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THERMODYNAMIC STUDIES OF THE POSSIBILITY OF FORMING INORGANIC MATERIALS BY SHS WITH A REDUCTION STAGE

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For synthesizing powders of refractory inorganic materials by the SHS method with a reduction stage, compounds of the necessary elements are used as an initial raw material. Thermodynamic analysis was used, which allows thermodynamically optimal conditions (initial temperature, pressure, component proportion) for synthesizing a required compound to be found.

The scientific and technological progress responsible for development of many important fields of technology in recent decades has increased the importance of materials. New and updated materials can be widely used under new operating conditions such as high temperatures, processes with sharp temperature gradients, aggressive media, etc.

In this respect ceramic materials are of particular interest.

The SHS method, in particular, that with a reduction stage, is among the most promising for production of such compounds. Unlike the classical SHS, in this case various compounds (oxides, halogenides, etc.) of the necessary elements are used instead of elements (metals and nonmetals) as initial raw materials for synthesis of refractory inorganic powders.

Schematically these processes can be presented as follows:

$$\sum_{i=1}^{q_i} \nu_i A_i + \sum_{j=1}^{q_j} \nu_j B_j + \sum_{k=1}^{q_k} \nu_k C_k \rightarrow \sum_{m=1}^{q_m} \nu_m D_m + \sum_{n=1}^{q_n} \nu_n E_n, \tag{1}$$

A_i are TiO_2, ZrO_2, CaO, B_2O_3, WO_3, SiO_2, La_2O_3, $LaCl_3$, ZrF_4, KBF_3, ..., B_j are Mg, Ca, Al, CaH_2, Zn, ..., C_k are B, Si, N_2, C, SiO_2, B_2O_3, ..., D_m are carbides, borides, silicides, nitrides, ..., E_n are corresponding compounds of the reductant.

It follows from scheme (1) that SHS processes with a reduction stage are essentially multicomponent ones, yielding multiphase products.

Due to the evident complexity of the theoretical analysis of the relations governing the combustion process in complex heterogeneous systems, thermodynamic analysis, which determines thermodynamically optimal conditions of the process in every case, has become popular [1, 2].

The problem of the thermodynamic analysis of a combustion process can be formulated in the following way: on the basis of a prescribed proportion of the initial components, pressure or volume of the gas phase, and initial temperature, it is necessary to obtain the equilibrium composition of the products and the adiabatic temperature of combustion, corresponding to a minimum thermodynamic potential of the system and the energy conservation equation. It should be noted that the set of possible condensed and gaseous products of the synthesis is determined by the level of knowledge on the existence of compounds of elements and their thermodynamic properties at a particular temperature. Thermodynamic functions and constants borrowed from known sources [3-6] were used in the calculations. All the calculations were carried out on a PC AT 286, using a program specially developed for calculation of thermodynamic equilibrium in complex multicomponent heterophase systems.

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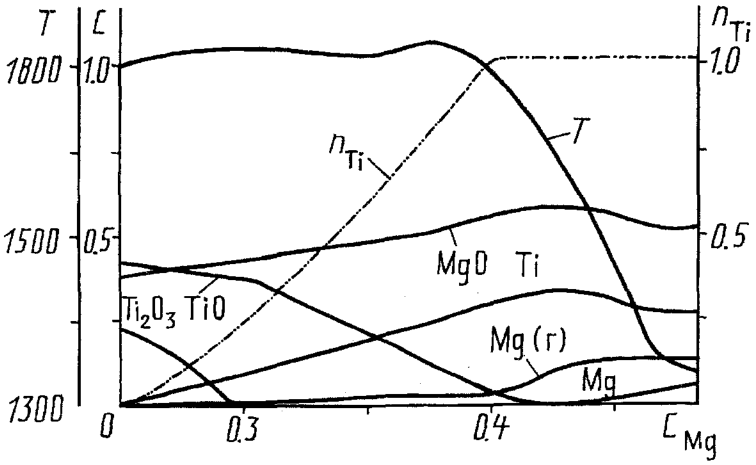

Fig. 1. Equilibrium diagram of combustion products in the TiO_2-Mg system, T_0 = 298.15 K, P_0 = 0.1 MPa: C) mass fraction of the combustion products, C_{Mg}) mass fraction of magnesium in the initial charge, n_{Ti}) titanium yield (in fractions). T, K.

TABLE 1

System	Component ratio, wt.%		T_{max}, K	$\eta_{prod.}$ at T_{max}, %	T_c (K) at η_{prod} = 100 %
	at T_{max}	at η = 100%			
TiO_2+Ca	0.449: 0.501	0.490: 0.510	2400	99.6	2360
ZrO_2+Ca	0.606: 0.394	0.590: 0.410	1570	99.8	1520
Ta_2O_5+Ca	0.688: 0.312	0.688: 0.312	2860	100	2860
WO_3+Ca	0.658: 0.342	0.640: 0.360	3650	98.5	3580
TiO_2+Mg	0.600: 0.400	0.580: 0.420	1840	90.9	1760
ZrO_3+Mg	0.717: 0.283	0.717: 0.283	1154	100	1154
Ta_2O_5+Mg	0.750: 0.250	0.720: 0.280	2620	99.6	2150
B_2O_3+Ca	0.367: 0.633	0.300: 0.700	2626	91.3	2236
B_2O_3+Mg	0.488: 0.512	0.420: 0.580	2208	85.0	2080
H_3BO_3+Ca	0.330: 0.670	0.280: 0.720	2390	84.9	2140
H_3BO_3+Mg	0.450: 0.550	0.400: 0.600	2050	75.4	2000
SiO_2+Mg	0.550: 0.450	0.550: 0.450	2110	100	2110
ZrF_4+Ca	0.676: 0.324	0.676: 0.324	2253	100	2253
$TiCl_2$+Ca	0.720: 0.280	0.710: 0.290	2130	97.6	2110

The thermodynamic analysis of reductive SHS processes can be classified, depending on the type of initial system, as follows:

1. Formation of elementary (metal or nonmetal) materials.
2. Formation of refractory inorganic materials: a) carbides; b) nitrides; c) borides; d) silicides.
3. Formation of composite materials on the basis of refractory compounds with aluminum oxide.

As a rule, class 1 includes the following two-component reductive systems that can be singled out from the general scheme (1):

$$\sum_{i=1}^{q_i} \nu_i A_i + \sum_{j=1}^{q_j} \nu_j B_j + \sum_{k=1}^{q_k} \nu_k C_k \rightarrow \sum_{m=1}^{q_m} \nu_m D_m + \sum_{n=1}^{q_n} \nu_n E_n. \qquad (2)$$

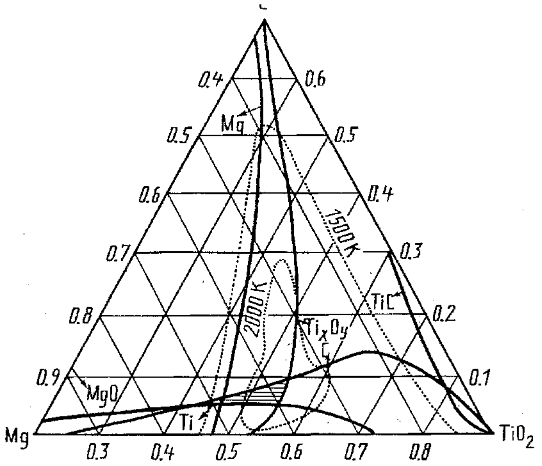

Fig. 2. Equilibrium diagram of condensed combustion products in the TiO_2-Mg-C system, $T_0 = 298.15$ K, $P_0 = 0.1$ MPa.

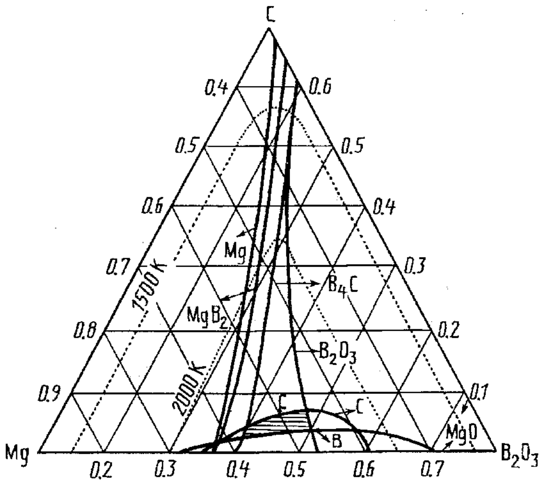

Fig. 3. Equilibrium diagram of condensed combustion products in the B_2O_3-Mg-C system, $T_0 = 298.15$ K, $P_0 = 0.1$ MPa.

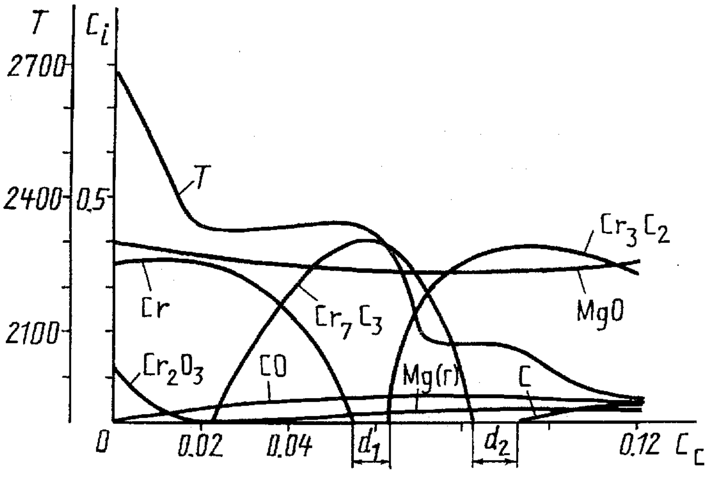

Fig. 4. Fragment of the equilibrium diagram of condensed combustion products in the Cr_2-Mg-C system, $C_{Mg} = 0.18 =$ const, $T_0 = 298.15$ K, $P_0 = 0.1$ MPa (C_c is the mass fraction of carbon in the initial charge, C_i is the combustion product mass fraction).

TABLE 2

System	Component ratio, wt. %		T_{max}, K	η_{prod} at T_{max}, %	Tc (K) at η_{prod} = 100%
	at T_{max}	at η = 100%			
TiO_2+Ca+C	0.46: 0.46: 0.08	0.46: 0.46: 0.08	2680	100	2680
TiO_2+Ca+CH_4	0.48: 0.48: 0.04	0.45: 0.45: 0.10	2200	41.4	1990
ZrO_2+Ca+C	0.57: 0.37: 0.06	0.57: 0.37: 0.06	2330	100	2330
ZrO_3+Ca+CH_4	0.58: 0.37: 0.05	0.55: 0.35: 0.10	1650	66.7	1400
Ta_2O_5+Ca+C	0.68: 0.31: 0.01	0.65: 0.29: 0.06	2860	TaC and Ta_2C	2370
Ta_2O_5+Ca+CH_4	0.67: 0.31: 0.02	0.62: 0.28: 0.10	2830	TaC and Ta_2C	1820
TiO_2+Mg+C	0.56: 0.35: 0.09	0.54: 0.32: 0.14	2250	91.7	2020
ZrO_2+Mg+C	0.65: 0.26: 0.09	0.65: 0.26: 0.09	2030	100	2030
Ta_2O_5+Mg+C	0.77: 0.21: 0.02	0.72: 0.20: 0.08	2950	TaC and Ta_2C	2020
$NbCl_5$+Mg+C	0.70: 0.25: 0.05	0.70: 0.25: 0.05	2110	100	2110
NbF_5+Mg+C	0.62: 0.33: 0.05	0.62: 0.33: 0.05	2200	100	2200
ZrF_4+MG+C	0.72: 0.21: 0.07	0.71: 0.20: 0.09	1940	99.6	1890
$NbCl_5$+Ca+C	0.64: 0.33: 0.03	0.64: 0.33: 0.3	2950	100	2950

TABLE 3

System	Component ratio, wt. %		T_{max}, K	η_{prod} at T_{max}, %	Tc (K) at η_{prod} = 100%
	at T_{max}	at η = 100%			
TiO_2+Ca+N_2	0.450: 0.450: 0.100	0.200: 0.200: 0.600	2820	71.2	1870
TiO_2+Ca+NH_3	0.450: 0.450: 0.100	0.400: 0.400: 0.200	2560	85.9	2170
ZrO_2+Mg+N_2	0.653: 0.257: 0.090	0.358: 0.142: 0.500	2190	75.7	1719
Ta_2O_5+Ca+N_2	0.660: 0.300: 0.040	0.413: 0.187: 0.400	3115	65.8	2185
ZrB_4+Ca+N_2	0.642: 0.308: 0.050	0.439: 0.211: 0.350	2770	92.3	2290
ZrB_4+Mg+N_2	0.721: 0.209: 0.070	0.426: 0.124: 0.450	2130	91.2	1640
$NbCl_5$+Mg+N_2	0.703: 0.247: 0.050	0.629: 0.221: 0.150	2270	89.9	2120
$ZrCl_4$+Mg+N_2	0.786: 0.164: 0.050	0.654: 0.136: 0.210	1654	96.2	1530
B_2O_3+Mg+N_2	0.336: 0.464: 0.200	0.168: 0.232: 0.600	2310	78.0	2040
B_2O_3+Ca+N_2	0.255: 0.535: 0.150	0.165: 0.338: 0.445	2600	82.5	2340
BCl_3+Mg+N_2	0.657: 0.243: 0.100	0.474: 0.176: 0.350	2410	85.2	2140

Scheme (2) differs from (1) in that D_m denotes not carbides, borides, silicides, nitrides, etc., but elements Ti, Zr, B, Si, ... For example, $TiO_2 + 2Mg = Ti + 2MgO$, $ZrF_4 + 2Ca = Zr + 2CaF_2$, $2KBF_4 + 3MG = 2B + 3MgF_2 + 2KF$.

Results of thermodynamic calculations of combustion of these systems can be expressed by a diagram of the equilibrium combustion products. As an example, results of calculating the equilibrium characteristics for the system $TiO_2 + 2Mg = Ti + 2MgO$ are given in Fig. 1. In a fragment of the diagram of the equilibrium combustion products, the temperature and composition of the combustion products are shown as a function of the magnesium content in the initial mixture. The percentage of magnesium in the initial mixture influences the yield of reduced metallic titanium, which amounts to 1.0 (100%) with a certain content of initial magnesium. The calculations were carried out for a large class of systems and some of the results are presented in Table 1. For each system the table contains the maximum values of the combustion temperature and the corresponding yields of products, the combustion temperatures at the maximum product yield, and the component ratios in the initial mixture at a pressure of 0.1 MPa.

Formation of Carbides. In Figs. 2 and 3 results of the thermodynamic calculations are presented as diagrams of equilibrium condensed combustion products for the TiO_2-Mg-C and B_2O_3-Mg-C systems, respectively.

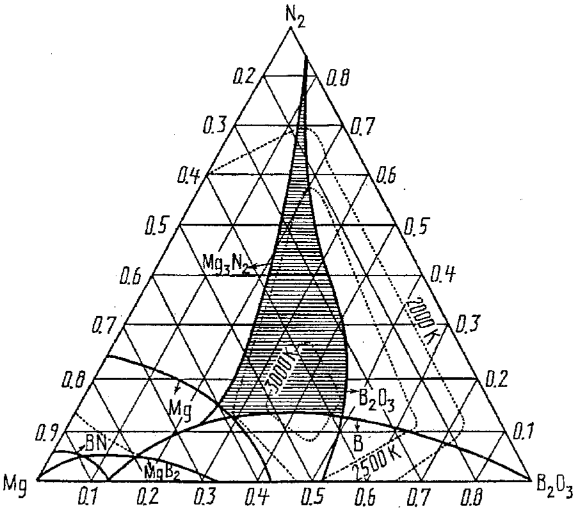

Fig. 5. Equilibrium diagram of condensed combustion products in the B_2O_3-Mg-N_2 system, $T_0 = 298.15$ K, $P_0 = 0.1$ MPa.

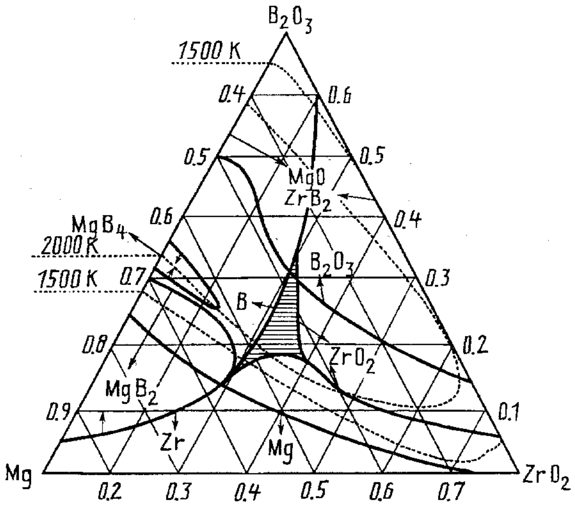

Fig. 6. Equilibrium diagram of condensed combustion products in the ZrO_2-Mg-B_2O_3 system, $T_0 = 298.15$ K, $P_0 = 0.1$ MPa.

In the diagram the areas of the existence of condensed combustion products are shown as a function of the initial component ratio. The crosshatched areas show the initial component ratios for which the titanium carbide or boron carbide end product is formed without side products, except for magnesium oxide which may be separated from the end product by acid enrichment. In the diagrams isotherms of adiabatic combustion temperatures temperatures (dotted lines) are also presented, from which it can be inferred whether SHS combustion is possible.

Contents of gaseous and condensed products and temperature as a function of the initial component contents are shown in the section of the diagram of condensed combustion products for the Cr_2O_3-Mg-C system (Fig. 4). It is seen from Fig. 4 that at a constant value of the magnesium content in the initial mixture ($C_{Mg} = 0.18$ = const), depending on the carbon proportion, there are areas δ_1 and δ_2 where the Cr_2C_3 and Cr_7C_3 end products are formed without side products, except for magnesium oxide.

Table 2 contains the predicted adiabatic temperatures and the corresponding carbide yields in combustion of particular systems (at $P_0 = 0.1$ MPa, $T_0 = 298.15$ K).

Formation of Nitrides. The equilibrium diagram of condensed combustion products (the end product is boron nitride) for the B_2O_3-Mg-N_2 system is presented in Fig. 5. The crosshatched area in the diagram shows the optimal region of boron nitride production without side products (except for magnesium oxide).

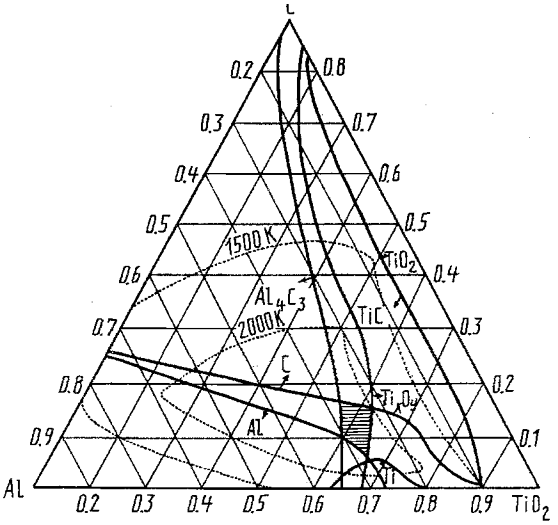

Fig. 7. Equilibrium diagram of condensed combustion products in the TiO_2-Al-C system, $T_0 = 298.15$ K, $P_0 = 0.1$ MPa.

Results of the thermodynamic analysis (maximum adiabatic combustion temperatures and nitride yield) of combustion for particular systems are given in Table 3. As follows from the results, the nitride yield at the maximum combustion temperature is not always 100%. This fact is due to dissociation of the end product at high combustion temperatures. As thermodynamic calculations show, nitride dissociation can be decreased by decreasing the temperature or increasing the nitrogen pressure in the reaction medium.

Formation of Borides. Thermodynamic calculations showed that borides of many metals of the second, fourth, fifth, and sixth groups of the periodic table could be formed in the SHS process with a reduction stage. Results of the thermodynamic calculations of combustion of the ZrO_2-Mg-B_2O_3 system are given in Fig. 6. The optimal region of variation of the initial component contents is crosshatched. In this region zirconium diboride is formed without side products (except for magnesium oxide).

Formation of Silicides. Thermodynamic calculations of combustion of reductive systems in which metal silicides are formed were carried out in a similar way. They showed that Ti, Zr, V, Nb, Ta, Cr, Mo, W, etc. silicides could be produced in combustion, using oxides of these metals and silicon oxide as raw materials.

Adiabatic combustion temperatures of these systems are sufficiently high. In systems with titanium and zirconium oxides T_{ad} is about 2000 K and in systems with chromium and molybdenum oxides the combustion temperature amounts to nearly 2500-2600 K (at $P_0 = 0.1$ MPa).

Formation of all silicides of the metals mentioned was taken into account in determining the optimal regions. Using the MoO_3-Mg-SiO_2 system as an example, according to the practical importance of the end products (molybdenum silicides), three regions of variation of the initial component contents for which $MoSi_2$, Mo_5Si_3, and a composition of these silicides can be synthesized can be distinguished.

Formation of Composite Materials Based on Refractory Compounds with Aluminum Oxide. Thermodynamic calculations showed that under conditions of combustion of reductive SHS systems nitride, carbide, boride, and silicide compositions with aluminum oxide could be synthesized. These compositions can be expressed by the formula $MeX \cdot Al_2O_3$, where Me is B, Si, Ti, Zr, Nb, Cr, ...; X is N, C, B, Si. B and Si function as nonmetals (X) in boride and silicide compositions and as metals (Me) in the other systems, for example, $B_4C \cdot Al_2O_3$, $SiC \cdot Al_2O_3$, $TiB_2 \cdot Al_2O_3$, and $ZrSi_2 \cdot Al_2O_3$.

Results of thermodynamic calculations for the TiO_2-Al-C system are presented as an equilibrium diagram of condensed combustion products in Fig. 7. As in the systems considered above, the crosshatched area is that with the initial component content for which the pure end product is formed ($TiC \cdot Al_2O_3$ composition). As can be seen from the diagram, sufficiently high combustion temperatures (> 2000 K) occur in this region and consequently, the conclusion can be made that for this ratio of the initial components SHS can be implemented.

It follows from the results presented that thermodynamic analysis is a reliable means for testing the feasibility of SHS in complex heterophase systems and can be used for determining optimal conditions (initial temperature, pressure, component ratios) for synthesis of a particular compound.

Results of the calculations were used for conducting the synthesis of the materials mentioned here and showed good agreement with experiment [7-11].

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