

THERMODYNAMIC ANALYSIS OF PREPARATION OF TWO KEY REFRACTORY BORON COMPOUNDS

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ABSTRACT

Thermodynamic calculations are performed to determine the optimal conditions for carrying out two chemical reactions to obtain boron carbide and titanium diboride, important refractory boron compounds, in combination with aluminum oxide. The accompanying phase transformations at a fixed pressure are established as a function of temperature.

KEYWORDS: thermodynamic analysis, temperature, enthalpy, Gibbs free energy, chemical reaction, boron carbide, titanium diboride, aluminum oxide

INTRODUCTION

Boron compounds have many promising industrial applications [1]. Many of them are materials based on boron carbide B_4C [2–4]. Perhaps the second most common boron compound is titanium diboride TiB_2 , which is often found in composites containing boron carbide as well [5–8]. In this paper, we consider two examples of chemical reactions of the formation of B_4C and TiB_2 , respectively, together with aluminum oxide Al_2O_3 , an important component of boron-containing composite ceramics.

It should be emphasized that the present introduction of this short communication does not aim to exhaust the vast number of reports on composites containing boron carbide and titanium diboride. The above are only citations of recent works by authors on boron containing composite materials, which led them to the problem considered here.

In general, thermodynamic calculations allow us to determine the conditions for various chemical reactions in a given system of reagents and the nature of the accompanying phase transformations depending on temperature. In this paper, such an analysis is carried out for the processes of obtaining two important refractory boron compounds – boron carbide and titanium diboride – in combination with aluminum oxide.

APPROACH

We used a standard approach in which the energy and spontaneity of chemical reactions are described by thermodynamic parameters. The key parameters are enthalpy H , entropy S , and Gibbs free energy G , which are responsible for heat release, disorder, and overall spontaneity, respectively. They help predict

whether a reaction will occur spontaneously and under what conditions.

Enthalpy represents the heat content of a physical system at constant pressure. A negative enthalpy change ΔH indicates an exothermic reaction (heat is released), while a positive ΔH indicates an endothermic reaction (heat is absorbed). Entropy measures the disorder or randomness of a system. A positive entropy change ΔS indicates an increase in disorder, while a negative ΔS indicates a decrease. Gibbs free energy combines enthalpy and entropy to determine the overall spontaneity of a reaction. A negative Gibbs free energy change ΔG indicates a spontaneous reaction, while a positive ΔG indicates a non-spontaneous reaction. The Gibbs free energy equation $\Delta G = \Delta H - T\Delta S$ shows the interplay between enthalpy, entropy, and temperature T in determining spontaneity. A reaction is more likely to be spontaneous at lower temperatures if it is exothermic (negative ΔH) and increases in disorder (positive ΔS).

Understanding these parameters is crucial for:

- Predicting reaction feasibility or determining whether a reaction will occur under given conditions.
- Optimizing reaction conditions or adjusting temperature, pressure, and concentrations.
- Designing chemical processes via developing efficient and sustainable chemical reactions.

As 3 parameters ΔH , ΔS , and ΔG at fixed temperature T are related with each other, only 2 of them are independent. Following a standard approach, we chose ΔH and ΔG to characterize chemical reactions under the study. In particular, a general scheme of possible reactions was developed.

Thermodynamic calculations were carried out using the complex program ASTRA-4 in the temperature range of 800–6000 K at a pressure of 1 atm.

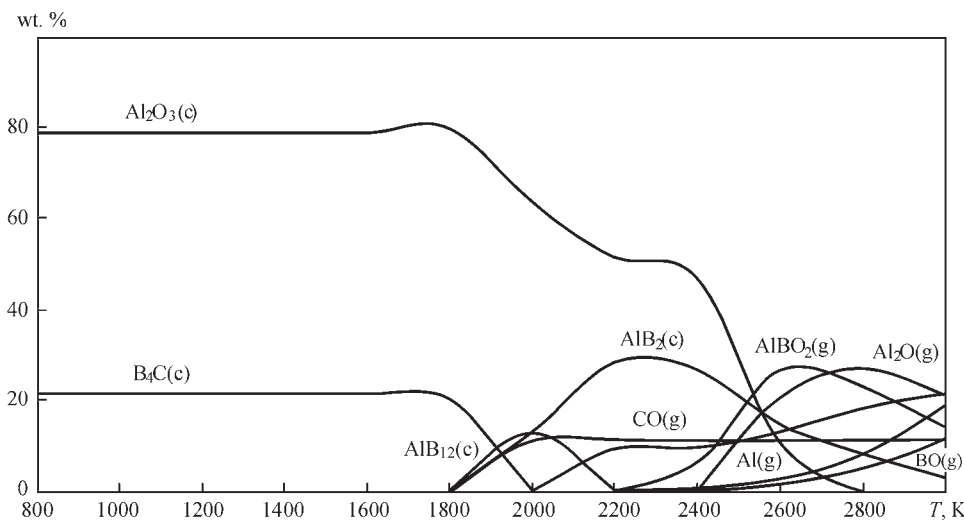
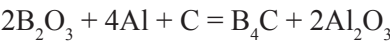


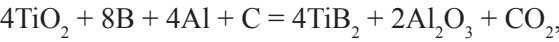
Figure 1. Change in content of gaseous (g) and condensed (c) phases formed during the process of obtaining boron carbide in temperature range of 800–3000 K

RESULTS OF THERMODYNAMIC CALCULATIONS AND THEIR DISCUSSION

The processes of obtaining boron carbide B_4C and titanium diboride TiB_2 selected for investigation are based on the reactions



and



respectively. Below, the results of the thermodynamic analysis performed are presented in the form of diagrams (Figures 1 and 2) and Tables 1, 2, 3 and 4.

The process diagram for obtaining B_4C (Figure 1) shows that the reaction products are mostly released in condensed form in the temperature range of 800–2800 K, while above 1800 K, the gas phases are mainly obtained. The optimal temperature range for synthesizing the target products, i.e. boron carbide and aluminum oxide, is 800–1600 K.

For this case, we calculated the reaction enthalpy ΔH (Table 1) and Gibbs free energy ΔG (Table 4) at some different temperatures, which allowed us to determine the possibility of its conduction and the nature of the process.

From this it can be seen that, on the one hand, the process is exothermic ($\Delta H < 0$) in the entire temperature range of the study: 800–3000 K. On the other hand, in the range 800–2400 K, $\Delta G < 0$ and, therefore, the reaction proceeds, but above 2400 K, when $\Delta G > 0$, it ceases.

The diagram of Figure 2 shows that the main products of the reaction to produce TiB_2 are mostly released in condensed form in the temperature range of 800–4000 K, while above 2400 K, gaseous phases are predominantly obtained. The optimal temperature range for synthesizing the target phases (in this case, titanium diboride and aluminum oxide) can be considered to be 1200–2000 K.

Table 1. Calculated enthalpy of reaction to produce boron carbide

Temperature T , K	Enthalpy ΔH , kcal
800	–201
1000	–203
1200	–211
1400	–230
1600	–267
1800	–332
2000	–437
2200	–594
2400	–821
2600	–1135
2800	–1556
3000	–2104

Table 2. Calculated Gibbs free energy of reaction to produce boron carbide

Temperature T , K	Gibbs free energy ΔG , kcal
800	–183
1000	–178
1200	–173
1400	–165
1600	–154
1800	–136
2000	–109
2200	–69
2400	–12
2600	+68
2800	+176
3000	+317

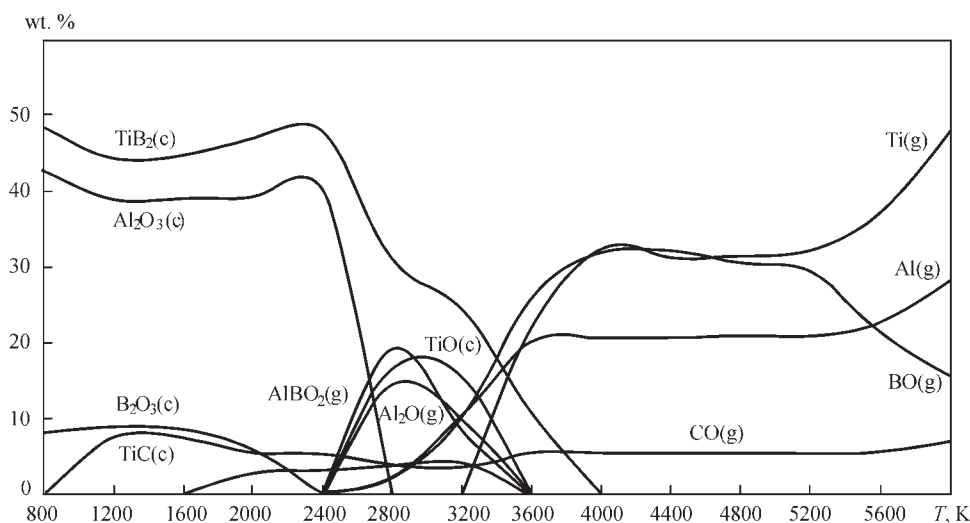


Figure 2. Change in gaseous (g) and condensed (c) phases formed during the process of obtaining titanium diboride in temperature range of 800–6000 K

Table 3. Calculated enthalpy of reaction to produce titanium diboride

Temperature T , K	Enthalpy ΔH , kcal
800	–264
1200	–269
1600	–281
2000	–307
2400	–353
2800	–417
3200	–489
3600	–541
4000	–514
4400	–278
4800	+438
5200	+2119
5600	+5567
6000	+11992

The values obtained by calculating the ΔH (Table 3) and ΔG (Table 4) parameters of this reaction determine the possibility of its conduction at different temperatures and the nature of its course.

As can be seen from the results obtained, the process is exothermic in the temperature range of 800–4400 K, where $\Delta H < 0$ (Table 3). The reaction itself proceeds completely in the studied temperature range, since always $\Delta G < 0$ (Table 4).

CONCLUSIONS

The first of above-considered high-temperature reactions, $2\text{B}_2\text{O}_3 + 4\text{Al} + \text{C} = 2\text{Al}_2\text{O}_3 + \text{B}_4\text{C}$, is often carried out using SHS (Self-propagating High-temperature Synthesis) to efficiently produce boron carbide and its composites. It is a thermite-type metallothermic reduction where boron oxide B_2O_3 is reduced by aluminum Al with carbon C, as a carbide producing

Table 4. Calculated Gibbs free energy of reaction to produce titanium diboride

Temperature T , K	Gibbs free energy ΔG , kcal
800	–269
1200	–271
1600	–271
2000	–265
2400	–253
2800	–232
3200	–200
3600	–161
4000	–119
4400	–88
4800	–97
5200	–201
5600	–494
6000	–1129

reactant, to form boron carbide B_4C and aluminum oxide Al_2O_3 . First, aluminum acts as a strong reducing agent for boron oxide, removing oxygen. The carbon then reacts with the boron to form the desired boron carbide product.

The methods of synthesis of boron carbide powders were surveyed in the mini-review [9]. Based on the morphological peculiarities of the products obtained, in particular, by metal- and carbothermic reductions, it was found [10] that the chemical oven method can readily heat reactants used in combustion synthesis of B_4C powder (as well as forming sintered $\text{TiC}-\text{Al}_2\text{O}_3$ as a precursor for composite material). Finer powder of B_4C was formed under higher compacting pressure on green compact. In addition, since the extent of expansion of reactant compact increased as the theoretical density of the reactant compact increased, a higher

packing compact can easily be crushed to powders after combustion reaction.

Composite of $B_4C-Al_2O_3$ was prepared [11] by SHS from ball-milled powder mixture $B_2O_3/Al/C$ with components ratio corresponding to the reaction: $2B_2O_3 + 4Al + C = B_4C + 2Al_2O_3$. $B_4C-Al_2O_3$ composite was also produced [12] by aluminothermic reduction in $Al/B_2O_3/C$ system using microwave heating of ball-milled powder.

Using B_4C , Al , and C powders as the raw materials, phase pure $Al_8B_4C_7$ nanoparticles were obtained [13] after firing via a molten-salt-mediated route. The synthesis mechanism can be described as follows. In a eutectic liquid medium, Al partially dissolved and diffused onto the surfaces of C and B_4C to form Al_4C_3 and $Al_3BC-AlB_2$, respectively. B from the decomposition of AlB_2 also slightly dissolved in the salt, diffused onto the surface of Al_4C_3 formed earlier, and reacted with it to form $Al_8B_4C_7$. On the other hand, the Al_3BC formed earlier also decomposed to give Al , B , and Al_4C_3 . The latter two would similarly react to form $Al_8B_4C_7$. Compared to the conventional techniques, the synthesis temperature in this case was significantly (about 500 K) lower.

Another considered high-temperature reaction, $4TiO_2 + 4Al + 8B + C = 4TiB_2 + 2Al_2O_3 + CO_2$, is used to produce titanium diboride and its composites.

In the dissertation [14], an exothermic reaction was designed to synthesize Al_2O_3 and TiB_2 from TiO_2 particles and elemental B in an Al melt, and the mechanism of such boro- and aluminothermic reduction of titanium oxide together with *in situ* synthesis of micro- and nanoparticles via solidification processing was investigated. Microstructural examination in combination with theoretical analysis indicated that the formation of TiB_2 and Al_2O_3 proceeds through several complex non-equilibrium reactions. According to the multi-stage reaction model proposed to describe the process by which the TiO_2 surface reduces to form Al_2O_3 and TiB_2 , nanosized TiO_2 powder was found to promote the formation of smaller size reinforcing phases. A solidification route was designed to fabricate *in-situ* aluminum composites reinforced with submicron Al_2O_3 and TiB_2 particulates. In the dissertation [17], the chapter devoted to the synthesis of TiB_2 to be alloyed with Al contains a thermal analysis of the corresponding reaction mixture.

In-situ composite coatings of $TiC-Al_2O_3$, as well as $TiB_2-TiC-Al_2O_3$, were applied [15] on the surface of stainless steel by using combining, welding, and self-combustion synthesis. In all heat inputs, cubic titanium carbide particles formed heterogeneously on Al_2O_3 particles or spontaneously in the austenitic matrix of stainless steel. The reinforcing of TiC and TiB_2

particles formation in both $3TiO_2-4Al-3C$ and $3TiO_2-4Al-B_4C$ layers led to an increase in surface hardness and wear resistance versus the substrate. The reaction process in an $Al-TiO_2-C$ system was studied in [16]. TiC and Al_2O_3 were finally formed in the Al matrix. $TiAl_3$ and Al_4C_3 were found to be transitional phases during the *in situ* reaction process, which involves two steps: (1) $3TiO_2 + 13Al = 3TiAl_3 + 2Al_2O_3$ and $4Al + 3C = Al_4C_3$ and (2) $3TiAl_3 + Al_4C_3 = 3TiC + 13Al$. Quasi-adiabatic combustion synthesis of optimized $3TiO_2 + 4Al + (3 + x)C$ mixture in the presence of oxygen was carried out [17] to produce $TiC-Al_2O_3$ composite and the influence of Al_2O_3 diluent in combusted reactant mixture $6TiO_2 + 8Al + 7C + 2yAl_2O_3$ was investigated. Thermodynamics studies showed that self-sustaining mode of combustion wave propagation can occur for large amounts of diluents ($y = 2.5$). Adding Al_2O_3 diluent increased density that resulted in better thermal conductivity and reduced combustion temperature and rate of reaction. The effect of TiO_2 on some of Al_2O_3 -containing systems was considered as well [18].

Summarizing these literature data, we can conclude that the study of chemical reactions of aluminothermic reduction to obtain high-temperature boron compounds is an important materials science problem. In this paper, the thermodynamic analysis allowed us to determine the possibilities and conditions for the conduction of specific reactions, $2B_2O_3 + 4Al + C = B_4C + 2Al_2O_3$ and $4TiO_2 + 8B + 4Al + C = 4TiB_2 + 2Al_2O_3 + CO_2$, for the production of two boron compounds of particularly high practical interest — titanium diboride and boron carbide, and also determine the expected phase composition of their products, which allows to optimally select the compositions of the reagents.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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