A Review on Corrosion of Metallic Implants: Titanium

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Abstract - *Corrosion is characterised as the destructive attack of a metal by chemical or electrochemical reaction within its environment with water, oxygen, sulphur and so on. Human bodies use metals and alloys as biomaterials for decades to fix, substitute, or uplift tissues and structures. The corrosion activities of these materials have to deal with the metals which are implanted within a human body. Alloys based on Magnesium, titanium Co-Cr-Mo, and stainless steel consists of large numbers of metals and is of great significance, used in medical devices such as in orthopaedic, dentistry, and related to heart and blood vessels through vast class of uses. Every single of these experience tough and separate environments. Such conditions involve the electrochemical environment which is produced by the functioning body i.e. "biological environment" and the mechanical environment. By concentrating on implant reclamation, following report will provide a concise summary of the corrosion, corrosion in humans and its types which can be seen in the human body. Corrosion in cardiovascular and orthopaedic implants will be described. Why titanium is mostly used as an implant specially as a dental implant and finally the current and future development of the biomaterials will be described.*

Key words: Titanium, Corrosion, Electrochemical Reaction, Orthopaedic Implants, Biomaterials

1. Introduction

In the field of material science, the metallic implant is a boon for mankind as some of the unlucky humans born with cardiovascular disease and some old age people require these metallic implants to raise their lifetime. The main disease normally faced by the old age people is arthritis. Sometimes young people also face this disease which causes resistance to mobility and crucial pain. Since now, the cause of this disease is unknown even after so much advanced equipment and technologies[1]. Sometimes people who are young like sports person also need replacements, reason being fracture disintegrate and wrenched[2]. The concept of biomaterials is 4000 years old when Egyptians and Roman people used linen for stitches or to close a cut or a wound[3]. For replacement of limbs they used wood as a bio metallics material and they had no idea of corrosion of these implants[4], [5]. Biomaterials such as Ti, stainless steel are some other examples of materials which we are using till now after the World War II. To fabricate the bio Metallic implants some other materials are used such as alloys, metals, polymers, composites and ceramics[6]–[8]. These materials experience different biological surroundings and these materials have different physical and chemical complexion. And complicated problem arises whenever these materials interact with body tissues and bones[9]–[11]. At first test of implants bio material was carried out on animals that results to the generation of good biomaterials that could be implanted in the human beings[12], [13]. Following are some prior and foremost requirements that are required to implant a biomaterial: -

1. The implant bio material must not catalyze unfavorable impact.
2. It must provide or enough strength and to withstand the force and do not go through crack while performing their task.
3. It must have property to resist wear and corrosion.
4. It must remain in contact with the other bones or tissue for a longer span and must not cut out until the death of the receiver.

Corrosion-related failure of an implant is one of the biggest challenges and this research subject is addressed by a different penman in their books and in articles. One who is willing to know more about corrosion of implants can read these [1-15].

The important factor while giving preference to metals and designing of metals and alloys for in vivo use is Corrosion. Different corrosion mechanisms can cause loosening and failure of implants[14]–[19].

2. Corrosion in Humans

Corrosion, the rapid decay of substance by electrochemical attack is of very much importance especially when a bio metallic implant is interpolated in the human body's active electrolyte atmosphere. An implant confronts serious corrosion contexture which contains blood and other component of the body fluent that include various components such as water, amino acids, Na, proteins, Cl etc. and aqueous part of human body exist of different anions, cations and organic substance[20], [21]. Upon absorbing the products due to anodic or cathodic reaction, the biological molecules disrupted the implant's corrosion reaction equilibrium. Proteins are attracted towards the ions of metal and transfer them fro from the implant shell and affix equipoise throughout the surface binary layer which is created by the e^- on the shell and extra cations in the solution. Hydrogen produced by cathodic reactions serves as an inhibitor of corrosion, though; the existence of bacteria appears to alter this activity by consuming the hydrogen in the vicinity of the implant to increase corrosion. Corrosion is also influenced by change in the value of the pH. Although, the pH value of the body of human is generally sustained at seven, this value varies between three and nine because of various reasons, likewise injuries, any disease imbalances the biological system, infections from ineffective agent. The pH-value around the implant after operation usually ranges from 5.3 to 5.6. As can be seen by the fact that a large number of the materials used are shielded from the surrounding attack by surface oxide layers, there is scientific proof of metal ions emitted from the implants and this leaching was due to the corrosion cycle [22]. Following are the most common occurring corrosion:

- Pitting
- Intergranular
- Galvanic
- Stress
- Fatigue
- Wear and fretting

Thermodynamic forces that causes corrosion by oxidation or by reduction and kinetic obstacle like surface oxide layer which in real obviate corrosion reaction are two physical qualities which judges the corrosion of the implants[23], [24].

'Pitting corrosion' is a sort of local corrosion that occurs at a more bounded space while the bulk of the passive top is complete. It is recognized in many cases by the form of pits the depth of which is greater than the diameter. This tends to occur in the company of halogen family which includes bromine, chloride and iodine ions on passive alloys. The defects of films are attacked by species of halogens which results in the breaking of the film. Some of the pitting corrosion are shown in Fig:1

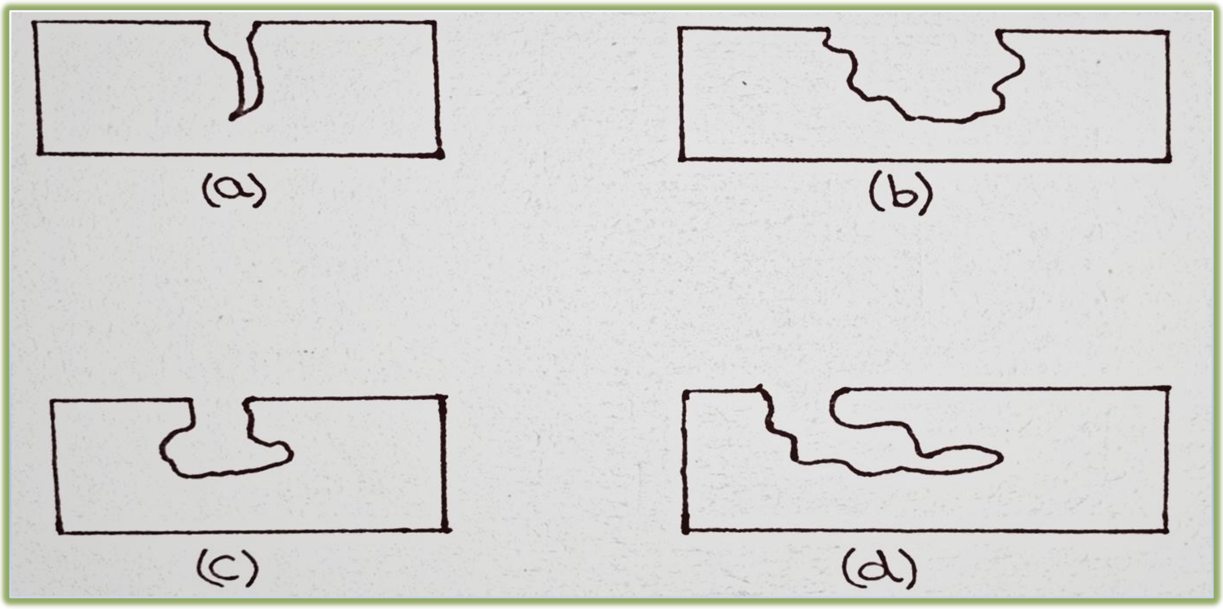

Fig -1: (a) Narrow Deep (b) Elliptical (c) Subsurface (d) Undercutting

Intergranular corrosion is a form of corrosion that progresses particularly and profoundly at the edges of the grain, while the interior of the grain is intact as shown in Fig:2

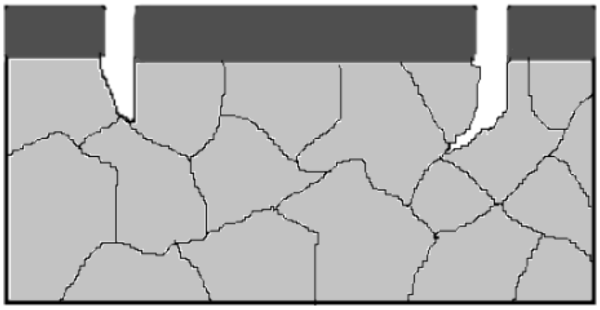

Fig -2: Intergranular Corrosion

Galvanic corrosion is a type of corrosion that occurs when different corrosion potential is shown by two different types of metal individually and kept in contact with electricity one another in an electrolyte. Less noble potential is seen on the metal and the protection of cathode takes place on the other metal at noble potential as shown in Fig:3

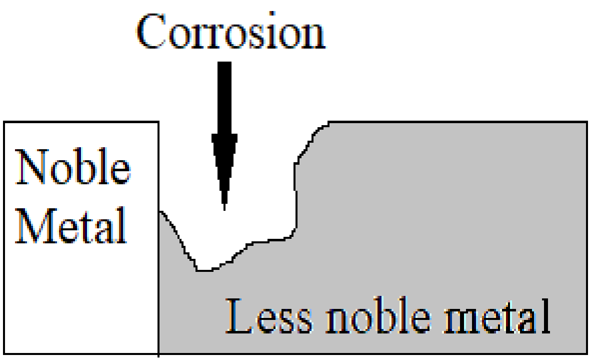

Fig -3: Galvanic Corrosion

Stress (Fig:4), fatigue (Fig:5), and wear and fretting corrosion (Fig:6) are the corrosion which occurs when the implant is under some mechanical loading like static load, tensile or compressive load or cyclic stress and wear and fretting. Due to this the surface of an implant is distorted and the passive layer is broken by repetition. Corrosion of metal under the load of mechanical frequently takes place at the area where absorption of stress is more.

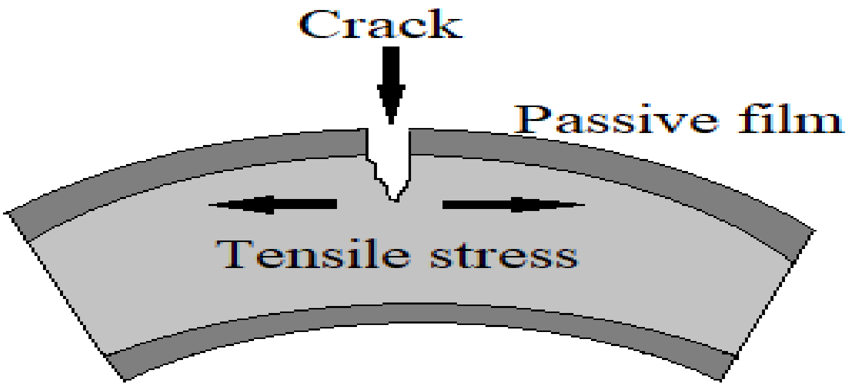

Fig -4: Stress corrosion cracking

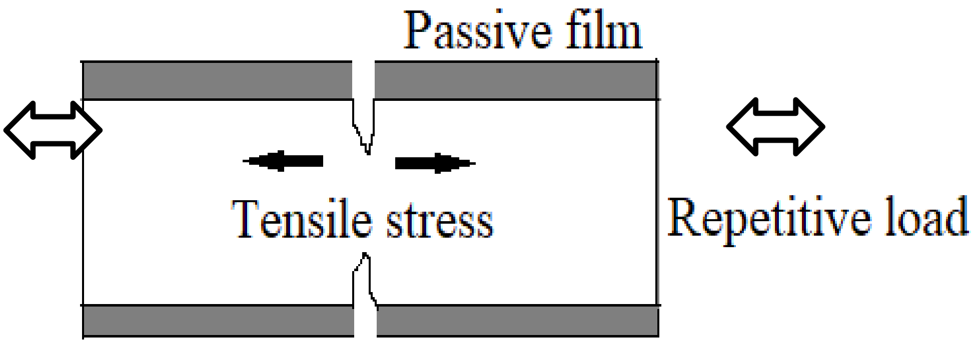

Fig -5: Fatigue corrosion

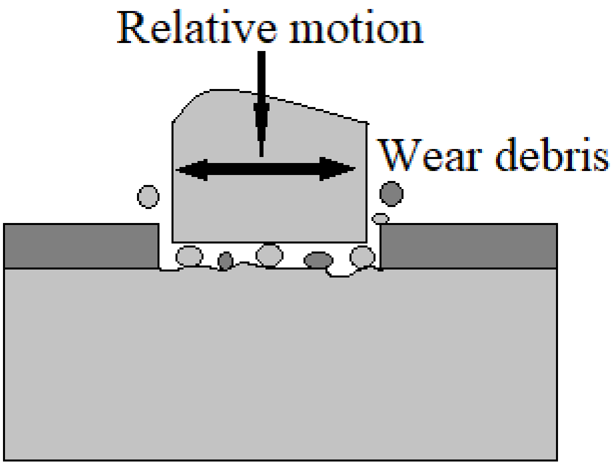

Fig -6: Wear and fretting corrosion

Surface Oxide Film on Bio Metallic Implants

When a metallic substance disrupts the surface oxide layer, corrosion occurs and metal ions are emitted constantly until the layer is transformed. The time which is taken by a layer for repassivation is also called regeneration time and it is variable in different substance that is being used. The regeneration time is found to be longer in stainless steel and takes less time in Ti-6Al-4V, an alloy that is widely better recognized and extensively applied for orthopaedic implementations; that indicates the fact that more metal ions are emitted from stainless steel than the Ti6Al4V, That takes out one of the supreme characteristics that this alloy possesses, other than its other beneficial characteristics. In Hank's solution the repassivation rate of Ti is observed to be shorter than that in saline and continues to remain unburdened by the solution's pH. A covering provided on the implants is therefore desirable in specific, as it will slow down the process of corrosion.

A layer on metal material is generated which act as crucial role as an inhibitor which cause metal ions to come out and this layer is known as surface oxide layer. When the metal ions are released this cause in the change of the gest of the surface oxide. The structural alteration of the surface oxide film depends on the reaction that occurs between the living tissue and implant material. The Number of ions Unleash is decided by the regeneration time of the surface oxide layer after disintegrate. Surface oxide layer which is on metallic implant have a very crucial part to play, not only to resist corrosion but also for compatibility of tissues. Therefore, it is necessary to observe the property of the surface of the implants when it is a case of corrosion and compatibility of tissues. Biomaterials are used in vitro as well as in vivo research for their uses[25]–[27].

Corrosion of Cardiovascular Implants

Cardiac diseases, and especially Coronary artery disease, cause annual expiration of about 18 lac people in the Europe and over 5 lacs in the United States and that is the primary cause for middle-aged people to die prematurely[28], [29]. A stent is supposed to be an answer for this and they are made up of metal mesh and are expandable tubes which treat narrow arteries in human body. The process of placing stent in narrow arteries is called angioplasty. Implants in cardiovascular system must have specific biocompatibility in the blood to make sure that the system do not excluded due to unexpected "thrombogenic" or blood reactions. While bio metallic implants of cardiovascular may be manufactured by the use of natural tissues, there is clinical apprehension about the eventual calcification of these bio medical prostheses resulting to gradual tightening and ripping of the implants. Non-bioprosthetic implants are made from pyrolytic graphite coated with carbon, pyrolytic titanium coated with carbon, stainless steel, alloys of cobalt and chrome, alloys of cobalt and nickel, polypropylene-coated alumina and PTFE. Other than the boundaries on materials assess by the necessity of blood biocompatibility and the issues related with sketches assess by the required to replenish blood run in the veins, proper heed must be carried out in all circumstances to dodge the danger of another procedure of surgery. Moreover, if the device which is implanted fails disastrously, it will surely lead to the death of the recipient[30].

Corrosion of Orthopedic Implants

The implants of bones consist of ad interim implants for example: - plates, nut & bolts and permeant implants that is used to substitute hip, knee, lumbar, shoulders, toes, fingers, etc. The mechanisms of corrosion that happens in artificial implants are split corrosion at protective areas in the screw and disc interaction, and this is under the head of screw repairing and implant corrosion pitting made of stainless steel[31]. The primary reason of orthopedic implant failure is worn and tear, which in turn speeds up the corrosion. Strong abrasion defiance materials like ceramics, thus, Co-Cr is also used to make orthopedic bioimplants. Alloys of titanium are used in hip implants only to make the femoral part, and the ball is composed of Cobalt-Chromium and some other tough ceramics. Sometimes even the 'femoral' structures are covered with powdery cement to ensure proper bonding. Once implanted with bone cement, the scientist, Waller had noticed crevice corrosion in femoral structures composed of Ti-6Al-4V and Ti6Al-7Nb[32].

Titanium Implant and its Performance

If we talk about using Titanium as a dental implant, then it is the only metal that is accepted worldwide and given preference due to its strong strength and less density as compared to Steel and other metals which are tested earlier internal applications. Titanium metal has perfect capability of assimilation into bones where other materials are incompetent or unfit for this job. Our body has unique ability to nix all unwanted elements that raid on it. There are various methods by which we can Discover them. The first and foremost case is with unwanted proteins that are swiftly removed or excluded by our body. By this process our body is forfend against harmful viruses and bacteria. This process is also accountable for refusing the other harmful germs from other human beings the second case is the modification which is done by metal ions that are present in our proteins which activates a self-protective chemical process and nix the unwanted metallic particles. All metals that are attached to body fluids attain oxides and oxygen molecules and go through a process called ionization. This leads to oxidation of the outermost layer of atoms, (which are not oxidized) and separate themselves from the structure. After the separation, the next layer of metal atoms comes in contact with oxygen and the same chemical reaction i.e. oxidation occurs to that layer causing a separation from the rest of the structure. This process of releasing ionized metals keep repeating and the metallic implant. This happens because of instability of ions and they attached to server protein to regain their stability. By doing so they develop a complex of metal protein which is mis knowingly identified by the body as an attacking harmful substance like bacteria or virus. And if the body is attacked by an antigen, it starts to produce antibody by activating the immune system to guard itself from it. Multiplication of lymphocytes starts to clash with the very attacker. Stainless steel that contains too much irons also produces same kind of reaction and same kind of response against it but Titanium does not show any response or react like that. No doubt, the oxygen reacts with its very upper layer but the strong attraction between the layers does not allow the layer to get separated from the rest of the structure. Those layers of atoms of Titanium stay strong and steady in their position which does not result in atom separation. And if the separation of atom will not occur then it will be considered as no activity took place which will be unnoticed by the immune system. Bones and tissues will repair their damage without being aware of the invader and construct a firm protective layer with that invisible substance. It is some kind of boon for our human body that it gives permission of Titanium material to be used as medical implant in various areas of the body like in dental, orthopaedic and cardiovascular implants. Therefore, the term "Nix" is incorrect, because the body cannot nix something if it is not detected by the body.

Current and Future Development

The area of rusting and corrosion is very wide. According to dentistry, orthologs and cardiology these medical implants encounter several obstacles because there are lot of trouble to figure out. Now a day, research is concentrating on the manufacturing of materials that are composite and are used for medical implants which will copy the nature of its surrounding as our bone and cartilage are congenital composites. Although to attain the more knowledge about the comportment of composite materials, scientist and researchers are learning and exploring this field in vivo as bio fluent consuming nature, in vivo condition the relationship between the metal matrix and mounting under load is not fully understand till now Another category of materials is ceramics that have a strong biocompatibility and an improved vulnerability to corrosion. These ceramics are used in great extent now a days in changing of hip, tooth implants, valves of heart, filler of bones and scaffolds for tissue optimization, these have some disadvantages also like their brittleness, elastic modulus is high and can easily deform as they have less plasticity. Additionally, they left out ions in the body of humans when they are exposed to oxygen, and that can indicate to the implant’s degradation[33]. For load-bearing applications, alumina and zirconia are regarded as alternative options for metallic materials as they do not illustrate corrosion in the human body and also possess heavy wear opposition. Nevertheless, mechanical defects of these metallic implants are also recorded and additional work and study is therefore required in order to suggest these material groups for actual purposes. Biologically functional crystal founded in 1969 and is still commonly used for bone maintenance and bone rejuvenation. Fused quartz, aluminosilicates, certain borosilicate, alkali-resistant glass, soda-lime glass, titanium frit, arsenic trisulfide, aluminosilicates of magnesium and lithium and glass ceramics seem to be better allowable and adequate for the firmly implanted tissue. Although they show a little bit of corrosion and a much more sensitive technique is yet to be developed to examine low glass corrosion rates[34]. At the atomic level, it should be understood several conversations previously mentioned which give rise to biological corrosion. Although there are guidelines present for testing the corrosion efficiency of the materials being produced, the approach followed by various research groups often varies. A standardized approach must be followed to compare and contrast of the various groups operating towards this end. Since the in vitro test can only be regarded as a screening test because it cannot represent the actual sketch, a simulator has to be formed by all kinds of amenities to calculate corrosion in the simulated body situation such as hip simulator and knee simulator that are frequently accustomed only to check the tribological characteristics of the components. The existing simulators that are used must also involve research facilities to calculate tribological corrosion, in order to attain the real image of the different methods are taking place over time. Although there are lots of results showing the harmful effects of corroded goods, yet a technique needs to be implemented to determine the exact compositions, the form of the metal that will cause contamination and other harmful impacts. The biomedical implants often undergo surface alterations to enhance corrosion defiance, wear and tear defiance and surface shape and biological compatibility[35]–[37]. All of the changed layers will inevitably be checked for their corrosion demeanour aside from enhancing other desirable characteristics. A full knowledge of intercourse that take part on the atomic situation on the layer of metallic implant, the implant and the environment of the human body that involve various types of small movements of the metallic implant inserted in the body of human must be observed cautious in detailed manner to get implants that can prolong for coon's age in humans. Now a days various biological and mechanical dereliction are seen in the surgical operations due to corrosion in orthopaedic implants but it also provides an opportunity to the future development of biomaterials. Most of the alloys which are generally used as an implant at present were modified 60-80 years ago; not for the implant in body but for the other applications such as automation, electrical and electronics equipment. These were not precisely designed to use as an implant. Although this concept is changing now. At present biomaterial implant depends upon two major factor which are engineering material science and biology. Any development in the medicinal and biological field will give us a crystal-clear image on the geometry and performance of many different organs and tissues in microscopic levels. Interaction of biomaterial will lead the vision of various newly formed alloys in detail. The past refinement in modelling of material will guide the researchers to increase the speed of development of the modern alloys and biomaterials. The area of corrosion in biological system is new and fruitful as men know very less about their anatomy and its communication with non-native particle is so much more complex and the task or research will be going on.

Conclusion

As compared to stainless steel and alloys of cobalt; the use of Ti alloys in biomaterials is increasing day by day because of its low modulus, fantastic biocompatibility and increased resistance to the corrosion. Due to these appealing properties, commercially pure α Ti alloys and (α+β) Ti alloys were introduced earlier and β Ti alloy is developed recently which is stable for orthopaedic applications. The Ti alloys holds increased biocompatibility, control strain and resistant to repetitive load. Various improvements are shown in β Ti alloys for wear resistance when a comparison is made between β and α+β Ti alloys. After all, more research and thorough development is required to use Ti alloys as orthopaedic implant in the case of wear and its mechanism.

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