

LOW-POWER BLUE DIODE LASER NITRIDING OF Ti-6Al-4V ELI AND Ti-6Al-7Nb

Deyan Veselinov^{1,2✉}, Yanko Yankov¹, Veneta Koeva¹,
Radostina Yankova¹, Ivan Rusev¹, Hristo Skulev^{1,2}

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Abstract

Laser-induced nitriding was applied to Ti-6Al-4V ELI and Ti-6Al-7Nb alloys using a low-power blue diode laser (455 ± 5 nm, 22 W) under localized high-purity nitrogen delivery. The effect of laser power on the microstructure, phase composition, and microhardness of the treated layers was systematically investigated. A multilayer structure consisting of a TiN-rich compound layer, a remelted zone, and a heat-affected zone was formed. The total modified depth increased with increasing laser power, reaching approximately 160–170 μm . X-ray diffraction analysis confirmed the formation of titanium nitride phases, with TiN reflections becoming more pronounced at higher laser power levels. A substantial increase in surface hardness was achieved, with maximum values of approximately 1758 HV for Ti-6Al-4V ELI and 2233 HV for Ti-6Al-7Nb, compared with substrate hardness values of approximately 300–330 HV. The hardness gradually decreased with increasing depth, reflecting the transition from the nitride-rich compound layer toward the substrate. The results demonstrate that low-power blue diode laser processing enables the controlled formation of TiN-based surface layers on biomedical titanium alloys and represents an efficient approach for localized surface modification.

Key words: laser surface treatment, titanium nitriding, TiN, microhardness, surface modification

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Introduction. Titanium and its alloys are extensively used in biomedical applications such as orthopedic and dental implants due to their favourable combination of low density, high specific strength, excellent corrosion resistance, and good biocompatibility [1]. Among them, Ti-6Al-4V ELI and Ti-6Al-7Nb are widely employed implant materials, where the extra-low interstitial (ELI) grade is preferred for load-bearing applications due to its improved fracture toughness, while Ti-6Al-7Nb has been developed as a vanadium-free alternative to enhance long-term biocompatibility [2, 3]. Despite these advantages, the relatively low hardness and poor wear resistance of titanium alloys remain critical limitations, particularly in articulating or fretting environments, where wear debris may lead to adverse biological responses and implant failure [4].

Surface modification techniques have therefore been widely investigated to improve the tribological performance of biomedical titanium alloys without compromising their bulk mechanical properties. Among these approaches, thermochemical treatments such as nitriding, oxidation, and oxynitriding have proven effective in enhancing surface hardness and wear resistance through the formation of hard ceramic phases including TiN, Ti₂N, and TiO₂ [5]. However, conventional gas nitriding and oxidation processes typically require high processing temperatures and long treatment times, which may result in grain coarsening, distortion, or degradation of mechanical properties, particularly in metastable $\alpha + \beta$ titanium alloys [6, 7].

Laser surface engineering has emerged as a powerful alternative for thermochemical surface modification due to its localized energy input, high heating and cooling rates, and precise controllability. Laser-assisted nitriding and oxidation of titanium alloys have been shown to produce hardened surface layers with refined microstructures and minimal thermal influence on the substrate [8, 9]. In reactive laser processing, the interaction between the laser-induced melt pool and a reactive gaseous atmosphere enables in-situ formation of nitride, oxide, or oxynitride layers, depending on processing conditions and gas composition [10].

Most previous studies on laser-assisted nitriding and oxynitriding of titanium alloys have focused on high-power laser systems, such as CO₂ or fibre lasers, often exceeding several hundred watts [11, 12]. In contrast, investigations employing low-power diode lasers remain limited, despite their advantages including high electrical efficiency, compact design, and suitability for precise surface treatment of biomedical components [13]. Furthermore, comparative studies addressing the influence of alloying elements, particularly aluminum, vanadium, and niobium, on nitride layer formation and surface-hardening behaviour remain limited in the literature. The use of low-power blue diode lasers for reactive nitriding of biomedical titanium alloys remains largely unexplored.

In this study, reactive laser nitriding of Ti-6Al-4V ELI and Ti-6Al-7Nb alloys was performed under a nitrogen atmosphere using a low-power (22 W) diode laser equipped with a custom-designed nozzle for localized nitrogen delivery. The

microstructural evolution, phase composition, and microhardness distribution of the treated surfaces were systematically investigated. Particular attention was given to the relationships between laser-processing conditions, nitride layer development, and surface-hardening behaviour, as well as to the comparative response of the two biomedical titanium alloys.

Experimental. Biomedical titanium alloys Ti-6Al-4V ELI and Ti-6Al-7Nb were used as substrate materials. The nominal chemical composition (wt.%) of Ti-6Al-4V ELI was 5.5–6.5 Al, 3.5–4.5 V, ≤ 0.25 Fe, ≤ 0.13 O, ≤ 0.08 C, ≤ 0.05 N, ≤ 0.012 H, balance Ti, while Ti-6Al-7Nb contained 5.5–6.5 Al, 6.5–7.5 Nb, ≤ 0.25 Fe, ≤ 0.20 O, ≤ 0.08 C, ≤ 0.05 N, ≤ 0.012 H, balance Ti.

Cylindrical specimens were machined from bar stock with a height of 5 mm and diameters of 16 mm (Ti-6Al-4V ELI) and 12 mm (Ti-6Al-7Nb). Prior to laser processing, the samples were mechanically prepared by sequential grinding with SiC abrasive papers of increasing grit size, followed by polishing with diamond suspensions to obtain a mirror-like surface. The samples were then rinsed with distilled water and air dried. For metallographic examination, the polished cross-sections were etched with Kroll's reagent for 30 s.

Laser surface treatment was performed using a blue diode laser (455 ± 5 nm) with a maximum power of 22 W, equipped with a coaxial nozzle for localized nitrogen delivery (Fig. 1). High-purity nitrogen (99.9999%) was used as the reactive atmosphere at a constant flow rate of 25 L/min. The samples were processed at 30%, 50%, 70%, and 90% of the nominal maximum laser power of 22 W, corresponding to actual power settings of approximately 6.6, 11.0, 15.4, and 19.8 W,

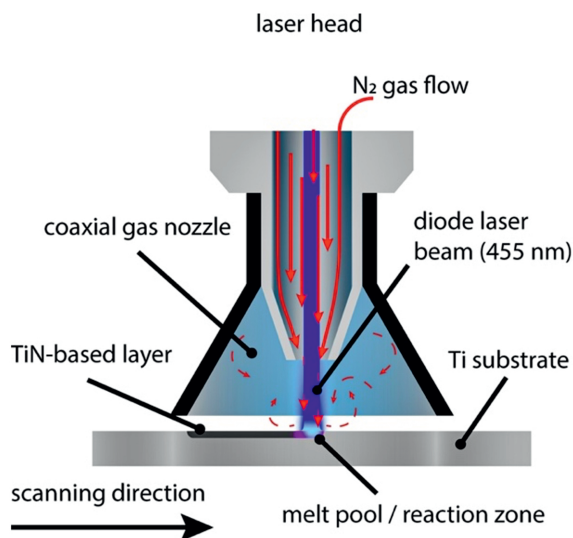


Fig. 1. Schematic illustration of the laser surface treatment setup with coaxial nitrogen gas delivery

respectively. A beam spot of approximately 100 μm and a scanning speed of 1000 mm/min were used for all processing conditions.

The microstructure and thickness of the modified layers were examined by optical microscopy on cross-sections prepared perpendicular to the scanning direction using standard metallographic procedures. The thicknesses of the compound layer and the total modified region were determined from the cross-sectional optical micrographs by measuring the distance from the treated surface to the corresponding microstructural boundaries. The compound-layer thickness was identified from the near-surface nitride-rich region, whereas the total modified depth included the compound layer, remelted zone, and heat-affected zone. Phase composition was analyzed by X-ray diffraction (Tongda TDM-10, Cu $K\alpha$ radiation, $2\theta = 20\text{--}80^\circ$), and phase identification was performed using reference databases.

Microhardness profiles were measured on polished cross-sections using a Vickers indenter (HV0.01) with indentations applied from the surface toward the substrate.

Results and discussion. Microstructure. Representative cross-sectional micrographs (Fig. 2) reveal that laser processing in nitrogen produces a multilayer structure consisting of a compound layer, remelted zone, and heat-affected zone (HAZ), followed by the substrate. The thickness of the modified region increases with laser power in both alloys.

At 30% power, only a shallow modified layer is formed ($\sim 40\text{--}45\ \mu\text{m}$), indicating near-threshold melting. Increasing the power to 50% leads to a substantial increase in depth ($\sim 95\text{--}100\ \mu\text{m}$) and the formation of a stable melt pool with cellular and columnar structures. At 70%, the compound layer reaches $\sim 55\text{--}57\ \mu\text{m}$, while the total modified depth increases to $\sim 135\text{--}145\ \mu\text{m}$.

At 90%, the compound layer thickness remains nearly constant ($\sim 56\text{--}57\ \mu\text{m}$), whereas the HAZ expands significantly, resulting in a total depth of $\sim 170\ \mu\text{m}$. Local surface irregularities and cracking are observed at this condition. The occurrence of local cracking at 90% power suggests that the highest energy input introduces excessive thermal loading of the surface. The rapid heating and cooling associated with laser processing can generate high local thermal stresses, particularly within the hard nitride-rich surface layer. In addition, the nearly unchanged compound-layer thickness between 70% and 90% power, together with the pronounced increase in HAZ depth, indicates that the additional laser energy primarily promotes deeper thermal modification rather than further compound-layer growth. Consequently, intermediate laser power provides a more favourable balance between nitride layer formation, surface hardening, and preservation of surface integrity.

The results indicate a transition from limited melting at low power to stable reactive melting at intermediate power, followed by saturation of compound layer growth at higher power, where further energy input primarily increases the HAZ depth.

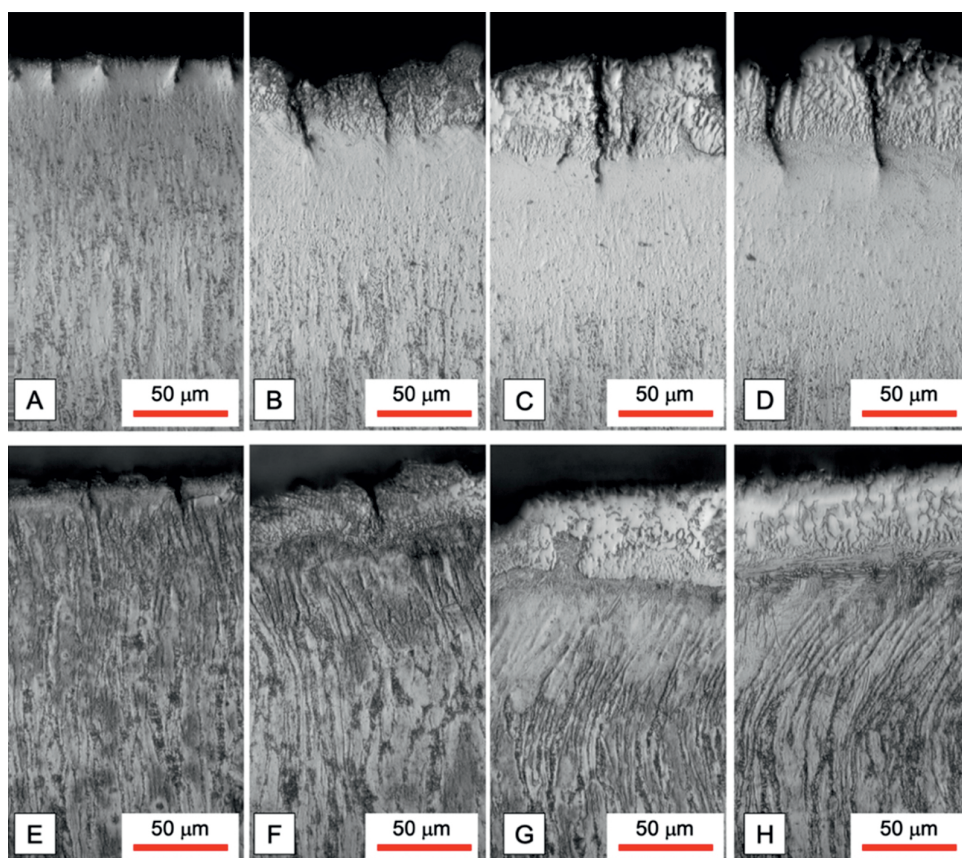


Fig. 2. Cross-sectional microstructures of Ti-6Al-4V ELI (A–D) and Ti-6Al-7Nb (E–H) after laser nitriding at 30%, 50%, 70%, and 90% of 22 W

The evolution of the multilayer structure is governed by laser power, which controls melt pool temperature and nitrogen incorporation. At low power, limited melting produces a thin compound layer, while increasing power leads to a stable melt pool and enhanced nitride formation. At higher power, the compound layer thickness approaches saturation (~ 55 – 57 μm), and further energy input mainly increases the HAZ depth, indicating diffusion-limited growth, consistent with previous studies [14,15].

Phase analysis. Figure 3 presents the XRD patterns of the untreated and laser-treated samples. The untreated alloys are dominated by α -Ti reflections, with minor β -phase contributions.

After laser nitriding, additional diffraction peaks corresponding to TiN are observed, confirming the formation of nitride phases. The TiN reflections generally become more pronounced with increasing laser power. At 30% power, the nitride reflections are relatively weak, whereas at 50–70% they become clearly defined and are most pronounced at 90% power. This evolution is consistent

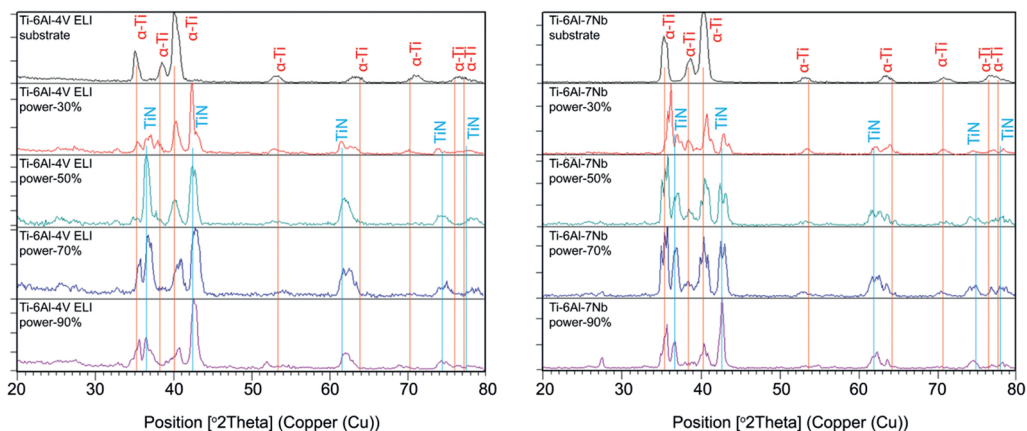


Fig. 3. XRD patterns of Ti-6Al-4V ELI (left) and Ti-6Al-7Nb (right) substrates and samples laser-treated under nitrogen at 30%, 50%, 70%, and 90% of the nominal 22 W power

with the progressive development of the TiN-containing surface layer. However, because XRD peak intensity may also be influenced by phase fraction, crystallographic texture, and measurement conditions, the changes in peak intensity are interpreted qualitatively rather than as a direct quantitative measure of nitrogen concentration. Minor contributions from Ti_2N cannot be excluded because of peak overlap, whereas no distinct TiO_2 reflections are detected. A small uniform peak shift is attributed to sample displacement during measurement.

Overall, the XRD results confirm the formation and progressive development of TiN-based surface layers during laser processing in nitrogen. The increasingly pronounced TiN reflections are consistent with enhanced nitride formation at higher laser power. The absence of distinct oxide reflections indicates that nitriding is the dominant reaction under the applied processing conditions, although minor contributions from Ti_2N cannot be excluded.

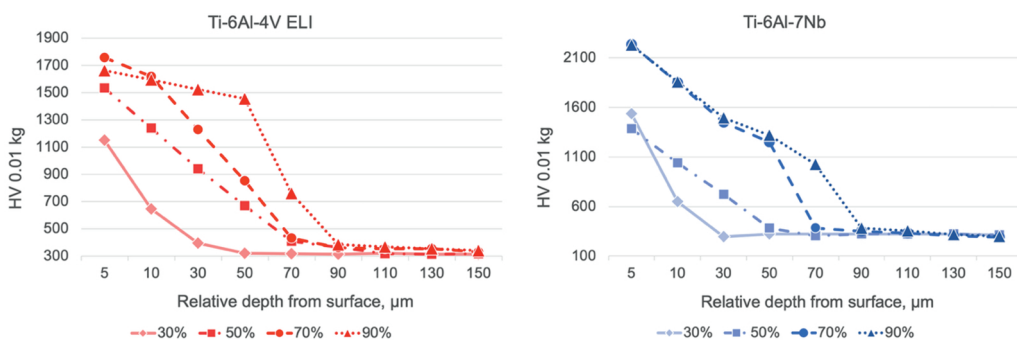


Fig. 4. Cross-sectional microhardness profiles (HV0.01) of Ti-6Al-4V ELI (left) and Ti-6Al-7Nb (right) as a function of depth from the laser-treated surface under nitrogen at 30%, 50%, 70%, and 90% of the nominal 22 W power

Microhardness. The microhardness profiles (Fig. 4) show a significant increase in surface hardness after laser nitriding for both alloys. Maximum values are observed near the surface ($\sim 5 \mu\text{m}$), reaching ~ 1758 HV for Ti-6Al-4V ELI and ~ 2233 HV for Ti-6Al-7Nb, compared to ~ 300 – 330 HV for the substrates.

Hardness decreases gradually with depth, reflecting the transition from the nitride-rich compound layer to the remelted and heat-affected zones. The hardened region extends up to $\sim 70 \mu\text{m}$ in Ti-6Al-4V ELI and $\sim 90 \mu\text{m}$ in Ti-6Al-7Nb at higher laser powers.

Increasing laser power leads to higher surface hardness and deeper hardened layers, with maximum values at $\sim 70\%$ power and slight saturation at higher power. Ti-6Al-7Nb exhibits consistently higher hardness than Ti-6Al-4V ELI.

The results confirm that laser nitriding produces pronounced surface hardening consistent with the formation of TiN-based layers and the observed microstructural evolution. The high hardness values are attributed to the formation of TiN-based phases, consistent with literature data for laser-nitrided titanium alloys [15]. Maximum hardness is achieved at $\sim 70\%$ power, while slight reduction at higher power may be related to remelting or defect formation.

Conclusions. Laser-induced nitriding of Ti-6Al-4V ELI and Ti-6Al-7Nb alloys was successfully achieved using a 455 nm diode laser under a nitrogen atmosphere. The treatment produced a multilayer surface structure composed of a nitride-rich compound layer, a remelted zone, and a deeper heat-affected zone. The thickness of the modified region increased with increasing laser power, reaching total depths of approximately 160–170 μm at the highest processing conditions.

X-ray diffraction analysis confirmed the formation of TiN-based phases on the treated surfaces. The TiN reflections became progressively more pronounced with increasing laser power, consistent with enhanced development of the nitride-containing surface layer. No distinct TiO_2 reflections were detected under the applied processing conditions, although minor contributions from Ti_2N cannot be excluded.

Laser nitriding resulted in a substantial increase in surface microhardness. Maximum values of approximately 1758 HV for Ti-6Al-4V ELI and 2233 HV for Ti-6Al-7Nb were obtained, compared with substrate hardness values of approximately 300–330 HV. The hardness gradually decreased with increasing depth, reflecting the transition from the nitride-rich compound layer through the remelted and heat-affected zones toward the unaffected substrate.

Among the investigated processing conditions, approximately 70% of the nominal laser power provided the most favourable combination of nitride layer development and surface hardness. Increasing the power to 90% produced only a limited further increase in compound-layer thickness while increasing the heat-affected depth and promoting local surface irregularities and cracking. These results demonstrate that low-power blue diode laser nitriding is an effective approach for localized surface hardening of Ti-6Al-4V ELI and Ti-6Al-7Nb alloys.

REFERENCES

- [1] MARIN E., A. LANZUTTI (2023) Biomedical applications of titanium alloys: a comprehensive review, *Materials*, **17**(1), 114.
- [2] ABD-ELAZIEM W., M. A. DARWISH, A. HAMADA et al. (2024) Titanium-based alloys and composites for orthopedic implant applications, *Mater. Des.*, **241**(65), 112850.
- [3] BESISA N. H. A., T. YAJIMA (2024) Titanium-based alloys: classification and applications. In: *Titanium-Based Alloys*, IntechOpen.
- [4] RABBITT D., V. M. VILLAPÚN, L. N. CARTER et al. (2025) Rethinking biomedical titanium alloy design: a review of challenges from biological and manufacturing perspectives, *Adv. Healthc. Mater.*, **14**(4), e2403129.
- [5] VESELINOV D. (2022) *Titanium for Biomedical Applications: Surface Treatment and Anodizing*, Sofia, Prof. Marin Drinov Publ. House of BAS, 324 pp.
- [6] CUTHILL J. R., W. D. HAYES, R. E. SEEBOLD (1960) Nitriding phenomena in titanium and the 6Al-4V titanium alloy, *J. Res. Natl. Bur. Stand. A Phys Chem.*, **64A**(1), 119–125.
- [7] FUJITA K., M. IJIRI, Y. INOUE et al. (2021) Rapid nitriding of titanium alloy with fine grains at room temperature, *Adv. Mater.*, **33**(20), e2008298.
- [8] FEDOROV R., F. LEDERLE, M. LI et al. (2021) Formation of titanium nitride, titanium carbide, and silicon carbide surfaces by high power femtosecond laser treatment, *ChemPlusChem*, **86**(9), 1231–1242.
- [9] KAMAT A. M., S. M. COPLEY, A. E. SEGALL et al. (2019) Laser-sustained plasma (LSP) nitriding of titanium: a review, *Coatings*, **9**, 283.
- [10] ABOUD J. H., A. F. FIDEL, K. Y. BENYOUNIS (2008) Surface nitriding of Ti-6Al-4V alloy with a high power CO₂ laser, *Opt. Laser Technol.*, **40**(2), 405–414.
- [11] DAVID R., P. K. BANNARAVURI, G. B. RAO et al. (2023) Effects of fiber laser treatment of Ti-64 alloy, *Mater. Today Proc.*, <https://doi.org/10.1016/j.matpr.2023.10.060>.
- [12] YILBAS B. S., H. ALI, A. AL-SHARAFI et al. (2019) Laser processing of Ti-6Al-4V alloy, *Heliyon*, **5**, e01211.
- [13] TUMKUR T. U., R. LI, V. KORAKIS et al. (2025) A review of laser materials processing paradigms, *MRS Bull.*, **50**, 1519–1538, <https://doi.org/10.1557/s43577-025-01021-7>.
- [14] LISIECKI A. (2015) Titanium matrix composite Ti/TiN produced by diode laser nitriding, *Metals*, **5**, 54–69.
- [15] GUO J., Y. SHI, P. GENG et al. (2020) The surface morphology of a Ti-6Al-4V fiber-lasered nitride layer, *Coatings*, **10**(5), 451, <https://doi.org/10.3390/coatings10050451>.

¹*Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Centre “Acad. A. Balevski”, Bulgarian Academy of Sciences, 67 Shipchenski Prohod Blvd, 1574 Sofia, Bulgaria*

e-mails: dveselinov@ims.bas.bg, yankov@ims.bas.bg, koeva@ims.bas.bg, radyankova@ims.bas.bg, rusev@ims.bas.bg, skulev@ims.bas.bg

²*National Centre of Excellence Mechatronics and Clean Technologies, Akad. Georgi Bonchev St, Bl. 29, 1113 Sofia, Bulgaria*