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A review on Ti-based metal matrix composite coatings

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A B S T R A C T

Lightweight high-strength Ti-based metal matrix composites (Ti-based MMCs) have a multitude of application applications, e.g., biomedical engineering, aerospace, and automotive, due to their good sustainability, high specific strength/stiffness, high elevated temperature strength, high wear, and corrosion resistance. Although there are metal matrix composite coatings comprised of polymers, composite, and ceramics materials, the paper primarily focuses on titanium-based composite coatings. This review also discusses the different coating techniques including electrodeposition, thermal spray, plasma spray, vapor deposition, and laser cladding to achieve high hardness and roughness, wear resistance and corrosion resistance. Totally, we attempt to bring out Ti based materials scenario for its current applications.

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1. Introduction

Aerospace and automotive industries are among the industries that have been considered and investigated as titanium and titanium alloy consuming industries. Light weight, high biocompatibility, good chemical resistance and high specific strength are the characteristics of these materials. According to the said properties, there are applications such as biomedical, marine, petrochemical, chemical and structural for these materials [1, 2]. Simultaneous, the heat resistance and wear resistance of titanium materials are lower than nickel-based alloys and steel [3, 4]. By using Ti-based MMCs, these shortcomings have been overcome.

In MMCs, reinforcements are embedded in a alloy matrix or ductile metal. The reinforcement can be ceramics, carbon materials, or other metallic materials, in the form of particulates, platelets, whiskers, or fibers. The capabilities of high service temperature and higher strength in compression and cutting are among the properties of MMCs. These properties are a combination of reinforcing properties, such as high modulus and greater strength for ceramics, as well as metallic properties such as toughness and ductility. The thermal and strength stability and high specific modulus of MMCs have been proven in various documents. Owing to these benefits exhibited, these materials are widely used in severe working conditions such as high temperature, high friction/wear and high load conditions [3, 5, 6]. They are also very popular commercially. In other industries such as: high-end engineering industries in bearing

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components and machining tools [7, 8], electronics in transducersand insulators [9], aerospace in heat-resistant tiles and engine components and biomedical components [9] are used in dental restoration frameworks and acetabular cups [10, 11]. During the last three decades, particular attention was paid to Ti-based MMCs for the purpose of manufacturing airframe and engines [5, 6]. Due to their high specific strength, they are used in airplane engines and due to their high specific modulus, they are used in airframe. Ti-based MMCs based on titanium aluminides (with a temperature capability of nearly 760°C) weigh half the weight of nickel-based superalloys (used in high-temperature compressors) [10, 11] .

In this review, we will focus on Ti-based MMCs coating status. In the following, we deeply examine the considerations that are important in the stages of fabricating of Ti-based MMCs coating, such as the processing parameters and the materials used. In this review, the preparation of powders and physical properties are emphasized. Then the corresponding enhancing mechanisms and mechanical properties of Ti-based MMCs coatings are investigated in order to better understand these coatings. At the end, future research trends are described.

2. Metal matrix composite coatings

MMC coating, which combines high ceramic phase strength and hardness with sound matrix toughness, is frequently used for surface repair and strengthening of engineering metal components. The addition of a reinforcing particle can be accomplished using one of two methods. ex situ or external addition has its own intrinsic problem in the bonding between matrix and particles. This is due to the weak wetting property that exists between the metal and ceramic phases. In contrast, in situ synthesis, elements of the precursor undergo a chemical reactions at a very high temperatures. In situ nucleation and growth are performed in the next step. Finally, the ceramic reinforcing phase is produced in the coating. These particles are therefore more thermodynamically stable and lighter than hard particles that are added externally. By choosing the suitable ceramic and coating matrix materials, procedures, and relevant process parameters, one can produce composite coatings of various sorts, forms, sizes, and characteristics [3].

Aluminum, iron, magnesium, titanium, nickel, beryllium and cobalt are just a few of the materials that can be used as the matrix in MMCs [4, 5]. One very challenging and intriguing metal matrix is the Ti-based MMC coating, which is covered in the next section. The advantages of metal matrix composite coatings (MMCCs) are not only the relatively low cost of metal materials, high flexibility and toughness, but also corrosion and wear resistance and high hardness [1, 2]. Such advantages make these materials to be considered for mechanical components with harsh service conditions. High wear resistance, good wettability, excellent hardness and high melting point are the characteristics of tungsten carbide particles [3, 4]. These features allow it to be used as a reinforcing phase to protect against wear. Reinforced MMCCs have wide applications in industry. Among these applications are cutting tools [10], hot work molds [6] and mining tools [5]. In additionIn addition, they are used as coatings in dies, high pressure valves, engine cylinders, in the production of car accessories, drill fittings and musical instruments, microelectromechanical systems, aerospace, marine, small aircraft microelectronics, precision engineering, mining, nuclear fields, agriculture and medical equipment are used [7-9, 11-13].

3. Coating methods for MMCs

A large number of research has been done to fabricate MMCs coatings [14-16]. Among the ways of applying these wear-resistant coatings on protected surfaces, we can mention electroplating, vapor deposition, thermal spray, and laser cladding [17-19], and among the matters that limit the use of these coatings are metallurgical phase transformation, decarburization, tensile thermal stresses, oxidation and higher deposition temperature [19-22].

3.1. Electrodeposition

Composites have a metal matrix in which the particles are dispersed. Compared to mechanical and thermal methods such as vacuum deposition, nitrogen deposition, metal spraying, powder metallurgy and magnetron sputtering for preparing composite layers, electrical deposition is a very versatile and suitable method [23].

Inclusion plating is another name used for the field of composite plating. The word inclusion is used to refer to the presence of pollutants and unwanted particles, which has a traditional background. Among these particles are inorganic materials for example metal oxides that are sedimented in the bath and are entrained in the electrolyte flow and become deposited simultaneously e.g., Lansdell and Farr [24]. Electrodeposition along with electrophoresis is a method that is used for coating and sometimes electroforming a wide range of matrix materials and inclusion. Among these materials are ceramic matrices containing polymer or metal, conductive polymers, hybrid and ceramic particles of aqueous electrolytes [25, 26].

Losiewies designed and implemented an experiment for electroplating Ni-P + TiO_2 composite coatings. These coatings were porous and the experiment was conducted under galvanostatic conditions with a cathodic current density of 0.05 A cm^{-2} and at a temperature of 40 °C [27]. It had proper adhesion to the substrate and there was no internal stress that would cause cracks or defoliation of the copper plate. The metal surface was mat-grey and rough. White velvet tarnish related to embedded TiO_2 powder grains were observed on the surface.

Ni-P-TiO_2 nanocomposite coatings were electrodeposited on a copper substrate by Safavi and Rasouli [28]. The effect of heat treatment and current density on the morphology of coatings has been investigated. Their investigation indicated the uniform formation and distribution of Ni_3Ti intermetallics throughout the microstructure of the nanocomposite coatings. In the electrodeposited coatings, they were compact and free of cracks, and many globular grains were formed. With increasing current density, the morphology did not change significantly, although the volume fraction was different between $NiTi_3$ intermetallics. In another study conducted by Ma et al. [29], Ni-P-TiN nanocomposite was deposited on 45 steel sheets, examined at a temperature of 42 degrees Celsius. The intensity of magnetic was in the range of 0.1 to 0.5 T, the density of current was 4 A/dm^2 and pH=7.5. At 0.1 T, the deposited particles were coarse with crystal structure like cauliflower. The nanostructure formed at 0.3 T was uniform among small areas. It showed a uniform and finer structure and finally, at 0.5 T, an extremely exiguous and compact microstructure of surface was formed, which was much smaller than other composites, and its approximate average grain size was 80 nm. Fig. 1 shows the electrodeposition method, in this method, electrochemical cells in which composite coating is installed by current flowing from cathode to anode.

3.2. Thermal spray

In thermal spray coating, coating materials such as metal alloys, carbides, and ceramics are heated, become molten or semi-melted, and are propels to the substrate. The temperature of the flame in this method is between 3000 and 16000 degrees Celsius and the temperature of the substrate depends on the thermal spray processes used and is usually less than 500 degrees Celsius. Coating materials are feed into the spray gun in the form of wire, rod or powder.

The objectives of thermal coating can be stated as follows: 1. Increase wear and corrosion resistance 2. Protection against electrostatic and electromagnetic 3. Resistance to radio frequency interference 4.

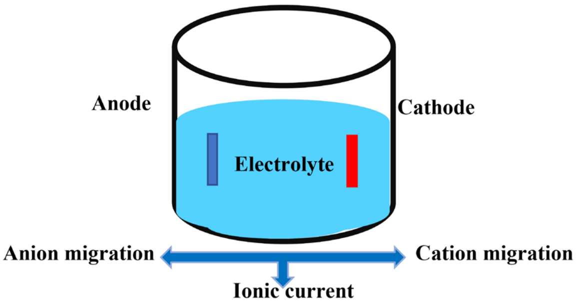

Fig. 1. Electrochemical deposition .

Metal buildup 5. Cosmetic.There are five common processes in thermal spray coating: Detonation gun, high-speed oxy-fuel andnplasma arc spraying, electric and flame [30]. The most likely reason for the higher friction torque for MMCs is the increased viscosity friction by the functional surface of the cylinder liner

$Ti(Al,O)/Al_2O_3$ coating with HVAF and wear resistant was created by Salman et al. [31] by thermal spraying method on tool steel (H13). This material is used in making high pressure die casting aluminium and aluminum extrusion of dummy blocks. A mixture of ball milled Al and $TiO2$ powders and then thermally processed was used for $Ti(Al,O)/Al_2O_3$ composite powder feedstock. This coating had wear resistance performance at room temperature and higher temperature. TiAl-(Cr, Nb, Ta) coatings were fabricated by thermal spraying in Ar atmosphere in Y_2O_3 crucibles in induction coil with high frequency and different nitrogen flow rates by Sienkiewicz et al. [32]. All coatings had relatively small porosity, which was located between the particles and during spraying, the particles hitting the substrate and form microstructures. These microstructures consist of stacked particles. The increased oxidation of the in-flight particles in the HVOF method, which is caused by higher temperature, can prevent deformation in order to have a good bond between the particles. Thermal spray coating is schematically showed in Fig. 2.

3.3. Cold spray

In deposit coating by cold spraying method, using Laval nozzle, nano powder particles are accelerated at a speed between 300 m/s and 1200 m/s per second. Due to the impact that is applied to the powder particles, they deform plastically and adhere to the substrate, accumulate and create a coating on the surface. Coatings that fabricate in coating with other spray processes may have defects, but cold spray method at a temperature lower than the melting temperature of the feedstock powder particles devoid of defects [17, 33, 34].

One of the types of deposition processes in the solid state is cold spray, during which plastic deformation of the sprayed particles and adhesion to the coating substrate is created. This method is used to deposit materials that are sensitive to oxygen or high temperature, such as Ti, Al, Cu and nanostructured and amorphous powders [35]. By maintaining the temperature of the particle below solidus, the undesirable phase transformation of the deposited particles is minimized. Compared to other spray processes, this method improves fatigue properties by creating compressive residual stresses with work hardening throughout the coating [36]. Cold spray is more suitable for producing dense coating of aluminum and copper and other materials that have low mechanical strength and low melting point than materials with higher melting point and higher mechanical strength. Due to the significant softening at high temperature and low yield strength in order to deposit these materials, gas pre-warming is not necessary or low temperature is used for the process. These materials have been well established in a number of studies [37-40].

The composite coating that can be used to optimize the functionality of the coating can be made in the following three ways: deposition of clad or coated powders, deposition of composite powders by mechanical milling or agglomerate- sintering , and deposition of a mixture of different powders [41].

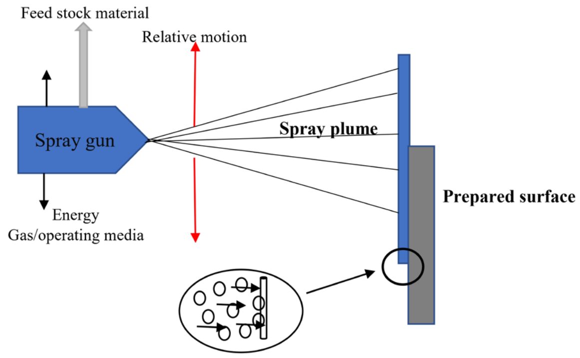

Fig. 2. Thermal spray coating .

In the last method, the cost is reduced due to the spraying of a mixture of commercial powders, and it is possible to control the composition of the coating by changing the composition in the spraying blend. If this approach does not show a favorable performance, the first and second approaches could be used to make a special composite coating. Deposition of different powders is an approach whose success has been proven in the literature. Huang et al. [42] deposited the Ni-Ti coating by cold spray method and post-treated to form intermetallic phases.

Friction stir processing was used to modify the Ni-Ti coatings. The SEM images taken from the surface of the as-sprayed coating confirmed the uniform distribution of deformed nickel particles in the titanium matrix and the coating had a relatively thick and compact structure. The mechanical properties and microstructure of as-sprayed coating can be improved by applying FSP. The macrostructure by the deformed layer and the alloyed layer after FSP were characterized. Synthesized Ni-Ti intermetallic compounds were obtained in the alloyed layer in-situ and there were no obvious defects. Shen et al. [43] were able to coat the $TiAl_3$-Al composite by cold spraying and post-heat treatment with high bonding strength and high micro-hardness.

As mentioned before, mixing powders is a simple method for fabricating composite and intermetallic coatings in conventional cold spray. This method has some advanegess in improving the cold spray ability of component powders, such as reducing porosity, increasing deposition efficiency and coating/substrate adhesion. These advantages are achieved usually by adding a ceramic component such as alumina into a metal powder such as aluminum. According to research, mixing two metal powders can also create the aforementioned advantages [44].

Adding a ceramic component to the metal powder allows to reduce the porosity. The addition of 10% w.t % Ti to Ti-6Al-4V has reduced the porosity of the coating from 7.5% to 1.75% [45], and in another study, with the increase of feedstock iron [46], the deposition efficiency of mixed iron and steel (316L) powders increased. It can be concluded that adding ceramic particles to feedstock is not necessary to fabricate a coating. Three different fields for biomedical applications of cold spray processing in studies aimed at increasing the corrosion resistance of metal implants while degradation rate control exists: hydroxyapatite (HA) and HA composites biocoatings (HA + Ti, Ti + Al + HA) [47, 48], ceramic-based bio-coatings such as TiO_2 [49], and metal-based biocoatings (Ti, Ti + Mg, Stainless steel + L605 Co-Cr alloy) [50-52]. On the other hand, it is possible to improve the stress shielding between bone and a metallic material by fabricating these coatings and improving bioactivity. For example, it is possible to facilitate the attachment of bone cells and ingrowth. Until today, enough studies in the field of using the cold spray method has not been done in order to modify the surface by adjusting the metal content, which results in reducing the amount of debris during sliding and providing sufficient toughness for the bearing surface of the artificial hip joint and knee [53].

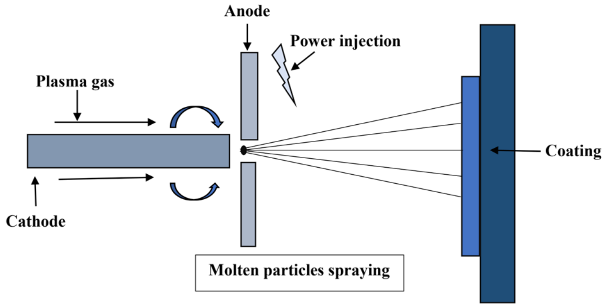

Fig. 3. represents a schematic of the plasma spray coating process. Plasma spray coating .

3.4. Plasma spray

A highly anisotropic coating with a layered structure was built up by particle-by-particle plasma spraying. Micro and macro cracks, residual stresses, oxide content, porous distribution and size are affected by the spraying parameters. These factors have a great impact on the final failure and performance of the coating. The capabilities of thermal spray coatings can be extended. For this purpose, plasma spraying can be used by accommodating materials such as superalloys, refractory alloys, cermets and ceramics that have a very high melting point. These actions mostly can be performed in the field of mechanical engineering [54, 55]. Many modeling and measurements have been done on the study of particles in flight and how these parameters are affected by plasma jets and macroscopic parameters of particle injection [55].

Ti6Al4V matrix composite coatings reinforced with in situ synthesized TiB-TiN by plasma spray method by depositing Ti6Al4V powder + 15 wt. % BN on titanium substrate by Anand et al. [56]. To coating Ti6Al4V, pulsed plasma transferred arc surfacing was used. To form TMC and B4C, B4C powder and Ti6Al4V were cofed in a melting pool. B4C grains in the matrix were dispersed homogeneously by relatively thick and deposited layers [57]. The deposits were metallurgically connected to the Ti6Al4V substrate. The use of this method led to an increase in wear resistance. In order to improve the wear resistance and hardness of the TiN surface, TiA16V4 and TiA15Fe2.5 were plasma sprayed. Using plasma nitriding and then plasma-assisted deposition Chemical vapor deposition the TiN layer was coated and a layering system of Ti_2AlN, Ti_2N, TiN and nitrogen-stabilized α phase was created. In this way, the biocompatibility, corrosion resistance and surface hardness of the samples increased [58].

3.5. Vapor deposition

Two important coating techniques are physical and chemical vapor deposition PVD and CVD respectively which by applying them, the coated surface has completely different property, structure and chemistry compared to the substrate [59]. In the physical vapor deposition method, the coating metal is evaporated and then deposited on the substrate. The temperature of the substrate in this method is several hundreds of degrees Celsius and it is accomplish in high vacuum chambers. The vaporization of the coating metal is done by the induction coil in such a way that the electron beam or electrical resistance causes the source to heat up and in Continued covering materials are vaporized in the presence of reactive gases. Often, N_2, nitride compounds are deposited on the surface of the substrates [60-63].

In the chemical vapor deposition method, there is a source of several reactive gases that are deposited on the substrate by performing chemical reactions [64]. The surface of the substrate on which the thermal deposition reaction is to be performed is heated and the gaseous compounds of the materials to be deposited are transported there and the reaction of gases occurs on the surface of the hot substrate to produce solid deposit. The description of the chemical vapor deposition mechanism includes chemical reactions in the vapor phase that occur before

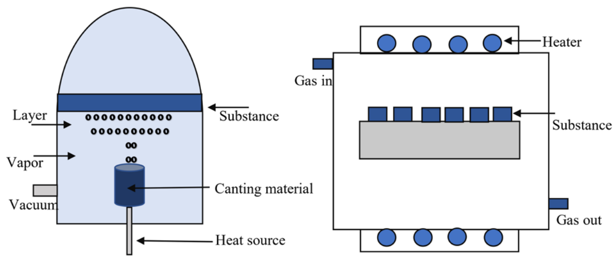

Fig. 4. Physical and chemical vapor deposition .

absorption and the surface diffusion of reactive adsorbents. It is possible to control the extent of these processes and, as a result, to control the deposit morphology using the most advanced chemical vapor deposition systems. Compared to the physical vapor deposition process, this method has a higher throwing power, and by using this method, even intricately shaped parts can have a uniform coating [65].

The high temperature of the classic chemical vapor deposition process, which is necessary for the formation of coatings by this method, is the main disadvantage of this process. This temperature is in the range of 800-1400 degrees Celsius. With Plasma Assisted chemical vapor deposition, the coating can be performed at a lower temperature. In this process, by applying low-temperature plasma to the gas/substrate system, the activation energy of the reaction is provided. By using plasma, the temperature used is lower and in the range of 450-650 degrees Celsius [66].

The PVD coating process in which the vapors generated under heat are deposited is shown, as well as the CVD process, and according to the requirements of different pressures, different gas flows, and required temperatures is slected and is shown in Fig. 4.

In a study conducted by Fortuna et al. [67], the surface of TiN-coating in the chemical vapor deposition method was much smoother than the coating produced by physical vapor deposition method. Doerfel et al. [68] produced (Ti, Cr)N coating by physical vapor deposition method and investigated the microstructural properties of the coatings. A somewhat columnar microstructure was obtained for the resulting wear-resistant coatings. The properties of TiN coatings with NH_3 plasma pre-treatment by plasma-enhanced chemical vapor deposition were investigated by Kim et al. [69]. The produced coatings had higher wear resistance, adhesion strength and hardness than untreated coatings.

3.6. Laser cladding

Laser cladding is an industrial method that is not completely known and is used to manufacture metal matrix components. The powder materials injected into the molten pool are melted by the laser beam on the surface of the substrate, and as a result, a coating with a metallurgical bond with a thickness of 0.5-3 mm is created [70]. This coating is fully dense. MMCs are produced by blowing hard powder, which is usually carbide, along with metal powder in the molten pool created by the laser. The goal is to keep the carbides intact with minimal dissolution and also Only the matrix material is melted, this is possible due to the low input heat of the laser if the difference in the melting temperature of the carbides and the matrix is high. There is a quantity of information in scientific articles about laser coating of metal matrix composites.

Ti/TiN metal matrix composite coatings on commercial pure titanium composite surface were synthesized by Cui et al. [71] using a continuous wave laser In another study, Hu et al. [72] analyzed the phases developed by Ti-6Al-4V laser cladding and found that the microstructure mostly contained TiN phase and α-titanium in the matrix. Ti-6Al-4V alloy was produced by using TiCqNiCrBSi and TiC powders using laser cladding, and the profile of microhardness and microstructure in the clad layers were investigated by Sun et al. [73] .Due to the increase of specific laser energy, the microhardness in the coating areas and di-

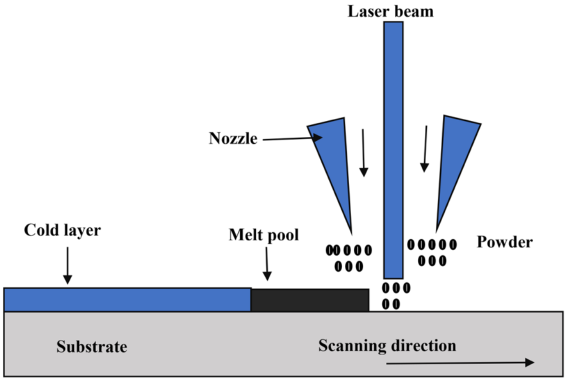

Fig. 5. Laser cladding .

lution decreased and The dilution effect of the titanium alloy substrate increased. The clustering of TiC particles in the clad zone was observed by increasing the volume fraction of TiC to more than 50%, which reduced the homogeneity of the microstructure and the microhardness distribution in the clad zone. Using an environment of 60% argon and 40% nitrogen, a combination of laser surface nitriding and alloying by pre-placing SiC on a Ti-6Al-4V alloy was performed by Selamat et al. [74]. The Ti-Al-Si/NbC composite coating was deposited on the titanium alloy substrate with laser cladding by Wang et al. [75]. According to the reported results, the addition of NbC made the structure denser and more uniform and improved the wear resistance and hardness of the coating. The method is carried out in two steps; Fig. 5 shows the laser cladding process.

4. Properties of Ti-based MMC coatings

The following classification is provided for common TMCs. This classification is based on the form of the reinforcements : 1. Discontinuously reinforced TMCs 2. Continuously reinforced TMCs

Recently, discontinuously reinforced titanium composites (DRTCs) have received more attention and have been developed more and more. These composites are expected to have better thermal stability and durability against high temperature, wear resistance, specific stiffness and specific strength compared to their corresponding titanium alloy counterpart. These advantages cause the application potential of DRTCs in the automotive industry. and aerospace. The focus of this review is on this types of TMCs. Boron carbide, titanium oxide, silicon carbide, and aluminum oxide are among the ceramic materials that are used as reinforcement Because of its poisson's ratio and thermal expansion coefficient similar to Ti6Al4V [76, 77], high elasticity modulus, high thermal stability, and high hardness (HV 3200) are reasons why TiC with typical NaCl-type FCC structure is often chosen as the particle reinforcing phase of titanium alloy matrix composites.

TiCp/Ti6Al4V composite coatings on Ti6Al4V thin plate were prepared by laser melting deposition method by Wang et al. [78]. The coating of TMCs prepared with TiC-coated Ti6Al4V raw material powder compared to mechanical powder mixing method due to the presence more uniformly distributed eutectic TiC phases showed higher tensile strength and toughness. In another study, the dry sliding wear behavior of Ti6Al4V-TiC metal-based composite coating and cold sprayed Ti6Al4V coating has been compared by Munagalama et al. [79] at a static temperature of 25–575◦C. Due to the presence of TiC reinforcing particles, at lower temperatures the formation of a wear-resistant layer that resists local deformation leads to less wear.

The formation of a glaze layer at high temperatures exhibits a negative wear rate and Ti6Al4V-TiC metal matrix composite coatings perform better wear resistance compared to Ti6Al4V coatings. According to the studies, it has been determined that the wear-resistant layer composed of oxides of TiC and Ti particles increases the stress bearing capacity of the metal matrix composite coating and prevents further peeling in the wear process.

The high cost of some conventional ceramic reinforcements, recycling difficulties, unwanted chemical reactions, poor wettability/interfacial adhesion, high abrasiveness, fracture toughness, and low ductility are the limitations of using ceramic reinforcements in the development MMCs [80]. High dimensional instability and poor thermal fatigue in composites under high cyclic thermal loading are caused by the mismatch between the thermal coefficient of expansion between metallic materials and ceramic [81, 82].

Due to today's applications of MMCs as stress-bearing and structural materials in high-tech applications the need for safety and maintaining structural integrity are crucial service demands. Thus the limitations of ceramic reinforced MMCs have increased. The mentioned background helps to understand the motivation of the studies that have been carried out in order to substitute new tools to increase the functionality and properties of MMCs. Recently, most attention has been paid to the in-situ synthesis of MMCs. In this method, the reaction products are hard ceramic phases that are formed during laser processing [1,6,14]. In this way, it is possible to achieve a strong interface without contaminants and defects between the metal matrix and ceramic reinforcements. These interfaces improve the tribological performance of composite coatings [15 18].

titanium borides (TiB/TiB_2) [17,19,20,22] titanium nitrides (TiN/Ti_2N) [3,9,25,26] and Titanium carbide (TiC) [19–24] are usual reinforcement phases of MMCs coatings on Ti alloys which is in situ synthesized. That is due to their excellent wear resistance and high hardness between 1500 to 3400 HV) [9,21,27].

Zhang and his colleagues [83] synthesized in situ TiC coating on Ti6Al4V matrix using laser cladding technique. Their investigations showed that the eutectic reaction resulted in the forming of β-Ti. Needle alpha martensite was formed from β-Ti through the cooling method. They also found that a metallurgical bond formed among the substrate and the composite coating formed with feathery TiC.

Zhao and his colleagues [84] also used the laser cladding method and deposited wear-resistant TiOxNy/α-Ti composite coating using titanium oxide powder on Ti-6Al-4V in air. As a result of the reaction between Ti, TiO_2 and N_2 reinforcements dendritic TiOxNy synthesized in situ. The α-Ti matrix is formed by mixing the ceramic melt and the semi-melted substrate. This matrix has a chemical bond with the reinforcements. Stacking faults were found in TiOxNy grains, which are caused by thermal stress. These faults apply strain hardening impact. The mean microhardness of the coating was four times that of Ti-6Al-4V, equivalent to 1417 HV0.3. The wear resistance of the composite coating was calculated to be 3.7 times wear resistance of Ti-6Al-4V. Ti .That was asosiated with coating/substrate and TiOxNy/α-Ti interfaces and the coating high hardness.

Cr_3C_2 ceramic reinforcing particles are suitable for improving corrosion and wear resistance in coatings [85]. Adding chromium to coatings by forming a protective oxide layer containing chromium on the surface of the material leads to improved resistance to oxidation and corrosion.

The raw materials used in this method were Cr_3C_2 powder and pure Ti powder, and in-situ , modified and reinforced TiC coatings fabricated on Ti6Al4V substrate using PTAW technology.

The following results were obtained from the analysis and research:

i: The cooling rate of PTAW was uneven and it causes the formation of a temperature gradient. This resulted in a different structure of the TMC coating in various regions. A fine dendritic phase TiC coated with β-Ti was formed on top of the coating. This phase was uniformly distributed under the structure layer of $TiCr_2$ and α-Ti, which was a needle-like mixture structure substrate .ii: TMCs coatings under the effect of microjet and wave of stress maked by the consecutive collapse of bubbles of cavitation have a longer incubation of cavitation erosion time. This is because of the shock stress dissipation impact of the α-Ti + $TiCr_2$ substrate with good toughness and the anchoring effect of the β phase compared to hard TiC. TiC particles inhibit crack growth and reduce material loss after the incubation period due to high strength. In this way, the resistance of cavitation erosion of TMCs was better than Ti_6Al_4V.

iii: The corrosion potential of the TMCs coating compared to Ti6Al4V substrate was higher (216.5 mV and 323.4 mV respectively) they were obtained from artificial seawater but the corrosion current density was lower (5.96 μA/cm^2 and 10.92 μA/cm^2). This data were obtained from impedance test results and dynamic polarization curve. The rapid formation of a more dense and stable passive film inhibited corrosion and this means better corrosion resistance behavior of the TMCs coating.

iv: The specific wear rate of the Ti6Al4V substrate was 2.44 × 10^{-5} mm^3 . N^{-1}. m^{-1} and the specific wear rate of the TMCs coating was 1.36 × 10^{-5} mm^3 . N^{-1}. m^{-1} . Also, the mean the TMCs coating microhardness was 1325 HV0.2.The mechanism of wear of TMCs coating is mostly adhesive and abrasive wear, and the wear mechanism of Ti6Al4V substrate is abrasive wear. The TMCs coating whith surface modified has better resistance to plastic deformation, cutting and furrowing compared to Ti6Al4V. That was because of the anchoring effect of β-Ti and the in situ production of TiC particles.

One of the interesting MMCs is graphene reinforced MMCs [86] . According to experimental studies and simulations, it has been proven that the mechanical properties of composite materials such as aluminum [87, 88], magnesium [89], copper [90] and other materials can be greatly improved by using graphene as a reinforcement.

Zhang and his colleagues [91] prepared a graphene/Ti6Al4V composite coating trough a laser cladding method. They investigated the properties and microstructure of the composite coating. According to the obtained results, an in situ synthesis occurred between graphene and Ti and resulted to the forming of TiC. The distribution of TiC was homogeneous. During the fast solidification process Acicular martensite formed at the bottom of the coating. A well metallurgical bond was established among the coating and the substrate.

The wear resistance of the coating was improved by using TiC and graphene self-lubrication.

The mild wear mechanism with fine scratches replaced the more drastic adhesive and abrasive wear mechanism. At the same time, intense oxidative wear occurs in both coating and substrate under wear and also friction. This wear occurs at high temperature. The results indicated the improvement of the coating corrosion resistance and the morphology of the local pitting corrosion was replaced by pitting and denudation. Graphene and TiC in the coating reduce corrosion effectively.

Hybrid reinforcements can be used to improve mechanical properties. For example, Ti6Al4V composite (Ti64) reinforced with Ti6Al4V (Ti64) with 50 volume percent in-situ single TiB and hybrid TiB + TiC coatings were prepared using gas tungsten arc coating process. The hybrid coating (TiB+TiC)/Ti64 had an intergrowth ceramic structure and also higher hardness compared the TiB/Ti64 coating. It had more wear resistance at room temperature.

According to the results of the studies, the hybrid TiB + TiC reinforced Ti64 composite coating show a higher wear rate compare to the composite with TiB reinforcement. These measurements were performed at a temperature of 500 degrees Celsius. While the wear rate of TMC hybrid coating was somewhat lower at room temperature. The non-stoichiometric feature of the ceramic phase of TixC in the hybrid composite has an effect on the wear rate, which is oxidized at high temperature. It greatly reduce the wear resistance.

The amount of wear rate of TiB/Ti6Al4V coating at 500 degrees Celsius decreased as a result of the high thermal stability of TiB ceramics. In another study, they reinforced TiB particles with TiB 2 particles using in situ synthesis method by laser cladding method on the Ti6Al4V alloy surface with short TiB fibers. Some advantages of short TiB fiber are as follows: the small diameter of the short fiber led to less internal crystal defects and the atomic arrangement more regular, and the strength of TiB is very close to the theoretical value of the perfect crystal [92, 93].

Chemical reaction does not occur between Ti and TiB, and a constant orientation relationship can be obtained to improve fatigue performance and mechanical properties [93, 94]. Due to the proximity of density and thermal expansion coefficients between TiB and Ti, the residual stress of the composite coating can be reduced [95, 96].

The average microhardness of the coatings was twice that of the substrate, and the microhardness of the TiB_2 / TiB coating showed a decreasing gradient. The volume of wear of the coating center was about 30% less compared to the Ti-6Al-4V substrate, this was due to the reinforcing effect of TiB_2 particles and TiB short film. The coating wear mechanism was the detachment of mild fatigue particles.

Table 1.
Some Ti-based MMCs coatings and underlying features.

Matrix	Reinforcement	Processing Route	properties	Ref
Ti	TiN	gas nitriding technology	Improved wear resistance	[97]
Ti	TiN	nitriding and laser cladding	Improved wear resistance	[98]
Ti6Al4V	TiN	laser cladding	-Improved wear resistance (from 2.8 × 10^{-4} to 4.3 × 10^{-4} mm^3. N^{-1} m^{-1} by adding up to 20% TiN) - the superior cellular response compared to Ti6Al4V control	[99]
Ti	TiC	induction cladding	-good elasticity and excellent tribological properties	[100]
Ti	TiC	self-propagating high temperature synthesis	strong metallurgical bonding at the MMCs coating and the steel substrate interface	[101]
Ti6Al4V	TiC	Laser cladding	improved tribological properties (Wear rate of 0.26 ± 0.03 ·10−15(m^3/N m) and Friction coefficient of 0.65 ± 0.06 with 60%TiC)	[102]
Ti	TiB	wire-feed deposition	Improved wear resistance (23.64 mg) compared with the Ti substrate (50.13 mg)	[103]
Ti6Al4V	TiB	laser metal deposition	improved surface hardness values, wear resistance and corrosion resistance	[104]
Ti	TiC+TiN	selective laser melting	- a average COF amount of about 0.808 - a low wear rate of about 0.84 × 10^{-4} mm^3/N^{-1}m^{-1}	[105]
Ti	TiB +TiC	laser cladding	improved wear resistance	[106]
Ti	Ti_3Al + TiB	laser cladding	Improved wear resistance and high temperature oxidation property	[107]

The properties of TMC coating synthesized by different methods are shown in table 1.

There is a high variety for industrial sectors and coatings. With the expansion of metal alloy matrices, some applications such as battery, optical, electronic and magnetic materials have been expanded. Such applications add to traditional markets for example: cutting tools and tribological coatings [26].

Automotive and aerospace industries are among the industries where titanium and its alloys are used in their research. High specific strength, chemical resistance, biocompatibility and low weight are among the attractive properties of these materials. The said features have brought structural, petrochemical, marine, chemical and biomedical applications to these materials [108].

Ti-6Al-4V alloy is one of the commonly used titanium alloys used in the aerospace industry in the blades of engines. Among the disadvantages of titanium alloys that have limited their use, we can mention their weak wear resistance, high friction coefficient and low surface hardness [109, 110]. SCS-6 is an example of continuous SiC fibers that have been used to reinforce titanium alloys. Today, these alloys are commonly used in the aerospace industry as structural materials at high temperatures. Aerospace engine compressors, hollow fan blades and shafts are among these applications [111, 112].

High temperature aircraft engine use, including applications of TMCs reinforced with continuous SiC fiber. Their mechanical performance under fatigue and creep stress at high temperatures limits the structural integrity. Toyota has used discontinuous reinforced TMC to make intake and exhaust valves in its engines [113]. The applications of space propulsion are also among the potentials of this class of materials [114]. Such applications have made the fatigue resistance parameter one of the most important issues in design.

Titanium aluminum base alloy is a high- temperature structural material with light weight.

This material has high specific strength, well creep resistance and very good oxidation resistance at high temperature. It also has low density and high melting point. According to the mentioned features, the use of these materials in the new generation of airplanes has made it possible to reduce the weight of the airplane engine and improve its efficiency. At the same time, the applications of these alloys are limited due to their low fracture toughness and high brittleness at room temperature [115-118].

The magnetron sputtering method was used and Ti-6Al-4V composite coatings reinforced with 2% B4C were coated on AISI 1040 steel plates. AFM, EDS, XRD and SEM analyzes used to determine and investigate the morphology and microstructure of the surface of the coated specimen. For the coating time of half an hour, the thickness of the uniform coating was 75 nm, and for the coating time of one hour, the thickness of the coating was 110 nm. The wear analysis of Ti-Al-V-B4C coatings under two and three N normal loads was performed. Very good wear rate and lower friction coefficient was achieved.

The Ti–Al–V–B4C thin film with 7.2 GPa nano-hardness value during the half-hour coating time, and 9.7 GPa for the one-hour coating time. The measured elastic modulus was 204 GPa.

Also, during half an hour, the measured surface roughness was 3.93 and during one hour, it was 17.433 nm. Increasing the hardness of nano and reducing the friction coefficient and thus improving the wear resistance were the advantages of adding reinforced B4C particles to Ti-Al-V composite coatings. The heat generated amount during the test of wear is determined. Considering that Ti-Al-V-B4C composite coatings had the lowest amount of wear in all loading conditions, they are suitable alternatives for other hard coatings [119].

The TiN/Ti composite coating was formed in situ by laser remelting method in an inert nitrogen atmosphere on the commercial pure titanium (CP-Ti) surface. To remelt the surface,two amount of laser powers (425 W and 475 W) were considered and one or two scans at each power were used to fabricate the samples. The in situ coating formed on the surface was rich in nitride. Nitride-rich dendrites were dispersed in the α-Ti matrix at the uppermost region.

The structure changed with fewer dendrites and more heat under the influence of the α-Ti phase, maintaining a smooth interface. The size of the dendrites was larger at higher laser powers. In the samples where two laser scans were performed, there were more α-Ti phase and discontinuous dendrites than in the samples where one laser scan was performed. The composites obtained from tin with Ti_2N in α-Ti had significantly higher wear resistance and hardness compared to the untreated CP-Ti substrate. because of the surface nitriding, the friction coefficient decreased, and during the wear test, Ti^{4+} ions decreased in DI water medium.

Zhou et al. , applied composite coating (CC) of 20 wt. % HA/Ti on Ti substrates through an in-house developed system of argon atmospheric pressure plasma spray. A dense CC with typical HAp morphology was obtained which was uniformly distributed in the Ti matrix. Also the HAp decomposition was avoided during the plasma spray process. Strength of Bonding is considerably higher than Hap-reinforced Ti or HAp coatings, and the friction was comparable to Ti substrates. HAp/Ti composites showed more corrosion current than that of pure Ti coatings in SBF which is related to its good bioactivity.

This is proved by forming apatite layer in the in-vitro study. A apatite with tortoise-shell likestructure thick layer was formed on the whole top of the composite coating after 8 months of immersion. This investigation demonstrates the potential of the mentioned composites as materials of load-bearing implant .

Coating on metallic implants is a significant applications of HA. This application is included in the category of clinical applications. For instance HA can be applied on Ti substrate using the plasma spray method. Zheng et al. [120], increased the bond strength of HA coatings by formation of coating with Ti composite. They applied HA/Ti composite coatings through spraying of atmospheric plasma on Ti-6Al-4V alloy substrate. The results show that the bonding strength was significantly improved by adding Ti to HA. It was confirmed by X-ray photoelectron spectroscopy that in the SBF test, the surface of coating covered with carbonate apatite showed well bioactivity of the HA/Ti composite coating.

Li et al. [121] applied graphite and C nanotubes reinforced Ti-based MMCs through Powder metallurgy. They prepared 0-0.4% wt. % Ti and VGCF/graphite mixed powders by rocking mill, and they integrated the premixed powders at 1073 K by use of spark plasma sintering. They performed hot extrusion at 1273 degrees Kelvin with ratio of 37 to 1. When the VGCF/Gr content increased (0.1 to 0.4 wt. %), the mechanical strength, ultimate tensile strength and yield strength of Ti-VGCF/Gr composites increased.

Composites based on Al/TiO_2 have the potential to be used in extrusion industries and aluminum die casting. In these composites, due to high temperature stability, Al_2O_3 ceramic phase is not wetted by molten aluminum. The titanium phase makes the substrate binder like an adhesive.

The Al_2O_3 phase should increase the temperature strength, environmental stability and wear resistance, and the Ti-based phase should increase the thermal shock resistance and toughness.

Therefore, applications of die coating , the contact angle of the coating with molten aluminum should be large [122].

Today, DRTC is used to make engine valves and connecting rods in new cars of Toyota Motors [108]. The Ti-based MMCs [123] produced in Dynamet Technology Inc., which is merged with the international titanium segment, have various and numerous applications, including medical implants, sports knives, etc.

The field of medicine is one of the most widely used fields of titanium consumption. Among the applications of titanium in this field are replacement parts for knee, hip, wrist, elbow, spine and shoulder joints, dental implants, orthodontic surgery parts, housing devices for artificial heart valves and pacemakers, bone fixation materials such as Plates, screws, nuts and nails, components in high-speed blood centrifuges and surgical instruments [124-126].

Due to the good biocompatibility of Ti-6Al-4V, it is a material of standard for use in medicine. This alloy has a lower elasticity modulus than cobalt-chromium alloy and stainless steel [127, 128]. By increasing the survival of implants for a long-term, it reduces the effects of mismatch of elastic modulus between bone and implant and mechanical failure as much as possible [53].

The very good compatibility and non-allergenic nature of titanium alloys has led to the use of this material in healthcare products such as artificial legs, artificial limbs, medical wheelchairs, etc. Ti-4Fe-6.7Cr-3Al and Ti-4.2Fe-6.9Cr alloys are used to make the wheelchair frame. The chair weight which is made of these alloys have half the weight of the chair made of pure titanium [129].

5. Challenges and future perspective

Although a lot of research has been done in this field we are still at the beginning of the research. There are many challenges regarding the development of Ti-based MMCs. As a result, future research is recommended for a deeper and better understanding of technology and fundamental issues. It is necessary to develop experimental and numerical methods to clarify the new phenomena caused by nanoparticles. In order to be able to explicate the changes caused by nanoparticles, the behavior in molten pools should be simulated. These studies are currently very limited. Better understanding and proper manipulation of parameter optimization is realized with proper insight and understanding in physical modeling.

In recent years, High-speed synchrotron X-ray imaging is an *in situ* technique that have been used for real-time detection of defect formation. One of the applications of these techniques is in behavioral studies of nanoparticles. Rapid investigations in order to achieve various applications are the goals of further research.

6. Conclusions

Ti-based MMCs are lightweight, high-strength and wear resistant materials that have found widespread use in a great variety of industrial and biomedical applications.

In this article, the results of experimental investigations and the views of researchers in various literatures in the field of Ti-based MMC coatings were examined in detail. The result of researchers' and industrialists' attention to these materials is numerous studies. By reviewing and studying this literature, the understanding of the inter-relationship among the macroscopic behavior and the microscopic characteristics of the processing can be improved.

In the last two decades, various techniques have been developed to process Ti-based MMC coatings. The available techniques can be classified as follows by reviewing different literatures:

- Laser cladding, vapor deposition, plasma spray, cold spray, thermal spray and electrodeposition.
- Different processing routes, advantages and disadvantages and features are discussed. The mechanical and physical properties of Ti-based MMC coatings are investigated. To investigate these properties, special attention was paid to high temperature, static, dynamic behavior and reinforcement mechanisms.

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