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# Surface structure and properties of Ti6Al4V alloy laser melted at cryogenic conditions

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## ABSTRACT

**Purpose:** The research work has been to determine whether surface melting of the Ti6Al4V bioalloy with the high power laser, when immersed in liquid nitrogen, would result in an appearance of hard and thick surface layer, containing new structural constituents.
**Design/methodology/approach:** The laser melting of the Ti6Al4V alloy has been made by the CO2 laser at different laser beam energy and scan rate. The specimens have been immersed in liquid nitrogen bath during laser treatment. The Vickers microhardness of cross-sections of the surface layer has been measured, and the microscopic examinations have been performed with the SEM.
**Findings:** The laser melting at cryogenic conditions has resulted in creation of the modified surface layer, up to 1.5 mm thick with HAZ, of properties and structures different from those of the base metal. The layer has been well adjacent to base metal, its microhardness being significantly higher. The numerous zones have been observed within the surface layer, with nitrogen-containing martensite and titanium nitride structures. The negative effect has been an initiation of surface cracks. The laser beam energy has influenced the presence of different zones, their thickness, and number of cracks.
**Research limitations/implications:** So far research has shown that proposed technique can create thick and hard surface layer, containing new structural important components. The new research is necessary in order to establish the laser treatment parameters which permit to avoid cracking and determine the phase constituents and crystallinity within the surface layer.
**Practical implications:** The elaborated technique may be useful in order to improve the surface properties of the Ti alloys for biomedical applications.
**Originality/value:** The paper shows original in the world-scale results of laser treatment of the Ti bioalloy at cryogenic conditions.
**Keywords:** Surface treatment; Laser treatment; Titanium alloys; Aluminium alloys

## 1. Introduction

The application of titanium and its alloys in medicine has been directed towards obtaining the surface of appropriate roughness, increasing the growth of osteoblasts, creating the thick oxide (especially rutile) layers, laser treatment has been intensively applied for change on surface properties of titanium and its alloys for medical applications.

The number of works has been devoted to laser treatment. The short pulse Cr-F UV laser has been used for treatment of the Ti, Ti-6Al-4V i Ti-6.8Mo-4.5Fe-1.5Al in order to obtain nanocrystalline hard surface layer [1-4]. It has been assumed that very short pulses of laser beam would result in substantial heating of the alloy and then fast cooling in air, then in conditions corresponding to the ultrafast quenching. The relatively smooth, crack-free, nanocrystalline surface layer has been obtained containing a significant amount of martensite. In another papers the growth of osteoblasts has been stimulated by pulsed laser ablation [5], development of surface roughness and increase in oxide layer thickness [6-9], laser surface nitriding [10,11]. Although similar features of surface can be obtained by another techniques [12-15], laser treatment seems very promising as it can develop a lot of features simultaneously.

The present research has been aimed at creating of conditions of ultrafast quenching of melted layer in presence of nitrogen in such a way as to obtain the hard and thick surface layer of the Ti6Al4V alloy, the most frequently used Ti bioalloy, containing martensite and titanium nitride structures.

## 2. Experimental

The specimens were made of the Ti6Al4V alloy (TIMETAL 6-4), delivered as a sheet 12 mm thick. The material was investigated as received so that after previous hot rolling and annealing at 750°C. The chemical composition was as follows: 4.08% V, 6.39% Al., 0.17% Fe, 0.015% C, 0.1850% O, 0.0050% N, 0.0035% H, borium traces et al. The mechanical properties were: yield stress 1010 MPa, tensile strength 1072 MPa, relative elongation 13%.

The melting of the alloy was made, after immersion of the specimens in liquid nitrogen bath, with the molecular $CO_2$ TRUMPF TLF 6000 Turbo laser, working with the light wave 10.6 μm length. The rectangular laser beam 1x20 mm was used. The distance between laser beam and specimens surface was fixed at about 10 mm, and immersion depth of the treated surface was about 1 mm. The width of melted band approached 22-24 mm. The special absorbing agent was used. The laser melting was perfomed at Swietokrzyska University of Technology, Center of Laser Techniques. The treatment parameters are listed in Table 1.

Table 1.
Parameters of laser melting

| Specimens No. | Laser power input, kW | Scan rate, m/min |
|---|---|---|
| 1 | 3 | 1 |
| 2 | 4 | 1 |
| 3 | 5 | 1 |
| 4 | 6 | 1 |
| 5 | 5 | 0.5 |
| 6 | 6 | 0.5 |

The metallographic examinations were made with the Tesla SEM. The etching was carried out with the Kroll reagent.

## 3. Research results and discussion

Detailed examinations of cross-sections showed very complex structure of the melted layer and microhardness gradually decreased from the surface. The laser treatment parameters influenced the structure of layer, surface roughness and appearance of cracks.

In laser melted layer the number of zones has been observed which differed in color, structure, hardness and thickness. Beginning from the surface, the following zones were distinguished:

1. black graphite color zone: dendritic zone, dissolving in Kroll reagent, present on the surface together with some surface dendrites and thin cracks,
2. gold-yellow color zone: appearing usually as isolated areas or sometimes on longer distance, depending on melting parameters; identified as a zone of titanium nitride, with maximum grain size 1.4 μm, and hardness 1660 $HV_{0,05}$ as average, approaching even 2650 $HV_{0,05}$,
3. silver-white color zone: observed only locally when the gold-yellow zone was very thick, saturated with nitrogen, with average hardness 1440 $HV_{0,05}$,
4. dark zone: containing clear dendrites with randomly oriented axes and bright needle precipitates, the thickest zone in entire melted layer, with hardness 850 $HV_{0,05}$,
5. bright zone: thin or invisible, demonstrating lamellar structure, with numerous inclusions and hardness 715 $HV_{0,05}$,
6. border line of diffusion zone, present only in some specimens and in part of the total layer,
7. zone containing some grain boundaries of the previous β phase in lamellar α phase structure, with microhardness 515 $HV_{0,05}$,
8. heat affected zone (HAZ), of great width and small grain structure (likely only α phase), with microhardness from 480 $HV_{0,05}$ to 370 $HV_{0,05}$ at depth 1.65 mm, which corresponds to the base material.

The more distinct differences in thickness appeared rather as an effect of scan rate then of laser power. At the same laser power value the specimens scanned at a lower rate demonstrated higher thickness. The views of cross-sections of specimens melted at different parameters are show in Fig. 1.

The layer thickness measurements comprised both melting zone and heat-affected zone. The melted layer thickness comprised between 250 μm in specimen No. 1 to 470 μm in specimen No. 5. The melted layer was thicker at laser power 5 kW then 6 kW at both 1 m/s (Nos. 3 and 4) and 0.5 m/s (Nos. 5 and 6)scan rate. The thickest was layer obtained at 5 kW and 0.5 m/s. In this specimen the mostly developed gold zone of titanium nitride and silver zone containing titanium saturated with nitrogen (martensite) was observed. In specimen No. 6 the outer zone was mostly developed, possessing the highest tightness and uniformity. The zone was composed of bright dendrites on dark background of martensite.

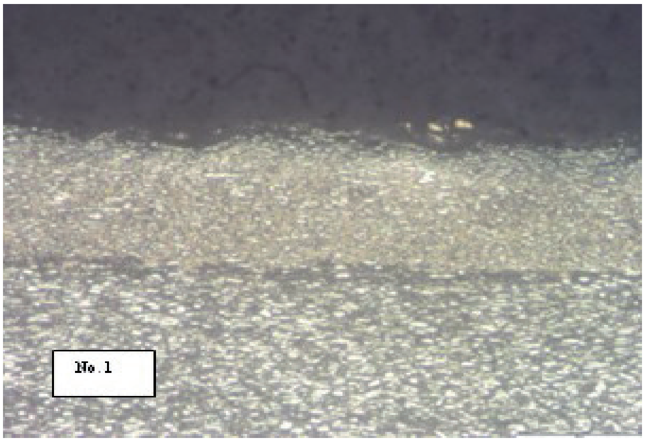
The gold-yellow zone was seen as a solid structure. The laser power clearly influenced its contribution to the whole layer: at weak laser energy, the gold layer was thin and irregularly dispersed, then becoming more and more tight and thick.

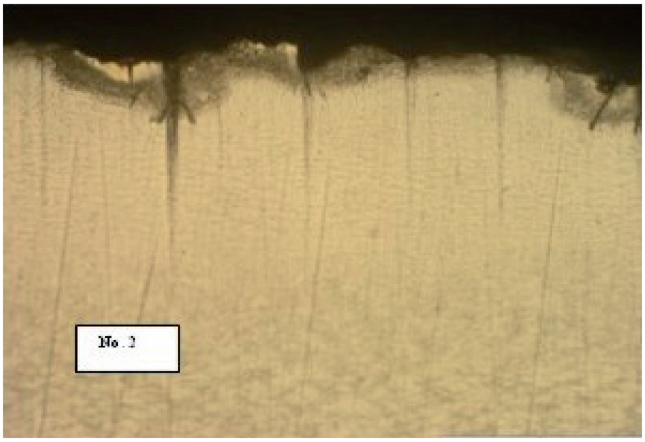
The laser melting at high scan rate resulted in greater discontinuity and inhomogeneity of melted layer. The increase in laser power resulted in more visible particular zones and enhanced their features.

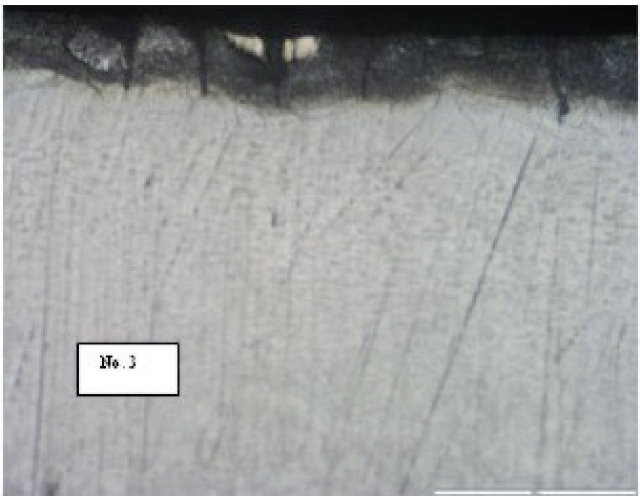
The network of cracks was observed for all specimens. The cracks sometimes propagated across entire layer, sometimes

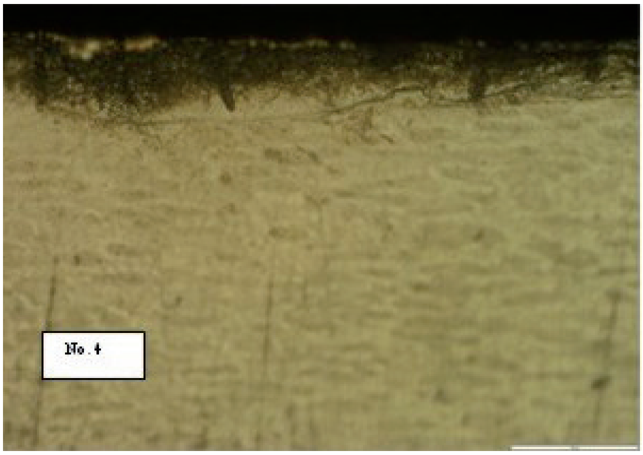
stopped in deeper zones, usually finished in diffusion area. The number of cracks ranged between 26 (No. 1) and 11 (No. 6).
The visual examinations of the surface (examples in Fig. 2) showed two overlapped passages of beam laser.

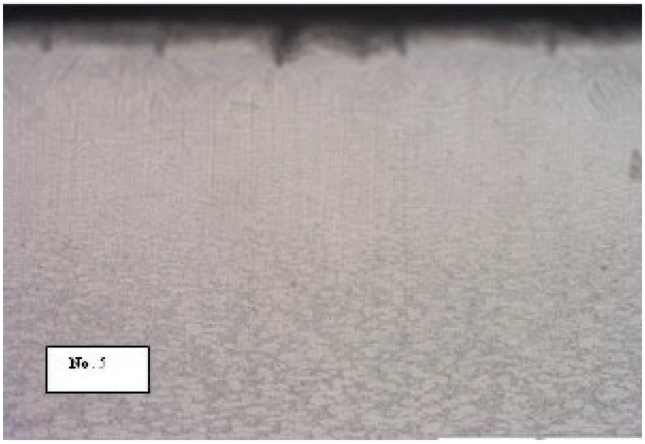
The surface of specimen No. 1 was the most black one, slightly glossy, with visible lines parallel to the beam direction, consisting of irregularly dispersed small pellets („islands”).



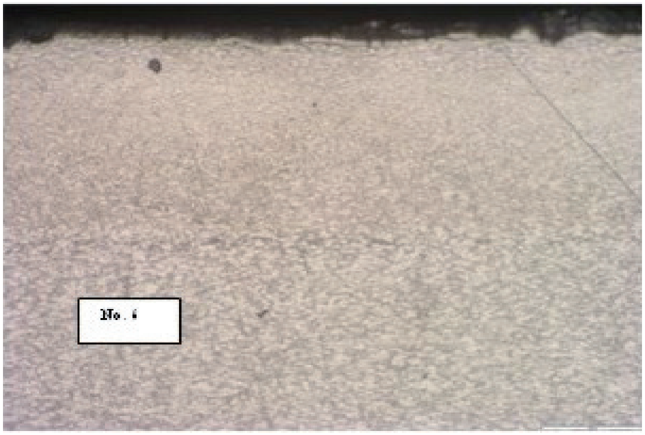




Fig. 1. View of cross-sections of specimens laser melted at different parameters. Scale bars 200 µm (Nos, 1,2,3,4,5,6) or 50 µm

The specimens Nos. 1 and 2 showed rough surface, and solidified metallic droplets, singular or in colonies. In cavities the dendritic crystallites were observed. The layer had not fully developed. The transcrystalline cracks formed network on the surface in area of a local stress concentration, e.g. at irregularities created during solidification.

The specimens Nos. 3 and 4 disclosed relatively uniform surface. In specimen No. 5 the large area of surface was seen as isolated droplets of solidified liquid surrounded by flat area. The cracks propagated in both flat and rough area, with dominating direction parallel to laser beam direction. In specimen No. 6 the roughness was the highest and droplets elongated.

The obtained results confirm that used laser treatment at cryogenic conditions is able to melt the layer and to transform it in very small grain structure, with creation of titanium nitride and titanium martensite structure saturated with nitrogen, also probably covered with titanium and vanadium oxides. All these processes cause substantial hardness of the surface layer. Thus, this process is an analogy to simultaneous processes of surface melting, nitriding and quenching.

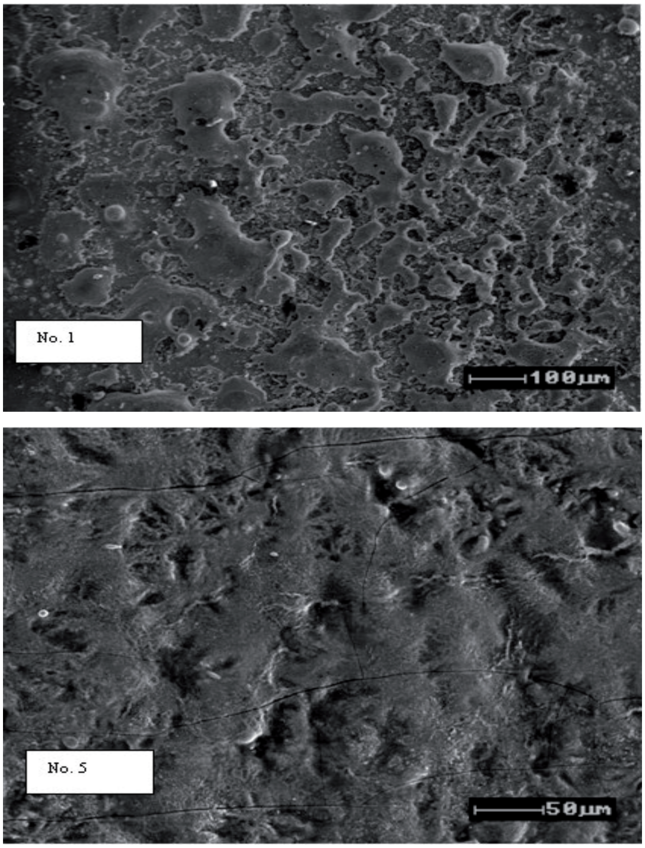



Fig. 2. View of some selected specimens` surfaces after laser melting

## 4. Conclusions

The melting of the Ti6Al4V alloy with high power laser at cryogenic conditions gives the thick and hard layer.

The structure of obtained melted layer is very complex and is composed of zones with dominant structures, among others, titanium nitride and titanium martensite saturated with nitrogen.

The creation of titanium nitride and nitrogen martensite is a positive effect caused by nitriding of surface zone.

The thickness of melted layer and its structure depend on laser beam energy, i.e. laser beam power and scan rate.

The appearance of network of cracks is likely a result of high compressive stresses, formation of martensite structure and high sensitivity of the alloy of brittle fracture.

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