

# Thermodynamic modelling of phase equilibrium in system Ti-B-Si-C, synthesis and phases composition of borides and carbides layers on titanic alloy VT-1 at electron beam treatment in vacuum

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**Abstract.** Composite layers on the basis of carbides and borides the titan and silicon on titanic alloy VT-1 are generated at diffused saturation in vacuum. Formation in a composite of MAX phase  $\text{Ti}_3\text{SiC}_2$  is shown. Thermodynamic research of phase equilibrium in systems Ti-Si-C and Ti-B-C in the conditions of high vacuum is executed. The thermodynamics, formation mechanisms of superfirm layers borides and carbides of the titan and silicon are investigated.

## 1. Introduction

Last year's interests to the titan-silicon-boron-carbon alloys increases, as they, possess ease, high durability, excellent electro conducting and stability at the raised temperatures. The development of new compositions according to phase diagrams of the Ti-Si-B-C system is one of the main ways to obtain and investigate new titanium alloys with improved properties. By present time of the MAX phases (double carbides of silicon and titan  $\text{Ti}_3\text{SiC}_2, \text{Ti}_5\text{Si}_3\text{C}_x$ ) are synthesized by various methods in a nano structural status in the form of layers, films or ceramic.

The crystal structure of thin layers and physical and chemical, mechanical properties etc. are investigated [1-4].  $\text{Ti}_3\text{SiC}_2$  is a rare example of so called "plastic ceramics". It combines properties typical of ceramic compounds, such as high melting temperature, thermal and chemical stability, with mechanical properties of metallic systems. The main difficulty while synthesizing  $\text{Ti}_3\text{SiC}_2$  is the loss of silicon during reaction. The reaction features depend on the  $\text{Ti}_3\text{SiC}_2$  crystal structure that consists of titanium carbide blocks divided by silicon layers. The inter-atomic dimension analysis shows that they are larger for silicon in  $\text{Ti}_3\text{SiC}_2$  than for other compounds Ti-Si-C. At the same time, Ti-C dimensions are close to those of titanium carbide. The weak bond of silicon in the  $\text{Ti}_3\text{SiC}_2$  lattice can be the cause of its loss in thermal reactions.

In [5] the conclusion is drawn on synthesis possibility complex carbide phases, analogues of MAX phases in system Ti-Si-C as a result of high-intensity influences, for example electron beams. To improve properties of the material, information about the phase diagram and thermodynamic properties in the Ti-Si-C system is essential [6]. The authors strongly recommend the simultaneous use of thermodynamic calculations and experiments in order to establish technologically important phase diagrams highly efficiently.



Certainly, modeling phase equilibrium and revealing a field of borides and carbides in ternary systems Ti-Si-S and Ti-B-C represents to crystallization certain scientific interest. It is physicochemical basis for working out of technology of functional coating formation at electron beam processing in vacuum.

In the present study revealed optimum conditions of formation the MAX phases at electron beam processing of titanic alloys.

## 2. Experimental procedures

*Modeling phase equilibrium and revealing of fields of crystallization borides and carbides in ternary systems Ti-Si-S and Ti-B-C.*

In the present study used interface of a program complex TERRA[7]. Calculations are spent in a temperature interval 300-4500 K at a variation of the general pressure in system in a range from  $10^5$  to  $10^{-3}$  Pa.

In calculations considered following phases: silicides  $Ti_3Si$ ,  $Ti_5Si_3$ ,  $Ti_5Si_4$ ,  $TiSi$ ,  $TiSi_2$ ; carbides  $B_4C$ ,  $SiC$ ,  $TiC$ ; borides  $TiB$ ,  $TiB_2$  and  $Ti_3SiC_2$ ,  $Ti_5Si_3C_x$ .

Layers of composites formed on preliminary prepared surface of the samples made of titanic alloy VT-1 in the form of square plates in the size 15x15 mm and height of 7 mm. It was used sating daubs. Sating daubs contained reactionary a component (Si:2C) and the organic binding. As the organic binding applied a solution 1:10 glue BF-6 in acetone. Electron beam processing was carried out in a vacuum at most  $2 \times 10^{-3}$  Pa at power electron beam  $W = 250-450$  W for 1-3 min.

X-ray phase analysis was carried out on the Phaser 2D Bruker ( $Cu\ K\alpha_1$  – radiation). The microstructure of layers was investigated by METAM PB-22 microscope with the program NEXSYS Image Expert. The Vickers (HV) microhardness measurements are made by pressing a diamond indenter, of a specified shape, into the surface with a known force.

## 3. Results and discussion

Phase equilibrium and revealing of of crystallization fields of borides and carbides of the titan and silicon in ternary systems Ti-Si-C and Ti-B-C and their analysis representations about mechanisms and laws of education боридов and carbides in the conditions of vacuum allow to systematize and expand modeling. On fig. 1 the concentration tetrahedron of system Ti-Si-B-C is presented.

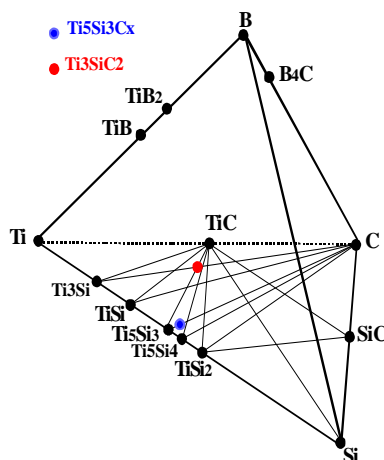
Phase equilibrium and revealing of of crystallization fields of borides and carbides of the titan and silicon in ternary systems Ti-Si-C and Ti-B-C and their analysis representations about mechanisms and laws of education боридов and carbides in the conditions of vacuum allow to systematize and expand modeling. On fig. 1 the concentration tetrahedron of system Ti-Si-B-C is presented.

### 3.1. Phase equilibrium in system Ti-Si-C.

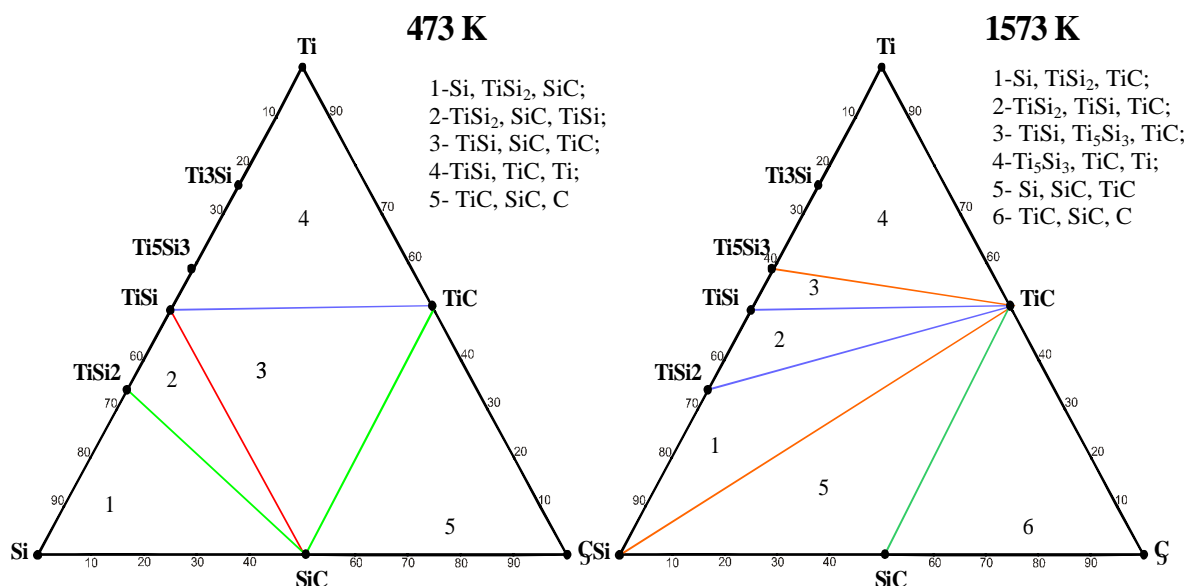
On fig. 2 are presented phase balance in system Ti-Si-C at pressure  $P=10^{-3}$  Pa. Areas of co-existing phases are allocated. It is shown, that the titan silicides titans of various compositions form квазибинарные cuts with titan carbide, instead of with silicon carbide.

### 3.2. Phase balance in system Ti-B-C.

In this system cut  $Ti-B_4C$  is not binary. At him there can be various phases from ternary system Ti-B-C. Phase balance (isothermal sections at 1000 K) in system Ti-B-C are presented on fig. 3 at pressure  $10^{-3}$  Pa, besides on fig. 4 are presented isotherms of this system at discussed pressure. Formation of ternary compounds is not revealed.



**Figure 1.**Concentration tetrahedron of system Ti-Si-B-C.



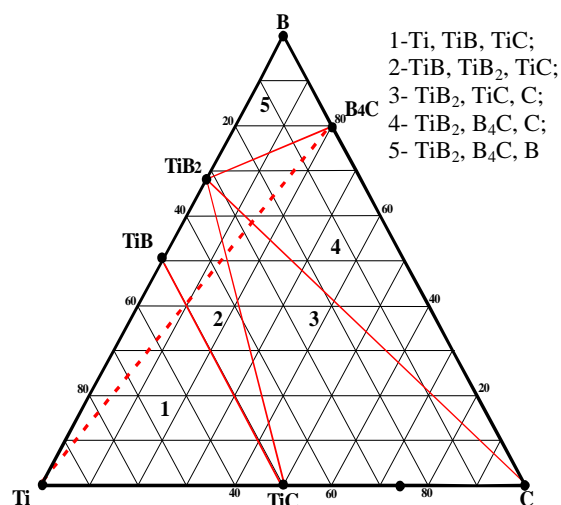
**Figure 2.**Phase equilibrium in system Ti-Si-C at  $10^{-3}$  Pa.

According to thermodynamic calculations the coexistence of various areas of crystallization is possible:  $B_4C$ ; C;  $C+TiB_2$ ;  $B_4C+C+TiB_2$ ;  $C+TiB_2+TiC$ ;  $TiC$ ,  $TiB_2+TiC$ ,  $TiB+TiB_2+TiC$ ;  $TiB+TiC$  and  $Ti+TiB$  (at pressure below 1 Pa). At atmospheric pressure at heats (above 3000K) areas single-phase boride  $TiB_2$ , boron, their joint presence, and three-phase area with B, C and  $TiB_2$  are found out.

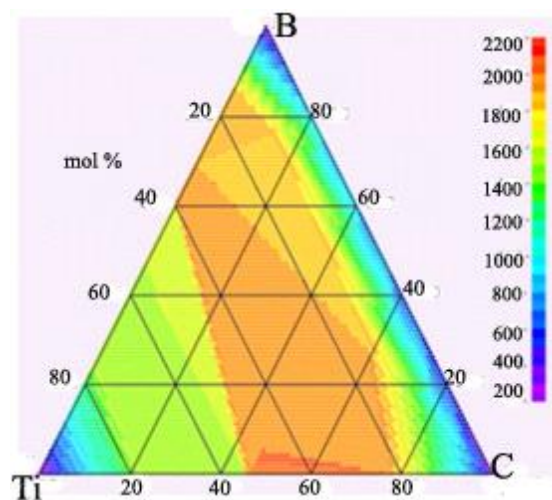
Formation processes of the carbides and borides titan proceed with allocation of a significant amount of energy, thereby raising temperature in system to 2000÷2150 K ( $P=10^5$  Pa) and 1600÷1725 K ( $P=10^{-3}$  Pa).

### 3.3. Titanic alloy VT-1.

Initial alloy VT-1 was represented a mix of two forms of the titan ( $\alpha$  - and  $\beta$ -Ti). Titanic alloy VT-1 after electron beam treatment was also many phases. Lattice parameters of cells  $\alpha$ -Ti:  $a=0,29504$  nm and  $c=0,46833$  nm (P63/mmc, PDF 03-065-3362), and parameters of a cubic cell  $\beta$ -Ti:  $a=0,3306$  (Im-3m, PDF 00-044-1288).



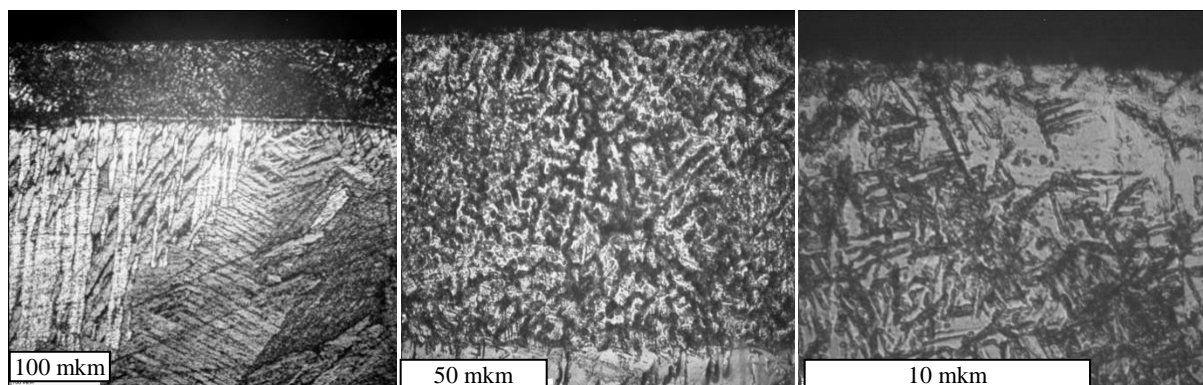
**Figure 3.** Phase equilibrium in system Ti-B-C at T=1000 K ( $P=10^{-3}$  Pa).



**Figure 4.** Isotherms in system Ti-B-C at  $P=10^{-3}$  Pa.

*Composite layers on the basis of titan and silicon carbides.*

Layers of composites 80-100 microns are formed. A layers structure iseutectic (fig. 5).



**Figure 5.** Structure layer Ti-Si-C on titan VT-1.

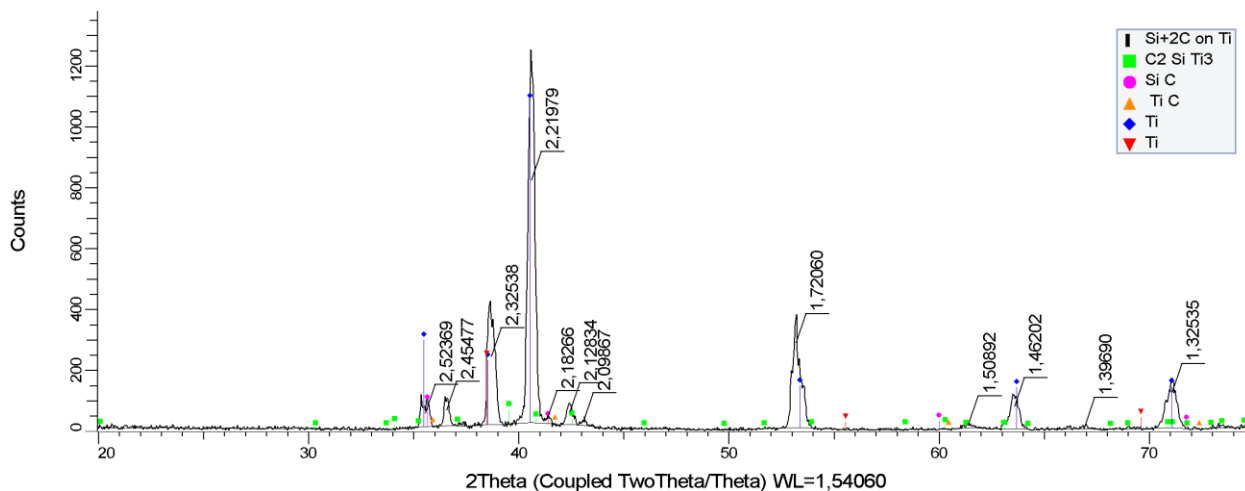
According to XRD results the composite layer are contain 76,5 mas. % crystalline and 23,5 mas. % amorphous phases. Thus the metal basis consists from 84,06 mas. %  $\beta$ -titan with and 4,06 mas. %  $\alpha$ -titan. The layer contains double carbide  $\text{Ti}_3\text{SiC}_2$  and silicon carbide  $\beta\text{-SiC}$  (PDF01-073-1665, F43m), with a cubic cell  $a=0,4358 \text{ nm}$ .

### 3.4. Solid state boriding from sating daub of amorphous boron.

X-ray presence disordered phases of titan  $\alpha\text{-Ti}$  and boride titan  $\text{TiB}_2$  (PDF 01-073-2148) is revealed. There is no reflexes  $\beta\text{-Ti}$  that testifies to heats on a surface of a titan alloy at electron beam boriding. The considerable thickness of the modified layer (more than 700-900 microns) is observed.

Attempt of synthesis  $\text{Ti}_6\text{Si}_2\text{B}$  from sating daub of composition Si-B-2C is made. Layers of thickness 30-80 microns are reformed.

Measurement of microhardness of composite layers has shown achievement of values to 10 GPa.



**Figure 6.** X-ray phase analysis of composite layers Ti-Si-C on titan alloy VT-1.

#### 4. Conclusions

In summary, preliminary results of electron beam boriding of titan alloy VT-1 are presented. The thermodynamic investigation of equilibrium in systems Ti-B-C-Si is carried out with the purpose of formation conditions optimization of functional layers on a surface of titan alloys as a result of electron beam boriding in vacuum. The thickness of MAX phase  $\text{Ti}_3\text{SiC}_2$  coating is received 100  $\mu\text{m}$ . Composite layers will consist from  $\text{Ti}_3\text{SiC}_2$ . Research by means of a metallographic microscope has shown that carbide borides layers formation is difficult physical and chemical process. Their formation is difficult physical and chemical process. The structure, phase structure and strength characteristics are investigated.

#### Acknowledgements

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