



# Advances in Laser-Clad, Particle-Reinforced Wear-Resistant Coatings: Enhancing Durability Through Material Innovation



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**Abstract:** The quest for superior wear-resistant coatings has led to significant advancements in laser cladding technology, yet the escalating requirements for durability under operational conditions challenge the efficacy of existing solutions. This investigation delves into the enhancement of wear resistance in coatings through the integration of particle reinforcement phases, identified as a cost-effective strategy for augmenting coating performance. Emphasis is placed on the systematic classification of particle reinforcements and the methodologies employed for their incorporation. The focus is particularly cast on the incorporation of hard and self-lubricating particles into laser-clad wear-resistant coatings, highlighting innovations in particle addition techniques. An examination of the mechanisms through which hard particles—comprising oxides, carbides, nitrides, borides, and their multifaceted compounds—reinforce coatings is presented, delineating the influence of particle content, size, and morphology on wear resistance. Additionally, the paper explores the state of research on the self-lubricating properties imparted by sulfides, fluorides, graphite, and MAX phase particles under varied thermal conditions. A critical analysis of the benefits and limitations associated with the use of hard and self-lubricating particles in the enhancement of coating durability is conducted. This comprehensive review serves not only to elucidate the current landscape of particle-reinforced, laser-clad coatings but also to inform future research directions aimed at developing coatings capable of withstanding high temperatures and exhibiting exceptional hardness. The commitment to leveraging in situ synthesis for the development of these advanced materials underscores the potential for significant breakthroughs in the field of wear-resistant coatings.

**Keywords:** Laser cladding; Particle reinforcement; Wear resistance; Self-lubricating; In-situ synthesis

## 1 Introduction

Laser cladding technology, following thermal spraying and electroplating, represents another surface modification technique. Its principle is essentially identical to thermal spraying, utilizing a high-density laser as the heat source to melt materials and solidify them on the substrate surface to form a coating. Laser cladding technology first emerged in the 1970s [1], but due to technological limitations, it did not gain widespread attention until the late 80s and 90s, when it gradually entered the public eye. Today, laser cladding technology is widely applied in surface protection of vulnerable components, rapid repair of worn surfaces, and re-manufacturing of parts [2, 3].

Although coatings prepared by laser cladding exhibit excellent performance, the increasingly complex conditions of working environments mean that laser-clad coatings can no longer meet performance needs, especially wear-resistant coatings, which must withstand faster speeds and higher temperatures. To meet the wear resistance of coatings under complex conditions, it is often chosen to add particles to enhance the wear resistance of the clad coating. For example, cladding nickel-based coatings reinforced with (Ti, W) C particles on the surface of centrifugal pump impellers eliminates grooving on the impeller surface, reduces wear, and significantly extends the life of the centrifugal pump [4]. Creating a cobalt-based coating reinforced with WC on the surface of mining picks improves

the wear resistance of the pick surface, extending the life of the parts [5]. Due to the discontinuous particle reinforcement, material homogeneity, and simplicity of preparation, particle-reinforced coating technology has become an important technique for preparing wear-resistant coatings on components. This article briefly outlines the classification of particle-reinforced wear-resistant coatings and methods of particle addition, focusing on the research of different particles in enhancing the wear resistance of coatings, and summarizes and prospects the development of particle-reinforced coatings' wear resistance, to promote the development and application of particle reinforcement technology in wear-resistant coatings.

## 2 Classification of Wear Resistance in Particle-Reinforced Coatings

The common mechanisms of wear resistance enhancement in particle-reinforced coatings include fine grain strengthening, solid solution strengthening, second phase strengthening, and anti-wear strengthening. There are multiple strengthening mechanisms during the process of enhancing the performance of particle-reinforced coatings. A comprehensive analysis of the mechanisms of wear resistance in particle-reinforced coatings shows that the enhancement of wear resistance mainly falls into two categories: wear resistance enhancement and friction reduction enhancement.

Wear resistance enhancement refers to the ability of the coating to resist deformation after the addition of particles, generally reflected in the enhancement of the coating's hardness to achieve a wear-resistant effect. Friction reduction enhancement refers to the reduction of the coating's surface roughness after the addition of particles, achieving resistance to material removal by reducing frictional forces, thus enhancing the wear resistance of the coating.

## 3 Methods of Particle Addition

The effect of strengthening varies with different methods of particle addition. Currently, there are two main approaches to adding particles: direct addition and in-situ synthesis.

Direct addition involves directly mixing the reinforcing particles into the cladding powder. This method is simple and convenient, but the reinforcing particles are prone to oxidation with oxygen in the air under the high temperatures of the laser or to react with substances in the powder, reducing the corresponding particle-reinforced phase in the coating. In severe cases, brittle phases may form. To avoid this, particle encapsulation technology is often used to encapsulate the particles, thus preventing melting and decomposition.

In-situ synthesis utilizes the particle addition technology that fully takes advantage of melting, decomposition, and then reaction, by placing substances that can generate particle-reinforced phases into the cladding powder. During the coating preparation, a reaction occurs to synthesize the reinforcing phase. This technology often results in coatings that have good wettability with the substrate and uniform particle distribution. The drawback is that the control is relatively poor, the content of the reinforcing phase is difficult to control, and the interaction of mixing enthalpy between elements needs to be considered.

## 4 Application Research on Particle-Reinforced Wear-Resistant Coatings

### 4.1 Application Research on Coating Wear Resistance Enhancement

Wear resistance enhancement often aims to increase the hardness of the coating to enhance its wear resistance. To achieve such an outcome, hard particles are commonly used as additives, including oxides, nitrides, carbides, borides, and Ti (B, C, N) compounds.

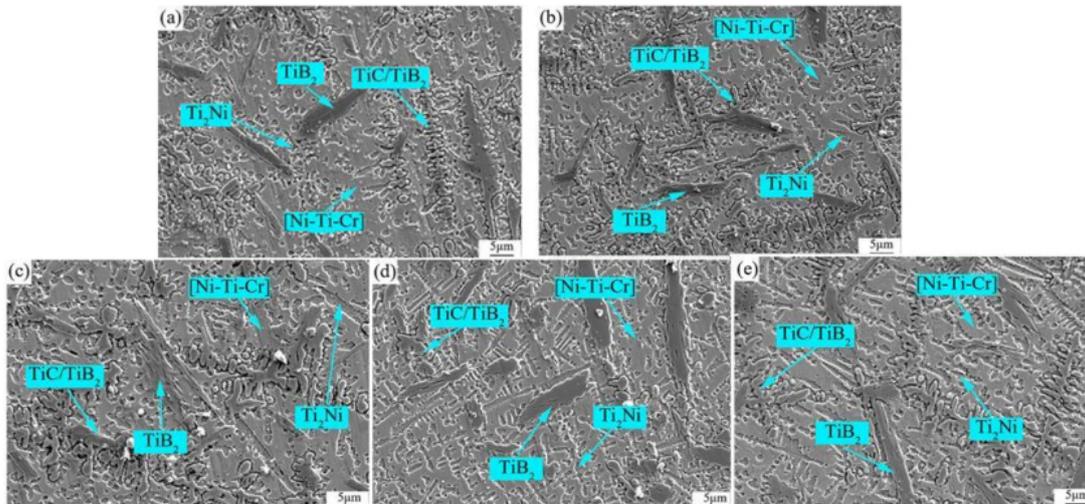
#### 4.1.1 Oxide hard particles

The most commonly used oxide for hard particle reinforcement is  $Al_2O_3$ .  $Al_2O_3$  is inexpensive and high-temperature resistant, with a hardness second only to diamond in nature, fitting perfectly with the mechanism of enhancing wear resistance.  $Al_2O_3$  can induce undercooling at the dendrite interface, promoting nucleation of the liquid metal and hindering further growth of dendrites, resulting in a finer and denser coating structure. The highest microhardness that can be achieved by  $Al_2O_3$  reinforced nickel-based coatings can reach 1127HV [6]. In the study of the structure of reinforced coatings, the presence of  $Al_2O_3$  reinforcing phase was not found in coatings prepared under different granularities and energy densities [7, 8]. As shown in Figure 1, element analysis was conducted on the four major structures in coatings prepared with different laser energy densities. The gray structure A, gray-white structure B, gray-black strip structure C, and dendritic structure D all lack aluminum oxide, indicating that aluminum oxide completely decomposes, contributing to solid solution strengthening and fine grain strengthening.

#### 4.1.2 Carbide hard particles

Commonly used carbide reinforcing particles include SiC, TiC, and WC. TiC, known for its high melting point and hardness, possesses a thermal expansion coefficient compatible with iron-based materials, offering good wettability and interfacial bonding strength with iron-based substrates, making it frequently used as a reinforcing particle for iron-based coatings. WC, with its high melting point, high hardness, and low thermal expansion coefficient,

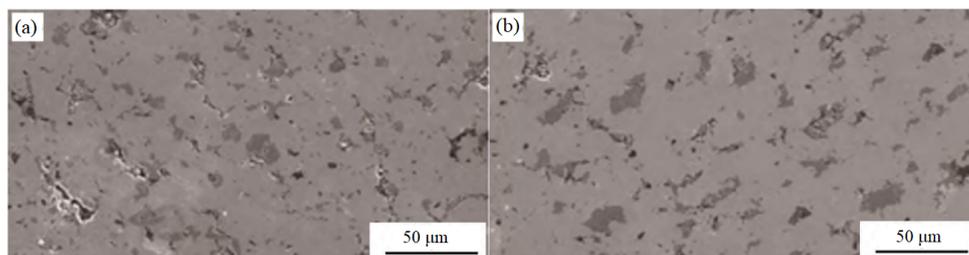
exhibits good wettability with nickel-based materials and is often used as a reinforcing particle for nickel-based coatings [9, 10].



**Figure 1.** High magnification of microstructure in the middle of Ni60A-Al<sub>2</sub>O<sub>3</sub> cladding layer under different laser energy densitie [7] (a) 108.4 j/mm<sup>2</sup> (b) 116.7 j/mm<sup>2</sup> (c) 125 j/mm<sup>2</sup> (d) 133.3 j/mm<sup>2</sup> (e) 141.7 j/mm<sup>2</sup>

(1) SiC

Adding SiC particles to cobalt-based materials can improve the wear resistance of cobalt-based coatings. However, SiC/Co coatings are composed of a  $\gamma$ -Co and Cr<sub>23</sub>C<sub>6</sub> eutectic structure, without the presence of SiC hard particle phase [11]. Subsequent research found that the size of SiC particles plays a different role in the wear resistance of the coating [12]. Micron-sized silicon carbide is not completely decomposed during the laser cladding process and can act as a hard point to enhance the coating’s wear resistance. Nano-sized silicon carbide is completely decomposed, producing high-hardness compounds that increase the hardness of the coating. However, both nano and micron-sized silicon carbide are prone to react with the substrate at high temperatures, and the difference in thermal expansion coefficients can significantly reduce the coating’s performance [13]. To address this issue, Zhong et al. [14] successfully improved the density of the coating and mitigated interface defects between SiC particles and the substrate by electroless copper plating on  $\alpha$ -SiC powder, reducing the interfacial reactions and mismatches between SiC particles and the substrate. As shown in Figure 2, a comparison of the coating morphology between coated and uncoated particles reveals that coatings prepared with coated particles have significantly reduced porosity and cracks.

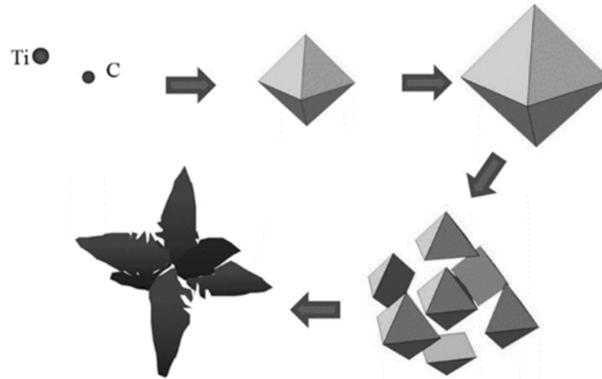


**Figure 2.** Microstructure of iron matrix composites before and after  $\alpha$ -SiC copper plating [14] (a) Before copper plating (b) After copper plating

(2) TiC

Ertugrul et al. [15] utilized TiC to reinforce 316L stainless steel composite materials, finding that the hardness enhancement of the TiC-reinforced coating was mainly due to titanium carbide powder dissolving in the austenite, precipitating carbides, and thus increasing the coating hardness by 100 HV. The wear resistance of the coating first increased and then decreased with the addition of TiC. At higher concentrations, TiC tended to agglomerate, leading to cracks forming along the edges of the particles [16]. Generally, in-situ synthesis yields better reinforcement effects, but under low power pulse conditions, in-situ synthesized TiC in iron-based coatings was found to be less effective than direct addition. Zhang et al. [17] discovered that at low power, Fe and Ti react more readily, producing

too little TiC to significantly enhance the wear resistance of the clad layer. Zhang et al. [18] observed the growth pattern of TiC crystals formed by in-situ synthesis of Ti and C. As shown in Figure 3, Ti and C synthesize octahedral TiC crystals that grow and split upon encountering undercooled liquid in the coating. The split crystals continue to grow and split again, eventually forming dendritic TiC structures. In-situ synthesized TiC has an excellent thermal conductivity, which facilitates rapid heat dissipation, can inhibit grain growth, promote the formation of fine-grained structures, and also produce a stable  $\alpha$ -Ti/TiC interface bonding mode. Guo et al. [19] used titanium powder and carbon powder for in-situ synthesis of titanium carbide to reinforce nickel-based coatings, but this method requires high precision in the process. Subsequent researchers developed methods using SiC+Ti and B<sub>4</sub>C+Ti for in-situ synthesis of titanium carbide to enhance the wear resistance of nickel-based coatings [20, 21].



**Figure 3.** Diagram of in situ TiC growth [18]

### (3) WC

Guo et al. [22], in a study on the impact of WC content on the wear resistance of nickel-based coatings, found that the enhancement of wear resistance and hardness in the coating is primarily due to the solid solution strengthening of  $\gamma$ -Ni and the precipitation of hard phases such as WC, Cr<sub>23</sub>C<sub>6</sub>, and W<sub>2</sub>C. The optimal wear resistance of the coating was achieved when the WC addition was 45%. The grain size and shape of WC also significantly affect the coating's reinforcement performance [23, 24]. The smoother and smaller the WC particles, the more tightly they are encapsulated within the coating, making the hard particles less likely to detach during friction. The optimal wear resistance of the coating, which can be up to five times that of NiCrBSi, is achieved with WC particles of 1  $\mu$ m in size.

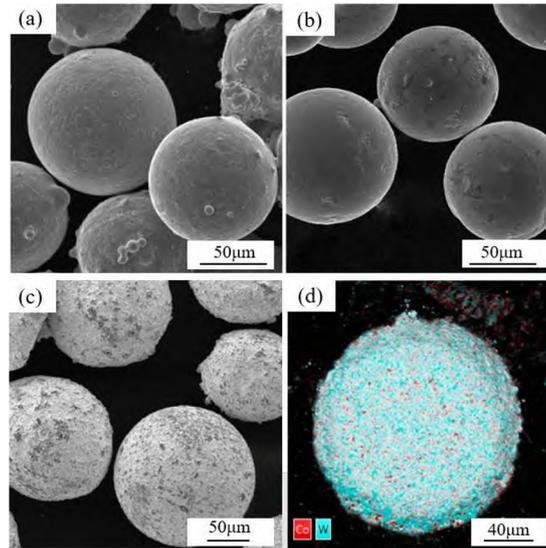
WC undergoes decomposition in laser cladding, with part of the carbon oxidizing to form gas that cannot escape, affecting the coating's density. The method of encapsulating WC in nickel can prevent the decomposition of WC. As the content of nickel-encapsulated WC increases, the effect of fine-grain strengthening in the coating becomes very apparent, further enhancing the wear resistance of the coating [25]. There are also methods of attaching Co to the surface of WC. Figure 4 is a comparison between WC and Co-encapsulated WC, where Co encapsulation improves the sphericity of the particles and prevents the decomposition of WC. The microhardness of the prepared WC-Co/HEA composite coating reached 882.55 Mpa, exhibiting superior wear resistance compared to WC/HEA composite coatings and also outperforming Ni60/WC composite coatings prepared by vacuum diffusion bonding [26].

In-situ synthesis of WC hard particles commonly utilizes carbon (C) and tungsten (W) powders. Due to the lower Gibbs free energy of W<sub>2</sub>C, prolonged laser irradiation is required to provide the energy necessary for WC synthesis. Research has found that the synthesis of WC from C and W results in more WC production and finer particles with smaller grain sizes of W powder. When W powder is 23  $\mu$ m in size, the produced WC is hexagonal, and its wear resistance can reach 602 times that of the substrate [27].

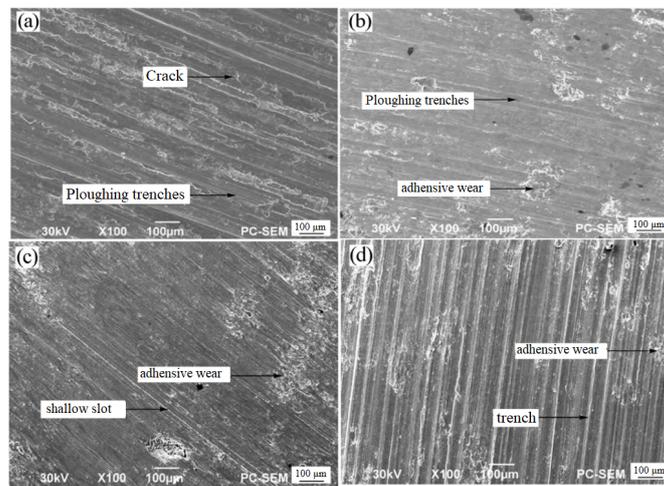
#### 4.1.3 Nitride hard particles

Commonly used nitride particles for reinforcement include TiN, which is characterized by high hardness, high wear resistance, and high melting point, and is less expensive than WC, making it a promising substitute for WC. Like other hard particles, titanium nitride also decomposes; upon decomposition of TiN, Ti preferentially reacts with C to precipitate TiC hard phases. TiN and TiC particles have good compatibility and low internal stress, meaning that using TiN to reinforce cobalt-based materials actually forms a dual-phase reinforcement [28–30]. Wang and Hu [31] utilized the “pre-nitridation + pulsed laser cladding” method to leverage the rapid heating and cooling characteristics of laser cladding, refining large-sized particles to form a novel intrinsic reinforced phase with micro and nano TiN “nested” within each other, improving hardness characteristics more effectively in depth. Comparing coatings made of nano TiN and sub-micron TiN, the morphology of the coatings after friction wear, as shown in Figure 5, reveals that coatings with nano-level TiN only show shallow grooves left by friction, while those without nano-level TiN

reinforcement exhibit plough-shaped grooves [32]. Increasing the content of nano TiN can further refine the coating structure and enhance its hardness, but it can weaken the bonding strength between the hard phase and the surrounding matrix; nano TiN particles may also collide and aggregate in the melt pool, gradually increasing in size [33]. To address the issue of particle aggregation, laser cladding technology has been combined with ultrasonic technology to form the “ultrasonic-laser cladding technology”. Xia et al. [34] successfully suppressed particle aggregation using this technique, preparing reinforced coatings with fine particles and uniform distribution.



**Figure 4.** Surface morphology and element distribution of particles [26] (a) (c) Surface morphology and element distribution of WC (b) (d) Surface morphology and element distribution of Co-WC



**Figure 5.** Wear morphology of different types of TiN reinforced coatings (a) Zirconium alloy coating (b) Submicron TiN (c) 5% nanoscale TiN+95% submicron TiN (d) Submicron nitrogen-rich TiN [32]

Research on in-situ synthesis of titanium nitride is scarce. Wang and Hu [31] mixed titanium powder with nickel-based alloy and conducted nitridation in a nitrogen-rich atmosphere, resulting in a golden-yellow titanium nitride reinforced coating. Ma et al. [32] used titanium powder and aluminum nitride for in-situ synthesis, finding that the shape of synthesized titanium nitride could change from rod-like to particle-like under the influence of powder ratio and laser power. Ding et al. [35] synthesized titanium nitride reinforced cobalt-based wear resistance using vanadium nitride and titanium powder; after a heat treatment at 650°C for five hours, the coating’s grains were refined, and its microhardness was enhanced, improving the wear resistance of the reinforced coating.

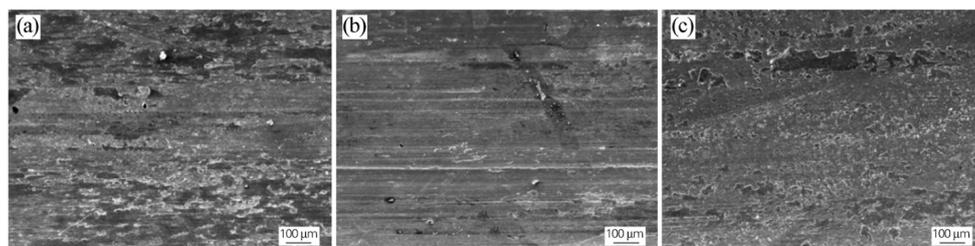
#### 4.1.4 Boride hard particles

The commonly used borides include TiB and TiB<sub>2</sub>. TiB<sub>2</sub>, with its high hardness and thermal expansion coefficient close to that of nickel-based materials, is often used to reinforce nickel-based coatings. Meanwhile, TiB,

with a thermal expansion coefficient and density similar to that of titanium and not chemically reacting with titanium, is generally used to reinforce titanium-based coatings.

Adding  $\text{TiB}_2$  particles to nickel-based alloys can cause the structure to grow into fine equiaxed crystals, forming a polycrystalline grain array. Under stress, the particles coordinate with each other, enhancing the resistance to deformation, hindering the further expansion of cracks, and improving the hardness and wear resistance of the coating [36, 37]. Besides forming a polycrystalline grain array, the boron element decomposed from  $\text{TiB}_2$  can strengthen grain boundaries, and the titanium element can produce hard phases like  $\text{TiB}$  and  $\text{TiC}$ , increasing the hardness of nickel-based coatings by 15.4% [38]. When reinforcing cobalt-based materials with  $\text{TiB}_2$ , un-melted  $\text{TiB}_2$  acts as heterogeneous nucleation sites in the cobalt base, causing  $\gamma\text{-Co}$  to radiate growth around  $\text{TiB}_2$ , forming a dense and uniform “plum blossom-shaped” dendritic structure. Titanium synthesized  $\text{TiC}$  is distributed between dendrites, which oxidizes into  $\text{TiO}_2$  self-lubricating particles during friction, enhancing the wear resistance of the coating. Co and Ti can also form an intermetallic compound  $\text{Co}_3\text{Ti}$  with excellent ductility, improving the coating’s resistance to adhesive wear. According to the wear morphology of the coating shown in Figure 6, coatings at 2 wt% and 4 wt% show spalling wear, indicating that the optimal particle addition amount of  $\text{TiB}_2$  should be 4 wt% [39, 40].

For the in-situ synthesis of  $\text{TiB}_2$ , the commonly used materials are titanium powder and boron powder. From thermodynamic and kinetic perspectives, the tendency to form  $\text{TiB}_2$  from titanium powder and boron powder is stronger than forming  $\text{TiB}$  [41, 42]. Zhang et al. [43] studied the preparation process of  $\text{TiB}_2$  from boron powder and titanium powder, finding that coatings synthesized in-situ from titanium and boron powder always exhibited cracks and pores regardless of the laser power, scanning speed, and defocus amount used in the experiment. Wang et al. [44] investigated the phenomenon of cracking in in-situ synthesis and found that cracks originated from the solidification process, interface stress, and particle segregation, making cracks difficult to avoid. Overall, coatings reinforced with in-situ synthesized  $\text{TiB}_2$  are not as effective as those with directly added hard particles.



**Figure 6.** SEM morphology of wear surface of cladding layer with different  $\text{TiB}_2$  content [41] (a) 2% (b) 4% (c) 6%

For the direct addition of  $\text{TiB}$  particles to enhance titanium alloy coatings, achieving wear-resistant coatings with good wear loss and friction coefficients requires an increase in laser power [45]. For in-situ synthesis of  $\text{TiB}$ , both increasing the laser power and the scanning speed can reduce defects in the coating and improve its wear resistance. Although  $\text{B}_4\text{C}$ ,  $\text{BN}$ ,  $\text{ZrB}_2$ ,  $\text{LaB}_6$  can all synthesize  $\text{TiB}$  with titanium powder, other substances are produced during synthesis, leading to many uncertainties in the formation of  $\text{TiB}$  [46–48]. Currently, the best method of synthesis is using  $\text{TiB}_2$  and  $\text{Ti}$  powder to synthesize  $\text{TiB}$ . Lin et al. [49] conducted in-situ synthesis of  $\text{TiB}$  on a titanium alloy substrate using  $\text{TiB}_2$  and found that the coating had a gradient distribution; the upper layer was primarily reinforced with  $\text{TiB}_2$  phase, the middle contained both  $\text{TiB}_2$  and  $\text{TiB}$  phases, and the bottom layer was mainly  $\text{TiB}$ . There exists a fixed orientation relationship between  $\text{TiB}$  and  $\text{Ti}$ , with the interface mostly in coherency or semi-coherency, and the bottom layer of  $\text{TiB}$  significantly enhances the bonding strength between the coating and the substrate [50, 51]. Since the hardness of  $\text{TiB}$  is less than that of  $\text{TiB}_2$  [52], the hardness of the coating shows a gradient distribution, with microhardness 2-3 times greater than that of the substrate. In-situ synthesized  $\text{TiB}$  reinforced coatings also exhibit cracks, mainly due to the high melting point of the added  $\text{TiB}_2$ , which does not easily dissolve in the titanium melt. Adding more titanium powder can help encapsulate  $\text{TiB}_2$ , reducing the formation of cracks within the coating [53].

#### 4.1.5 Ti (B, C, N) compounds

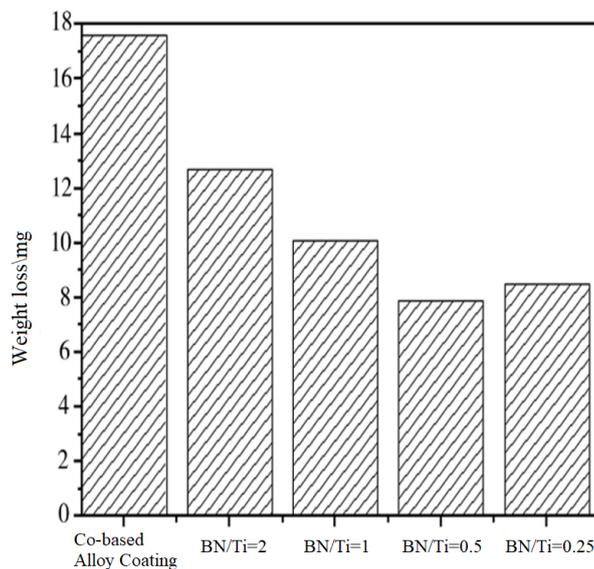
The performance of commonly used hard particles and in-situ synthesized materials are shown in Table 1. Although individual particles can improve the wear resistance of coatings, the enhancement by a single type of particle is always limited. Moreover, the addition of a single type of particle does not only produce a single hard reinforcing phase, and the study of multi-element reinforcing particles is an important direction. The research by Qi et al. [54] primarily focused on the in-situ synthesis of Ti (C, N) ternary compounds to reinforce iron-based coatings for wear resistance, utilizing fine  $\text{TiN}$  particles and graphite powder. The coatings prepared by laser cladding mainly consisted of  $\alpha\text{-SiC-Fe}$ ,  $\text{Ti (C}_{0.3}\text{N}_{0.7})$ , and  $\text{Ti (C}_{0.2}\text{N}_{0.8})$ . The reinforcing phase Ti (C, N) formed by  $\text{Ti (C}_{0.3}\text{N}_{0.7})$  and  $\text{Ti (C}_{0.2}\text{N}_{0.8})$  has smooth outer edges and disperses throughout the coating, achieving hardness levels

between 800-900HV. Ti ( $C_{0.3}N_{0.7}$ ), either in rhombic shape or irregular form, not only formed smooth, clean, and tightly bonded interfaces with the substrate and cladding layer but also pinned at the grain boundaries to inhibit grain growth, thereby refining the microstructure [54–56]. Li [57] used Ti and BN powders for in-situ synthesis of TiB-TiN reinforcing phases and found that increasing the laser power, reducing scanning speed, and adding more BN particles led to a greater number of uniformly dispersed TiB-TiN reinforcing phases, as shown in Figure 7. When the Ti:BN ratio was 4:1, the coating experienced the least wear loss, with numerous and evenly distributed reinforcing phases, achieving the best wear resistance. Zhao et al. [58] applied TiB-TiN reinforcing phases to cobalt-based materials, which could increase the hardness of the cobalt base by 1.45 times and reduce wear by 55.11%, but the coating produced brittle  $Co_2Ti$  phases and exhibited particle aggregation. Jiang et al. [59] used carbon powder, boron nitride, and titanium alloy powder for in-situ synthesis of Ti (B, C, N), producing coatings that formed a metallurgical bond with the TC4 substrate and generated reinforcing phases such as TiB, TiN, and AlN. Under the effects of dispersion strengthening and fine grain strengthening, the coating's microhardness could reach up to 1454 HV.

**Table 1.** Commonly used reinforcing particles

Granule	Melting Point (°C)	Density (g/mL)	Coefficient of Thermal Expansion (K)	Moh's Hardness	In-situ Synthetic Material	References
$Al_2O_3$	2045	3.5 – 3.9	-	-	-	-
SiC	2830	3.25	-	-	-	-
TiC	3140	4.93	$7.74 \times 10^{-6}$	9 ~ 10	Ti + C	[19]
WC	2870	15.63	-	9	Ti + SiC	[20]
TiN	3290	5.43	$9.35 \times 10^{-6}$	8 ~ 9	Ti + $B_4C$	[21]
TiB <sub>2</sub>	4.50	2930	-	-	W + C	[27]
					Ti + Ni	[60]
					Ti + AlN	[61]
					Ti + VN	[37]
					Ti + B	[45]

Data sources: <http://www.basechem.org/>



**Figure 7.** Grinding weight loss of Ti-BN/Co composite coatings with different BN/Ti molar ratios [60]

Su et al. [62] utilized nitrided TiCB particles as reinforcing particles for titanium bases, preparing coatings with in-situ synthesized hard phases such as TiC, TiN, and TiB<sub>2</sub>, significantly enhancing the coating's hardness and wear resistance. Xu et al. [63], when using Ti (B, C, N) reinforcing particles, achieved uniform and dense coating structures by adding Mn powder, which encapsulated and dispersed the Ti (B, C, N) compounds evenly with the molten pool flow. The experiments also revealed that Al in the substrate could partially replace titanium, forming Ti(Al)BCN multicomponent solid solutions. The wear resistance of the particle-reinforced coatings was found to be

four times higher than that of the titanium alloy.

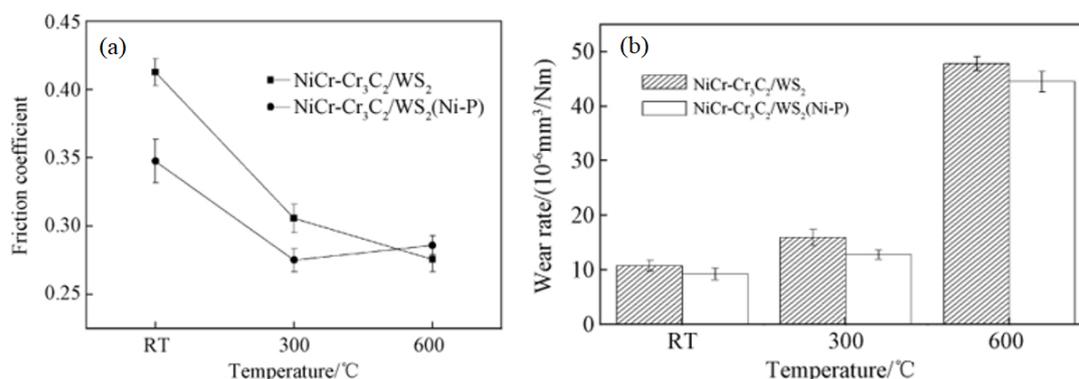
The difference in wear resistance of coatings is greatly related to the particle size and uniform distribution of hard particles. The smaller and more uniformly distributed the hard particles, the denser the coating structure and the higher its wear resistance. Although in-situ synthesis may introduce some defects in certain particles, overall, in-situ synthesized hard particle-reinforced wear-resistant coatings tend to have better bonding strength, more uniform distribution, and fewer impurities compared to coated particles and direct additions. Selecting appropriate in-situ synthesis materials to precipitate pure compounds and form metallurgical bonds with the substrate is key to in-situ synthesis. However, this method works well for particles with low melting points, while for high-melting-point particles like titanium boride, the effect of in-situ synthesis is poor, and particle encapsulation techniques yield better results for high-melting-point particles.

## 4.2 Anti-Wear Enhancement Application of Coatings

The wear resistance of anti-wear enhanced coatings primarily involves adding self-lubricating particles that can reduce the friction coefficient, thereby diminishing friction and reducing wear. Common self-lubricating particles include sulfides, fluorides, graphite, hexagonal boron nitride, and MAX phase self-lubricating particles.

### 4.2.1 Sulfide self-lubricating particles

Sulfides are widely used, with  $WS_2$  being the most common. In coatings reinforced with  $WS_2$ , lubricating phases such as  $Ti_2CS$  and  $CrS$  are produced [64, 65], with no residual  $WS_2$  found, indicating that  $WS_2$  decomposes entirely during laser cladding. Besides forming sulfides, the decomposition of  $WS_2$  also generates  $SO_2$  gas, severely affecting the coating's density. The high density of W generally causes it to settle at the bottom of the coating, affecting the uniformity of the coating structure. Zheng et al. [66] used Ni-P alloy to encapsulate  $WS_2$ , finding that the prepared coating performs best at temperatures up to  $300^\circ C$ . As shown in Figure 8, whether encapsulated or not,  $WS_2$ -based coatings operate optimally at  $300^\circ C$ , and at temperatures above  $600^\circ C$ , friction and wear can double.



**Figure 8.** Performance test of NiCr-Cr<sub>3</sub>C<sub>2</sub>/WS<sub>2</sub> and NiCr-Cr<sub>3</sub>C<sub>2</sub>/WS<sub>2</sub>(Ni-P) coatings at different temperatures [66] (a) Microhardness (b) Wear rate

### 4.2.2 Fluoride self-lubricating particles

Given the operational temperature limitations of sulfides, it is necessary to find wear-resistant particles suitable for temperatures above  $300^\circ C$ . Yan et al. [67] found that coatings prepared with added  $CaF_2$  exhibited excellent wear resistance both physically and chemically at  $400^\circ C$ , physically preventing adhesive wear and chemically limiting the formation of new compounds at high friction temperatures, stabilizing the structure of the organization, and preventing deterioration of coating properties due to thermal decomposition. At  $500^\circ C$ ,  $CaF_2$  undergoes a ductile-brittle transition, where it can exhibit its high-temperature lubricating effects, significantly aiding in enhancing the coating's wear resistance [68, 69]. Other fluorides like  $BaF_2$ ,  $LaF_3$ , and  $CeF_3$  possess similar properties, with  $CaF_2$  and  $BaF_2$  capable of forming eutectic structures that generate self-lubricating effects below  $500^\circ C$  [70].  $CaF_2$  can also be used in conjunction with  $WS_2$  to produce new self-lubricating phases; under laser action,  $WS_2$  and  $CaF_2$  decompose entirely, forming  $CaSO_4$  and  $CaWO_4$ , which exhibit good lubricating properties at  $600^\circ C$  [71, 72]. Wu et al. [73] studied the effect of force on  $CaF_2$  self-lubricating particles and found that coatings prepared with  $CaF_2$  show self-lubricating advantages under forces less than 5 N. When the pressure exceeds 8 N, the wear resistance of the coating is even inferior to the inherent wear resistance of the  $Ti_5Al_4V$  alloy.

### 4.2.3 Graphite and hexagonal boron nitride self-lubricating particles

Graphite is known for its good lubricating properties, but graphite was not found in the coating structure in in-situ synthesis experiments, as it easily oxidizes or reacts with other substances to form compounds. Ma and Wang [74] used a method of nickel encapsulating graphite to enhance the coating, which not only improved the hardness of the coating but also played a lubricating role, enhancing the coating's wear resistance from two aspects. Currently, white graphite (h-BN) or hexagonal boron nitride is commonly used in laser cladding. Similar to graphite, h-BN easily decomposes during laser cladding, with studies showing that the coating's hardness and wear resistance improve with increasing h-BN content [75–78]. Wang and Ye [79] utilized high-power laser cladding to encapsulate Ti liquid around h-BN, introducing self-lubricating particles into the coating, but most of the h-BN still decomposed, limiting the self-lubricating effect. Yan et al. [80] improved the preservation of h-BN self-lubricating particles within the coating and the compatibility between the particles and the Ni base by using nano-nickel encapsulated h-BN.

### 4.2.4 MAX phase self-lubricating particles

MAX phases consist of three elements, represented by M, A, and X, as shown in Figure 9 [81]. The bond between M and A is weak, while M and X are connected by strong covalent bonds. The weak interactions between A and the M-X along with the layered structure contribute to the MAX phase's self-lubricating properties [82, 83]. Common MAX phases include  $Ti_3SiC_2$ ,  $Ti_2AlC$ , and  $Cr_2AlC$ , with  $Ti_3SiC_2$  often used in laser cladding.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo

Figure 9. Corresponding elements of M, A and X [80]

When enhancing Ni-based coatings with  $Ti_3SiC_2$ , the highest coating hardness was achieved at a content of 7.5 wt%, while coatings prepared with a content of 10 wt% experienced a frictional weight loss of 1.2 mg [84]. Subsequent research found that self-lubricating coatings made with 10 wt%  $Ti_3SiC_2$  only performed well in terms of frictional properties at 600°C, whereas at room temperature, coatings made with 15 wt%  $Ti_3SiC_2$  exhibited the least wear [85]. Although the addition of  $Ti_3SiC_2$  can enhance the wear resistance of the coating, it also reduces the fluidity within the melt pool, causing the interfaces to become wavy and the highest hardness layer of the coating to shift downwards [86]. For cobalt-based coatings reinforced with  $Ti_3SiC_2$ , a 15 wt% addition provided the best wear resistance both at room temperature and at 600°C [87]. When  $Ti_3SiC_2$  reinforced Fe-based materials, the defect of  $Ti_3SiC_2$  inhibiting melt pool fluidity was amplified, causing the grains within the coating to grow coarser and the hardness to decrease, yet the coating's wear resistance was still improved through the formation of TiSi [88]. During in-situ synthesis, Ti-Si-C materials are primarily used. The optimal performance of the coating prepared by Qin et al. [89] was achieved with a Ti-Si-C content of 50 wt%, where the frictional loss was 6.2 mg, nearly half that of the substrate. The enhancement effect of  $Ti_3SiC_2$  via in-situ synthesis technology is not as effective as direct particle addition, possibly due to the difficulty in accurately synthesizing the compound from the three elements.

To further leverage the application of self-lubricating particles in wear-resistant coatings, the materials chosen for self-lubricating particles should produce a lubricating effect at room temperature, and when the temperature exceeds 600°C, the self-lubricating phase should not decompose or denature, maintaining its lubricity or the material could liquefy or even vaporize to dissipate heat generated by friction. Generally, self-lubricating particles have lower melting points and decompose easily during laser cladding, but research on in-situ synthesis and particle encapsulation technologies is significantly less developed than that on hard particles. Future research on self-lubricating phases could focus more on these areas.

As shown in Table 2, whether hard phases or self-lubricating phases, their performance improves after encapsulation. Comparing their hardness, the self-lubricating phase coatings are less hard than the hard phase coatings. In terms of friction coefficients, self-lubricating phases at temperatures of 300°C and 600°C are similar to, or even lower than, the friction coefficients of hard phase coatings at room temperature. From these aspects, a complementary relationship exists between self-lubricating and hard particles, suggesting that leveraging the complementarity between hard and self-lubricating phases could produce high-temperature, high-hardness wear-resistant coatings.

**Table 2.** Performance list of partial particle reinforced phase coatings

Experimental Temperature (°C)	Granule	Coating	Hardness HV	Friction Coefficient	Friction Weight Loss (g)	References
Room Temperature	Al <sub>2</sub> O <sub>3</sub>	Ni	1127	-	0.0275	[8]
	SiC	Co	-	0.31	-	[11]
	TiC	Fe	401	0.65	-	[16]
	WC	Ni	530	0.54012	0.00172	[25]
	Ni-WC	Ni	570	0.53631	0.00132	[26]
	Co-WC	HEA	-	0.4	0.002	[29]
	TiN	Co	582	-	0.0057	[34]
	TiN	Ni	833	0.42	-	[40]
	TiB <sub>2</sub>	Ni	855.8	0.363	0.0035	[64]
	WS <sub>2</sub>	NiGr–Cr <sub>3</sub> C <sub>2</sub>	-	0.3	-	[66]
300	(Ni-P)-WS <sub>2</sub>	NiGr–Cr <sub>3</sub> C <sub>2</sub>	-	0.27	-	[85]
	WS <sub>2</sub>	Cr <sub>3</sub> C <sub>2</sub>	-	-	-	[87]
	Ti <sub>3</sub> SiC <sub>2</sub>	Ni	450	0.38	-	[87]
600	Ti <sub>3</sub> SiC <sub>2</sub>	Co	463.8	0.46	-	[87]

## 5 Conclusion

Friction is an inevitable presence in mechanical structures, and in the pursuit of higher speeds, the loss of parts due to wear is becoming increasingly severe. Under the grand scheme of carbon neutrality, wear-resistant coatings will undoubtedly assume their historical mission. Besides improving wear resistance, these coatings must also possess high-temperature resistance to continue playing a role in environmental protection and cost savings. Future research will persistently aim at discovering new materials, but a crucial direction currently is to maximize the performance of existing materials through component design, preparation processes, and structural design.

(1) Hard particles enhance wear resistance through increased hardness, while friction leads to temperature rises; self-lubricating particles exhibit good lubricity at high temperatures but lack hardness. The performance of hard particles and self-lubricating particles is complementary in these scenarios. Encapsulating self-lubricating particles with hard particles can both increase coating hardness and produce a lubricating effect when friction causes temperatures to rise. Future studies could explore encapsulating self-lubricating particles with hard particles or co-encapsulating both types to prepare coatings that are both high-temperature and high-hardness resistant.

(2) The uniformity of particle distribution and the shape of the structure play a crucial role in enhancing coating performance. A “plum blossom-shaped” grain distribution can withstand forces from various directions. Particle distribution involves using ultrasonics or magnetic fields to disperse aggregated particles within the cladding layer, achieving a uniform distribution effect. There is no definitive research on the formation of specific grain shapes in coating structures, and control over particle distribution and structure shape remains in the preliminary exploration stage. The shaping and control of particles and structure shapes could become a direction for future research. For example, during the process of powder spraying onto the substrate, particles could be interfered with to melt onto the substrate in a specific arrangement, combined with the heterogeneous nucleation function of particles to control the organizational structure.

(3) An optimal coating structure can surpass the capabilities of the particle-reinforced coating itself. Current particle-reinforced gradient coatings are prepared based on the amount of particle addition, resulting in a somewhat simplistic structure that mostly produces a gradient effect. Coating structure design should be based on performance gradients, not merely transitional gradients. Different particle-reinforced coating performances vary; some enhance bonding strength with the substrate, some increase coating hardness, and others enhance coating toughness. Coatings should be designed according to the different wear conditions of the working parts of the coating, arranging the corresponding reinforced coatings to prepare performance gradient coatings.

## Data Availability

The data used to support the research findings are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare no conflict of interest.

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