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O.M. Borysenko [a], S.M. Logvinkov [a], G.M. Shabanova [b], I.A. Ostapenko [c]*

THERMODYNAMICS OF PHASE TRANSITIONS IN THE SUBSOLIDUS DOMAIN OF THE $FeO-MgO-TiO_2$ SYSTEM

[a] Simon Kuznets Kharkiv National University of Economics, Kharkiv, Ukraine
[b] National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine
[c] Druzhkivskyi Vognetryvkyi Zavod, Druzhkivka, Ukraine

This paper gives consideration to the three-component $FeO-MgO-TiO_2$ system that is a part of the four-component $MgO-Al_2O_3-FeO-TiO_2$ system which serves to produce materials with valuable properties. The structure of binary $FeO-TiO_2$ and $MgO-TiO_2$ systems is described and the available data on the $FeO-MgO-TiO_2$ system are analyzed. We present the thermodynamic data on all system compounds and calculate change of the free Gibbs energy in the temperature range of 800 to 1900 K for three exchange reactions. It was established that the triangulation of the $FeO-MgO-TiO_2$ system changes in three following temperature ranges: at the temperatures of up to 1115 K, at 1115 to 1413 K (the restructuring of conodes here occurs) and above 1413 K (stable pseudobrookite is formed). It was shown that the following two-phase equilibria are stable: $MgTi_2O_5-FeTiO_3$, $FeTiO_3-MgTiO_3$, $MgTiO_3-Fe_2TiO_4$, $Fe_2TiO_4-Mg_2TiO_4$ and Mg_2TiO_4-FeO at the temperatures of up to 1115 K; $MgTi_2O_5-FeTiO_3$, $FeTiO_3-MgTiO_3$, $FeTiO_3-Mg_2TiO_4$, $Fe_2TiO_4-Mg_2TiO_4$ and Mg_2TiO_4-FeO in the temperature range of 1115 to 1413 K; and $MgTi_2O_5-FeTi_2O_5$, $MgTi_2O_5-FeTiO_3$, $FeTiO_3-MgTiO_3$, $FeTiO_3-Mg_2TiO_4$, $Fe_2TiO_4-Mg_2TiO_4$ and Mg_2TiO_4-FeO at the temperatures of above 1413 K.

Keywords: phase equilibrium, change of free Gibbs energy, ulvospinel, ilmenite, pseudobrookite, quandilite, karroite, geikelite.

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Introduction

The $FeO-MgO-TiO_2$ system has an auxiliary value to study different multicomponent systems. For example, it forms a part of a four-component $MgO-Al_2O_3-FeO-TiO_2$ system that serves as a basis for the production of materials with such valuable properties (high refractoriness, enhanced mechanical strength and resistance to the chemical impacts, and an improved heat resistance). This system has been studied insufficiently, especially in terms of its structure and the processes that occur in it at different temperatures.

The binary $FeO-TiO_2$ contains three thermodynamically stable compounds: ulvospinel Fe_2TiO_4, ilmenite $FeTiO_3$ and pseudobrookite $FeTi_2O_5$ [1–3]. According to ref. [4], Fe_2TiO_4 and $FeTiO_3$ melt at 1668 K and 1673 K, respectively. Pseudobrookite is stable at above 1408 K [5]; research [6] showed that this temperature is equal to 1413 K.

The phase diagram of the $MgO-TiO_2$ system was investigated in a number of works [7–9]. Early studies mentioned two compounds: quandilite Mg_2TiO_4 and karroite $MgTi_2O_5$. Later on, the stochiometric geikelite compound ($MgTiO_3$) was described. There was a lot of discussion about the melting temperatures and the temperatures at which appropriate compounds are decomposed. Ref. [9] summarized all studies done to address this issue. Mg_2TiO_4 melts incongruently at 2033 K, $MgTiO_3$ is decomposed at 1933 K and the third compound, $MgTiO_3$, melts congruently at 1933 K.

Berezhnoi [10] plotted the phase diagram with three series of the solid solutions in $FeO-MgO-TiO_2$ system (Fig. 1). According to this diagram, the system has four series of continuous solid solutions. These are as follows: magnesiowustites (Mg, Fe)O, inverted spinelides $(Mg, Fe)_2TiO_4$, ilmenites (Mg, Fe)TiO_3, and pseudobrookites (Mg, Fe)Ti_2O_5.

This work was aimed at establishing the existence of mutual combinations of phases in the

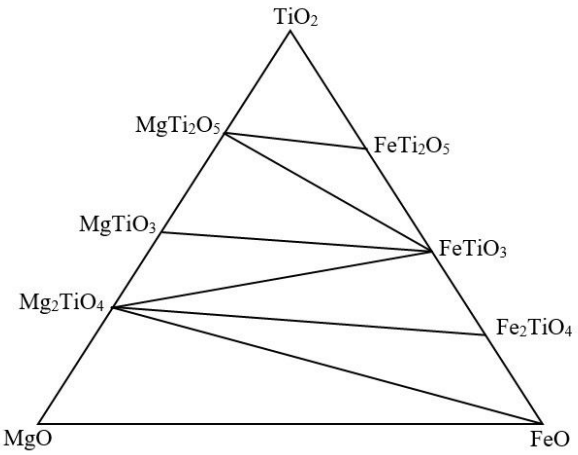

Fig. 1. Phase diagram of the FeO–MgO–TiO_2 system [10]

three-component system FeO–MgO–TiO_2 and studying its subsolidus structure.

Results and discussion

This paper reports the thermodynamic analysis of the subsolidus structure of the FeO–MgO–TiO_2 system by considering temperature dependences of free Gibbs energy (ΔG vs. T) for the solid-phase reactions of the type 2–2 and 2–3, i.e. where two initial compounds and two or three interaction products may exist) using the methods described elsewhere [11]. Calculations were performed in the temperature range of 800 to 1900 K using thermodynamic data given in Table 1. The following model exchange reactions were investigated:

$$MgTiO_3 + FeTi_2O_5 = MgTi_2O_5 + FeTiO_3, \quad (1)$$

$$2MgTiO_3 + Fe_2TiO_4 = Mg_2TiO_4 + 2FeTiO_3, \quad (2)$$

$$2MgO + Fe_2TiO_4 = Mg_2TiO_4 + 2FeO. \quad (3)$$

Table 2 shows the calculated data on the values of the changes in the Gibbs energy for solid-state exchange reactions (1)–(3) as a function of temperature.

First, we will give consideration to reactions (2) and (3), because the $FeTi_2O_5$ compound is stable above 1413 K. According to the obtained data (Table 2), reaction (2) is reversible at 1115 K and it provides the stability for the combinations of initial $MgTiO_3$ and Fe_2TiO_4 compounds up to this temperature and the phase combination of Mg_2TiO_4 and $FeTiO_3$ is stable above 1115 K. As for reaction (3), the combination of Mg_2TiO_4 and FeO phases is stable in the entire temperature range (Table 2). Hence, we will triangulate the FeO–MgO–TiO_2 system up to the temperature of 1115 K (Fig. 2) and in the temperature range of 1115 to 1413 K (Fig. 3). At the temperature above 1413 K, we will take into consideration reaction (1), according to which the compounds $MgTi_2O_5$ and $FeTiO_3$ are stable and this system can be triangulated (Fig. 4).

Conclusions

The subsolidus structure of the system under consideration is complicated and is characterized by the phase changeability. Above 1115 K, the solid phase interaction occurs with the transformation of

Table 1

Initial thermodynamic data [11]

Compound	$-\Delta H^0_{298}$, kJ mol^{-1}	ΔS^0_{298}, J mol^{-1} K^{-1}	$C_p = a + bT + c'T^{-2}$, J mol^{-1} K^{-1}		
			a	$b \cdot 10^3$	$-c \cdot 10^{-5}$
FeO	272.044	60.752	48.785	8.37	2.80
MgO	601.241	26.924	42.59	7.28	6.19
$MgTiO_3$	1571.93	74.56	118.37	13.27	27.32
$MgTi_2O_5$	2507.89	138.91	170.21	38.49	30.75
Mg_2TiO_4	2163.55	115.1	154.64	35.73	28.83
$FeTiO_3$	1236.37	105.86	116.61	18.24	20.04
$FeTi_2O_5$	2190.7	145.6	192.59	22.01	31.00
Fe_2TiO_4	1510.42	163.18	139.5	63.10	14.23

Table 2

The results of the calculated changes in the Gibbs energy for the reactions in the system FeO–MgO–TiO_2 at different temperatures

Reaction number	ΔG, kJ mol^{-1}						
	800 K	1000 K	1200 K	1400 K	1600 K	1800 K	1900 K
1	4.260	2.833	1.552	0.239	–1.228	–2.941	–3.912
2	5.218	1.845	–1.298	–4.133	–6.605	–8.671	–9.541
3	–16.531	–24.268	–32.138	–39.941	–47.538	–54.825	–58.327

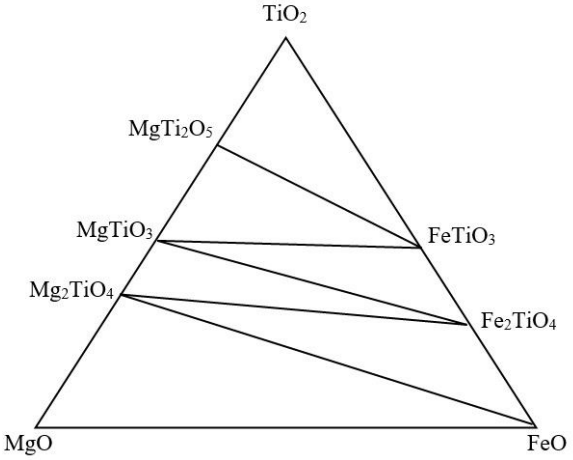

Fig. 2. Triangulation of the FeO–MgO–TiO_2 system at temperatures up to 1115 K

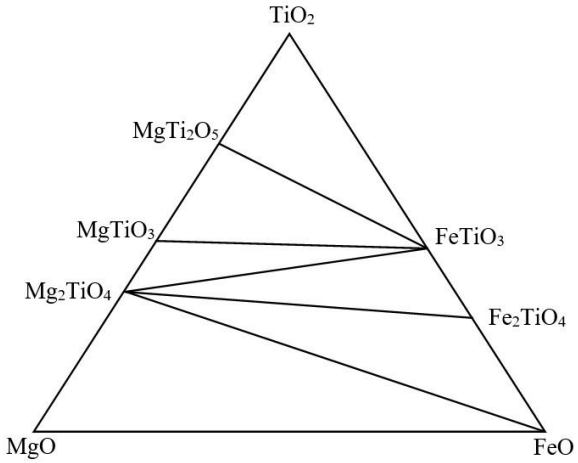

Fig. 3. Triangulation of the FeO–MgO–TiO_2 system in the temperature range of 1115–1413 K

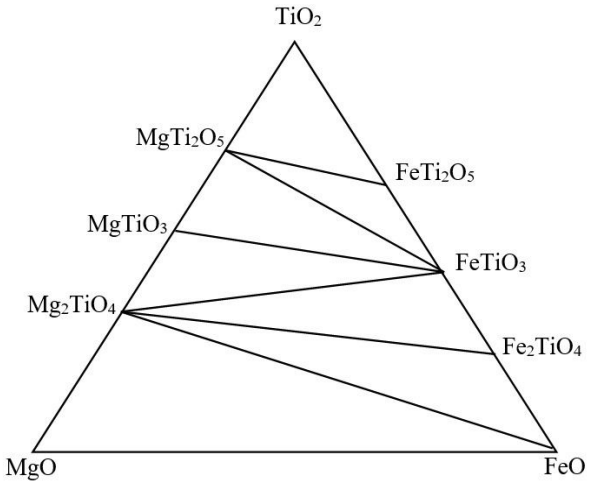

Fig. 4. Triangulation of the FeO–MgO–TiO_2 system at temperatures above 1413 K

the $MgTiO_3$–Fe_2TiO_4 conode into Mg_2TiO_4–$FeTiO_3$ one. Pseudobrookite is not stable up to 1413 K and the solid solutions of a pseudobrookite type can be formed only on the basis of karroit with a similar type of the crystalline lattice. Magnesium ferrite solid solutions coexist with quandilite and are not stable in the combination with ulvospinel. These data can be further used to develop scientific basis for fabricating new materials with specified operational properties.

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ТЕРМОДИНАМІКА ФАЗОВИХ ПЕРЕТВОРЕНЬ НА СУБСОЛІДУСНІЙ ДІЛЯНЦІ СИСТЕМИ $FeO-MgO-TiO_2$

О.М. Борисенко, С.М. Логвінков, Г.М. Шабанова, І.А. Остапенко

У статті розглядається будова трикомпонентної системи $FeO-MgO-TiO_2$, що входить до складу чотирикомпонентної системи $MgO-Al_2O_3-FeO-TiO_2$, на основі якої одержують матеріали з цінними властивостями. Описано будову бінарних систем $FeO-TiO_2$, $MgO-TiO_2$, а також проаналізовані відомі дані стосовно системи $FeO-MgO-TiO_2$. Наведено термодинамічні дані всіх сполук системи, на основі яких виконано розрахунок зміни вільної енергії Гіббса в інтервалі температур 800–1900 K для трьох реакції обміну. Встановлено, що тріангуляція системи $FeO-MgO-TiO_2$ змінюється в трьох температурних інтервалах: до 1115 K, 1115–1413 K (відбувається перебудова конод) і вище 1413 K (утворюється стабільний псевдобрукіт). Показано, що стабільними є наступні двофазні рівноваги: $MgTi_2O_5-FeTiO_3$, $FeTiO_3-MgTiO_3$, $MgTiO_3-Fe_2TiO_4$, $Fe_2TiO_4-Mg_2TiO_4$ і Mg_2TiO_4-FeO при температурі до 1115 K; $MgTi_2O_5-FeTiO_3$, $FeTiO_3-MgTiO_3$, $FeTiO_3-Mg_2TiO_4$, $Fe_2TiO_4-Mg_2TiO_4$ і Mg_2TiO_4-FeO в температурному інтервалі 1115–1413 K; та $MgTi_2O_5-FeTi_2O_5$, $MgTi_2O_5-FeTiO_3$, $FeTiO_3-MgTiO_3$, $FeTiO_3-Mg_2TiO_4$, $Fe_2TiO_4-Mg_2TiO_4$ і Mg_2TiO_4-FeO при температурі вище 1413 K.

Ключові слова: фазова рівновага, зміна вільної енергії Гіббса, ульвошпінель, ільменіт, псевдобрукіт, кванділіт, карроїт, гейкеліт.

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[a] Simon Kuznets Kharkiv National University of Economics, Kharkiv, Ukraine

[b] National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine

[c] Druzhkivskyi Vognetryvkyi Zavod, Druzhkivka, Ukraine

[*] e-mail: onborisenko@ukr.net

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