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Phase equilibrium in system Ti-Si-C-B and synthesis of MAX phase layers in vacuum under the influence of electron beam

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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 by electron beam treatment in vacuum. Formation in a composite of MAX phase Ti_3SiC_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 Ti_3SiC_2, $Ti_5Si_3C_x$) are synthesized by various methods in a nanostructural 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]. Ti_3SiC_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 Ti_3SiC_2 is the loss of silicon during reaction. The reaction features depend on the Ti_3SiC_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 Ti_3SiC_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 Ti_3SiC_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, modelling 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 in ternary systems Ti-Si-S and Ti-B-C were carried out. 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: silicide's Ti_3Si, Ti_5Si_3, Ti_5Si_4, TiSi и $TiSi_2$; 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:2 C) 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 $2x10^{-3}$ Pa at power electron beam W = 250-450 W for 1-3 min.

X-ray phase analysis was carried out on the Bruker Phaser 2D diffractometer with a Cu Ka radiation source of a wavelength of 1.504 Å over a 2θ range from 20º to 100º. The microstructure of layers was investigated by METAM PB-22 microscope with the program NEXSYS Image Expert. The microhardness of composite layers was measured by indentation technique using a Vicker's indenter.

3. Results and discussion

Phase equilibrium and revealing 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 borides and carbides in the conditions of vacuum allow systematizing and expanding modeling. On the figure 1 the concentration tetrahedron of system Ti-Si-B-C is presented.

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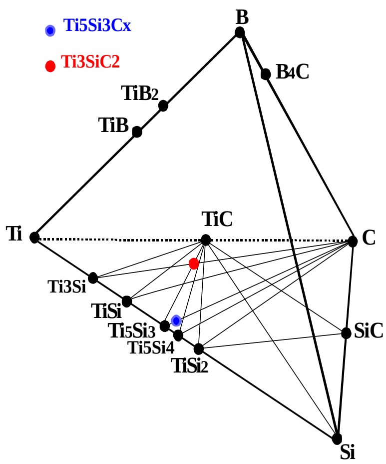

Figure 1. Concentration tetrahedron of system Ti-Si-B-C.

Phase equilibrium in system Ti-Si-C was calculated. On the figure 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 silicide's titans of various compositions form quasi-binary cuts with titan carbide, instead of with silicon carbide.

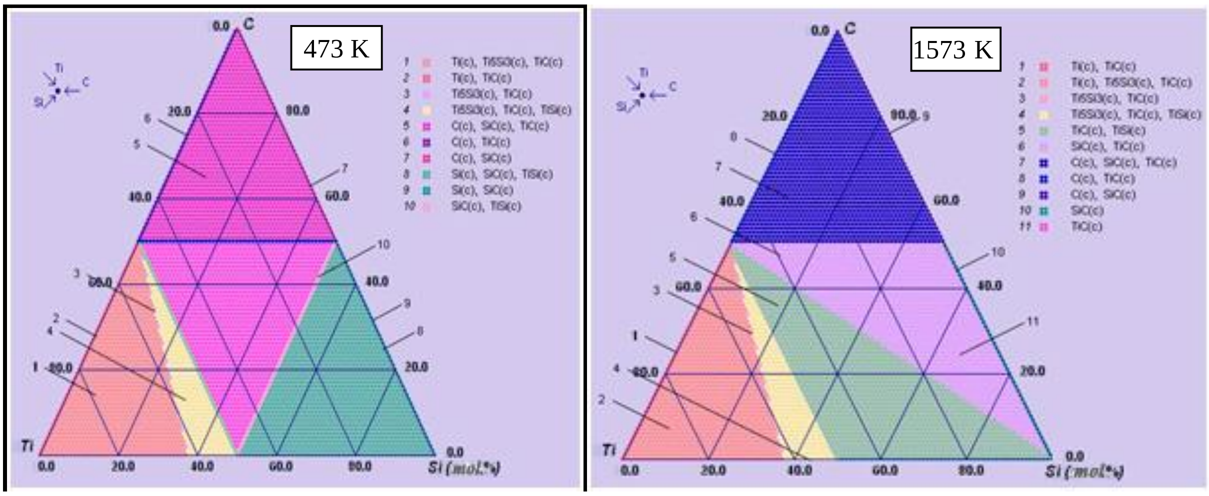

Figure 2. Phase equilibrium in system Ti-Si-C at 10^{-3} Pa.

Phase balances in system Ti-B-C were studied. 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 the figure 3 at pressure 10^{-3} Pa, besides on the figure 4 are presented isotherms of this system at discussed pressure. Formation of ternary compounds is not revealed.

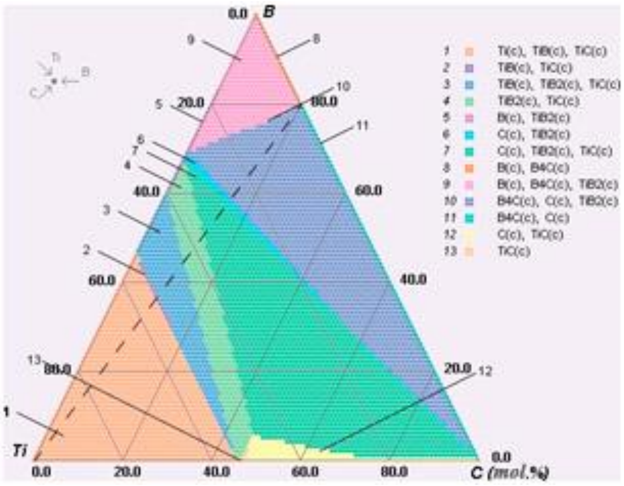

Figure 3. Phase equilibrium in system Ti-B-C at T=1000 K (P=10^{-3} Pa).

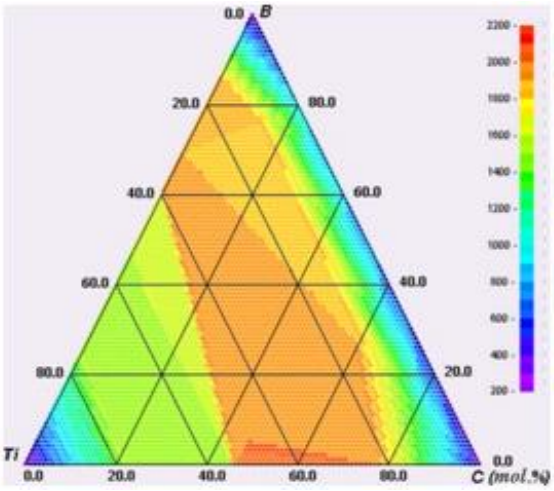

Figure 4. Isotherms in system Ti-B-C at P=10^{-3} Pa.

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).

Titanic alloy VT-1 was carried out by power electron beam. The diffraction results were compared with the results published by the International Centre for Diffraction Data (ICDD), and the measured values were close to the d values published by ICDD in the Powder Diffraction File (PDF). Initial alloy VT-1 was represented a mix of two forms of the titan (α - and β-Ti). Titanic alloy VT-1 after electron beam treatment was also many phases. Lattice parameters of cells α-Ti: *a*=0,29504 *nm* and *c*=0,46833 *nm* (P63/mmc, PDF 03-065-33 62), and parameters of a cubic cell β-Ti: *a*=0,3306 (Im-3m, PDF 00-044-1288).

Composite layers on the basis of titan and silicon carbides were formed. Layers of 80-100 microns are formed. Figure 5 showed the microstructures of the overview cross-section of the composite layers in sample. It was noted that there was a metallurgical combination between the coating and VT-1 substrate in sample 1. A layers structure is eutectic.

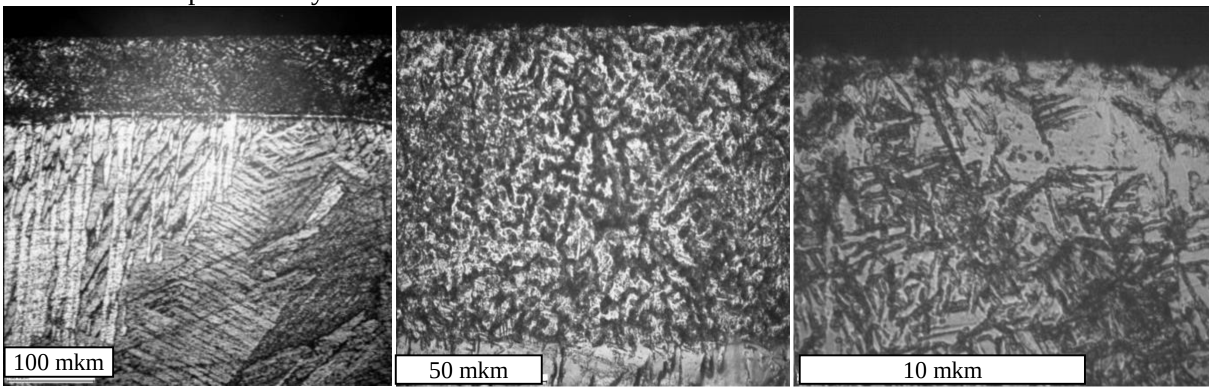

Figure 5. Structure layer Ti-Si-C on titan VT-1.

According to XRD studies the composite layer are containing 76,5 mas. % crystalline and 23,5 mas. % amorphous phases. Thus the metal basis consists from 84,1 mas. % β- titan with and 4,1 mas. % α-titan. The layer contains double carbide Ti_3SiC_2 and silicon carbide β-SiC (PDF01-073-1665, F43m), with a cubic cell *a*=0,4358 nm.

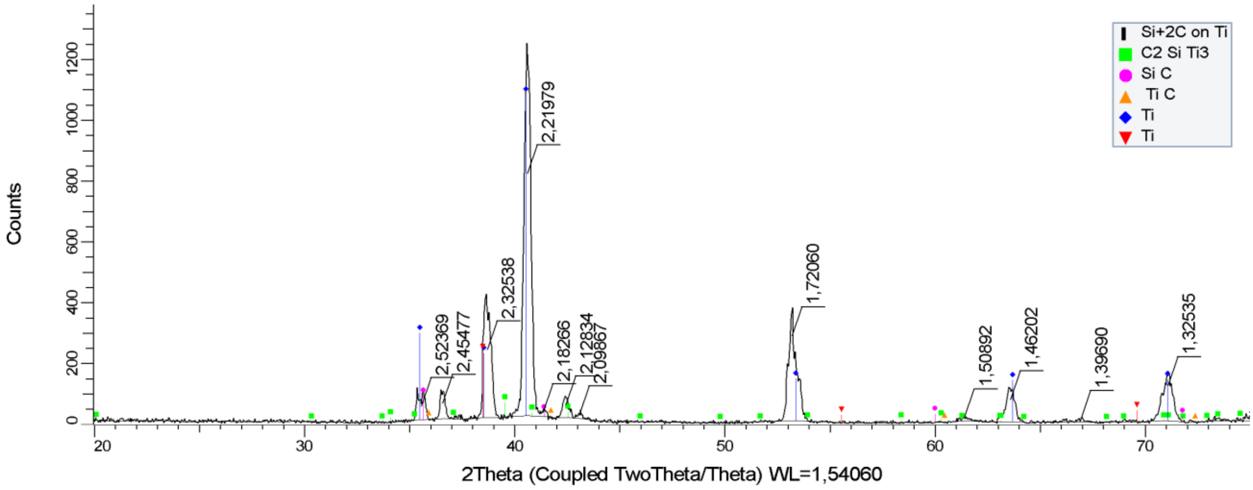

Figure 6. XRD pattern of composite layers Ti-Si-C on titan alloy VT-1.

Solid state boriding from sating daub of amorphous boron were carried out. On XRD patterns the disordered phases of titan α-Ti and boride titan TiB_2 (PDF 01-073-2148) are presented There is no reflexes β-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 Ti_6Si_2B from sating daub of composition Si-B-2C is made. Layers of thickness 30-80 microns are formed.

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

4. Conclusion

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 Ti_3SiC_2 coating is received 100 μm. Composite layers will consist from Ti_3SiC_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.

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