N. NURGALI, O. SARIEV, A. MUKHAMBETKALIYEV, B. MOMENOV, A. KUANDYKOVA, R. ABDRASHEV

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PHASE COMPOSITION OF TITANIUM-CONTAINING RAW MATERIALS DEPENDING ON ITS TITANIUM OXIDE CONTENT

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The article deals with the phase equilibrium in titanium-containing slag from metallurgical processing of ilmenite concentrates of Shokash deposit on the basis of five-component system TiO_2-Al_2O_3-SiO_2-MgO-CaO have been studied by thermodynamic analysis (TDA). The phase equilibria in two four-component systems CaO-MgO-Al_2O_3-SiO_2 and TiO_2-MgO-Al_2O3-SiO_2, which are part of the five-component system TiO_2-Al_2O_3-SiO_2-MgO-CaO were clarified and corrected. Thus, the data on the phase compositions of congruently (stably) melting compounds of titanium slag and slag of aluminum- and aluminosilicothermic ferrotitanium as well as slag melts from melting of titanomagnetite ores, etc. have been obtained.

Keywords: titanium slag, phase composition, TiO2-Al2O3-SiO2-MgO-CaO system, multicomponent oxide systems, thermodynamic-diagram analysis

INTRODUCTION

Study of the phase structure of multicomponent solid and liquid solutions formed at various stages of raw material processing is part of the fundamental science in the theory of metallurgical processes. As a rule, initial raw materials, whether ore or concentrate, contain complex oxide compounds instable in the liquid state [1], i.e. decomposing into stable constituent parts after overcoming their liquidus temperature. Generally accepted thermodynamic studies of processes in multicomponent systems are quite complex and require extensive mathematical calculations and are directly related to the need to determine the thermodynamic functions of a large number of independent reactions. In many cases, some data on the properties of compounds required to determine the free energy of Gibbs reactions

are limited or absent, which in such cases excludes the applicability of thermodynamic analysis for the study of multicomponent systems [2].

RESEARCH METHODOLOGY

Real rich titanium slags (RTS), intended mainly for production of sponge titanium, and slags from ferrotitanium production are multi-component system of oxide products for pyrometallurgical treatment of ilmenite concentrates, but they are based on relatively small amount of oxides. The phase composition of RTS and ferrotitanium slags can be characterized by the five-component system TiO_2-Al_2O_3-SiO_2-MgO-CaO. Extensive data on this system and its constituent subsystems are described by A.S. Berezhny [3]. It consists of five quadruple systems: TiO_2-CaO-MgO-Al_2O_3, TiO_2-CaO-MgO-SiO_2, TiO_2-CaO-Al_2O_3-SiO_2, TiO_2-MgO-Al_2O_3-SiO_2 and CaO-MgO-Al_2O_3-SiO_2.

The phase composition of the TiO_2-Al_2O_3-SiO_2-MgO-CaO system and its analytical expressions of secondary components are discussed in [4]. The authors found that this five-component system, taking into account incongruent (unstable) compounds, consists of 58 elementary pentatopes of coexisting phases. Numerical values of coefficients *a*, *b*, *c*, *d* and *e* were found for each of the pentatopes. This allows to calculate the equilibrium phase composition for any combination of TiO_2, Al_2O_3, SiO_2, MgO and CaO oxides in the feed or intermediates.

The complexity of the phase composition of the TiO_2-Al_2O_3-SiO_2-MgO-CaO system, which describes the compositions of titanium-containing raw materials or slags, represented by its boundary quaternary subsystem CaO-MgO-Al_2O_3-SiO_2. This sub-system has been repeatedly corrected and clarified, corrections were related to the high-alumina area [4]. There are also contradictions in its phase composition due to the presence of a SiO_2-MgO·Al_2O_3 binary line (flintstone -spinel) on its boundary triple system MgO-Al_2O_3-SiO_2, which implies the formation of quadruple compounds not existing in nature.

The Thermodynamic analysis (TDA) of complex systems, developed at Zh. Abishev Institute of Chemistry and Metallurgy, has proved to be a simple and thus sufficiently accurate method of studying phase patterns

N. Nurgali, O. Sariev (rafhatsson@mail.ru), A. Mukhambetkaliyev, B. Momenov, Kuandykova A., Abdrashev R, Aktobe regional of university named K.Zhubanov, Aktobe, Kazakhstan

Table 1 **Three and five tetrahedron in the CaO-MgO-Al_2O_3-SiO_2 and TiO_2-MgO-Al_2O_3-SiO_2**

TiO_2-MgO-Al_2O_3-SiO_2	CaO-MgO-Al_2O_3-SiO_2
1 $MgO·2TiO_2$-$MgO·Al_2O_3$-$Al_2O_3·TiO_2$-SiO_2 (0,19) 2 $MgO·2TiO_2$-$Al_2O_3·TiO_2$-TiO_2-SiO_2 (0,11) 3 $MgO·2TiO_2$-$2MgO·SiO_2$-$MgO·Al_2O_3$-SiO_2 (0,33)	1 MgO-$2CaO·SiO_2$-$2CaO·Al_2O_3·SiO_2$-$CaO·Al_2O_3$ (0,046) 2 MgO-$2CaO·SiO_2$-$2CaO·MgO·2SiO_2$-$2CaO·Al_2O_3·SiO_2$ (0,05) 3 MgO-$2CaO·Al_2O_3·SiO_2$-$CaO·Al_2O_3$-$MgO·Al_2O_3$ (0,055) 4 MgO-$2CaO·SiO_2$-$2CaO·MgO·2SiO_2$-$2CaO·Al_2O_3·SiO_2$- $MgO·Al_2O_3$ (0,064) 5 MgO-$2MgO·SiO_2$-$2CaO·MgO·2SiO_2$-$MgO·Al_2O_3$ (0,125)

in comparison with classical thermodynamic studies of metallurgical processes [5-10].

The phase equilibria in two four-component systems CaO-MgO-Al_2O_3-SiO_2 and TiO_2-MgO-Al_2O_3-SiO_2, which are part of the five-component system TiO_2-Al_2O_3-SiO_2, have been specified and corrected by theoretical studies [11-14]. Based on the new data obtained, three and five new tetrahedrons are formed in the CaO-MgO-Al_2O_3-SiO_2 and TiO_2-MgO-Al_2O_3-SiO_2 systems, respectively (their relative volumes are given in parentheses) Table 1.

The sum of the relative volumes of stable tetrahedrons including each boundary subsystem calculated using the «center of gravity» and «Heath» methods identically must be 1. Phase composition of each of the tetrahedrons can be described by substituting the corresponding coefficients in equation [15]:

$$X_i = a_i C_o + b_i M_o + c_i A_o + d_i S_o \qquad (1)$$

which is the Heath equation of transformation, where X_i – is the quantity of the secondary phase produced; a_i, b_i, c_i, d_i – transformation ratios; C_o, M_o, A_o, S_o – the amount of primary oxide components in the melt.

Thus, the phase equilibrium data obtained from the congruent (stable) melting compounds of the pentacle system TiO_2-Al_2O_3-SiO_2-MgO-CaO, which simulates the compositions of titanium slags and aluminium, aluminosilicothermal ferrotitanium slags, as well as slag melts from smelting titanium magnetite ores, etc., led to the conclusion that this system consists of 30 stable pentatopes (pentameters).

RESULTS RESEARCH

The practical application of TDA results in relation to titanium slags is to find elementary pentatopes, inside which their compositions are located. The normative distribution of the primary phases between the secondary compounds for them is equal to 100″% of the pentatope under the study. To determine the phase composition of slags or other titanium-containing industrial products, it is necessary to recalculate their weighted average material compositions from Table 1 into five primary oxides of the TiO_2-Al_2O_3-SiO_2-MgO-CaO system.

Using the input data from Table 2 in thermodynamic and diagram analysis of phase composition calculation, the results presented in Table 3 are obtained. The table shows the chronology of changes in relative phase compositions as a function of TiO2 content in materials ranging from titanium ore to RTS.

In some cases, with an increase in silica content of slags (SiO_2 of more than 5 %), in all RTS the pheno phase ($CaO·TiO_2$) prevails over the perovskite phase ($CaO·TiO_2·SiO_2$) and their compositions are transferred to the pentatope $MgO·2TiO_2$-$CaO·TiO_2·SiO_2$-$Al_2O_3·TiO_2$-TiO_2-SiO_2.

When processing RTS compositions and slags from ferrotitanium production (Table 2) from concentrates of the Shokash deposit by means of TDA, it was established that:

1 RTS is modeled by pentatope $MgO·2TiO_2$-$Al_2O_3·TiO_2$-$CaO·TiO_2$-TiO_2-SiO_2 (V = 0,046). The transformation equations to calculate the equilibrium ratios of secondary components through the primary component are as follows:

Table 2 **Weighted average chemical composition of slags received from melting of Shokash concentrates**

Slag	TiO_2	CaO	MgO	Al_2O_3	SiO_2
Shokash RTS	88,86	0,27	0,3	6,254	4,31
High percentage FeTi•	17,5	20	3,7	56,3	2,5
Low percentage FeTi ••	22,95	17,4	3,45	45,8	10,4

Note• - using the technology of obtaining high percentage ferrotitanium by aluminium-thermal method from rich titanium slag;
Note•• - using a technology to produce low-percent ferrotitanium using ferrosilico-aluminium

Table 3 **Change in relative phase compositions as the amount of TiO_2 increases**

Contents TiO_2, %	Pentatopes and their volumes	
From 5 to 25	MgO-$2CaO·MgO·2SiO_2$-$2MgO·SiO_2$-$CaO·TiO_2$- $MgO·Al_2O_3$	(0,074)
from 25 to 45	$2MgO·SiO_2$-$CaO·Al_2O_3·2SiO_2$-$CaO·TiO_2$-$MgO·2TiO_2$-$MgO·Al_2O_3$	(0,065)
from 45 to 60	$MgO·2TiO_2$-$MgO·Al_2O_3$-$Al_2O_3·TiO_2$-$CaO·TiO_2$- SiO_2	(0,078)
from 60 to 65	$Al_2O_3·TiO_2$-$CaO·TiO_2·SiO_2$-$MgO·2TiO_2$-$CaO·TiO_2$-TiO_2	(0,014)
from 65 to 75	$MgO·2TiO_2$-$CaO·TiO_2·SiO_2$-$Al_2O_3·TiO_2$-TiO_2-SiO_2	(0,032)
from 75 and above•	$MgO·2TiO_2$-$Al_2O_3·TiO_2$-$CaO·TiO_2$-TiO_2-SiO_2	(0,046)

Note • - SiO_2 content is assumed to be less than 5 % in the calculation.

$$MgO \cdot 2TiO_2 = 4{,}97512 \cdot M_0$$

$$Al_2O_3 \cdot TiO_2 = 1{,}78253 \cdot A_0$$

$$CaO \cdot TiO_2 = 2{,}42718 \cdot C_0$$

$$TiO_2 = 1{,}0 \cdot T_0 - 0{,}78253 \cdot A_0 - 3{,}97512 \cdot M_0 - 1{,}42718 \cdot C_0$$

$$SiO_2 = 1{,}0 \cdot S_0$$

where: M_0, A_0, C_0, S_0 and T_0 - primary oxides content in slags. Relative pentatopic volume V = 0,046458.

It follows that RTS in the area of liquidus temperatures includes the phases, %: carcite ($MgO \cdot 2TiO_2$) - 1,5; tealite ($Al_2O_3 \cdot TiO_2$) - 11,14; perovskite ($CaO \cdot TiO_2$) - 0,65; free rutile (TiO_2) - 82,38 and silica (SiO_2) - 4,31.

2 Slags of low percentage ferrotitanium using ferrosilico-aluminium technology are located in pentatope $Al_2O_3 \cdot TiO_2$-$CaO \cdot Al_2O_3 \cdot 2SiO_2$-$MgO \cdot Al_2O_3$ -$CaO \cdot TiO_2$-Al_2O_3. Transformation equations have been derived to calculate the equilibrium ratios of secondary components of this system. Relative pentatopic volume V = 0,022061.

$$Al_2O_3 \cdot TiO_2 = 2{,}27790 \cdot T_0 + 1{,}52367 \cdot S_0 - 3{,}25099 \cdot C_0$$

$$CaO \cdot Al_2O_3 \cdot 2SiO_2 = 2{,}32019 \cdot S_0$$

$$MgO \cdot Al_2O_3 = 3{,}53357 \cdot M_0$$

$$CaO \cdot TiO_2 = -1{,}13757 \cdot S_0 + 2{,}42718 \cdot C_0$$

$$Al_2O_3 = -1{,}27790 \cdot T_0 + 1{,}0 \cdot A_0 - 1{,}70628 \cdot S_0 - 2{,}53357 \cdot M_0 + 1{,}82381 \cdot C_0$$

Slags generated in the area of liquidus temperatures include phases, %: tealite ($Al_2O_3 \cdot TiO_2$) - 11,55; anonymite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) - 24,12; spinel ($MgO \cdot Al_2O_3$) - 12,19; perovskite ($CaO \cdot TiO_2$) - 30,4 and free alumina (Al_2O_3) - 21,72.

3 Aluminium-thermal high percentage ferrotitanium slags from RTS from the processing of ilmenite concentrates from the Shokash deposit are located in pentatope $CaO \cdot 2Al_2O_3$-$MgO \cdot Al_2O_3$-$2CaO \cdot Al_2O_3 \cdot SiO_2$-$Al_2O_3$-$CaO \cdot TiO_2$. The equations calculating the phase composition of the slag generated through primary component are as follows:

$$CaO \cdot 2Al_2O_3 = -3{,}24389 \cdot T_0 - 8{,}64620 \cdot S_0 + 4{,}62963 \cdot C_0$$

$$MgO \cdot Al_2O_3 = 3{,}53357 \cdot M_0$$

$$2CaO \cdot Al_2O_3 \cdot SiO_2 = 4{,}56621 \cdot S_0$$

$$Al_2O_3 = 2{,}54321 \cdot T_0 + 1{,}0 \cdot A_0 + 5{,}07999 \cdot S_0 - 2{,}53357 \cdot M_0 - 3{,}62963 \cdot C_0$$

$$CaO \cdot TiO_2 = 1{,}70068 \cdot T_0$$

The relative volume of pentatopes is equal V = 0,007872.

Consequently, the resulting slags in the area of liquidus temperatures consist of phases, %: ibonite ($CaO \cdot 2Al_2O_3$) - 14,21; spinels ($MgO \cdot Al_2O_3$) - 13,07; gelenit ($2CaO \cdot Al_2O_3 \cdot SiO_2$) - 11,41; perovskit ($CaO \cdot TiO_2$) - 29,76 and free alumina (Al_2O_3) - 31,54.

CONCLUSION

It follows from presented theoretical data, that TDA, which neglects a complex mathematical apparatus, allows to use diagrams of multi-component systems phase structure to determine the optimal areas of more technological slag compositions. Further, taking into account data on the melting temperatures of secondary components and their ratios in the elementary volume, it is possible to predict the relative melting temperatures and viscosity of the resulting slags.

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