

Properties of Ti/TiN composite layers made with an “in situ” method using a high-power diode laser

Introduction

Titanium and its alloys, due to their special properties such as low specific gravity, high strength even at heightened temperatures and excellent corrosion resistance, are commonly used in many industries [1÷4,7÷9]. However, titanium alloys, in spite of having numerous advantages in comparison with other engineering materials, are not characterised by satisfactory tribological properties, e.g. resistance to abrasive and erosive wear [3,4,5,16]. For this reason, while manufacturing machinery parts made of titanium and titanium alloys, exposed to abrasion- or erosion-induced wear, it is often necessary to use additional treatment in order to improve the functional properties of surface layers on work surfaces [4,6÷9]. One of the most technologically advanced and effective methods of shaping the properties of the surface layers of engineering materials is laser surface alloying. A particular case of laser surface alloying is laser gas nitriding of the surface layers of parts made of titanium and its alloys [1,10]. Laser gas nitriding consists in heating a metal surface with a laser beam or partially melting a surface while in an atmosphere of nitrogen, i.e. a gas active to a metal, e.g. titanium [7]. In the case of titanium and its alloys the process of nitriding is very effective owing to the high chemical activity of titanium and

high susceptibility to nitrogen absorption at a heightened temperature, even in the solid state. In the case of laser gas nitriding of titanium and its alloys in the solid state, i.e. without the partial melting of a surface, the surface layer is strongly nitrated and the structure of the surface layers is mainly composed of a titanium solid solution strongly supersaturated with nitrogen $Ti\alpha$ and a slight amount of titanium nitrides separated during nitriding. In turn, in the case of the partial melting of a titanium or titanium alloy surface with a laser beam in a gas atmosphere, particularly in the atmosphere of pure nitrogen, the process of nitrogen absorption and separation of nitrides is very intense, and the surface layer has the structure of a composite layer with nitrides deposited in the metallic matrix of the solid solution $Ti\alpha$ supersaturated with nitrogen. The process of composite layer formation is a result of dissociation and absorption of nitrogen through titanium, and, next, the separation of nitrides in a reaction e.g. $Ti+N \rightarrow TiN$, already in a liquid phase, within a metal pool. Due to this fact the process of the surface layer formation with titanium nitrides is an *in situ* process as it takes place as a result of the reaction of the separation of titanium nitrides in a liquid metal pool. Tests of laser nitriding of titanium and its alloys have been conducted worldwide for many years,

yet they have been mainly concerned with the process of nitriding in the solid state by means of CO₂ gas lasers and solid-state rod lasers Nd:YAG with a circular cross-section of a laser beam. Physical phenomena, the mechanisms of nitrogen absorption and separation of titanium nitrides during laser nitriding in the liquid state i.e. as a result of titanium surface melting are dynamic, very complex and difficult to describe by means of mathematical or physical dependences. That is why the knowledge of this subject is still very limited. Besides, in most publications authors indicate the basic problem, i.e. the high brittleness of surface layers as well as the presence of micro-cracks and cracks which are difficult or even impossible to eliminate.

In turn, the knowledge related to nitriding of the surface layers of titanium and titanium alloys by means of a diode laser beam is fragmentary and very few publications, the majority of which are available only overseas, are usually limited to the presentation of the results of simple tests and preliminary investigations, indicating the advantages of using a rectangular laser beam of the multi-mode and uniform distribution of energy on the focus area and a wavelength within the range of very near infrared from 800 to 900 nm [11÷16].

Test material and methodology

The tests involved the use of samples made of titanium alloy Ti6Al4V (Grade 5 according to ASTM B265), prepared in the form of 3mm-thick rectangular plates (70mm x 40 mm) as well as disks with a diameter of 46.0 mm (Fig. 1, 2, Tables 1 and 2). In order to ensure the complete control of the gas atmosphere, the laser nitriding of the surface layers of string beads were carried out in a chamber with a controlled gas atmosphere filled with high-purity nitrogen (99.999%) under approximately 1 atmosphere of pressure with a nitrogen flow rate of 5.0 l/min (Fig. 1). In order to fully remove the air from the chamber and fill the latter with nitrogen, the flow of nitrogen was activated approximately 3.0 minutes before activation of the laser beam and the commencement of the nitriding process. In turn, the disks with a diameter of 46.0 mm, which were subjected to laser nitriding with girth beads having a diameter of 30.0 mm, were fixed in a manipulator. Nitrogen was blown by means of a cylindrical nozzle with a diameter of 12.0 mm; the nitrogen flow rate was 18 l/min (Fig. 2).

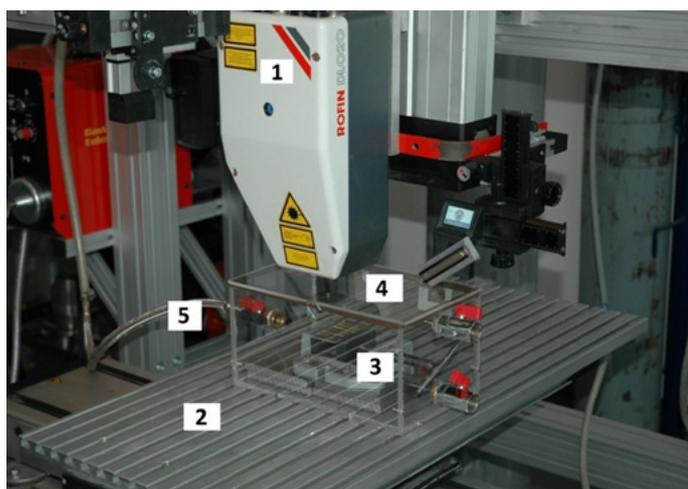


Fig. 1. Testing station with diode laser HPDL ROFIN SINAR DL020:

- 1 – laser head, 2 – positioning table, 3 – sample fixing device, 4- chamber with controlled gas atmosphere,
- 5 – conduits supplying gas mixture

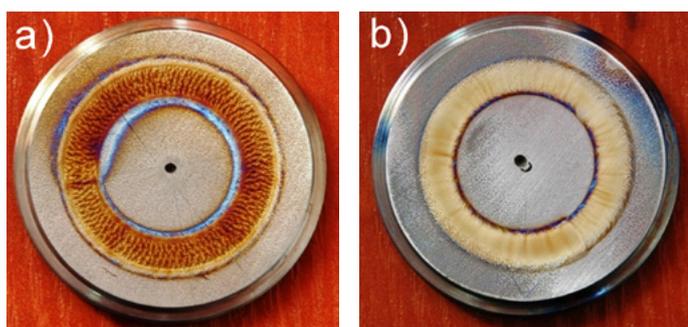


Fig. 2. Face of a single bead of the surface layer nitrided with laser HPDL on the surface of a 3.0mm-thick disk made of titanium alloy Ti6Al4V (Table 3);
a) bead no. 3, b) bead no. 4

The laser nitriding tests were carried out using an automated laser station equipped with a high-power diode laser HPDL DL 020 ROFIN SINAR, emitting radiation in the near infrared range of a wavelength amounting to 808 nm. The radiation had a rectangular focal shape (1.8 mm× 6.8 mm) and a multi-mode, uniform distribution of energy along the longer side of the focus (Fig. 1). The surface layers of the titanium alloy plates were made with single string beads, and the beam of the di-

Table 1. Chemical composition of technical titanium (Grade 2) and titanium alloy Ti6Al4V (Grade 5) according to standard ASTM B 265-99 (Table 2)

Material	Content, % by weight							
	C	Fe	O	N	H	Al	V	Ti
Technical titanium (Grade 2)	max 0,1	max 0,3	max 0,25	max 0,03	max 0,015	-	-	rest
Titanium alloy Ti6Al4V (Grade 5)	max 0,08	max 0,25	max 0,2	max 0,05	max 0,015	5,5÷6,76	3,5÷4,5	rest

de laser was focused on the upper surface of the plates in such a manner that the longer side of the 6.8 mm-long focus was positioned crosswise in relation to the direction of travel (Fig. 1, 2). In order to remove surface impurities and the layer of oxides, the surfaces of the titanium alloy plates and disks were cleaned mechanically and degreased with acetone. The nitriding of the surface layers with string and girth beads was carried out using various linear energy (Table 3). The process was followed by metallographic tests, macro- and microscopic observations, hardness and micro-hardness measurements and tests of resistance to abrasive and erosive wear.

Resistance to erosive wear was tested on the surface of laser-nitrided surface layers and on the surface of a plate made of titanium alloy Ti6Al4V (parent metal - PM), which was adopted as a comparative sample (Fig. 2, 5, 12). The erosion resistance tests were carried out in accordance with standard

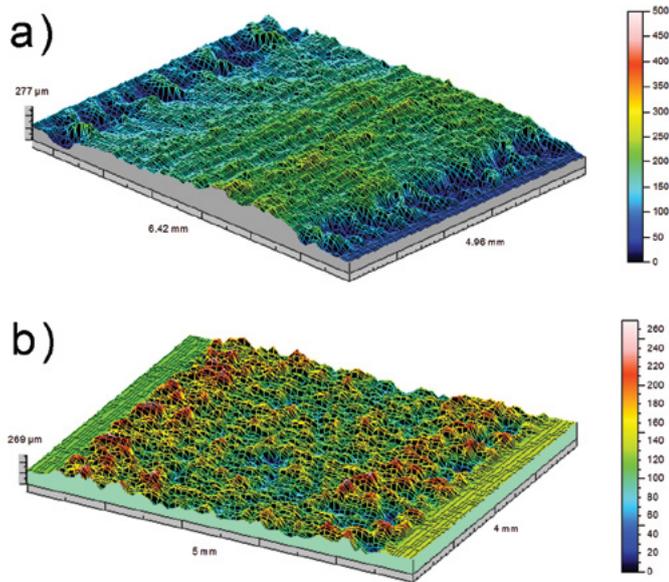


Fig. 3. Surface topography of the face of a single bead of the surface layer nitrided with laser HPDL on the surface of a 3.0mm-thick disk made of titanium alloy Ti6Al4V (Table 3); a) bead no. 1, b) bead no. 3

Table 2. Physical and mechanical properties of technical titanium (Grade 2) and titanium alloy Ti6Al4V (Grade 5) according to standard ASTM B 265-99 (Table 1)

Material	Density g/cm ³	Melting point °C	Rm MPa	Rp _{0,2} MPa	Elongation A %	Contraction Z %	Hardness	
							HV	HRC
Technical titanium (Grade 2)	4,51	1665	345÷450	275÷410	20	35	145	-
Titanium alloy Ti6Al4V (Grade 5)	4,43	1649	880÷950	820÷910	10÷18	20÷36	349	36

Remarks: Other physical properties of titanium alloy Ti6Al4V: specific heat: 560 J/kg×K, thermal expansion coefficient: 8.6×10⁻⁶, electrical resistance: 170 Ω×cm, thermal conductivity: 7.2 W/m×K

ASTM G76: at an erosive agent flow rate of 70 m/s, a distance between the nozzle and the surface of 10.0 mm, an erosive agent feeding rate of 2.0 g/min and incidence angles of 90° and 15° (Table 4). Resistance to abrasive wear was tested on the surface of laser-nitrided surface layers using the ball-on-disk method according to standard ASTM G99 (Table 5). Prior to the ball-on-disk testing, the surfaces of the disks were evened up by means of a flat-surface grinder. The test results are presented in Tables 2 to 5 and Figures 2 to 17.

The measurements of micro-hardness on the cross-sections of single beads of the surface layers made as a result of laser nitriding of the surface of a plate made of titanium alloy Ti6Al4V were carried out according to the scheme presented in Figure 8.

Table 4. Results of measurements of mass decrements of samples after erosion resistance tests of the plate made of titanium alloy Ti6Al4V and of surface layers nitrided with laser HPDL (Table 3)

Bead/sample designation	erosive agent incidence angle [°]	Initial mass of sample* [g]	Final mass of sample* [g]	Sample mass decrement [mg]	Remarks
Sc 1/1	90	43,4671	43,459	8,1	GD
Sc 1/2	15	43,3245	43,3224	2,1	GD
Sc 2/1	90	48,2674	48,2603	7,1	RK
Sc 2/2	15	48,2324	48,2279	4,5	RK
Sc 3/1	90	29,3764	29,3716	4,8	GD
Sc 3/2	15	29,2456	29,2424	3,2	GD
Ti6Al4V	90	45,1639	45,1545	9,4	GD
Ti6Al4V	15	45,0924	45,0792	13,2	GD

Remarks: * - average value from three measurements, test conditions and parameters: test time 10 min, the distance between the nozzle and the surface of 10.0 mm, an erosive agent flow rate of 70 m/s, an erosive agent feeding rate of 2.0 g/min, SB – smooth crater bottom, LB – laminations at crater bottom

Table 3. Parameters of laser gas nitriding of 3mm-thick flat plates and disks made of titanium alloy Ti6Al4V with a beam of high-power diode laser HPDL ROFIN SINAR DL020 (Fig. 1)

Bead no.	Laser beam travel rate mm/min	Laser beam power W	Linear energy J/mm	Power density kW/cm ²	Remarks
1	200	1000	300	8,17	CH, BP
2	200	800	240	6,54	CH, BP
3	200	600	180	4,90	CH, NW, BP
4	200	400	120	3,27	GL, BP

Remarks: other laser nitriding parameters: laser beam focus dimensions 1.8×6.8 mm, focal length: 82 mm, nitrogen flow rate: 5 l/min, nitrogen pressure in the chamber - 1 atmosphere, beam focused on the upper surface of the plate, rectangular focus positioned crosswise in relation to travel direction. Bead quality assessment: HR – high roughness, SF – smooth face, NF – non-uniform fusion, NC – no cracks

Analysis of test results

Melting the surface layer of the plates made of titanium alloy Ti6Al4V (Grade 5 according to ASTM B265) by means of a high-power diode laser with a rectangular beam while in an atmosphere of high-purity nitrogen within a tested range of process parameters leads to intense absorption of nitrogen through a liquid metal pool and to the separation of titanium nitrides in the surface layer, i.e. to the *in situ* formation of a

composite layer consisting of high-hardness titanium nitrides uniformly distributed in the metal matrix of the solid solution Ti α (MMC Metal Matrix Composite), (Fig. 2÷7). The thickness of the composite surface layer with the separations of titanium nitrides as well as the vo-

lume fraction of titanium nitrides in the surface layer is clearly dependent on the nitriding process parameters (melting), and primarily on linear energy (Fig. 4, 6). Likewise, the roughness and the topography of the surface of the surface layers laser-nitrided on the titanium alloy Ti6Al4V base clearly depend on the linear energy of the laser nitriding process (Fig. 2, 3). At the minimum linear energy of the laser nitriding of the surface of 3.0 mm-thick plates made of titanium alloy Ti6Al4V, when the power of a laser beam is 400 W and the travel rate amounts to 200 mm/min, the roughness of the surface layers is similar to that of the surface of the parent metal, and the surface of the face is a golden colour, characteristic of the separation of titanium nitrides (Fig. 2, 3). Along with an increase in the laser nitriding linear energy, at a travel rate of 200 mm/min and the power of a laser beam of 600 W, the roughness of the face of the surface layers increases (Fig. 2, 3). In turn, the highest nitriding linear energy, at a speed of 200 mm/min and a power of 1000 W, is accompanied by the development of laminations on the surface of the face of the surface layers of the plate made of titanium alloy Ti6Al4V (Fig. 2÷4, Table 3). However, the metallographic tests as well as observations of ma-

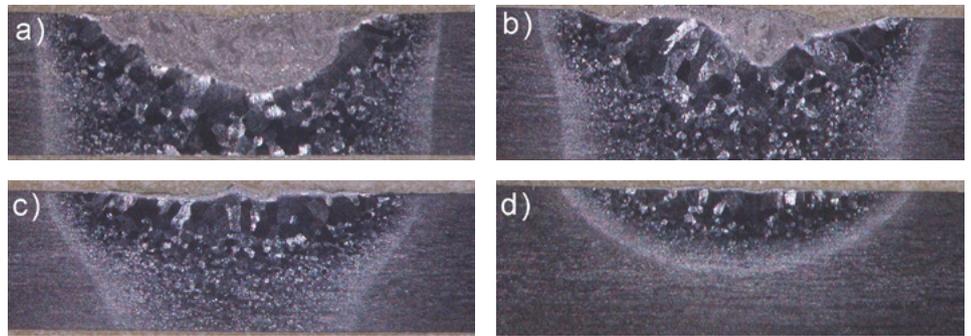


Fig. 4. Macrostructure of a single string bead of the surface layer nitrided with laser HPDL on the surface of a 3.0mm-thick disk made of titanium alloy Ti6Al4V (Table 3); a) bead no. 1, b) bead no. 2 c) bead no. 3, d) bead no. 4

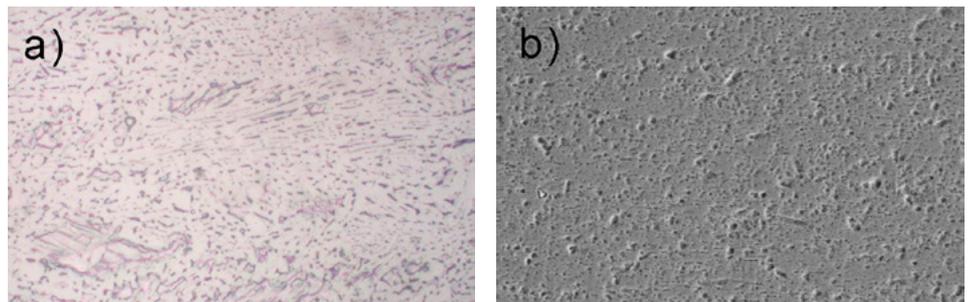


Fig. 5. Microstructure of a 3.0mm-thick plate made of titanium alloy Ti6Al4V (parent metal), (Table 1 and 2), etching: Kroll's etchant; a) image recorded with a light microscope, magnification 500x, b) image recorded with a scanning microscope SEM

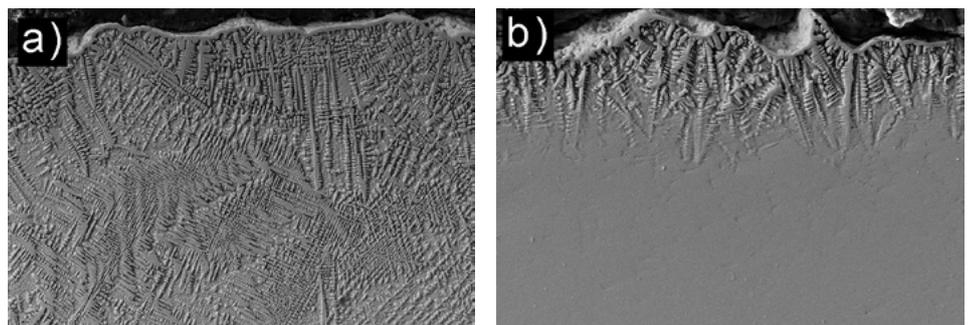


Fig. 6. Structure of the surface layer of a 3.0mm-thick plate made of titanium alloy Ti6Al4V nitrided with laser HPDL, (Table 3); a) bead no. 1, b) bead no. 3

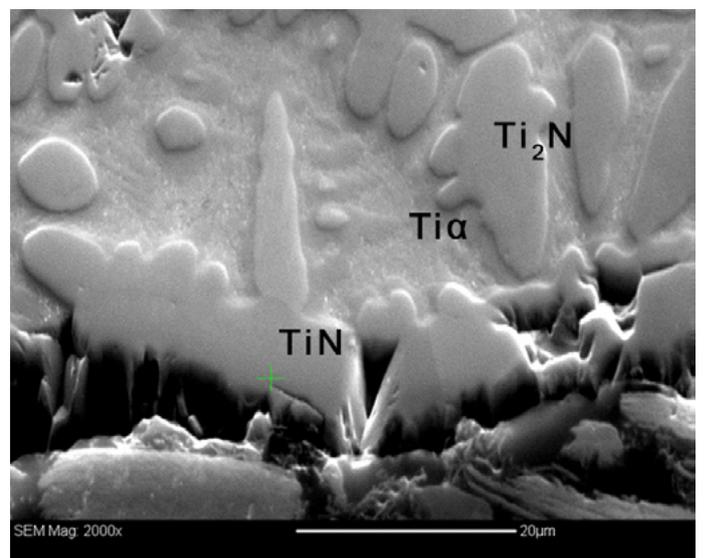


Fig. 7. Titanium nitrides in the base of a solid solution $Ti\alpha$ of the surface layer of a plate made of titanium alloy Ti6Al4V nitrided with laser HPDL, (Table 3); a) bead no. 1

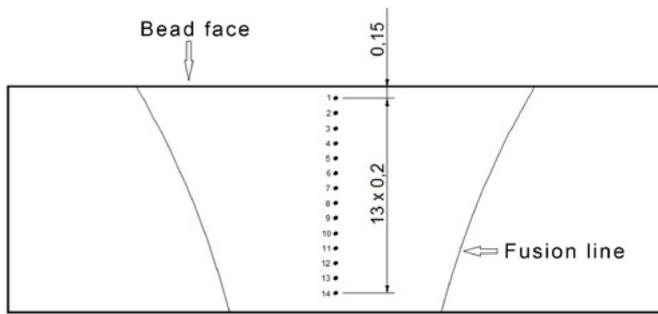


Fig. 8. Scheme of micro-hardness measurement on the cross-section of a single string bead of the surface layer of a plate made of titanium alloy Ti6Al4V nitrided with laser HPDL

cro- and micro-structure did not reveal any cracks of the surface layers on the cross-sections, but only face surface irregularities (Fig. 2÷4, 6, 7).

Micro-hardness measurements revealed a significant micro-hardness increase in the area of the surface layers, and particularly, near the face of the bead, in comparison with the micro-hardness of the parent metal

of titanium alloy Ti6Al4V amounting to approximately 350 to 360 HV0.1 (Fig. 8÷10). The highest micro-hardness, i.e. over 2300 HV0.1, was measured directly under the surface of the face of the surface layer made with the highest linear energy of laser nitriding of the plate made of titanium alloy Ti6Al4V, of a power of 1000 W and a travel rate of 200 mm/min (Fig. 9). At the same time it was possible to observe that a decrease in the linear energy of the nitriding process is accompanied by a decrease in the micro-hardness of the surface layers. The lowest micro-hardness, i.e. almost 380 HV0.1, was measured in the surface layer made with a power of 400 W and a travel rate of 200 mm/min (Fig. 10).

The tests of the erosion resistance of the laser-nitrided surface layers and of the parent metal of titanium alloy Ti6Al4V re-

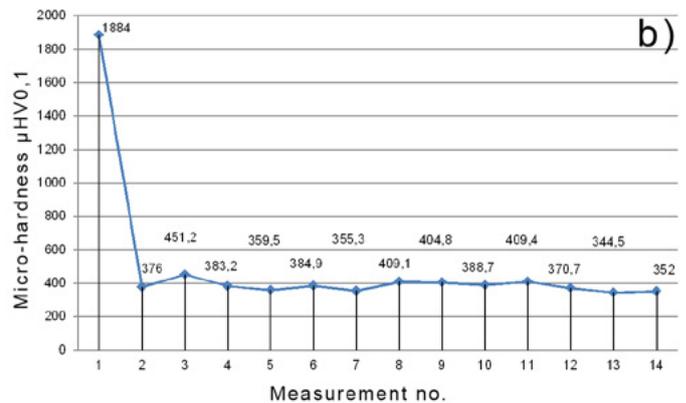
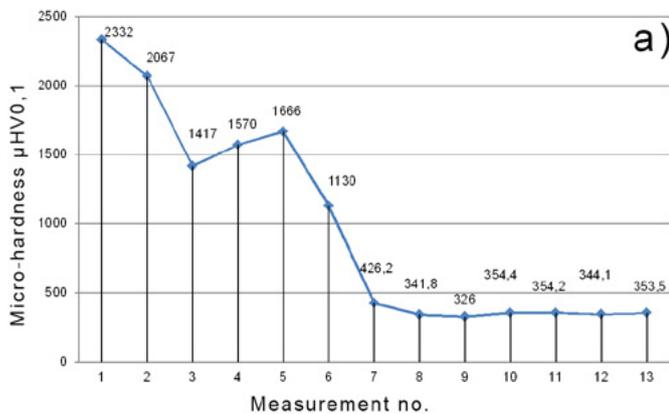


Fig. 9. Change in micro-hardness on the cross-section of a single string bead of the surface layer of a 3.0mm-thick plate made of titanium alloy Ti6Al4V nitrided with laser HPDL (Table 3); a) bead no. 1, b) bead no. 2

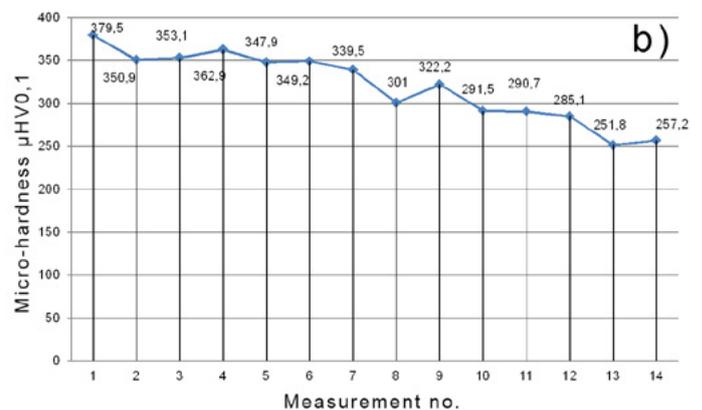
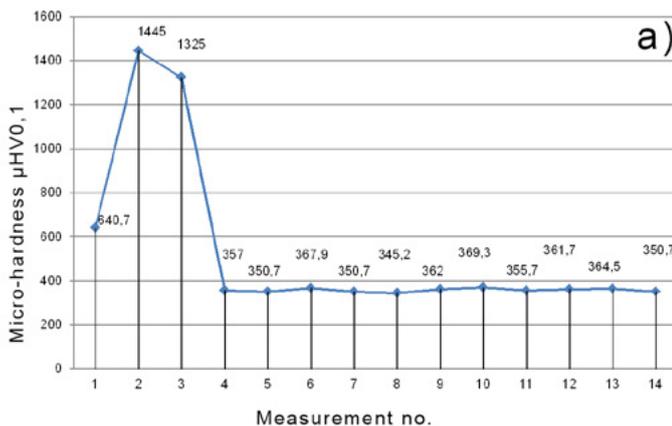


Fig. 10. Change in micro-hardness on the cross-section of a single string bead of the surface layer of a 3.0mm-thick plate made of titanium alloy Ti6Al4V nitrided with laser HPDL (Table 3); a) bead no. 3, b) bead no. 4

vealed that the resistance to erosive wear, both of the nitrated surface layers and of the titanium alloy parent metal, significantly depend on an erosive agent incidence angle (Table 4). The sample mass decrement from the parent metal of titanium alloy Ti6Al4V at an erosive agent incidence angle of 90° amounts to 9.4 mg, and increases by 40% to 13.2 mg at an angle of 15° (Table 4, Fig. 12÷14). In turn, in the case of laser-nitrated surface layers, a mass decrement resulting from erosive wear decreases along with a decreasing erosive agent incidence angle (Table 4, Fig. 12÷14).

In the case of an erosive agent incidence angle of 90° the lowest mass decrement of 4.8 mg, two times lower than in the case of the sample of the parent metal, was observed in the case of the nitrated surface layer made with a low linear energy, with a power of 600 W and at a travel rate of 200 mm/min

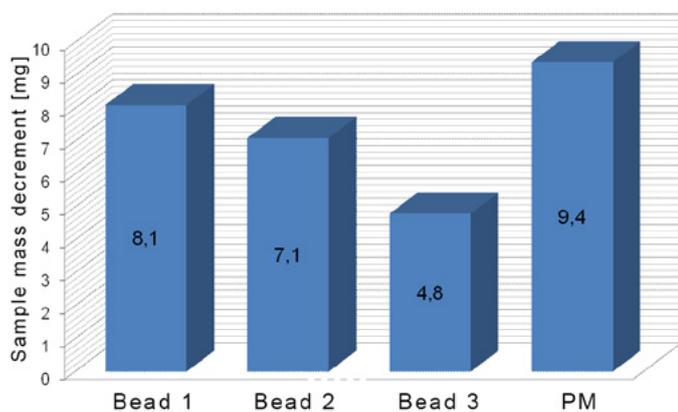


Fig. 13. Results of mass decrement measurements for samples after the erosion resistance tests of the surface layers of plates made of titanium alloy Ti6Al4V nitrated with laser HPDL and the parent metal (PM) of a plate made of titanium alloy Ti6Al4V, at an erosive agent incidence angle of 90°, (Table 1÷3, 4)

(Fig. 13, 14). In turn, in the case of an erosive agent incidence angle of 15°, the mass decrement of the surface layer made with the lowest linear energy of 2.1 mg is over six times lower if compared with the sample of the parent metal made of titanium alloy Ti6Al4V (Fig. 13, 14).

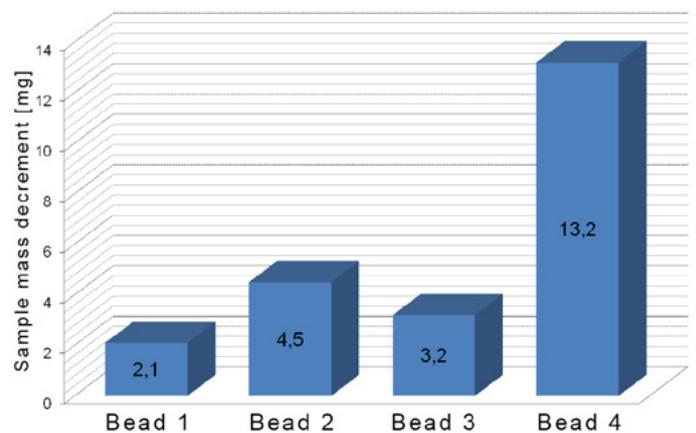


Fig. 14. Results of mass decrement measurements for samples after the erosion resistance tests of the surface layers of plates made of titanium alloy Ti6Al4V nitrated with laser HPDL and the parent metal (PM) of a plate made of titanium alloy Ti6Al4V, at an erosive agent incidence angle of 15°, (Table 1÷3, 4)

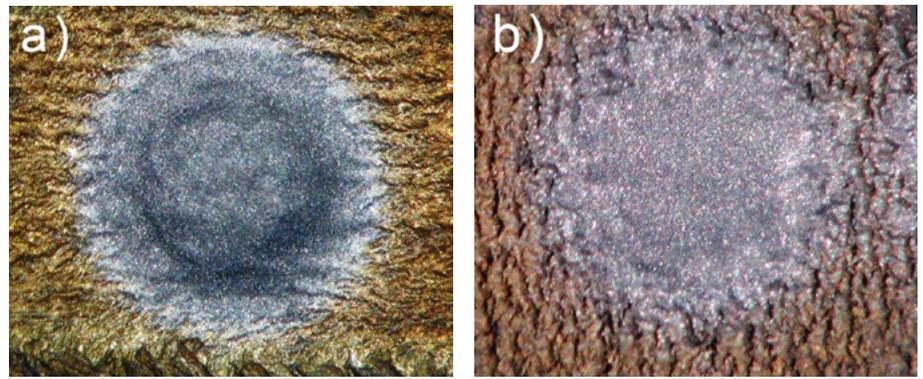


Fig. 11. Crater on the surface layer of a plate made of titanium alloy Ti6Al4V nitrated with laser HPDL after the erosion resistance test, erosive agent incidence angle 90° (Table, 3, 4); a) bead no. 1, b) bead no. 3

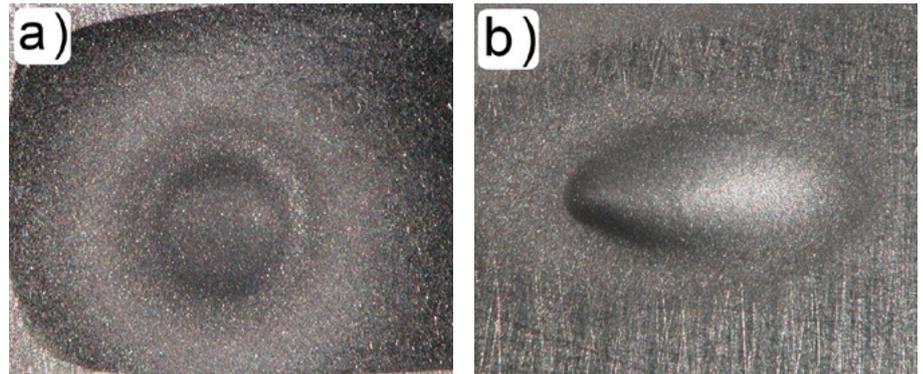


Fig. 12. Crater on the surface layer of a plate made of titanium alloy Ti6Al4V after the erosion resistance test (Table 1, 2); a) erosive agent incidence angle 90°; b) erosive agent incidence angle 15°

The tests of resistance to metal-metal abrasive wear of the nitrided surface layers on the base of the plates made of titanium alloy Ti6Al4V revealed a clear impact of the laser nitriding process parameters on the resistance expressed by sample mass decrement (Table 5, Fig. 15÷17). The highest resistance

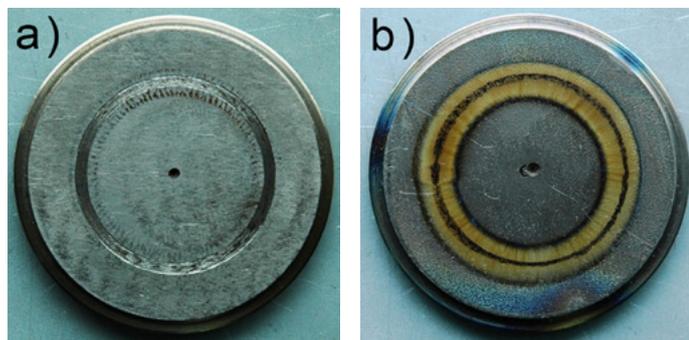


Fig. 15. Single girth bead of the surface layer nitrided with laser HPDL on a disk made of titanium alloy Ti6Al4V (Table 3, 5); a) bead no. 3, b) bead no. 4

to metal-metal abrasive wear in the ball-on-disk test, with the smallest sample mass decrement – 0.39 mg, could be observed in the case of the surface layer nitrided with the lowest linear energy of the nitriding process, made using a laser beam with a power of 400 W and at a travel rate of 200 mm/min (Fig. 16, 17). The mass decrement of the surface layer which was the most resistant to abrasion in the ball-on-disk test is over 15 times lower than in the case of the surface

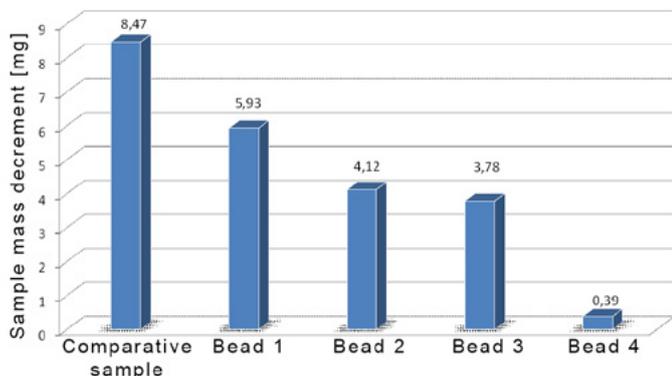


Fig. 16. Results of mass decrement measurements for samples after the ball-on-disk abrasion resistance tests of the surface layers of disks made of titanium alloy Ti6Al4V nitrided with laser HPDL and the parent metal (PM) of titanium alloy Ti6Al4V (comparative sample), (Table 1÷3, 5)

Table 5. Results of mass decrement measurements for samples after the ball-on-disk abrasion resistance tests of disks made of titanium alloy Ti6Al4V and the surface layers nitrided with laser HPDL on the plates made of titanium alloy Ti6Al4V, (Table 3)

Sample designation	Ball mass decrement* mg	Disk mass decrement * mg
Ti6Al4V	0,16	8,47
Sc 1	0,58	5,93
Sc 2	0,56	4,12
Sc 3	0,41	3,78
Sc 4	0,39	0,39

Note: * - average value from three measurements

layer nitrided with the highest linear energy, a power of 1000 W and at a travel rate of 200 mm/min, and almost 22 times lower if compared with the sample of titanium alloy Ti6Al4V (Table 5, Fig. 16, 17).

Conclusions

On the basis of the investigation into the laser nitriding of the surface layers of the plates made of titanium alloy Ti6Al4V (Grade 5 according to ASTM B265) with a high-power diode laser beam HPDL and within the tested range of nitriding parameters, the following could be observed:

1. One can *in situ* prepare composite surface layers with separations of high-hardness titanium nitrides as well as control the quality and properties of surface layers within

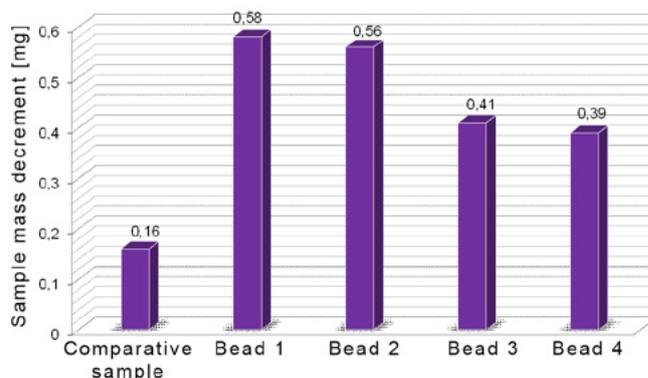


Fig. 17. Results of mass decrement measurements for a ball made of steel ŁH 15 after the ball-on-disk abrasion resistance tests of the surface layers of disks made of titanium alloy Ti6Al4V nitrided with laser HPDL and the parent metal of titanium alloy Ti6Al4V (comparative sample), (Table 1÷3, 5)

a wide range of process parameters of nitriding with a diode laser beam, mainly linear energy.

2. Micro-hardness of laser-nitrided composite surface layers clearly depends on nitriding process parameters. Under the surface of the face of surface layers it can reach even 2300 HV0.1.

3. Ensuring the highest resistance of surface layers to erosive wear at small erosive agent incidence angles, more than six times higher if compared with that of the titanium alloy Ti6Al4V, requires nitriding at a high linear energy, with a power of 1000 W and at a travel rate of 200 mm/min. In turn ensuring the highest resistance of surface layers to erosive wear at an erosive agent incidence angle of 90° requires a low linear energy, a power of 600 W and a travel rate of 200 mm/min.

4. The highest resistance to metal-metal abrasive wear, over 22 times higher than in the case of titanium alloy Ti6Al4V, characterises the surface layers nitrided with a diode laser beam on the Ti6Al4V alloy base, with the lowest linear energy, a power of 400 W and a travel rate of 200 mm/min.

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