Structural studies of surface-alloyed layers of the Cr-B4C system, formed on Ti-6Al-4V titanium alloy

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Abstract. The paper presents studies of the structure of surface-alloyed layers obtained by the method of non-vacuum electron-beam cladding of the Ti-Cr-B4C and Cr-B4C powder mixture systems. Structural analysis allowed to identify the dependence of the initial powder portion on the shape and size of the phases formed. It is noted that the presence of titanium (10 wt. %) in the composition of the surfacing mixture leads to the formation of large primary crystals of titanium carbide and boride. The absence of titanium contributes to the formation of chromium carbide coating and small eutectic particles on the grain boundaries on the surface.

1. Introduction
Titanium and its alloys are among the most promising structural materials in modern engineering. Due to its excellent corrosion resistance, physiological inertness, high specific strength, plasticity and satisfactory heat resistance, titanium-based alloys are widely used in aircraft, rocket production, shipbuilding, chemical industry and medicine [1-2].

The use of titanium alloys in the manufacturing of various kinds of products, is quite extensive, but, despite the unique combination of characteristics, is not recommended to use it under the wear conditions. The relation between the crystal lattice and the electronic structure of materials with its properties is proved in many scientific works [3-5]. It is shown that the tribotechnical characteristics of titanium alloys depend on the axial ratio of its crystal lattice [6]. Despite the fact that α-Ti has a HCP lattice, its axial ratio is far from ideal (for α-titanium = 1.588; for an ideal HCP lattice = 1.633), which is associated with the compression of the titanium lattice along the C axis. Thus, an increase in the axial ratio of the crystal lattice should lead to an increase in the tribotechnical properties of titanium alloys.

Research studies have shown that to improve the tribotechnical properties of titanium alloys, it is necessary to form a wear-resistant coating on the surface of the blanks, since it is the surface layers that are affected by the external environment during operation. Highly concentrated heat sources, such as a laser [7-9], a plasma [10-11], and an electron beam [12-13], are promising methods for surface hardening. However, the use of these heating sources for the formation of surface-alloyed layers has several disadvantages. These include low adhesion properties (plasma spraying), low level of efficiency and thickness of the alloyed layer (laser processing) and overall limitations (vacuum electron-beam cladding). To avoid the above disadvantages, it is possible to use a unique technology
of non-vacuum electron-beam treatment. Due to the high power (100 kW), electron-beam treatment in the atmosphere makes it possible to obtain uniform coatings up to 5 mm thick that include high-strength particles of carbides, borides, nitrides and oxides [14-15]. Also, the non-vacuum electron-beam treatment allows to avoid the use of expensive vacuum chambers, due to the possibility of the output of a relativistic electrons beam into the air atmosphere [13].

A literature review showed that the formation of particles such as titanium carbides (TiC) and borides (TiB) in the surface-alloyed layers can lead to 2-fold increase in hardness, and wear resistance can be increased by 6-9 times [16].

In this work, surface hardening of titanium alloy Ti-6Al-4V is implemented by the method of non-vacuum electron-beam treatment. Structural transformations and features of the samples obtained by cladding powder mixtures of the Ti-B₄C-Cr and B₄C-Cr systems are also studied.

2. Materials and Methods

The technology of non-vacuum electron-beam treatment was used to implement the surface treatment of titanium blanks. The method was implemented on an industrial electron accelerator of the ELV-6 type. This accelerator was developed at the Budker Institute of Nuclear Physics SB RAS and has a power of up to 100 kW. A three-stage vacuum pumping allows a concentrated beam of relativistic electrons to be output without significant energy loss, which makes it possible to form refractory particles on the surface of materials.

The plates of titanium alloy Ti-6Al-4V with the size of 12 × 50 × 100 mm were used as the blanks. The formation of wear-resistant coatings was carried out by cladding a powder mixture containing boron carbide, chromium and titanium as a wetting component. To protect the molten bath from air, fluorine fluxes (CaF₂ and LiF) were used. These fluxes are not prone to hot cracking. Table 1 presents the modes and compositions of the cladding mixtures for a series of samples.

| No. | Cladding mixture, wt. % | Blank | Specific surface energy, kJ/cm² |
|-----|------------------------|-------|-------------------------------|
| 1   | B₄C+Cr+CaF₂+LiF (20+30+40+10) | Ti-6Al-4V | 3 |
| 2   | B₄C+Cr+CaF₂+LiF (30+20+40+10) | Ti-B₄C-Cr | 5 |
| 3   | Ti+B₄C+Cr+CaF₂+LiF (10+20+20+40+10) | Ti-B₄C-Cr | 3 |

Structural studies of the formed samples were carried out using optical and scanning microscopy. Analysis of the coatings on a Carl Zeiss Axio Observer Alm microscope at magnifications up to 1000 times allowed to estimate the quality of the samples, the thickness of the surface-alloyed layers and the distribution of the formed phases. More in-depth studies were carried out using a Carl Zeiss EVO50 XVP electron microscope equipped with an EDS X-Ast add-on device.

3. Results and discussion

Analysis of the structure of the formed surface-alloyed layers showed that it can be divided into 2 zones: the coating and the heat-affected zone (HAZ). The thickness of the surface-alloyed layer (the 1st and the 2nd samples) was 2.2 ... 2.6 mm. The addition of titanium to the initial powder mixture leads to an increase in the thickness of the surface-alloyed layer up to 2.9 mm.

It should be noted that in the structure of the samples obtained by cladding of the B₄C-Cr powder mixture, a thin layer of chromium carbide was fixed in the upper part of the coating (Figure 1 a, d). Cladding of a powder mixture containing chromium (30 wt. %) contributes to the formation of a uniform layer over 100 µm thick over the entire surface of the coating. Reducing the chromium
concentration in the initial cladding mixture by 10 wt. % makes it possible to form only local areas with chromium carbide with a maximum thickness of up to 80 µm.

These carbide crystals have a dendritic structure, which is similar to the structure obtained in the foundry. Dendrites have an axis of the first and second order and crystallize in the direction of heat removal. At high magnifications, the axes of dendritic chromium carbide crystals have an irregular shape, which is formed by merging of the primary round particles in the crystallization process (Figure 2 a).

Figure 1. Structural features of coatings of the sample formed by cladding the powder mixtures using non-vacuum electron-beam treatment: a, b, c – the 1st sample (30Cr + 20B₄C); d, e, f - the 2nd sample (20Cr + 30B₄C); g, h - the 3rd sample (10Ti + 10Cr + 20B₄C)
Figure 2. The microstructure of the surface-alloyed layers obtained using a scanning electron microscope: a, b, c - coatings formed by cladding of the Cr-B₄C powder mixture; d, e, f - coatings formed by cladding of the Ti-Cr-B₄C powder mixture

During the electron-beam treatment, the surface of the blank receives significant heating; a molten bath is forming, which forms a surface-alloyed layer during crystallization that is tightly bound to the base material by a heat-affected zone. However, the electron beam effect occurs only on the surface, so that the remaining volume of the titanium base remains intact. This leads to rapid heat transfer from the coating deep into the base material, and therefore the main structure of the coatings consists of eutectic particles located along the grain boundaries, elongated in the direction of heat removal (Figure 1c, e; 2c). Changing the concentration of boron carbide in the initial powder mixture from 20 to 30 wt. % leads to a slight increase in the density of these eutectic crystals for the first and second samples, respectively (Figure 1b, f). More in-depth studies of the microstructure showed that eutectic particles consist of small needle-like crystals of titanium boride, and dispersed crystals of titanium carbide, which are close to round in shape (Figure 2b).

The structure of the sample obtained when titanium was added to the initial powder mixture is significantly different. This type of coating is homogeneous and consists of large crystals of titanium boride, in a form close to hexagonal, and titanium carbides of dendritic morphology (Figure 1g – h; 2d).

A distinctive feature of these surface-alloyed layers is the formation of titanium carbide crystals on the walls of boride particles (Figure 2d-f). Such a structure is explained by a more active interaction
of boron atoms with titanium, which leads to the initial formation of titanium boride. Subsequently, with a decrease in temperature, carbide crystals form on the already formed particles of titanium boride, which significantly reduces the required energy of formation. In addition to the primary phases, eutectic small particles are fixed in the entire volume of the coating (Figure 2 b).

The apparent structural differences of the samples of the B₄C-Cr and Ti-B₄C-Cr systems can be explained by the negligible presence of titanium in the molten bath during the treatment of the first samples by the electron beam. For the formation of large primary crystals of titanium carbide and boride, a larger amount of free titanium atoms is needed, however, when treated by an electron beam, chromium, added to a powder, is the first that reacts with boron and carbon atoms. After the powder mixture is melted, the surface layer of the titanium blank melts; however, due to the rapid heat removal, only small eutectic particles are formed in the coating. The introduction of titanium (10 wt. %) into the initial cladding mixture leads to the nucleation of primary crystals of titanium boride and carbide, which after melting of the base material increases in size.

4. Conclusion
The formation of wear-resistant coatings containing solid ceramic particles of titanium carbides and borides by the method of non-vacuum electron-beam treatment of the Ti-6Al-4V alloy is a unique process. Due to the sequence of fusion of the powder mixture and the base material in the process of cladding, the interaction of the components significantly influences the final structure of the surface-alloyed layers, which is proved by the research data. Samples of the B₄C-Cr system during treatment have a smaller amount of free titanium atoms in the molten bath, in comparison with the samples obtained with the titanium (10 wt. %) addition to the initial powder mixture. Thus, fine eutectic crystals of titanium carbide and boride are formed in the coatings, while large primary crystals of these phases are fixed in the layers alloyed with Ti + B₄C + Cr. In addition, the main feature of samples without titanium in the initial cladding mixture was the dendritic chromium carbide layer, formed due to the primary interaction of chromium and carbon.

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