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Influence of Nanomodifying Additives and Strengthening Phase on the Structure and Properties of Laser Coating of Porous Titanium

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Abstract. The results of an experimental study of the influence of nanomodifying additives on the structure and mechanical properties of coatings during laser surfacing of a composite powder with a strengthening phase on porous titanium are presented. Titanium alloy of the Ti–V–Al system with a strengthening phase of titanium carbide was used as a surfacing material, and nano-sized refractory titanium nitride powders were used as a modifying additive. An analysis of the morphological and structural characteristics of a deposited single track was carried out, and the influence of modifying additives on the intensity of dissolution of the strengthening phase and the mechanical characteristics of the deposited layer was established.

Keywords: nanopowders, composite materials, laser surfacing, strengthening phase, microhardness, nanomodification.

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Introduction

Porous metals are a new promising material with unique properties, such as low specific gravity, high specific strength, resistance to impact loads and rigidity, due to which they have great prospects for practical applications [1–4]. Properties such as lightness and resistance to shock loads, low and high temperatures are of interest when creating screens to protect spacecraft from the impact of meteorites and objects of artificial origin [5, 6]. Some metals, for example, titanium alloys, have shape memory, which, in combination with porous technologies, is useful

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for healing holes caused by impacts from cosmic micro-objects. The effectiveness of shockproof, tribotechnical and anti-corrosion resistance of porous structures can be increased by the use of strengthening coatings obtained by surfacing powder materials with strengthening additives using highly concentrated technologies (laser, electron beam, etc.) [7, 8]. The development of surface hardening processes for porous products makes it possible to increase both the strength characteristics of structural equipment as a whole and other functional properties (impact and wear resistance, heat resistance, corrosion resistance, etc.). Therefore, the study of the patterns of structure and phase formation in strengthening layers on the surface of porous materials is of important scientific and practical importance. The purpose of this study is to experimentally analyze the formation of the structure and properties of a protective coating of porous titanium obtained by laser surfacing of a nanomodified composite powder with a strengthening phase.

1. Materials and methods of research

The surfacing of the compositions was carried out on plates of porous titanium Grade5(6Al4V), size $50 \times 20 \times 2$ mm, porosity 32%. Chinese-made plates were used, made by pressing followed by sintering of titanium alloy (Fig. 1).

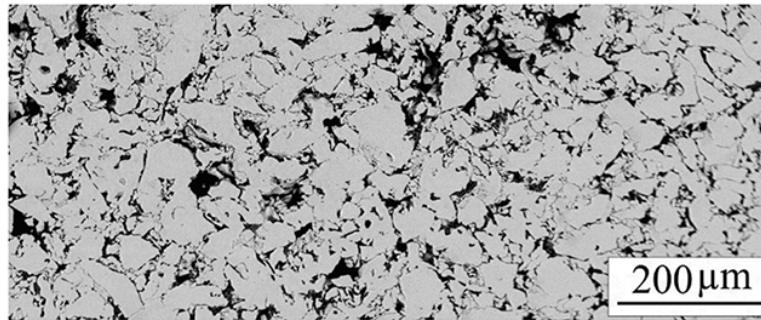


Fig. 1. Morphology of the internal structure of a porous titanium plate

Compositions based on Grade5(6Al4V) alloy with the addition of dispersed particles of titanium carbide TiC (20% by weight, 65–80 μm in size) and nanoparticles of titanium nitride TiN (size 30–50 nm) clad with titanium in the ratio 1 were used as surfacing material: 3 in a centrifugal planetary mill for 3 minutes. The powder composition was processed in a mixer for 6 hours and dried in a vacuum oven for 2 hours at a temperature of 120 °C before the experiment. Preparation of the plates for experiments consisted of grinding and treatment with acetone. Surfacing in the form of single beads was carried out in a neutral atmosphere (helium) using a solid-state laser.

The work used an IPG Photonics ytterbium fiber laser with a radiation wavelength of 1.07 μm and a maximum power of 3 kW. Laser processing mode: radiation power $W = 0.2$ kW, beam speed $v = 0.85$ m/min, beam diameter on the substrate surface 2 mm.

The surfacing composition was poured in a layer of 0.6 mm onto a test plate measuring $30 \times 30 \times 2$ mm, located on the laser work table, pressed and moved at a constant speed relative to the laser beam. A diagram of the surfacing process is shown in Fig. 2.

Tab. 1 shows the chemical composition of the Grade 5(6Al4V) alloy used as the basis for the surfacing composition.

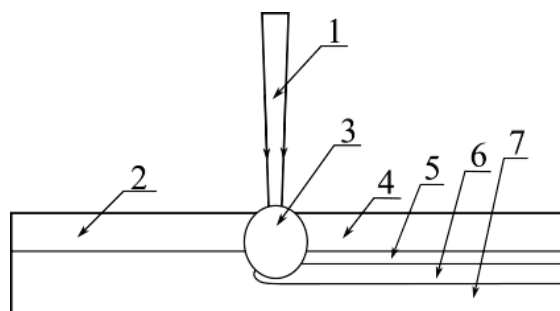


Fig. 2. Scheme of laser cladding of powder: 1 – laser beam, 2 – layer of composite powder, 3 – weld pool, 4 – weld bead, 5 – fusion zone, 6 – heat-affected zone, 7 – substrate

Table 1. Chemical composition of Grade 5(6Al4V) alloy, mass. %

Fe	C	Si	V	Zr	Ti	Al	N	O
0.6	0.1	0.15	3.5 - 5.3	0.3	86.45 - 90.9	5.3 - 6.8	0.05	0.2

Alloy Grade 5(6Al4V) belongs to two-phase ($\alpha + \beta$) – alloys of the martensitic class with a small amount of β -phase, the presence of which determines their ability to strengthening heat treatment. The alloy is alloyed with aluminum and vanadium. Aluminum in the Grade 5(6Al4V) alloy strengthens and stabilizes the α -phase, increases the strength and heat-resistant properties, the Ac3 temperature, and also reduces the specific gravity of the alloy. Vanadium, which is β -stabilizer, reduces the temperature. $\alpha - \beta$ – titanium transformations. With an increase in its content, the amount of increases β -phase, which is more plastic at high temperatures compared to α -phase, which helps improve manufacturability when applying the coating. Vanadium is one of the few alloying elements in titanium that increases not only strength properties, but also ductility. The beneficial effect of vanadium on plastic properties is associated with its specific effect on the lattice parameters α -titanium [9].

Powder compositions of various compositions were used as surfacing material for single tracks: No. 1 – Grade 5(6Al4V) + TiC, No. 2 – Grade 5(6Al4V) + NP (0.1%) + TiC, No. 3 – Grade 5(6Al4V) + NP (0.2%) + TiC. The ratio of titanium alloy Grade 5(6Al4V) and the strengthening phase TiC is taken in the proportion 8:2. Nano-sized refractory TiN particles 30–50 nm in size, clad with titanium in an AGO-2 centrifugal planetary mill for 3 minutes were used as a nanopowder additive (NP).

2. Methods for studying the structure of materials

The structure of materials with deposited coatings determines their physical, mechanical and operational properties. To analyze structural transformations in the surface layers of the porous titanium alloy and the surfacing layer, methods of metallographic analysis and scanning electron microscopy were used.

Samples for metallographic studies were prepared using standard methods, including grinding and polishing operations. To carry out the final polishing operation, a solution was used, which included 20 ml of colloidal silicon oxide, 5 ml of hydrogen peroxide H_2O_2 and 2.5 ml of Kroll's reagent ($H_2O - 18.4$ ml, $HNO_3 - 1.2$ ml and $HF - 0.4$ ml). To study the structure of materials, as well as the features of structural transformations of the deposited layers,

a Zeiss EVO MA 15 scanning electron microscope was used. The studies were carried out in secondary and backscattered electron modes in the magnification range from 50 to 30,000 times. To determine the chemical composition of local microvolumes of deposited layers, an Oxford Instruments X-Max 50 micro-X-ray spectral analyzer was used. To carry out durometric tests, a Nanoscan4D+ Nanoindenter was used according to the Vickers method at a load of 300 g.

3. Analysis of the research results

The structure of materials with deposited coatings determines their physical, mechanical and operational properties. To analyze structural transformations in the surface layers of the porous titanium alloy and the surfacing layer, methods of metallographic analysis and scanning electron microscopy were used.

In Fig. 3 shows microphotographs of the cross-section of tracks of compositions No.No. 1–3, characterizing the features of the formation of a composite powder deposited on porous titanium with a strengthening carbide phase without the addition and with the addition of titanium nitride nanopowder.

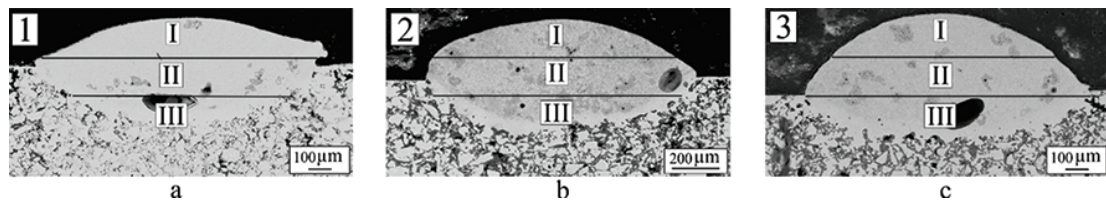


Fig. 3. General view of cross sections of single tracks from composition compositions: No. 1 (a), No. 2 (b), No. 3 (c), solid lines indicate the boundaries of the structural zone

It has been established that the treatment of powder with a beam of radiation power ≤ 0.2 kW is accompanied by the formation of deposited layers, which are characterized by the formation of symmetrical tracks with a defect in the form of individual pores and undissolved particles of titanium carbide. As the specific energy increases, the initial TiC particles dissolve in the superheated melt and, during crystallization, dispersed titanium carbide particles are released in it. In Fig. 4 shows of the microstructure in the characteristic structural zones of the track of composition No. 1 are presented.

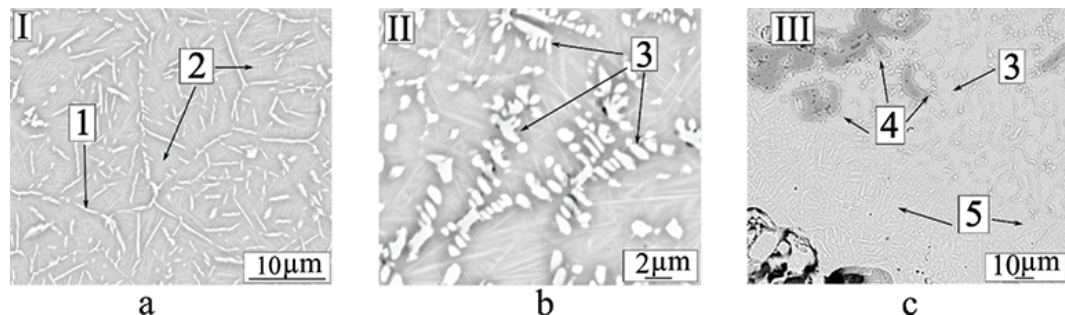


Fig. 4. Microstructure in characteristic zones of single tracks of the deposited mixture with the composition: No. 1 – Grade 5(6Al4V) + TiC: a – zone I, c – zone II, d – zone III. 1 – α -phase Ti; 2 – β -phase Ti; 3 – dendritic crystals; 4 – carbide phase; 5 – martensitic structure

The results of metallographic analysis of deposited tracks obtained using laser cladding technology show the formation of a structure characteristic of layers with a cast structure. In a general photograph of the microstructure of the strengthened material in the direction from the coating to the substrate, three characteristic zones are identified (Fig. 3). Each zone is characterized by its own structural features, depending on the surfacing parameters (radiation power, surfacing speed, etc.) and chemical composition. Let us consider the structural features of the sample obtained by surfacing mixture No. 1. Zone *I* has a two-phase ($\alpha + \beta$) structure with an α -phase of mixed structure (Fig. 4 a, 1). The main features of the structure of zone *I* is the lamellar intragranular structure of the alloy (Fig. 4 a, 2), due to the presence of the β phase (Fig. 4 a, 2), which is preserved along the boundaries of the α plates. Taking into account the diffusion nature $\beta \rightarrow (\alpha + \beta)$ of the transformation, one can expect the formation of nonequilibrium states and concentration inhomogeneities, as well as a martensitic-type grain structure.

The structural features recorded in zone *II* of the surfacing layer are determined by the degree of heterogeneity of the chemical composition, which is associated with the crystallization process and the formation of dendrites (Fig. 4, b) in combination with a β -phase of variable composition. Fig. 4, b shows cases of growth of round crystals [10–12].

Of particular interest are the local microvolumes of zone *III* (Fig. 4c, 4), complex titanium compounds in the form of particles ranging in size from 20 to 60 μm . The morphology of the phases represents fused agglomerates of titanium carbide. The process of interaction of titanium carbide with a titanium matrix can be described as follows.

During the processing of composite powders with a radiation power of less than 0.2 kW, the dissolution of fine and partly large agglomerates of TiC powders occurs, and during crystallization, dispersed particles of titanium carbide are released from the melt, which leads to strengthening of the surfacing layer according to the dislocation model of strengthening by dispersed phases [13]. If the composition of titanium carbide is close to stoichiometric, carbon predominantly passes into the melt, and if it is far away, then titanium. TiC_x carbide dissolves in titanium congruently, i.e. without noticeable changes in the composition of the matrix.

In the presence of TiN, the mechanism of phase and structure formation processes in the system under consideration changes qualitatively. The initial stage of interaction of the components in this system is characterized by the predominant dissolution of the carbon of the carbide phase in the melt. In addition, in Figs. 3 b, 3 c, 5 b and 5 c, there are conglomerates of primary particles of titanium carbide. Moreover, in composition No. 1 (without the addition of nanopowder) they are practically absent, which is probably due to their possible dissolution due to exposure to a laser beam. A similar result was discovered earlier when surfacing nickel powder with a strengthening phase Grade 5(6Al4V), modified with TiN nanoparticles, in to a steel substrate [14]. The mechanism of their preservation can be explained as follows. Modifying nanodispersions introduced into the melt increase the effective viscosity of the melt and, accordingly, reduce the mass transfer coefficient, so that under a given processing mode, particles of the strengthening phase of the appropriate size do not have time to completely dissolve during the solidification of the melt [15].

When the composition is cooled from the melt, primary and eutectic phase precipitates based on titanium carbide crystallize. Under high temperature conditions, the maximum rates of carbon diffusion in titanium are reached, and the presence of vanadium and aluminum leads to the formation of complex carbide phases based on the original titanium carbide particles (Fig. 4, c).

At the interface of the deposited layer with the substrate, the nucleation of crystals as a

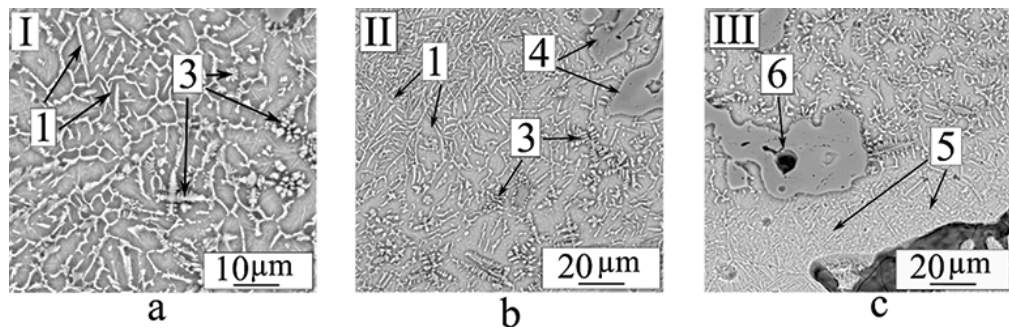


Fig. 5. Microstructure in characteristic zones of deposited single tracks of the deposited mixture with the composition: No. 2 – Grade 5(6Al4V) + NP (0.1%) + TiC: a – zone 1, c – zone 2, d – zone 3: 1 – α -phase Ti; 3 – dendritic crystals; 4 – carbide phase; 5 – martensitic structure; 6 – a pore

result of submelting of the substrate and a high cooling rate occurs mainly on the elements of the substrate partitions. The resulting grains have an elongated structure (zones s II and III, Fig. 6) and grow in the direction opposite to the direction of heat removal. It should be noted that the first-order axes of dendritic crystals are predominantly oriented perpendicular to the contact boundary of the deposited layer and the substrate. In zones III (Figs. 4, c – 6, c) structures of the martensitic type are recorded, which can be explained by the high rates of heat removal and crystallization of the melt at this boundary.

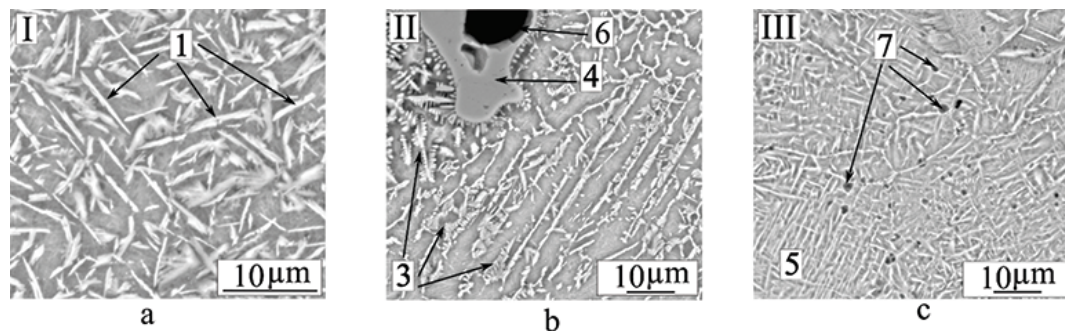


Fig. 6. Microstructure in characteristic zones of deposited single tracks of the deposited mixture with the composition: No. 3 – Grade 5(6Al4V) + NP (0.2%) + TiC: a – zone I, b – zone II, c – zone III; 1 – α -phase Ti; 3 – dendritic crystals; 4 – carbide phase; 5 – martensitic structure; 6 – a pore

From an examination of the structure of the resulting coatings, it is clear that the use of nanomodifying additives significantly refines the structure of the deposited metal compared to surfacing without a nanomodifying additive, which affects the hardness of the samples. The level of microhardness values in the upper region of the track for nanomodified samples is 14–18% higher than for unmodified samples (Fig. 7).

The observed effect of material strengthening is due to the formation of a highly dispersed heterophase structure, the mechanism of which consists primarily of two components: grain-boundary strengthening and strengthening due to the presence of dispersed particles of the carbide phase in the matrix. The jumps in microhardness observed in the experimental depen-

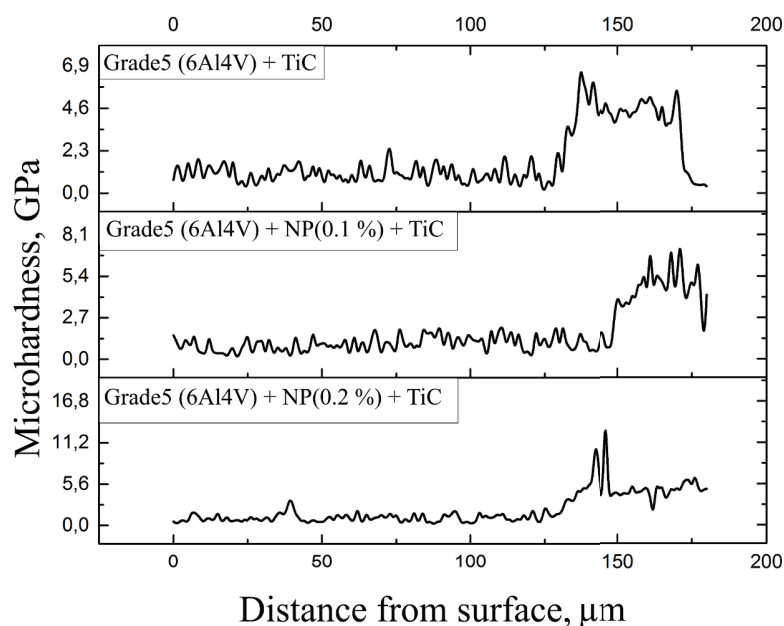


Fig. 7. Distribution of microhardness along the depth of deposited layers of powder compositions without the use of nanopowder and with the use of nanopowder additives

dences are due to the fact that when applying injections, the indenter may get into large particles of titanium carbide or into their clusters. Similar jumps are characteristic of coatings containing a high-strength phase with a hardness significantly different from the hardness of the matrix material [17–19].

Conclusion

The analysis showed that the use of nanomodifying additives significantly affects the processes of phase and structure formation of the coating material. A small amount of specially prepared refractory powders contributes to the formation of a highly dispersed structure in the deposited composite layer, reducing the intensity of dissolution of the strengthening phase, which has a positive effect on the strength properties of the protective layer.

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Влияние наномодифицирующих добавок и упрочняющей фазы на структуру и свойства лазерного покрытия пористого титана

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Аннотация. Приведены результаты экспериментального исследования влияния наномодифицирующих добавок на структуру и механические свойства покрытий при лазерной наплавке композиционного порошка с упрочняющей фазой. В качестве наплавочного материала использовался титановый порошок системы Ti–V–Al с упрочняющей фазой из карбида титана, а в качестве модифицирующей добавки — наноразмерный тугоплавкий порошок нитрида титана. Проведен анализ морфологических и структурных характеристик наплавленного одиночного трека, установлено влияние модифицирующих добавок на интенсивность растворения упрочняющей фазы и механические характеристики наплавленного слоя.

Ключевые слова: нанопорошки, композиционные материалы, лазерная наплавка, упрочняющая фаза, микротвердость, наномодифицирование.