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Recent Development of Laser Based Treatment on Titanium Alloys: From Coating to Treatment – A Review

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Abstract: **-- The tribological properties, in specific, oxidation and hot corrosion behavior were found to be a dominant property to improve the surface characteristics of titanium alloys and many researchers tried different methods to improve it. In order to achieve a better coating, there are numerous surface treatment techniques have been performed. The techniques, such as nitriding, carburizing, oxidation, physical vapor deposition (PVD) and chemical vapor deposition (CVD) executed to improve the surface properties of titanium alloys. In addition to this, laser was also used in surface modification. The coatings made by laser techniques exhibited strong metallurgical bonding with the substrate materials, owing to their high energy density. It was also found that the technique satisfied the industrial requirements for all applications.**

***Index Terms*— Microhardness, Laser Surface Melting, Laser Metal Deposition, Microstructure, Ti6Al4V.**

I. INTRODUCTION

Titanium is the most significant metal of major industrial applications. The exceptional properties of titanium alloys incorporate high strength and astonishing erosion resistance. Titanium alloys are found in aviation applications where the mix of quality and corrosion resistance is unavoidable. The one of the major utilization for titanium alloys is in the aviation gas turbine motor compressor blades. The compressor disks and blades of the first stages are used at low temperatures about 300°C (low pressure compressor) are made from Ti-6Al-4V, a titanium alloy [1]. Ti-6Al-4V is extensively used alloys in aero engine turbine blades. These aero engine blades, after thousands of operating hours are mostly encountered fatigue and creep which are reducing the actual service life of the component. The blades subjected to wear and fretting are most of the times getting replaced rather than refurbished [2]. There are extensive research work to improve the material properties through various coatings, in order to the service life of Inconel 718 and Ti-6Al-4V [3].

II. COATING ON TITANIUM ALLOYS

The tribological properties of pure titanium (cp-Ti) was improved by deposition of Ti-Si-N coating through laser (LENS) processing [4]. The evaluated microstructures were evidenced in the coating along with in-situ shaped stages. The dendritic microstructure of the coatings was greatly influenced by the Si, as accumulation of Si impacted the solidification behavior of the melt pool. Increase in Si accelerates the solidification rate and in this way it prompted to better and more discernable dendrites. This influenced the mechanical properties of the deposited region. The experiment further demonstrated that the changes in microstructural varieties and phase impacted on hardness and wear resistance specifically. The top surface of the coating exhibited with higher hardness qualities and the same was reported in all specimens. Besides, the sample without Si had relatively high wear rate and it was reported that Si enhanced the tribological execution of the coatings.

Similar performance improvement was achieved with nanocomposite deposition WC1-x/C on titanium alloys is depicted in figure 1 [5].

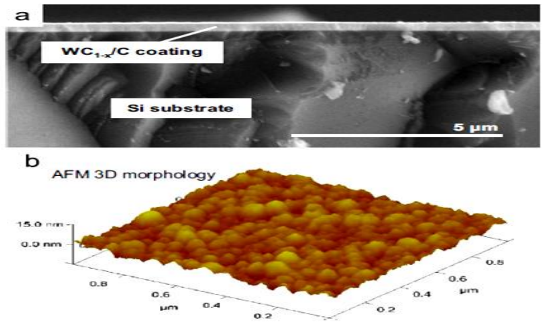
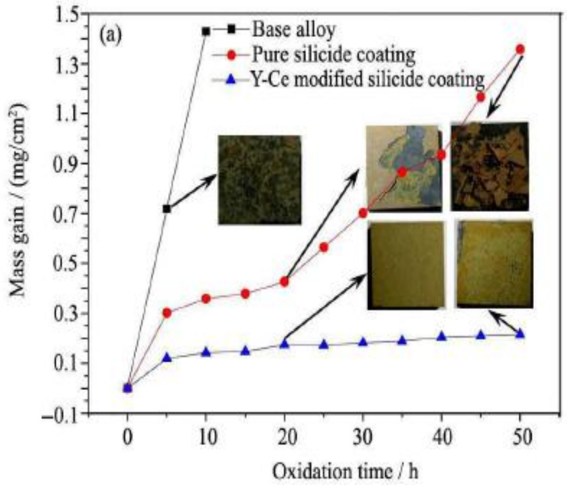


Fig. 1. Nanocomposite deposition WC1-x/C (a) SEM image of coating (b) AFM morphology [5].

The reactive arc evaporation method was implemented to deposit 2 µm thick titanium, carbon and nitrogen (TiCxNy) layer on the base material which was diffusion hardened and outside a very thin nanocomposite coating was performed using responsive magnetron sputtering. This approach enhanced the surface hardness of the diffusion treated Ti6Al4V substrate material and greater bonding between the base material, the middle TiCxNy layer and the outer nanocomposite coating was accomplished. The created multilayer covering framework achieved nearly 95% more wear resistance than the uncoated titanium base material. The multilayer framework coated on titanium alloys revealed a favorable technique to essentially enhance the wear resistance.

The oxidation behavior of titanium alloy was excellently controlled with silicide coating using pack-cementation method [6]. To understand the effect of isothermal oxidation behavior on titanium alloy; the substrate material was separately coated with pure silicide and the Y-Ce jointly modified silicate. The coating was prepared with TiSix coating in inner, middle and outer regions. The experimental outcomes demonstrated that Y-Ce jointly modified silicide covering had much preferable oxidation resistance over the plain silicide coating. It was inferred that Y and Ce are having excellent impact on oxidation resistance of the deposition. A thick layer of TiO2 and SiO2 formed externally and internally, respectively on Y-Ce jointly modified silicide at the end of oxidation. The TiO2 and SiO2 layers further offered great protection against oxidation effect (Fig. 2) in titanium alloys.



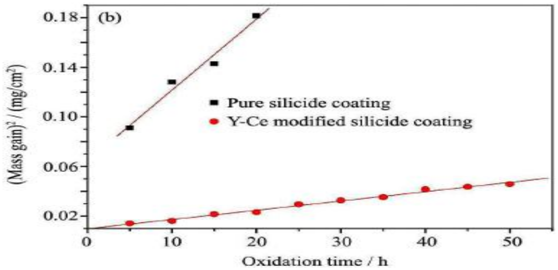


Fig. 2. Oxidation kinetics at 1000 °C (a) Mass gain Vs Oxidation time (b) (Mass gain)2 Vs Oxidation time [6].

Aluminuim and Silica based nanocomposite coatings were performed on carbide tools to evaluate the performance against titanium alloys. [7]. Experiment was carried out with deposition of two different coatings on carbide tools to enhance the tribological properties of the tool material. In this examination, two different combination of Aluminuim and Silica based nanocomposite coatings were used with two different conditions of dry and minimum quality lubrication. The noteworthy impact was reported by using minimum quality lubrication (MQL) condition especially in enhancing the service life when contrasted with dry condition. Besides that the tools coated with nanocomposite exhibited significant improved quality of performance in the machining of titanium alloys. The coated tools also accentuates the coordination between cutting fluids and materials. Comes about demonstrated that MQL condition, significant protective layer was formed on nanocomposite deposited tool. Also MQL condition exhibited that the nanocomposite deposited tools encountered with adhesive and oxidation wears. As an alternative, nanocomposite with Ti addition coating restricted the oxidation and diffusion wears. The MQL condition imprecate that the major type of wear the tools suffered was adhesive wear. Interestingly, oxidation and adhesive wear were the principle wear encountered in dry condition when turning tests were performed.

III. LASER TREATMENT ON TITANIUM ALLOYS

The laser surface treatment was performed on titanium alloys to enhance the surface properties and to strengthen wear resistance resulting from dry-sliding contact [8]. The laser treated region indicated that the concentration of carbon content was greatly influenced by laser energy density. The aggregated grouped carbon content helped in greater extend to improve tribological properties of the laser melt zone. Along with carbon inclusion, the surface region was evidenced with aggregation of graphite which further offered the effect of solid lubrication. The laser treatment process indicated that the friction was reduced tremendously compared to base material and the material is also encountered with nil or less adhesive wear. The laser treatment process considerably reduced the anticipated wear by adopting the self-lubrication effect in the composite coating.

The performance of laser surface treated titanium alloy was compared against with cobalt chromium alloy [9]. The Nd:YAG laser was used to perform surface treatment on cast titanium specimen materials. The laser treatment offered increase in tensile strength on treated specimens compared with untreated specimens. The exhibited higher tensile strength in treated sample was near equivalent to the tensile strength of cobalt chromium alloy. The hardness was low in the treated specimen; however, it maintained uniform hardness until the depth upto 400 microns. The untreated specimen had more hardness than treated specimen but it shown decremented rate towards depth of 200 microns. The treated specimen also showed most astounding modulus of elasticity compared with untreated specimen. The cast titanium material properties were fundamentally enhanced by the laser treatment through enhancement of surface integrity.

The laser surface treatment has shown greater influence in the mechanical properties of titanium alloys, similar effect was analyzed on titanium based alloys using laser nitriding technique under argon nitrogen gas mixture atmosphere [10]. It was found that the martensite phase matrix was formed during laser nitriding of titanium, while δ-matrix phases were reported during nitrating of the gamma aluminum based titanium alloy. The laser nitrating process increased the melt volume ratio of the specimen; this was ascribed to the increment in the absorption rate of laser power. The rate of laser power absorption was solely actuated by nitride development and not related with the heat development. The pulsed Nd:YAG laser was also used to perform nitriding process on pure Ti [11]. In this approach, two phases TiN - $TiN_{0.3}$ and/ or Ti - TiN were formed during the laser nitriding process. The dendritic microstructures were formed in the laser-melted zone. The laser surface nitriding process produced improved tribological property with increased microhardness up to 1700 HV in the nitride zones.

The laser nitriding effect on microstructural behavior of titanium based alloys was analyzed with changes in laser beam positions. The experiments were performed with two different laser beams arrangement, one at idle beam and another one was arranged as spinning beam [12]. The experiment revealed that the dendrites structures along with α' phases were produced during the rotary laser beam setup. All together, the heat affected region evidenced with the presence of α' phases mixed with additional needle like structures. The similar α' phases with larger dendrites structures were developed during the stationary laser beam setup. Though the larger dendrites were developed the size was steadily diminished with respect to the depth. The nitrogen diffusion was reported uniform upto 50 microns depth in the rotary laser beam setup. After 100 microns depth the level of nitrogen diffusion was equal to that of base material. The level of nitrogen diffusion in stationary beam was comparatively lesser than the rotary beam setup. Similarly the level of diffusion was equal to base material after depth of 100 microns. This nitrogen diffusion plays a vital role in laser processing, as the vanadium and aluminum solely depends on nitrogen concentration in molten region.

The metallurgical and tribological properties of laser surface melted commercial pure Ti parts were analyzed to understand the effect of laser treatment on titanium alloys [13]. A combination of low laser scan speed and high energy density resulted in microscopic balling phenomenon and interlayer thermal cracks, because of various factors like higher thermal stresses and low liquid viscosity. With increase in laser scan speed, a relatively coarsened α phase refined to α' martensitic phase later again reduced to zigzag α' martensitic phase. The transformation occurred because of higher thermal rate, kinetic undercooling and solidification process. Both these inadequate densification caused by thermal microcracks and interlayer micropores and the formation of relatively coarsened α grains caused reduction in hardness and wear rate. Figure 3 indicates the effect of laser scan speed in nanohardness and wear rate of the laser surface melted titanium.

The coating of boron nitride on titanium alloy using CO2 laser was performed to improve the tribological properties of titanium alloy [14]. The coated boron nitride induced the formation of TiN intermetallic during the process. The intermetallic matrix formed with Ti and TiN were harder, due to laser melting. It was found that the laser treatment surface induced phases of TiB, Ti_3B_4 and Ti_2N phases. The needle shape and dendrite phases were evidenced in the laser melt region; it induced formation of boride and nitride phase in titanium. The boride and nitride phases' of titanium possess higher hardness level which helped to attain enhanced tribological and mechanical properties of titanium alloy together with higher temperature steadiness.

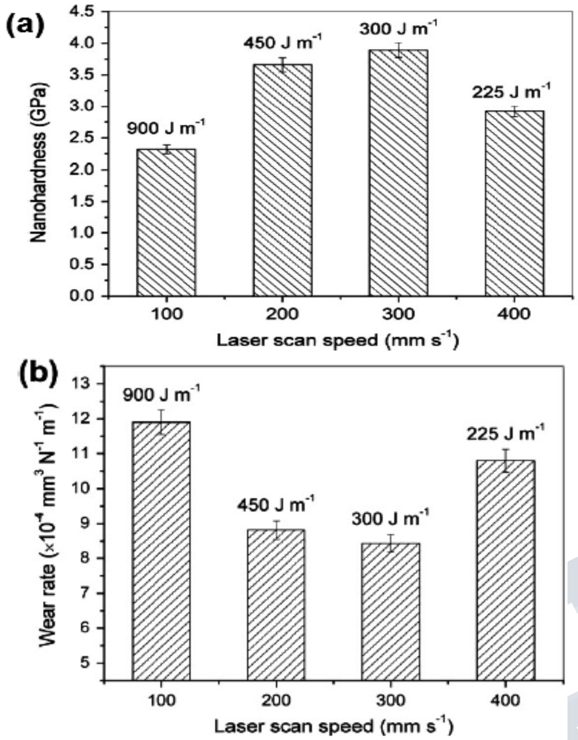


Fig. 3. Effect of laser scan speed in surface melting of Ti (a) Nanohardness against various laser scan speed (b) wear rate at various laser scan speeds [13].

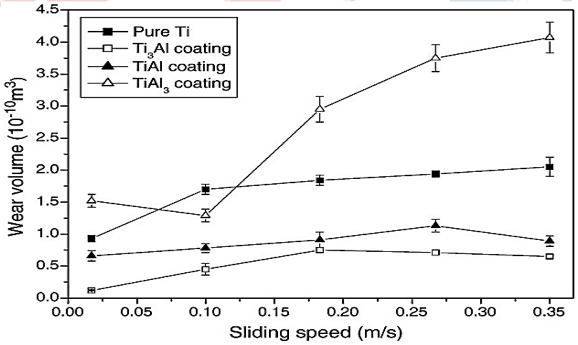


Fig. 4. Variation of wear volume of pure Ti and its coatings [15].

Similar to boron nitride coating, aluminum coating was performed on titanium substrate using laser surface melting technique. Alike the formation of boron and nitride of titanium phases in BN coating process here titanium aluminide coatings was prepared [15]. The major intention was to perform coting to enhance the tribological properties of titanium specimen. There are three different coatings Ti3Al, TiAl and TiAl3 were formed. Unlike in BN coating here Ti3Al and TiAl exhibited higher hardness than pure titanium but TiAl3 exhibited non-uniform hardness and some region recorded with lower hardness than base material. The uncertainty in hardness of TiAl3 coating caused poor tribological properties compared with other Ti3Al and TiAl coatings. The tribological properties of Ti3Al and TiAl coatings were better than base material (Fig. 4).

Alike BN and aluminum coating in previous cases, Niobium coating was also performed on pure Ti sheets through laser surface alloying technique [16]. The procedure was performed to enhance the service life of titanium component by considerably bringing down the internal fatigue and the induced stresses at surface level. The less rigid β and α" phases were obtained while niobium was brought into coating with titanium. The developed new phases helped to achieve 100% more hardness than base material.

The coating powders exhibited their respective influence on titanium alloys; comparably the selection of laser process parameter has its own influence on base material. It was reported that the laser scanning velocity influenced the mechanical properties of titanium alloy during laser surface melting process [17]. The experiment resulted that the wear resistance of the titanium alloy was directly proportional with laser scanning velocity upto 0.065 m/s later it shown inverse effect. In the same way, the surface roughness shown positive trend at initial stage and later it shown negative trend with laser scanning velocity. Both the wear resistance and surface roughness maintained the bell curve against scanning velocity. The low wear resistance was obtained at low scanning velocity, as the time availability to melt carbide particle was more. However, at higher scanning velocity, the time availability to melt all carbide particles would be less. It induced the presence of unmelted carbide particle in the laser treated zone, which resulted to poor wear resistance property.

IV.LASER METAL DEPOSITION ON TITANIUM ALLOYS

Detailed studies were carried in the previous sections to understand the different coating performance and effect of laser treatment. The effect of laser medium was investigated for additive manufacturing of titanium alloy [18]. Two different laser medium solid laser (Nd:YAG laser) and gas laser (CO2 laser) were used to perform the laser glazing operation. The major study was focused to compare the macrostructure formation with respect to solidification process. The physical phenomenon of solidification process was further analyzed with FEM based theoretical modeling technique. The metallurgical studies were reported that the solid laser induced the development of columnar grain structure, while those of gas laser triggered the development of mixed grain structures in the laser glazed region. It was also interpreted the bands as colonies of secondary alpha with varying grain size and correlated to specific thermal cycles.

The titanium blocks manufactured by solid state laser was investigated to understand the mechanical and physical properties of the manufactured titanium blocks as depicted in figure 5 [19]. The 3.5 kW solid state laser Nd:YAG with titanium alloy wire was used to prepare titanium alloy blocks at three different conditions. The first, as deposited condition of titanium alloy found that the deposited material properties were superior than the base material and satisfied the industrial requirement standards. The second heat treated at 600°C for 4 hours shown improved strength in the deposition region, however, it lacked with ductile property. The final heat treated at 1200°C for 2 hours also decreased the alloy’s strength because of collapse in grain dislocations. The experiment results indicated that the titanium blocks manufactured through laser based additive manufacturing technique was not required any further heat treatment process, as the heat treated sample resulted with inferior material property which are not recommended for industrial applications.

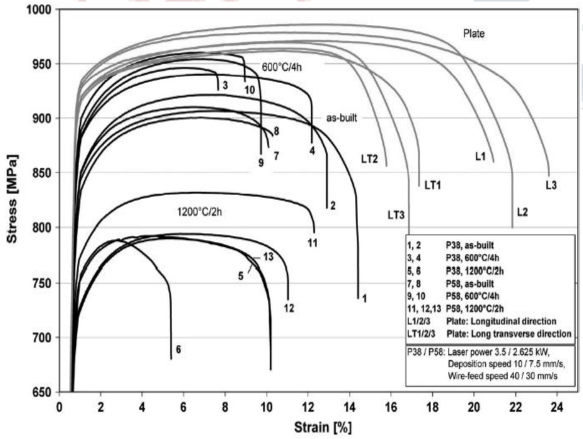


Fig. 5. Tensile properties of solid state manufactured Ti blocks at three different conditions [19].

The successful progression of laser based fabrication inspired to continue the work with titanium alloys. The metallurgical properties accomplished through laser based deposition was comparable and the same as achieved in other additive manufacturing techniques [20]. The laser treated titanium alloy microstructure; phase and surfaces were similar to that of shape obtained from shaped metal deposition technique also the top region exhibited finer, lamellar α / β microstructure. The hardness gradients present in the top region of laser fabricated specimen were not evidenced in the shaped metal deposition, which resulted with inferior hardness quality. It was correlated with higher tensile property experienced in the laser treated specimen. Similar to previous scenarios, the heat treatment processes did not helped any improvement in physical properties of the fabricated specimen. However, the strain failure rate was considerably increased while the sample was heat treated to 843°C.

The laser free form fabrication process is another promising laser technique for fabrication of superior quality titanium alloys. The titanium alloyed prepared with this technique proved superior tensile strength [21]. The development of micro cracks and distortions at surface region led to inferior mechanical property during manufacturing. However, uniform tensile strength was reported on entire location of the laser free form fabricated specimen. Though the properties were inferior to the wrought material, still isotropic tensile strength is indeed for industrial applications.

Sui et al. [22] investigated the mechanical properties of laser based deposition of titanium alloy wire on titanium alloy substrates. Single bead walls were deposited. The experimental results indicated that the metal deposition direction influenced the grain growth in clad region. The reported grains were columnar in structure while the interface region found with α grains and Widmanstätten structure. The laser scan speed played vital role in the physical property of specimen. The specimen found with more hardness at higher speed compare to lower speed for a same laser power. As the deposition was anisotropic nature the reported tensile properties were superior along the orientation built layer. The laser treatment induced internal residual stresses in the specimen. Though the stress was developed, it didn’t affect the tensile behavior of the specimen; the same was confirmed by testing the specimens before and after stress relieved. Similar phenomena was experimented on titanium alloys by some other researchers [23]. The process was carried out with varying traversing speed between 300 mm/min and 1500 mm/min. It was found that the decrease in the laser traversing speed induced refinements of the Widmanstätten in the HAZ and increase in clad zone martensite thickness (Fig. 6).

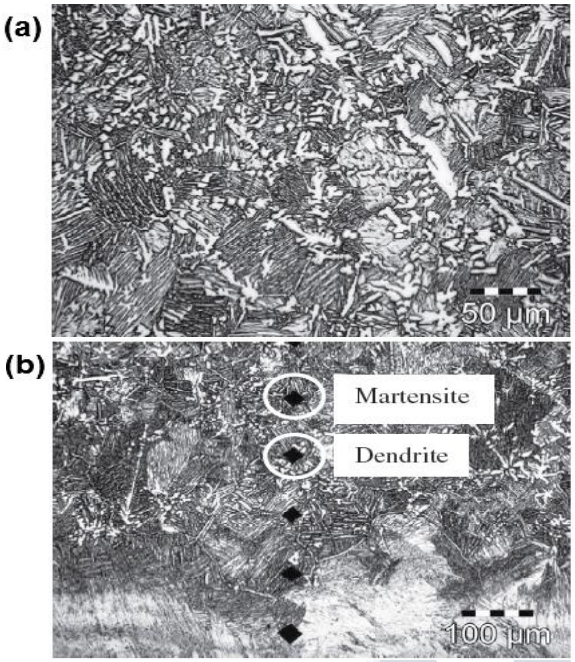


Fig. 6. Optical micrographs of clad region (a) OM image (b) Hardness impressions [23].

Jun et al. [24] investigated the laser metal deposited (LMD) Ti-6Al-4V parts. The microstructure of the fabricated parts contained prior columnar β grains consisting of acicular α' martensite due to the rapid cooling of the melt pool. The microstructure was less consistent and heat-affected zone was low. The hardness and other tensile properties of the LMD parts were superior to the cast and annealed wrought material. The wear behavior of the laser cladding of TiB whiskers and TiC particles on Ti-6Al-4V for a titanium based coating was studied [25]. The coating was mainly composed of α-Ti cellular dendrites and a eutectic in which a large number of needle-shaped TiB whiskers and a few equiaxial TiC particles were uniformly embedded. The TiB and TiC particles helped to improve the contact between the coated part and counter body and thus decreased the friction. This improved the coating wear resistance under dry sliding condition. TiVCrAlSi coatings was also laser clad on Ti-6Al-4V alloy to test the wear resistance property [26]. The (Ti,V)5Si3 precipitates were dispersed in the TiVCrAlSi coating, it also formed the intermetallic compound in due respect with more enthalpy variations. The hard silicide in (Ti,V)5Si3 phase played a vital role in wear resistance and encountered with nil or mild wear regime. The regime was suffered with oxidation, slight adhesive wear and fragmentation. The dry sliding wear test indicated that the TiVCrAlSi coating has improved the wear resistance property of the Ti-6Al-4V alloy.

Titanium metal matrix composite was prepared on Ti-6Al-4V substrate using laser cladding technique by Ochonogor et al. [27]. The process was performed to improve the hardness and wear properties of Ti-6Al-4V substrates. The homogeneous distribution of TiC particles was evidenced in the microstructure. The results indicated that the Ti and TiC powders had helped the surface modification and microstructure of the coatings at a greater extend.

The effect of Ti-6Al-4V powder preparation processes also studied to understand its impact on laser direct metal deposition process [28]. The powders prepared with two processes namely gas-atomization (GA) and plasma rotating electrode (PREP). The deposited Ti-6Al-4V PREP powder exhibited α + β microstructure in the deposited regions and subsequent laser power affected the (Sα + β) the lamellar spacing of α + β phase. As the microhardness of the clad was mainly depends on the Sα + β, the hardness exhibited by the PREP Ti-6Al-4V powder was lesser than GA Ti-6Al-4V powder deposition.

The performance of metal matrix composite coating on titanium was performed to enhance the tribological properties of titanium alloy [29]. The laser cladding process was performed to fabricate TiC particle reinforced Ti-6Al-4V composite coatings on titanium alloy hot rolled samples. At the time of solidification, titanium carbide dendrites were produced in the laser deposition zone due to precipitation of partially dissolved carbide particles in the molten titanium. Increased laser specific energy induced the dissolved particles to form dendrites in the deposition region. Increase in titanium carbide volume fraction resulted with improved the physical and tribological properties. The presence of coarse TiC primary carbides favored the oxide formation and retained the debris at the sliding contact. As a massive dilution of TiC primary particles occurred at high specific energy conditions, the wear behavior was not improved.

V. CONCLUSION

A detailed literature survey was conducted relevant to the surface treatment and coatings on titanium alloys and their associated characterization relevant to tribological properties. The coatings made by laser techniques exhibited strong metallurgical bonding with the substrate materials, owing to their high energy density. Especially in recent times, there is more interest created towards laser based metal deposition on titanium alloys. Despite that, the residual thermal stress induced as a result of rapid heating and cooling showed more attention required on selection of laser process parameters. The selection of optimal parameters helped to exhibit very good metallurgical bonding and improved mechanical properties in the deposited region. Few researchers also performed and proved the suitability of the laser metal deposition technique for manufacturing and repairing titanium based aeronautical components.

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