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Subsolidus of the $MO–Cr_2O_3–V_2O_5$ systems, where M = Ni, Mg

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Abstract

Phase relations in the system: $MO–Cr_2O_3–V_2O_5$, where M = Ni and Mg, were determined up to the solidus lines over the whole components concentration range. On the basis of this, a division of both systems into subsidiary subsystems was performed. The melting temperatures of individual areas were also established.

Keywords: A. Inorganic compounds; A. Oxides; C. X-ray diffraction; D. Phase equilibria

1. Introduction

The development of industry poses a considerable threat. Therefore, increasingly, all sorts of enterprises aiming at minimizing the negative consequences of industrial activity are undertaken. Owing to the fact that norms permitting the values of harmful HCl, NO_x molecules and others are being tightened, one can expect much stricter boundary values of exhaust gas emissions. Therefore, their effective purification, thanks to DENOX filters and catalysts, will become highly necessary. In the years 1970–1980, the bloc d metal oxides, implemented as catalysts removing NO_2, were found to be highly selective [1]; thus, the research on further improvement of the catalysts' selectivity is far flung. The oxide multicomponent systems are the area of search for the catalysts characterized by high selectivity and activity. For many years, the vanadates of bivalent metals [2] have been known owing to their interesting properties. Thoroughly conducted studies have revealed that the catalytic characteristics are connected with the presence of isolated tetrahedra VO_4 in vanadates'(V) molecules [2].

During the works conducted on $M_2V_2O_7$ reactivity in relation to $CrVO_4$, where M = Ni, Mg, Zn, it was demonstrated that, in the solid phase, these compounds react with forming a new phase of the general formula $M_2CrV_3O_{11}$ [3–5]. The $M_2CrV_3O_{11}$ compounds, where M = Ni, Mg crystallize in the triclinic system and melt congruently at the temperatures: $Ni_2CrV_3O_{11}$–940 ± 5 °C [5], $Mg_2CrV_3O_{11}$–900 ± 5 °C [3].

Until today, phase relations corresponding to the solidus line, settling in three intersections of the ternary $NiO–Cr_2O_3–V_2O_5$, i.e. $NiV_2O_6–NiCr_2O_4$, $Ni_2V_2O_7–CrVO_4$ and $Ni_3V_2O_8–NiCr_2O_4$ system [4,5] have been examined. The results of these investigations made it possible to draw a few lines of the division of the triangle of the ternary $NiO–Cr_2O_3–V_2O_5$ system concentrations (Fig. 1a) [4,5]. This figure implies that the NiV_2O_6—$NiCr_2O_4$ system is the actual bivalent system up to the 25 mol% $NiCr_2O_4$ content only. Above the content of 25 mol% $NiCr_2O_4$, the $NiV_2O_6–NiCr_2O_4$ system constitutes the cross-section of the $NiO–Cr_2O_3–V_2O_5$, going through two subsidiary subsystems: $Ni_2CrV_4O_{11}–Ni_3V_2O_8–Cr_2O_3$ and $Ni_3V_2O_8–NiCr_2O_4–Cr_2O_3$. The investigation into the $Ni_2V_2O_7–CrVO_4$ system demonstrated that it is the real binary system where the $Ni_2CrV_3O_{11}$ compound is formed.

The studies on the three intersections, $MgV_2O_6–MgCr_2O_4$, $Mg_2V_2O_7–CrVO_4$ and $Mg_3V_2O_8$, [3] allowed the determination of the partial division of the components concentration triangle of the $MgO–V_2O_5–Cr_2O_3$ system into subsidiary subsystems (Fig. 1b.) The figure implies that the $MgV_2O_6–MgCr_2O_4$ system is not the real binary one. In the samples containing up to 50.00% mol MgV_2O_6, $Mg_2V_2O_7$, Cr_2O_3 and $MgCr_2O_4$ coexist at equilibrium, while within the concentration range from 50.00 up to 75.00% mol MgV_2O_6 the products of $Mg_2CrV_3O_{11}$, $Mg_2V_2O_7$ and Cr_2O_3 reactions coexist at equilibrium, whereas above 75.00% mol MgV_2O_6: $MgCrV_3O_{11}$ and

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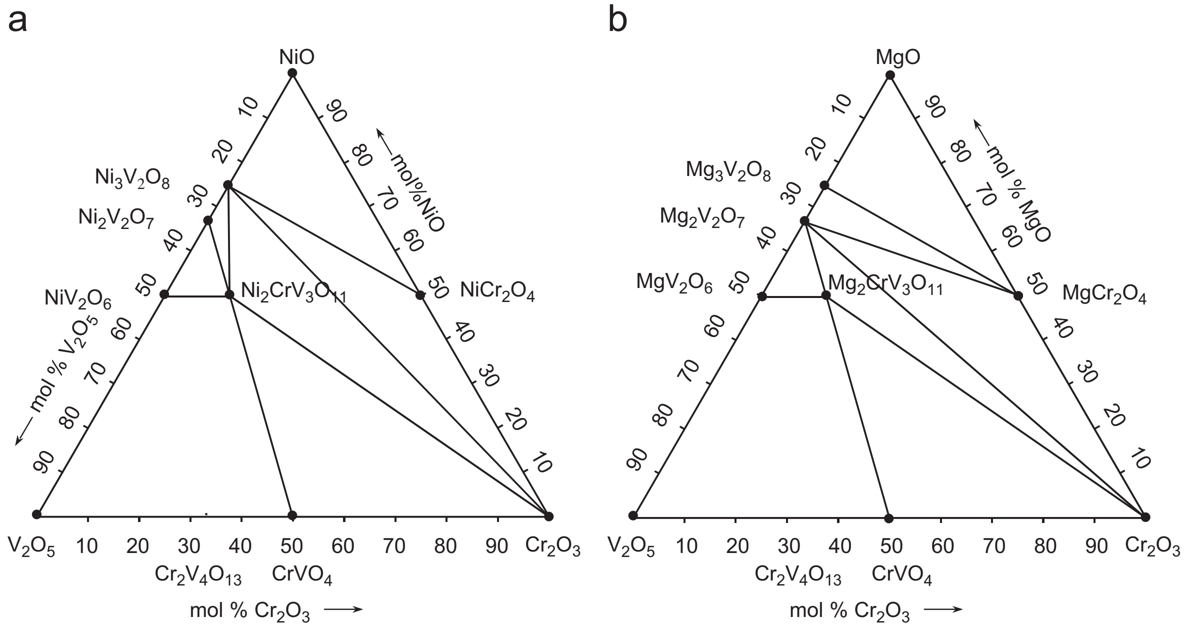

Fig. 1. Preliminary division of the investigated ternary systems into subsidiary subsystems: a— $NiO–V_2O_5–Cr_2O_3$, b—$MgO–V_2O_5–Cr_2O_3$.

MgV_2O_6 [3]. However, the $Mg_2V_2O_7$–$CrVO_4$ is the real binary system where the $Mg_2CrV_3O_{11}$ compound is formed [3]. Also, the $Mg_3V_2O_8$–$MgCr_2O_4$ system is binary, in which the components do not react with one another [4].

The aim of this work was to complete the phase relations determined so far, settling to the solidus line in two ternary systems: $MO–Cr_2O_3–V_2O_5$, where M = Ni, Mg all over their components concentration range. On the basis of this data, a division of these two systems into subsidiary subsystems was carried out. Another objective was to obtain samples, at equilibrium, of the compositions belonging to particular subsidiary subsystems and binary intersections of the investigated ternary systems, and next determining the melting temperatures of both the subsidiary subsystems and the binary intersections.

2. Experimental

The following compounds were used in the investigations:

- V_2O_5, analytically pure, Riedel-de Haën, Germany—manufacturer;
- Cr_2O_3, analytically pure, Aldrich, Germany—manufacturer;
- $2NiCO_3 \cdot 3Ni(OH)_2 \cdot H_2O$, analytically pure, POCh Gliwice; Poland—manufacturer;
- $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$, analytically pure, POCh Gliwice, Poland—manufacturer.

Also, MV_2O_6, $M_2V_2O_7$, $M_3V_2O_8$, MCr_2O_4, where M = Ni, Mg as well as $CrVO_4$ and $Cr_2V_4O_{13}$ were used as reacting substances in the conducted studies. The syntheses of the mentioned compounds have been related in works [3,5–8].

Adequate weighed amount of substrates were homogenized by grinding, forming into pellets and heating in air atmosphere in several stages, until the state of equilibrium was obtained. After each heating stage, the samples were homogenized and examined by the X-ray diffraction (XRD) method and later formed into pellets and heated once again. The conditions of heating particular samples, depending on the composition of the initial mixtures, differed by both the heating temperature and the time of heating at a given temperature.

After the final heating stage, all samples and the furnace were slowly cooled down to ambient temperature. Next, they were ground and tests were applied by means of the DTA and XRD methods. The samples were then pelletized again and further heated at the temperature of the last stage of the synthesis within 24 h. Later, they were rapidly cooled down to room temperature and, after grinding, were DTA tested. Their composition was determined with the XRD method. This procedure allowed the establishment of types of phases being generated in the investigated system and also the ranges of their coexistence in the concentration solid state.

The DTA tests were carried out with the help of the F. Paulik—L. Paulik—L. Erdey derivatograph (MOM, Budapest). The samples weighing 1000 mg each were placed in quartz crucibles. All measurements were run in air atmosphere, in the temperature range 293–1273 K, at the samples' heating rate 10 K/min. Some chosen samples were examined by DTA method using an instrument of METLER TOLEDO TGA/SDTA 851. Samples of 5 mg each, measured by DTA method in air, in the temperature range 1173–1673 K, were placed in platinum crucibles and heated at a rate of 10 K/min.

The phases occurring in the samples were identified on the basis of the results of the XRD investigations (DRON—3 diffractometer, CoKα radiation Fe filter), and the information included in the PDF cards [9] and works [3,5]. When a diffraction pattern was being worked on, a package of computer programs DHN/PDS (Program Packing for Powder Diffraction) was used.

3. Results and discussion

3.1. The NiO–Cr_2O_3–V_2O_5 system

In order to carry out the studies, 22 samples of compositions exhibited in Table 1 were prepared. Table 1 demonstrates the heating conditions of particular samples and the phases detected in the equilibrium state as well. The information obtained by means of the XRD method, concerning the samples with compositions lying within the area of a polygon characterized by the $CrVO_4$, $Cr_2V_4O_{13}$, V_2O_5, NiV_2O_6 and $Ni_2CrV_3O_{11}$ compounds (samples 1–5), implies that reaction:

$$2CrVO_{4(s)} + V_2O_{5(s)} = Cr_2V_4O_{13(s)} \quad (1)$$

does not occur, while other components of the examined polygon react with one another according to the following reaction:

$$V_2O_{5(s)} + Ni_2CrV_3O_{11(s)} = CrVO_{4(s)} + 2NiV_2O_{6(s)}. \quad (2)$$

The results of these studies allowed to determine the division of the polygon into two subsidiary subsystems, NiV_2O_6–$NiCrV_3O_{11}$–$CrVO_4$ and NiV_2O_6–$CrVO_4$–V_2O_5, and finally state that, in the solidus area of the investigated

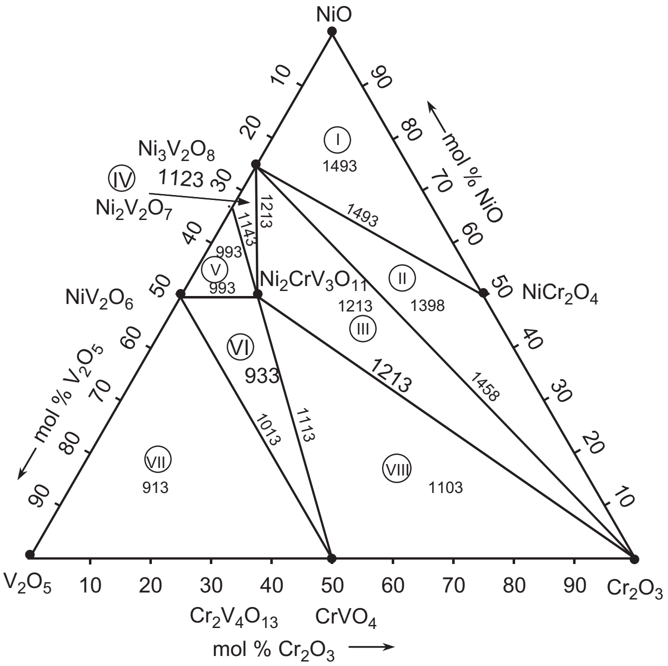

Fig. 2. The division of concentration components triangle of the NiO–V_2O_3–Cr_2O_3 system into subsidiary subsystems and the melting temperatures (K) of the subsidiary subsystems and binary systems.

Table 1
The composition of initial mixtures per system's components, heating stages and phases detected in the samples in the state of equilibrium in binary and ternary systems belonging to the NiO–Cr_2O_3–V_2O_5 system

Sample no	Mixtures' composition per system's components [mol%]			Heating conditions (K × 24 h)	Phases detected in the state of equilibrium
	NiO	V_2O_5	Cr_2O_3		
1	85.00	10.00	5.00	863→923→973	$CrVO_4$, NiV_2O_6, $Ni_2CrV_3O_{11}$
2	60.00	15.00	25.00	863→923→943	
3	40.00	55.00	5.00	863→923→943→993	NiV_2O_6, $CrVO_4$, V_2O_5
4	10.00	80.00	10.00	863→(×)	
5	37.00	54.00	9.00	989 (× 4)	NiV_2O_6, $CrVO_4$, V_2O_5
6	60.00	35.00	5.00	973	$Ni_2V_2O_7$, $Ni_2CrV_3O_{11}$
7	45.00	35.00	20.00	973→1073	$Ni_2CrV_3O_{11}$, Cr_2O_3
8	30.00	27.00	43.00		$Ni_2CrV_3O_{11}$, $CrVO_4$
9	65.00	15.00	20.00	973→1073→1093	$Ni_3V_2O_8$, $NiCr_2O_4$
10	53.00	17.00	30.00	973→1073	$Ni_3V_2O_8$, Cr_2O_3
11	28.00	22.00	50.00	973	$Ni_2CrV_3O_{11}$, Cr_2O_3
12	60.00	20.00	20.00	973→1073	$Ni_3V_2O_8$, Cr_2O_3
13	85.00	10.00	5.00	863→923→1073→1123→1223	NiO, $Ni_3V_2O_8$, $NiCr_2O_4$
14	70.00	10.00	20.00		
15	60.00	15.00	25.00	863→923→943→1123	$Ni_3V_2O_8$, $NiCr_2O_4$, Cr_2O_3
16	35.00	20.00	45.00	863→923→943→1073→1093	$Ni_3V_2O_8$, $Ni_2CrV_3O_{11}$, Cr_2O_3
17	15.00	10.00	75.00		
18	33.00	33.00	34.00	863→923→973→943	$Ni_2CrV_3O_{11}$, Cr_2O_3, $CrVO_4$
19	15.00	30.00	55.00		
20	55.00	40.00	5.00	863→923→943→993	$Ni_2V_2O_7$, $Ni_2CrV_3O_{11}$, NiV_2O_6
21	60.00	30.00	10.00	973→1073→1093	$Ni_2CrV_3O_{11}$, Cr_2O_3, $Ni_3V_2O_8$
22	25.00	42.00	33.00		$Ni_2CrV_3O_{11}$, Cr_2O_3, $CrVO_4$

$NiO–Cr_2O_3–V_2O_5$ system, eight subsidiary subsystems, where three solid phases coexist, can be distinguished (Fig. 2).

Area I	$NiO–NiCr_2O_4–Ni_3V_2O_8$
Area II	$NiCr_2O_4–Cr_2O_3–Ni_3V_2O_8$
Area III	$Cr_2O_3–Ni_2CrV_3O_{11}–Ni_3V_2O_8$
Area IV	$Ni_2CrV_3O_{11}–Ni_2V_2O_7–Ni_3V_2O_8$
Area V	$Ni_2CrV_3O_{11}–NiV_2O_6–Ni_2V_2O_7$
Area VI	$NiV_2O_6–CrVO_4–Ni_2CrV_3O_{11}$
Area VII	$NiV_2O_6–V_2O_5–CrVO_4$
Area VIII	$Ni_2CrV_3O_{11}–CrVO_4–Cr_2O_3$

3.2. The $MgO–Cr_2O_3–V_2O_5$ system

Fourteen samples of the compositions presented in Table 2 were prepared. Table 2 also has the heating conditions of particular samples and the phases detected in the equilibrium state. In order to determine the phase relations establishing in the quadrilateral described by the V_2O_5, MgV_2O_6, $Mg_2CrV_3O_{11}$ and $CrVO_4$ phases, it was necessary to investigate the mutual reactivity of $Mg_2CrV_3O_{11}$ towards V_2O_5 and $Mg_2CrV_3O_{11}$ towards $Cr_2V_4O_{13}$. Thus, two samples 1 and 2 were subjected to the reactivity investigations (Table 2). After obtaining the samples in the equilibrium state, it was concluded that substrates of sample 1 responded completely, according to equation:

$$Mg_2CrV_3O_{11(s)} + V_2O_{5(s)} = 2\ MgV_2O_6 + CrVO_{4(s)}, \tag{3}$$

whereas sample 2 responded in accordance with equation:

$$2Mg_2CrV_3O_{11(s)} + 3V_2O_{5(s)} = 4MgV_2O_{6(s)} + Cr_2V_4O_{13(s)}. \tag{4}$$

It can be concluded that the quadrilateral described by the $V_2O_5–MgV_2O_6–CrVO_4$ $Cr_2V_4O_{13}$ compounds can be divided into two subsidiary subsystems: $V_2O_5–MgV_2O_6–Cr_2V_4O_{13}$ and $Cr_2V_4O_{13}–MgV_2O_6–CrVO_4$.

The investigations conducted resulted in isolating, in the ternary $MgO–Cr_2O_3–V_2O_5$ system, nine subsidiary subsystems, where in the equilibrium state there coexist three solid phases. These are the following subsidiary subsystems:

Area I	$MgO–MgCr_2O_4–Mg_3V_2O_8$
Area II	$Mg_3V_2O_8–MgCr_2O_4–Mg_2V_2O_7$
Area III	$Mg_2V_2O_7–MgCr_2O_4–Cr_2O_3$
Area IV	$Mg_2V_2O_7–Cr_2O_3–Mg_2CrV_3O_{11}$
Area V	$Mg_2CrV_3O_{11}–Cr_2O_3–CrVO_4$

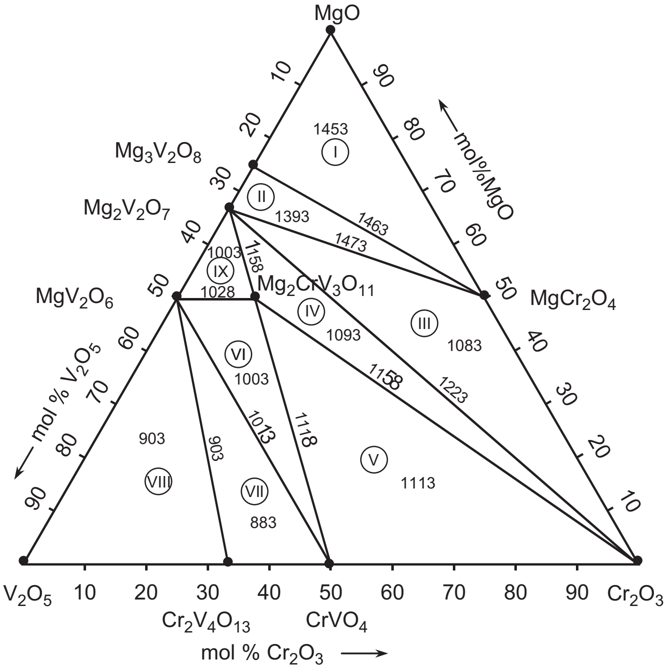

Fig. 3. The division of concentration components triangle of the $MgO–V_2O_5–Cr_2O_3$ system into subsidiary systems and the melting temperatures (K) of subsidiary and binary systems.

Table 2
The composition of initial mixtures per system's components, the heating stages and the phases detected in the samples in the state of equilibrium in binary and ternary systems belonging to the $MgO–Cr_2O_3–V_2O_5$ system

Sample no	Mixtures' composition per system's components [mol%]			Heating conditions (K × 24 h)	Phases detected in the state of equilibrium
	MgO	V_2O_5	Cr_2O_3		
1	40.00	50.00	10.00	823→853→873	MgV_2O_6, $CrVO_4$
2	28.57	50.00	21.43	868→893→903	
3	36.36	54.54	9.09	868→868→893	MgV_2O_6, $Cr_2V_4O_{13}$
4	66.66	16.67	16.67	923→973→1023→1073	$Mg_3V_2O_8$, $MgCr_2O_4$
5	60.00	20.00	20.00		$Mg_2V_2O_7$, $MgCr_2O_4$
6	50.00	25.00	25.00		$Mg_2V_2O_7$, Cr_2O_3
7	40.00	30.00	30.00		$Mg_2CrV_3O_{11}$, Cr_2O_3
8	80.00	10.00	10.00		MgO, $Mg_3V_2O_8$, $MgCr_2O_4$
9	65.00	20.00	15.00		$Mg_3V_2O_8$, $MgCr_2O_4$, $Mg_2V_2O_7$
10	55.00	40.00	5.00	923→973→1023	$Mg_2V_2O_7$, $Mg_2CrV_3O_{11}$, MgV_2O_6
11	40.00	45.00	15.00		MgV_2O_6, $Mg_2CrV_3O_{11}$, $CrVO_4$
12	20.00	65.00	15.00	823→853→873→883	V_2O_5, MgV_2O_6, $Cr_2V_4O_{13}$
13	25.00	55.00	20.00		MgV_2O_6, $CrVO_4$, $Cr_2V_4O_{13}$
14	20.00	30.00	50.00	823→873→923→948	$Mg_2CrV_3O_{11}$, Cr_2O_3, $CrVO_4$

Area VI	$Mg_2CrV_3O_{11}$–$CrVO_4$–MgV_2O_6
Area VII	MgV_2O_6–$CrVO_4$–$Cr_2V_4O_{11}$
Area VIII	MgV_2O_6–$Cr_2V_4O_{13}$–V_2O_5
Area IX	MgV_2O_6–$Mg_2V_2O_7$–$CrVO_4$

In order to determine the melting temperatures of particular subsidiary subsystems in the ternary MO–Cr_2O_3–V_2O_5 systems, where $M = Ni$, Mg, the melting temperatures of all samples prepared for particular systems of the compositions demonstrated in Tables 1 and 2, were determined. The melting temperatures of phases, being at equilibrium in a given binary or ternary system, were marked out on the basis of the onset temperatures of first endothermic effects, not being the temperatures of polymorphous transformations, recorded on the DTA curves. The conducted measurements, completed with the results of the tests run earlier, facilitated working out complete phase diagrams of the NiO–Cr_2O_3–V_2O_5 systems and MgO–Cr_2O_3–V_2O_5 in the solidus area (Figs. 2 and 3).

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