

## Phase Transformations and Thermodynamics in the System $\text{Fe}_2\text{O}_3$ – $\text{V}_2\text{O}_5$ – $\text{MnO}$ – $\text{SiO}_2$ of Non-Isothermal Heating

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### ABSTRACT

Thermodynamic characteristics in the system  $\text{Fe}_2\text{O}_3$  –  $\text{MnO}$  –  $\text{V}_2\text{O}_5$  –  $\text{SiO}_2$  have been investigated. Two mixtures have been prepared. The first mixture was synthetic, prepared from pure oxides in proportion according to the chemical composition of the waste catalyst and manganese concentrate. The second one contained the waste vanadium catalyst and manganese concentrate. The synthetic mixture has been used as a standard in order to establish the influence of impurities in the concentrate, and the waste catalyst on the thermodynamics of the studied system.

Experiments carried out in the temperature up to 1473 K for the system containing waste vanadium catalyst and manganese concentrate occur to formation of new phases formation as  $\text{FeV}_2\text{O}_4$  and Iron Vanadium Oxide type and Jacobsite types  $\text{MnFe}_2\text{O}_4$  and  $(\text{Mn}_6\text{Fe}_4)(\text{Mn}_4\text{Fe}_{1.6})\text{O}_4$ . EMF method with difference reference electrode ( $\text{Ni}/\text{NiO}$ ,  $\text{Mo}/\text{MoO}_2$  and air) relationship of  $\Delta G^\circ = f(T)$  in the temperature range 1073 – 1173 K of mixtures was obtained. The experimental data for the system show that the reference electrodes air and  $\text{Ni}/\text{NiO}$  are more suitable than  $\text{Mo}/\text{MoO}_2$ .

The obtained results will be used as an investigations base to the production of complex iron vanadium manganese alloy using the waste materials.

**Keywords** – thermodynamics, DTA, EMF method, vanadium catalyst, manganese concentrate.

### I. INTRODUCTION

From a metallurgical point of view, the study of binary and ternary systems has great practical significance even for ferroalloy production to obtain alloys. Complex alloys are becoming more and more widely used in metallurgy for deoxidation, alloying, modifying and desulfurization; they also improve the mechanical, physical and chemical properties of steel and iron. It is more effective to obtain elements as a complex ferroalloy than as separate elements.

In the present studies, the waste vanadium catalyst was used. Annually, between 500 and 1000 tons vanadium catalyst are released from sulphuric acid production which contains a significant quantity of deficit vanadium. The toxicity of the vanadium causes certain environmental problems which is an additional consideration to look for ways to utilize this valuable waste product.

The complex systems are used in various fields of Chemistry and Metallurgy. Ternary systems of the type  $\text{MeO}-\text{V}_2\text{O}_5-\text{Fe}_2\text{O}_3$  are used as catalysts because vanadates, which are formed, as a result, catalyze the oxidation processes of many compounds [1]. The similar systems is also used in the electrode materials preparation, and glasses with relatively

high electrical conductivity and high thermal stability or for correction of the phase diagram. [1, 2, 3, 4, 5, 6, 7, 8].

Other studies have focused on the structure of complex compounds produced by the solid-phase method -  $\text{Co}_4\text{Fe}_{3.33}(\text{VO}_4)_6$  [9],  $\text{Mn}_3\text{Fe}_4(\text{VO}_4)_6$  [9, 11] and  $\text{Zn}_3\text{Fe}_4\text{V}_6\text{O}_{24}$  [10]. The equilibrium in the system  $\text{V}_2\text{O}_5-\text{Fe}_2\text{O}_3-\text{Mn}_2\text{O}_3$  ( $\text{MnO}$ ) was examined by some authors [12]. They found out the formation of the solid solution of the type  $\text{Fe}_2\text{Mn}_2\text{V}_4\text{O}_{15}$  based on manganese pyrovanadat. DTA and XRD analyses were used in the investigation of all these systems.

In the binary system  $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ , containing manganese oxides, the heat capacity for different values of “x” was determined as well as the entropy changes [13]. The phase equilibrium of the Mn-Fe-O system ( $\text{Fe} / \text{Mn} = 2$ ) and the partial pressure of oxygen of  $10^{-1}$  Pa to  $10^5$  Pa were examined in the temperature range from 1223 to 1393 K, by measuring the electrical conductivity and the mass of the sample [14]. The enthalpy and Gibbs free energy of  $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$  at 298 K were defined calorimetrically [15].

Some other authors analyzed the thermodynamics of the processes in the ternary

system  $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5\text{-MnO}$  using data for the binary systems respectively or some known thermodynamic parameters.

To determine the oxidation potential of the system  $\text{Fe} + \text{FeV}_2\text{O}_4\text{-V}_2\text{O}_5$ , K.T. Jacob and C.B. Alcock [16] used the EMF method. The same method was used to determine the thermodynamic data for  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$  [17, 18]. A.N. Grundy et al. [19] studied the thermodynamics and the phase diagram of system  $\text{Mn-O}$ , using CALPHAD method. A. Petric and K.T. Jacob determined the activity of  $\text{Fe}_3\text{O}_4$  in the solid solution  $\text{Fe}_3\text{O}_4\text{-FeV}_2\text{O}_4$  [20]. In this paper [21] the authors analyzed in detail the reactions occurring in the system  $\text{FeO-V}_2\text{O}_5$  and their Gibbs energy respectively.

The standard Gibbs energy of spinel phase  $\text{MnV}_2\text{O}_4$  formation in the temperature range 1200-1600°C was calculated using the equation of mixtures in the liquid iron or liquid copper and the known thermodynamic parameters [22, 23].

The purpose of these investigations is to describe the phase changes that occur in the non-isothermal heating synthetic ternary system ( $\text{Fe}_2\text{O}_3\text{-MnO-V}_2\text{O}_5$ ), and ternary system containing waste vanadium catalyst, manganese concentrate, and  $\text{Fe}_2\text{O}_3$ . The thermodynamic characteristics of this system will be used as a basis for the production of complex alloy with the participation of waste material.

## II. EXPERIMENTAL AND DISCUSSION

### 2.1. Materials and Apparatus

The chemical composition (mass %) of manganese concentrate is shown in Table 1.

Table 1 Chemical composition of manganese concentrate, %.

MnO	FeS2	$\text{Fe}_2\text{O}_3$	$\text{P}_2\text{O}_5$	$\text{SiO}_2$	MgO	CaO	$\text{Al}_2\text{O}_3$
44,56	2,25	1,79	0,31	12,4	2,00	3,90	2,10

The chemical composition (mass %) of waste vanadium catalyst is shown in Table 2.

Table 2 Chemical composition of waste vanadium catalyst, %.

$\text{V}_2\text{O}_5$	$\text{Fe}_2\text{O}_3$	$\text{SiO}_2$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{Al}_2\text{O}_3$	$\text{SO}_3$
4,12	3,4	57,12	6,71	3,93	0,82	23,88

Experiments were carried out using manganese concentrate, waste vanadium catalyst and chemically pure oxides  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$  ( $\text{MnO}_2$ ),  $\text{V}_2\text{O}_5$ ,  $\text{SiO}_2$ .

The synthetic Mix 1 is composed of pure oxides. The quantitative ratio between oxides is calculated so as to be correlated with Mix 2 containing manganese concentrate and the waste vanadium catalyst. In this mixture are given only oxides, which could influence the process of the complex alloy obtaining.

Mix 1 – pure oxides -  $\text{V}_2\text{O}_5$  -  $\text{MnO}$  -  $\text{Fe}_2\text{O}_3$  –  $\text{SiO}_2$ .

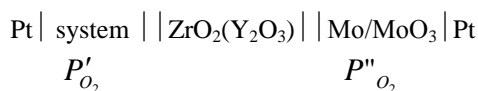
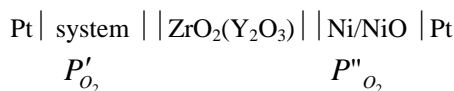
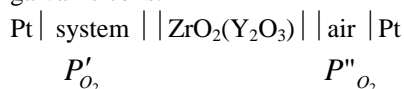
Mix 2 – waste vanadium catalyst, manganese concentrate, and  $\text{Fe}_2\text{O}_3$ .

The composition of the mixtures is as follows: 2,5%  $\text{V}_2\text{O}_5$ ; 22,5 %  $\text{MnO}$ ; 35 %  $\text{SiO}_2$  and 40 %  $\text{Fe}_2\text{O}_3$ .

The mixtures were investigated by DTA method within the temperature range 293 K – 1473 K using thermogravimetric apparatus STA PT1600.

The thermodynamics of mixtures were also studied by EMF method using galvanic cells with a solid electrolyte  $\text{ZrO}_2$  ( $\text{Y}_2\text{O}_3$ ) and reference electrodes  $\text{Ni/NiO}$ , air, and  $\text{Mo/MoO}_2$

The equilibrium of oxides in the system  $\text{Fe}_2\text{O}_3$  -  $\text{MnO}$  -  $\text{V}_2\text{O}_5$ -  $\text{SiO}_2$  was studied with the following galvanic cells:



$P''_{\text{O}_2} = 0,2095 \text{ atm}$ ;  $\lg P''_{\text{O}_2} = -0,6788$  for the air electrode.

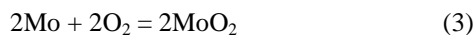
The  $\Delta G^\circ_{\text{T}}(\text{NiO})$  values reported by some other authors [24 - 26] were used in this paper.



$$\Delta G^\circ(\text{NiO}) = -233651 + 84.893 T, \text{ J / mol}$$

$$\lg P_{\text{O}_2} = \frac{-12225}{T} + 4,44 \qquad (2)$$

The  $\Delta G^\circ_{\text{T}}(\text{MoO}_2)$  values reported by some other authors [27, 28] were also used in this paper.



$$\Delta G^\circ(\text{MoO}_2) = -570563 + 173.T$$

$$\lg P_{O_2} = \frac{-29852}{T} + 9,051 \quad (4)$$

## 2.2. DTA Results

The derivatogram of Mix 1 (pure oxides  $\text{Fe}_2\text{O}_3$ - $\text{MnO}_2$ - $\text{V}_2\text{O}_5$ - $\text{SiO}_2$ ) is presented in Fig.1. The DTA curve shows two low-temperature endothermic effects. The first one ( $T \sim 107^\circ\text{C}$ ) corresponds to the evaporation of physical moisture and the second one ( $T \sim 348^\circ\text{C}$ ) – to partial dissociation of  $\text{MnO}_2$  to  $\text{Mn}_2\text{O}_3$ . In the temperature range from  $T \sim 582^\circ\text{C}$  to  $T \sim 667^\circ\text{C}$  solid solution between  $\text{Fe}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$  from a peritectic type was formed. The peritectic solution decomposes at about  $930^\circ\text{C}$ . A solid solution between  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  is formed which can be confirmed by the phase diagram ( $\text{Fe}_2\text{O}_3$  -  $\text{Mn}_2\text{O}_3$ ) [30]. The X-ray analysis (Fig.2) shows that in the end product the following phases were found: cubic  $\text{Mn}_2\text{O}_3$ , rhombic Hematite  $\text{Fe}_2\text{O}_3$ , tetragonal Hausmannite ( $\text{Mn}_3\text{O}_4$ ) as well, tetragonal  $\alpha$ -Cristoballite ( $\text{SiO}_2$ ).

Derivatogram of Mix 2 (waste vanadium catalyst, Mn-concentrate, and  $\text{Fe}_2\text{O}_3$ ) is presented in Fig.3. The DTA curve shows one intensive endothermic effect and three less intensive endothermic effects. One of them at about  $T \sim 715^\circ\text{C}$

corresponds to  $\text{FeV}_2\text{O}_4$  or  $\text{FeV}_2\text{O}_6$  formation. In this sample, the formation of these ferrovanadates is possible at low temperature and even at low vanadium oxide concentration in the system Fe-V-O these compositions could be formed [29]. In waste vanadium catalyst (as opposed to pure  $\text{V}_2\text{O}_5$  in mix 1), vanadium oxides are in the form of  $\text{V}_x\text{O}_y$  ( $\text{V}_2\text{O}_3$ ,  $\text{VO}$ ,  $\text{V}_2\text{O}_4$ ,  $\text{V}_6\text{O}_{13}$ ) and formation of these vanadates is possible by reason of its repeated thermal transformations. X-ray analysis confirms the fact (Fig.4), that except for rhombic Hematite ( $\text{Fe}_2\text{O}_3$ ), tetragonal Cristalloballite ( $\text{SiO}_2$ ), cubic Bixbyite ( $\text{Mn}_2\text{O}_3$ ), tetragonal Hausmannite ( $\text{Mn}_3\text{O}_4$ ), Coulsonite  $\text{Fe}_2\text{VO}_4$  ( $\text{Fe}_2\text{O}_3$ . $\text{VO}$ ) is also present. In the temperature range from  $T \sim 575^\circ\text{C}$  to  $T \sim 680^\circ\text{C}$  solid solution is formed between  $\text{Fe}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$  from a peritectic type that decomposes at about  $930^\circ\text{C}$  to solid solution between  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$ , which can be confirmed by the phase diagram ( $\text{Fe}_2\text{O}_3$  -  $\text{Mn}_2\text{O}_3$ )[30].

The melting phase in Mix 2 was registered upon heating up to  $1200^\circ\text{C}$ . The X-ray analysis (Fig.5.) of the obtained product from Mix 2 treated at this temperature, showed mainly presence of Jacobsite ( $\text{Mn}_6\text{Fe}_4(\text{Mn}_4\text{Fe}_{1.6})\text{O}_4$ , as well as vanadium oxide ( $\text{V}_3\text{O}_4$ ), Coulsonite  $\text{Fe}_2\text{VO}_4$  ( $\text{Fe}_2\text{O}_3$ . $\text{VO}$ ), Hematite and  $\alpha$ -Quartz.

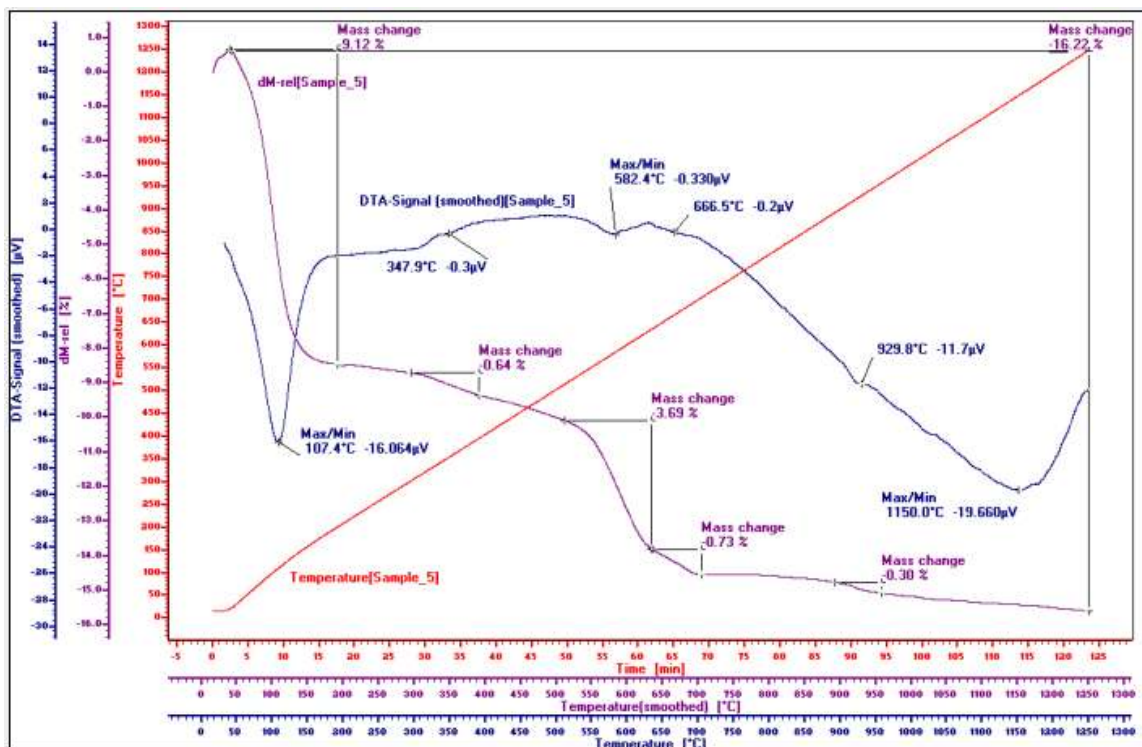


Fig.1. Derivatogram of Mix 1 (pure oxides  $\text{Fe}_2\text{O}_3$  -  $\text{MnO}_2$ - $\text{V}_2\text{O}_5$  –  $\text{SiO}_2$ )

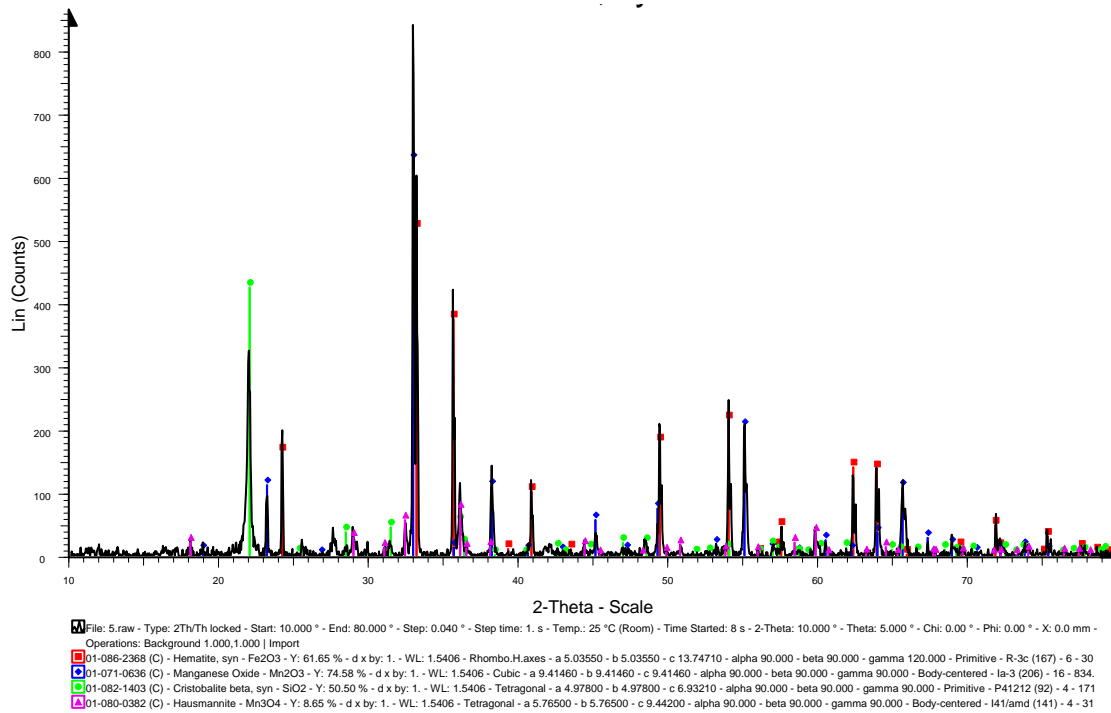


Fig.2. X- ray analysis of obtained product of Mix 1 (heated up to T= 1198K).

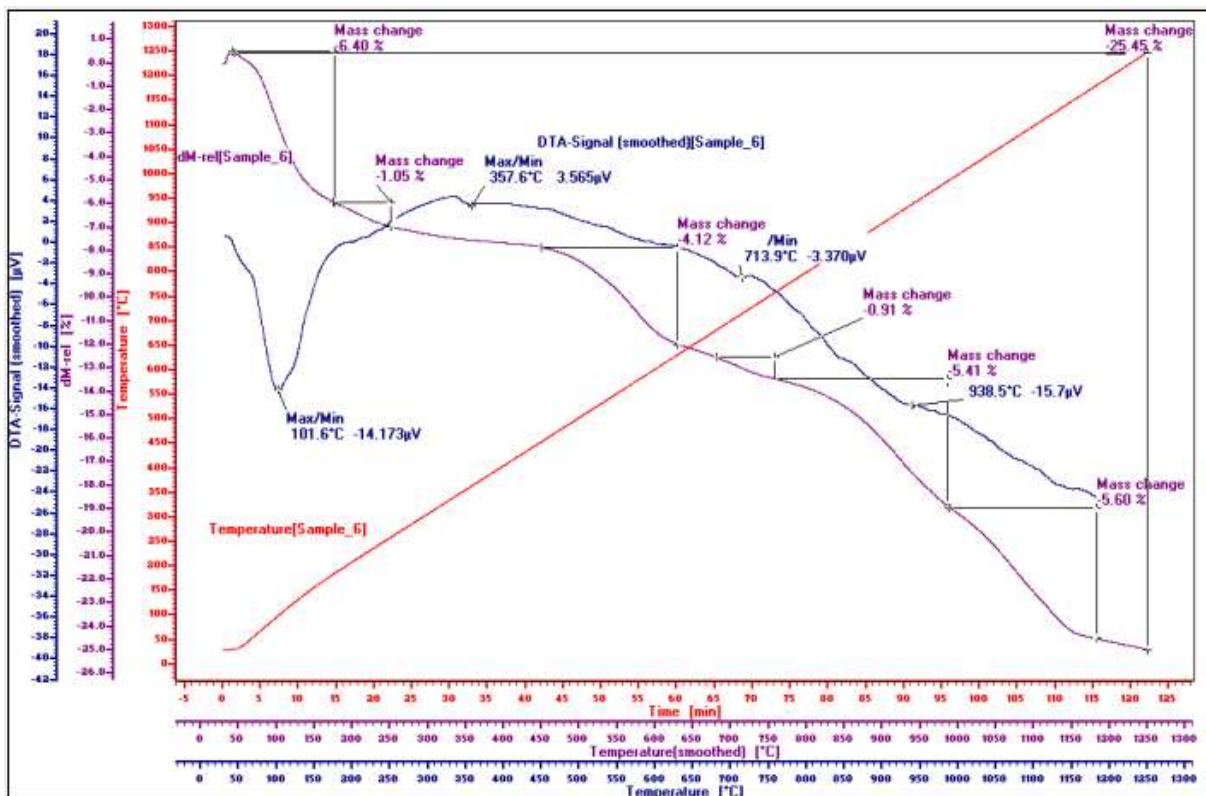


Fig.3. Derivatogram of Mix 2 (Fe<sub>2</sub>O<sub>3</sub>, waste vanadium catalyst and manganese concentrate).

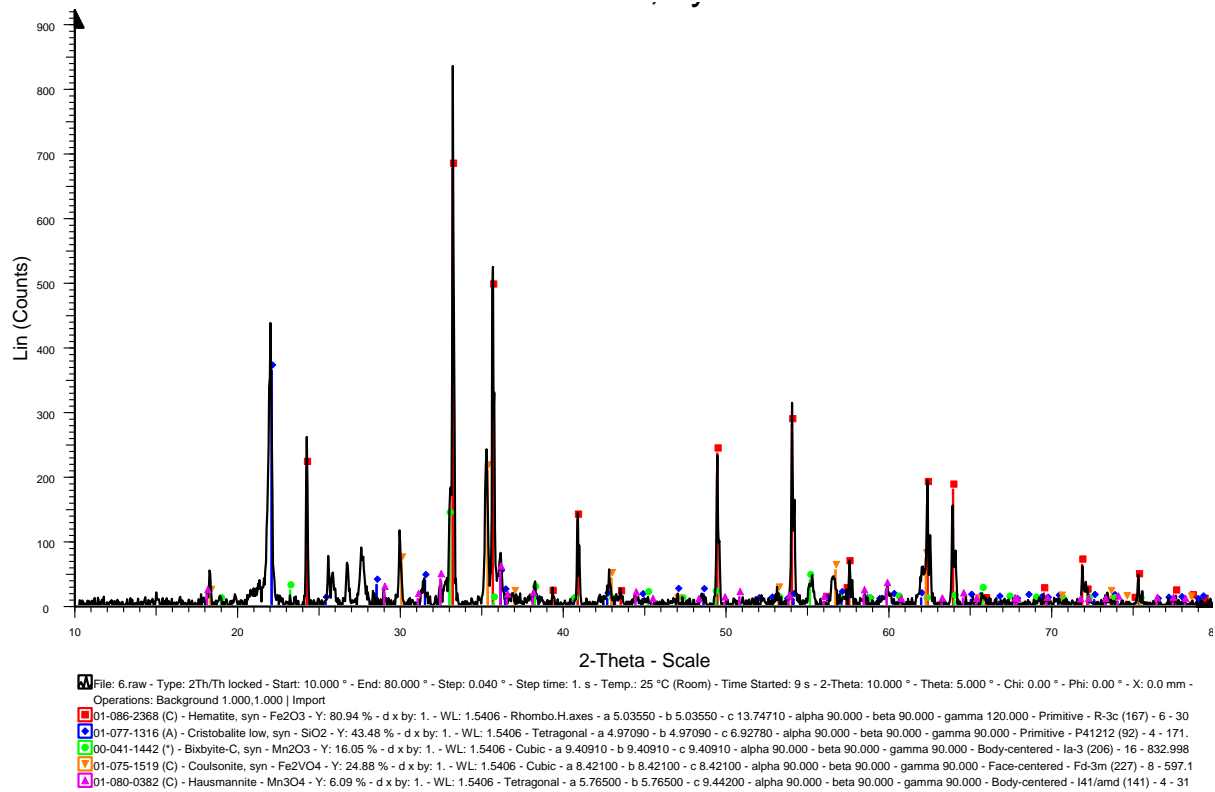


Fig.4. X- ray analysis of the obtained product of Mix 2 (heated up to T= 1183K).

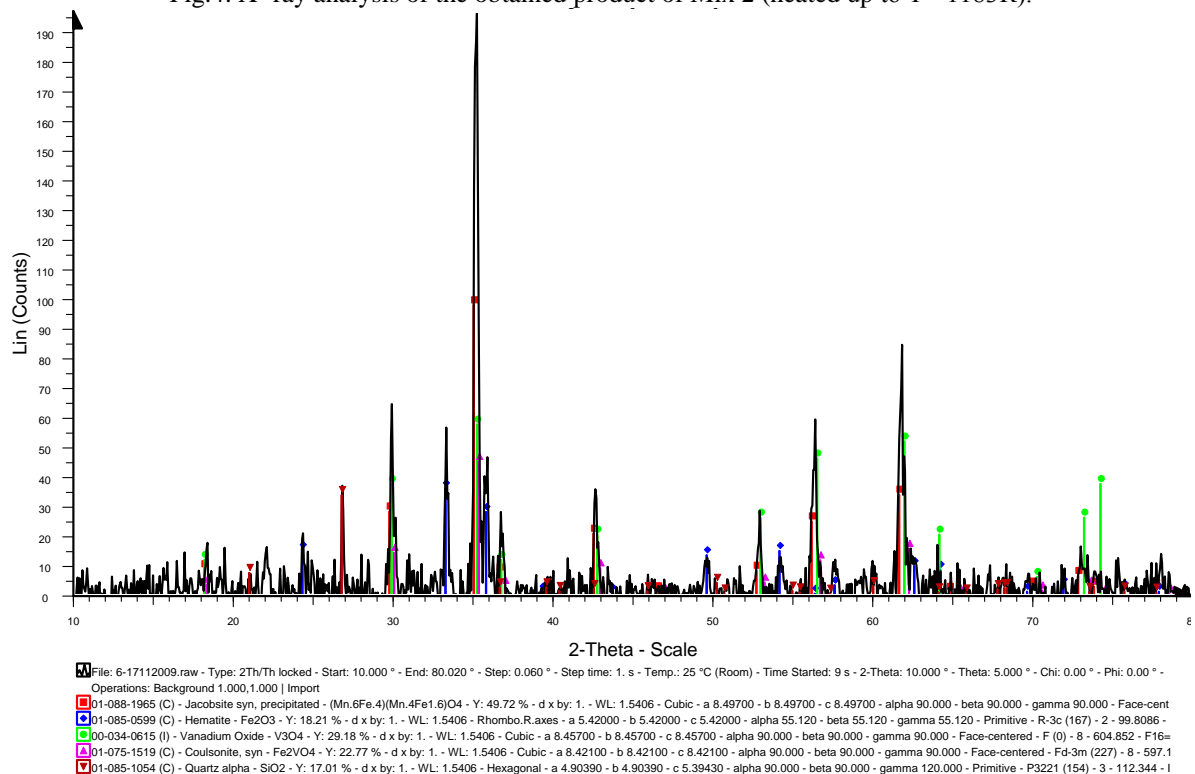


Fig.5. X- ray analysis of obtained product of Mix 2 (heated up to T= 1498K).

### 2.3. EMF results

Partial pressure of the oxygen in the mixtures was calculated by the following equations:

For air reference electrode

$$\lg P'_{O_2} = -\frac{E.20193}{T} - 0.6788 \quad (5)$$

For reference electrode Ni/NiO

$$\lg P'_{O_2} = -\frac{E.20193}{T} - \frac{12225}{T} + 4.44 \quad (6)$$

For reference electrode Mo/MoO<sub>2</sub>

$$\lg P'_{O_2} = -\frac{E.20193}{T} - \frac{29852}{T} + 9.051 \quad (7)$$

The obtained results of the EMF experimental data is shown in Table 3. The values are an average result of six measurements.

In the studied system Fe<sub>2</sub>O<sub>3</sub>-MnO-V<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub>, a number of reactions could take place. Equations ΔG = f (T) were deduced for the main reactions, using

thermodynamic data for H<sup>o</sup>, S<sup>o</sup> and C<sub>p</sub> obtained by some authors [23, 24]. The calculated results for these reactions and the reported ones by some other authors were compared with our results obtained experimentally. The dependences of ΔG = f (T) for the investigated mixtures in air, Ni/NiO and Mo/MoO<sub>2</sub> as reference electrode are shown in Fig. 6, 7 and 8.

The proposed reactions (shown in Table 4), were accorded with the results of X-ray analysis (Figure 2.4, 5) of the obtained products of both tested mixtures.

Table 3. EMF experimental data of both mixtures

Mix 1								
air			Ni/NiO			Mo/MoO <sub>3</sub>		
T, K	E, V	lg P'' <sub>O<sub>2</sub></sub>	T, K	E, V	lg P'' <sub>O<sub>2</sub></sub>	T, K	E, V	lg P'' <sub>O<sub>2</sub></sub>
1093	0.588	- 25.64	1113	0.376	- 22.22	1093	0.463	- 37.92
1123	0.546	- 23.24	1123	0.373	- 21.86	1123	0.444	- 35.88
1133	0,497	- 21.03	1133	0.370	- 21.50	1133	0.437	- 35.19
1143	0,488	- 20.49	1143	0.363	- 20.99	1143	0.436	- 34.77
1153	0,482	- 20.08	1153	0.362	- 20.73	1153	0.435	- 34.35
1163	0,478	- 19.75	1163	0.360	- 20.43	1163	0.436	- 34.01
1173	0,472	- 19.35						
Mix 2								
air			Ni/NiO			Mo/MoO <sub>3</sub>		
T, K	E, V	lg P'' <sub>O<sub>2</sub></sub>	T, K	E, V	lg P'' <sub>O<sub>2</sub></sub>	T, K	E, V	lg P'' <sub>O<sub>2</sub></sub>
1083	0.564	- 24.84	1123	0.406	- 23.22	1093	0.494	- 39.23
1093	0.548	- 23.94	1133	0.390	- 22.32	1103	0.424	- 35.85
1103	0,526	- 22.81	1143	0.359	- 20.83	1123	0.390	- 33.65
1113	0,520	- 22.36	1153	0.328	- 19.36	1133	0.359	- 32.00
1123	0,518	- 22.08	1163	0.320	- 18.84	1143	0.356	- 31.52
1133	0,498	- 21.07	1173	0.314	- 18.40	1163	0.354	- 30.74
1143	0,470	- 19.76						
1153	0.462	- 19.27						

The deduced dependences ΔG = f (T) based on experimental data are as follows:

#### Mix 1

- for air reference electrode  $\Delta G_{\text{exp.}} = -864\,166 + 580,74.T, \text{ J.mol}^{-1}$  ( $R^2 = 0,8922$ ),
- for Ni/NiO reference electrode  $\Delta G_{\text{exp.}} = -393\,685 + 169,11.T, \text{ J.mol}^{-1}$  ( $R^2 = 0,9722$ )
- for Mo/MoO<sub>2</sub> reference electrode  $\Delta G_{\text{exp.}} = -594\,159 + 230,08.T, \text{ J.mol}^{-1}$  ( $R^2 = 0,9215$ ).

**Mix 2**

- for air reference electrode  $\Delta G_{exp.} = -808\,621 + 540,62.T, \text{ J.mol}^{-1}$  ( $R^2 = 0,9633$ )
  - for Ni/NiO reference electrode  $\Delta G_{exp.} = -1.10^6 + 809,18.T, \text{ J.mol}^{-1}$  ( $R^2 = 0,9473$ )
  - for Mo/MoO<sub>2</sub> reference electrode  $\Delta G_{exp.} = -2.10^7 + 35776.T - 15,513. T^2, \text{ J.mol}^{-1}$  ( $R^2 = 0,9706$ )
- where R is a correlation coefficient

Table 4 Gibbs Energy Equations of the expected reactions.

<b>Mix 1</b>		
$2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 = 3\text{Fe}_2\text{O}_3$	$\Delta G_1 = -586770 + 340.2.T, \text{ J.mol}^{-1}$	[34]
$6\text{MnO} + \text{O}_2 = 2\text{Mn}_3\text{O}_4$	$\Delta G_2 = -563241 + 1761.758.T - 220.490.T.\ln T + 0.101819.T^2$	[18]
$Mn_{1-x}O + \frac{1}{2}O_2 = \frac{1-x}{1-4x} Mn_3O_4$	$\Delta G_3 = -222470 + 111,1.T, \text{ J.mol}^{-1}$	[19]
$\frac{6}{(1-4x)} Mn_{1-x}O + O_2 = \frac{2(1-x)}{(1-4x)} \alpha Mn_3O_4$	$\Delta G_4 = -445606 + 221,70.T \text{ J.mol}^{-1}$	[17]
$6\text{MnO} + \text{O}_2 = 2\text{Mn}_3\text{O}_4$	$\Delta G_5 = -443067 + 0,7.10^6.T^{-2} + 144,4.T - (22,1.10^{-3}).T^2 + 15.67.\ln T, \text{ J.mol}^{-1}$	[33]
$6\text{MnO} + \text{O}_2 = 2\text{Mn}_3\text{O}_4$	$\Delta G_6 = -541,31 + 0,3593.T, \text{ J.mol}^{-1}$	in this work
<b>Mix 2</b>		
$2\text{Fe} + \text{O}_2 + 2\text{V}_2\text{O}_3 = 2\text{FeV}_2\text{O}_4$	$\Delta G_7 = -577500 + 124,7.T, \text{ J.mol}^{-1}$	in this work
$\text{Fe}_2\text{O}_3 + \text{MnO} = \text{Fe}_2\text{MnO}_4$	$\Delta G_8 = -17669 - 6,8286.T, \text{ J.mol}^{-1}$	in this work
$4\text{Fe}_3\text{O}_4 + \text{O}_2 = 6\text{Fe}_2\text{O}_3$	$\Delta G_9 = -417348 + 147,73.T, \text{ J.mol}^{-1}$	in this work
$\text{V}_2\text{O}_3 + \text{FeO} + \text{O}_2 = \text{FeV}_2\text{O}_6$	$\Delta G_{10} = -449912 + 35,441.T, \text{ J.mol}^{-1}$	in this work
$2\text{FeO} + \text{V}_2\text{O}_4 = \text{Fe}_2\text{O}_3 + \text{V}_2\text{O}_3$	$\Delta G_{11} = -77323 + 48,84.T, \text{ J.mol}^{-1}$	[21]
$\text{FeO} + \text{V}_2\text{O}_3 = \text{FeV}_3\text{O}_4$	$\Delta G_{12} = -24700 - 2,25.T, \text{ J.mol}^{-1}$	[21]

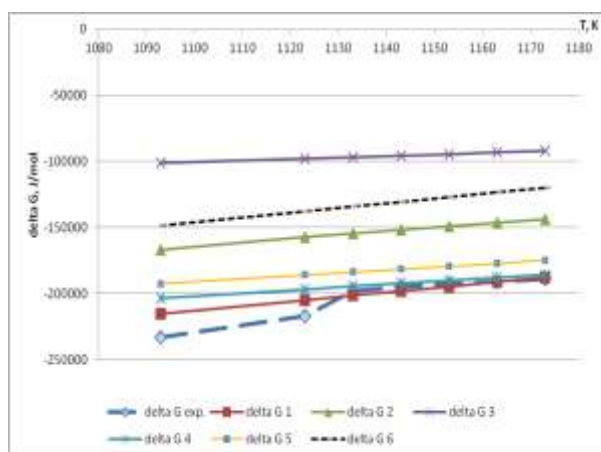


Fig.6. Dependence of  $\Delta G = f(T)$  for Mix 1 (air as a reference electrode)

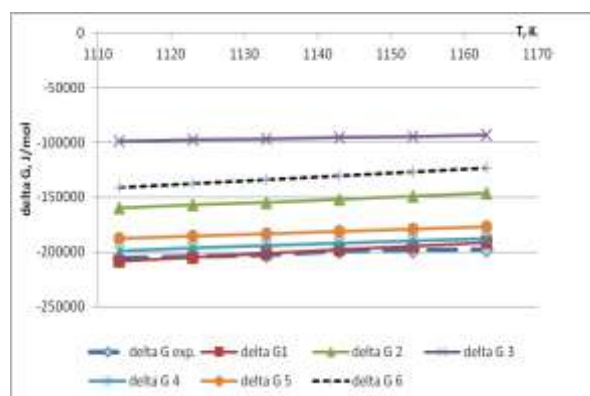


Fig.7. Dependence of  $\Delta G = f(T)$  for Mix 1 (Ni/NiO as a reference electrode)

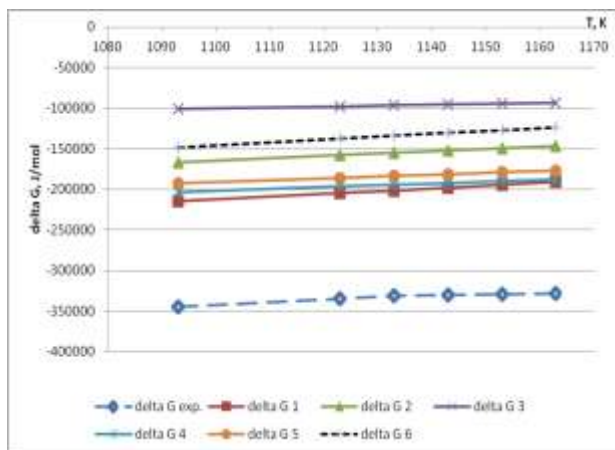


Fig.8. Dependence of  $\Delta G = f(T)$  for Mix 1 (Mo/MoO<sub>2</sub> as a reference electrode)

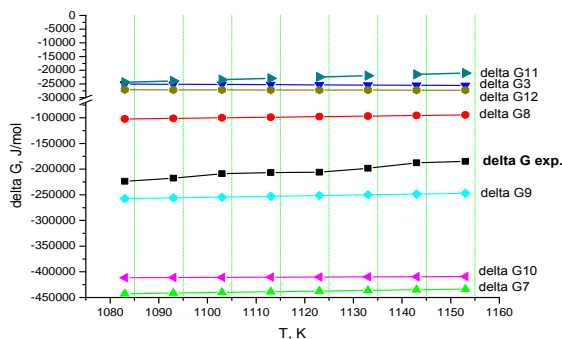


Fig.9. Dependence of  $\Delta G = f(T)$  for Mix 2 (air as a reference electrode)

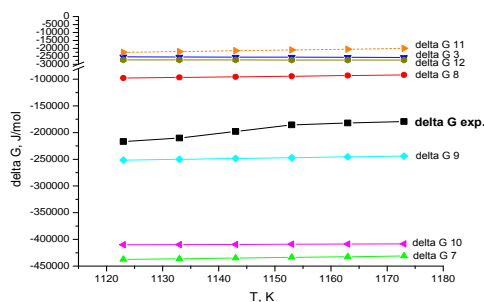


Fig.10. Dependence of  $\Delta G = f(T)$  for Mix 2 (Ni/NiO as a reference electrode)

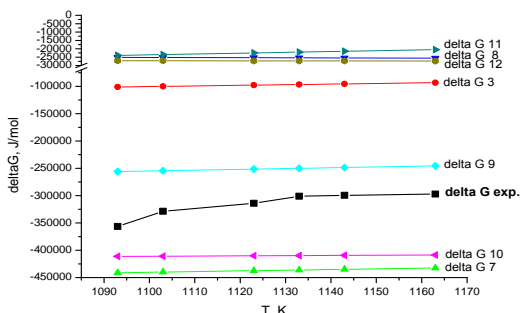


Fig.11. Dependence of  $\Delta G = f(T)$  for Mixture 2 (Mo/MoO<sub>2</sub> as a reference electrode)

The comparison of the experimental data of the three types of reference electrodes with the theoretically calculated values for Hematite showed that the obtained results with reference electrodes air and Ni/NiO were very close to the theoretical values (particularly for Mixture 1), while those of Mo/MoO<sub>3</sub> essentially differed. That is why when thermodynamics of the processes including iron oxides is studied; these two reference electrodes are more suitable than molybdenum.

### III. CONCLUSION

1. It was found out that the phase transformations up to 1473 K and forming of new phases in the mixtures, for example FeV<sub>2</sub>O<sub>4</sub> (coulsonite) (at ~1173K) and Iron Vanadium Oxide type (Fe<sub>6.5</sub>V<sub>11.5</sub>O<sub>35</sub>) (at ~1473K) and Jacobsite types MnFe<sub>2</sub>O<sub>4</sub> (at ~1173K) and (Mn<sub>6</sub>Fe<sub>4</sub>)(Mn<sub>4</sub>Fe<sub>1.6</sub>)O<sub>4</sub> (at ~1473K) could happen only if in the initial materials contained waste vanadium catalyst and manganese concentrate. The X-ray analysis confirmed the presence mainly of hematite phase, cubic and tetragonal Mn<sub>2</sub>O<sub>3</sub>, hausmanit (Mn<sub>3</sub>O<sub>4</sub>).

2. Based on the experimental results obtained after the heating of mixtures containing oxides of iron, manganese and vanadium the relationship of  $\Delta G^{\circ}_T = f(T)$  in the temperature range 1073 – 1173 K was obtained, using EMF method with the three different reference electrodes (Ni/NiO, Mo/MoO<sub>3</sub> and air). Gibbs energy for Mix 1 and Mix 2 were very close to the theoretically calculated values for Fe<sub>2</sub>O<sub>3</sub> using reference electrodes Ni/NiO and air while that of Mo/MoO<sub>2</sub> essentially differed. The X-ray analysis confirmed the presence of hematite phase.

3. It was proved that waste vanadium catalyst and manganese concentrate were more appropriate precursors for the production of complex iron vanadium manganese alloy than the pure oxides - V<sub>2</sub>O<sub>5</sub> and MnO<sub>2</sub>.

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