The importance of Co-Cr alloys in bioimplants for hip joints: A review

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ABSTRACT

The metallic materials such as titanium alloys, cobalt Chromium alloys and, 316 stainless steel are mainly used as implant materials. The necessity of Co-Cr alloys in the orthopedic field due to its incomparable corrosion resistance and wear properties. These are majorly applicable for artificial hip and knee joints. Corrosion of implants in the biological environment is one of the major issues affecting the lifespan of orthopedic devices. Several surface modification techniques are employed to enhance corrosion resistance. This review highlights an ample summary of different coating methods to improve the performance of Co Cr alloys. Plasma spraying technique is reported as one of the best suitable methods to coat different alloys using hydroxyapatite and other reinforced powders to boost corrosion resistance and biocompatibility. Other than the corrosion and mechanical properties, selection of materials in bioimplants also plays a major role depending upon the life span and human body environment.

1. Introduction

Biomaterials are considered to be artificial joints for the human body. These are employed in place of a damaged body parts or to restore the diseased part. Thus to enhance the quality of life biomaterials are engaged. Currently, due to aging population and increased accidents, there is a rapid rise in demand for implants. In the human body, biomaterials are used as replacement embeds in shoulders, knees, hips, elbows, ears and orthodental structures [1-3]. Among all the maximum replacement of implants are for knee and hip joints. Arthritis in the human body leads to disfunction or pain in body joints. Due to excessive loading or lack of self-healing process leads to less mechanical functioning and degradation of bone. According to the survey, about 90% of the people aged 40 or beyond are suffering from the above-mentioned diseases. The demand is budding day by day as there is a seven times increase in demand from the year 2002 to 2010 [4]. These problems are solved by using artificial biomaterials and the above-mentioned alloys are employed as surgical implants of required shapes and sizes. Generally, the life of an implant also varies according to age limits as according to literature implant life of the older patients was around 15 to 20 years whereas more than 20 years for the younger patients [5]. The blood, as well as other constituents present in the corrosive environment of human body, adversely affects the biocompatibility and mechanical behavior of the implant [6]. To avoid mechanical failure, high corrosion resistant biomaterials are required to escape the dissolution of surface oxide film that leads to supplementary ions in the body [7]. The success of the implant replacement does not consider only on the surgery executed by surgeon but also depends upon the selection of the materials used as a replacement. The selection is based on the condition of patient related to its health, weight, recovery time and age [8]. This signifies proper knowledge is required replacement materials and also the performance of the material. In addition to these various factors such as design, surface properties and biocompatibility of the selected material were also considered [9]. An implant material

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should have high tensile, compressive, shear strength to prevent fractures and improve functional stability. It should have high yield strength and fatigue strength to prevent brittle fracture under cyclic loading. Electrical and thermal conductivity, on the other hand, should be minimum to prevent thermal expansion, contraction, and oral galvanism [10]. The implant material should have the ability to form direct contact or interaction with the bone (osseointegration). This is largely dependent on the biocompatibility and surface composition of biomaterial [11].

2. Basic Implant Materials

Since the 19th century the use of metallic implants was introduced for biomedical uses. Earlier in the 1860's a surgical technique was developed by Lister. After Lister, it was then amended by Lane in the 1900's by introducing a fracture plate of steel and further the stress concentration was reduced by Sherman [12]. From 1900s onwards metallic implants turn out to be an essential part of the orthopedic industry and are employed in the body for both permanent and temporary joints [13]. These are extremely suitable for bone repair due to enhanced properties. High tensile strength along with young's modulus makes them 20 times tougher than ceramics. Metallic corrosion is one of the major aspects and it can be reduced by proper selection of materials as some of the metals hold sound corrosion resistance [14]. The knack of alloys makes them appropriate for required applications as their properties such as wear, mechanical and corrosion behavior can be altered. Similarly, the biocompatibility can also be enriched via those elements which show no contrary effects in the body. Hereafter metals have established relatively expedient for implantable device applications and it is expected that this trend is not going to change any time soon [15]. The advantages and disadvantages of various metallic implants are shown in Table 1. [16].

2.1.Titanium and its alloys

In 1950-1960s titanium was firstly designed for aerospace applications and later it was developed for surgical implants. Currently, 2% of titanium is used in medical applications. Titanium possesses outstanding mechanical and biocompatible properties that make it's a popular bioimplant [17]. Pure titanium and Ti-6Al-4V alloy are the furthermost used implants in biomedical applications. However, Titanium alloys possess poor wear resistance and hence are not used for the manufacturing of femoral head. As a component made of titanium suffers wear on the surface as well as on the stem that results in loosening of the implant. This loosening further upshots the metal fragments in the neighboring tissues and advances infection [18].

Table 1
Features of metallic orthopedic implants.

Materials	Advantages	Disadvantages	Application
Ti and Ti based alloys	Biocompatible, corrosion resistance, fatigue strength, low modulus, light weight	Low wear Resistance	Total joint replacement, fracture fixation elements
Cobalt based alloys	Better wear and corrosion resistance, fatigue strength	High modulus, Expensive, Biologically toxic	Total hip replacement, bone plates and wires
Stainless Steel	Low cost, easily available, acceptable biocompatibility	High modulus, Low corrosion resistance, Allergic reaction	Temporary devices plates and screws
Magnesium based alloys	Biocompatible, biodegradable, low Young's modulus	Low corrosion resistance, hydrogen evolution during degradation	Biodegradable orthopaedic devices, bone pins and plates

2.2.Stainless steels

In many countries, stainless steels (316L) grade used a temporary implant. These alloys possess high mechanical strength and ductility. On the other hand, it releases ions and also gets corroded in a biological environment [19]. Due to these ion releases it affects the body and causes powerful allergens. According to the previous studies, it was noticed that around 90% of 316L implant failures are only because of corrosive behavior[20]. This causes loosening of the implant even for temporary use. So, it is appropriate that some other enhanced materials were chosen for orthopedic implants with feasible mechanical as well as biological properties [21].

2.3.Cobalt and its alloys

Cobalt, Chromium, Molybdenum alloy serene of identical elements as vitallium. CrO offers corrosion resistance whereas molybdenum delivers strength. Co-Cr alloys retain extraordinary mechanical strength, outstanding corrosion resistance and low ductility [22]. These alloys reveal balance among mechanical properties as well as biocompatible nature. As compared to stainless steel both parameters i.e. corrosion resistance and mechanical behavior are superior [23]. On the other hand, these alloys are slightly costly than steels but are far better in concern to its corrosion stability. Co-Cr alloys are divided into two types namely Co–Cr–Mo alloy and Co–Ni–Cr–Mo alloy. For permanency of artificial joints in the field of dentistry, cast Co-Cr-Mo alloy was employed as at the time of surgery these can't be shaped in a certain form [24]. While wrought Co–Ni–Cr–Mo alloy is capable of heavily loaded joints and is employed in developing the stems of prostheses namely, the knee and hip. On the other hand in the annealed form, it displays stress parallel to the more brittle cast with enriched ductility, and the tensile strength rate is equal to heavily cold-worked Stainless steel [25]. Moreover, the wrought alloy can be fetched to attain required ductility and strength by applying appropriate working and annealing situations to triumph it as an implantable alloy [26]. But has a disadvantage over Co-Cr-Mo alloy, as wrought alloy has increased incidence of crevice corrosion. Improvement of electrochemical as well as mechanical properties of the biomaterial has been done by thermal dealings to Co–Cr–Mo alloys [27]. For medical purposes, the supreme used material is cast version of Co28Cr6Mo (ASTM F75) and the wrought versions ASTM F799 and ASTM F1537. The hardness of produced F75 composition alloy is nearer to that of ceramic biomaterials consumed for hip replacement device creation. Wrought Co–Ni–Cr–Mo alloy due to its grander fatigue and absolute tensile strength make it capable for applications those demand a lifelong service deprived of fracture [28].

2.4.Other precious metals

Precious metals consist of gold, platinum, and palladium. These are noble metals unaffected by air, moisture, heat and most solvents. These do not depend on surface oxides for their inertness [29]. These materials retain high ductility and possess low mechanical properties. These are limited in use due to the high cost per unit when paralleled to other implant materials [30].

3. Human Bone

Human bone is a type of connective tissue consisting of fibers and cells which further gives internal support and protection to the vital organs in the form of the rib cage and also serves as a site for the attachment of the muscles. Furthermore, the bone helps to maintain calcium homeostasis as well as hematopoiesis. To aid these purposes the bone must be inflexible. On the contrary side, it needs to be flexible for energy absorption. Cortical and trabecular are the only two categories of bone tissues found in a human skeleton. Cortical bone displays high compressive strength as it has low porosity and delivers more strength and rigidity to the bone, whereas, trabecular bone offers high porosity. Thus, signifying the lower value of Young's modulus and lacks basic compressive strength [31]. However, it supplies an enhanced surface area to permit the contact of blood vessels and red bone marrow. To practice cobalt implant in exchange for human bone, it must be confirmed that the mechanical manners of both are alike [32]. Mechanical properties of implant alloys and human bone are presented in Table 2. [33].

4. Surface Coatings Techniques

In today's era, various kinds of techniques are available in which the implant surface is smeared with different coatings which further magnifies the surface area and roughness. Moreover, it enhances biocompatibility and attachment strength at bone-implant border.

4.1.Plasma spray

As shown in fig. 1. Electric arc builds a plasma flame over which an argon gas stream is circulated to heat the coating powder to a temperature of approximately 12000 to 16000°C. This amount of heat produced to melt the particles which are further sprayed on the samples and harden to create round interconnected pores between the bone and the implant which allows straight chemical bonding leading to a durable bond. Additionally, this supports the implant to achieve good corrosion resistance and biocompatibility and better recovery time after surgery. To increase the weight-bearing ability of the bone neighboring the implant it is prepared and mineralized in a superior way [34].

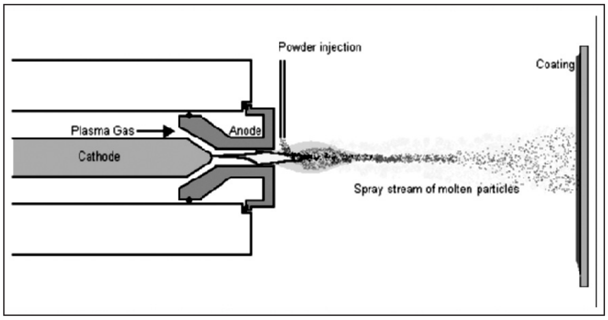

Fig. 1. Plasma spray technique [35].

4.2. Electrophoretic deposition

Fig. 2. Shows the setup for electrophoretic technique. The first part of the process consists of mineral ions dissolved in the electrolytic

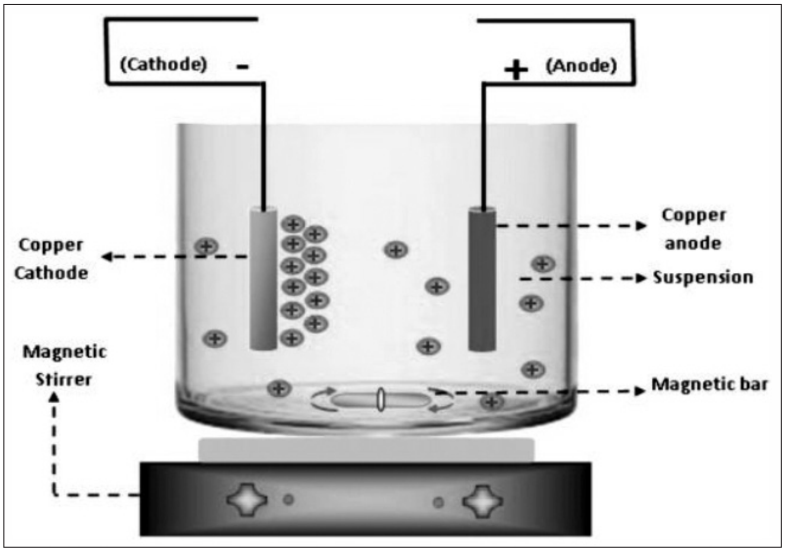

Fig. 2. Electrophoretic deposition setup [37].

Table 2
Mechanical properties of the implant alloys and human bone.

Material	Tensile Strength (MN/m)²	Yield Strength (MN/m)²	Elongation at fracture	Vickers hardness (H_v)	Young's modulus (GN/m)²	Fatigue limit (GN/m)²
316 SS	650	280	45	190	211	0.28
Wrought Co-Cr alloy	1540	1050	9	450	541	0.49
Cast Co-Cr alloy	690	490	8	300	241	0.30
Titanium	710	470	30	-	121	0.30
Ti-6Al-4V	1000	970	12	-	121	-
Human bone	137.3	-	1.49	26.3	30	-

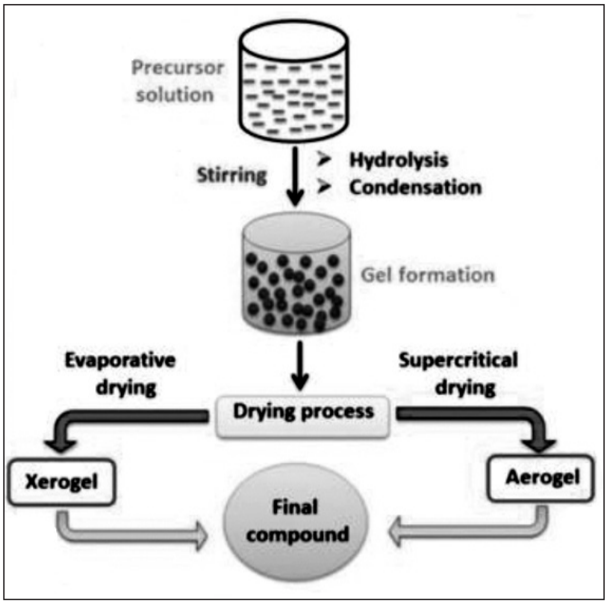

Fig. 3. Sol Gel deposition method [39].

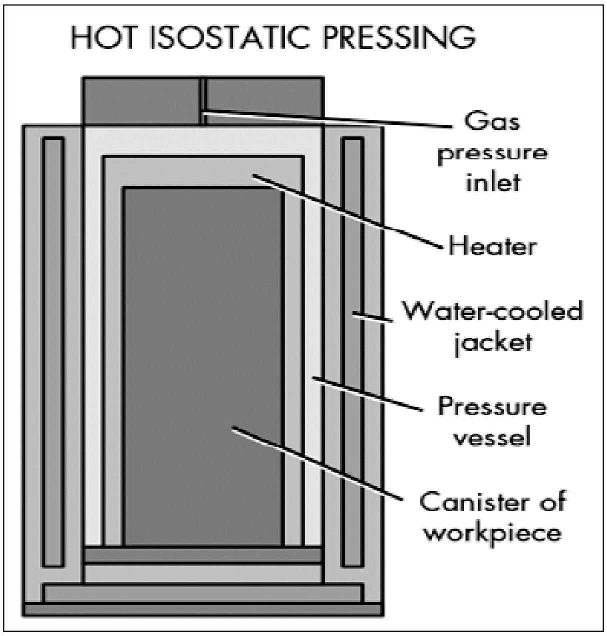

Fig. 4. Hot isostatic processing [41].

bath in which the electric current is applied and the particles get electrically charged that start traveling to one of the electrodes. In the second part of the process, a coherent deposit is formed near to the electrode by the accumulation of the particles in the shape executed by the electrode which is obtained in the form of the green ceramic body by removing and drying it from the electrode. A ceramic component is designed by firing the green ceramic body. The only shape drawback is the likelihood to take away the deposit from the electrode after deposition [36].

4.3. Sol gel deposition

This technique shown in fig. 3. is applied for making solid materials from small molecules. The supreme materials for this development are oxides of silicon and titanium. Transformation of monomers was done into colloidal solution (sol) which deeds as the originator for acombined network (gel) of any discrete particles or network polymers. Low cost, as well as easy control factors, makes this a favorable technique. On the other hand, thin films are prepared by sol-gel method, demonstrates outstanding antiwear and act friction reduction. Commonly it is used in methodical applications such as monolithic gels and thin films.

Monolithic gels can be simply geared up by pouring sol into the flask. As soon as the processes gelation and drying are done, the primed piece is formed by the flask in which it was poured [38].

4.4. Hot isostatic pressing

The basic fundamental of this process hot isostatic pressing (Fig. 4.) is to drop the porosity of metals and upsurge the density of numerous ceramics ingredients, results in enhancing mechanical properties as well as workability. Firstly the material is focused on a higher temperature as well as at raised isostatic gas pressure in a controlled vessel. Argon is generally used as pressurizing gas. To protect the material from chemical reactions inert gas was applied. The pressure inside the chamber rises to a content results in heating. Various systems use allied gas pumping to attain the required pressure value. As the pressure is smeared for entire directions, therefore, it demonstrates isostatic. The powder is hot pressed around 850°C and a dense coating was created which results in higher shear strength [40].

4.5. Pulsed laser deposition

From many years this process is accomplished in producing materials with superior quality films. High power laser pulses effect the material to melt, evaporate and ionize from the surface of the target. PLD (Fig. 5.) works on an extremely plain technique in which material is removed from the surface of the target by using pulses of laser energy. Laser produced plasma plume is a vaporized material consisting of neutrons, ions, electrons which quickly grows away from the

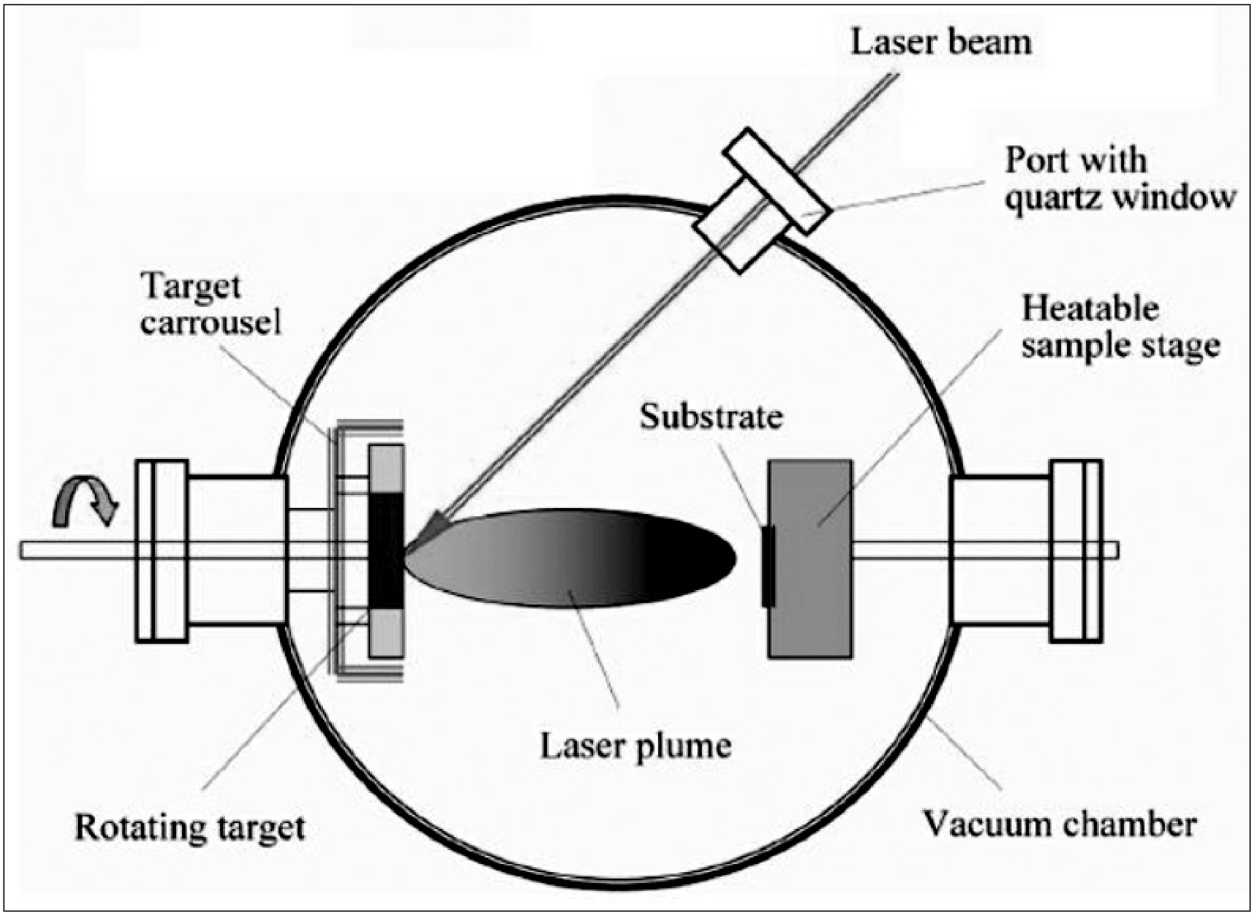

Fig. 5. Pulsed laser deposition [43].

target surface in vacuum plume material recondenses and a film is formed upon the substrate. But practically condition is complicated, with a multiple numbers of variables influencing the behavior of the film, such as laser fluence, background gas pressure, and substrate temperature. These variables permit the film behaviors to be modified slightly to suit singular applications. However, a great amount of time and effort is involved in optimization [42].

4.6. High-Velocity Oxygen Fuel

To achieve better properties the process is carried out by heating the material and then accelerated to a constituent's surface by a gas stream which is made in a combustion chamber by burning the combination of oxygen and fuel as shown in Fig. 6. It further allows the high-pressure gas to escape via nozzle. A powder is heated and hastened towards the surface of the component by bringing it into the steam. The subsequent thermal spray coating involves thin overlapping platelets. Almost perfect surface finish is obtained by dense spray coating produced by spraying the molten or semi- molten matter on

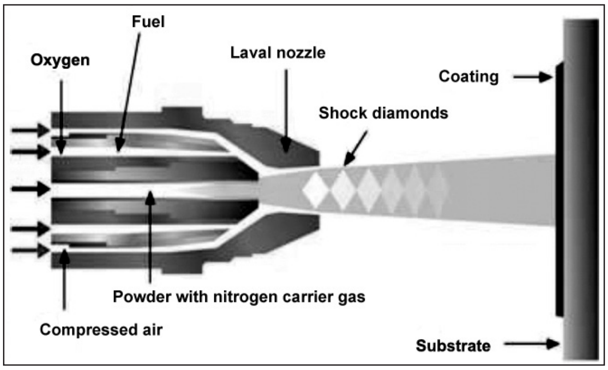

Fig. 6. High velocity oxygen fuel setup [46].

the surface through high temperature or high-velocity gas stream [44-45].

Inspite of numerous coating practices exists, but plasma-spray technique is used most commonly for HA coating on substrates.

5. Studies Related To Co-Cr Alloys

H. Minouei et al., [47] reported that to produce orthopedic implants cobalt-based alloy coatings are extensively consumed. Subsequent to casting, the alloy demands homogenization as well as solutionizing heat processes. In addition to this, bioactivation of the surface was also performed to raise the potential of tissue bonding. This article signifies that ASTM F-75 cobalt alloy was heated to a temperature of 1220°C for one hour along with the hydroxyapatite-bioglass powder. This tends to raise the surface bioactivation, solutionize and homogenize the microstructure. The heat conducted samples were submerged in SBF to acquire bioactive evaluation. SEM and XRD were carried out before and after the samples were submerged. After heat treatment, the outcomes displayed that a suitable microstructure was produced on the surface. The results obtained from in vitro evaluation as well as a bone-like apatite layer formed on substrates signifies that heat-treated cobalt samples were prospectively acceptable for orthopedic implants.

R. Liang et al., [48] applied vacuum plasma spray to form Ag coating on CoCr alloy. The corrosion behavior, wear properties and consequences of Vitro antibacterial on Ag coatings were analyzed. SEM, XRD, EDS and XPS studies were also carried out. SEM micrographs presented that the coatings were dense and no visible cracks were found. XRD results signify the surface contains mostly Ag and Cr. Also, a little content of Ag_2O and Cr_2O_3 were observed. According to EDS studies, Ag and Cr were consistently distributed. Ag coatings deliver alike wear behavior to that of CoCr alloys. On the other hand, corrosion resistance increases marginally. These results demonstrate Ag coating depicts better surface as well as antibacterial properties. Hence, CoCr alloys possess optimistic appliances in the biomedical field.

D. Cetiner et al., [49] in this study developed the TiO_2 layer on CoCr alloy to upgrade biological features to make it suitable for orthopedic implants. The titanium coating was employed on the substrates and there after oxidized in air at a temperature of 600°C for 60hrs. Surface classification was achieved by SEM and XRD techniques. Also, various properties such as wear, hardness, roughness, and bioactivity were examined. The obtained results revealed that the formation of TiO_2 on the CoCr surface led to enhance wear resistance as well as bioactivity.

M.H. Hassimet et al., [50] reported that CoCr alloys incorporated as one of the significant bioimplant having magnificent mechanical properties. In this study, CoCr alloy was coated with nanostructure TiO_2-Ag employing air plasma spray and HVOF approaches. The coated substrates exhibit remarkable hardness as well as preferable wear resistance when correlated to bare CoCr. The CoCr substrate coated with the HVOF technique displays low porosity when compared with the APS technique and results in superior wear resistance of CoCr alloy makes it a promising candidate for medical use.

H. Kheimehsari et al., [51] treated sol-gel method on CoCr implant to coat HA and various properties such as surface morphology and corrosion resistance were explored. Sintering was executed at four distinct circumstances. Crystalline phase of HA powder developed on CoCr alloy as confirmed by XRD. To analyze the corrosion resistance substrates were coated using two distinct thicknesses of 78µm and 142µm. After sintering these are examined in SBF by potential dynamic polarization and spectroscopy. The results signify that the corrosion rate was influenced by the thickness of the coating. On the other hand sintering practice of coated layer on CoCr shows a note worthy performance in upgrading the corrosion resistance. The sample with a coating thickness of 142µm reveals better surface morphology in comparison to uncoated and other treated surfaces. This makes CoCr suitable for various medical functions.

F.A. Vechietti et al., [52] employed a brushing method to coat CoCr alloy by HA mixed with pine oil and following heat treatment. The substrate was coated at four distinct surfaces to estimate the effect of roughness on wettability values and influence amidst substrate as well as coating. SEM and XRD are used to characterize the coated samples. PO shows the contact angle of 23° and metal implant of 68° signifies better homogenous coating. The response of heat treatment on the bonding strength of the coating was also examined. After heat treatment, the thermal and chemical investigation resulted that only the phases of pure HA were observed and no significance of PO was found. Among all the surface morphologies of the coatings with smoother surfaces exhibits enhanced adhesiveness as compared to rough surfaces. This derives HA-coated CoCr alloy is familiar to be advisable for medical utilization.

B. Singh et al., [53] described that CoCr alloys are broadly employed in implant materials. The corrosion behavior in bodily circumstances leads to allergic reactions. In this study CoCr alloy coated with NbTa alloy coating using plasma spray at three distinct compositions. The substrates were also coated with pure Nb and Ta. In SEM micrographs, for pure coatings, some microcracks were recognized. While crack free micrographs are obtained from reinforced alloy coatings. The results report that the coated substrates show higher corrosion resistance than uncoated and also the substrates coated with reinforced alloy coatings are far better than pure coated. These findings suggest that CoCr alloy with surface modifications is encouraging access for biomedical applications.

B. Singh et al., [54] reported that in total joint replacements CoCr alloys are broadly employed owing to their outstanding mechanical and wear properties. The extreme discharge of Co and Cr ions leads to various health problems. In this article, CoCr alloy was coated with pure HA and HA reinforced Ta to enhance the corrosion resistance of the substrate. The corrosion performance was analyzed by electrochemical values in Ringer's solution. The parallel behavior of surface hardness and Ta content was obtained along with satisfactory roughness and wettability standards. The aid in corrosion resistance was also observed as the Ta content rises. The obtained results indicate that on reinforcement of Ta in HA coatings assembles CoCr alloy suitable for bioimplants.

R. Liu et al., [55] reported that CoCr alloys are listed as the supreme tools for biomedical uses because of high mechanical properties and satisfactory corrosion resistance. The development of nano debris due to ion releases results in toxic behavior of the body. Various studies are carried out to enhance wear and corrosion resistance of CoCr alloy for clinical use. This article aimed to enrich hardness, wear as well as corrosion properties by plasma spray surface alloying with Ni as well as with both Ni and C at 300-400°C. All the layers coated with alloys are categorized and the outcomes exhibit the employed treatment settings developed very favorable surface layers on the CoCr material for biomedical and clinical purposes.

6. Conclusions

In this paper, the properties of various biomaterials are discussed with their mechanical and corrosion behavior. A previous literature on cobalt-based alloys was also discussed for advanced bone-implant replacement studies. The data delivered above clarifies that the design and selection of the materials are key factors along with the corrosion and other surface properties of the substrate. The leading origins for hip joint diseases are loosening of the implant due to wear debris, unstable implant and adverse reaction of a prosthesis with host tissue. Mainly implant materials are affected by degradation due to corrosion, as noticed the release of by-products which results in opposing the biological effects. In the case of cobalt-based alloys due to the development of chromium oxide (Cr_2O_3) passive layer and alloying additions, good mechanical properties along with the excellent corrosion resistance were achieved. Various coating methods along with coating materials discussed in this article also support CoCr based alloys to enhance parallel properties that are in demand for the orthopedic field. Moreover in the future, taking into consideration the increasing demand there is a need for higher life span of the orthopedic implants. Therefore, it is necessary to highlight the detailed studies to determine the behavior of advanced biomaterials, their clinical use, and a detailed methodology to enhance the biocompatible behavior that follows after implantation. Still handy cooperation in dynamic order is required among orthopedic surgeons, biologists and engineers to reach to great success with this challenging future of joint replacements.

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