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THERMODYNAMIC PRECONDITIONS OF THE TITANIUM COMPOUNDS FORMATION WITH INTERSTITIAL ELEMENTS (C, N, O, B) DEPENDING ON TEMPERATURE AND PRESSURE OF GASEOUS MEDIUM

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Summary. Results of the thermodynamic analysis of the probability of formation of chemical compounds in the «Ti-C-N-O-B» system are presented in this paper. The ranking of the formation of chemical reactions as a function of temperature ($T = 100...1200^{\circ}\text{C}$) and air pressure ($P = 1.33 \cdot 10^{-8}...1 \cdot 10^5 \text{ Pa}$) is carried out. It is shown, that titanium will interact with oxygen most actively, forming a interstitial solid solution with the subsequent $T = 900^{\circ}\text{C}$ titanium boride. Reduction of air pressure is not likely to reduce the formation of compounds containing formation of oxides; following the probability, nitrides will be formed, then carbides and up to temperature oxygen and nitrogen. Thus, at the temperature $T = 800^{\circ}\text{C}$, the available compound B_2O_2 will be decomposed and will not be formed at the pressure below $P = 1.33 \cdot 10^3 \text{ Pa}$.

Key words: titanium, oxygen, nitrogen, carbon, boron, thermodynamic analysis, binary chemical compounds.

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Statement of the problem. The structure and properties of the metal surface layer specify the most service properties of products. Development of the surface engineering technology for modification of the surface layers makes possible to form films and coatings, which comprise the specific combination of properties, which differ from those of the basic metal. One of these methods is the thermodiffusion saturation of the gaseous medium. This problem is urgent for the products made of the titanium compounds as well, as despite the high values of the specific strength some other operation properties (such as wear and corrosion resistance) are not good enough [1 – 3]. Nowadays traditional materials for creation of high-quality operation coatings are the binary compounds of titanium (oxides, nitrides and carbides) [4 – 8]. One of the first stages, provided for the investigation of the chemical compounds formation, is the thermodynamic analysis. That is why to find the possibility of formation of binary compounds during thermodiffusion saturation of titanium from the oxygen, nitrogen, carbon and boron medium, as well as to estimate the processes in the gaseous phase, the thermodynamic calculations in the «Ti-C-N-O-B» system were carried out.

Analysis of the available results of investigations. The main criteria for choosing these compounds are, beside high melting temperature, which, as a rule, is below 1500°C , the thermodynamic strength at high temperatures and some special properties, possessing by them, which are of paramount importance in certain operation conditions (hardness, wear resistance, thermal expansion, scale resistance, heat resistance, corrosion resistance, electric resistance, etc.). According to the scientific-technological literature the interstitial compounds of titanium oxides, nitrides and carbides are similar in their crystalline structure, the type of

chemical bonds, electric and chemical properties. Besides, it should be noted, that the interstitial compounds mentioned above possess a great deal of homogeneity [9 – 11].

Thermodiffusion saturation from the gaseous medium is still the most efficient and versatile from the point of view of possibility to form binary interstitial compounds in titanium in great range of interstitial element/titanium. Formation of binary interstitial compounds (titanium oxide, nitride, carbide) of different interrelation depends on the technological factors of the saturation medium. One of such key factors are the temperature and the pressure of the chemically active gases (oxide, nitrogen, carbon). Lately the investigation attention was directed to the accumulation of data on the effect of chemical binary compounds on the physical-mechanical properties of titanium for carrying out calculations being able to estimate preliminarily the possibility to form these or those binary interstitial compounds in titanium.

The objective of the paper is to carry out theoretical calculations in order to reveal the possibility to form chemical titanium compounds with the interstitial elements (C, N, O, B). To reach the goal the system «Ti-C-N-O-B» has undergone the thermodynamic analysis. The changes of the characteristic functions of the system state with the change of temperature and the partial pressure of the gas components (O₂, N₂) were analyzed. In the calculations the table values of the thermodynamic parameters [12 – 15] were used as well as the following available dependencies for finding the free energy of chemical reactions [16].

Statement of the task. In the paper the table values of the thermodynamic parameters and the following available dependencies for finding the free energy for the chemical reactions were used to carry out theoretical calculations in order to reveal the possibility to form the titanium chemical compounds with the interstitial elements (C, N, O, B). It made possible to present in the paper the results of analytical calculations of formation the binary embodied compounds of titanium basing on oxygen, hydrogen, carbon and boron. To carry out the calculations we took advantage of the platform MathCad.

Results of investigations. For the thermodynamic analysis let us analyze the changes of the characteristics functions of the system state, when the temperature and partial pressure of the gaseous components (O₂, N₂) are changed. With this purpose the table values of the thermodynamic parameters [12 – 15] and the following known dependencies were used

$$\Delta G_T = \Delta H_T^o - T \cdot \Delta S_T^o + R \cdot T \cdot \ln(1/p_A) = \Delta G_T^o - RT \cdot \ln(1/p_A), \quad (1)$$

where ΔH_T^o – the change of the investigated system enthalpy, resulted from the reaction at the temperature T in normal conditions, J/mole, T – temperature, K, ΔS_T^o – the change of the system enthalpy at the temperature T in the normal conditions, J/(mole·K); R – versatile gas constant; $R = 8,314$ J/(mole·K); p_A – partial pressure of the components in the saturating medium, *atm*.

$$\Delta H_T^o = \Delta H_{298}^o + \int_{298}^T \Delta C_p dT; \quad \Delta S_T^o = \Delta S_{298}^o + \int_{298}^T \frac{\Delta C_p}{T} dT, \quad (2)$$

where ΔC_p – the change of the system heat capacity.

The comparison criterion is assumed to be the level of similarity between the chemical elements ΔG_T , that is, the reactions with more minus values of the free energy change will prevail.

The system «Ti-C-N-O-B» will be analyzed under such initial states: Ti – is in the condensed state – solid metal; C – is in the condensed state – solid graphite; N₂ – is in the gaseous state – gas; O₂ – is in the gaseous state – solid gas; B – is in the condensed state – powder-like.

Let us analyze the thermodynamic characteristics of interrelation the mentioned above system components within the temperature range 100...1200°C under the pressure of 1 atm.

Preliminary analysis of the reactions probability will be performed according to the molar enthalpy of the chemical compounds formation at the temperature 25°C (298,15 K) and under the normal conditions.

Table 1

Molar enthalpy of the chemical compounds formation at the temperature 298,15 K from the regular elements under normal conditions [13]

№	Compound	$\Delta_f H^\circ(298,15 K),$ J/mol	№	Compound	$\Delta_f H^\circ(298,15 K),$ J/mol
1	BC	838161,905	13	CO	-110535,196
2	BC ₂	801258,725	14	TiB	-160247,000
3	B ₂ C	800432,614	15	TiC	-184096,000
4	CNN	633484,056	16	BN	-251000,000
5	C ₄ N ₂	529200,000	17	TiB ₂	-279491,000
6	CN	438683,552	18	BO ₂	-309121,947
7	C ₂ N ₂	309100,000	19	TiN	-337648,800
8	B ₂ O	192798,018	20	CO ₂	-393510,000
9	N ₂ O ₃	86630,595	21	B ₂ O ₂	-457711,486
10	N ₂ O	81600,000	22	TiO	-542000,000
11	BO	20406,404	23	B ₂ O ₃	-835382,271
12	B ₄ C	-62000,000	24	TiO ₂	-944000,000

The exothermal reactions, which take place releasing energy, prevail in forming compounds, that is why let us analyze the reactions of formation compounds from 12 till 24 (Table 1).

1. Ti + 1/2O₂ = [O]_{Ti} – formation of the solid solution of the oxygen interstitial in titanium;
2. Ti + 1/2O₂ = TiO;
3. Ti + 1/2N₂ = TiN;
4. Ti + C = TiC;
5. Ti + B = TiB;
6. B + 1/2 N₂ = BN;
7. 2B + O₂ = B₂O₂;
8. 2B + 3/2O₂ = B₂O₃;
9. 4B + C = B₄C;
10. C + 1/2O₂ = CO.

For the changed conditions (temperature, pressure) let us analyze the change of the isobaric-isothermal potential of the formation of these compounds.

The dependence of change of the isobaric-isothermal potential of these compounds formation under the pressure 1 atm (taking into account the portion of oxygen and nitrogen) is presented in Fig. 1, the calculation was performed on g-atom of the oxidant.

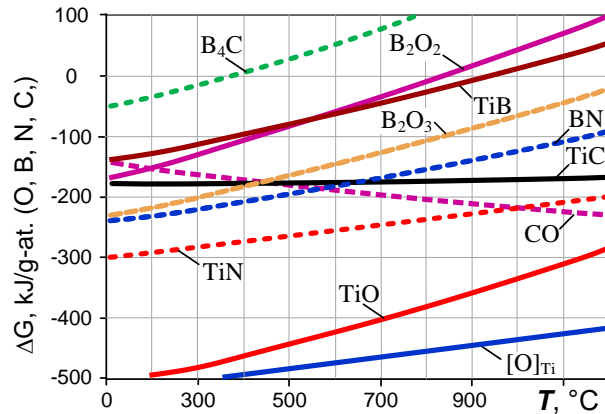


Figure 1. Temperature dependences of the isobaric-isothermal potential change of simple compounds formation under the pressure $1 \text{ atm } (1 \cdot 10^5 \text{ Pa})$

According to the obtained dependences it can be assumed, that the titanium will interact with the oxygen the most actively, forming solid penetration solution with the further formation of oxides, further the nitrides are likely to be formed, then carbides and borides till the temperature 900°C . Above the temperature 900°C the compound TiB must have not been formed, the diffusion saturation of the titanium by boron can take place. When the titanium contacts with the boron nitrite, its dissociation is likely to take place and formation of the titanium nitrite and titanium boride. When B_2O_3 and B_2O_2 contact with the titanium, these oxides will be decomposed and form the titanium oxide and titanium boride correspondingly.

Up to the temperature 800°C the following procedure is possible: B_2O_3 being in contact with the titanium releases the oxygen atom forming B_2O_2 and the titanium oxide. When the amount of oxygen is enough, the probability of formation B_2O_2 is high enough within all the temperature range. Carbon boride B_4C being in contact with the titanium will be treated as the boron donor, and above 700°C it will be decomposed into the components: boron and carbon. Above the temperature 500°C , oxygen being available, the formation of the carbon oxide will prevail over the titanium carbide, but the carbon oxide being in contact with the titanium, it becomes the oxygen donor for formation of the solid solution of oxygen in the titanium and titanium oxide. And carbon, when oxygen being available, form the carbon oxide again. Oxygen being not available, the titanium carbide is formed.

Let us analyze these processes under the lower general air pressure up to $1 \text{ mm Hg } (133,33 \text{ Pa})$.

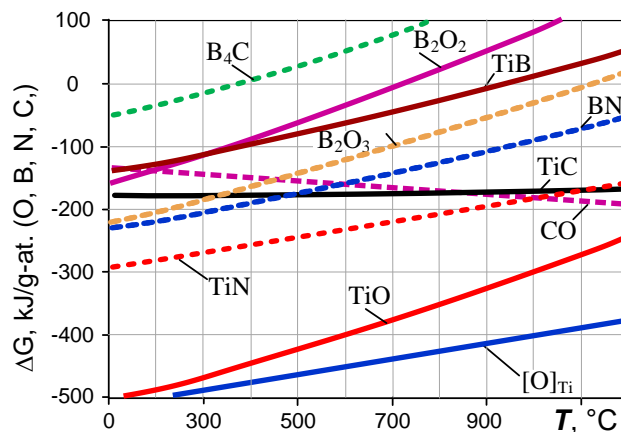


Figure 2. Temperature dependencies of the isobaric-isothermal potential change of simple compounds formation under the residual pressure of the rarefied air $1 \text{ mm Hg } (133,33 \text{ Pa})$

The decrease of the gaseous components pressure does not change effectively the situation, but the stability of compounds, possessing oxygen or nitrogen, decreases. Thus, at the temperature above 1100°C the formation of B_2O_3 becomes impossible. At the temperature above 1100°C the formation of the titanium carbide prevails over the formation of nitride. Decreasing of pressure results in prevailing of the carbon oxide over the titanium carbide, the temperature being above 900°C .

The interrelation of the gaseous components in the gas solution under available technical conditions can change from 1 atm ($133,33 \cdot 10^5\text{ Pa}$) till $1 \cdot 10^{-6}\text{ mm Hg}$ ($1,33 \cdot 10^{-8}\text{ Pa}$). That is why let us analyze the dependencies of the isobaric-isothermal potential change of the compounds formation depending on the pressure of the gaseous medium. The rarefield air will be analyzed, that is why the interrelation of partial pressures of the oxygen and nitrogen were taken into account in the calculations.

Let us analyze the isobaric-isothermal potential change of the compounds formation at the temperature 750°C within the range of pressures $1 \cdot 10^6 \dots 760\text{ mm Hg}$ ($1,33 \cdot 10^8\text{ Pa} \dots 101,324\text{ Pa}$) (Fig. 3).

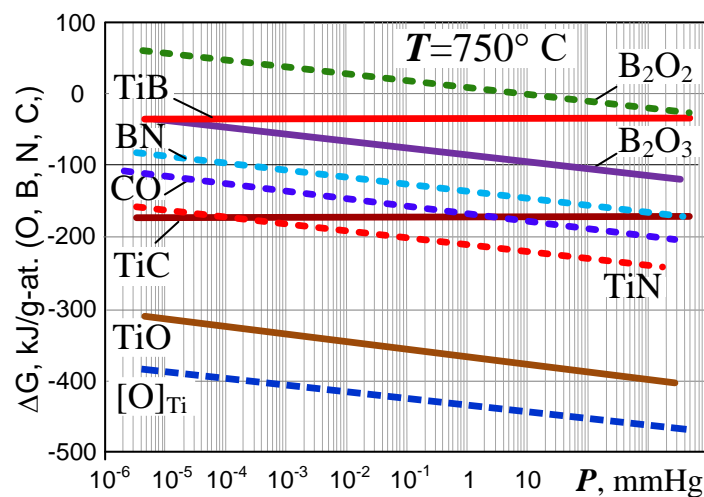


Figure 3. Dependencies of the isobaric-isothermal potential change of simple compounds formation on the residual pressure of the medium at the temperature 750°C

According to the obtained dependencies it can be concluded, that the decrease of the air pressure decreases the probability of formation the compounds, possessing the oxygen and nitrogen. Thus, at the temperature 750°C the available compound B_2O_2 will be decomposed and a new compound will not be formed, if the pressure is below 10 mm Hg ($1,33 \cdot 10^3\text{ Pa}$).

Similar situation is for B_2O_3 , if the temperature is 950°C (Fig. 4) – the compound can not be formed, if the pressure is below $5 \cdot 10^{-4}\text{ mm Hg}$ ($6,66 \cdot 10^{-2}\text{ Pa}$). The decrease of pressure till $1 \cdot 10^{-2}\text{ mm Hg}$ ($1,33\text{ Pa}$) at the temperature 950°C results in the greater probability to form TiC than TiN .

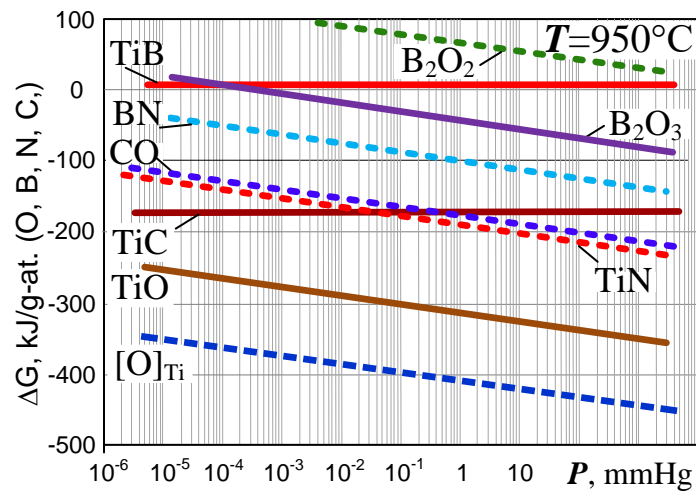


Figure 4. Dependencies of the isobaric-isothermal potential change of simple compounds formation of the residual pressure of the medium at the temperature 950°C

The decrease of pressure at the temperature 1150°C (Fig. 5) results in the fact, that the formation of B₂O₃ is impossible under the residual pressure below 1 mm Hg (133,33 Pa). If the pressure is below 1·10⁻² mm Hg (1,33 Pa), the titanium carbide is more stable than the carbon oxide and titanium carbide. The boron nitride is not formed, if the pressure is below 1·10⁻⁵ mm Hg (1,3310⁻³ Pa).

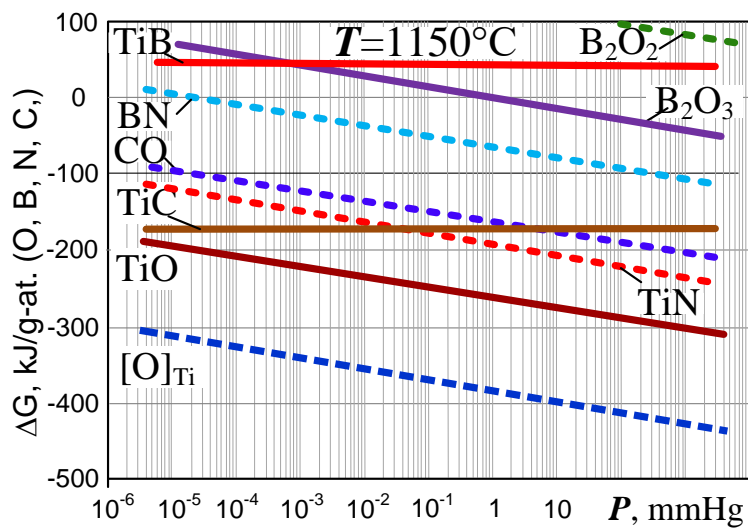


Figure 5. Dependencies of the isobaric-isothermal potential change of simple compound, formation on the residual pressure of the medium at the temperature 1150°C

From the point of view of the possibility to deliver the boron to the titanium surface, let us analyze the pressure of the saturated steam of the pure B and B₂O₃ (Fig. 6).

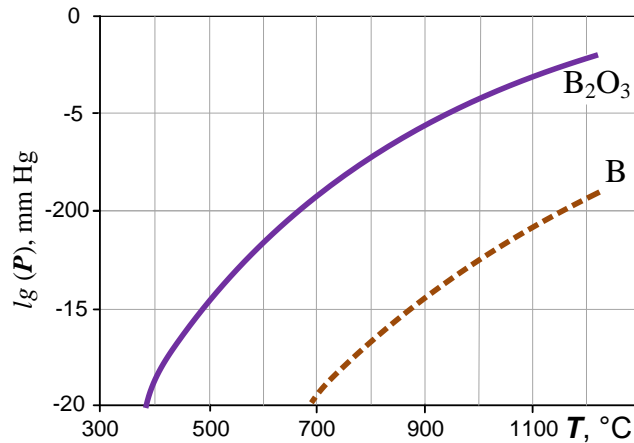
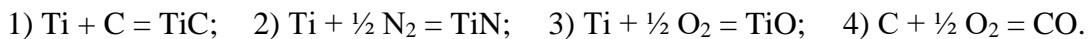


Figure 6. Pressure of saturated steam B and B₂O₃ depending on temperature

The delivery of boron through the oxide B₂O₃ is possible, if the temperature is above 950°C and the pressure of saturated steam is more than $1 \cdot 10^{-5} \text{ mm Hg}$ ($1,3310^{-3} \text{ Pa}$), because such pressure of the residual gaseous medium can be used during the chemical-thermal treatment.

As the saturated medium is complex and contains oxygen, nitrogen and carbon, the probability of formation of the triple compounds is possible [17, 18].

As the source of the thermodynamic data is different, let us present the basic data curves for the comparison. That is why let us calculate the change of isobaric-isothermal potential for the reactions:



In Fig. 7 the change of the Gibbs energy for formation of these compounds, depending on the temperature, is presented.

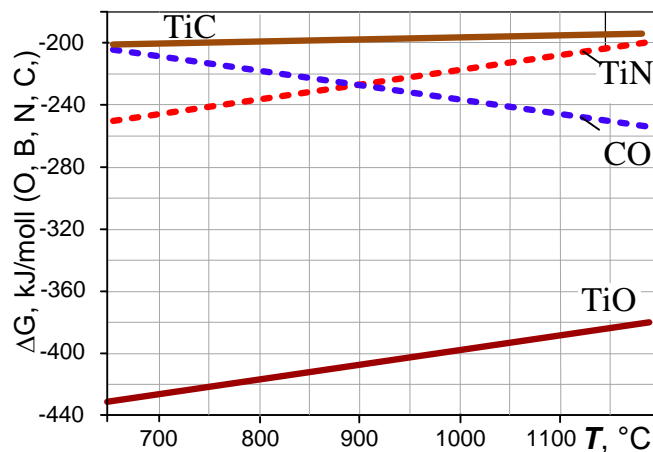
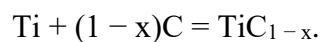


Figure 7. The change of the isobaric-isothermal potential of the chemical compounds formation depending on temperature under normal conditions

Let us analyze the change of the isobaric-isothermal potential of the reaction of formation of non-stoichiometric carbides (Fig. 8)



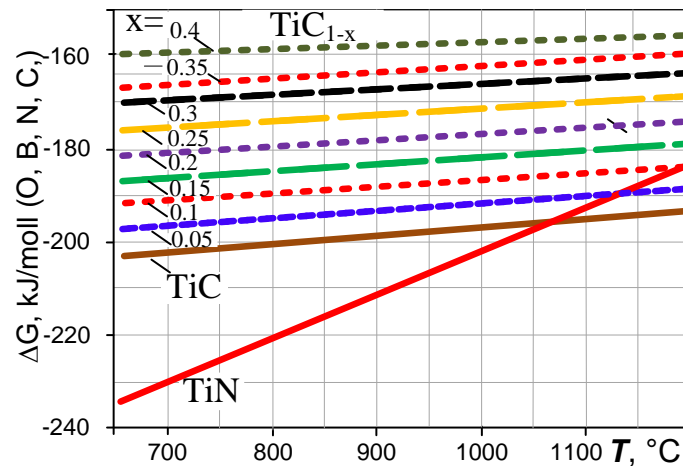


Figure 8. The change of the isobaric-isothermal potential of non-stoichiometric titanium carbides formation depending on temperature

According to the Fig. 8 the raising of temperature will result in the prevailing formation of the titanium carbides of the stoichiometric composition, if the delivery of carbide is not enough. The formation of carbides of non-stoichiometric composition will be slower, because of the formation of nitrides of the stoichiometric composition.

The results obtained in the paper make possible to estimate and reveal the regularities of formation of the interstitial binary compounds (oxides, nitrides, carbides, borides) of the titanium depending on such technological factors as temperature and pressure of the saturated gaseous medium.

Because of that the further investigation of the thermodiffusion saturation kinetics of the titanium alloys from the combined (gaseous + powder-like) medium, depending on the temperature and pressure of the gaseous components, as well as the comparison of the obtained results with the theoretical ones, the study of wide range of physical, chemical, mechanical and service properties of the modified layers, is worth being investigated in future.

Conclusion. The presented above results are of the probability nature and absolutely real for the balanced state. Under the real conditions of the chemical-thermal treatment the vital role in formation of these or those compounds is that of the kinetic factor, that is, the rate of delivery and the amount of the chemical element being delivered to the titanium surface. That is, the deviation may happen to be and the probability of formation the complex compounds with the admixtures of boron and carbon cannot be excluded, which can be delivered from the powder-like filling itself, being diffused into the depth of the metal, reacting with the other chemical compounds and being fixed in the defects.

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ТЕРМОДИНАМІЧНІ ПЕРЕДУМОВИ УТВОРЕННЯ СПОЛУК ТИТАНУ З ЕЛЕМЕНТАМИ ВТІЛЕННЯ (С, N, O, B) ЗАЛЕЖНО ВІД ТЕМПЕРАТУРИ І ТИСКУ ГАЗОВОГО СЕРЕДОВИЩА

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Резюме. Титан належить до легких металів, які внаслідок низької питомої густини та низького модуля пружності мають значні переваги при використанні в автомобільній та авіаційній промисловостях. Застосування методів інженерії поверхні дозволяє розширити сфери використання титанових сплавів, забезпечити надійність та роботоздатність виробів з них, суттєво підвищити економічність їх експлуатації. Проведення попередніх термодинамічних розрахунків у системі «Ti-C-N-O-B» дозволить оптимізувати вибір схем та режимів обробок для формування тих чи інших сполук на метал, що підтверджує актуальність теми даної роботи. Наведено результати термодинамічного аналізу ймовірності утворення хімічних сполук у системі «Ti-C-N-O-B». Проведено ранжування утворення хімічних реакцій залежно від температури ($T = 100 \dots 1200^\circ\text{C}$) й тиску повітря ($P = 1,33 \cdot 10^8 \dots 1 \cdot 10^5 \text{ Pa}$). Показано, що найактивніше титан буде взаємодіяти з киснем, утворюючи твердий розчин втілення з подальшим утворенням оксидів. Наступними за ймовірністю будуть утворюватися нітриди, потім карбіди і до температури $T = 900^\circ\text{C}$ – бориди титану. Виявлено, що вище температури $T = 900^\circ\text{C}$ сполука TiB утворюватися не повинна, може відбуватися лише дифузійне насичення титану бором. Показано, що за контакту B_2O_3 та B_2O_2 з титаном ці оксиди будуть розпадатися й утворювати відповідно оксиди титану та бориди титану. За контакту титану з нітридом бору ймовірно буде відбуватися його дисоціація та утворення нітриду титану й бориду титану. Карбід бору B_4C за контакту з титаном буде виступати як донор бору та вуглецю, а вище $P = 700^\circ\text{C}$ він буде розкладатися на бор та вуглець. Зниження тиску повітря зменшує ймовірність утворення сполук, що містять кисень та азот. За температури $T = 800^\circ\text{C}$ існуюча сполука B_2O_2 буде розкладатися і не буде утворюватися за тиску нижче $P = 1,33 \cdot 10^3 \text{ Pa}$. Подібна ситуація складеться для B_2O_3 за температури $T = 1000^\circ\text{C}$ – ця сполука не може утворюватися за тиску нижче $P = 0,133 \text{ Pa}$. Зниження тиску до $P = 1,33 \text{ Pa}$ за температури $T = 1000^\circ\text{C}$ призводить до збільшення ймовірності утворення TiC ніж TiN. Доставляння бору через газову фазу оксиду B_2O_3 стає ймовірним вище температури $T = 950^\circ\text{C}$, коли тиск його насиченої пари стає вищим за $P = 1,33 \cdot 10^3 \text{ Pa}$.

Ключові слова: титан, кисень, вуглець, азот, бор, термодинамічний аналіз, бінарні хімічні сполуки.

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