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A Comprehensive Review on Carbon-Based Thermal Sprayed Coatings for Orthopedic Implants

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ABSTRACT

The use of orthopedic implants is increasing worldwide as the population of older people is growing. Metals and their alloys like stainless steel, cobalt-chromium alloys, and titanium alloys are widely used as implant biomaterials for the treatment of orthopedic joint failure because of their biocompatibility and good mechanical properties. However, these materials offer poor osseointegration due to their bio-inert nature. Hydroxyapatite, a bioactive material, has similar properties to bone tissue and helps in improving bone regeneration. It has good osseointegration properties, but it lacks mechanical properties. It has low fracture toughness, wear resistance and poor tensile strength. The carbon reinforced hydroxyapatite can have better mechanical properties as well as biocompatibility. The addition of graphene and carbon nanotubes in HA can also provide antibacterial effects and induce osteogenic differentiation of stem cells. The surface modification process like surface coatings involves the addition of composite materials to have desirable properties. The hydroxyapatite coatings produced by thermal spray are commercially accepted by FDA (Food and Drug Administration). Thermal spray materials can play a vital role in enhancing orthopedic implants' biocompatibility, wear, and corrosion resistance. The coatings can improve the optimal integration to the surrounding tissues and result in increasing the life of implants. The study will focus on the various thermal spray techniques like flame spray, HVOF (High-Velocity Oxygen Fuel), cold spray, and plasma spray that are commonly used in bio-implant applications. The paper will also discuss the different types of biomaterial coatings produced with thermal spray processes by the researchers. Moreover, the comparison of various thermal spray coatings for biomedical applications are also covered.

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Introduction

Biomaterials can be defined as the natural or synthetic materials used to restore the shape and function of the degraded biological structure or replace the existing part. With the growth in aged population, the demand for biomaterials also increased at rapid rate[1]. The artificial heart valves, cardiac simulator, stents, dental and orthopedic implant are various types of biomaterials used in human body[2]. From all these, the maximum use is of knee, hip and shoulder implants. These synovial joints suffer from degenerative diseases like osteoarthritis that result in breakdown of cartilage. The damaged cartilage leads to severe pain and ultimately losses its function. 90% of the population over the age of 40 suffer from these diseases which are still increasing at an alarming rate[3]. The data analysis from the records of ISHKS (Indian Society of Hip and Knee Surgeons) reveals that there is a steady rise in the number of total knee replacements being reported to the registry from a mere 1019 in 2006 to around 27000 in 2019 as shown in fig1. The majority of patients were diagnosed with osteoarthritic knee[4].

The main requirements of load bearing implants are mechanical properties like tensile strength, hardness, modulus and elongation. The mismatch of modulus and stiffness between bone and implant can lead to higher stress concentration to the adjacent bone which is known as stress shielding effect[5]. Therefore, the similar properties to bone can prevent implant loosening and the risk of revision surgery is reduced. The biocompatibility of the implants is the other major necessity. It must be non-toxic, and any kind of inflammatory reaction should not be produced in the body. It should be hemocompatible and have favorable immune response. Apart from above, the implant should have high corrosion and wear resistance[6]. The poor corrosion resistance can result into release of toxic ions in the body. The integration of implant with adjacent bone is also essential and can lead to the success of implantation[7].

The currently used materials for orthopedic implants are stainless steel 316l, cobalt-chromium alloys, titanium, and its alloys. The SS316l and Co-Cr alloys can release toxic Ni, Co, Cr ions because of the corrosive human body fluid[8]. These alloys can also lead to stress transfer to bone and implant loosening due to their higher modulus than bone. Titanium alloys have high corrosion resistance, strength, better biocompatibility, and lower modulus than SS316l and Co-Cr alloys. However, titanium has poor wear resistance and lacks osseointegration[9].

Surface engineering can play a major role in enhancing the integration of implants with adjacent bone. Surface modification techniques like thermal spray coatings can increase the biocompatibility of materials like titanium by coating with bioactive material and hence, improve the osseointegration. The main advantage of thermal spray coatings is the high deposition rate, varying coating thickness and good bonding strength. The surface roughness and surface topology can be varied to increase the cell attachment. Moreover, the poor wear resistance of titanium can also be improved by coating with desired materials. Hydroxyapatite is a bioceramic material having properties like bone tissue and can provide

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osteoinductivity of the implants. The HA coatings by thermal spray techniques are commercially accepted and approved by FDA(Food and Drug Administration) and used in knee, hip, shoulder, ankle and dental implants[10][11]. But, HA has low fracture toughness, weak wear resistance and poor tensile strength. The carbon reinforced HA composites can improve the mechanical properties along with biocompatibility. CNTs have ultra-high strength around 100 times the tensile strength of steels and is a prominent reinforcement material for coatings.

The mechanical and biological evaluation of graphene-based materials for biomedical applications has been increasing in the past few years. Graphene is a 2D nanosheet of hexagonally bonded sp^2 hybridization carbon atoms having excellent mechanical properties, high conductivity, large surface area and good biocompatibility. It can originate the osteogenic and chondrogenic differentiation of stem cells and hence, can be the promising candidate for bone repair and regeneration[12].

This study will discuss the commonly used thermal spray techniques like flame spraying, HVOF (High velocity oxygen fuel) spraying, cold spray and plasma spray for biomedical applications. The main emphasis is given on the carbon reinforced composite coatings for orthopedic implants.

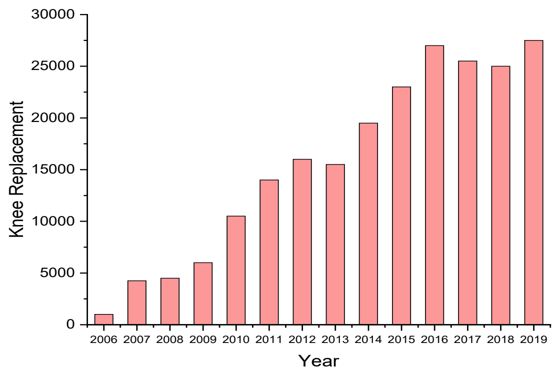

Figure 1: Total number of knee replacements in India [4]

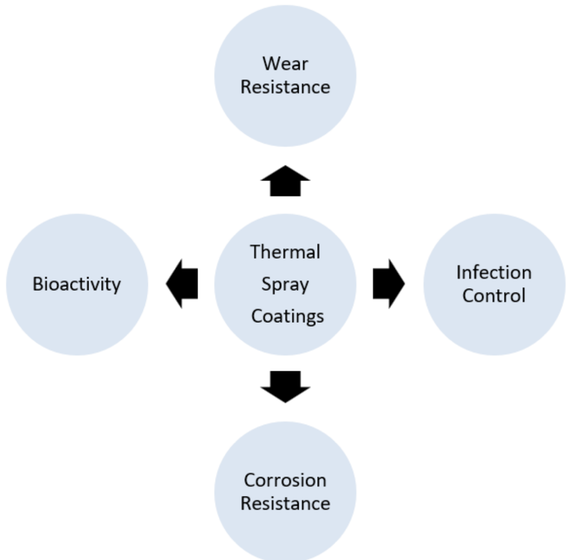

Figure 2: Applications of thermal spray coatings for orthopedic implants

Coating Processes

Powder flame spraying

In powder flame spraying, the feedstock powder is melted by flame in combustion chamber. It is a low velocity thermal spray process having particle velocity around 100m/s. The characteristics of such type of coatings is high porosity, low cohesive strength and high surface roughness[13]. The increased porosity in coatings can enhance cell adhesion and proliferation. The pore size between 100µm to 300µm according to cell size helps in cell migration and transport[14]. The porous titanium coatings produced by flame spraying have 34% porosity and high fraction of pores helps in significant cell growth. The surface roughness of flame spray coatings is highest with R_a 11.19µm and have oxidized surface. The formation of spheroid globules was observed on surface of coatings after immersion in simulated body fluid for 14days and Ca/P ratio was 1.61 [15].

Table 1: Parameters of different thermal spray processes used for biomedical applications.

	Flame spray	HVOF	Cold spray	Plasma spray
Temperature	3500°C	3000°C	25°C-1000°C	15000°C
Velocity	50m/s	500-1000m/s	300-1200m/s	300m/s
Pressure	3.5 bar	3.5 bar	40-50bar	Vacuum/ Atmospheric
Carrier gas	Argon	Acetylene and Oxygen	Nitrogen	Argon
Coating porosity	35%	1%	0.5%	30%
Spray rate	30-50g/min	15-50g/min	20-80g/min	50-150g/min

HVOF (High velocity oxygen fuel) spraying

In this process, the mixture of fuel like acetylene or propane and oxygen are ignited in high pressure combustion chamber with temperature 3000°C and velocity of gas jet is around 2000m/s. The supersonic gas velocity stream carrying the melted or partially melted feedstock powder is accelerated towards the substrate. The coatings developed by this technique have low porosity and high bond strength because of higher particle velocity and lower temperature than flame spray[16]. The HVOF coatings are used in biomedical application to overcome wear and corrosion failure[17]. The HA and HA-TiO2 HVOF sprayed coatings were used to examine the corrosion resistance by performing electrochemical tests in Hanks solution for 24 hours. The addition of TiO_2 in HA can provide improved adhesion strength to Ti substrates and better mechanical properties like high hardness and low porosity[18]. The concentration of TiO_2 was increased from upper layer of coating to bottom layer on the substrate. This type of functionally graded coatings can provide long life to implants without decreasing the bioactivity of HA[19].

The alumina-1wt%graphene coatings were deposited by suspension HVOF for wear testing. The good distribution of graphene was achieved, and graphene was retained even when the combustion gases reached at 2800°C. Raman spectroscopy revealed the increase in the level of defectiveness of graphene due to increase in Id:Ig ratio. The low specific wear rate was observed for 1wt% of graphene than alumina coatings during sliding wear testing. The alumina-1wt% graphene suffers brittle fracture and grain pullout between 30N to 35N while pure alumina sample fractures between 5N to 7.5N. The improved wear resistance of 1wt% graphene can be attributed to decrease in coefficient of friction during wear test and reduced absolute intensity of raman peaks of graphene[20].

Cold Spraying

Cold spray is a solid-state process that minimizes high temperature reactions and can be suitable for biomedical applications. The high-pressure gas stream (He, N2 or compressed air) containing solid feedstock powder is expanded through a converging-diverging nozzle. The convergent part of nozzle causes the gas stream to be compressed and attained the sonic speed at throat area and further expanded to supersonic speed at the exit of divergent part of nozzle[21]. The minimum velocity required to attain the coating deposition in cold spray is called as critical velocity[22]. As the cold spray always works at temperature lower than melting point of feedstock powder the problems associated with thermal degradation are minimized[23]. The low-pressure cold spray have a maximum pressure of 10 bar and temperature between room temperature to 1000^{0}C and has air as carrier gas. The high-pressure cold spray can achieve pressure upto 70bar and temperature upto 1100°C. With the increase in gas temperature, the particle impact temperature rises, and it decreases the critical velocity. The adhesion strength of high pressure and low-pressure cold spray copper coatings was 36MPa and 13MPa respectively. The thick and dense coatings can be achieved by this process. The optimization of process parameters like carrier gas temperature and pressure, selection of carrier gas and standoff distance can lower the critical velocity and increase the deposition efficiency[24].

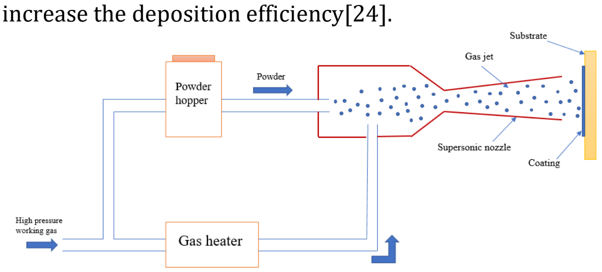

Figure 3: Schematic diagram of cold spray coating process

The cold sprayed Ti coatings were produced on Co-Cr alloy substrate for examining the corrosion resistance. The coatings acted as a barrier providing the protective effect. The HA-Ti composite coatings on Ti were found to have bond strength of 24.45MPa. However, increasing the HA incorporation in Ti beyond 30% results in the crushing of HA particles into fragments due to high velocity of gas stream causing high impacts and shocks[25]. The HA-Ag coatings deposited on Ti substrate for antibacterial applications. The antibacterial activity was improved by increasing the concentration of Ag nanopowder[26]. The Ti-Baghdadite (BAG) composite coatings deposited on SS316l for analyzing the corrosion resistance in simulating body fluid. BAG has better biological as well as mechanical properties. Corrosion resistance is enhanced by increasing the BAG content and thickness of coating beyond 200µm act as a barrier to corrosion[27].Further, Ti-15%BAG has lowest wear rate where wear debris and plastic deformation is less. The micro hardness at this composition is best and is recommended for orthopedic implants[28]. HA has poor mechanical properties and HA-Graphene composite cold sprayed coatings prepared on Ti substrate for load bearing and biocompatibility tests. Graphene has high mechanical strength and adding with HA enhanced elastic modulus, fracture toughness and adhesion strength of coatings. HA-1wt% graphene enhances the cell behavior and has the highest cell proliferation rate. Graphene provides more adhesion sites on the surface of coatings and the filopedia of cells incline to approach graphene which results in improved spreading and proliferation of cells. Also, the fibronectin protein adsorbs on graphene and facilitates the cell attachment[29].

Plasma Spraying

Plasma spraying involves the melting of feedstock powders due to generation of gaseous plasma and the liquid spray is accelerated towards the substrate to form the coatings. Nitrogen, helium, argon and hydrogen gases are used as DC electric arc heat source for generation of plasma[30]. The temperature range is between 10000°C to 15000°C and particle velocity is between 100 to 300m/s. Vacuum plasma spraying is preferred for biomedical coatings as it show high adhesion and high densities to provide robust bonding between orthopedic implants and neighboring bones or tissues. Plasma spray coatings have high surface roughness and porous microstructure and are beneficial for bone tissue engineering. Moreover, both metal and ceramic coatings can be produced in plasma spray and are suitable for orthopedic prosthesis[31].

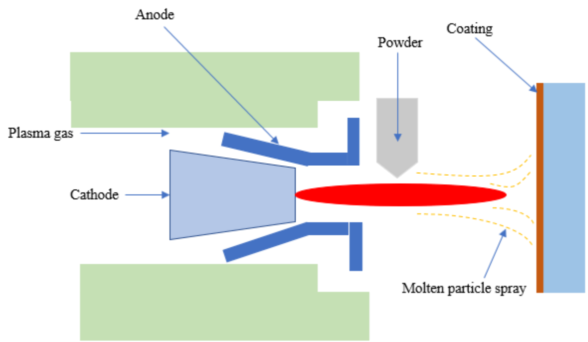

Figure 4: Schematic diagram of plasma spray coating process

The Carbon nanotubes (CNT) reinforced in HA on Ti-6Al-4V substrates provide the strength and toughness to brittle HA coatings. The HA-4wt%CNT plasma sprayed coatings increased the crystallinity by 27% and fracture toughness by 56%. The uniform dispersion of CNT results in osteoblast hFOB 1.19 cell growth and ensures the HA-CNT coatings are non-toxic. Further, CNT enhanced the mineralization and precipitation of apatite[32]. The electrochemical behavior of graphene nanoplatelets reinforced HA plasma sprayed coatings were examined in simulated body fluid. The porosity measurement of HA coatings was 15% and with addition of 1wt% graphene it reduced to 13% and further reduced to 10% with 2wt% graphene. After plasma spraying, defects like voids, porosity and microcracks occurs which can be minimized as graphene fills the gaps at inter-splat region and hence the porosity is reduced. Moreover, the corrosion resistance was enhanced by 67% with 1wt%graphene and by 87% with 2wt%graphene. The reason behind this can be the increased water contact angle of coating due to hydrophobic nature of graphene[33].

Table 2: Main characteristics of carbon reinforced thermal spray coatings

Author	Coating technique	Coating material	Substrate	Test performed	Key finding	Remarks
Murray et al.(2018) [20]	HVOF	Al-Graphene nanoplatelets	Stainless steel	Wear testing	1wt% graphene showed low specific wear rate.	
Khan et al.(2023) [37]	Plasma spray	HA-Graphene Composite	Ti-6Al-4V	Tribocorrosion behavior	Shallow wear scar showed increase in tribocorrosion resistance with graphene addition	2wt% graphene has shown best biocompatibility.
Balani et al.(2007) [32]	Plasma spray	HA-CNT composite	Ti-6Al-4V	Fracture toughness and biocompatibility	Fracture toughness increased by 56% and osteoblast hFOB1.19 cell growth occurs	Mineralisation and precipitation of apetite
Singh et al.(2020) [33]	Plasma spray	HA-Graphene	Ti	Porosity and Corrosion resistance	Porosity reduced by 5% and corrosion resistance enhanced by 87%.	Graphene fills the gaps, voids formed in coatings
Chen et al. (2010) [38]	Cold spray	Al-CNT composite	Al	Wear resistance	Wear rate decreased drastically with the addition of CNT	
Lieu et al.(2014) [29]	Cold Spray	HA-Graphene composite	Ti	Load bearing and biocompatibility	Enhanced fracture toughness, elastic modulus and adhesion strength of coatings	Graphene-HA composite increased the attachment and proliferation of osteoblast cells

The mechanical properties, chemical properties and phase composition of BAG and HA plasma sprayed coatings were evaluated. The BAG coatings on Ti-6Al-4V have more uniform structure and better mechanical properties than HA. The presence of zirconium results in better hardness and toughness of BAG. The BAG has uniform features on the surface and well melted spherical splats without splashes while HA shows irregular splat shapes with large splashes and fragmentation. However, the crystallinity levels of BAG coatings and HA coatings were 21.8% and 64.7% respectively. The microhardness value of BAG coatings was 325.5HV which was comparatively higher than HA coatings with 118.3HV. The BAG coating promotes the cell adhesion and proliferation of osteoblast like cells MG-63 and hence, better osseointegration properties than HA and Titanium[34].
The tribological behavior of CNT-reinforced HA coatings in simulated body fluid environment was examined. The wear resistance was improved with the addition of CNT. The micro cracks induced during abrasive wear test of HA-CNT coatings was restricted by CNT. The weight and volume loss during wear was significantly reduced for HA-CNT coatings due to the self-lubricating nature of CNT. Further, the wear debris pinning was assisted by the bridging and stretching of CNT[35].
Graphene nanosheets reinforced HA plasma spray coatings were deposited for evaluating strength and toughness. The homogenous distribution of graphene in coatings was observed in microstructure and acts as a binder between individual HA splats. Graphene nanosheets addition results in an increase in fracture toughness by 32.3% and indentation yield strength by 54.7%. The crack propagation is resisted during contact with graphene nanosheets and results in crack deflection. The strengthening mechanisms like load transfer, graphene nanosheets pull out and bridging, crack branching and inter-layer sliding of graphene nanosheets give rise to increase in strength[36].
The varying wt% of graphene 0.5%,1% and 5% with HA was deposited on Ti-6Al-4V by plasma spraying for tribocorrosion behavior and biocompatibility. Mechanical properties do not change significantly with the increasing graphene percentage. The shallower wear scar was observed in graphene-HA coatings that shows the better tribocorrosion resistance than pure HA coating. The cell viability of HA-2wt%graphene was maximum with 89.6% as compared to 0.5wt% graphene and 5wt% graphene with cell viability 87.3% and 85.4% respectively. The study depicted the optimum graphene wt% in HA for best biocompatibility for implants was 2wt%[37].

Conclusions

This study intended to give an overview of different thermal spray coatings techniques for orthopedic implants applications. The process of various techniques has been explained and major focus is drawn on the carbon reinforced composite coatings for mechanical, electrochemical, and biocompatible evaluations. The review study can be summarized in following points-

1. Graphene and CNT reinforced coatings can be successfully deposited by thermal spray techniques. The plasma spray is the well-established method for implant coatings and suitable biocompatibility is achieved as compared to other thermal spray processes.
2. The mechanical properties like hardness, wear resistance and fracture toughness is increased by addition of graphene in HA coatings irrespective of the thermal spray process.
3. Raman spectroscopic studies ensured the retention of CNT in matrix after thermal spraying.
4. Graphene and CNT can be ideal candidate for reinforcing in HA coatings for achieving both mechanical as well as bioactivity of orthopedic implants.

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