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REVIEW

Advancements and Applications of Laser Surface Treatment on Titanium Alloys

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Abstract: Titanium and its alloys, characterized by light weight, excellent corrosion resistance, high strength, low elastic modulus, superior biocompatibility, and outstanding osseointegration, have become one of the mostly widely used metallic materials in aerospace and biomedical fields. However, their relatively low plasticity, hardness, and wear resistance constrain further development and applications. Laser surface treatment (LST) technology, which enhances surface properties without altering the bulk material, has emerged as a beneficial approach to modify the surface of titanium alloys. The research advancements and current applications of LST in surface modification of titanium and its alloys were reviewed. The mechanisms, process parameters, surface characteristics, and microstructures of various LST methods were analyzed, including laser transformation hardening (LTH), laser surface remelting (LSR), laser shock peening (LSP), laser surface alloying (LSA), laser cladding (LC), and composite LST techniques. The applications of LST in aerospace and medical domains were also clarified, as well as existing limitations, future research directions, and insights into the developmental trends of LST for titanium and its alloy materials. The objective is to advance LST innovation and to pave new avenues for the application of titanium alloys in various sectors.

Key words: laser surface treatment; titanium alloy; aerospace; medical treatment

Due to its high specific strength, excellent fatigue resistance, and corrosion resistance, Ti alloy has extensive application in high-end sectors such as biomedicine, aerospace, marine engineering, petroleum drilling, and the automotive industry. However, within these domains, particular emphasis is placed on the surface properties of Ti alloys. In aerospace engineering applications, for instance, the inherent low hardness and poor wear resistance of Ti alloy[1–2] render it susceptible to damage of fatigue delamination and abrasive wear[3], making frictional wear a principal contributor to failure in aerospace motion mechanisms[4]. Similarly, in the field of biomedicine, challenges arise like the corrosion of Ti alloy implants within bodily fluids, micro-motion wear against bones, and issues of biocompatibility[5]. Moreover, challenges related to wear and corrosion are also encountered in marine engineering, petroleum industries, and the automotive industry, as well as other domains. Consequently, there is a quest for efficient and precise surface treatment techniques aimed at enhancing the surface performance of Ti alloy components, ultimately prolonging their lifespan and diminishing maintenance costs.

Laser surface treatment (LST) has garnered significant attention due to its potential in enhancing material surface performance[6–7]. The history of LST can trace back to Albert Einstein's pioneering work on laser physics, where he introduced the concept of stimulated emission[8]. However, the first functional laser, which emits the world's inaugural coherent beam of laser light, was not invented until 1960 by Maiman[9]. This marked a pivotal shift in diverse fields, including materials processing and surface treatment. A notable milestone emerged in the 1970s for LST with the integration of high-power lasers into industrial production [10].

LST works by focusing a high-intensity laser beam onto the Ti alloy surface. The energy from the laser heats the surface to a specific temperature, which can cause localized phase changes or melting. After the laser beam is removed, the

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material rapidly cools down, resulting in modified surface properties. This controlled heating and cooling process can lead to a variety of beneficial effects, including heightened hardness, enhanced wear and corrosion resistance, surface alloying, modified residual stress, improved adhesion, and selective surface alteration.

LST offers advantages like the flexibility to process materials with diverse shapes, strong material adhesion, and a compact heat-affected zone[11–13]. Furthermore, LST boasts exceptional attributes in energy efficiency, speed, environmental friendliness, and precise automation[14]. Laser transformation hardening (LTH), laser surface remelting (LSR), laser shock peening (LSP), laser surface alloying (LSA), and laser cladding (LC) have emerged as LST techniques alongside the development of high-energy laser systems[15–21]. They have extensive applications in the reinforcement of Ti alloy surfaces. Besides, the hybrid surface treatment[22–25] based on abovementioned LST techniques is also increasingly applied in the surface treatment of Ti alloys. This work provided an overview of the development of these LST techniques and their contributions in the surface modification of Ti and its alloys. It includes a brief introduction, theoretical studies, processes, performance, and applications in aerospace and medical treatment aeras for different LST techniques. The future of LST techniques for Ti and its alloys is offered at the end.

1 Laser Surface Treatment

As shown in Fig.1, LST is primarily categorized into LTH, LSR, LSP, LSA, and LC. Additionally, there are hybrid LST techniques, i. e., the combination of these LST methods or their joint application with other surface treatment methods. LTH, LSR, and LSP can be classified to laser hardening (LH). In contrast to LH, LC involves incremental coating, while LSA forms non-incremental alloying layers, often termed as alloying layers and coatings, respectively[26].

1.1 Different techniques

1.1.1 Laser hardening

LH is a LST technique that enhances surface performance by irradiating material surfaces with laser beams at various parameters.

LTH uses a high-energy laser ($10^4 – 10^5$ W/cm^2) to rapidly heat a metal surface at 10^4–10^6 °C/s, reaching a phase transformation point below melting point. Instantaneous quenching ($10^4 – 10^8$ °C/s) of the cold base results in high martensite dislocation density, and increases carbon solubility. This yields a highly hardened surface, improving wear and fatigue resistance[27–28]. Fig. 2a shows cross-sectioned LTHed pure Ti microstructure. LTH zone has larger grain size, revealing acicular α' martensite, as shown in Fig.2b and 2c[29].

The LSR is another LH technique, by which the material surface is partially melted by a high-energy laser beam (10^5–10^7 W/cm^2), which is much higher than that of LTH, and the metal liquid in the molten pool quickly cools down through the thermal conduction of the substrate at a cooling rate of $10^5 – 10^8$ °C/s[30]. LSR refines grains, elevates hardness, reduces segregation, and densifies structure, improving surface integrity[31–37]. Fig.3 illustrates the refinement of Ti alloy grains after LSR. However, surface friction coefficient may increase[38].

In LSP[39–41], ultra-short high-energy pulses create surface vaporization, generating intense high-pressure shockwaves, and the energy density exceeds 10^{10} W/cm^2. The shock wave induces ductile deformation, resulting in hardening. LSP offers deeper residual stress, improves microstructure, integrity, and thermal stability, and enhances fatigue, wear, tensile, and corrosion properties[42–47].

1.1.2 Laser surface alloying and laser cladding

LSA uses a high-energy laser to fuse pre-sprayed ultrafine metal or ceramic materials onto Ti alloy surfaces. LSA rapidly homogenizes solute elements through liquid convection, enabling broader alloy composition choices beyond traditional elements.

LC and LSA processes exhibit similarities, but LC employs lower laser energy than LSA. In LC, the cladding material fully melts while substrate melting is limited (typically ≤10% dilution), minimally affecting cladding composition[48–49]. LC avoids using substrate metal as a solvent. Alloy powder, interacting synchronously with the surface, swiftly melts via laser, forming a molten pool that solidifies into a dense, controlled thick bond[50]. Laser operates at $10^3 – 10^6$ W/cm², between that of LTH and LSA[51]. This technique offers

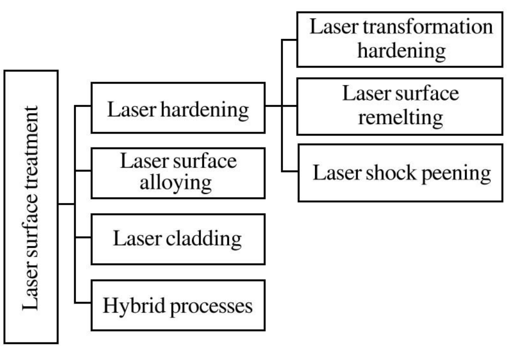


Fig.1 Classification of LST

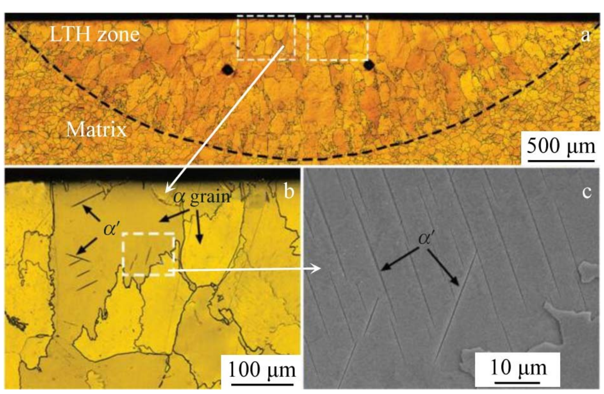


Fig.2 Cross-section microstructure of LTH zone (a), higher magnification image of dashed rectangle box area in Fig.2a (b), and SEM image of dashed rectangle box area in Fig.2b (c)[29]

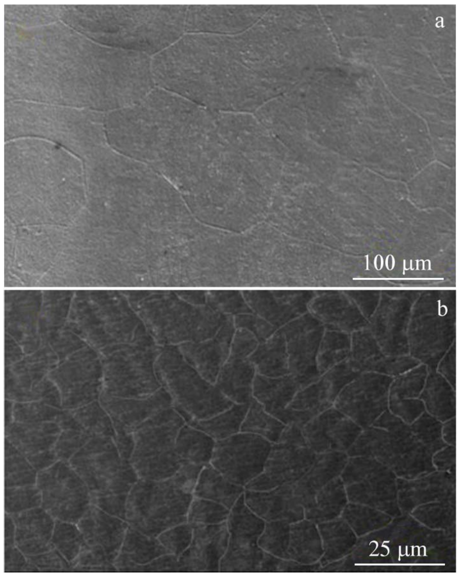


Fig.3 Micro-topographies of Ti-Zr alloy based on LSR: (a) substrate area and (b) remelting area[31]

diverse materials precise shaping, smooth surfaces, strong bonding, and ecofriendly energy use.

1.2 Processing and performance

1.2.1 Laser hardening

LH adjusts parameters to create a robust surface layer, enhancing performance without altering core properties.

Nanosecond, picosecond, and femtosecond lasers yield distinct surface performance improvements. Femtosecond/picosecond treatment enhances wear resistance, while nanosecond treatment yields extended metal-oxide foam surface with wear resistance, showing α-Ti to β-Ti transformation and fragmentation[52].

LTH process parameters, including laser power, scanning speed, and spot size[53], profoundly influence material surface performance[54]. Typically, larger laser power leads to increased surface hardness and deeper hardening layers[53,55]. Zhang et al[56] found that laser-quenched alloy gains super elasticity and microhardness, but loses toughness. Zhang et al[57] found that micro-fretting fatigue of TC11 after LTH shows more noticeable effect, increasing fatigue life by 110.78% at low stress and by 17.56% at high stress.

Likewise, laser power, scanning speed, and spot size are vital parameters of LSR. Another essential factor that must be noticed is the duration[58]. Comparing adhesion, hardness, microstructure, wear, and corrosion resistance, it can be found that LSR enhances material surface properties[59–62]. For example, Zhu et al[63] analyzed laser re-melted TC11 titanium alloy microstructure, and achieved increased strength compared with forging. Adjusting laser parameters like power and speed yields desired surface properties, as demonstrated by Li et al[64].

Laser power, exposure time, and the number of impacts are vital in Ti alloy surface modification via LSP. Surface features intensify with laser power. LSP significantly enhances residual stress, hardness, and fatigue life, especially post multiple treatments. Nanosecond laser shock improves fatigue life by 47% (1 impact) and 85% (3 impacts)[65–66]. The TEM photographs of TC6 Ti alloy after LSP with different laser impacts are shown in Fig.4.

1.2.2 Laser surface alloying and laser cladding

LSA induces refined composition, fine microstructure, high hardness, and excellent wear resistance[67]. Applicable to cost-effective base materials, LSA replaces pricey bulk alloys, reducing costs and accelerating production efficiency.

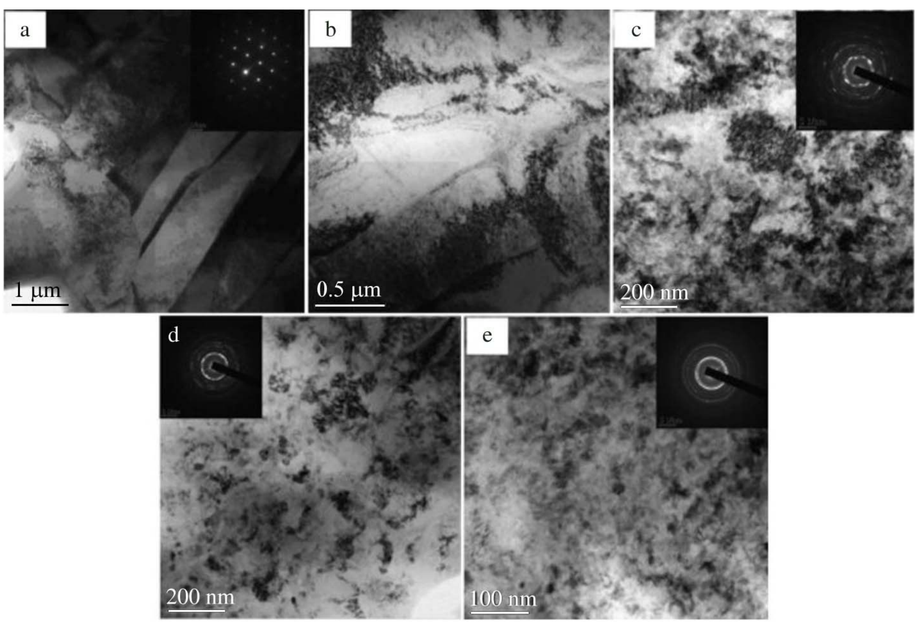


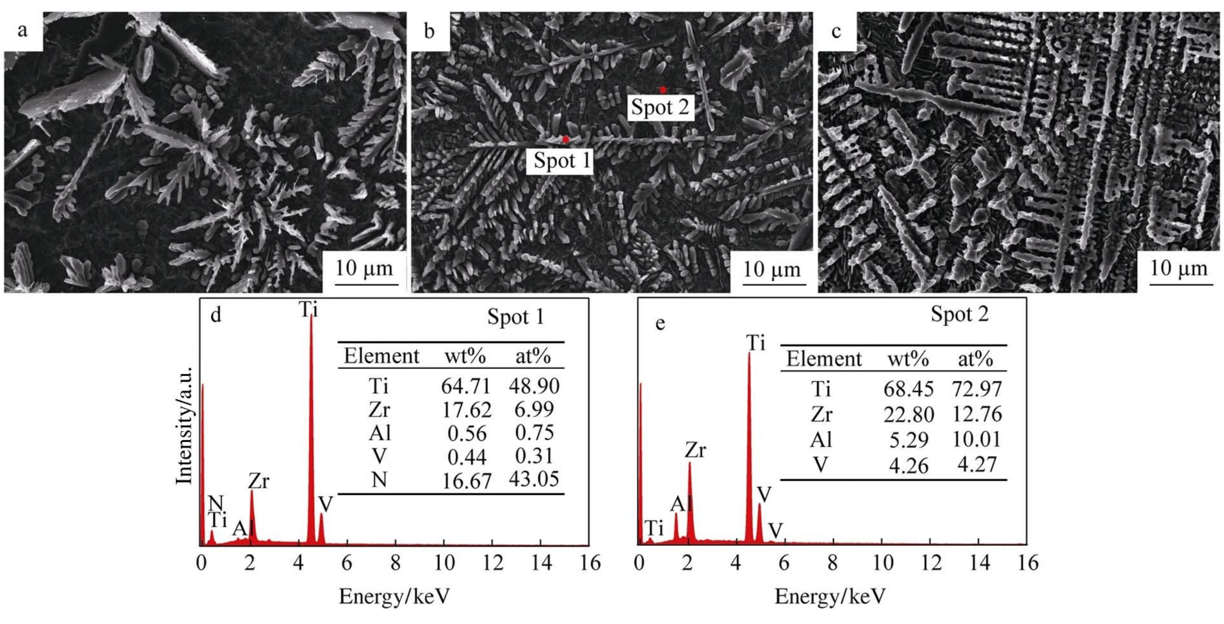
Fig.4 TEM images and diffraction patterns of TC6 Ti alloy after different LSP impacts: (a) without impact, (b) 1 impact, (c) 3 impacts, (d) 5 impacts, and (e) 10 impacts[43]

Parameters like alloying powder thickness, laser power, scanning speed, spot size, and lap rate influence substrate surface performance during LSA.

In laser gas-phase alloying, Zeng et al[68] nitrogenized pure titanium under nitrogen, forming TiN dendrites and enhancing corrosion resistance. In air, Zeng et al[69] laser-irradiated pure titanium, yielding TiN and TiO_2 on the surface. Oxygen is enriched in the outermost layer due to slower diffusion in titanium, and nitrogen is mainly concentrated below. For the first time, the high-temperature diffusion coefficients of O_2 and N_2 into laser-irradiated Ti samples in air at 1843–2930 °C are estimated, which are 4.00×10^{-5}–4.24×10^{-2} cm^2/s and 8.00×10^{-7} – 1.00×10^{-5} cm^2/s, respectively, while the diffusion coefficient of oxygen in TiN is 4.34×10^{-9} cm^2/s. Zong et al[70] studied laser nitriding on TA2, and found that nitride layer thickness increases with cycles. After three cycles, layer thickness reaches about 56 μm. Feng et al[71] employed laser nitriding on Ti-20Zr-6.5Al-4V alloy. Increasing laser power from 120 W to 240 W leads to distinct microstructures (as shown in Fig. 5): dense TiN dendrites, $\alpha+\beta$ Ti (alloy layer), and nanoscale α platelets in HAZ. Higher power amplifies TiN dendrite content due to energy input. HAZ exhibits self-quenching effects, forming nanoscale α platelets and residual β phase. At 240 W, re-melted region shows the highest HV microhardness (about 8984.64 MPa).

In laser solid-state alloying, Fogagnolo et al[72] treated TC4 with Cu and Nb by LSA, forming diverse modified surface structures. At laser power of 200 W, Cu alloying exhibits dendritic and platelet microstructure, while Nb shows needle-like morphology. Adebiyi et al[73] laser-alloyed TC4 with Mo+Zr+S_6, enhancing hardness ($HV_{0.1}$) from 3263.4 MPa to 11 222.96 MPa and wear resistance.

Similar to LSA's laser parameters, LC is closely tied to laser power, scanning speed, spot size, laser dwell time, etc[74]. Beyond laser parameters, coating material is pivotal. Alloy, ceramic, and composite materials often serve as cladding layers, enhancing surface performance of Ti and its alloys. Additionally, powder feeding rate, powder layer thickness, and protective gases influence the surface performance of Ti and its alloy after LC[75–78]. Ali et al[79] investigated the effects of scanning speed, spot size, and dwell time in the LC process of NiCrBSi+WC powder on Ti-6Al-4V alloy surface using 1000 W laser power. The resulting surface hardness under different parameters is illustrated in Fig. 6. Liu et al[80] examined LC of Ti-Ni gradient coatings on TA2 substrates. They varied laser power (1000–1400W) and scanning speeds (300 – 500 mm/min). At low laser power or high scanning speed, the coating exhibits good thickness and adhesion to the substrate, although incomplete melting of powder is observed on the surface. When laser power increases to 1400 W, higher penetration occurs, leading to more Ti atoms entering the coating. This raises the possibility of excessive intermetallic compound formation and cracking. The grain size is refined, element dilution rate decreases, and microhardness increases with higher laser scanning speed[81]. Due to higher dilution rate, corrosion potential of cladding layer at 100 mm/s in scanning speed is lower after immersion in 3.5wt% NaCl solution for 2 h. Jiang et al[82] investigated the influence of laser power on Ti-6Al-4V composite coatings, aiming to enhance the wear resistance of Ti alloys in deep and ultra-deep petroleum field, as shown in Fig. 7. Dense WC-Co coatings demonstrate strong metallurgical bonding. The cross-section microstructures of WC-Co composite coatings are shown in Fig. 8. At laser power of 2000 W, exceptional bonding and refined microstructure yield high microhardness ($HV_{0.5}$) of 15 052.8 MPa and low wear rate of 1.5 g/h.



Element	wt%	at%
Ti	64.71	48.90
Zr	17.62	6.99
Al	0.56	0.75
V	0.44	0.31
N	16.67	43.05

Element	wt%	at%
Ti	68.45	72.97
Zr	22.80	12.76
Al	5.29	10.01
V	4.26	4.27

Fig.5 SEM images of nitrided T-20Zr-6.5Al-4V samples at different laser powers: (a) 120 W, (b) 180 W, and (c) 240 W; EDS point analysis results of Spot 1 (d) and Spot 2 (e) marked in Fig.5b[71]

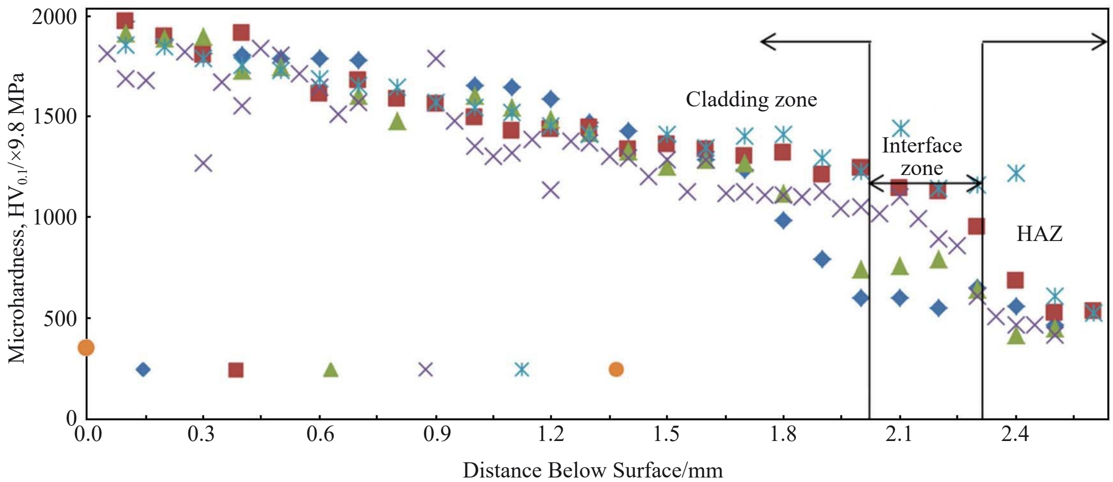


Fig.6 Microhardness profiles of samples under different laser interaction conditions (dwell time, scanning speed, spot size: 0.3 s, 7.45 mm/s, 2.2361 mm; 0.5 s, 5.766 mm/s, 2.8867 mm; 0.7 s, 4.883 mm/s, 3.4156 mm; 0.9 s, 4.3 mm/s, 3.8729 mm; 1.1 s, 3.9 mm/s, 4.2817 mm, respectively)[79]

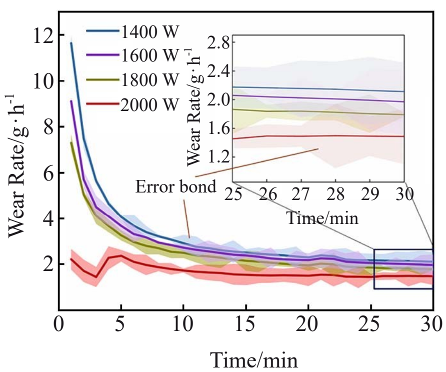


Fig.7 Wear rate distribution[82]

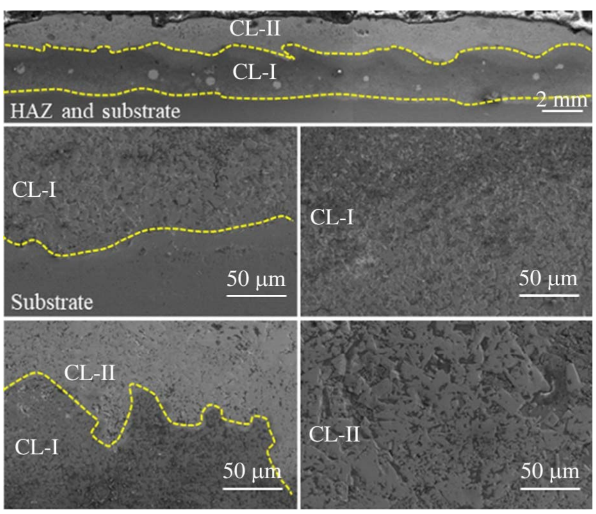


Fig.8 Cross-sectional microstructures of WC-Co composite coatings[82]

1.2.3 Hybrid processes

The surface performance enhancement achieved through standalone LST techniques may fall short of desired outcomes. Hence, researchers proposed laser hybrid processes to further augment surface properties. The study of Kashyap et al[83] demonstrated that the hybrid process of LST and heat treatment can enhance the surface hardness and adhesion of Ti-6Al-4V.

Combining LSP with shot peening (SP) significantly enhances Ti alloy fatigue performance. This hybrid treatment leads to at least 126.4-fold increase in fatigue life for TB6[22] and 9.3-fold increase for Ti-6Al-4V[24]. Yao et al[84] employed LTH with low temperature liquid nitrogen cooling (LTH+LNC) to treat titanium sheets, as shown in Fig.9. The resulting nitrogenized layer, consisting of TiN and α-Ti phases, exhibits improved hardness and wear resistance compared to conventional LTH. The refined grain structure also addresses rapid solidification-induced cracking.

1.3 Summary

The process parameters of LST and the performance index after surface treatment are stated, and LTH, LSR, and LSP are promising methods to achieve deeper hardening layers, especially for complex components with stringent surface quality and stability requirements. In contrast, LSA and LC create distinctive alloy or cladding layers, diverging from the initial composition. The performance of LC and LSA[85] hinges on laser parameters, alloying/cladding material characteristics, auxiliary gases, absorption coatings, and other factors. The LST process parameters to be considered during laser surface strengthening of Ti alloys as well as the evaluation parameters for LST performance (including geometric and physical properties) are depicted in Fig.10.

However, optimizing laser parameters for attaining the optimal surface performance remains challenging. The influence of processing parameters is still uncertained, often leading to a trial-and-error approach in parameter determination.

Simultaneously, considering the escalating performance demands in fields such as aerospace and healthcare, relying solely on a single LST technique might be insufficient. The

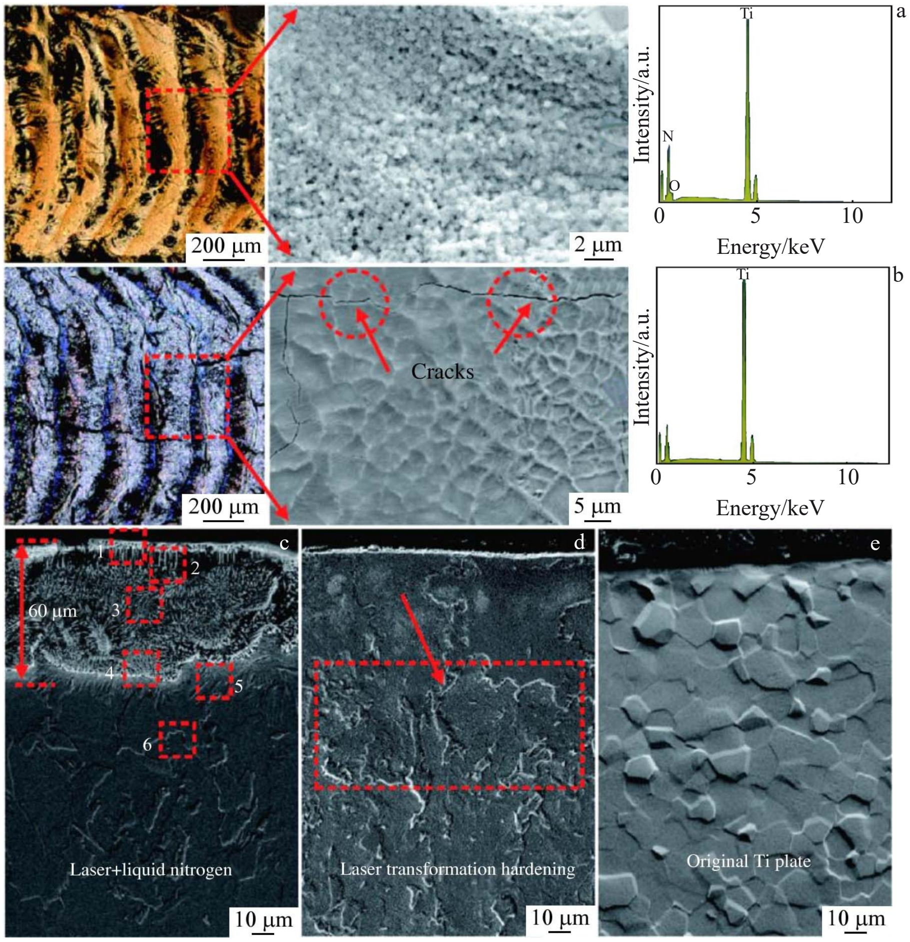


Fig.9 Morphologies and EDS analysis results of titanium plate after LTH+LNC (a) and LTH (b) treatments; cross-sectional morphological features: after LTH+LNC treatment (c), after LTH treatment (d), and original titanium plate (e)[84]

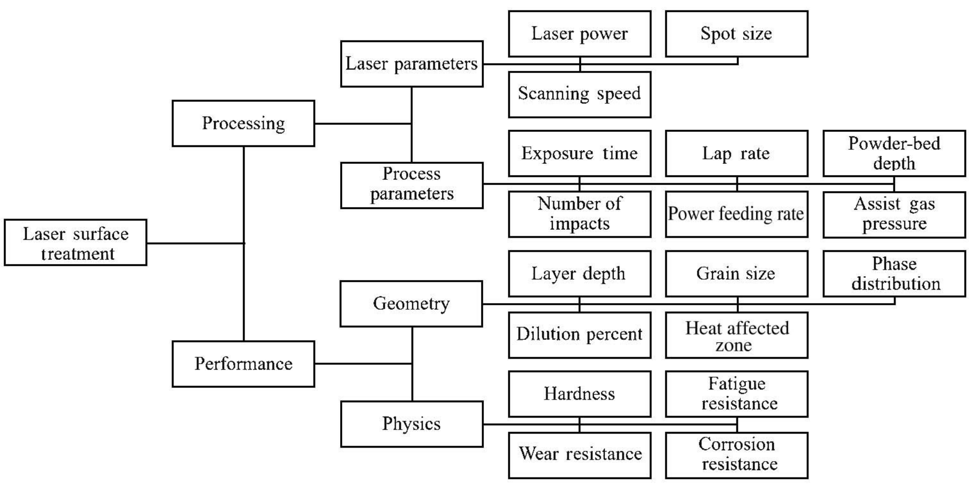


Fig.10 Processing and performance of LST

emergence of laser hybrid processes as a solution to enhance surface performance necessitates further exploration of LST process selection, diverse process interaction mechanisms, and applicability on Ti alloys.

LST primarily aims to functionalize material surfaces. Extensively, Ti and its alloys serve as substrates. Table 1 illustrates various LST examples of Ti and its alloys and scientific rationale behind property enhancements.

2 Application

Ti and Ti alloys find extensive applications across various sectors, including aerospace, medical industry, providing lightweight, durable, and superior performance as various

Table 1 Different LSTs for titanium and its alloys

Substrate	Processing	Research results	Ref.
Pure Ti	LTH	Phase transformation zone is composed of fine plate structures induced by $\beta\rightarrow\alpha$ martensitic transformation, and the hardness increases by 130%.	[27]
Ti plate (Fe: 0.3; C: 0.08; N: 0.03; H: 0.015; O: 0.25)	LTH+LNC	Surface hardness and wear resistance are improved, and mitigating cracking is related to single LTH, owing to grain refinement in the nitrided layer (60 μm, TiN and α-Ti phases).	[83]
TC11	LTH	The fretting fatigue life is increased by 110.78% at low stress level and 17.56% at high stress level.	[56]
Pure Ti	LTH	Grain boundary migration behavior of pure titanium under laser-induced non-isothermal conditions is the same as that under isothermal conditions, but the prior β grain growth kinetics is largely accelerated due to the high heat input from the laser beam.	[29]
Ti-6Al-4V	LSR	Melted zone is composed of fine martensitic plates with dense $\{10\bar{1}1\}$ nanotwins inside them. Heat affected zone is comprised of β particles, martensitic plates, and untransformed bulk α grains. Hardness increases in melted zone due to grain refinement, nanotwins, and solid solution.	[13]
Ti-Zr-Hf-Ta-Nb	LSR	The average grain size in gradient nanostructured layer is refined from 200 μm of matrix to only 8 nm of the top surface. The gradient nanostructure shows significantly enhanced wear resistance, reducing the wear rate with an order of magnitude.	[34]
Ti-47Al-2Cr-2V	LSR	Dendrite arm spacing of TiAl alloys mainly depends on the temperature gradient.	[33]
Ti-6Al-4V	LSR	The acicular martensite α' phase occupies the microstructure of the sample before and after laser remelting.	[36]
TC17	LSP	As the laser energy increases, the surface roughness decreases and the residual stress increases.	[86]
Ti-6Al-4V	LSP+SP	Gradient microstructure with dislocations and novel CRS distribution can be induced. Fatigue crack initiation can be hindered by the high-density dislocation layer. Fatigue crack growth rate can be retarded by the dislocation proliferation layer.	[24]
Ti-6Al-4V	LSP+SP	Dislocations and deformation twins are induced in the subsurface layer and the original coarse grains are refined, especially at 15 μm near-surface location.	[25]
Ti-6Al-4V	LSP	Enhanced tribological performance results from a synergy among laser-induced periodic surface structures, titanium oxide, high compressive residual stress, and gradient grain size distribution in laser surface treatment.	[45]
Pure Ti	LSA (N_2+O_2 in air)	The phase transformation steps during the laser melting and cooling process are found to be α-Ti→β-Ti→α-Ti+β-Ti→α-Ti+TiN+TiN_x (+LTO)→liquid+TiN (+LTO)→TiN+TiO_xN_y (+LTO)→TiO_2+TiN.	[69]
Ti-20Zr-6.5Al-4V	LSA (N_2)	Dense TiN dendrites and (α+β)-Ti (remelting zone, RMZ) and nanoscale α laths are doped with part of β phase (heat-affected zone). Increasing laser power raises TiN dendrite content, resulting in higher surface hardness.	[71]
TA2	LSA (N_2)	The thickness of the alloying layer and the depth of the lath zone increase with the increase in nitriding passes.	[70]
Ti-6Al-4V	LC (WC+ NiCrBSi powder)	Laser cladding for 0.3 s produces a high-quality layer with uniform WC dispersion in the NiCrSiB matrix, which is nonporous and crack-free, and exhibits high microhardness (13 563.2 MPa) and superior wear resistance due to low dilution (25%).	[79]
Ti-6Al-4V	LC (Ni, B_4C, graphite, Si_3N_4)	Wear resistance is improved due to high hardness, excellent lubrication and toughness.	[87]
TC21	LC (5Ti:4Ni: 1SiC)	The composite coatings consist of Ti_2Ni, TiNi, Ti_5Si_3, and TiC phases. Nano-SiC coating has better hardness and wear resistance due to TiC reinforcement and compact microstructure.	[75]
TA2	LC (WS_2-TiC-Ti powders)	α-Ti, TiS, Ti_2SC, (Ti, W)C_{1-x}, and TiC are in-situ synthesized. The microhardness of the coating is improved significantly due to the formation of carbide ceramics Ti_2SC, (Ti,W)C_{1-x}, and TiC, and exceptional wear resistance is observed at 500 °C.	[76]
Ti-6Al-4V	LC (Ni-based alloy+TaC)	TaC addition forms Ta_2O_5 in the passive film, improving corrosion resistance of titanium coating due to its superior stability.	[77]

Table 1 Different LSTs for titanium and its alloys (continued)

Substrate	Processing	Research results	Ref.
Ti-6Al-4V	LC (Ti+B_4C powders)+ heat treatment	Phase composition and microstructure of the heat-treated coatings are virtually identical to those of the untreated coatings; however, the precipitation of acicular TiB enhances mechanical properties of the heat-treated coatings.	[78]
Ti-6Al-4V	Laser texturing+ heat treatment	Combination of LST and heat treatment improves rutile phase fraction, surface hardness and adhesion. Anatase to rutile transformation is prominent mechanism in laser-textured heat treated Ti-6Al-4V surface.	[83]

product components. This section will delve into the LST application for modifying Ti alloy surfaces in aerospace and medical treatment fields.

2.1 Aerospace

Ti alloys play vital roles in aviation[88]. In aircraft engines, their high strength and heat resistance enhance combustion efficiency and thrust[89]. For aircraft structures, they reduce mass and improve fuel efficiency. Ti alloys also meet extreme demands for spacecraft shells, structures, and propulsion. They are used for aerospace tools, lightweight instruments, sensors, and connectors. Leveraging laser surface treatment can further enhance the application of Ti alloys in the aerospace field.

For example, in aircraft operations, foreign objects like birds and debris ingested by engines cause foreign object damage (FOD) to fan/compressor blades[90]. Ti alloy's notch sensitivity intensifies stress concentration, weakening fatigue resistance, risking engine blade fractures, and jeopardizing safety[91]. LSP is pivotal in enhancing blade FOD resilience. It employs laser shock waves to induce plastic deformation, bolstering fatigue strength through residual stress and structural alteration[92]. Acknowledging LSP's fatigue improvement, the US incorporates it in Aircraft Engine Structural Integrity Programs (ENSIP – 1783B) to enhance aircraft adaptability and safety[93].

Furthermore, research by Nie et al[94] demonstrated that after simulating air cannon-induced damage to TC17 Ti alloy blade leading edges, and LSP leads to a fatigue strength increase of approximately 28% after 10^7 cycles. Wu et al[95] investigated LSP-enhanced TC17 Ti alloy fan blade leading edges against FOD. Compared with non-treated notched specimens, after 10^7 cycles, double-sided single-pass LSP on TC17 notched specimens raises fatigue strength from 180 MPa to 280 MPa, achieving an improvement by approximately 55.6%. Lu et al[96] employed air cannon tests on LSP and non-LSP specimens for FOD. LSP reduces pit depth, induces grain fragmentation post-impact, elevates residual stress, refines microstructures, and improves microhardness, effectively countering foreign object impact.

Wang et al[25] applied combined LSP+SP treatment, and surface microhardness is increased by 20% to a depth of about 400 μm, as shown in Fig. 11. Residual stress reaches –843.2 MPa at around 640 μm in depth. High cycle fatigue strength rises by nearly 35% after LSP+SP treatment. LSP+SP induces significant subsurface plastic deformation, refining grain layer

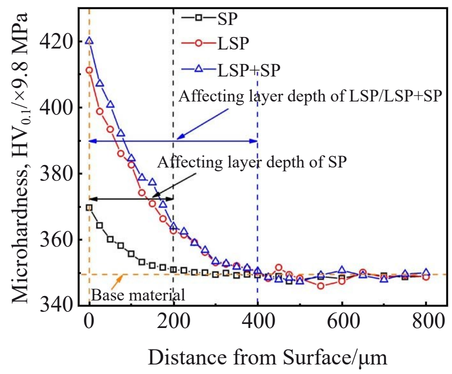


Fig.11 Average microhardness distributions at cross section of Ti-6Al-4V alloy aerofoil specimens[25]

within about 60 μm. FOD tests showcase enhanced hardness against low-energy impacts, but limited effect against high-energy ones. This improvement is stemmed from maximized microhardness and induced residual stress fields. However, full LSP region edge coverage can reduce fatigue life[39], as edges tend to introduce discontinuities, shortening fatigue life further[97–98].

Application of LC technique in aerospace is also notably significant. Addressing aerospace's imperative for high specific strength, high-temperature resistance, and wear-resistant alloys, Jiang et al[99] employed LC techniques to fabricate boron-containing TC4 composites. Increasing boron content can remarkably reduce grain size (from 1294 μm to 28.6 μm), minimize columnar grain formation, and elevate hardness and strength. Microhardness (HV) surges from 3069.654 MPa to 3520.552 MPa, and tensile strength increases by 32.02% from 848 MPa to 1119.5 MPa.

In aerospace and gas turbine environments, temperatures have reached high-temperature alloy limits. Thermal barrier coatings merge metal performance with ceramic high-temperature resistance[100]. Xu et al[101] improved TC4 alloy oxidation resistance by applying NiCrNiSi mixed powders through LC, forming an oxide film of continuous Al_2O_3 and NiO. Liu et al[102] used LC to produce an in-situ TiN/Ti_3Al composite coating on Ti-6Al-4V alloy, primarily comprising α-Ti, TiN, and Ti_3Al phases. The coating exhibits relative oxidation resistance values of 6.83 and 1.94 at 600 and 800 °C, respectively. Shan et al[103] used LC to create coatings with high-temperature oxidation resistance using Nb, Al, and Ti mixed powders. Coating performance relies on Ti segregation and Nb_2Al content. An optimal Ti content of 15.18wt% minimizes segregation. Briguente et al[104] conducted laser nitriding on Ti-6Al-4V (700, 750, 800 W), and this processing can reduce secondary creep. TiN layer prevents oxygen diffusion, enhancing creep resistance. Compared with the base material, at 700 and 750 W, the final fracture time is longer. At 800 W, the time to fracture is shorter because thicker nitrided layer increases hardness and reduces the creep time to fracture.

2.2 Medical treatment

Ti and its alloys, with superior mechanical properties, corrosion resistance, and biocompatibility, find extensive applications in biomedicine, especially as implant materials due to their low elastic modulus and high biocompatibility[105–106]. Pires et al[107] observed potential benefits of LST for cell proliferation and maturation in the Ti-15Mo alloy based on preliminary biological in vitro analyses. Li et al[108] enhanced the bioactivity of Ti-6Al-4V medical implants by LC of a hydroxyapatite (HA)/TC4 composite coating. The contact angle with simulated body fluid (SBF) reduces, indicating improved wettability compared to Ti and its alloy substrate. Chakraborty et al[109] successfully synthesized a nickel-free calcium-titanium cladding layer on nitinol's top surface through LC and alloying. This approach aims to prevent nickel from diffusing into live tissues/cells when applied to metal implants. Shi et al[110] observed no noticeable cracks or holes in the HA/HT/T gradient cladding layers. These coatings exhibit a gradient structure from dense to loose from the interface to the surface. The Ca/P ratio is 1.64, which closely resembles the natural bone's Ca/P value. Shaikh et al[111] used a femtosecond laser (energy density: 0.6 J/cm²) to create Ti-1 and Ti-2 microstructures on Ti-6Al-4V surface (scanning speeds: 25 and 800 μm/s). They cultivated S. aureus, S. mutans, and P. aeruginosa, and found that Ti-1 resists S. aureus and S. mutans, and Ti-2 inhibits S. mutans and P. aeruginosa growth but allows S. aureus colonies growth.

However, both pure Ti and its alloys encounter post-implantation inflammation. Even alloys with Young's modulus closely matching that of bone lack reactivity, leading to mechanical fixation-related micro-motion and debris-induced inflammation[5]. After micro-motion friction, surface structure damage makes them susceptible to ion corrosion, resulting in reduced mechanical properties like corrosion cracking and increased oxide layer thickness[112].

Hence, numerous researchers use LST to enhance surface properties of Ti alloys, aiming to extend their lifespan in medical applications. For instance, Attar[113] and Li[114] et al used LSR to pure Ti, forming α' phase and elevating microhardness, compressive, and ultimate tensile strength. Nelea et al[115] employed pulsed laser deposition to implant and to densify hydroxyapatite coatings on Ti alloys. Jiang et al[116] used continuous laser treatment in a nitrogen atmosphere on Ti-64 alloy, forming TiN dendrites on surface layers that significantly improve wear resistance. Balla et al[117] found enhanced surface hardness and wear resistance of Ti-64 alloy through continuous laser treatment under argon. Chen et al[118] explored pulsed laser surface modification, revealing links among surface hardness, wear resistance, and laser power, supported by finite element simulation. Xue et al[119] studied the LST effects on Ti-20Zr-10Nb-4Ta (TZNT) alloy and found that laser treatment can create grooved structures, improving corrosion resistance and maintaining cell compatibility, making TZNT alloy a potential alternative for implants. The SEM images of MC3T3-E1 cells cultured on the untreated and laser-treated TZNT alloys are shown in Fig.12.

2.3 Summary

Ti and its alloy as the advanced materials capable of withstanding extreme conditions are crucial in aerospace, medical, and other sectors. LST's notable role in these fields highlights its significance, showcasing its promising potential across these applications. Typical applications of titanium alloy LST in the aerospace and medical fields are listed in Table 2 and Table 3, respectively. However, certain limitations must also be acknowledged.

In the field of aerospace, the surface strengthening effect of LST may not be obvious for some parts that are often subjected to friction, because the thickness of the hardened layer, alloy layer, and cladding layer is limited and cannot adapt to rapid and massive wear.

In the field of medical treatment, Ti and its alloys are crucial for enhancing biocompatibility of medical implants, while actual requirements extend beyond good biocompatibility alone[120]. Ensuring enduring strength, hardness, and corrosion resistance is essential. Balancing diverse mechanical properties while preserving the biocompatibility of titanium alloy implants remains a focal point of research in the field of LST technique for future applications in the biomedical sector.

Besides, Ti alloys have an expanding role in maritime

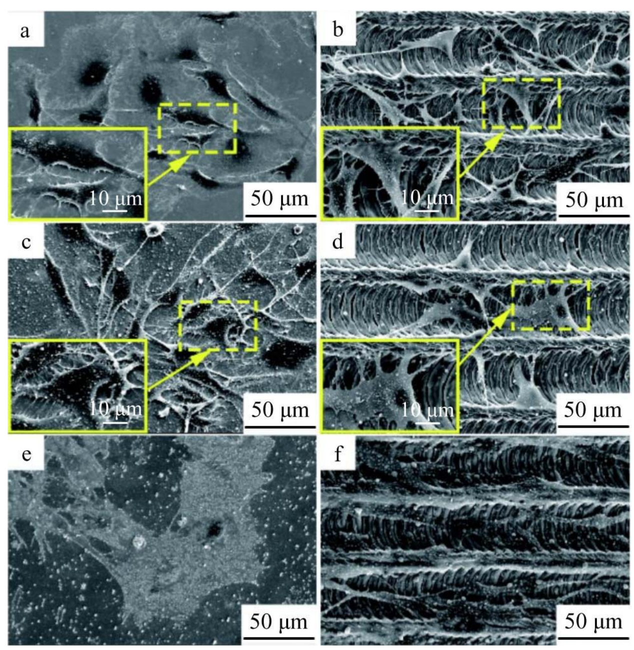


Fig.12 SEM images of MC3T3-E1 cells cultured on untreated (a, c, e) and laser-treated (b, d, f) TZNT alloys: (a–b) 12 h, (c–d) 24 h, and (e–f) 72 h[119]

Table 2 Applications of LST on titanium alloys in the aerospace field

Application	Alloy	Processing	Performance	Ref.
Resisting FOD in airraft engine fan blades	TC17	LSP	Fatigue strength increases after FOD compared to the non-LSP condition.	[94–95]
	TC11	LSP	Laser shock peening effectively reduces the depth of damage pits.	[96]
	Ti-6Al-4V	LSP+SP	The damage caused by low energy impact can be effectively resisted.	[25]
Surface modification of aerospace parts with complex structures	TC11	LTH	The fretting fatigue life is increased.	[56]
	Ti-6Al-4V	LC (Ni-based+TaC)	With increasing the TaC content, the corrosion trend gradually decreases.	[77]
	Ti-6Al-4V	LC (B)	Microhardness increases, and tensile strength rises.	[99]
Aerospace and gas turbine engine oxidation-resistant coatings	Ti-6Al-4V	LC (NiCrAlSi)	The oxide film composed of continuous dense Al_2O_3 and NiO effectively prevents oxygen atoms from corroding the substrate, significantly enhancing oxidation resistance.	[101]
	Ti-6Al-4V	LC	Relative oxidation resistance values of 6.83 and 1.94 can be achieved at 600 and 800 °C, respectively.	[102]
	Ti-6Al-4V	LC (Ni-Al-Ti)	Reducing the extent of Ti segregation in the alloy leads to increased coating oxidation resistance.	[103]
	Ti-6Al-4V	LSA (N2)	The secondary creep rate reduces for all laser nitriding conditions.	[104]

Table 3 Applications of LST on titanium alloys in the medical field

Application	Material	Processing	Performance	Ref.
Enhancing biocompatibility	Ti-6Al-4V	LC (Ti powder)	The in vitro test in Hank's solution confirmed that leaching is inside the preferred values.	[126]
	Ti-6Al-4V	LC (HA/HT/T gradient cladding layers)	The Ca/P ratio is closer to that of natural bone, indicating superior biocompatibility.	[110]
Improving the surface performance of implants	Pure Ti	LSA (N_2+Ar)	Electrochemical experiments in SBF confirm the improved corrosion resistance.	[68]
	Ti-20Zr-10Nb-4Ta	Laser treatment creating grooved structures	Improving corrosion resistance and maintaining cell compatibility can both be achieved.	[119]
	Ti-6Al-4V	LC (HA/TC4)	The surface is uniform, smooth, exhibits good wear resistance, and has excellent biocompatibility.	[108]
	Pure Ti	LSR	Microhardness, compressive strength, and ultimate tensile strength are enhanced.	[113–114]
	Ti-64	LSA (N_2)	Formation of TiN dendrites in the surface layer significantly improves wear resistance.	[116]
	Nitinol	LC ($CaCO_3$+$Ca_3(PO_4)_2$)	Surface modulus of elasticity is found in 6–30 GPa range, similar to that of natural bone.	[109]

applications, the petroleum industry, the automotive industry, and chemical equipment[121–125]. LST technique can enhance their utility in these sectors, notably improving corrosion resistance and mechanical properties.

3 Future Development

Although laser surface strengthening technologies like LTH, LSR, and LSP are mature and widely used for Ti alloy, choosing a best laser parameter to maximize surface performance strengthening remains an ongoing challenge. Both single and hybrid LST methods induce alterations in the microstructure of Ti and its alloy surface layers, thereby resulting in changes in macroscopic mechanical properties. The comprehensive impact of single and hybrid LST techniques on Ti alloys is not fully understood at present. Currently, research primarily involves experimental methods to investigate the influence of LST on the mechanical properties of Ti and its alloy materials[13,127]. There is an urgent need for enhanced research on the multiscale relationship between microstructure and macroscopic performance.

In contrast to the hardened layers produced by LTH, LSR and LSP, LSA or LC generates new alloying or cladding layers, altering composition. LC and LSA[85] performance relies on laser parameters and the properties of alloying/cladding materials. LC offers surface modification advantages, but has some typical defects such as cracks, gas-induced porosity, and partial alloy melting[128]. Auxiliary methods play a crucial role in defect elimination[37,129–131], as shown in Fig.13 and Fig.14. Future research should focus on this aspect to fully eradicate processing flaws of LC and LSA.

Interdependencies between processing parameters and performance parameters are intricate. Understanding interaction mechanisms between LST parameters and Ti alloy properties to reduce trial-and-error costs is a key goal. In the future, researchers should consider the internal relation among geometric attributes after LST, material properties, microcosmic characteristics and mechanical performance.

Furthermore, gradient coatings can further advance the prospects of LC applications[110,132–133]. In the future developments of LST, there should be increased attention towards gradient coating materials and corresponding laser processes suitable for titanium alloys. This includes a focus on

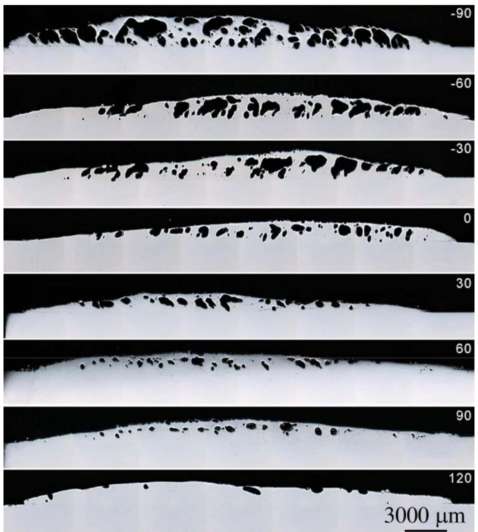


Fig.13 Utilizing electric-magnetic compound fields to restrict pore formation in LC process[130]

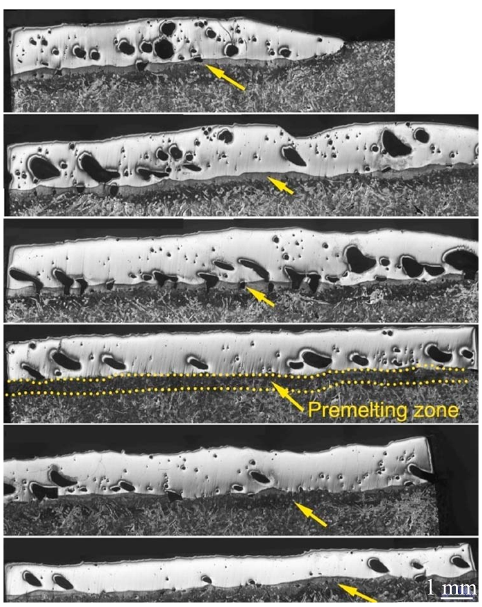


Fig.14 Utilizing LSR compound fields to restrict pore formation in LC process[131]

interface performance related to microstructures and bonding strength[85].

Attention to LST numerical simulation technology is also rising. It is essential to uncover intricate interplay between input parameters and outcomes. Relationships need to be established among laser parameters, materials' properties, and the surface performance after LST[29,32]. The development of numerical simulation technology can greatly reduce the additional costs caused by experimental methods and greatly improve the efficiency of LST for Ti alloy surface modification.

4 Conclusions

1) LST significantly improves the surfaces of Ti and its alloys, selectively altering surface layers to improve durability, to enhance efficiency, and to reduce maintenance costs. LST can improve surface properties through alloy phase transformation and enhance surface performance by incorporating external substances or altering alloy surface composition to prepare coatings. LST is comprehensively reviewed, aiming to inspire advancements of Ti alloy surface modifications in various applications. LST boasts adaptable geometry, strong adhesion, and minimal heat impact. Its repeatability and control allow tailored modifications while preserving internal properties. Precision is achieved through power, speed, and path adjustments. Hybrid LST techniques have enhanced efficiency, and an increasing number of LST applications are no longer confined to a single specific technology.

2) The LST technique for enhancing the surface properties of titanium alloys has wide applications in the aerospace and medical fields. Research on the application of LST technique in aerospace engine components primarily targets complex parts such as fan/compressor blades and turbine blades, and high-temperature oxidation-resistant coatings[25,40,56,103–104]. Each component possesses distinct structural characteristics and fatigue failure modes, necessitating research from various perspectives. In the medical treatment field, the regulation of titanium alloy composition combined with LST can be applied to multiple body parts, including human skeletal structures and teeth[68,109,113,120,126].

3) An inescapable challenge in the research of LST technique for surface modification of Ti and its alloys is related to equipment development and cost, the demand for highly skilled labor, safety concerns, and the selection of optimal processing parameters[85]. If these challenges are effectively addressed, LST surface modification of titanium alloys has great potential in the industrial development.

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钛合金激光表面处理的进展及应用

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摘 要：钛及其合金由于质轻、耐腐蚀性能好、强度高、弹性模量低、生物相容性佳和骨整合性优异，已成为应用最广泛的航空航天与生物医学金属材料之一。然而，较低的塑性、低硬度、和耐磨损性能限制了其发展和应用。激光表面处理（LST）技术在不改变材料体积的情况下增强表面性能，成为钛合金表面改性的一种有利手段。综述了利用LST技术对钛及其合金材料进行表面改性的研究进展和应用现状。分析了激光相变硬化、激光表面重熔、激光冲击喷丸、激光表面合金化、激光熔覆和复合LST的机理、工艺参数、表面特性和微观结构。总结了LST在航空航天、医学等领域的应用，介绍了现有的局限性，提出了未来的研究方向，并对LST在钛及其合金材料上的发展趋势进行了展望，以推进LST创新，为钛合金在多领域中的应用开辟新途径。
关键词：激光表面处理；钛合金；航空航天；医疗

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