, namely CoMoO_4 . Its melting temperature is 1180°C [5], but our investigations have shown that CoMoO_4 melts at $1110\pm 10^\circ\text{C}$. The phase relations in the CoO – V_2O_5 system are also well known. In this system there exist three compounds, all of them melting incongruently. The melting temperature of cobalt vanadates amount respectively to CoV_2O_6 – 740°C [8], $\text{Co}_2\text{V}_2\text{O}_7$ – 830°C [8], $\text{Co}_3\text{V}_2\text{O}_8$ – 1216°C [9]. The ternary CoO – V_2O_5 – MoO_3 system was comprehensively investigated as well with respect to the phase equilibria and properties of the phases present in this system [3]. It was shown that in the CoO – V_2O_5 – MoO_3 system there exists a solid solution MoO_3 in CoV_2O_6 exhibiting the brannerite structure type [3]. The diagram of the CoO – V_2O_5 – MoO_3 system has been constructed, except for the CoV_2O_6 – CoMoO_4 – CoO section. The area of this section was not discussed in the above-mentioned work in detail [3]. Our aim was, therefore, to investigate the phase equilibria in the subsolidus area of

the $\text{CoV}_2\text{O}_6\text{-CoMoO}_4\text{-CoO}$ system, in which a compound of $\text{Co}_{2.5}\text{VMoO}_8$ is formed in the $\text{Co}_3\text{V}_2\text{O}_8\text{-CoMoO}_4$ section [1, 2].

Experimental

18 samples were prepared from CoCO_3 (Aldrich, Germany), V_2O_5 (POCh, Gliwice) and MoO_3 (POCh, Gliwice) i.e., their composition having been chosen for the sake of phase relationships investigation of the $\text{CoV}_2\text{O}_6\text{-CoMoO}_4\text{-CoO}$ system in the solid state. Reactants were weighed in appropriate amounts, homogenised, shaped into pastilles, and then heated in a sylvite furnace, in air. On each heating stage the pastilles were ground again, were examined by using DTA method and their content was determined by means of XRD method. Afterwards, the samples were re-shaped into pastilles and heated again. This procedure was continued till equilibrium state was reached. Two identical results obtained were taken as an indication of the equilibrium state having been established and then the heating of samples was finished. The conditions of calcination were different depending on the sample composition. After the last heating stage all samples were cooled for 12 h to ambient temperature and then DTA and XRD were examined. Compositions of the samples thus prepared were determined by using XRD method (diffractometer DRON-3, CoK_α radiation, Fe filter) and on the data included in PDF cards [10], and found in literature [2, 3, 11]. The XRD patterns were handled by means of the programs from DHN/PDF package (Program Package for Powder Diffraction).

With the use of the TA Instruments STD 2960 apparatus the DTA examinations of the samples were performed. These measurements were carried out in air, with the use of platinum crucibles at a heating rate of $10^\circ\text{C min}^{-1}$.

Results and discussion

In the face of discrepancies in literature data we decided to start verifying the melting temperature of all cobalt vanadates and cobalt molybdates. It was found that both the melting temperature and the temperature of polymorphic transition of CoV_2O_6 were

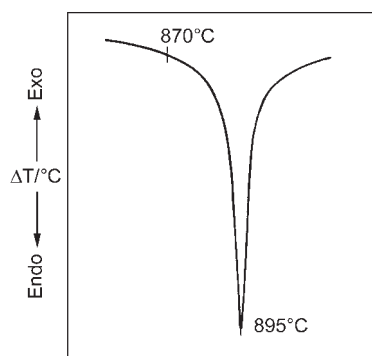


Fig. 1 DTA curve of $\text{Co}_2\text{V}_2\text{O}_7$

in accordance with the literature data [8] i.e. cobalt metavanadate melts at 740°C, whereas the polymorphic transition takes place at 662°C. On the other hand, Co₂V₂O₇ melts at 870°C (Fig. 1) according to our research results, i.e. by 40° higher than other papers reported [8]. We have also found out that the melting temperature of Co₃V₂O₈ is equal to 1120°C, while of CoMoO₄ amounts to 1110°C.

Table 1 The compositions of initial mixtures, calcination and XRD results for samples after the final heating cycle

No.	Compositions of initial mixtures/mol%			Condition of calcination	Phase detected
	CoO	MoO ₃	V ₂ O ₅		
1	65	30	5	600°C (24 h)	Co _{2.5} VMoO ₈ ,
2	80	15	5	+650°C (24 h)	CoMoO ₄ , CoO
3	70	20	10	+700°C (24 h)	Co _{2.5} VMoO ₈ ,
4	85	10	5	+750°C (24 h)	CoO
5	75	10	15	+900°C (24 h)	Co _{2.5} VMoO ₈ ,
6	85	5	10	+1000°C (24 h)	Co ₃ V ₂ O ₈ , CoO
7	68	5	27	600°C (24 h)	Co _{2.5} VMoO ₈ ,
8	67	13	20	+650°C (24 h)	Co ₃ V ₂ O ₇ , Co ₂ V ₂ O ₇
				+700°C (24 h)	
				+750°C (24 h)	
				+800°C (24 h)	
9	65	13.5	21.5	+810°C (24 h)	Co _{2.5} VMoO ₈ ,
10	62.6	16.5	21		Co ₂ V ₂ O ₇
11	60	25	15	600°C (24 h)	Co _{2.5} VMoO ₈ ,
12	58	30	12	+650°C (24 h)	CoMoO ₄ , Co ₂ V ₂ O ₇
				+700°C (24 h)	
13	55	35	10	+750°C (48 h)	CoMoO ₄ ,
14	60	20	20	+770°C (48 h)	Co ₂ V ₂ O ₇
15	52.5	30	17.5	550°C (24 h)	
16	55	20	25	+600°C (24 h)	CoMoO ₄ ,
17	55	10	35	+600°C (24 h)	Co ₂ V ₂ O ₇ ,
				+650°C (24 h)	CoV ₂ O ₆
18	60	5	35	+650°C (48 h)	
				+680°C (48 h)	

Composition of initial mixtures, conditions of preparation and XRD results for all samples after the final of stage heating are presented in Table 1. Figure 2 shows a scheme for the fragment CoV₂O₆-CoMoO₄-CoO of the ternary system CoO-V₂O₅-MoO₃ in subsolidus area. This phase diagram was determined on the basis of XRD results, DTA curves and reported data [2, 4, 5]. It follows from the phase diagram that in the CoV₂O₆-CoMoO₄-CoO system five subsidiary partial systems can be separated, each of them containing three solid coexisting phases. These are the following partial systems:

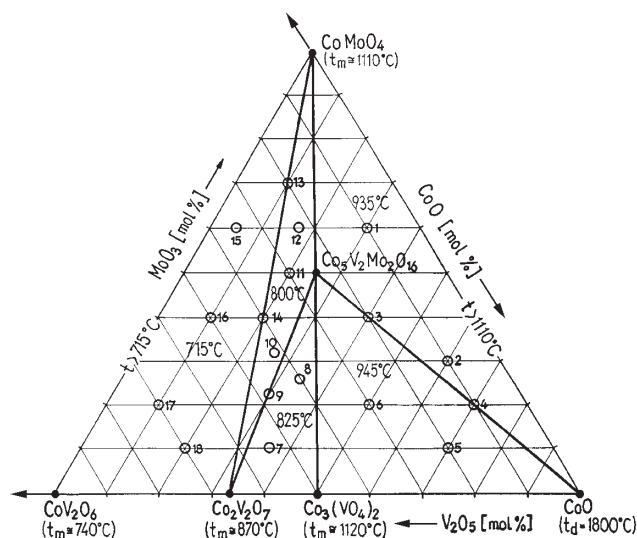
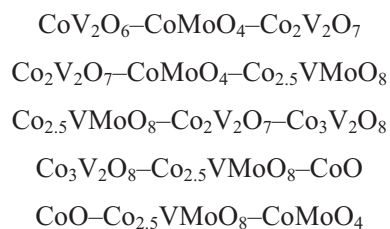


Fig. 2 Subsolidus portion of the phase diagram of the CoV_2O_6 – CoMoO_4 – CoO systems divided into subdiagrams. Open circles represent the composition of the studied samples

In Fig. 2 there are marked the melting temperatures for the individual areas of partial subsidiary systems that were determined on the basis of onset temperatures of DTA effects corresponding to the samples, respectively.

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