Materials Science Forum
ISSN: 1662-9752, Vol. 1038, pp 177-184
doi:10.4028/www.scientific.net/MSF.1038.177

Submitted: 2021-03-21
Accepted: 2021-03-30
Online: 2021-07-13

Thermodynamics of Solid-Phase Exchange Reactions Limiting the Subsolidus Structure of the System $MgO-Al_2O_3-FeO-TiO_2$

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Keywords: the multicomponent systems, the thermodynamic analysis, the subsolidus structure.

Abstract. The basis of modern materials science is multicomponent systems, on their basis it is possible to create various combinations of phases in structural materials with a set of specified properties. The investigated system $MgO – Al_2O_3 – FeO – TiO_2$ is promising for the production of periclase-spinel refractories used as lining of rotary kilns during cement clinker firing, which are highly resistant to chemical corrosion when exposed to a gas environment and cement clinker components; thermomechanical stresses. However, in the reference literature and scientific articles, no information was found on the structure of the four-component diagram of the state of the $MgO – Al_2O_3 – FeO – TiO_2$ system, partial elements of its structure are given only in the composition of multicomponent systems [1-3]. Thus, research to the study of the subsolidus structure of the $MgO – Al_2O_3 – FeO – TiO_2$ system, which is the physicochemical basis for the development of compositions of periclase-spinel refractories, is urgent.

Introduction

We carried out a thermodynamic analysis of the subsolidus structure of the $MgO – Al_2O_3 – FeO – TiO_2$ system by comparing the Gibbs free energy in the temperature range 800 – 2076 K according to the method [4], using the thermodynamic data presented in table. 1, for model solid-phase exchange reactions [5, 6]. The calculation of the change in the Gibbs free energy with temperature makes it possible to judge the direction of the solid-phase reactions and the preference for the formation of certain combinations of phases [7].

Materials and Methods

In the three-component subsystem $MgO – TiO_2 – FeO$, according to the calculations of the change in the Gibbs free energy (Table 2) according to reaction (1):

$$2MgTiO_3 + Fe_2TiO_4 = Mg_2TiO_4 + 2FeTiO_3, \quad (1)$$

up to a temperature of 1115 K, the combination of the starting compounds $MgTiO_3$ and Fe_2TiO_4 is stable.

Changes in Gibbs free energy for reaction (2):

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

are negative in the entire temperature range (Table 2), which indicates the stability of the combination of the Mg_2TiO_4 and FeO phases in the interaction products.

Table 1. Thermodynamic constants of compounds [1, 4, 8-10]

Compound	$-\Delta H^0_{298}$ [kJ/mol]	S^0_{298} [J/(mol·K)]	$C_p = a + bT + c'T^{-2}$, [J/(mol·K)]		
			a	$b \cdot 10^3$	$-c \cdot 10^{-5}$
Al_2O_3	1676.0577	50.95	115.072	11.80	35.06
MgO	601.241	26.924	42.59	7.28	6.19
FeO	272.044	60.752	48.785	8.37	2.80
TiO_2 anatase	912.53	34.727	44.225	15.062	7.782
TiO_2 rutile	943.492	49.915	74.6	2.092	17.698
$MgAl_2O_4$	2297.02	80.58	153.97	26.78	40.92
$FeTiO_3$	1236.37	105.86	116.61	18.24	20.04
$MgTiO_3$	1571.93	74.56	118.37	13.27	27.32
Mg_2TiO_4	2163.55	115.10	154.64	35.73	28.83
$MgTi_2O_5$	2507.89	138.91	170.21	38.49	30.75
$FeTi_2O_5$	2190.7	145.6	192.59	22.01	31.00
Fe_2TiO_4	1510.42	163.18	139.5	63.10	14.23
$FeAl_2O_4$	1982.4	106.3	156.48	26.15	31.34
Al_2TiO_5	2607.47	109.62	182.55	22.18	46.91
Al_4TiO_8	4194.883	211.576	$395.84 - 1.1634 \cdot 10^7 \cdot T^{-2} - 1925.3 \cdot T^{-0,5} + 1.505 \cdot 10^9 \cdot T^{-3}$		

For the model reactions considered below the calculated values of $\Delta G = f(T)$ are presented in table 2.

In the MgO – Al_2O_3 – FeO subsystem, the only reaction that determines the subsolidus structure is:

$$FeO + MgAl_2O_4 = MgO + FeAl_2O_4. \quad (3)$$

Reaction (3) is reversible at a temperature of 1141 K (Table 2), and the combination of the MgO and In the Al_2O_3 – TiO_2 – FeO subsystem, reaction (4) is the most thermodynamically probable and ensures the stability of the combination of the starting compounds Al_2O_3 and $FeTiO_3$ (positive and maximum values of ΔG in modulus according to Table 2), according to reaction (5), the combination of compounds in the reaction products is more stable: $FeAl_2O_4$ and $FeTiO_3$ (negative values of ΔG in the entire investigated temperature range (see Table 2):

$$Al_2O_3 + FeTiO_3 = FeAl_2O_4 + TiO_2 \text{ (anatase)}, \quad (4)$$

$$Fe_2TiO_4 + Al_2O_3 = FeTiO_3 + FeAl_2O_4. \quad (5)$$

$FeAl_2O_4$ phases is stable up to this temperature.

The structure of the MgO – Al_2O_3 – TiO_2 subsystem in the low-temperature region (before the polymorphic transformation of anatase – rutile) is determined by the following reactions:

$$MgAl_2O_4 + 2TiO_2 \text{ (anatase)} = MgTi_2O_5 + Al_2O_3, \quad (6)$$

$$MgAl_2O_4 + TiO_2 \text{ (anatase)} = MgTiO_3 + Al_2O_3, \quad (7)$$

$$Al_2O_3 + Mg_2TiO_4 = MgAl_2O_4 + MgTiO_3. \quad (8)$$

In reactions (6), (7), the values of ΔG up to 1400 K are negative (Table 2), which indicates the thermodynamic preference of their flow in the forward direction and the stability of pair combinations of compounds in the reaction products.

For reaction (8), the ΔG values are negative over the entire temperature range. Thus, we find stable two-phase combinations: Al_2O_3 and $MgTi_2O_5$, Al_2O_3 and $MgTiO_3$, $MgTiO_3$ and $MgAl_2O_4$, Mg_2TiO_4 and $MgAl_2O_4$.

To simplify the calculations, the first temperature interval for the analysis of the subsolidus structure of the $MgO – Al_2O_3 – FeO – TiO_2$ system is chosen – 800 – 1141 K. For the tetrahedration of the system under study, it is also necessary to take into account the following reactions:

$$Mg_2TiO_4 + 2FeAl_2O_4 = 2MgAl_2O_4 + Fe_2TiO_4, \quad (9)$$

$$FeAl_2O_4 + MgTiO_3 = MgAl_2O_4 + FeTiO_3. \quad (10)$$

The results of calculating ΔG for reaction (9) indicate the thermodynamic stability of the starting compounds (Table 2), which determines the presence in the subsolidus structure of the system of the "internal" connode Mg_2TiO_4 and $FeAl_2O_4$. According to the positive values of ΔG for reaction (10) – the starting compounds coexist (Table 2), which establishes the "internal" $FeAl_2O_4 – MgTiO_3$ connode.

Thus, when three-component subsystems are combined into a concentration tetrahedron and in the presence of two "internal" connodes, we determine the presence of 10 elementary tetrahedra in the subsolidus structure of the system under study in the temperature range 800 – 1141 K: $Al_2O_3 – TiO_2 – FeTiO_3 – MgTi_2O_5$, $Al_2O_3 – FeTiO_3 – MgTi_2O_5 – MgTiO_3$, $Mg_2TiO_4 – FeAl_2O_4 – MgO – MgAl_2O_4$, $Mg_2TiO_4 – FeAl_2O_4 – MgO – FeO$, $Mg_2TiO_4 – FeAl_2O_4 – FeO – Fe_2TiO_4$, $FeAl_2O_4 – MgTiO_3 – MgAl_2O_4 – Mg_2TiO_4$, $FeAl_2O_4 – MgTiO_3 – Mg_2TiO_4 – Fe_2TiO_4$, $FeAl_2O_4 – MgTiO_3 – Fe_2TiO_4 – FeTiO_3$, $FeAl_2O_4 – MgTiO_3 – MgAl_2O_4 – Al_2O_3$, $FeAl_2O_4 – MgTiO_3 – Al_2O_3 – FeTiO_3$.

In the $MgO – TiO_2 – FeO$ subsystem above a temperature of 1115 K, the connodes are rearranged (reaction (1), Table 2): $MgTiO_3 – Fe_2TiO_4$ changes to $Mg_2TiO_4 – 2FeTiO_3$. Above 1141 K, in the $MgO – Al_2O_3 – FeO$ subsystem, according to Eq. (3), there is also a rearrangement of the connodes (Table 2): $MgO – FeAl_2O_4$ disappears and $FeO – MgAl_2O_4$ appears. These circumstances make adjustments to the structure of $MgO – TiO_2 – FeO$ and $MgO – Al_2O_3 – FeO$. In ternary subsystems, which include the binary subsystem $FeO – TiO_2$, above a temperature of 1413 K, it is necessary to take into account such a compound as pseudobrookite ($FeTi_2O_5$), which is stable above this temperature [11]. It is also necessary to take into account the anatase – rutile phase transition and, to simplify the calculations, we take it ~ 1413 K. Thus, the second temperature interval for considering the subsolidus structure of the four-component system $MgO – Al_2O_3 – FeO – TiO_2$ is taken – 1141 – 1413 K. When combining all three-component subsystems into concentration tetrahedron, we take into account reactions (9) and (10), which determine the presence of two "internal connodes" and the four-component system is divided into 10 elementary tetrahedra: $Al_2O_3 – TiO_2 – FeTiO_3 – MgTi_2O_5$, $Al_2O_3 – FeTiO_3 – MgTi_2O_5 – MgTiO_3$, $MgO – MgAl_2O_4 – Mg_2TiO_4 – FeO$, $FeAl_2O_4 – Mg_2TiO_4 – MgAl_2O_4 – FeO$, $FeAl_2O_4 – Mg_2TiO_4 – FeO – Fe_2TiO_4$, $FeAl_2O_4 – Mg_2TiO_4 – Fe_2TiO_4 – FeTiO_3$, $Mg_2TiO_4 – MgTiO_3 – FeTiO_3 – FeAl_2O_4$, $FeAl_2O_4 – MgTiO_3 – MgAl_2O_4 – Mg_2TiO_4$, $FeAl_2O_4 – MgTiO_3 – MgAl_2O_4 – Al_2O_3$, $FeAl_2O_4 – MgTiO_3 – Al_2O_3 – FeTiO_3$.

Table 2. The results of calculating the change in the values of Gibbs free energy depending on temperature

№ reaction	ΔG, [kJ/mol], at temperature, [K]						
	800	1000	1200	1400	1600	1800	1900
1	5.218	1.845	-1.298	-4.133	-6.605	-8.671	-9.541
2	-16.531	-24.268	-32.138	-39.941	-47.538	-54.825	-58.327
3	-5.718	-2.475	1.046	4.756	10.660	12.711	14.801
4	40.445	50.675	61.770	73.492	–	–	–
5	-32.588	-32.826	-32.600	-31.781	-30.276	-28.019	-26.591
6	-106.866	-124.409	-143.450	-163.383	–	–	–
7	-57.037	-66.189	-76.144	-86.639	–	–	–
8	-21.213	-19.157	-16.928	-14.499	-11.855	-8.982	-7.458
9	27.966	29.182	30.046	30.429	30.237	29.402	28.725
10	16.592	15.513	14.374	13.147	11.816	10.365	9.591
11	–	–	–	–	-1.228	-2.941	-3.912
12	–	–	–	-7.998	-6.614	-5.138	-4.367
13	–	–	–	39.779	36.891	33.158	30.959
14	–	–	–	-12.205	-12.735	-13.079	-13.182
15	-13.643	-10.378	-7,088	-3.790	-0.493	2.801	4.446
16	–	–	–	-12.908	-13.044	-13.307	-13.504
17	–	–	–	–	-0.867	-1.868	-2.416
18	–	–	–	-10.312	-9.536	-8.584	-8.031
19	–	–	–	–	-0,558	-1.640	-2.094
20	–	–	–	–	-0.335	-6.340	-9.343
21	–	–	–	–	-30.900	-26.600	-24.45
22	–	–	–	–	-19.600	-18.900	-18.550
23	–	–	–	-17.354	-17.054	-16.418	-15.969
24	–	–	–	13.160	10.948	8.497	7.175
25	–	–	–	50.104	45.560	39.874	36.574
26	–	–	–	–	–	-106.178	-122.732
27	–	–	–	–	–	-136.999	-157.771
28	–	–	–	–	–	-127.835	-141.756
29	–	–	–	–	–	-120.179	-136.612
30	–	–	–	–	–	-134.198	-149.324
31	–	–	–	–	–	-404.102	-229.125
32	–	–	–	–	–	-273.356	-303.490
33	–	–	–	–	–	-396.760	-443.761
34	–	–	–	–	–	-105.656	-120.216
35	–	–	–	–	–	257.828	289.522

In subsequent studies, we take into account the pseudobrookite compound, which introduces corresponding changes in the rearrangement of the subsolidus structure of the three-component subsystems Al_2O_3 – TiO_2 – FeO and MgO – TiO_2 – FeO. Above a temperature of 1413 K in the MgO – TiO_2 – FeO subsystem, we take into account the reaction (11):

$$MgTiO_3 + FeTi_2O_5 = MgTi_2O_5 + FeTiO_3, \quad (11)$$

according to which (Table 2) the combination of the $MgTi_2O_5$ and $FeTiO_3$ phases is stable. In the Al_2O_3 – TiO_2 – FeO subsystem, we take into account the following reactions:

$$Al_2O_3 + FeTiO_3 = FeAl_2O_4 + TiO_2 \text{ (rutile)}, \quad (12)$$

$$2FeAl_2O_4 + TiO_2 \text{ (rutile)} = 2Al_2O_3 + Fe_2TiO_4, \quad (13)$$

$Al_2O_3 + FeTi_2O_5 = FeAl_2O_4 + TiO_2$ (rutile), (14)

$Al_2O_3 + 2FeTiO_3 = FeAl_2O_4 + FeTi_2O_5$. (15)

In reactions (12) – (14) (Table 2), the coexistence of hercynite ($FeAl_2O_4$) and rutile (TiO_2) is found, reaction (15) up to a temperature of 1630 K is thermodynamically probable in the forward direction and the combination of compounds in the products of the interaction of $FeAl_2O_4$ and $FeTi_2O_5$ is stable, reaction (5) ensures the coexistence of hercynite and ilmenite ($FeTiO_3$) (Table 2), which automatically establishes the stability of the hercynite – ulvospinel (Fe_2TiO_4) combination.

The thialite compound (Al_2TiO_5) is stable above 1537 K [12-13]. Based on the stability of pseudobrookite and thialite, as well as the anatase – rutile phase transition, we determine the following temperature range in the structure of the four-component system – 1413 – 1537 K. To determine the subsolidus structure of the four-component system in this interval, we take into account reactions (9) and (10), as well as:

$MgAl_2O_4 + FeTi_2O_5 = FeAl_2O_4 + MgTi_2O_5$, (16)

according to which (Table 2) the third "internal" connode $FeAl_2O_4 – MgTi_2O_5$ is found.

Accordingly, the $MgO – Al_2O_3 – FeO – TiO_2$ system in the temperature range of 1413 – 1537 K is divided into 12 elementary tetrahedra: $MgO – FeO – Mg_2TiO_4 – MgAl_2O_4$, $FeAl_2O_4 – Mg_2TiO_4 – MgAl_2O_4 – FeO$, $FeAl_2O_4 – Mg_2TiO_4 – FeO – Fe_2TiO_4$, $FeAl_2O_4 – Mg_2TiO_4 – Fe_2TiO_4 – FeTiO_3$, $FeAl_2O_4 – MgTiO_3 – Mg_2TiO_4 – MgAl_2O_4$, $FeAl_2O_4 – MgTiO_3 – Mg_2TiO_4 – FeTiO_3$, $FeAl_2O_4 – MgTiO_3 – MgAl_2O_4 – Al_2O_3$, $FeAl_2O_4 – MgTi_2O_5 – MgTiO_3 – Al_2O_3$, $FeAl_2O_4 – MgTi_2O_5 – MgTiO_3 – FeTiO_3$, $FeAl_2O_4 – MgTi_2O_5 – FeTiO_3 – FeTi_2O_5$, $FeAl_2O_4 – MgTi_2O_5 – FeTi_2O_5 – TiO_2$, $FeAl_2O_4 – MgTi_2O_5 – TiO_2 – Al_2O_3$.

Above 1537 K, thialite changes the structure of the $Al_2O_3 – TiO_2 – FeO$ and $MgO – Al_2O_3 – TiO_2$ subsystems.

In the temperature range above 1537 K, reactions (17) – (19) should be taken into account in the $MgO – Al_2O_3 – TiO_2$ subsystem:

$MgAl_2O_4 + 2TiO_2$ (rutile) $= MgTiO_3 + Al_2TiO_5$, (17)

$MgAl_2O_4 + Al_2TiO_5 = 2Al_2O_3 + MgTiO_3$, (18)

$Al_2O_3 + MgTi_2O_5 = Al_2TiO_5 + MgTiO_3$. (19)

According to the negative values of ΔG (Table 2) for reaction (17), the stability of the combination of the $MgTiO_3$ and Al_2TiO_5 phases is ensured, which is also tested by the reaction of the "2 = 3" type (two initial components – three reaction products):

$6MgAl_2O_4 + 13TiO_2$ (rutile) $= MgTi_2O_5 + 6Al_2TiO_5 + 5MgTiO_3$. (20)

The negative value of ΔG for reaction (18) (Table 2) does not violate the stability of the combination of Al_2O_3 with $MgTiO_3$, which is also tested and confirmed in the calculations of ΔG (Table 2) for solid-phase reactions:

$2Al_2TiO_5 + Mg_2TiO_4 + MgAl_2O_4 = 3Al_2O_3 + 3MgTiO_3$, (21)

$Al_2TiO_5 + MgTi_2O_5 + 2MgAl_2O_4 = 3Al_2O_3 + 3MgTiO_3$. (22)

According to reaction (19), according to the ΔG values (Table 2), the combination of the $Al_2TiO_5 – MgTiO_3$ phases is stable.

When analyzing phase equilibria in the $Al_2O_3 – TiO_2$ - FeO subsystem, we also take into account the effect of thialite. The calculation results ΔG (Table 2) for the following reactions:

$Al_2TiO_5 + FeTi_2O_5 = FeAl_2O_4 + 3TiO_2$ (rutile), (23)

$FeAl_2O_4 + 2TiO_2$ (rutile) $= Al_2TiO_5 + FeTiO_3$, (24)

$2FeAl_2O_4 + 3TiO_2$ (rutile) $= 2Al_2TiO_5 + Fe_2TiO_4$, (25)

indicate the coexistence of rutile with hercynite. If the combination of TiO_2 and $FeAl_2O_4$ is stable, the stability of the combination of $FeAl_2O_4$ and Al_2TiO_5 has no alternative.

According to reaction (15), which is described above, up to a temperature of 1630 K, the combination of $FeAl_2O_4$ – $FeTi_2O_5$ compounds is stable.

Thus, the fourth temperature range, in which the subsolidus structure of the investigated four-component system changes, is 1537 – 1630 K. In accordance with reactions (9), (10), and (16), we establish three “internal” connodes: Mg_2TiO_4 – $FeAl_2O_4$, $FeAl_2O_4$ – $MgTiO_3$ и $FeAl_2O_4$ – $MgTi_2O_5$, which determines the division of the MgO – Al_2O_3 – FeO – TiO_2 system into 13 elementary tetrahedra: MgO – FeO – Mg_2TiO_4 – $MgAl_2O_4$, $FeAl_2O_4$ – Mg_2TiO_4 – FeO – Fe_2TiO_4, $FeAl_2O_4$ – Mg_2TiO_4 – Fe_2TiO_4 – $FeTiO_3$, $FeAl_2O_4$ – Mg_2TiO_4 – $MgAl_2O_4$ – FeO, $FeAl_2O_4$ – $MgTiO_3$ – Al_2TiO_5 – Al_2O_3, $FeAl_2O_4$ – $MgTiO_3$ – Mg_2TiO_4 – $MgAl_2O_4$, $FeAl_2O_4$ – $MgTiO_3$ – Mg_2TiO_4 – $FeTiO_3$, $FeAl_2O_4$ – $MgTiO_3$ – $MgAl_2O_4$ – Al_2O_3, $FeAl_2O_4$ – $MgTi_2O_5$ – $MgTiO_3$ – Al_2TiO_5, $FeAl_2O_4$ – $MgTi_2O_5$ – Al_2TiO_5 – TiO_2, $FeAl_2O_4$ – $MgTi_2O_5$ – $FeTiO_3$ – $FeTi_2O_5$, $FeAl_2O_4$ – $MgTi_2O_5$ – TiO_2 – $FeTi_2O_5$, $FeAl_2O_4$ – $MgTi_2O_5$ – $MgTiO_3$ – $FeTiO_3$.

Above a temperature of 2076 K, we assume the existence of a compound Al_4TiO_8 [12], which determines the fifth temperature range – 1630 – 2076 K and the sixth – above 2076 K.

In the temperature range of 1630 – 2076 K, we take into account reaction (15) according to which (Table 2) above a temperature of 1630 K, the phases Al_2O_3 and $FeTiO_3$ coexist, which introduces its own changes in the subsolidus structure of the three-component subsystem Al_2O_3 – TiO_2 – FeO, and as a consequence, the structure of the investigated four-component system changes. In this case, we take into account reactions (10) and (9), which determines the presence of two "internal" connodes and, accordingly, the partition of the system into 12 elementary tetrahedra: MgO – FeO – Mg_2TiO_4 – $MgAl_2O_4$, Al_2TiO_5 – TiO_2 – $MgTi_2O_5$ – $FeTi_2O_5$, Al_2TiO_5 – $MgTi_2O_5$ – $FeTi_2O_5$ – $FeTiO_3$, Al_2TiO_5 – $MgTi_2O_5$ – $FeTiO_3$ – $MgTiO_3$, Al_2TiO_5 – $MgTiO_3$ – $FeTiO_3$ – Al_2O_3, $FeAl_2O_4$ – $MgTiO_3$ – $MgAl_2O_4$ – Al_2O_3, $FeAl_2O_4$ – $MgTiO_3$ – Al_2O_3 – $FeTiO_3$, $FeAl_2O_4$ – Mg_2TiO_4 – $MgAl_2O_4$ – $MgTiO_3$, $FeAl_2O_4$ – Mg_2TiO_4 – $MgTiO_3$ – $FeTiO_3$, $FeAl_2O_4$ – Mg_2TiO_4 – $FeTiO_3$ – Fe_2TiO_4, $FeAl_2O_4$ – Mg_2TiO_4 – Fe_2TiO_4 – FeO, $FeAl_2O_4$ – Mg_2TiO_4 – FeO – $MgAl_2O_4$.

In the temperature range above 2076 K, the results of calculations of ΔG (Table 2) for reactions involving Al_4TiO_8 unambiguously indicate its maximum thermodynamic stability in combinations with all iron titanates (26) – (28), wustite (29), hercynite (30), magnesium titanates (31) – (33), periclase (34) and aluminum-magnesium spinel (35):

$2Al_2O_3 + 2FeTiO_3 = Fe_2TiO_4 + Al_4TiO_8$, (26)

$2Al_2O_3 + FeTi_2O_5 = FeTiO_3 + Al_4TiO_8$, (27)

$FeTiO_3 + 2Al_2TiO_5 = FeTi_2O_5 + Al_4TiO_8$, (28)

$2Al_2O_3 + FeTiO_3 = FeO + Al_4TiO_8$, (29)

$3Al_2O_3 + FeTiO_3 = FeAl_2O_4 + Al_4TiO_8$, (30)

$MgAl_2O_4 + 5Al_2TiO_5 = 3Al_4TiO_8 + MgTi_2O_5$, (31)

$MgAl_2O_4 + 3Al_2TiO_5 = 2Al_4TiO_8 + MgTiO_3$, (32)

$2MgAl_2O_4 + 4Al_2TiO_5 = 2Al_4TiO_8 + Mg_2TiO_4$, (33)

$MgAl_2O_4 + Al_2TiO_5 = Al_4TiO_8 + MgO$, (34)

$MgAl_2O_4 + 2Al_4TiO_8 = 5Al_2O_3 + MgTi_2O_5$. (35)

Consequently, the four-component system MgO – Al_2O_3 – FeO – TiO_2 is divided into 11 elementary tetrahedra: Al_2O_3 – Al_4TiO_8 – $FeAl_2O_4$ – $MgAl_2O_4$, Al_4TiO_8 – $FeAl_2O_4$ – $MgAl_2O_4$ – FeO, Al_4TiO_8 – $MgAl_2O_4$ – MgO – FeO, Al_4TiO_8 – MgO – FeO – Mg_2TiO_4, Al_4TiO_8 – FeO – Mg_2TiO_4 – Fe_2TiO_4, Al_4TiO_8 – Mg_2TiO_4 – Fe_2TiO_4 – $FeTiO_3$, Al_4TiO_8 – Mg_2TiO_4 – $FeTiO_3$ – $MgTiO_3$, Al_4TiO_8 – $FeTiO_3$ – $MgTiO_3$ – $MgTi_2O_5$, Al_4TiO_8 – $FeTiO_3$ – $MgTi_2O_5$ – $FeTi_2O_5$, Al_4TiO_8 – $MgTi_2O_5$ – $FeTi_2O_5$ – Al_2TiO_5, $MgTi_2O_5$ – $FeTi_2O_5$ – Al_2TiO_5 – TiO_2.

Conclusions

Thus, the conducted thermodynamic analysis of reactions that limit the subsolidus structure of the four-component system MgO – Al_2O_3 – FeO – TiO_2 indicates phase changes in this system occurring in six temperature ranges:

I – 800 – 1141 K, in which the system is divided into 11 elementary tetrahedra;
II – 1141 – 1413 K, with which the system is divided into 10 elementary tetrahedra;
III – 1413 – 1537 K, with which the system is divided into 12 elementary tetrahedra;
IV – 1537 – 1630 K, in which the system is divided into 13 elementary tetrahedra;
V – 1630 – 2076 K, in which the system is divided into 12 elementary tetrahedra;
VI – above 2076 K, in which the system is divided into 11 elementary tetrahedra.

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