Features of formation of structural-phase states on the surface of titanium alloy VT1-0 after electron-ion-plasma treatment

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Abstract. Complex modification of a surface of commercially pure titanium is realized. Firstly plasma is created by electrical explosion of a carbon-graphite fiber, of which surface was placed nanosized TiB_2 powder. Then the surface of technically pure titanium is processed with this plasma. Finally, the modified surface was irradiated by an electron beam. Formation of multi-layer multiphase nanosized structure is revealed. It is shown that the maximum microhardness reached in a near-surface layer exceeds microhardness of a initial material more than by 10 times. Wear resistance of a blanket increases in 7.5; the friction coefficient decreases by 1.15 times.

1. Introduction

Currently, one of the most promising approaches to creation of wear-resistant coatings is a method of formation of composite materials with titanium diboride. Such a composite material has a high load-bearing capacity combined with high physical and mechanical properties (high hardness, low values of the thermal expansion coefficient, low sensitivity to heat shock) and is not subject to plastic deformation which contributes to accumulation of defects in a crystalline lattice and the subsequent damage during a tribological contact. Such a surface is possible to create using pulsed melting with simultaneous saturation of the material surface layers with doping elements followed by crystallization and formation of strengthening phases, carried out by plasma formed during an electric explosion of a conductive material (electroexplosive doping), is one of the promising methods for modification of the structure and properties of metals and alloys.

This paper presents the results of the study on the combined treatment effect, which includes electroexplosive doping and the subsequent exposure to a high-intensity pulsed electron beam, on the structural-and-phase state of the surface layer of the alloy based on titanium VT1-0.

2. Materials and methods of study

Doping of the surface layer of the alloy based on titanium VT1-0 was carried out by exposure to plasma formed during an electric explosion of a graphitized carbon fiber, on the surface of which in the explosion area a sample of the powder of titanium diboride TiB_2 was placed. Additionally, pulsed melting of the modified layer was carried out with a high-intensity electron beam on the installation

"Solo", under the mode: electron energy 18 keV, energy density of the electron beam (45-60) J/cm^2, duration and the number of exposure pulses 100 ms, 10 pulses; 200 ms, 20 pulses, the pulse repetition rate 0.3 s^{-1}. Structural studies were carried out using methods of scanning and electron diffraction microscopy, X-ray analyses; physical-and-mechanical properties of the surface layer were studied by measuring the microhardness, the wear resistance, and the friction coefficient.

3. Experimental results and their discussion

According to the literature data on the enthalpy, formation of compounds in systems Ti-B [1] and Ti-C [2] is significant and it indicates a high stability of compounds TiB_2 and TiC_X (Fig. 1).

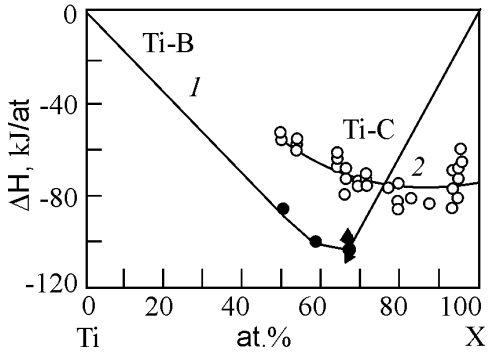

Figure 1. The enthalpy of compound formation in systems Ti-B (curve 1) [1] and Ti-C (curve 2) [2] at 298 K

In the system Ti-B during the crystallization three intermediate phases from the side B are formed: TiB, Ti_3B_4, TiB_2 [3] (Fig. 2). Mutual solubility of components in the solid state is virtually absent. At a temperature of 1540 ± 10 °C the eutectic (βTi) + TiB is crystallized. The compound TiB_2 melts congruently at 3225 ± 25 °C, it has a small homogeneity range. Compounds Ti_3B_4 and TiB are formed by peritectic reactions at temperatures of 2200 °C and 2180 °C, respectively [4]. Titanium is a transition metal and has an unfilled 3*d*-band [5]. Among elements of the group IVA it is the most electronegative metal and has an atomic radius (R_{Ti} = 0.1462 nm). Formation of compounds with a variety of elements of the periodic system is characteristic of titanium; as well as formation of limited solid solutions.

There are several known crystalline modifications of boron (Fig. 2) [6]. For example, in the structure of silver boron atoms form a three-dimensional framework, whose basic structural unit is an icosahedron with 12 boron atoms at its vertices. Icosahedra are interconnected by means of intermediate boron atoms, which are not part of any of the icosahedron, and boron atoms that are part of icosahedra. This leads to the fact that boron atoms in crystals have different coordination numbers: 4, 5, 6, and 5 + 2 (5 near "neighboring" and 2 more distant). According to the electronic configuration $1s^2 2s^2 2p^1$ there are three electron atoms of boron on the outer shell, and this leads to the fact that each bond in the crystalline boron has less than 2 electrons. Thus, in the crystalline state the main bond type for boron is covalent with electron deficiency [6].

In the system Ti-C there is one carbide compound TiC(δ) with a structure B1 (prototype NaCl, Pearson symbol sF8, sp. gr. *Fm3m*) [4]. The compound TiC(δ) melts congruently at 3073± 25 °C and the content is ~44% (at.) C. The homogeneity range of the phase TiC near the solidus is from 32 up to 50% (at.) C. Carbon decreases the melting point of Ti from 1663 to 1653±7 °C - the temperature of eutectic crystallization L ↔ βTi + TiC(δ); a eutectic contains 1.5% (at.) [4]. From a structural point of view, the compound TiC (δ) is a solid solution of nonmetal atoms in octa-interstitial sites of the FCC-lattice of metal [7]. Consequently, in the literature carbide TiC (δ) is often referred to as TiC_x. Structural parameters of the compound TiC_x depending on the carbon content are shown in Table 1.

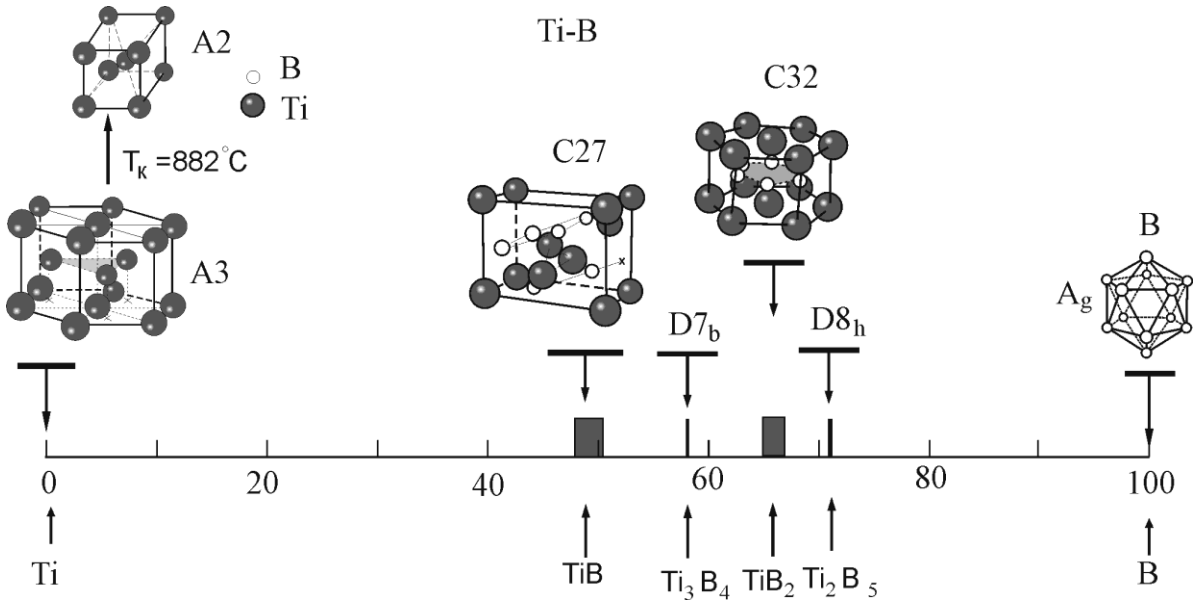

Figure 2. Elementary cells of borides in the binary system Ti-B, depending on the concentration and their homogeneity range.

Table 1. Structural data on ordered phases as a result of PT δ↔δ' [4]

Composition	Syngony	Sp. gr.	Elementary cell parameters	T_C, °C δ↔δ'
Ti_8C_5	trigonal	*R3m*	a = 0.6115 nm, c =1.490 nm in hexagonal axes	
$TiC_{0.67}$	rhombic		$a= 2a_0$	785±5
$TiC_{0.58}$	rhombic		$a= 2a_0$	
$TiC_{0.53}$	rhombic		$a= 2a_0$	
$TiC_{0.46}$ - $TiC_{0.60}$				590

We shall note the following important points that reflect features of the crystalline structure of the phase TiC_x:

1) an important role of the size factor in formation of carbide TiC_x is evident, i.e. arrangement of non-metal atoms in octa-interstitial sites of the FCC-lattice of metal (Fig. 3), which is determined by the well-known Hagg's rule (for TiC_x the size factor is $R_C / R_{Ti} = 0.62$);

2) the presence of a very wide homogeneity range of titanium carbide ($TiC_{0.48}$ - $TiC_{1.0}$);

3) the compound TiC_x belongs to non-stoichiometric compounds of the interstitial phase type (or non-stoichiometric interstitial compounds), the concentration of defects (vacancies) in which provides the interaction among atoms;

4) in the system Ti-C the symmetry of the metallic sublattice of non-stoichiometric compounds is different from the symmetry of the crystalline lattice of corresponding transition metals because titanium carbide crystallizes in the FCC structure in which a succession of layers of Ti atoms is well traced (Fig. 3);

5) at a temperature below 1000 °C the presence of ordering in the carbon sublattice (transition δ↔δ'-transformation) as in conventional solid solutions [4];

6) during the transition δ↔δ'-transformation, as a result of ordering of structural vacancies of the nonmetallic sublattice, a decrease in the symmetry of the space group of the crystal takes place, which results in crystallographically nonequivalent variants of joints of octahedra MS6 (in the structure B1 octahedra are joined by ribs);

7) the solid-solution nature of TiC_x and the structure-forming role of bonds of the nearest neighbors Ti-Ti is confirmed by data value and their physical properties [7];

8) according to modern concepts, a combined covalent-metal-ion type of chemical bond is implemented in non-stoichiometric interstitial compounds MC_x.

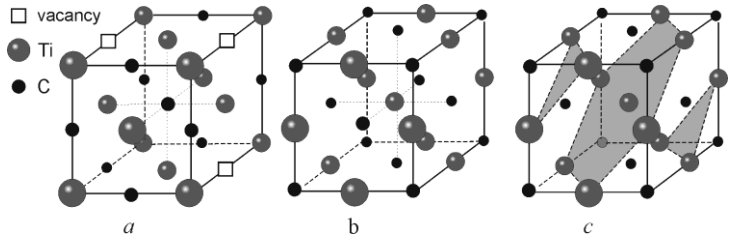

Figure 3. The crystalline structure of carbide TiC_x: *a* – structure B1 with vacancies; *b* –structure B1 without vacancies with a displaced origin of coordinates relative to the represented elementary cell; *a, c* – structure B1 with successively allocated alternating atomic layers of Ti atoms perpendicular to the direction of the type $[111]_{B1}$

Since the compound TiC_x belongs to non-stoichiometric compounds with a wide homogeneity range of the interstitial phase type, the arrangement of structural vacancies leads to formation of a wide variety of crystalline structures. Fig. 4 shows variants of these crystalline structures. It should be noted that the published data on thermodynamic properties of non-stoichiometric titanium carbide is extremely limited. On the other hand, theoretical calculations predict a whole range of crystalline structures based on titanium carbide. Thus, Fig. 5 presents a cubic superstructure of the type M_8X_7. It belongs to a perfectly ordered cubic phase with a space group $R4_332$, which is predicted in [8].

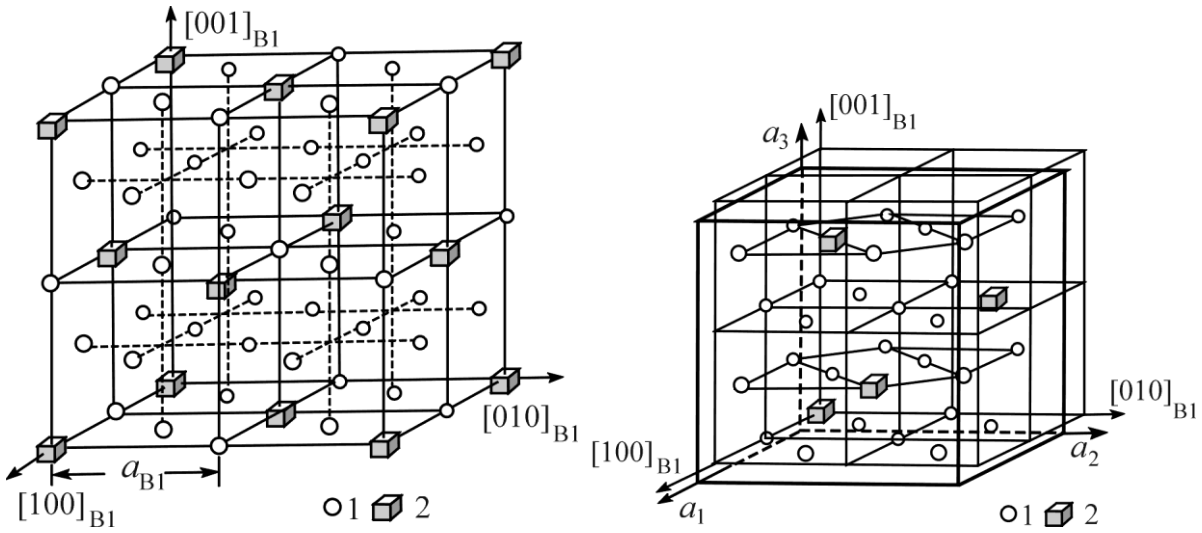

Figure 4. Arrangement of cubic (space group *Fm3m* (*a*) and sp. gr. $P4_332$ (*b*)) elementary cells of the superstructure M_8X_7 in the lattice with a structure Bl (NaCl) and (metallic sublattice is not shown) 1 – interstitial atoms; 2 – vacancies [7].

Fig. 5 shows an isothermal section of the system Ti–B–C. On this diagram it can be seen that the mutual solubility at temperatures below 1400 °C is insignificant. The solubility of boride TiB_2 in carbide TiC_{1-X} is highly dependent on the stoichiometry of the carbide. This is reflected in the form of a non-uniform, in thickness, homogeneity range of carbide TiC_{1-X} on the isothermal diagram. It also finds support on the quasi-binary section between the two coexisting phases TiC_{1-X} and TiB_2 (Fig. 6).

[9] This diagram is characterized by a eutectic transformation at a temperature of 2500 °C and low mutual solubility in TiC_{1-X} of boron atoms and carbon atoms in TiB_2 at temperatures below 2000 °C. In the case of $TiC_{0.95}$ it is nearly 3% (mol.), and in the case of $TiC_{0.68\ it}$ is nearly 7% (mol.) TiB_2. Furthermore, the given isothermal section of the ternary diagram Ti–B–C indicates the absence of ternary intermediate compounds inside the isothermal triangle (Fig. 5).

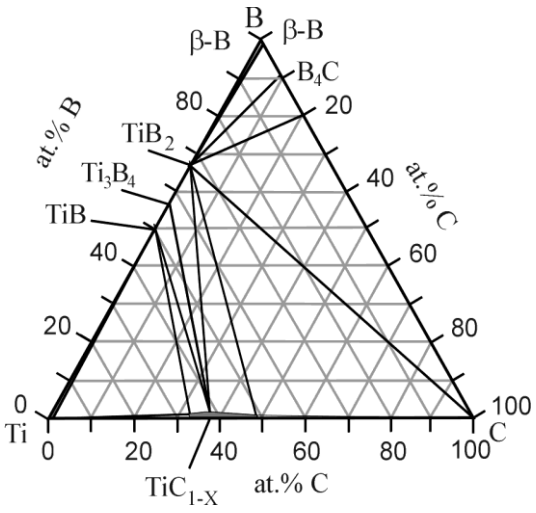

Figure 5. Isothermal section of the system Ti-B-C at 1400 K [9]

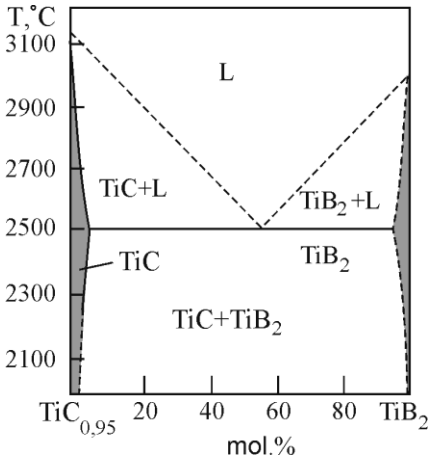

Figure 6. Quasi-binary section $TiC_{0.95}$–TiB_2 of the system Ti-B-C [3]

As previously noted, the system Ti-B-C was formed by doping of commercially pure titanium with plasma formed during an electric explosion of a graphitized carbon fiber, on the surface of which a sample of the nanoscale powder TiB_2 was placed. An additional heat treatment of the modified in such a manner surface layer was carried out by irradiation with an intense pulsed electron beam in the melting mode of the surface layer with a thickness of (20-30) micrometers.

Methods of the X-ray analysis revealed the phase composition of the complex modification of a surface of commercially pure titanium: α–Ti - 17 %, TiC - 60 %, TiB_2 - 14 %, Ti_3B_4 - 2 %, C - 6 %, (B_8C + $B_{25}C$) - 1 %. The total volume fraction of second phases (δ) after EED is 50%; an additional irradiation with an electron beam results in a non-linear change of the value δ: with an increase in the energy density of the electron beam from 45 J/cm^2 to 60 J/cm^2, δ ranges from 25% to 83% reaching a maximum value at the energy density of the electron beam of 60 J/cm^2 (pulse duration of the electron beam exposure is 200 ms).

The study of the phase composition and the defect substructure of the surface layer of titanium modified using the combined method (plasma doping and the subsequent irradiation with an electron beam) was carried out using methods of electron diffraction microscopy of thin foils. It has been established that as a result of the combined treatment in the surface layer of commercially pure titanium a structure of dendritic crystallization based on titanium is formed; the section size of dendritic branches varies from 100 nm to 250 nm. Second-phase inclusions (predominantly titanium carbide of the composition TiC) are located in interdendritic spaces, particle sizes vary from 30 nm to 50 nm.

The structure of the layer located at a depth of 40...50 micron (the intermediate layer separating the melting zone from the heat affected zone) is formed by titanium grains with sizes varying from 80 nm to 200 nm. Second-phase particles with sizes varying from 10 nm to 25 nm are located on grain boundaries and junctions of grain boundaries. Indexing of micro-electron-diffraction patterns obtained from particles allows to conclude that they are, primarily, carbides and titanium borides.

Modification of the structure of the surface layer led to a multiple increase in mechanical and tribological properties of titanium. It has been established that the maximum microhardness achieved in the near-surface layer exceeds the microhardness of the basis by more than 10 times. The thickness of the hardened layer, the micro-hardness of which exceeds the micro-hardness of the basis by ≈5 times, reaches ≈90 microns The wear resistance of the surface layer increases (relative to the wear resistance of the initial material) by ≈8 times. The friction coefficient decreases (relative to the friction coefficient of the initial material) by ≈1.2 times. Having analyzed the results obtained after constructing microhardness profiles it may be noted that one – three maxima of the microhardness, located at the surface and in layers at a depth of 30...50 microns and 80...90 microns, are formed depending on the mode of electron beam treatment.

The carried out studies of the defect substructure and the phase composition of the modified surface layer allow to express opinions about physical mechanisms responsible for a significant increase in mechanical and tribological properties of titanium. It has been established that the main mechanisms responsible for an increase in mechanical and tribological properties of the material are solid-solution (saturation of the crystalline titanium lattice with atoms of carbon and boron); dispersion (allocation of nanoscale particles of carbide, boride, and carbide-boride phases); grain boundary (formation of a grain structure with submicron dimensions).

4. Conclusion

The surface of commercially pure titanium was processed by plasma generated by the electric explosion of the carbon-graphite fibers, the surface of which is placed nanosized TiB_2 powder. Additional heat treatment of the modified in such a manner surface layer was carried out by irradiation with an intense pulsed electron beam in the mode of the surface layer melting. Formation of a multilayer multiphase nanoscale structure with high values of hardness and wear resistance is revealed. It is shown that the maximum micro-hardness achieved in the near-surface layer exceeds the micro-hardness of the basis by more than ≈10 times; the thickness of the hardened layer, the micro-hardness of which exceeds the micro-hardness of the basis by ≈5 times, reaches ≈90 microns. The wear resistance of the surface layer increases (relative to the wear resistance of the initial material) by ≈7.5 times; the friction coefficient decreases by ≈1.15 times. Based on the study results of the phase composition and the defect substructure, physical mechanisms ensuring high strength properties of the modified layer of titanium are proposed.

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