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Advances in TiO_2-based composite coatings: Phase control, deposition methods and tribological performance

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ABSTRACT

In sectors such as maritime, mining, and power generation, components frequently encounter severe tribological and corrosive environments that accelerate surface degradation. Titanium dioxide (TiO_2) coatings, particularly when applied via thermal spray techniques such as Atmospheric Plasma Spray (APS), Suspension Plasma Spray (SPS), and High-Velocity Oxy-Fuel (HVOF), demonstrate significant potential for wear and corrosion protection. This review focusses on the influence of TiO_2 crystalline phases, particularly rutile, on hardness, wear resistance, and chemical stability. The emphasis is on TiO_2-based composites reinforced with oxides (such as Al_2O_3, Cr_2O_3, and ZnO) or carbides (such as WC). These compounds enhance the durability of the composites by synergistically increasing their strength. The processing parameters, including temperature, voltage, and cooling rate, are highlighted as critical factors influencing phase stability and tribological outcomes. Furthermore, innovative methods like hybrid MAO-laser surface texturing and nanostructured sol-gel deposition are acknowledged as promising but inadequately explored strategies for tailoring microstructure and improving service longevity. The findings indicate that rutile-rich TiO_2 composites, when employed with contemporary deposition techniques, represent the optimal choice for fabricating next-generation wear-resistant coatings suitable for high-stress, high-temperature environments.

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1.0 INTRODUCTION

In numerous heavy industries, such as mineral processing, oil and gas, power generation, aerospace, and marine engineering, critical machinery is consistently subjected to extreme circumstances. These components must withstand both mechanical stress and continuous exposure to abrasive particles and substances that cause degradation (Khare et al., 2024). Over time, this intense exposure significantly degrades the surface, typically by abrasion or erosion. The materials gradually deteriorate, resulting in diminished performance, reduced longevity, and increased repair costs.

Certain components, such as pipelines, slurry pumps, valves, turbine blades, and ship hulls, are more susceptible to damage than others. They deteriorate more rapidly due to constant exposure to rapidly moving fluids or solid particulates. In slurry systems, abrasive particles repeatedly impact surfaces, leading to rapid degradation. Saltwater corrosion, coupled with the abrasive influences of sand, marine life, or ice, significantly complicates conditions in offshore and marine environments. Due to these issues, organizations always seek innovative materials and surface coatings to safeguard their equipment and enhance its reliability.

A possible approach involves altering the surface with protective coatings. These coatings can enhance surface hardness and chemical resistance while preserving the component's natural structure. Numerous coating techniques exist; however, thermal spray methods like as plasma spraying and high-velocity oxy-fuel (HVOF) have gained prominence (Singh et al., 2021) These technologies are particularly advantageous as they produce durable, thick coatings that adhere effectively to various surfaces. This renders them ideal for components subjected to significant wear.

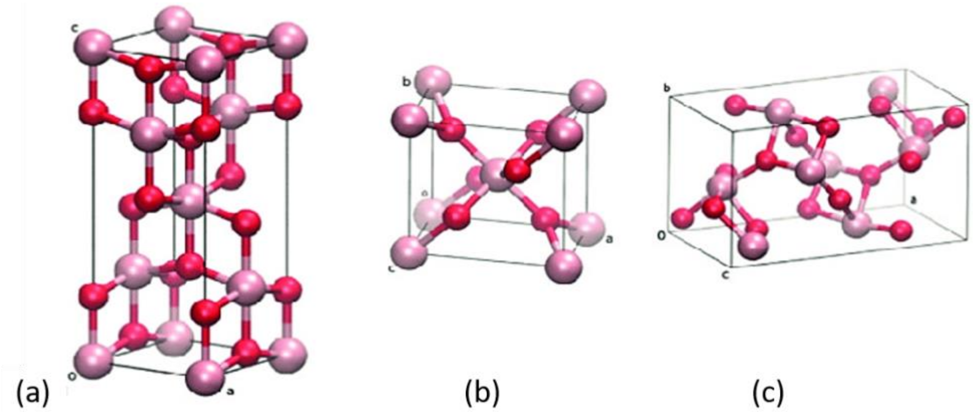
Researchers have extensively investigated titanium dioxide (TiO_2) as a coating material because to its exceptional hardness, stability, and environmental resistance. The rutile variant of TiO_2 is characterized by its robust, densely packed crystalline structure. It typically ranges from 6 to 6.5 on the Mohs scale (Eddy et al., 2023). This design renders it sufficiently robust to withstand surface abrasion under relatively adverse operating conditions. The rutile phase is generally attained using high-temperature deposition techniques such as plasma spraying, wherein the elevated temperature facilitates the transformation from other phases, including anatase and brookite (Zhang et al., 2020).

The transition from anatase or brookite to rutile occurs at elevated temperatures, typically ranging from 600 to 800 °C (Zeng et al., 2025). Plasma spraying readily achieves or exceeds this range, rendering it an effective method for producing TiO_2 coatings with a high rutile content. These coatings exhibit enhanced durability and superior resistance to heat cycling due to their robust, cohesive structure and little porosity. Consequently, they maintain their form despite fluctuations in temperature or repeated mechanical stress.

Titanium dioxide (TiO_2) possesses a significant advantage over alternative materials due to its exceptional chemical stability. Due to the presence of titanium in its highest oxidation state (Ti^{4+}), it exhibits inherent resistance to additional oxidation or chemical degradation (Yang, 2021). This renders it very suitable for corrosive or oxidative environments, such as petrochemical industries or offshore platforms. Despite its several advantageous properties, TiO_2 is not optimal. Its wear performance may be suboptimal in extremely adverse conditions. Researchers have explored methods to enhance its strength, such as combining it with other materials or including additional elements, to increase its durability and wear resistance. This paper examines recent advancements and provides a critical review of TiO_2-based coatings, emphasizing their current capabilities and potential future applications for wear protection in industrial settings.

2.0 TiO_2 PHASES AND PHASE CONTROL IN RELATION TO WEAR RESISTANCE

Titanium dioxide (TiO_2) can crystallise in three primary forms: anatase, rutile, and brookite (Figure 1). Anatase and rutile are the predominant forms of coatings utilised in practical applications. Anatase is metastable at ambient temperature and often transforms into rutile when subjected to temperatures ranging from 600 to 800 °C. The precise temperature at which this occurs depends on several factors, including particle size, dopant chemistry, and oxygen stoichiometry. Rutile, the thermodynamically stable phase, possesses a greater density (4.25 g/cm^3 against anatase's 3.89 g/cm^3) and exhibits increased hardness, both of which enhance its resistance to wear under tribological loading.



(a) (b) (c)

Figure 1: Schematic sketch for Crystal structures of TiO_2 (a) Anatase (b) Rutile (c) Brookite (Adapted from Ref. Godbert et al', 2018)

Coatings rich in rutile typically exhibit greater longevity than those dominated by anatase due to their increased compactness and enhanced weight-bearing capacity (Zuo et al., 2020). A dual-phase system integrating anatase and rutile has demonstrated a synergistic effect. Kusior et al. (2023) said that coatings containing around 30–40% anatase within a rutile matrix exhibited superior adhesion and reduced fracture propagation compared to pure rutile coatings. This is due to anatase enhancing the bond strength between surfaces, whereas rutile fortifies the overall structure. The anatase to rutile ratio is not just a thermodynamic need but also a modifiable variable that directly influences tribology.

2.1 Effect of Deposition Methods and Parameters on Phase Composition

The crystalline phase composition of TiO_2 coatings is significantly influenced by the deposition method and its associated processing parameters, which together dictate the thermal history, oxygen availability, and cooling pace of the material. In high-temperature deposition techniques like as plasma spraying and high-velocity oxy-fuel (HVOF) spraying, feedstock powders are subjected to flame or plasma jets exceeding 2000 °C. This fully liquefies the particles and subsequently solidifies them rapidly upon impact. Under these conditions, rutile formation is highly probable due to elevated enthalpy and prolonged thermal exposure. Most plasma-sprayed coatings consist of over 80% rutile and exhibit considerable hardness, ranging from 7 to 8 GPa, rendering them highly resistant to wear in severe tribological conditions (Mohamed et al., 2020). Nevertheless, modifications in the process, such as the spray distance and particle velocity, influence the cooling rate and hence affect phase retention. For example, extended stand-off distances can accelerate the quenching process, potentially preserving a portion of the anatase phase, typically limited to 20%.

Conversely, low-temperature synthesis methods such as sol-gel deposition typically maintain anatase as the predominant phase during initial crystallization. Rutile exclusively forms after thermal post-treatment. Upon heating to 400–500 °C, sol–gel-derived coatings typically transform into anatase. Upon heating to approximately 600 °C, they commence transformation into rutile, completing the process around 900 °C, contingent upon the heating rate and particle size. The use of dopants such as SiO_2, Al_2O_3, or Fe_2O_3 has been shown to postpone the transition from anatase to rutile by over 200 °C. This occurs as they immobilize grain boundaries and prevent lattice reconfiguration. From a tribological perspective, mixed-phase sol-gel coatings have superior wear resistance compared to single-phase anatase coatings. Zhang et al. (2020) demonstrated that sol-gel TiO_2 coatings with an anatase-to-rutile ratio of around 60:40 exhibited 30% reduced wear rates when sliding against steel counterparts, highlighting the advantages of phase coexistence.

The phase composition can be modified more readily by physical vapour deposition (PVD) and chemical vapour deposition (CVD) techniques by adjusting the substrate temperature, plasma energy, and oxygen partial pressure. Magnetron sputtering at substrate temperatures under 400 °C often produces coatings that are either amorphous or mostly anatase-rich. Upon elevating the substrate temperature to 500–600 °C, a composite anatase–rutile microstructure is generated (Kongsri at al., 2019). Nonetheless, when the temperature exceeds 600 °C, the growth of rutile is encouraged. Another significant impact is the quantity of oxygen present. In the presence of abundant oxygen, anatase remains stable during its growth. Rutile nucleation occurs in the absence of sufficient oxygen as the lattice reorganises to occupy the voids. These modifications significantly impact tribology. Sputtered films predominantly composed of rutile exhibit hardness values over 9 GPa and wear rates of 10^{-6} mm^3/Nm. This far surpasses anatase-rich coatings, which typically exhibit hardness values of approximately 5 GPa and wear rates of about 10^{-5} mm^3/Nm (Kaczmarek at al., 2012).

Micro-arc oxidation (MAO) is a distinctive deposition technique wherein voltage and discharge parameters govern the phase composition. Localised plasma discharges produce coatings predominantly composed of anatase at lower voltages (200–300 V). At elevated voltages (>500 V), intensified thermal effects facilitate the transition to rutile. Quadros et al. (2025) shown that the rutile concentration in MAO coatings increases approximately linearly with the applied voltage, attaining over 85% rutile content at 600 V, accompanied by hardness levels surpassing 12 GPa. Tribological investigations demonstrated that MAO coatings rich in rutile exhibited up to 40% reduced wear compared to those abundant in anatase under same sliding conditions. The results demonstrate the sensitivity of TiO_2 phase formation to processing conditions and the strong correlation between deposition-induced phase composition and tribological performance.

2.2 Comparative Observation and Phase Control Strategies

A comparative investigation of deposition processes reveals a clear association among processing, structure, and properties in TiO_2-based coatings. Plasma spraying and high-voltage micro-arc oxidation are instances of high-energy thermal processes that consistently provide microstructures predominantly composed of rutile (Ma et al., 2025). These coatings exhibit excellent hardness, increased density, and exceptional wear resistance. This renders them suitable for applications involving substantial loads or elevated temperatures. However, its brittleness may pose an issue, particularly when subjected to cyclic stress or impact loads. Conversely, low-energy or solution-based methods such as sol-gel or sputtering at reduced substrate temperatures facilitate the stabilisation of anatase. Anatase-rich coatings enhance adhesion, surface reactivity, and occasionally fracture deflection. Nevertheless, they typically lack the durability to withstand challenging tribological conditions.

Intermediate-energy methods, including controlled-annealed sol-gel coatings and PVD coatings placed at moderate substrate temperatures, can produce mixed anatase-rutile microstructures. These dual-phase solutions are gaining popularity because to their amalgamation of the mechanical strength of rutile with the adhesive and functional advantages of anatase (Pedrini, et al., 2020). The resulting synergy can prevent crack propagation, enhance coating strength, and significantly reduce wear rates compared to single-phase coatings. The ability to modify deposition temperature, oxygen partial pressure, dopant chemistry, and voltage provides numerous possibilities for tailoring TiO_2 coatings to meet specific requirements.

The research indicates that phase control is not merely a byproduct of deposition; rather, it is an essential design element that requires meticulous planning. By meticulously selecting the deposition technique and modifying the process parameters, it is possible to alter the anatase–rutile ratio to create coatings optimal for high-load tribological applications, surfaces requiring robust adhesion, or surroundings necessitating multifunctionality. Thus, comprehending and applying the correlation among processing, phase composition, and tribological behaviour remains crucial for enhancing TiO_2-based coating technologies.

3.0 TiO_2 COMPOSITE COATING

TiO_2 composite coatings have garnered significant attention in advanced surface engineering due to their exceptional mechanical, chemical, and tribological properties. Researchers have enhanced the hardness, wear resistance, and thermal stability of coatings by incorporating TiO_2 into composite matrices such as polymers, metals, or ceramics. This renders them suitable for aerospace, medical, and maritime applications requiring durability. The combination of TiO_2 with secondary reinforcements such as alumina (Al_2O_3), chromium oxide (Cr_2O_3), or carbon-based compounds enhances the material's strength and reduces its propensity to slip. The crystalline phase of TiO_2, particularly the predominance of rutile, is crucial in determining the material's performance. Plasma spraying, high-velocity oxy-fuel (HVOF), and micro-arc oxidation (MAO) are established methods for producing TiO_2 composite coatings with controlled microstructure and phase composition. These coatings exhibit superior resistance to mechanical wear and corrosion compared to other coatings, and they may possess photocatalytic and self-cleaning capabilities, enhancing their utility in multifunctional applications.

3.1 Pure TiO_2 Coating

Titanium dioxide (TiO_2) possesses advantageous features for surface engineering, including a reduced coefficient of friction (COF), oxidation resistance, and self-lubricating capabilities. Pure TiO_2, although promising, typically exhibits lower wear resistance compared to more resilient oxides such as aluminium oxide (Al_2O_3). The incorporation of TiO_2 into AA5083 aluminium alloys has demonstrated a decrease in the coefficient of friction by as much as 22.95%, indicating its tribological efficacy (Karmiris-Obratański et al., 2024). Nevertheless, this advantage alone does not enough compensate for the wear restrictions inherent to TiO_2 coatings independently.

To overcome this limitation, research has focused on the integration of TiO_2 with secondary oxides or metals to produce composite or hybrid coatings. The use of chromium oxide (Cr_2O_3) significantly enhances wear resistance by promoting the development of denser and more resilient microstructures (Grimm et al., 2020). These multiphase solutions surpass pure TiO_2 coatings for sliding applications due to their enhanced hardness, increased adhesion, and prolonged durability. Consequently, TiO_2 is being utilised more extensively in composite and hybrid arrangements, where its advantageous tribological properties are combined with those of other metals or oxides. This approach enhances the durability of pure TiO_2 and facilitates the production of innovative coatings that exhibit greater strength and longevity in challenging tribological and protective environments.

3.2 TiO_2 Metal Composite Coating

TiO_2 metal-composite coatings have gained significant acceptance due to their ability to enhance the wear and heat resistance of softer metal matrices. The incorporation of TiO_2 into metal–ceramic composites enhance their hardness and wear resistance, rendering them suitable for demanding mechanical applications. TiO_2 exhibits exceptional thermal stability, maintaining its crystalline structure even at elevated temperatures. This prevents heat transfer through the composite matrix. The thermal barrier effect enhances the longevity of the coating when employed at elevated temperatures. The mechanical and functional properties of the coating are contingent upon the precise composition and quantity of metal and ceramic phases, including TiO_2. This enables tailored performance for various industrial applications. Table 1 presents selected examples of TiO_2 metal–composite coatings that have been investigated by various researcher.

Table 1: TiO_2 metal composite coating.

TiO_2 metal composite coating	**Coating properties**	**Findings**	**Wear testing**	**Reference**
WC+TiO_2	Improve abrasion resistance and mechanical durability	Tungsten carbide incorporated into TiO_2 coating matrix can resist plastic deformation	Slurry erosion testing	Haque et al., 2021
WC-10Co-4Cr + 2% TiO_2	Improve mechanical strength (elasticity)	Dense coating and improve in mechanical strength (elasticity)	Slurry jet erosion testing	Pradhan et al., 2024
Cu-TiO_2	Better surface roughness and COF value	Cu particle act as binder that fills pore in coating	Coating morphology	Toibah et al., 2023
Al – TiO_2	Dense coating, low porosity, good adhesion to substrate	Good mechanical interlocking between coating and substrate	Coating morphology, Pin on disk	Salimi et al., 2020

3.2.1 Tungsten Carbide (Wc) + TiO_2 Coating

The incorporation of tungsten carbide (WC) into titanium dioxide (TiO_2) coatings significantly enhances their wear resistance due to the superior mechanical properties of WC. WC exhibits a hardness ranging from 2000 to 2500 HV, significantly surpassing that of pure TiO_2. This establishes an effective reinforcing phase within the coating matrix, enhancing its resistance to plastic deformation and abrasive forces. WC-TiO_2 composite coatings exhibit superior performance when applied via high-velocity oxy-fuel (HVOF) deposition techniques. Haque et al. (2021) demonstrated that WC+TiO_2 coatings exhibit superior resistance to fly ash erosion, particularly with particles ranging from 106 to 150 μm in size.

In addition to enhancing the hardness of the coating, WC also increases its weight-bearing capacity by distributing surface stress more uniformly. During thermal spray deposition, WC particles can infiltrate and occupy voids within the TiO_2 matrix. This reduces porosity and enhances overall coating density. Pradhan et al. (2024) demonstrated that HVOF-deposited WC-10Co-4Cr + 2% TiO_2 coatings exhibit superior mechanical integrity and flexibility. The dense microstructure produced by this composite formulation is crucial for enhancing adhesion strength and durability under mechanical stress.

Flexibility is a crucial attribute that influences the efficacy of wear-resistant coatings, particularly in scenarios with variable or cyclical loads. An ideal coating must accommodate minor shape alterations without compromising its structural integrity. The incorporation of WC into the TiO_2 matrix enhances stiffness due to WC's superior modulus of elasticity, enabling the coating to more effectively absorb and redistribute stress. This structural strengthening diminishes the likelihood of crack propagation and delamination, hence enhancing the material's performance under repeated use.

Coatings containing WC have demonstrated characteristics of ductile wear behaviour. Qiao et al. (2021) observed that WC-CoCr coatings exhibit signs of plastic deformation, including the creation of grooves and the propagation of cracks. This indicates that they can assimilate greater energy as they deteriorate. These findings demonstrate the effective synergy between WC and TiO_2 in composite systems, wherein the optimal amalgamation of hardness, stiffness, and ductility significantly enhances wear resistance. The amalgamation of these attributes renders WC-TiO_2 composite coatings a formidable contender for applications involving elevated tribological stresses.

3.2.2 Copper (Cu) – TiO_2 Coating

The incorporation of copper (Cu) into titanium dioxide (TiO_2) coatings has markedly enhanced their mechanical strength and wear resistance, particularly in thermally sprayed systems. Copper facilitates the formation of a protective CuO oxide layer at elevated temperatures. This layer prevents the substrate from direct exposure to erosive conditions (Mukanov et al., 2023). The self-lubricating oxide layer, combined with copper's inherent ductility and affordability, renders Cu an advantageous element in wear-resistant coatings. The efficacy of copper, conversely, is significantly contingent upon its concentration. Insufficient Cu will hinder the appropriate formation of the protective layer, while excessive Cu may diminish wear resistance at elevated temperatures. The appropriate quantity of copper is crucial to maximise the tribological advantages of Cu-TiO_2 composite coatings (Toibah et al., 2023).

The thermal characteristics of Cu and TiO_2 are crucial for ascertaining the coating's microstructure and performance. Given that copper melts at 1083 °C and titanium dioxide melts at 1843 °C, it is crucial to meticulously observe the behaviour of each component during deposition. The application of the atmospheric plasma spray (APS) technique to deposit a Cu–TiO_2 composite containing 30% Cu yields a coating that exhibits reduced porosity compared to pure TiO_2. Due to its lower melting point, copper can liquefy and occupy the interstitial spaces between particles during the spraying process, resulting in a denser and more uniform coating. Toibah et al. (2023) observed a 28.7% increase in deposition efficiency, indicating that copper can enhance the thickness and strength of coatings.

The use of Cu enhances the surface quality and tribological performance of the coating. The molten copper functions as a binder, enhancing particle cohesion and resulting in a smoother surface. The densification effect reduces the coefficient of friction (COF), hence enhancing the wear resistance of the composite layer. The interaction between Cu and TiO_2 enhances the uniformity and durability of the coated surface, improving its resistance to thermal and mechanical stress. Cu–TiO_2 composites exhibit potential for the development of high-performance coatings in applications where erosion, friction, and thermal stability are critical.

3.2.3 Aluminum (Al) – TiO_2 Coating

Aluminium (Al) flame-sprayed coatings are employed in various industrial applications due to their exceptional corrosion resistance. Nonetheless, their inherent tribological performance remains insufficient, restricting their application in environments prone to wear. Titanium dioxide (TiO_2) has been used into aluminium matrices to enhance their wear resistance and durability. Microstructural analysis of Al–10% TiO_2 coatings reveals a dense morphology marked by little porosity and strong adhesion to the substrate. Scanning electron microscopy (SEM) images demonstrate that the coating and substrate exhibit effective mechanical interlocking, hence enhancing the integrity of the bond and structure

The ASTM G99 pin-on-disk tribological testing method indicates that including TiO_2 in quantities ranging from 5% to 10% significantly enhances the wear resistance of aluminium coatings (Salimi et al., 2020). The incorporation of hard TiO_2 particles into the aluminium matrix facilitates these improvements. They prevent the removal of material during sliding contact. Exceeding the optimal TiO_2 concentration, particularly beyond 15%, deteriorates wear resistance. This decline is likely due to the inadequate cohesion of the splats, resulting in the detachment of TiO_2 particles under stress.

Excessive TiO_2 might adversely affect the microstructural characteristics of the coating. An increase in TiO_2 correlates with heightened porosity, resulting in diminished strength and increased susceptibility to wear in the composite. The diminished cohesion among splats at elevated TiO_2 concentrations may result in weak points that initiate wear and delamination. Maintaining a balanced TiO_2 content is crucial for achieving a dense, well-adhered coating with excellent tribological performance (Kasach et al., 2021).

Delamination is the primary mechanism by which Al–TiO_2 composite coatings degrade. This is influenced by the microstructure of the coating and the distribution of the particles. Optimising the quantity of TiO_2 enhances the coating's hardness and resistance to sliding wear, while also reducing the likelihood of splats detaching and the coating deteriorating (Kalinowski et al., 2025). The results underscore the necessity of optimising both the composition and processing parameters to enhance the performance of flame-sprayed aluminum-based coatings in tribological applications.

3.3 TiO_2 Ceramic Composite Coating

Experts involved with surfaces are particularly interested in TiO_2 ceramic composite coatings due to its exceptional hardness, thermal stability, and superior performance in tribological assessments. TiO_2-based composites have superior strength, enhanced wear resistance, and improved oxidation protection compared to monolithic TiO_2 coatings when reinforced with secondary phases such as ZnO, Al_2O_3, Cr_2O_3, or metallic particles. The enhancements result from the synergistic interactions between the ceramic matrix and the reinforcing phase, which reduce grain size, increase toughness, and decrease porosity. Plasma spraying and high-velocity oxy-fuel (HVOF) spraying are two conventional deposition techniques employed to produce these coatings. They enable fine control over microstructure and phase distribution. TiO_2 ceramic composites are advantageous in high-temperature and corrosive environments, rendering them suitable for aerospace, marine, and energy sectors where durability under extreme conditions is essential. Table 2 presents selected examples of TiO_2 ceramic coatings that have been investigated by various researcher.

Table 2: TiO_2 Ceramic composite coating.

TiO_2 Ceramic composite coating	**Coating properties**	**Findings**	**Wear testing**	**Reference**
ZnO-TiO_2	Improve wear resistance	Better wear resistance properties can be achieved by addition of ternary oxide	Ball on disc test	Shi et al., 2023
Al_2O3-TiO_2	High fretting wear resistance	Serve as good transitional layer Boost adhesion between substrate and coating High fretting wear resistance	High frequency micro dynamic friction and wear tester	(Wu *et al.*, 2021)(Hanifi *et al.*, 2024)
Cr_2O_3- TiO_2	Coating had a denser structure	Demonstrated the highest corrosion resistance, with minimal weight gain and rust formation	Simulated marine environment using artificial seawater prepared per ASTM D1141 – 98.	Raj Sharma et al., 2022

3.3.1 ZnO-TiO_2 Coating

Zinc oxide (ZnO) works as either a solid lubricant or a high-hardness oxide layer in protective coatings, contingent upon the conditions and its application. Although the two roles operate differently, they both protect the substrate surface from abrasion (Kołodziejczak-Radzimska et al., 2014). ZnO creates a robust, protective barrier that safeguards against external mechanical damage. As a solid lubricant, ZnO forms a smooth, low-shear surface layer that reduces interfacial friction and prevents material loss (Nassef et al., 2024). These wear resistance processes are particularly effective at elevated temperatures, where the production and transformation of ZnO phases are thermally induced.

The use of titanium dioxide (TiO_2) and zinc oxide (ZnO) into composite coatings has proven to enhance their wear resistance, particularly in elevated temperature environments. This enhancement results from the synergistic interaction of both oxides, which diminishes friction and better maintains the surface (Shi et al., 2023). The atmospheric plasma spray (APS) technology was employed to apply TiO_2–ZnO coatings on GH4169 alloy substrates in a recent study. A ball-on-disc tribometer was employed to evaluate the performance of these coatings at varying temperatures. The coatings exhibited low coefficients of friction at both ambient temperature and 400 °C; yet, their wear rates remained elevated.

Notably, the wear rate remained elevated even at 800 °C, a temperature typically optimal for oxide-based lubrication. The unexpected outcome resulted from insufficient oxide formation, which hindered the coating's ability to establish a solid lubricating film. The lack of adequate lubrication at elevated temperatures led to increased material deterioration, indicating a need for compositional improvement. The coating's capacity to endure wear under intense thermal stress was constrained due to the absence of ternary oxides or other lubricating elements.

Shi et al. (2023) performed supplementary research that supports this finding, demonstrating a significant improvement in tribological performance with the incorporation of molybdenum trioxide (MoO_3) into the TiO_2–ZnO combination. The incorporation of MoO_3 enhanced lubrication at elevated temperatures by forming layered oxides capable of deforming under stress, so reducing both friction and wear. These results demonstrate the significance of oxide composition and phase interactions in determining the efficacy of thermally sprayed ceramic coatings. Meticulous material design and the use of complementary oxide lubricants for high-temperature applications can significantly enhance the performance of TiO_2–ZnO coatings.

3.3.2 Al_2O_3-TiO_2 Coating

Fabrication of Al_2O_3-based ceramic matrix composites is a useful route to increase the fracture toughness of the material by adding secondary phases like metal and ceramic particles (Yıldız et al., 2023). Researchers extensively examine air plasma sprayed (APS) ceramic composite coatings due to their exceptional durability and wear resistance, particularly in challenging environments. Wu et al. (2021) investigated the fretting wear characteristics of AT40 (Al_2O_3-40 wt.% TiO_2) and Al_2O_3/AT40 composite coatings on TC6 titanium alloy substrates. Wu and teams employed APS to apply the coatings, followed by utilising a ball-on-flat tribometer to evaluate their wear under varying normal loads and displacement amplitudes. The findings indicated that both coatings exhibited significant resistance to fretting wear. The Al_2O_3/AT40 composite exhibited superior wear stability and a reduced friction coefficient compared to the monolithic AT40 covering.

The superior wear resistance of the Al_2O_3/AT40 composite can be attributed to its dense microstructure and robust interfacial bonding, which inhibited crack propagation and material separation during repeated contact. The microstructural analysis revealed uniformly distributed TiO_2 particles within the Al_2O_3 matrix (Michalak et al., 2020). These particles facilitated load distribution and mitigated surface damage. The composite coating exhibited reduced wear depth and volume loss, indicating that the amalgamation of Al_2O_3 and TiO_2 phases collaboratively enhanced the tribological performance under stressing conditions. This research validates the effectiveness of Al_2O_3-based composites for applications involving oscillatory motion and contact stress.

Concurrently, Hanifi et al. (2024) investigated the mechanical and tribological characteristics of NiAl/Al_2O_3-40 wt.% TiO_2 coatings fabricated by atmospheric plasma spraying on metallic substrates. This coating method employs a ductile NiAl matrix combined with a hard ceramic reinforcement phase to enhance its fracture toughness while maintaining exceptional wear resistance. The research revealed that incorporating Al_2O_3-40 wt.% TiO_2 significantly enhanced the coating's resistance to sliding and abrasion wear. This was due to its formation of a microstructure that adhered effectively and prevented the propagation of cracks. Fracture toughness assessments indicated that the NiAl matrix possesses sufficient ductility to withstand stress without compromising the coating.

Both researches demonstrates that Al_2O_3-TiO_2 systems can enhance the tribological properties of thermal spray coatings in various manners. Wu et al. examined the enhanced resistance of Al_2O_3/AT40 composites to fretting, whereas Hanifi et al. demonstrated that the incorporation of a NiAl matrix further augments their mechanical strength and stability under substantial loads. These findings offer critical insights for the improvement of ceramic-metal composite coatings designed for aerospace, marine, and industrial applications, where fretting, abrasion, and high contact stresses pose considerable challenges.

4.0 THERMAL SPRAY METHODS FOR TIO_2-BASED WEAR-RESISTANT COATINGS

Thermal spray techniques have emerged as efficient and versatile methods for applying TiO_2-based coatings to metal surfaces, enhancing their wear resistance under harsh conditions. Atmospheric Plasma Spraying (APS), Suspension Plasma Spraying (SPS), High-Velocity Oxy-Fuel (HVOF), and Solution-Precursor HVOF (S-HVOF) are various technologies, each offering distinct advantages regarding the microstructure, phase composition, and mechanical properties of coatings. APS and SPS facilitate high-temperature deposition, resulting in coatings that are thick and adhere effectively. HVOF and S-HVOF provide coatings that exhibit reduced porosity and increased hardness due to the accelerated velocity of their particles. The selected procedure significantly influences the hardness, wear rate, and coefficient of friction of TiO_2 coatings. The spraying technique must be customised to meet the application's requirements. These thermal spray techniques are extensively utilised in industries such as aerospace, marine, and energy because to their cost-effectiveness and versatility.

4.1 Atmospheric Plasma Spray

Atmospheric Plasma Spray (APS) is a prevalent thermal spray technique that employs a high-temperature plasma jet to melt and deposit feedstock materials, often in powder form, onto a substrate (Figure 2). The characteristics of the resultant coating are significantly influenced by many processing parameters, including the rate of powder feed, the distance from the spray to the surface, and the composition of the carrier gas. A higher powder input rate generally results in a thicker coating. Płatek et al. (2025) assert that a feed rate of 20 g/min produced a thicker coating compared to a feed rate of 10 g/min. A feed rate of 15 g/min yielded the most substantial outcome, indicating a non-linear correlation. Porosity is a common characteristic of APS coatings and is significantly influenced by the process parameters. Reduced hydrogen flow, a diminished feed rate, and an extended spray distance together contribute to increased porosity levels. Conversely, increased hydrogen flow has been demonstrated to reduce porosity, hence enhancing the strength of the coating (Shi et al., 2023; Płatek et al., 2025).

The chemical composition of the feedstock powder is equally significant as the process parameters for the final coating's mechanical and microstructural properties. Altering the concentration of TiO_2 in Al_2O_3–TiO_2 coatings affects their performance. AT13 (Al_2O_3 + 13 wt.% TiO_2) and AT40 (Al_2O_3 + 13 wt.% TiO_2) coatings exhibit significantly reduced porosity compared to AT0 coatings. This is mostly due to their higher TiO_2 content, which alters their melting characteristics. The increased TiO_2 concentration in AT40 enhances the efficacy of heat treatment during deposition, resulting in a denser microstructure (Nowakowska et al., 2021). The hardness of AT0 (AT13 (Al_2O_3 + 0 wt.% TiO_2) remains superior, as it lacks TiO_2, which is inherently softer. The surface roughness is also influenced. AT40 has the lowest roughness because to its bimodal microstructure, which facilitates a smoother surface.

Wear resistance is a critical performance metric when evaluating coatings for erosive environments. When utilised using the APS process, the AT13 coating exhibits superior wear performance compared to all Al_2O_3–TiO_2 compositions. In dry sliding wear tests, AT13 demonstrated minimal wear, with just slight delamination seen, outperforming coatings with different TiO_2 concentrations. AT13's exceptional wear resistance renders it an optimal selection for protective coatings in mechanical applications subjected to significant stress. These findings highlight the importance of deposition environments and material composition in improving APS-applied coatings for specific functional requirements. Table 3 shows selected examples of the use of the Atmospheric Plasma Spray method for the deposition of TiO_2-based coatings.

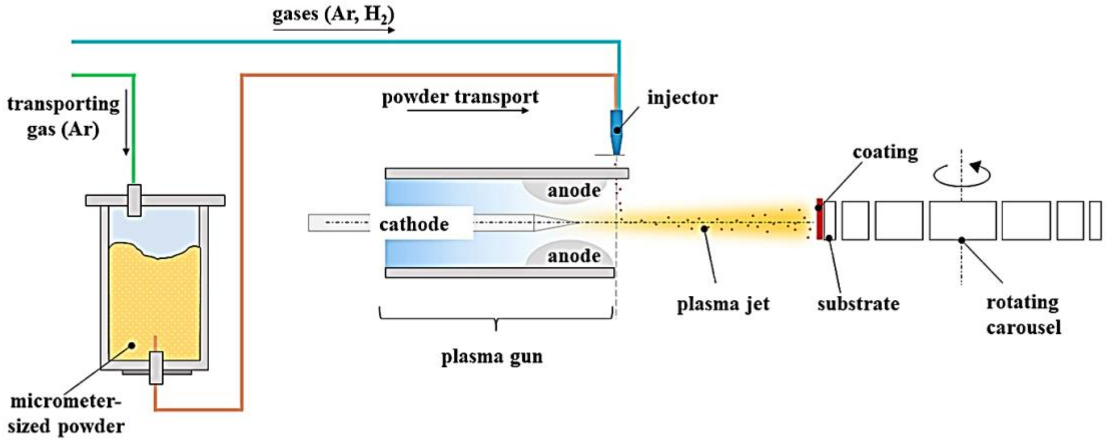


Figure 2: Configuration of deposition system based on Płatek et al., 2025.

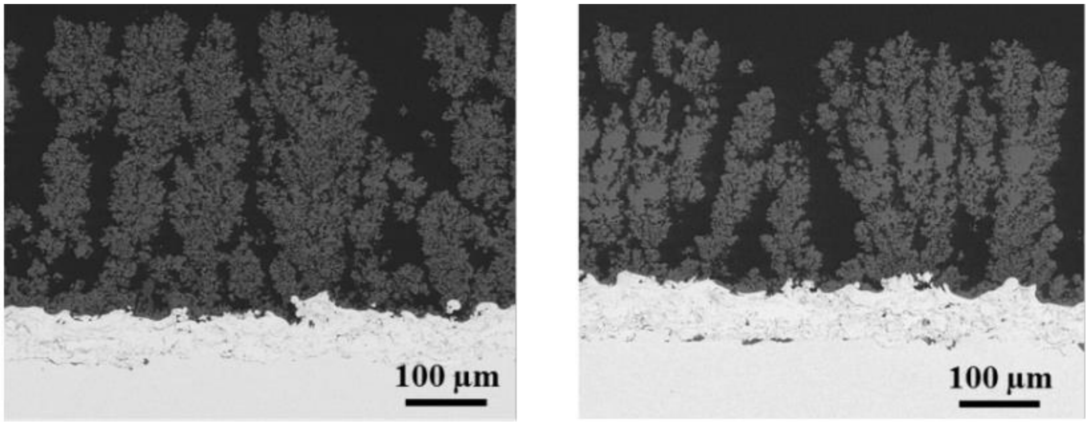
4.2 Suspension Plasma Spray

Suspension Plasma Spray (SPS) is an advanced thermal spray technique that employs nano-sized feedstock powders dispersed in a liquid medium. The particles are then introduced into a plasma plume and deposited onto a substrate. SPS facilitates the production of finely structured coatings with superior functional properties compared to conventional methods. A cross-sectional scanning electron microscopy (SEM) analysis of Al_2O_3–TiO_2 coatings with varying TiO_2 concentrations revealed a significant presence of uniformly distributed pores, characteristic of SPS processing (Nowakowska et al., 2021) (Figure 3). The AT40 coating exhibited a relatively low surface roughness in comparison to the other compositions. Nonetheless, its Ra value remained slightly higher than that of coatings produced by Atmospheric Plasma Spray (APS). This divergence arises from SPS depositing nano-sized particles that expose the bond coat from prior APS processes. The AT0 coating exhibited a tougher surface compared to other coatings due to its increased density and absence of additional TiO_2, which could compromise the matrix.

In dry sliding wear testing, the primary mechanism of degradation for SPS coatings was fatigue-induced deterioration. The AT0 coating experienced significant material loss due to smearing effects, resulting in a less steady wear response. Conversely, AT40 coatings exhibited less dispersion of wear products, indicating superior stability in tribological performance. AT13 coatings exhibited little smearing and shown enhanced wear resistance. This likely occurred due to the formation of a homogeneous and protective tribofilm layer on the surface during sliding, preventing direct contact between the materials and subsequent degradation (Nowakowska et al., 2021). These results demonstrate the significance of optimising the TiO_2 concentration and coating architecture for enhanced performance in tribological applications.

Table 3: Atmospheric Plasma spray for TiO2- based coatings.

Coating Types	**Scope of study**	**Findings**	**Reference**
TiO_2	Varying parameter variable: Hydrogen flow (SLPM) Powder feed rate (g/min) Spray distance (mm)	Low porosity coating can be achieved by: Increase hydrogen flow (SLPM) Low powder feed rate (g/min) Increase spray distances	Płatek et al., 2025
AT0,AT13,AT40	Using different type of coating with constant spraying parameter	AT13 and AT40 shows lower porosity AT0 has the highest hardness value AT40 has lowest surface roughness AT13 has lowest wear rates	Nowakowska et al., 2021
AT40	Varying parameter variable: Different standoff distance Torch scanning speed	Shorter standoff distance (80mm): Increase hardness and wear resistance Lower COF value Increase torch velocity (500mm/s): Decrease porosity Improve cavitation erosion resistance	Łatka et al., 2023



(a) (b)

Figure 3: Cross-sectioned images of SEM (a) AT3 (b) AT40 (Nowakowska et al., 2021).

4.3 High Velocity Oxy Fuel (HVOF)

High Velocity Oxy-Fuel (HVOF) spraying is a thermal spray technique that utilises the combustion of fuel gases, often hydrogen, propane, or kerosene, combined with oxygen to generate a high-temperature, high-pressure gas stream. This stream accelerates the feedstock powder to velocities exceeding the speed of sound before impacting and adhering to the target substrate. The procedure occurs within a regulated combustion chamber, where the elevated kinetic energy of the particles facilitates the formation of thick, adherent coatings.

The HVOF technique offers a distinct advantage by producing coatings with superior mechanical and tribological properties. HVOF coatings often exhibit high hardness, exceptional wear resistance, and a clean surface finish. The qualities arise from the process's low-temperature input and high particle velocity, which diminish oxidation and porosity while enabling the molten or semi-molten particles to flatten and adhere efficiently upon impact.

The HVOF process exhibits a high flame temperature, ensuring that the feedstock powder sufficiently melts or attains a plastic state to enhance adhesion and bonding with the substrate. Consequently, coatings produced using HVOF spraying exhibit structural strength and the capability to endure demanding operational conditions. This renders the method particularly advantageous for wear-sensitive applications in the aerospace, marine, and heavy industries. Table 4 shows selected examples of the use of the High Velocity Oxy-Fuel method for the deposition of TiO_2-based coatings.

Table 4: High velocity oxy fuel (HVOF) spray for TiO2- based coatings

Coating	**Scope of study**	**Findings**	**Reference**
WC-10Co-4Cr + 2% TiO_2	Erosion wear performance of WC-10Co-4Cr + 2% TiO_2 coating using HVOF	High hardness (1230 HV) Reduce wear Ductile mass loss behaviour in erosion testing	Pradhan et al., 2024
Ni-20Cr2O3 Ni-20Al2O3 Ni-15Cr2O3-5TiO_2 Ni-15Al2O3-5TiO_2	Using different type of coating with constant spray parameter	All samples produced has increase slurry erosion resistance and better erosion resistance compared to uncoated substrate	Singh et al., 2021

CONCLUSIONS

TiO_2 coatings provide robust and adaptable protection for components against wear and corrosion in demanding industrial environments. The crystalline structure of these coatings significantly influences their performance. Structures containing a higher proportion of rutile have superior mechanical strength and thermal stability. The incorporation of TiO_2 into metal or ceramic composite systems, such as those including WC, Al_2O_3, or ZnO, enhances their wear resistance, hardness, and strength. Techniques such as APS, SPS, and HVOF influence the microstructural characteristics of coatings and significantly affect tribological outcomes, including the coefficient of friction and erosion resistance. Altering these features and compositions enables the creation of coatings that are optimal for certain applications and perform effectively in challenging situations. Current knowledge indicates that coatings comprising a rutile-rich TiO_2 phase, reinforced with secondary oxides such as Al_2O_3 or Cr_2O_3, and applied using high-energy techniques like micro-arc oxidation (MAO) or plasma spraying, exhibit the optimal balance of hardness, adhesion, and wear resistance. The results suggest that the continuous development of TiO_2-based composite coating technologies is vital for extending service life, reducing maintenance costs, and improving the efficiency of important industrial processes.

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