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# Laser Surface Modification — A Focus on the Wear Degradation of Titanium Alloy

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#### Abstract

Over the years, engineering materials are being developed due to the need for better service performance. Wear, a common phenomenon in applications requiring surface interaction, leads to catastrophic failure of materials in the industry. Hence, preventing this form of degradation requires the selection of an appropriate surface modification technique. Laser surface modification techniques have been established by researchers to improve mechanical and tribological properties of materials. In this chapter, adequate knowledge about laser surface cladding and its processing parameters coupled with the oxidation, wear and corrosion performances of laser-modified titanium has been reviewed.

Keywords: Surface modification technique, Laser surface cladding, Wear, Titanium

#### 1. Introduction

Considering the swift increase in fuel consumption around the globe, it is essential to recognize the need for lightweight and high specific strength materials as a suitable approach to resolve the growing energy demand [1]. The energy efficiency of aero-engines and automobiles can be enhanced by reducing the engine weight [2]. In addressing the issue of energy efficiency, titanium and its alloys have been the prime materials for aerospace (with a weight share of about 36% being applied mainly in the fan and compressor sections for disks and blades; other areas include landing gear, window frames, galleys, and lavatories) and nonaerospace sectors such as automobiles (in the case of Rolls Royce and Jaguar cars where titanium is being used for suspension springs, connecting rods, valve strings, and underbody panels). In addition, Ti-6Al-4V alloy has the ability to substitute steel in friction and wear-critical diesel engine components like connecting rods, intake valves, pistons, suspension strings, and movable



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turbocharger vanes. The distinctive properties of titanium alloy (Ti-6Al-4V) such as low density (from an economical point of view, a lower mass implies lower fuel consumption), its excellent combination of high specific strength ratio that is maintained at an elevated temperature, low modulus of elasticity, and corrosion resistance justify its applications in aerospace, automotive, and marine industries [3, 4]. For example, higher operating temperatures of cars and turbine engines allow more efficient energy (fuel) conversion with lower toxic emissions [5]. In addition, titanium also has a high melting point, 1678 °C, indicating that it shows good creep resistance over different range of temperatures [6, 7]. However, with the distinctive advantages, voiding catastrophic breakdown in application of titanium in higher service temperature and friction in aerospace and automobile industries justifies the need for surface engineering techniques for improving performance of engineering components, longer component life, and failure prevention. In this chapter, adequate knowledge about laser surface cladding (LSC), a type of laser surface modification, and its processing parameters coupled with the oxidation, wear and corrosion performances of laser-modified titanium will be discussed.



Figure 1. Titanium usage in the GE-90 aero-engine.

# 2. Titanium and its alloy

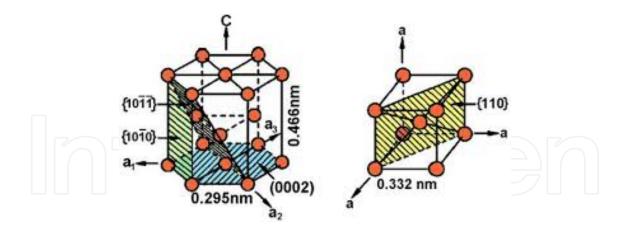
Titanium is richly available in the earth's crust at a level close to 0.6%, making it the fourth most abundant metal after the likes of aluminum, iron, and magnesium [8]. Rutile ( $TiO_2$ ) and ilmenite ( $FeTiO_3$ ) are important mineral sources of titanium alloy. Since their discovery in the early 1950s, titanium and its alloys have become choice materials for many (e.g., chemical, power generation, automobile, aerospace, and airframe) industries. Ti-6Al-4V is the most popular titanium-based alloy contributing to over 50% of global consumption [9], and it is 70% high in the United States. It has biocompatibility for biomedical implant applications, coupled with a good combination of mechanical and corrosive properties [10].

# 3. Properties and limitations

The unique properties of titanium and its alloys such as low density, excellent combination of high specific strength ratio, which is maintained at an elevated temperature, low modulus of elasticity, good compatibility, and good corrosion resistance, make them choice materials in a wide range of engineering applications such as aerospace, power generation, offshore, and chemical industries [5, 11]. While titanium possesses vast applications and excellent properties, its high relative cost, low hardness, poor oxidation resistance, its propensity to fail by galling, and poor tribological behavior in terms of high and unstable friction coefficient have retarded its engineering applications [2, 6, 12–15]. For example, numerous engineering components made of Ti-6Al-4V alloy are easily damaged at two surfaces in contact under load and in relative motion [4]. The atomic structure, crystal structure, and relatively low tensile and shear strength of titanium oxide film are fundamental causes for the high coefficient of friction and poor tribological properties of titanium [15].

# 4. Physical metallurgy of titanium and its alloys

Titanium is known to exist in two crystal states. Titanium and its alloys have a high melting point (1668 °C) and exist as a hexagonal closely packed (HCP) crystal structure alpha ( $\alpha$ ) phase below 882 °C, and above 882 °C they transform into a body-centered cubic (BCC) structure beta ( $\beta$ ) at higher temperatures.



**Figure 2.** Crystal structure of titanium as (a) HCP  $\alpha$  phase and (b) BCC  $\beta$  phase.

Titanium's properties are enhanced by its allotropic behavior characterized by alpha, alpha plus beta phase, and beta phases. They are microstructures and temperature dependent, which result from chemical composition and thermo-mechanical processing. The transformation temperature is strongly influenced by interstitial and substitutional elements and therefore depends on the purity of the metal [8]. The  $\alpha$ -phase alloys of titanium are known to be characterized by hard, tough properties such as good corrosion resistance, good weld ability,

creep resistance, and receptive to heat treatment coupled with ease of processing and fabrication. This justifies their application in fields such as aerospace for friction-related application. The  $\alpha$ -phase alloy is stabilized using elements such as Al, O, N, and C, while the  $\beta$ -phase alloy is characterized by soft and malleable properties with low Young's modulus and superior corrosion resistance.

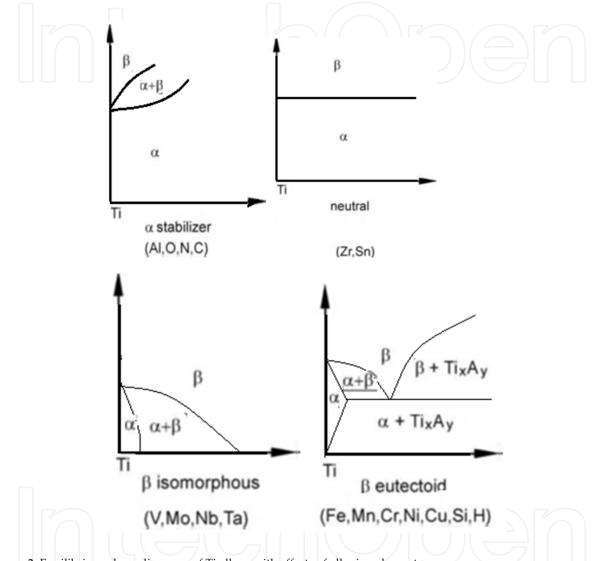


Figure 3. Equilibrium phase diagrams of Ti alloys with effects of alloying elements.

β-Phase alloys are stabilized in two stages, namely the isomorphus stage, using the elements Mo, V, Nb, and Ta; and the eutectoid stage, using the elements Fe, W, Cr, Si, Co, Mn, and H. In contrast, alpha + beta-phase alloys offer a combination of excellent ductility and strength when properly heat-treated, which makes them stronger than the alpha phase and even the beta-phase counterparts [10] due to the presence of both the *α* and β phases. *α* + β alloy is by far the most commonly used titanium alloy. The common type of Ti alloy containing *α* and β stabilizer is the Ti-6Al-4V alloy. In order to achieve the best combinations for a given application, an optimum control of the microstructure is essential. The properties of Ti-6Al-4V depend on various factors like composition, relative proportions of phases, heat treatment,

and thermo-mechanical process conditions [11]. A comparison of Ti-6Al-4V alloy with the commercial pure Ti (Cp Ti) microstructure shows that the Cp Ti microstructure contains grain boundaries, fine acicular  $\alpha$ , and Widmanstätten  $\alpha$  structures, while Ti-6Al-4V alloy shows the presence of grains and acicular structures. The alloy is characterized by high strength and resistance to wear and corrosion. These advantageous properties make Ti-6Al-4V to be employed in various industries. In the aerospace industry, the alloy provides high strength at elevated temperatures. Titanium alloys are regarded weak at high temperatures, because they do not function well in these conditions.

# 5. Surface engineering

Titanium's limited use in engineering applications is due to its poor tribological properties, which are susceptible to failure by galling and high and unstable friction coefficients when rubbing against bearing materials [2]. Wear, a common phenomenon in applications requiring surface interaction, leads to catastrophic failure of materials in the industry. Hence, preventing this form of degradation requires the selection of an appropriate surface modification technique. A technique of achieving the specified requirement is by the development of high-temperature resistance, improved hardness, and high wear-resistant coatings suitable to protect the base material against corrosion, wear, and erosion – corrosion at high temperatures. Surface modification techniques can be applied to address these limitations [16, 17], such as improvement in the functionality of a solid surface by altering its chemical composition or microstructure leading to increase in the surface hardness, decrease in coefficient of friction, and enhanced wear resistance of titanium alloys without altering the desirable bulk properties of the substrate [2, 14].

#### 5.1. Benefits of laser surface modification over conventional techniques

Various modification techniques are used to deposit the alloy layer onto the substrate such as pre-placing the alloy layer by electroplating, ion implantation, physical vapor deposition (PVD), chemical vapor deposition (CVD), carburizing, nitriding, thermal oxidation heat treatment, laser surface alloying (LSA), and laser surface cladding (LSC) [18]. The chemical heat treatment processes such as nitriding, carburizing, and boriding have some demerits such as long processing time and easy deformation of the substrate being treated [19]. In addition, thermal spray coatings possess low coating density and limited bond strength between the coating and the substrate. It is pertinent to note that these techniques give rise to many difficulties, such as poor adherence, lower bonding strength, and some defect at the interface [20]. However, laser surface modification techniques have been established by researchers to improve mechanical and tribological properties of materials. The main advantages of using laser as surface treatment are that the thermally affected regions are easily controlled in terms of depth, extent, and time above temperature [21]. Further, automation is possible due to lack of environmental disturbance while the radiant energy is delivered to the process.

# 6. Laser surface engineering

Laser was invented in 1960 as a new form of energy in industrial applications. Laser is one of the most flexible forms of energy that can be used to generate any required thermal experience on a substrate. Laser, an acronym for light amplification by stimulated emission of radiation, is known as a coherent, convergent, and monochromatic beam of electromagnetic radiation with wavelength ranging from ultraviolet to infrared [22]. Laser is an ideal tool for surface modification of metals in improving their corrosion and tribological properties [21, 23]. Laser generates radiant energy that is absorbed by top atomic layers of an opaque material, where it can either heat the surface or excite the surface atoms, leading to pyrolytic (thermo-chemical property of material at high temperatures) or photolytic processes (direct interaction of the photons by light or other radiant energy). If the photon energy is sufficiently high, the absorption of laser energy can result in phase transformations of the substrate [24]. The absorption process depends on the nature of the substrate and laser parameters used. A thin layer of the material could be heated, melted, or vaporized, and thereafter it solidifies to generate refinement or homogenization of the microstructure [25]. This takes place under various heat transfer processes such as conduction into the materials, convection, and radiation from the surface. This explains the advantage laser has over the available types of light sources, that is, the highly directional and high-intensity beam with an ability to focus on a small spot. The important properties that justify the use of laser in a wide variety of applications in manufacturing industries, electronics, medical, surveying, communication, and other industrial areas are: spatial and temporal coherence, low divergence, high continuous or pulsed power density, and monochromaticity [21].

# 7. Types of lasers

Lasers can be classified according to either the active medium, wavelength, or excitation mechanism into the following types: the  $CO_2$  laser (with a wavelength of 10.6  $\mu$ m), the neodymium yttrium aluminum garnet (Nd:YAG) laser (with a wavelength of 1.06  $\mu$ m), the high-power diode laser (HPDL; 800–950 nm), and the excimer laser (248 nm for KrF).

#### 7.1. The CO<sub>2</sub> laser

The  $CO_2$  laser has a wavelength of 10.6 µm and output power can range from 1 W to more than 10 KW. They are widely used in engineering and material processing due to their ability to produce very high power with relative efficiency that can be obtained and high-speed accuracy for cutting, welding, and marking both ferrous and nonferrous materials.

#### 7.2. Nd:YAG lasers (Solid-state type)

Nd:YAG laser consists of crystalline YAG with the chemical formula Y3Al5O12 and a wavelength of 1.06  $\mu$ m. Shorter wavelength, temperatures, and nature of the surface usually lead to a higher absorptivity for metallic materials [25]. The advantage Nd:YAG laser has over CO<sub>2</sub> laser is that it couples better. This type of laser has found major application in the automotive industry for high-speed welding of body parts [26]. The main advantage of Nd:YAG laser over  $CO_2$  laser relies on its shorter wavelength and its ability to deliver laser radiation through optical fibers. As a result of these advantages, the pulse Nd:YAG laser probably has a wider variety of applications (in various forms of material processing: alloying, cladding, drilling, spot welding, and laser marking) than any other type of laser.

#### 7.3. Excimer lasers

These types of lasers are available only as pulsed lasers, which produce intense output in the ultraviolet and deep ultraviolet regions. They are used extensively in micromachining and medical applications. The main advantage of an excimer laser over other types is its very short wavelength. Excimer lasers have good beam quality and focused ability to spot the diameter that is approximately smaller than  $CO_2$  laser beam with the same beam quality.

### 8. Laser surface modification

There are several laser surface modifications techniques, such as surface alloying, cladding, melting, hardening, direct deposition, physical deposition, and laser melt injection of laser surface. Laser surface modification techniques have been used extensively to improve the wear and corrosion resistance of mechanical components [27].

#### 8.1. Laser surface hardening

Laser surface hardening (LSH) is a heat treatment technique used on a material surface domain to increase hardness of a material by the use of laser beam energy. The purpose of LSH is to increase the hardness of the boundary layer of the substrate by rapid heating and then by quenching. The heated zone is quenched by self-cooling, and this leads to the desired hardening effect due to a change in the microstructure [28]. In ferrous material, the primary basic mechanism of surface hardening is by phase transformation to form the relatively hard martensitic phase in the surface layer. The advantages of LSH over conventional methods of hardening include its flexibility, ability to automate the hardening process, and contactless local heat treatment with no need for additional cooling media such as oil or water [29].

#### 8.2. Laser surface melting

Laser surface melting is a process where a thin layer of the substrate is melted by a high-power laser beam, which is then rapidly solidified without any attempt to modify the surface layer chemical composition [6]. The main advantage of this process over other laser modification processes is its ability to alter the microstructure without changing the composition [11].

#### 8.3. Laser surface alloying

Laser surface alloying is one of the modification methods for improving surface-dependent properties such as wear and corrosion resistance 46. Laser surface alloying is a process of incorporating additional alloying elements into the surface of a material by a high-power laser

beam to melt metal coatings and a small portion of underlying substrate). It involves high rate of melting, intermixing, and rapid solidification of the pre-placed or co-deposited alloying elements with part of the underlying substrate to form an alloyed layer. An LSA technique combines modification of both the microstructure and the chemical composition.

#### 8.4. Laser surface cladding

Laser surface cladding is a rapid solidification technique that could overcome the aforementioned difficulties with many advanced features, such as thick coatings, low dilution ratio, high cooling rate, crack-free layer, reduction or elimination of porosity, limited heat affected zone with low thermal distortion, high refined microstructure, and strong metallurgical bond between coating and substrate [30]. In order to overcome the restriction of titanium alloys in machinery performance and safety at low cost with high value elements, laser cladding is employed to fabricate coatings with advanced tribological properties and high-temperature oxidation resistance [31]. Laser cladding process is a surface modification process in which a defocused laser beam is used to fuse an alloy or powder on a substrate [32]. In LSC, alloy may be introduced onto the surface of a substrate as powder or wire either during (direct injection) or prior to processing (pre-placed). The beam energy melts and solidifies rapidly both the preplaced or injected powders and a thin layer of the opaque substrate [18]. Here, the powder and thin layer of the substrate rapidly reach their melting point causing homogenization to be achieved before solidification due to the photon energy absorption [33]. With this, vaporization is avoided due to rapid heating and solidification of the molten clad, which helps to inhibit long-range diffusion, avoid crystallization, achieve strong metallurgical bond with the substrate, and increase hardness [6, 34]. Laser beam-specific thermal characteristics induced by laser irradiation help generate specific microstructures, including metastable phases and nano-crystalline grains, which is an advantage over conventional techniques [35]. The most important factor to consider during cladding process is the melting of the alloying material to the substrate. This can be achieved by appropriate selection and control of laser processing parameter such as laser power (P), laser beam size (beam diameter D), laser scanning velocity (V), and thermal properties of the substrate, which also helps to achieve desirable properties such as degree of heating and phase transformation [18].

#### 8.4.1. Single-track clad

During laser cladding process, laser energy emitted by the laser beam melts the injected powder causing fusion between the clad material and the substrate. Two vital factors, clad height and dilution in single track, are subject to laser power variation, laser scan rate, mass flow rate, and type of powder being deposited. Laser single-track cladding is conducted with incident laser beam on the working substrate for a single pass. Here, the width of the track is smaller or equal to the laser spot size with the clad height depending variably on laser working parameters [23].

#### 8.4.2. Multi-track clad

In comparison to single-track cladding, multi-track laser cladding involves consecutive overlap of one track by the subsequent track. Morphologically, multi-tracks tend to exhibit

dendrites compared to a single track, which is subsequently attributed to longer exposure periods at elevated temperatures [36]. To give yield to a clad with required thickness and larger surface area, single-track clad has to be repeated at several increments. This increment significantly affects the clad height and dilution ratio.

#### 8.4.3. Forms of powder deposition: Cladding

Laser cladding process can be primarily differentiated by its means of introduction of clad material on the surface of the desired substrate. Powder and wire are two common forms in which clad material is introduced on the surface of the substrate. Powder deposition can be either coaxial or pre-placed where a mass of clad material is deposited on the substrate prior to introduction of a laser beam. Powder deposition approach uses a nozzle held separate from the laser beam that lays down powder mass ahead of the laser beam.

#### 8.4.3.1. Pre-placed powder method

During high laser deposition rate (typically 15 pounds/h), pre-placed powder introduction method is preferable since it is possible to maximize the amount of powder being melted. This ensures that the powder width equals the width of the area scanned by the laser, as powder melting is also advantageously maximized, creating an optimized stable clad. The powder must be mixed with a chemical binder so that it can adhere to the substrate during laser scanning. The chemical binder must evaporate as a result of the high energy emitted by the laser beam. However, this can result in porosity of the clad [37]. When cladding with preplaced powder, the melt pool is formed on top of the cladding material and proceeds downward to the substrate. Only when the substrate has been melted can a clad layer be formed. Therefore, it is difficult to control the depth of the melt pool, which results in a relatively high dilution.

#### 8.4.3.2. Wire feeding

The clad material can be introduced by wire feeding on the substrate where it simultaneously melts with the substrate under the laser beam. This process can be hard to control, especially in objects of complex shapes and eventually results in high dilution rates.

#### 8.4.3.3. Powder injection method

Powder delivery method requires a dedicated powder delivery system and a powder nozzle, which must direct the powder to the desired position. Powder injection method is a more flexible and easier method to control; however, changing the powder proved to be environmentally hazardous. The powder injection method resulted in good clad areas in recent research findings.

#### 8.4.3.4. Coaxial cladding

The clad material is supplied in the powder form mainly coupled with shielding gas to prevent reaction with the surrounding gases. This method is widely used due to the ease of automation

control and the minimal surface preparation it requires. It is divided into coaxial and side injection methods, differentiated by the method of powder injection into the process.

#### 8.4.3.5. Side laser cladding

In the side cladding method, the powder is introduced from a nozzle together with the shielding gas at an angle to the laser beam such that the powder gets in contact with the laser energy before reaching the substrate. The powder is heated to ignition state before reaching the substrate that is already being heated together forming an alloy of the set depth.

### 9. Influence of laser processing parameters

There are a number of varying parameters controlling the laser processes. Individual parameter has its own distinctive functions, which can affect the processing results and operation outcomes. Laser power, laser beam size (beam diameter), powder flow rate, and laser scanning speed are some of the important factors in achieving a thin clad layer with low dilution but sufficient bonding strength [27]. However, these factors are responsible for the temperature distribution, high-quality microstructure, the shape of the melt pool, and the final geometry of the laser clad layer. Vaziri et al. studied the effect of laser parameters on properties of surface alloyed Al substrate with Ni [38]. The influence of spot size and peak – power density of pulsed Nd:YAG laser on the depth of alloyed layer, the hardness and microstructure in LSA of Al with Ni. Results revealed that the hardness obtained was found to be 10-15 times the value of base Al. Reduction in the power density resulted in a decrease in the alloyed layer thickness, while increasing the peak power density increased the alloyed pool depth. The effect of laser beam diameter on the depth of the alloyed pool was examined; it showed that by increasing the laser beam diameters, the depth of the alloyed pool decreased. Hamedi et al. investigated the effect of pulsed laser parameters on in-situ Tic synthesis in laser surface treatment [39]. Here, effects of irradiated energy per unit length and pulse duration on mircostructure and hardness were investigated. Results showed improved hardness and fine dendritic morphology to cellular grain structure. The Marangoni convection flows in the melt pool allowed uniform distribution of carbon in liquid Ti because of decreasing peak power and increasing heat input. In order to achieve high volume fraction in laser-alloyed zone, the energy input to the melt pool is increased. Hardness value produced reached 1700 Hv, which is 10 times harder than the substrate.

#### 9.1. Laser power

Laser power is a very important factor in laser cladding as it is responsible for energy density transferred on the powder-substrate system. Optimum parameters during laser cladding are needed to yield microstructure and clad that are free from defects. Wu et al. carried out the effect of process parameters on the microstructure of laser-deposited Ti-6Al-4V [40]. It was observed that long columnar grains dominated the microstructure of the laser-deposited Ti-6Al-4V alloy for a large range of laser powers and is formed for all. The scale of columnar

grains also increases with decrease of the laser scan speed and when other parameters are maintained constant. The microstructure of the laser- deposited Ti-6Al-4V is influenced by laser power, scan speed, or powder feed rate.

#### 9.2. Laser scanning speed

Laser scanning speed generally refers to the speed at which laser beam travels along the working piece. Higher laser speeds lead to subsequent reduction in the amount of clad material particulates onto working piece leading to a thin clad layer. Hemmati et al. investigated into the effect of scanning speed on phase constituents and properties of laser-deposited coatings [41]; the investigation showed a significant refinement of dendritic structure that stabilized the phases and reduced the volume fraction of other phases at higher speeds. Laser cladding technology was used to deposit Co–Ti alloy on mild steel using different scanning velocities [42]. This resulted in a different rate of cooling of the clad variations in the microstructural characteristics and hardness of the clad layer. Good-quality clad layer was evident with no visible porosity or cracks. A fine microstructure was achievable with higher laser velocities while lower velocities yielded higher hardness due to a large fraction formation of hard intermetallic phase of TiCo<sub>3</sub>. The higher hardness of the clad layer compared to the substance is due to the formation of intermetallic compound TiCO<sub>3</sub>.

#### 9.3. Powder flow rate

Flow rate determines the thickness of the alloyed layer and dilution rate required. This tends to affect microstructural changes, homogeneity, cracking, porosity, and surface finish. Rajaram et al. studied the effect of feed speed and power on laser cut quality of 4130 steel [43]. Power and feed rate had a major effect on kerf width and size of HAZ. In addition, the surface roughness and striation frequency were affected most by feed rate. It was observed that at low power levels, the smallest kerf width and HAZ are obtained and the effect of feed rate is moderate. Low feed rates gave good surface roughness and low striation frequency.

# 10. Conclusion

Laser generates intense beam energy, which offers outstanding advantages over other conventional surface modification techniques. Laser techniques have become the choice for many industrial applications involving corrosion, wear, oxidation, and general repairs. Laser surface modification techniques overcome limitations such as poor adherence, lower bonding strength, serious crack propagation at the interface, and limitation of the thickness of coatings, which are associated with other forms of surface modification processes [44]. These techniques have known to modify surface composition and microstructure without altering the bulk substrate [25]. Laser cladding technique, a type of laser technique, has advantages over the traditional coating techniques, which include high precision, automation control with choices of clad thickness from about 0.1 millimeters to several centimeters, metallurgical bonding of the cladding material with the base material, lower deposition rate, minimal heat effect on the

substrate due to controlled laser energy and rapid cooling, a wide selection of homologous and non-homologous powder materials, and the ability to process virtually any type of metal alloy. Also, the energy input of laser cladding is low, resulting in finer microstructures with superior properties and minimal distortion [32].

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