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# Contemporary Progress in the Hybrid Coating of Titanium Alloys using the Liquid Additive Manufacturing Technique

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### ABSTRACT

This paper presents a review of the contemporary advancements in hybrid coating applications on titanium alloys using the liquid additive manufacturing technique. Hybrid coatings represent highly functional coatings with very good hardness, wear resistance, and adhesion properties with other tailored properties for the application of aerospace, automotive, construction, and maritime industries. Within this review, a comprehensive study of the foundational principles governing hybrid coatings is highlighted with the key aspects of the selection of metallic substrates, diverse coating methods, and the characterization of coatings. A perceptive segmentation of the merits and demerits attendant to diverse surface coating processes such as liquid additive manufacturing, sol-gel deposition, laser beam techniques, thermal spraying, and micro-arc oxidation are analyzed. Based on the literature review, it can be found that TIG torch LAM technology, appears as an encouragement rendering itself both cost-effective and ecologically sustainable, this methodology not only bequeaths a meticulous control over the mantle of coating thickness and composition but also bestows upon the resultant hybrid coatings an enhanced morphology and hardness, particularly within the realm of titanium alloys. Therefore, evident is the prospect of a transformative trajectory, wherein the higher costs associated with a laser beam, liquid deposition, and sol-gel techniques are supplanted by the greener, more sustainable embrace of liquid additive manufacturing. The hybrid coating on commercial purity titanium showed that hybrid coating enhances hardness value by a factor of three to fourfold accompanied by the development of a new microstructure. In conclusion, this paper explains the reflective impact of hybrid coatings and stresses the potential of TIG torch LAM technology in advancing the field of surface engineering, particularly in the context of hybrid coating on titanium alloy materials.

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## 1. Introduction

Titanium alloys are widely used in a variety of industries because of their strength, ductility and thermal conductivity but extremely vulnerable to environmental factors, which can significantly affect their mechanical performance, longevity, and usability, and constant contact friction between the surfaces can cause the wear, corrosion, and fatigue [1]. The researchers have been developing materials that endure severe environments and retain their properties over time. This can be accomplished by employing advanced coatings and suitable surface treatments to the surface quality and performance of metallic materials to enhance their wear and corrosion resistance, particularly within tribological conditions [2]. In addition, it is necessary to find suitable and effective protective coatings for the extended life of engineering components.

Titanium alloys are also utilized in a vast array of industrial uses through their advantages of its properties. However, these alloys are prone to problems such as wear, corrosion, and fatigue cracking [3]. As a remedy for these issues, hybrid coatings that consist of two or more coatings materials and have unique properties were introduced [4]. It was found from previous research that hybrid coatings can significantly enhance the properties of titanium alloys including their wear resistance [5]. This is achieved by boosting the hardness of Ti-alloy, decreasing friction, and also improving corrosion resistance [6].

Titanium alloys are an innovative structural material with excellent properties including high specific strength and fatigue strength, low-temperature toughness and density, and corrosion resistance [7]. However, their low wear resistance, softness, high coefficient of friction, and poor machinability make them poor tribological materials [8]. The application of surface coatings has been found to enhance the coefficient of friction, wear resistance, and hardness of titanium alloys [9]. Hence, material coating can last longer and perform better for the application of aerospace, automotive, machinery, biomedical, and oil and gas engineering. The recent study development demonstrated that the utilization of hybrid coating such as WC-Co, Ni-coated graphite,  $B_4C$  and  $CrNi/TiO_2$  can significantly increase wear resistance and decrease friction, which can be used to improve performance and broaden the use of titanium alloys [10-12].

Hybrid coatings are the most efficient when an appropriate mixture of coatings, thickness layer of coating, preparation of the surface coating, and the synthesis process are implemented. To ensure long-term efficacy, hybrid coatings must be tested in their actual operating conditions. The main problems that can ensure the effectiveness of hybrid coatings are processing cost and feasibility of coating materials whether it is environmentally friendly or not. Therefore, the main objective of this review paper is to discuss the recent advancement of hybrid coating on titanium alloys via liquid additive manufacturing methods.

## 2. Coating Materials

The coating material is a substance that is preplaced onto a metal surface to preserve it from wear, corrosion, or any damage that happens during service life. Coating materials are usually made from ceramics, metals, composites, polymers, and biodegradable polymeric materials or another natural source. The coating resists corrosive acid, ultraviolet (UV) lights, droplets of water, and heat temperature making it useful even in harsh conditions and protecting surface layers to boost the properties and performance [13]. Developments in technology and materials have produced a variety of coating options over time. Coatings are classified into several types, including organic coatings, inorganic coatings, metallic coatings, and composite coatings [14]. Each type has various qualities and advantages allowing tailored solutions to satisfy specific industry needs.

A recent investigation on the application of graphene-based coatings for corrosion prevention in marine applications was conducted by Wen *et al.*, [15]. The graphene coatings are revealed to have outstanding barrier properties that preserve corrosive substances from penetrating. Another study by Gao *et al.*, [16] assessed the impact of hard coatings on the structural, mechanical, and tribological characteristics. Hard coating has been found to maintain the dependable operation of workpieces, thereby extending their useful life and decreasing production costs. Furthermore, Lailatul and Maleque [17] investigated the fine Silicon Carbide (SiC) powder preplacement technique using a TIG torch. Based on the findings, it can be discovered that the dendrite microstructure was produced by the modified surface, which was created by melting SiC using a TIG torch, as a result of the preplaced SiC being completely melted and then re-solidified in the modified layer. In comparison to the substrate material, the hardness increment was 2 to 3 times higher. The enhanced hardness of the modified layer coating can be attributed to the presence of the dendritic microstructure across all melting conditions. This shows the potential of SiC as a coating material in the future. On the other hand, the study from Chenchen *et al.*, [18] employed laser processing and chemical assembly techniques to fabricate Ti-6Al-4V samples with varying groove widths and a graphene oxide (GO) coating on their surfaces. The findings indicate that the Ti-45-GO sample, which is coated with GO and has a groove width of 45  $\mu\text{m}$ , can enhance the resistance to corrosion in Ti-6Al-4V. This improvement is attributed to the homogenization of the surface microstructure from the Ti-45 substrate and the protective effect of the GO coatings. Consequently, the Ti-6Al-4V alloys exhibit enhanced properties in terms of both corrosion resistance and resistance to wear.

As has been demonstrated that coating materials provide many benefits to the surface of the substrate including increasing their durability, protection, and wear resistance. The development of a variety of coating materials has been facilitated for the improvement of coating technology. These advances boosted industry performance, cost-effectiveness, and sustainability to address environmental problems.

The future of silica carbide coatings appears promising as materials coating on alloy surfaces because of their enhanced hardness and wear characteristics [19]. Recent potential candidate materials for solid lubrication and low friction properties that are outstanding for surface coating are graphene oxide (GO), graphite, environmentally friendly SiC (eSiC), and other chemically derived materials [20, 21].

### 3. Coating Methods

The selection of a coating method and material is crucial in determining the success of the coating application and the overall performance of the coated material. Different coating materials possess different deposition mechanisms, therefore, a wide range of processes are available for the desired functionality. The suitable coating material and coating method are most crucial in accomplishing the ideal properties and performance like adhesion, durability, corrosion resistance, and cost of the coated surface. Some of the most common methods include physical vapor deposition (PVD), chemical vapor deposition (CVD) thermal spraying, etc. The choice of process depends on the properties required for the coating and the material being coated. These include dry, wet, and liquid state coating such as PVD coating, CVD coating, micro-arc oxidation (MAO), sol-gel, polymer coatings, thermal spraying, laser beam, and TIG torch welding [22]. The comparison of several coating methods can be seen in Table 1.

**Table 1**  
 Comparison of several coating methods (Adapted from ref. [23-27])

Parameters	TIG Torch LAM	Laser Beam	Thermal Spraying	Sol-gel Deposition	Micro Arc Oxidation
Typical coating material	TiC-CNT, TiC-Ni, hBN, TiN, SiC	TiNi, $Ti_2Ni$ , Zn	$ZrO_2$ , $TiO_2$ , NiCrBS	$Al_2O_3$ /Gr/HAP, $ZrO_2$ , $TiO_2$ , Li + Polyethylene glycol (PEG)	GO, $TiO_2$ , SDBS, chitosan (CS)
Substrates	Low alloy steel, Ti-alloy, stainless steel	Ti-6Al-4V, aluminum steel, stainless steel	Titanium alloys, aluminum alloy, carbon steel	Ti-6Al-4V alloys, aluminum alloy, stainless steel	Titanium, Al, and Mg alloys
Strengths	No defects at high energy density, smooth surface bonds well with substrate	Capable of synthesizing TiNi/ $Ti_2Ni$ intermetallic composites	Good coating quality	Control the coating composition precisely	Enhanced photocatalysis
Weakness	Depending on experimental conditions and parameters	Ti diffusion is limited to the deposition's upper level	Lack of significant variation in passivation rates	Post-treatment can be a time-consuming process	Expansion of micropores
Wear Resistance	Improved significantly	Improved wear resistance	Excellent wear resistance	Highly influenced	Better wear resistance
Hardness	Four times higher than the substrate	Improved hardness	Hardness increased	The hardness of the coating boosted	High hardness

In a nutshell, the process described makes use of multiple deposition mechanisms to produce a reliable coating. TIG torch LAM technology enables hybrid coating development by precisely controlling coating thickness and composition which can improve mechanical properties in a variety of metallic materials. LAM technology is also cost-effective and flexible compared to other coating methods [28, 29].

It is essential to take into consideration the potential adverse effects, including thermal effects, inclusion and contaminant penetration, melting point of coating materials, and biocompatibility. It is crucial to evaluate these factors thoroughly and select a process that will provide the desired properties and performance for the intended application. In addition, ongoing research and development in coating technology may result in the future development of processes that address these limitations.

#### 4. Sustainable Coating

The use of sustainable coating materials on alloy surfaces is a fundamental approach to improving performance and preventing premature failure of the automotive, aerospace, and tribological components. These components can be extended through improved protection, increased hardness and wear resistance, and improved thermal stability, resulting in improved performance and reliability. LAM is a cost-effective way to apply wear and corrosion-resistant coatings for advanced applications. LAM used lasers to melt and then fuse the metallic powders onto a substrate which resulted in a highly dense and uniform coating. This process has become more popular in many industries such as aerospace, defense, and automotive because of its capability to produce complex

geometries and reduce the waste of material. LAM also offers the potential for customization and on-demand production, making it a promising technology for the future. TIG torch melting is a suitable cladding or liquid additive manufacturing method for hard surface coating on metallic substrates. The TIG torch melting technique produces coatings with good melt pool geometry and strong substrate-coating bonding. A well-formed melt pool and good substrate adhesion result from the TIG torch's controlled heat input. Hard surface coatings on metallic substrates like Ti-alloy can be developed using the TIG torch melting technique. Its melt pool geometry, strong bonding, and selective surface modification make it suitable for many industrial applications, especially those that require improved surface properties.

Hybrid sustainable coatings with two ceramic materials have many benefits. These ceramic reinforcements complement each other to improve properties. This synergistic approach yields Ti-alloy coatings with balanced microstructure, hardness, and wear resistance. LAM can balance performance properties by carefully formulating materials and designing the operating process. In terms of cost-effectiveness, speed, and flexibility, this approach outperforms other coating techniques. The proposed method of using a TIG torch for LAM allows for a more efficient and cost-effective coating process. This hybrid sustainable coating allows metallic substrate materials to withstand wear and thermal loads. This helps in harsh dynamic and high-temperature environments where durability and strength are essential. The ceramic materials' unique properties and an optimized coating process improve wear resistance and thermal stress resistance.

The utilization of the LAM technique can facilitate the development of sustainable coating, consisting of different feedstocks and substrates, including hybrid formulations. This can lead to the advancement of sustainable coatings, which can provide unique coating mechanisms and improved tribological performance for coated materials.

## 5. Hybrid Coatings on Ti-alloy

Recently, hybrid coatings have been recognized as an efficient approach for reducing the wear and corrosion of titanium alloys. These hybrid coatings consist of two materials which are organic and inorganic. The unique property of their combination makes them different from the other types of frequently used coatings that generally are made from either organic or inorganic materials [30]. Flexible hybrid coatings provide the best corrosion resistance, adhesion, and chemical resistance.

Previous studies have shown that the use of various predecessors has produced a variety of hybrid coatings. To begin with, Naidoo *et al.*, [31] evaluated a novel hybrid coating of Ti-Al-Si-Cu for enhancement of the surface properties and prevent corrosion behavior preventing surface corrosion in titanium alloy grade 5 by laser metal deposition. The best optimum performance was determined to be Ti-9Si-3Cu alloy for 1 kW of laser power and 1.0 m/min scan speed. The enhancement of hardness and corrosion resistance was observed to be most effective when employing slower scanning speeds and higher laser intensity. This new successful composite coating strengthens titanium alloy in terms of microhardness and corrosion. Moreover, the study by Santana *et al.*, [32] examined the electrochemical characteristics and corrosion resistance of both a hybrid coating and an uncoated substrate using the sol-gel technique. According to the result, it can be observed that the SOM film, which is composed of a PMMA-SiO<sub>2</sub> hybrid material and coated onto a Ti-6Al-4V alloy substrate, exhibited strong adhesion and displayed a consistent surface topography. Additionally, the results indicate that the hybrid coating exhibited a superior corrosion protection barrier in comparison to the substrate that was not coated. This coating can be used in biomaterial applications and is corrosion-resistant. Furthermore, Bansal *et al.*, [33] conducted a study on the application of HA-Zn coating to improve the mechanical and corrosion resistance characteristics. The findings show

an increase in surface hardness and a decrease in surface roughness of the samples. The uncoated Ti13Nb13Zr alloy demonstrates hydrophobic characteristics, whereas all of the samples with coatings exhibit hydrophilic properties, leading to enhanced clinical efficacy. Among all samples, it was observed that the titanium substrate coated with a combination of hydroxyapatite (HA) and 12% zinc oxide (ZnO) showed the most superior corrosion resistance. Plasma-sprayed HA/ZnO coatings improved titanium substrate corrosion resistance and surface properties. The incorporation of pure hydroxyapatite (HA) with zinc oxide (ZnO) enhances the surface properties and corrosion resistance of Ti13Nb13Zr. The findings from the electrochemical and morphological analysis indicate that the application of HA/ZnO coatings holds promise for utilization in bio-implant materials.

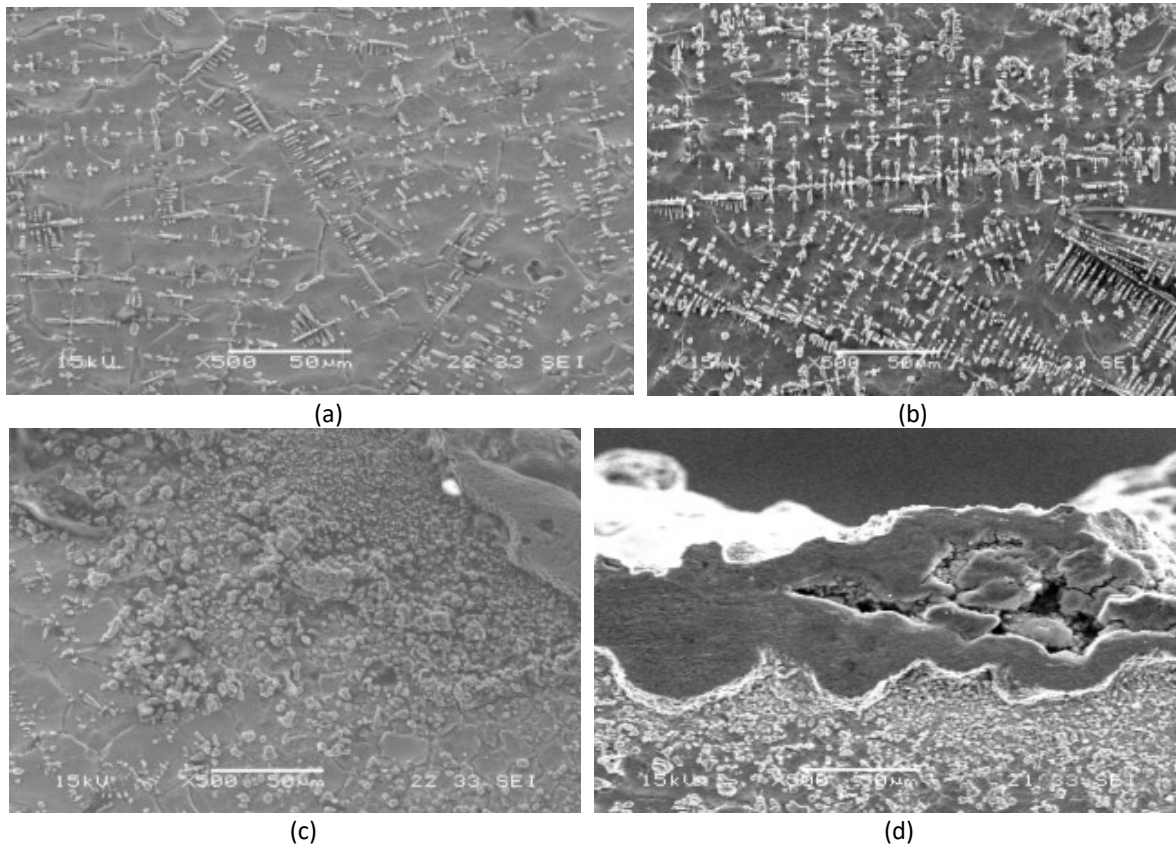
The wear behavior of TIG torch LAM hybrid coatings depends on the coating composition, microstructure, and process parameters. Reinforcement particles strengthen the coating, improving wear resistance. Optimizing process parameters like welding current and speed can also improve the coating's wear performance by controlling reinforcement particle distribution and orientation. TIG torch is commonly used in welding applications that require precision and control, such as aerospace, automotive, and medical industries. As a result of its low heat input and capacity to create welds of high quality, it is also preferred for welding thin materials. Successful past research discusses how TIG torch LAM technology was used. The study centered on the development of a composite consisting of Fe, C, and Si powders to alloy a commercial purity titanium (CP-Ti) substrate through the TIG torch melting process. The Fe:C: Si mixture was blended using a ball milling process for 1 hour, with a ratio of 82:12:6. Then, it was mixed with polyvinyl alcohol (PVA) before being placed on the substrate at a ratio of 1 mg/mm<sup>2</sup>. Table 2 displays the optimal process parameters for consistent adhesive coating, including current, energy, speed, depth, and width.

**Table 2**

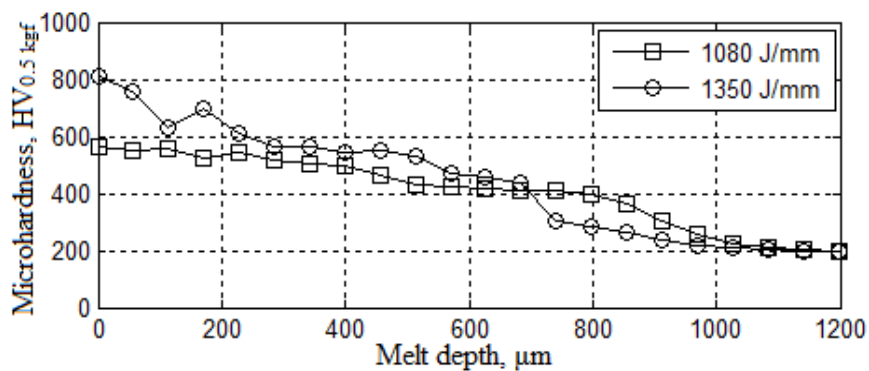
Melt dimension and conditions used for TIG torch LAM process (Adapted from ref. [34])

Powder Composition	Current (A)	Energy (J/mm)	Speed (mm/s)	Depth (mm)	Width (mm)
Fe:C: Si≡82:12:6	80	1080	1.0	1.14	5.95
	100	1350	1.0	1.20	9.06

Figure 1 shows the alloyed layer microstructure processed of 1080 J/mm and 1350 J/mm. Dendritic microstructures were observed to develop within the resolidified alloyed layer coating. in the resolidified alloyed layer. The extent of particulate agglomeration was observed to be greater at the periphery of the low-temperature region, as depicted in Figure 1 (c) and (d), in comparison to the melt pool layer located at the center. The microhardness test results of the surface-alloyed layers are presented in Figure 2, showcasing two distinct energy inputs: 1350 J/mm and 1080 J/mm. The presence of hybrid layers has resulted in an increase in microhardness value due to the formation of TiC. The substrate of CP-Ti has the lowest value of microhardness which was 200 HV<sub>0.5kgf</sub> compared to surface alloyed coating which was around 810 HV<sub>0.5kgf</sub>. The microhardness of hybrid coated alloy increases by 3 to 4 times higher than the CP of Titanium alloy substrate.



**Fig. 1.** SEM micrographs of the surface alloyed at two different energy inputs (a) 1080 J/mm (b) 1350 J/mm (c) melt microstructures at the edges showing unmelted particulates at 1080 J/mm and (d) 1350 J/mm (Adapted from ref. [34])



**Fig. 2.** Microhardness profile of the surface alloyed CP-Ti (Adapted from ref. [34])

## 6. Conclusions

In the current review paper, the most recent advances in surface engineering were primarily focused on hybrid coatings for titanium alloys. The coating materials and coating methods play a crucial part in ensuring the quality of the protective layers. TIG Torch LAM technique is a promising and fascinating way to develop hybrid coating onto metallic substrate. TIG torch LAM technology enables hybrid coating development by precisely controlling coating thickness and composition which can improve mechanical properties in terms of wear, morphology, and biocompatibility in titanium alloys. LAM technology is also cost-effective compared to other coating methods. Sustainable coating materials on alloy surfaces is a fundamental approach to improving performance

and preventing premature failure of the automotive, aerospace, and tribological components. It reveals that sustainable hybrid coatings performance and industrial applications can reduce environmental impact and contribute to a greener future that current research is focusing on. The successful development of a novel liquid additive manufacturing method for producing hybrid coatings can lead to the creation of new coating systems with enhanced properties. From the case study, it was found that hybrid coating implemented in CP-titanium alloy enhances morphology and the hardness properties by 3 times higher than the substrate.

In the future, it is believed that the TIG Torch LAM can be a cheaper, sustainable, and viable coating method for industrial applications to achieve the desired properties on the surface performance of the coated materials. The study's findings indicate that the critical factors for TIG torch LAM are the parameters of current and speed, which hold greater importance when compared to other processing variables. The utilization of this technology is expected to increase in the coming years.

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