Composition, structure and hardness of titanium after pulse laser processing in graphite

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Abstract. The structure, composition and hardness of the surface layer of titanium after laser processing in a solid carburizer (graphite) were studied. As a result of the processing, a coating containing Ti, C, O and characterized by a thickness of up to 10 μm, hardness up to 11.5±0.9 GPa and the presence of nano-sized structural elements was formed on the surface of titanium. The resulting diffusion layer with a fine dendritic structure consisted of Ti and C. The diffusion layer with a thickness of 130±20 μm was distinguished by a high microhardness of 16.7±0.6 GPa.

1. Introduction

Titanium alloys are widely used in the aerospace industry, shipbuilding, in the petrochemical and electronic industries, as well as in engine-building in the production of various structural elements, e.g. turbine blades [1,2]. To enhance the functional properties the working surfaces are strengthened by thermal, chemical-thermal or electrochemical treatment, as well as coating deposition. Titanium alloys are chemically active in a wide range of temperatures. For this reason, the following methods of surface treatment are widely used, in particular oxidation, cementation and nitriding. These strengthening methods can increase the hardness and wear resistance of products. The composition and properties of the formed layers depend on the processing temperature and composition of the reaction medium [3-6].

Among the methods of thermochemical treatment, cementation can be distinguished since it allows the formation of highly hard and wear-resistant carbide layers. Due to cementation performed using graphite powder and pulsed laser heating, a carbide layer is formed from non-stoichiometric titanium carbide (TiC), which makes allows the increase in the hardness of titanium to 1200 HV0.1 (about 11.8 GPa) [7]. In some cases, graphite powder is pressed with a metal base and subjected to electrocontact heating to 800 °C and subsequent exposure for 20 minutes. As a result, titanium carbide layers are formed, which are characterized by a carbon content of up to 36 at.% and a hardness of 6.53 GPa (Knoop hardness at 100 gf) [8]. Induction thermochemical treatment is also widely used, in which a titanium product is placed in a refractory container filled with graphite. During processing, the samples are heated up to the melting temperature. Due to the given treatment, TiC layers with a thickness of up to 14 μm and a hardness of up to 20 GPa are obtained [9,10]. Carbide layers are also
formed by electrospark alloying. Conducting the alloying of titanium with a graphite electrode allows the increase in the surface hardness to 20.0–20.4 GPa [11].

In some cases, it is more rational to strengthen the surface of titanium by applying carbide coatings. The layers of the WC-TiC-Co system obtained as a result of electrospark alloying of the titanium base with a hard alloy are characterized by a hardness of 18–22 GPa [12]. Carbide coatings are also formed by selective laser sintering, e.g. layers of TiC/TiB$_2$ system are produced by laser processing of titanium bases with a deposited TiC/TiB$_2$ powder mixture. These ceramic layers are characterized by hardness up to 11 GPa [13]. When using a mixture of powders of titanium, nickel and titanium carbide on the surface of titanium, coatings with a hardness of up to 6.84 GPa are formed by selective laser sintering [14]. A number of authors propose using carbon nanoparticles as a powder mixture [15].

Carbide coatings and layers formed on titanium by various methods are characterized by high hardness. Widely used technologies allow the process of cementation on the entire surface of the product. Local strengthening of the surface layer is performed by laser processing or electrospark alloying, however, the composition, structure parameters and hardness of the resulting carbide layers are not sufficiently studied.

2. Methodology

In the studies, samples with a diameter of 14 mm and a height of 2 mm from commercially pure titanium grade VT1-0 were used. The samples were cemented by laser processing of a carburizer deposited on the titanium surface. Graphite powder with a size of 10–35 µm was applied as a carburizer. Laser processing was performed on the "LRS-50A" setup with a pump lamp voltage of 250–300 V, pulse duration of 1–5 ms and a spot size of 0.75 mm. A special designation was introduced for the processing modes, e.g. "250_1", where: "250" – the pump lamp voltage, V; "1" – the pulse duration, ms.

The structure of the samples was studied using scanning electron microscopy (SEM). SEM combined with energy-dispersive X-ray analysis (EDX) of chemical composition of samples was performed on "MIRA II LMU" with "INCA PentaFETx3" detector. Hardness of the coatings was evaluated by microindentation using "PMT-3M" (at the load of 200 gf).

3. Results

After the laser processing at minimum modes, in particular "250_1", a coating consisting of carbon was formed on the surface of titanium (Figure 1a). There was a fusion of particles of graphite and they were fixed on the base material. The surface hardness was not high and amounted to 4.1±0.7 GPa. An increase in the voltage of the pump lamp led to the melting of the titanium surface and the appearance of cracks. Spherical particles with a size of more than 200 nm were also observed (Figure 1b). According to EDX the surface layer consisted of carbon (47.5 at.%), oxygen (3.7 at.%) and titanium (balance). A coating comprising titanium oxides and carbides was formed as a result of laser processing. This assumption was confirmed by high surface hardness up to 11.5±1.0 GPa.

An increase in the pulse duration to 5 ms led to a change in the composition of the coating. The carbon content decreased to 3.8 at.%, while that of oxygen and titanium grew to 37.6 and 58.6 at.%, respectively. The surface structure also changed, i.e. the size of cracks increased, the areas characterized by different reliefs were visualized (Figure 2a). In the course of analysis of SEM images, the presence of round grains with the size about 150 nm and more on the surface was established (Figure 2b). It was likely that an increase in the duration of laser effect resulted in a significant oxidation of the coating, which was confirmed by a decrease in hardness to 10.5±1.0 GPa.

As a result of laser irradiation a coating was formed on titanium and the structure of the surface layer changed. At "250_1" processing mode, the depth of structural changes was 21±5 µm. In this case no significant increase in the hardness of the surface layer was observed.
Figure 1(a, b). The surface of titanium after laser processing in graphite, "250_1" mode (a); the appearance of cracks, "300_1" mode (b).

The region of structural changes with a thickness of 79±5 μm and a hardness of 8.2±1.0 GPa was formed under "300_1" mode. In this area, along with the coating with a thickness within 5 μm, a diffusion layer with a thickness of 40±5 μm and the boundary of thermal effect were also observed.

Figure 2(a, b). The morphology of the titanium surface after laser processing in graphite, "300_5" mode (a); nano-sized elements of the morphology of the modified layer (b).

An increase in the pulse duration led to the formation of a region with a modified structure having a depth of up to 140±20 μm and the coating thickness reaching 10 μm (Figure 3a). This coating consisted of Ti (31 at.%), C (43 at.%) and O (26 at.%). A diffusion layer with a thickness of up to 130±20 μm, which, in addition to titanium, included up to 35 at.% carbon, was also visualized. The diffusion layer had a fine dendritic structure with the hardness about 16.7±0.6 GPa (Figure 3b).
Figure 3(a, b). The microstructure of the near-surface layer of titanium after laser processing in graphite, "300_5" mode (a); an enlarged fragment of the diffusion layer with dendrites (b).

4. Conclusion
As a result of laser irradiation affecting titanium placed in graphite, a coating containing Ti, C and insignificant amount of O was formed. During further processing, the content of O increased, which was probably associated with the oxidation of the carbide layer. The coating was characterized by the thickness up to 10 μm, hardness up to 11.5±1.0 GPa and the presence of nano-sized (50–150 nm) structural elements. In the course of processing, in addition to the coating, a diffusion layer consisting of Ti and C was formed, which was characterized by a fine dendritic structure and high hardness of 16.7±0.6 GPa.

Acknowledgments
The study of the processes of cementation of titanium was performed in the framework of additional research, which was supported by the Russian Science Foundation (project No. 18-79-10040).

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