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BIOMEDICAL APPLICATIONS OF TITANIUM AND ITS ALLOYS

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A B S T R A C T

Titanium and their alloys are biocompatible, corrosion resistant, good machinability, better fatigue strength and relatively low modulus of elasticity. Due to these desirable properties, they generally have cardiac and cardiovascular applications. For modern clinical requirements a proper tailoring of these materials can be done by surface modifications. This article gives a general perspective of surface modifications of titanium and its alloys. By allowing surface modifications of titanium and its alloys, properties of these materials can be changed in order to improve their biomedical applications.

1. INTRODUCTION

Titanium was discovered by Gregor (England) in 1790 (Braga et al., 2010). It was named by Klaproth in 1795 (Wang et al., 2014). It is a transition element in group IV and period 4 of Mendeleef's periodic table, with atomic number 22 and an atomic weight of 47.9 (Wilks and Wilks, 1991). It has an incomplete filled d shell in its electronic structure. That's why it has a tendency to form solid solutions with most substitutional elements (Leeet al., 1999). It has a high melting point of 1668°C with hexagonal closely packed crystal structure (α) up-to a temperature of 882.5°C (Tang et al., 2014). Above this temperature it transforms into a body centred cubic structure (β) (Saito et al., 2009). The density of titanium is 4.54 gcm^{-3} (Weng et al., 2013). The coefficient of thermal expansion (α) at 20°C is $8.4x10^{-6}k^{-1}$ with thermal conductivity of 19.2 W/mk (Bundy et al., 1955). The estimated boiling temperature is 3260°C (Panda et al., 2013). Its modulus of elasticity (α) is 105 GPa with yield strength and ultimate strength of 692 MPa and 785 MPa, respectively. Titanium alloys are classified as α, near α, metastable β, stable β, α+ β (Derjaguin et al., 1975).

Figure 1 shows the main characteristics of titanium alloys (Field et al., 1992). Although the α and near α titanium alloys show limited temperature strength, on the positive front they have a good corrosion resistance. α + β titanium alloys on the other hand exhibit good strength (Chrenko et al., 1975). There is a low modulus of elasticity and good corrosion resistance in case of β alloys (Berman et al., 1965). Titanium and its alloys are required in the military and aerospace industry, apart from medical, surgical and dental devices (Valentin et al., 1994). Due to lower modulus, better corrosion resistance and superior biocompatibility, it is a perfect material for biomedical applications (Veiga et al., 2012). It is preferred over conventional stainless and cobalt based alloys (J. Asmussenand D. Reinhard., 2002). Aging and accidents may cause damage to the hard tissues in a human body and animals (S. Rand, and L. Deshazer, 1985).

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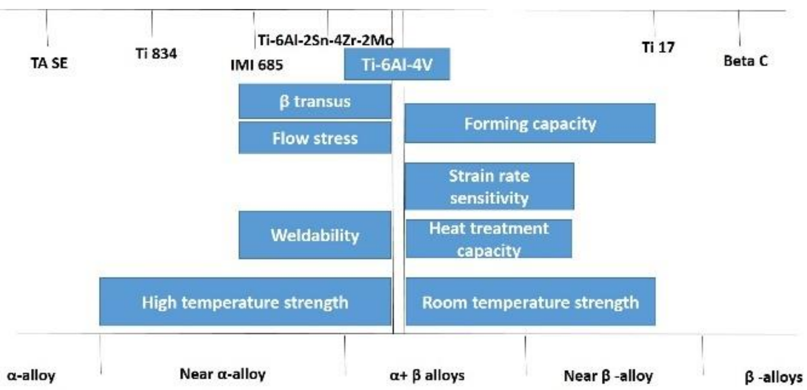

Figure1. Main characteristics of different titanium alloy family groupings

In such cases, artificial replacements of hard tissues are a common practice, which may be done by surgical approach (Whitfield et al., 1998). Different endoprosthetic materials are required which are biocompatible depending upon the functions and regions of the human body (Tzeng et al., 2013). Titanium and titanium alloys are used as hard tissue replacements in artificial bones, dental implants and joints (Murakawa et al., 1993). Due to smaller elastic modulus, it possesses low stress shielding (Aslam et al., 1992). These materials can be used in artificial hip joint which consists of articulating bearing (femoral head and cup) and stem. While designing this joint it is necessary to produce natural movement in the hip joint (Vescan et al., 1997). The stem is to be designed in such a way that it should secure the positioning of the femoral head with the other components (Gluche et al., 1997). These alloys are also used in knee joint replacement which consists of patella, femoral component and tibial component (Wang et al., 2014). Subperiosteal, endosseous and transosteal are the forms of dental implants of titanium and its alloys classified according to their shape and position (Migliorini et al., 2014). Subperiosteal implants comprise of custom-cast framework which rests on the surface of the bone (Zhecheva et al., 2006). In the oral cavity prosthesis is used on abutments penetrating the mucosa. In frontal lower jaw transosteal implants can be placed where as endosseous implants are used in both upper and lower jaws through mucoperiosteal incision (Zhecheva et al., 2006). These implants are most commonly used types and are either used as single implant or partial and total endentulism (Azevedo et al., 2005). The dental implants are designed to fuse with the bones (G. M. Swain et al., 2004). This requires good surface modifications such as chemical etching, plasma spraying and grist blast to improve the fusing capability of the dental implants with the bones (Diniz et al., 2003). In artificial hip and knee joints either bone cement fixation or cement-less implantation is employed (K. G. Budinski, 1991). Due to mixed lubrication regime wear occurs in articulation of artificial joints (Qu et al., 2005). During motion billions of microscopic particles are trapped inside the tissues of the joints (Lee et al., 1998). This may lead to unwanted body reactions. This results in the formation of granulonia. For device performance the material for femoral head and cup is important. In order to reduce the wear variety of materials have been used (Zitnansky et al., 2004). Different surface treatments have been suggested for this purpose (Ding et al., 2002). For load-bearing implants, the materials with high wear resistance and surface modifications are required (H. R. Ogden, 1961). This has attracted lot of scientific interest. The ideal materials should have good biocompatibility, chemical composition to avoid adverse chemical reactions with tissues, high wear resistance, low debris generation, anti-corrosion, good strength for cyclic loading and a low modulus to reduce bone resorption (E. W. Collings, 1984). A bio-inert material which is stable in the human body is preferred to avoid tissue reactions (Polmear, 1981). These reactions may be due to hard tissue replacement which react with body fluids and tissues (P. J. Bania, 1990). Polymethylmethacrylate (PMMA) is used in cemented prosthesis in which components are fixed to the body implant bed. At the time of surgery, the blood and medullary fats need to be removed, while the cement is usually prepared and applied to the body implant bed (R. W. Schutz, 1993). Due to exothermic reaction the cement hardens after the penetration into the cancellous bone structure (Morscher, 1995). Therefore, a continuous cement mantle is fixed in the bone structure. Because of their characteristics, titanium and its alloys are commonly used in protective cases in pacemakers, prosthetic heart valves, circulatory devices, artificial hearts (B. Yan et al., 1999). Stunts and occlusion coils in intravascular devices have received good appreciation (L. Pastewka et al., 2011). The use of shape-memory nickel-titanium (NITINOL) have received considerable attention. Since titanium is strong, non-magnetic and inert, that is why it can be used in cardiovascular applications (I. P. Hayward, 1991). In heart valves, disk is made of pyrolytic carbon while the ring and struts are made of titanium and its alloys. Knitted Teflon cloth is used around the ring for sewing ring which is placed around the main ring (D. H. Buckley, 1975). In order to enhance the blood compatibility, the metals used in prosthetic hearts are coated with a thin carbon film. Stents are used in cardiovascular disease, which dilate and keep narrowed blood vessels open (J. Black, and G. Hastings, 1998). Due to its special shape memory effects titanium nickel alloy is used in vascular stents.

This alloy is a stoichiometric compound of titanium and nickel. If subjected to macroscopic deformation this alloy exhibits the shape memory phenomenon (S. J. Bull, 1991). This results in total recovery of the material. After removal of load or heating this material shows complete shape recovery. NITINOL is an alloy of nickel and titanium which consists of 55 wt. % of nickel and 45 wt. % of titanium (P. Hedenqvist et al., 1990). NOL stands for Naval Ordinance Laboratory. NOL is the laboratory where this material was discovered by Buhler and his co-workers. In late 1960's the research on nickel-titanium alloys in the field of medicine was started (D. S. Rickerby and R. B. Newbery, 1988). It was seen that these alloys can be used for poisoning of tissues, tailored compressive fixation of bone fragments, dentures to the living tissues and anchoring of implants. Moreover, these alloys are used in surgical treatments, for biliary obstructions (A. Blomberg et al., 1994). Titanium and its alloys are used as bone-fracture fixation also known as osteosynthesis. The functions of the injured limb are disabled due to bone-fracture (A. Hirata, and M. Yoshikawa, 1995). Osteosynthesis is a process which can cure bone fracture and restore bones perfectly. Maxillofacial implants, bone screws and bone plates are the typical implants for osteosynthesis. The osteosysthesis applications require special properties which are possessed by titanium and its alloys (C. Rossington et al., 1984). The fracture gap is cured by lag screws which exert compression on the fracture gap. For direct bone fixation bone screws can be used. The bridging devices for skeletal areas are obtained from bone plates. Bone plates can be used as interior fixators (P. Andersson, and A. Blomberg, 1994). Many favourable properties of titanium alloys are due to the presence of the surface oxide. Upon exposure to air the native oxide film grows spontaneously on the surface. Chemical stability produces biocompatibility, excellent chemical inertness, re-passivation ability and corrosion resistance in titanium and its alloys (N. Axen, and S. Jacobson, 1994). The structure of nano-film of titanium oxide are responsible for the favourable properties. The oxide film is composed of TiO_2 and is typically 3-7 nm thick (S. J. Bull et al., 1994). Blood and interstitial fluids come in contact with materials implanted in vivo thereby resulting in corrosion. Corrosion is increased due to amino-acids and proteins present in body fluids (N. Lee, and A. Badzian. 1997). The property of corrosion resistance is important for biomaterials. Due to corrosion the metal oxides may diffuse in blood and cause mis-function of the tissues. Titanium dioxide protects the metal from oxidation which improves the corrosive resistance (S. J. Bull, 1995).

2. SURFACE MODIFICATIONS

Titanium has a high specific strength and low elastic modulus. However, it has low wear and abrasion resistance. It has low hardness. In order to improve these properties, it is suggested to have PVD coatings such as TiN and TiC, ion implantation N^+, laser alloying with TiC and thermal treatments such as nitriding, hardening and diffusion (M. Ali, and M. Urgen, 2011). The wear resistance and resistance to abrasion in Ti-6Al-4V can be improved by ion implantation. Due to surface treatment hard layers of various oxides are formulated which improve the lubrication capabilities. The ability of a material to perform a particular specific application in a host is biocompatibility (R. H. Dauskardt et al., 1998). Due to inertness and good corrosive resistance titanium and its alloys are considered as biocompatible. In biological environment they do not show any significant corrosion. They do adsorb proteins from biological fluids. Cell growth and differentiation is also supported by these materials (T. R. Anthony, 1997). Lot of research has been done to study the effect of cell interaction with the surfaces of titanium and its alloys. Neutrophils and macrophages are noted on the implants which are followed by foreign body giant cells from activated microphages. Under the proper conditions' titanium heals in close apposition to the mineralized tissues (N. Y. Tsubouchi et al., 2010). The bond of mechanical interlocking is formulated between the surface of the metal and the bones. For biological bonding, the methods of surface modifications are implemented to improve the bioactivity and bone conductivity of titanium and its alloys (K. Adachi et al., 1997). For a specific biomedical application fatigue strength, controlled degradability and non-toxicity are highly relevant for selection of biomaterials. For artificial medical devices material surface plays an important role (S. Chandrasekar, and B. Bhushan, 1992). There is a specific interaction between the biological environment and artificial material surfaces. The normal manufacturing steps in titanium made implants lead to contaminated surface layer. This layer is often plastically deformed, stressed, poorly defined and non-uniform (M. Chen et al., 2001). The solution for such problem is surface modification. This leads to specific surface properties. A good bone formability is required to accomplish biological integration. Blood compatibility is important for blood contacting devices such as artificial heart valves (T. Bell et al., 1998). The bulk attributes such as low modulus, machinability, formability and good fatigue strength are retained through surface modifications. They improve the specific surface properties such as wear resistance and corrosion resistance. Surface modifications can be done by mechanical methods such as grinding, shaping, polishing and blasting (G. Cabral et al., 2008). These methods remove surface contamination, improve adhesion in subsequent bonding steps and obtain particular surface topographies and roughness. Apart from mechanical methods, chemical methods can be also used for surface modifications. The methods include chemical vapour deposition, bio chemical modification, chemical treatment, electrochemical treatment and sol-gel. Chemical treatment involves chemical reactions, electrochemical treatment on the other hand involve electrochemical reactions and biochemical modifications involve biochemical reactions which take place at interface between the solution and the metal or alloy (S. Chowdhury et al.,2004). In chemical vapour deposition chemical reactions take place at the substrate surface between chemicals in the gas phase and the surface of the substrate.

Figure 2 shows the sol-gel process of titanium oxide-hydroxyapatite composite coatings. The high adhesion strength of TiO_2 and bioactivity of calcium phosphate is an advantage in coatings of composites such as titania/hydroxyapatite. Thses coatings can be prepared by the process depicted in figure 2. By mixing acetyl acetone, titanium isopropoxide, nitric acid, n-propane alcohol and distilled water, titania sol can be prepared. Anhydrous ethanol can be mixed with hydroxyapatite powders (V. A. Muratov et al., 1998). Therefore, TiO_2/HA composite coating can be produced which is homogeneous porous and rough. Ti-OH can be detected on the surface of the coatings. These coatings are found to be having good adhesion strength. In sol-gel process the chemical reaction takes place in the solution itself. Chemical treatment between titanium and other solutions take place at the interface (E. C. Pleuler et al., 2002).

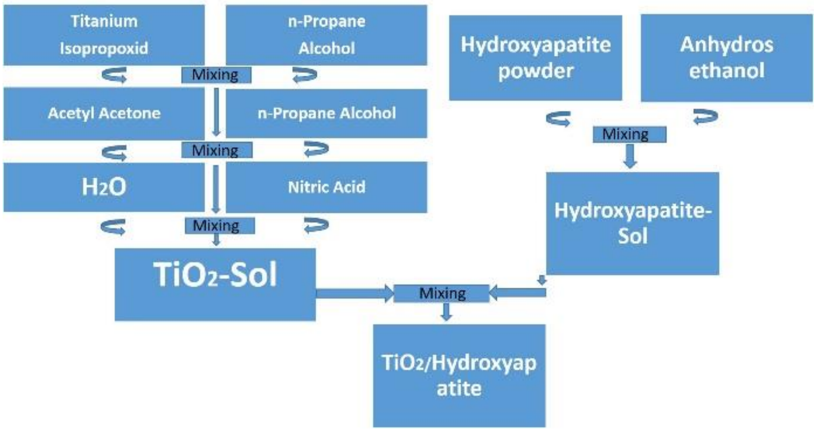

Figure 2. Sol-gel process of titanium oxide-hydroxyapatite composite coatings

The solutions generally used are H_2O_2, heat, alkali, acid and passivation treatments. One of the important surface modification process is acid treatment. It removes dirt, contamination and oxides from the surface. Many acids and combination of acids is used for pre-treatment (R. Chromik Richard et al., 2008). The standard solution for acid treatment of titanium is 10-30 vol. % of HNO_3 and 1-3 vol. % of HF in distilled water. HF acid reacts with titanium and forms titanium fluorides and hydrogen. TiO_2 is the oxide generally formed (H. Czichos et al., 1995). The residues form the etching solution is fluorine. Below the oxide it is examined that some treatments can lead to hydrogen incorporation. Many researchers suggest that titanium and its alloys can be etched properly by using HCl plus H_2SO_4 and alkaline solution. Titania gel can be used to improve bioactivity of titanium and its alloys. These can induce formation of apatite (K. Mallika, and R. Komanduri et al., 1999). Titanium peroxy gels are produced when H_2O_2 reacts with titanium surfaces. It actually offers a method for chemical dissolution, which results in titanium surface oxidation. If titanium is treated with H_2O_2/0.1 M HCl solution, an amorphous titanium gel layer can be formed. A layer of titania amorphous gel on the titanium surface is formed when the reaction between H_2O_2 solution and titanium takes place. Chemical treatment determines the thickness of the titania gel layer. This titania gel comprises of two layers (A. Fernandes et al., 1997). The inner layer is around 5 nm and outer layer is porous in nature. The gel can be transformed from amorphous to crystalline state by heat treatment above 300 °C. In this case the rutile phase is dominant over 700°C. The gel transformed to anatase below 600°C. the morphology of the pores of the gel layer can hardly be changed up to 600°C. After heat treatment of 700°C large spherical particles of titania are formed (T. E. Fischer, and H. Tomizawa, 1985). A fully densified titania layer is formed at around 800°C. The anatase structure of titania gel is found in the temperature range of 400°C to 500°C. This structure possesses a wonderful bioactivity. The degradation of bioactivity is seen at higher temperatures, which increases the rutile content in the structure (D. Ghosh et al., 2008). A titania gel layer on the surface of titanium is also found when chemically treated with $H_2O_2/TaCl_5$. This layer is generally amorphous. Between 300°C to 600°C the amorphous titania is transformed into anatase by heating. In simulated body fluids, this becomes active for apatite deposition. In thicker titania gel layers, cracks are found which are home to nucleation of apatite. A larger amount of apatite is found in thicker titania gel (P. Victor Astakhov, 2004). This happens when these layers are supposed to immerse in simulated body fluid up-to a period of one day. The whole surface is covered with apatite after two days. Bioactivity can be also improved by alkali and heat treatment. Bioactive ceramics such as bioglass, glass ceramic and hydroxyapatite can be used as surface which enable biologically active bone-like apatite layer to grow on their surfaces. In this process for 24 hours the material is immersed in 5-10 M NaOH and KOH. Then rinse in distilled water for five minutes (V. P. Astakhov, and S. V. Shvets, 2001). Dry the specimen in oven at 40°C for 24 hours. Heat to around 600-800°C for one hour. The heat treatment is performed at 10^{-4} to 10^{-5} torr. This prevents the titanium from oxidizing. A porous surface will be formed on the titanium surface after treatment. Sodium titanate hydrogel is formed on the treated titanium which can be acquired by XRD patterns (M. Z. Huq, and J. P. Celis, 2002). After 800°C for one-hour crystalline sodium titanate, anatase and rutile precipitate. Bone-like apatite is formed after treating titanium in simulated body fluid for four weeks. In simulated body fluid, the sodium titanate is highly negative charged. If the soaking time is increased the surface potential increases (J. Achard et al., 2005). Then it decreases with increasing time and finally remains constant at a negative value. Apatite formation plays a very imperative role in osteoblastic differentiation. For bone marrow cell differentiation, bone-like apatite formed titanium created the most favourable conditions. Surface apatite formation is the process by which alkali and heat-treated titanium bonds with the bones (N. A. Prijaya et al., 1994). Sodium removal enhances the bone-bonding strength of titanium if immersed in 5 M NaOH at 60°C for four to eight weeks. At fifteen to twenty-four weeks' bone bonding strength was inferior to alkali-heat treated titanium. In bioactive titanium removal of sodium resulted in acceleration in vivo bioactivity. This leads to faster bonding of bones due to structure of anatase surface. This also decreased the adhesive strength due to the complete removal of sodium. Porous network of sodium titanate is found on the surface of Ti-In-Nb-Ta and Ti-6Al-4V ELI alloys by vitro tests using simulated body fluids. This happens with surface modifications by alkali and heat treatments. It is found that the corrosion resistance of Ti-In-Nb-Ta is higher than Ti-6Al-4V ELI alloy (J. Isberg et al., 2004). Under simulated body fluids, titanium treated in NaOH formed non-uniform apatite. Apatite formation takes place when titanium is etched with HCl under inert atmosphere. It produced a uniform micro-roughened surface. Apatite nucleation was found to be homogeneous and its thickness increased in NaOH with increasing time (A. Tallaire et al., 2005). The surface bone bonding capability of titanium can be increased if treated with HCl followed by NaOH. For bone ingrowth plasma-sprayed titanium surface is found to be suitable. The shear forces that can damage the bones can be endured by the materials (M. Amaral et al., 2006). If such materials are alkali and heat treated, they lead to higher bonding shear strength. Such materials can be useful in cementless total hip anthroplastry and total knee anthroplastry. After alkali and heat treatment it is seen that a nanosized porous layer of sodium titanate is formed on titanium implants. This implant has a good bone-bonding strength. This happens due to mechanical interlocking and large bonding area of micro-sized rough surface (S. Schwarz et al., 2002). Using the sol-gel technique silica based coatings are produced which can be coated on titanium. Calcium phosphate, titanium oxide and composites such as TiO_2-CaP have been coated on titanium and its alloys and are highly recommended for biomedical applications (T. Yang et al., 2002). By the sol-gel process titania coatings can be synthesized. These have applications in catalytic electrical and optical fields. The sol consists of the following material: ethanol, hydrochloric acid and tetra isopropyl orthotitanate (W. Kulisch et al., 2006). The titanium is dip-coated in the sol after the mixture is prepared for around one hour. For slowing down the condensation reaction the temperature is maintained at zero-degreecelcius (S. Takeuchi et al., 2001). The sol is also added with valeric acid. The withdrawal speed of 0.3 mms^{-1} is maintained in titanium which is then heated to 600 °C for ten minutes. Finally, the samples are ultra-sonicated in acetone and ethanol (F. A. Almeida et al., 2007).

Chemical vapour deposition involves the deposition of a non-volatile compound on the substrate. This involves chemical reactions between the surface and the chemicals in the gas phase. It varies from physical vapour deposition since in physical vapour deposition there is no chemical reactions taking place. Physical vapour deposition on the other hand generally involves evaporation and sputtering.

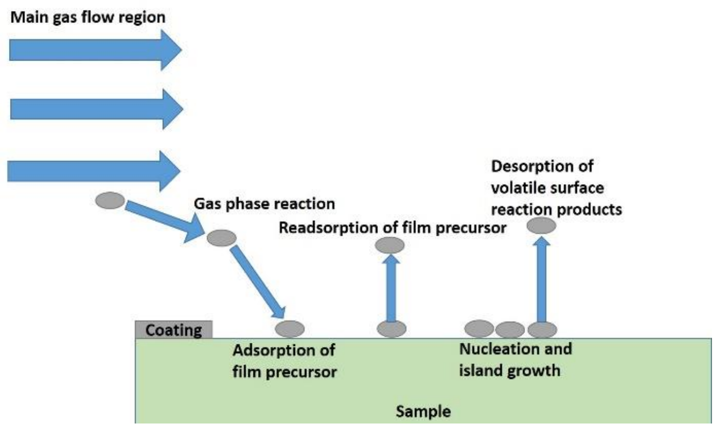

Figure 3. Sequence of gas transport and reaction processes contributing to CVD film growth

Chemical vapour deposition is a successful process used widely to deposit coatings or organic and inorganic compounds. These films can be deposited on metals, semiconductors and other materials. The steps involved in chemical vapour deposition are shown in figure 3. It involves transport of reactants to the reaction zone. Reactive species and by-products can be produced through chemical reactions. Transport of the reactant to the surface of the substrate. Adsorption and diffusion of these species on the surface of the substrate (W. Tan and T. A. Grotjohn, 1995). Homogeneous reactions leading to coatings. After surface reactions, adsorption of volatile products. Diffusive transport of by-products from the reaction zone. Tribological properties of titanium and its alloys can be improved by chemical vapour deposition, which involves the deposition of polycrystalline diamond coatings. These coatings exhibit highest hardness and highest heat conductivity. Thus, can prevent wear rate. Due to hydrogen-saturated surface, friction is lower in such coatings. These coatings are as biocompatible as titanium and its alloys and have been frequently and successfully used in biomedical implants (X. Wang et al., 2016).

Physical vapour deposition and thermal spraying are different from chemical vapour deposition as there is no chemical reactions taking place in these methods. The surface modified layers on titanium and its alloys can be attained due to thermal, electrical and kinetic energy. The material in thermal spraying is melted and coated on the surface at high speed. In thermal spraying a plasma jet is required to create a high temperature flame. It is divided into flame spray or plasma spray (M. Amaral, D. J. Silva et al., 2009). Thermal spraying methods are explained in figure 4.

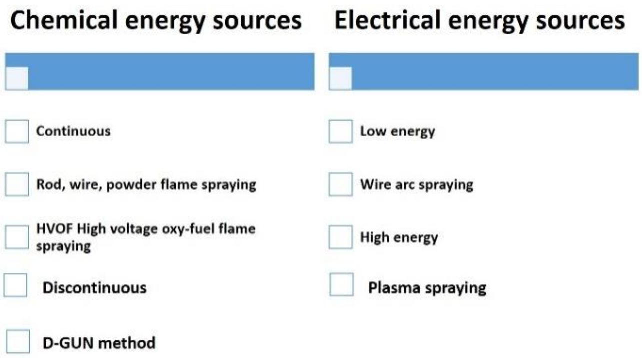

Figure 4. Thermal spray techniques divided by their principal energy sources

According to maximum temperature attained the thermal spraying is divided into flame spraying and plasma spraying. The flame spray torches heat the coating material and the plasmatrons attain the energy from electrical currents. In flame spraying oxyacetylene torches are used. These attain a temperature of 3000k (V. A. Sumant et al., 2007).

During 1970s and 1980s high velocity oxy fuel torch was developed. It a thermal spraying technique used to modify the surface of titanium and its alloys. Figure 5 shows a graph of high velocity oxy fuel technique. It portrays the dependence of mechanical properties and phase composition HVOF and HA/titania (YSZ) coatings on processing conditions.

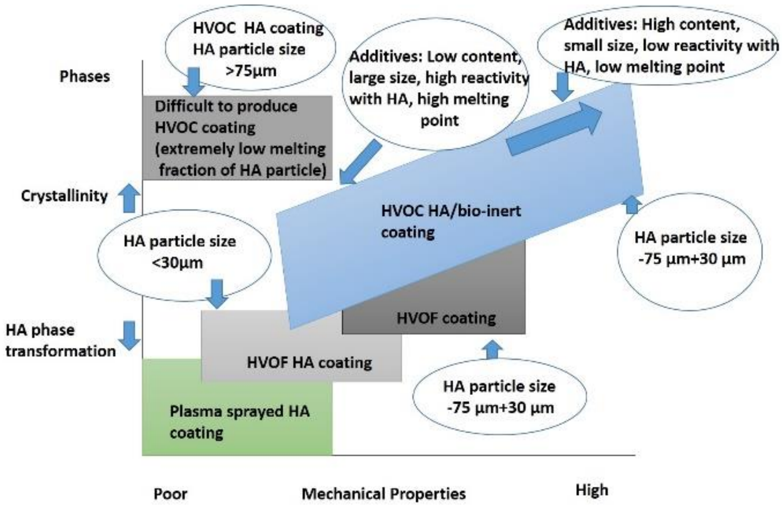

Figure 5. An overview of both mechanical properties and phase composition of HVOC sprayed bio-ceramic coatings on processing conditions

The comparison with plasma spray HA coatings is also shown in this figure. The technique of HVOC contains a carrier gas (S. Gupta et al., 2003). With the help of an injector the powder is injected into the carrier gas. It is allowed to burn in the combustion chamber. It flows out of the torch through a nozzle. This technique has been found to be very useful (S. Achanta et al., 2009).

3. CONCLUSION

In this review titanium and its alloys are discussed in detail. The applications of these materials in the industry especially medical field are elaborated. The discussion is further made strong by putting stress on the surface modification method. The properties such as mechanical, chemical and biological can be improved for biomedical applications. Physical, chemical and mechanical methods are discussed with effect of modified layer on the surface of the material. Suitable surface modification method can improve the properties of titanium and its alloys. For clinical needs these modifications can play a pivotal role.

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