PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 18, № 3 (2017) P. 358-364
DOI: 10.15330/pcss.18.3.358-364

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 18, № 3 (2017) С. 358-364

UDK 544.3:[661.862+661.657]

ISSN 1729-4428

O. Vasiliev[1,2], V. Muratov[1], T. Duda[2]

Thermodynamic Analysis of Perspective AlB_{12} Synthesis Reactions from Industrially Accessible Oxygen-Free Compounds

[1]Frantsevich Institute for Problems in Material Science NAS of Ukraine, Kyiv-142, Ukraine, 03680, Krzhyzhanovskogo str, 3, email: vasalexandr@gmail.com
[2]National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Kyiv-56, Ukraine, 03056, Peremogy av., 37, email: o.vasiliev@kznh.kpi.ua

Reactions of aluminum dodecaboride synthesis from oxygen free industrially available boron compounds by interaction of condensed and gaseous aluminum with boron nitride and carbide were the subject of thermodynamic analysis in this work. It was shown, that both reactions are thermodynamically advantageous at low temperatures rather than at high and the probability of their occurrence rises significantly for gaseous aluminum in comparison with condensed aluminum. Calculated values of Gibbs' free energy and equilibrium constants and the analysis of contributions into them clearly demonstrate the advantages of reaction with boron nitride. The probability of polyphase product composition imposes minimum temperature restrictions on the synthesis; it should be carried out at temperatures above 1000 °C. Hypothetical mechanisms of reactions between aluminum and boron containing compounds differ by the place of interaction — any place on the surface of each layer of BN and only open surface of B_4C — and by the transport of reaction participants in the reaction zone. From the results of analysis, we suggest indicative synthesis conditions: vacuum thermal synthesis to provide oxygen free environment and temperature above 1000 °C to avoid aluminum diboride formation.

Keywords: thermodynamic analysis, Gibb's energy, equilibriums constant, enthalpy, entropy, aluminum dodecaboride, aluminum, boron nitride, boron carbide, aluminum diboride.

Article acted received 02.08.2017; accepted for publication 05.09.2017.

Introduction

Boron compounds in which it forms icosahedral structural units B_{12} attract significant interest because uniqueproperties provided by such spatial atomic orientation. It is believed that this icosahedral boron configuration is the reason for high hardness values of these compounds and materials based on them and determines their belonging to superhard materials. Their main uses are impact resistant and armor materials [1], abrasive systems [2, 3], ceramic fillings in metal matrix composites [4] etc. Because ^{10}B isotope has large thermal neutron absorption cross-section, such high-boron materials are indispensable in nuclear energy applications. In particular, boron carbide B_4C is widely used in nuclear reactors' control rods [5–7]. Until now several such substances have been obtained; these include orthorhombic boron (γ-boron) and various chemical compounds, such as boron carbide B_4C ($B_{12}C_3$), boron suboxideB_6O, silicon hexaboride B_6Si(Si_2B_{12}), silicon tetraboride B_4Si (analogous to B_4C), aluminum dodecaboride $AlB_{12}$and others.

Aluminum dodecaboride is a typical representative of boron icosahedral compounds and has all the properties mentioned. But of an increased interest are its specifics. It has hardness comparable to boron carbide [8], but materials based on it are expected to have better stability under dynamic loading, which is a known disadvantage of B_4C as impact resistant material[9]. AlB_{12} boron content, about 83 % by mass, is one of the highest among boron compounds (boron carbide has theoretical boron content of 78 % by mass, but it is difficult to achieve because of residual equilibrium carbon) which is an important characteristic for nuclear applications. Solubility of AlB_{12}in aluminum melt (see phase diagram in [10]) determines special prospects for its use in aluminum matrix composites as it allows to control the size and particle distribution of the ceramic phase in metal matrix.

The main obstacle for wide application of $AlB_{12}$is an absence of a productive and technologically and economically rational method of production. Synthesis from elements can be realized by heating a mixture of powders in an evacuated sealed container or by addition of boron into aluminum melt [11]. These methods are neither simple nor productive and can be considered as laboratory technologies only. Besides, expensiveness and scarcity of elemental boron further reduces their attractiveness. Synthesis from oxygen containing compounds such as boron containing minerals and boron anhydride [11], is very attractive from economic point of view —such raw materials are accessible on industrial scale and are relatively cheap. Side products constitute the main problem here, especially aluminum oxide Al_2O_3, the formation of which is thermodynamically favorable in any reaction with oxygen participation. Separation of the main product from the subproductsis is a complicated technological process which requires a lot of physical, chemical and mechanical operations with thorough physical and chemical control. Apparently, the only rational way of aluminum dodecaboride synthesis is from oxygen free boron compounds in oxygen free environment. There are methods of synthesis from borofluorides of alkaline metals $MeBF_4$ (Me–alkaline metal) and boron halogenides (e.g., BF_3, BCl_3) that have some prospects of industrial application, but they are restricted by the raw materials expensiveness and increased environmental threats. We think that boron nitride BN and boron carbide B4C, oxygen free boron compounds of industrial mass production, are the most attractive for productive synthesis of aluminum dodecaboride.

Boron nitride and carbide are difficult to use as raw materials in a synthesis methods because of their remarkable thermodynamic stability. Studies of reactions between boron carbide and aluminum [12, 13] demonstrate their slow nature, small conversion rates, and polyphase products even at 1000-1500 ℃. In the case of boron nitride, the phase composition may be simpler, but other drawbacks will probably be the same.

The mentioned works are important because of their experimental results that show serious obstacles for the application of B_4C for aluminum borides synthesis. But each of them lacks a deep thermodynamic analysis of possible interaction conditions, which may be a key for successful search of the ways to increase the rates of interaction as well as conversion rate.

Evident necessity to understand thermodynamic conditions of reactions perspective for the synthesis of aluminum dodecaboride from accessible oxygen free boron compounds determines the goal of this work: to carry out a thermodynamic analysis of reactions between boron nitride BN and boron carbide B_4C with aluminum and assess the prospects of these interactions as key processes of productive aluminum dodecaboride AlB_{12} synthesis route.

I. Methods

Thermodynamic analysis was carried out for the reactions between boron nitride and carbide and elemental aluminum with the formation of aluminum dodecaboride and the product of complete interaction of aluminum with atoms of other chemical elements composing the boron compounds:

$$12\mathrm{BN} + 13\mathrm{Al}(\mathrm{cd, g}) \to \mathrm{AlB}_{12} + 12\mathrm{AlN}, \quad (1)$$

$$3\mathrm{B_4C} + 5\mathrm{Al(cd, g)} \to \mathrm{AlB}_{12} + \mathrm{Al_4C_3}. \quad (2)$$

Each interaction was considered in two realizations – with condensed (cd) and gaseous (g) aluminum.

Gibbs' free energy temperature dependences for the reactions (1) and (2) were calculated from the relation between the main isobaric thermodynamic potentials:

$$\Delta G(T) = \Delta H(T) - T\Delta S(T), \quad (3)$$

where $\Delta H(T)$ and $\Delta S(T)$ are temperature dependences of the enthalpy and entropy of the respective reactions. These were calculated as state functions at each temperature:

$$\Delta H(T) = \sum_i n_i \Delta_\mathrm{f} H^\circ(P_i,T) - \sum_i n_i \Delta_\mathrm{f} H^\circ(R_i,T), \quad (4)$$

$$\Delta S(T) = \sum_i n_i S^\circ(P_i,T) - \sum_i n_i S^\circ(R_i,T), \quad (5)$$

where $\Delta_\mathrm{f} H^\circ(P_i,T)$ та $\Delta_\mathrm{f} H^\circ(R_i,T)$ are enthalpies of formation at temperature T of the products and reactants respectively; $S^\circ(P_i,T)$, $S^\circ(R_i,T)$ are absolute entropies of the reactions' species at T; n_i is a stoichiometric quotient at i-th reaction participant. Enthalpies of formation at specific temperatures were calculated as the sum of standard enthalpies of formation and enthalpy increase from standard temperature to the temperature of interest

$$\Delta_\mathrm{f} H^\circ(T) = \Delta_\mathrm{f} H^\circ(298{,}15\,K) + (H^\circ(T) - H^\circ(298{,}15\,K)). \quad (6)$$

Values and temperature dependences of the thermodynamics functions required are present in original publications as well as reference sources, such as handbooks or databases. Data from the latter represent statistical assessment and generalization of the results of original publications, thus they were used whenever possible. Values of standard enthalpy, enthalpy and entropy of substances for BN, Al, AlNandAl_4C_3 at required temperatures were accepted from the hanbook[14];the source of AlB_{12}thermodynamic data is [15].

The order of magnitude for the reactions' equilibrium constants was calculated from the relation between equilibrium constant and Gibbs' free energy:

$$\ln K = \frac{-\Delta G}{RT} \quad (7)$$

where $R$is the universal gas constant.

II. Results and discussion

Calculated temperature dependences of Gibbs' free energy of interactions of born nitride and boron carbide with aluminum in the condensed and gaseous state according to the reactions (1)and(2) demonstrate (fig. 1) that both processes are thermodynamically advantageous in the overall analyzed temperature range. Absolute value of Gibbs' free energy or the reaction potential, are the largest at low temperatures and decrease with temperature increase, which is common in exothermic processes.

Such character of temperature dependence is determined by the decrease of entropy during the

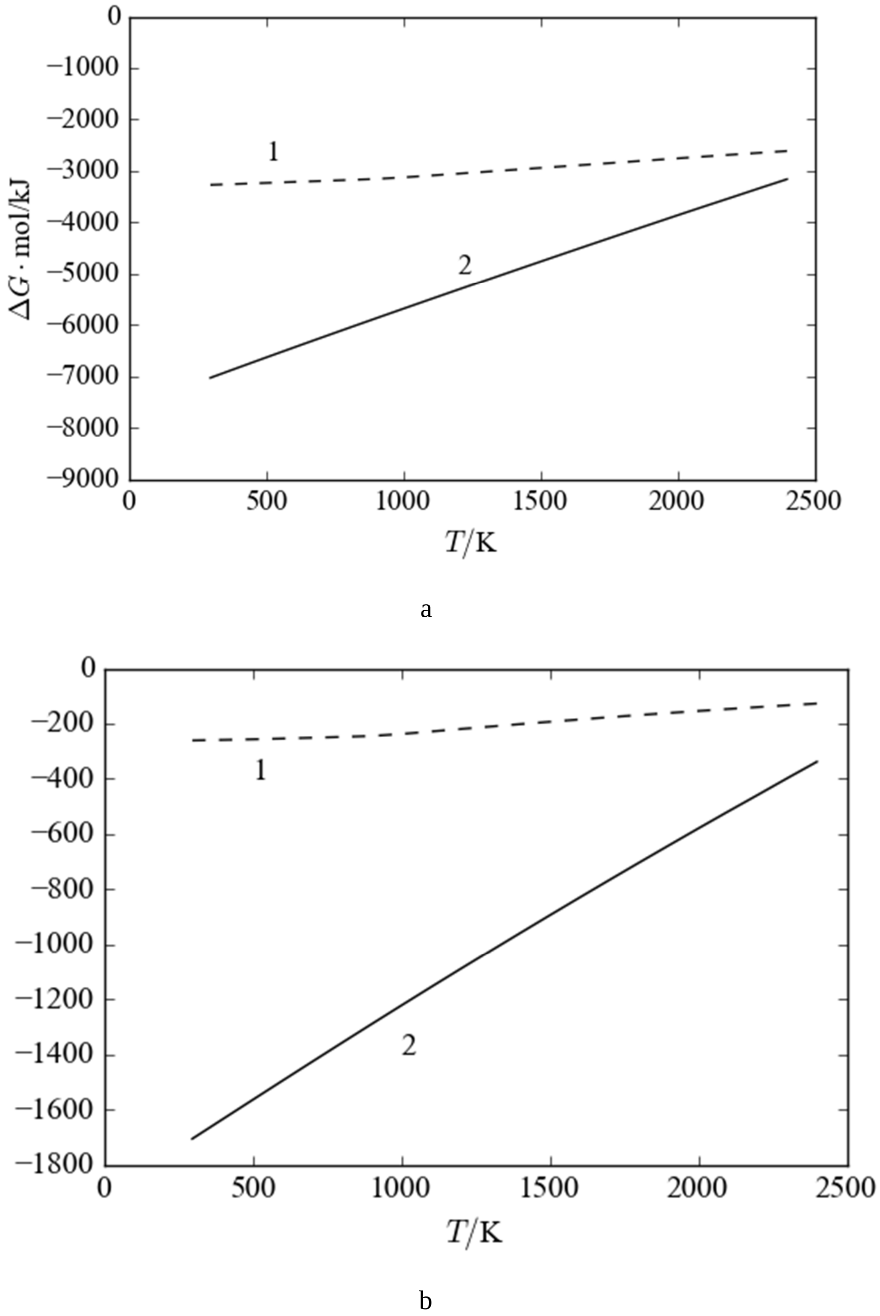

Fig. 1. Gibbs' free energy temperature dependences of reactions of boron nitride (a) and boron carbide (b) with aluminum in condensed (1) and gaseous (2) state.

reaction. Both reactions are exothermic ($\Delta H < 0$), and at low temperatures their heat determines the sign and absolute value of reactions' ΔG. But as a result of formation of product with high degree of atomic organization in the crystal lattice represented by the B_{12} pseudomolecules reactions proceed with entropy decrease. When temperature increases, the role of entropic constituent of the Gibbs' free energy of reaction $(-T\Delta S)$ becomes more significant, this is reflected by the absolute values of the reactions' potentials. Thus, low temperatures favor the formation of aluminum dodecaboride by the reactions (1)and(2).

On the other hand, phase diagram Al–B suggests the existence of two compounds: aluminum diboride $AlB_2$and aluminum dodecaboride AlB_{12}. There are a reliable data that at temperature around 970 °C these borides transform between each other[10,11]:

$$AlB_2 \rightleftarrows AlB_{12} + L, \qquad (8)$$

whereL is a liquid of variable composition containing aluminum and boron.There is a principal agreement on the proceeding of reaction (8)upon temperature increase — an incongruent melting of the diboride takes place in such a case. The reaction upon cooling is more ambiguous. Mirkovic*et al.* [10] experimentally demonstrated that even at very low cooling rates of about 2 K/min no traces of AlB_2in the interaction products were found; consequently, transformation (8) in the leftward direction does not occur. However, aluminum diboride will form upon cooling in equilibrium conditions. Therefore, any method of single phase

Table 1

Calculated thermodynamic properties of interactions of BN andB_4C with condensed and gaseous aluminum at temperatures of largest technological interest (per moleAlB_{12})

Reactant 1	Reactant 2	T/K	ΔG/kJ	ΔH/kJ	$\Delta S \cdot$ K/kJ	ln$K$
BN		1300	-3018.5	-3499.3	-0.36	279
	Al(cd)	1500	-2944.1	-3504.1	-0.37	236
		1700	-2869.5	-3504.0	-0.37	203
		1300	-5135.1	-7531.8	-1.84	475
	Al(g)	1500	-4768.1	-7508.1	-1.826	382
		1700	-4404.5	-7479.6	-1.808	312
		1300	-211.0	-325.7	-0.09	20
	Al(cd)	1500	-193.7	-320.2	-0.08	16
B_4C		1700	-177.3	-312.8	-0.08	13
		1300	-1025.0	-1876.6	-0.66	95
	Al(g)	1500	-895.2	-1860.2	-0.64	72
		1700	-767.7	-1841.8	-0.63	54

aluminum dodecaboride synthesis must take into account the probability of AlB_2impurities formation and provide the synthesis temperature over 1000 °C.

The state of aggregation of aluminum in a reacting mixture, as can be seen from fig. 1, critically influences the ΔG value of chemical reaction. For both reactions interaction is thermodynamically probable with both condensed and gaseous aluminum, but equilibrium constant K, which is related to the Gibbs' energy by (7), is much more informative here and has greater significance. According to tab. 1, interaction with gaseous aluminum leads to a drastic rise in equilibrium constant. In real reactions with solid participants, where kinetic factors (e.g., diffusion) have considerable influence, high values of equilibrium constant do not guarantee full reaction completion. Therefore, the noted difference of equilibrium constantfor condensed and gaseous aluminum may be a key to obtaining the product that does not contain reactants or contains them in acceptable amounts. It is important, that absolute values of Gibbs' free energy and equilibrium constant of interaction with Al(g) even at high temperatures are higher than the values for Al(cd) at low temperatures. Hence any variation of conditions that leads to interaction with gaseous aluminum is desirable despite possible relative reduction of the potential and equilibrium constant of reaction. From the kinetic point of view, individual aluminum atoms have higher mobility and penetrability into open pores of a solid reactant, providing the front of reaction on all the open surface of material, not only on the interface of two condensed phases. Thus, both thermodynamic and kinetic considerations indicate significant advantages of using gaseous aluminum in reactions (1) and (2).

It is obvious from fig. 1 and tab. 1 that the increase of synthesis temperature leads to the process suppression and lower the equilibrium constant and is undesirable. On the other hand, the only practical way to obtain gaseous aluminum is its evaporation, intensity of which increases with temperature. Thus, temperature during the synthesis of $AlB_{12}$by the reactions (1) and (2) should be controlled in such a way as to provide the balance between maximum value of the equilibrium constant and satisfactory aluminum evaporation.

Qualitatively, in the context of general thermodynamic patterns of reactions, interactions of aluminum with boron nitride and carbide are similar. Significant differences are revealed when analyzing absolute values of Gibbs' energy and equilibrium constant. Being negative for both reactions, absolute values of ΔG at the temperatures of interest deviate by a factor of 3 to 5 with larger values for the interaction with BN, making it much more attractive for the synthesis realization. The same applies to the equilibrium constant—upon interaction of boron carbide with aluminum probability of finding reactants in the final product is much higher than for boron nitride. Even in case of interaction with gaseous aluminum we can expect, that the results will be somewhat similar to [12], where the interaction of condensed aluminum (melt) with boron carbide was conducted during 160 hours to provide equilibrium conditions, but the products are highly polyphase. Remarkable difference in equilibrium constants suggests that for theAl(g)–BN system such phenomena won't occur to such a degree.

Detailed analysis of the contributions forming the Gibbs' free energy of the reactions (1) and (2) allows deeper understanding of their occurrence as well as prediction of the expected results. Because in both reaction entropy decreases, exothermic heat of reaction, that is enthalpic contribution, determines negative values of the reaction potentials. Some important specifics of these reactions are revealed upon comparison of the formation enthalpies of possible products. In the case of reaction(1) $\Delta_f H^\circ(\mathrm{AlB_{12}},\ \mathrm{cr},\ 298.15\ \mathrm{K}) = -244.76$ kJ/mol and $\Delta_f H^\circ(\mathrm{AlN},\ \mathrm{cr},\ 298.15\ \mathrm{K}) = -319.00$ kJ/mol, which, recalculated for one mole of atoms, is -18.3 and 159.5 kJ/molrespectively. Heat effect for one mole of atoms from the aluminum nitride formation is more than eight times higher than heat effect from aluminum dodecaboride. Additionally, there are almost two times more atoms binding into aluminum nitride. Formation of AlN, a sub product, determines the value of reaction's ΔG and, therefore, its proceeding in general.Boron carbide formation enthalpy is $\Delta_\mathrm{f} H^\circ(\mathrm{Al_4C_3}, \mathrm{cr}, 298.15\ \mathrm{K}) = -206.9\ \mathrm{kJ/mol}$ or 29.6 kJ per mole of atoms and its contribution into the heat of reaction is comparable to that of aluminum dodecaboride.

Contribution of the sub products into general heats of the reaction determines, in our opinion, key differences between the reactions(1)and(2). To discuss these differences, let us consider the processes that may take part at molecular level during the reactions and accompanying phenomena, or hypothetical mechanisms of reactions.

We suggest, that the interaction between gaseous aluminum and boron nitride begins with the transport of metal atoms to the place of interaction. For hexagonal boron nitride such place may be any point on the surface of every layer, because at high temperatures individual aluminum atoms are capable of intercalation into the interlayer gaps of BN. Further several processes may take place: forming of chemical bonds between aluminum and nitrogen atoms, which leads to breaking of bonds between the latter and neighboring boron atoms; interaction of aluminum atoms with released boron or, more probably, agglomeration of boron into twelve atom icosahedra; in case of icosahedra formation, their interaction with aluminum atoms.

All the processes mentioned are exothermic, and temperature of the system will rise. Approximate calculation with assumptions that the heat capacity of reacting mixture at the synthesis temperatures is close to the Dulong-Petit limit of 24.9 J/K per mole of atoms and reaction mixture is isolated shows that local temperature of the mixture during the reaction between BN and Al (g) may rise by about 8000 K for a short time. This should provide an effective transport of the reaction participants. Beside that, in case of a high rate of reaction (1) in the conditions of real synthesis, when masses of reactants are large, the process may be explosive and demands special control measures. One of such measures may be a restriction of gaseous aluminum introduction into the reaction zone for which the most apparent way is to control evaporation. Short time local temperature increase in case of reaction between boron nitride and solid aluminum could reach about 4000 K, but the release of heat here is significantly distributed in time because of the kinetic obstacles for such interaction.

In the case of B_4C expectations are somewhat different. Boron carbide structure does not allow an active incorporation of gaseous aluminum atoms into the bulk of material and interaction can occur on the surface only. Probably, the first thing that will happen is an interaction between aluminum and chain carbon atoms that connect boron icosahedra (the structure of B_4C see, for example, [9]) to form aluminum carbide. Additional aluminum atoms will fill in the space freed from carbon. These bulk products will have low mobility by themselves, but also will damp aluminum diffusion and facilitate the dissipation of heat released by exothermic processes. Heat effects of this reaction are also modest in comparison with boron nitride. Even without the heat dissipation short time local temperature increase in the case of condensed aluminum may be around 1000 K and resulting temperature is comparable to the temperature of hot pressing of B_4C, which occurs through a diffusive mechanism at elevated pressures. In the case of gaseous aluminum temperature increase may reach 2000 K, but it is improbable because of the kinetic obstacles for the reaction propagation.

The possibility of forming ternary compounds in the case of reaction (2) deserves special attention. There is a series of aluminum carboborides with icosahedral boron configuration in theAl-B-C system. Forming of such ternary compounds is typically thermodynamically advantageous because of entropy constituent, even in case of existence of binary compound with similar formation enthalpy. In the context of suggested mechanism, it means that incomplete substitution of carbon atoms by aluminum may occur and there will be neither favorable thermodynamic factors, nor transport possibilities to reach the desirable product — aluminum dodecaboride. Therefore, no matter what is the state of aggregation of the reacting aluminum, the real products of reaction will probably be aluminum carboborides and carbide, similarly to what is shown in[12].

All the stated considerations demonstrate, that the best prospects for the realization of rational aluminum dodecaboride synthesis from industrially accessible oxygen free boron compounds has reaction(1), that is the interaction of boron nitride and aluminum, particularly in the case of gaseous aluminum. The reaction should be done in vacuum to provide oxygen free environment and at temperatures exceeding 1000 °C to avoid the formation of aluminum diboride.

Conclusions

The results of thermodynamic analysis demonstrate that at least one of the considered reactions of aluminum dodecaboride synthesis from oxygen free compounds has significant prospects of practical realization. Reaction of boron nitride with aluminum, especially when the latter is in gaseous state, has significant thermodynamic probability and remarkably high values of equilibrium constant, which allows expecting high interaction intensity and product purity from reactants.The heats of the processes that occur upon such interaction are large enough to provide effective transport of reactants inside the reaction environment. Contrastingly, interaction between boron carbide and aluminum, although being thermodynamically probable, does not have significant thermodynamic drives and can be seriously dampened by kinetic factors.

Possible AlB_{12} synthesis method based on the reactions (1) and (2) has to take into account the technological restrictions imposed, first of all, by phase composition of initial substances and possible interaction products. In particular, the synthesis should be carried out in oxygen free environment, e.g. vacuum, and at temperatures over 1000 °C. Such conditions will allow avoiding alumina Al_2O_3 and aluminum diboride AlB_2 formationand increase aluminum evaporation.

Considering the results of this work, further efforts to develop a rational aluminum dodecaboride synthesis method should be directed at the search of possibilities to effectively obtain gaseous aluminum and control its input into the reaction environment, development of specific temperature modes of synthesis and, most importantly, the search of possibilities forproduct mixtures separation.

From the point of view of thermodynamic analysis, an undoubtable interest is specifics of the processes, described in hypothetical mechanisms of reactions (1) and (2) suggested in this work. Beside verification of the mechanisms, results of such analysis may be of use for fine tuning of synthesis' technological parameters and in the search of ways to eliminate the kinetic obstacles for the reactions realization. However, such analysis demands the knowledge of thermodynamic state of reacting system and its microscopic subsystems during the process and application of nonequilibrium thermodynamics approaches.

Acknowledgement

The work is done under the support of NATO Science for Peace and Security Programme, project G985070 "New shock-resisting boron-based ceramics: computer modeling, production, testing".

Vasiliev O. **-** PhD (candidate of chemical sciences), senior researcher, associate professor;
Muratov V. **-** PhD (candidate of chemical sciences), senior researcher;
Duda T. **-** PhD (candidate of chemical sciences), associate professor.

[1] B.A. Galanov, V.V. Kartuzov, O.N. Grigoriev et al., Procedia Eng. 58, 328 (2013).
[2] K.A. Schwetz, L.S. Sigl, J. Greim, and H. Knoch, Wear 181–183, 148 (1995).
[3] T. Murakami and H. Inui, Tribol. Int. 74, 38 (2014).
[4] Y. Kumart, G.A. Kumar, and T. Madhusudhan, International Research Journal of Engineering and Technology (5), 860 (2016).
[5] K. Sairam, J. K. Sonber, T. S. R. C. Murthy et al., Int. J. Refract. Met. Hard Mater. 35, 32 (2012).
[6] W. Dongshan, Y. He, Z. Ying, and X. U. E. Xiangxin, J. Chinese Ceram. Soc. 36(10), 2 (2008).
[7] C. Subramanian, A.K. Suri, Technol. Dev. Artic. (313), 14 (2010).
[8] P. Barvitski, T. Prikhna, V. Muratov et al., Bulletin of the National Technical University of Ukraine "ChPI" Mechanical-Technological Systems and Complexes 50(1222), 14 (2016).
[9] V. Domnich, S. Reynaud, R. Haber, M. Chhowalla, J. Am. Ceram. Soc. 94(11), 3605 (2011).
[10] D. Mirković, J. Gröbner, R. Schmid-Fetzer, O. Fabrichnaya, and H. L. Lukas, J. Alloys Compd. 384(1–2), 168 (2004).
[11] P Kisly, V. Neronov, T. Prikhna, Y. Bevza, Aluminum Borides (Naukova Dumka, Kyiv, 1990).
[12] J.C. Viala, J. Bouix, G. Gonzalez, and C. Esnouf, J. Mater. Sci. 32(17), 4559 (1997) .
[13] A. Koroglu and D.P. Thompson, J. Eur. Ceram. Soc. 32(12), 3501 (2012).
[14] V. Glushko, L. Gurvich, G. Bergman et al., Thermodynamic Properties of Individual Substances, 3-d ed. (Nauka, Moscow, 1981).
[15] A. Alekseev, G. Bovkun, A. Bolgar et al., Properties, obtaining and applications of refractory compounds (Metallurgia, Moscow, 1986).

О.О. Васільєв[1,2], В.Б. Муратов[1], Т.І. Дуда[2]

Термодинамічний аналіз перспективних реакцій отримання додекабориду алюмінію AlB_{12} із промислово-доступних безкисневих вихідних речовин

[1]*Інститут проблем матеріалознавства ім. І.М. Францевича НАН України, Київ-142, Україна, 03680, вул. Кржижановського 3, email:* vasalexandr@gmail.com
[2]*Національний технічний університет України «Київський політехнічний інститут імені І. Сікорського», м.Київ-56, Україна, 03056, проспект Перемоги, 37, email:* o.vasiliev@kznh.kpi.ua

В роботі здійснений аналіз термодинаміки перебігу реакцій синтезу додекабориду алюмінію із безкисневих промислово доступних реагентів, взаємодією алюмінію в конденсованому та газоподібному стані із нітридом та карбідом бору. Показано, що обидві реакції є термодинамічно вигідними за низьких температур в більшій мірі, аніж за високих, і ймовірність їх перебігу суттєво зростає при використанні алюмінію у газоподібному стані у порівнянні з конденсованим алюмінієм. Розраховані значення та аналіз внесків, які формують величину енергії Гіббса та констант рівноваги однозначно демонструють переваги реакції алюмінію з нітридом бору. Обмеження, що накладаються можливим поліфазним складом продукту за рахунок утворення диабориду алюмінію за температур нижче 970°С, вимагають застосування температури синтезу понад 1000 ^{0}С. Запропоновані гіпотетичні механізми взаємодії алюмінію з боровмісними сполуками за двома реакціями відрізняються місцем взаємодії — будь-яка точка поверхні кожного шару при використанні BN або тільки відкрита поверхня для B_4C — та характером транспорту учасників реакції в реакційній зоні. З результатів аналізу запропоновані орієнтовні технологічні умови синтезу: вакуумний термічний синтез для забезпечення безкисневого середовища та температура понад 1000 ^{0}С, для уникнення утворення диборду алюмінію AlB_2.

Ключові слова: термодинамічний аналіз, енергія Гіббса, константа рівноваги, ентальпія, ентропія, додекаборид алюмінію, алюміній, нітрид бору, карбід бору, диборид алюмінію.