A Review on Surface Coatings on 316L Stainless Steel to Improve Biomedical Properties

Goutham Murari V P
Centre for Nanoscience and Nanotechnology, Sathyabama University, Chennai, Tamilnadu, India

Abstract - Stainless steel 316L has widely used as bioimplants in cranial plates, dental implants, bone fracture fixation, prothestic joints. However, low wear resistance, in some cases susceptibility to pitting and crevice corrosion in body environment and release of toxic ions from the surface are the basic disadvantages which this material prone to be. It has still applied as a temporary biomaterial due to its excellent mechanical strength, acceptable corrosion resistance, good formability and cost-effectiveness. Surface engineering aims to improve surface-dominated properties, like resistance to corrosion, ion release or wear, without compromising the mechanical properties of the bulk. In this paper, some of methods for the surface coatings of the stainless steel as a biomaterial are reviewed.

Keywords: 316 L Stainless steel, surface engineering, coating.

I. INTRODUCTION

Biomaterials are commonly characterized as materials used to construct artificial organs, rehabilitation devices, or implants to replace natural body tissues. Biomaterials definitely improve the quality of life for an ever increasing number of people each year. The range of applications is wide and includes joint and limb replacements, artificial arteries and skin, contact lenses and dentures. To successfully apply implants in the human body, an adequate level of tolerance of the material used with the living organism is required, in other words a high grade of biocompatibility. Biocompatibility has been defined as ''the ability of a material to perform with an appropriate host response in a specific application'' [1, 2]. This means that the material or any leachable products from it do not cause cell death, chronic inflammation or other impairment of cellular or tissue functions. Mechanical property is the primary aspect for hard tissue replacements, to establish the mechanical formation of an implant. However, to achieve a high grade of compatibility of a material system with the host tissue, key factors are surface determined such as biocompatibility and corrosion resistance. Indirectly these surface factors also effect mechanical behaviour such as stress shielding, wear debris or fatigue failure. But most importantly, the surface of the synthetic device is in direct contact with the living organism. Therefore major attention must be paid to the surface of a material system as its reaction with the host tissue is often decisive on success or failure of implantation [3].

In the past few decades, increase in the utilization of self-operating machines, participation of many persons in sports, defence activities, increased interest in motorcycles and bicycles, and day-to-day increasing traffic, has resulted in enormous increase in the number of accidents. This has necessarily led people to opt for orthopaedic implants for early and speedy recovery and resumption of their routine activities [4]. Chemical stability, mechanical behaviour and biocompatibility in body fluids and tissues are the basic requirements for successful application of implant materials in bone fractures and replacements. Corrosion is one of the major processes affecting the life and service of orthopaedic devices made of metals and alloys used as implants in the body. Currently, orthopaedic implants make up the bulk of all devices implanted (approximately 1.5 million per annum worldwide) at a cost of around $10 billion [5]. Many researchers have looked for methods that will cost-effective 316 L stainless steel make good enough, especially for temporary implants, but also to create opportunities for the safe use of this material for permanent implants. The aim of this paper is to present current research in the field of surface engineering that improve the properties of AISI 316L stainless steel for medical application.

II. 316 L STAINLESS STEEL AS A BIOMATERIAL

Austenitic type AISI 316L stainless steel (SS) is a low-carbon version of the AISI 316 SS used extensively in many purposes due to its very good corrosion resistance, smoothness, biocompatibility and clean ability after electro polishing treatment. Stainless steel AISI 316LVM is molybdenum alloyed vacuum remelted stainless steel for the production of both temporary and permanent implants Beside its enormous application in the nuclear and processing industry, it has widely used for implants (orthopaedic fixation plates, screws, dental prostheses, vascular stents). 316LVM (using the American iron and steel industry nomenclature), is a more expensive than AISI 316L and posses higher corrosion resistance due to its purer structure. AISI 316L SS has reasonable corrosion resistance, biocompatibility, tensile strength, fatigue resistance, thus making this material a desirable surgical-implant material. SS is a widely used cost-effective orthopaedic implant material for internal fixation because of its mechanical strength and the possibility of bending and shaping the implant. Examples of SS applications include aneurysm clips, bone plates and screws, femoral fixation devices, intramedullary nails and pins, joints for ankles, elbows, fingers, knees, hips, shoulders and wrists [6]. However, major disadvantages of SS are well-documented. Upon prolonged contact with human tissue (elevated temperature and saline conditions) surface corrosion phenomena takes place resulting in a high rate of locally and systemically released corrosion products [7]. Release of large amount of certain metal ions may lead to harmful deceases [8]. The ions released from SS are mostly of iron, nickel and chromium. Specially nickel is recognized as a strong immunological reaction medium and may cause hypersensitivity reactions, contact dermatitis, asthma, and moderate cytotoxicity [9]. Keeping in mind previous considerations, SS is mostly used for temporary orthopaedic implants such as bone screws, plates and implanted medical devices, besides surgical instruments. Time period for bone healing, over which the host is exposed to the bone screw/plate is 3–12 months [10].

Principally, the nature and stability of a passive film on a particular biomedical metal or alloy depend on the environmental conditions, such as the composition of the electrolyte, the redox conditions, the exposure time and temperature. Depending on the type of oxide formed, the passive film may or may not remain stable and hence sustain passivity upon exposure to the biological environment. Under certain conditions, localized breakdown of passivity takes place, leading to fast dissolution at the site of breakdown. Localized corrosion typically starts at sites characterized by inhomogeneities either in the material, or in the surrounding environment. Even though most of the surface is still covered by the intact passive film, the corrosion rate at locally activated sites can reach very high values. Localized corrosion may thus lead to unexpected deterioration of the whole system with disastrous consequences, although the total mass loss is actually small. Therefore, localized corrosion processes are more dangerous in nature and far less easy to predict than uniform corrosion [11].

The passive state of a metal can be prone to localized instabilities, under certain circumstances. Localized corrosion is triggered by specific aggressive anions (halogenides) and typically starts at sites characterized by inhomogeneities either in the material, or in the surrounding environment. The final result is the formation of an active pit in the metal, an example for localized breakdown of passivity. Even though most of the surface is still covered by the intact passive film, the corrosion rate at locally activated sites can reach very high values. Localized corrosion may thus lead to unexpected deterioration of the whole system with disastrous consequences, although the total mass loss is actually small. Therefore, localized corrosion processes are more dangerous in biomedical applications and far less easy to predict than uniform corrosion [12]. Corrosion can have two effects: the first, the implant may weaken and the premature failure of the implant will occur; the second effect is the tissue reaction leading to the release of corrosion products from the implant. No metallic material is totally resistant to corrosion or ionization within living tissues.
Orthopaedic implants include both temporary implants such as plates and screws and permanent implants that are used to replace hip, knee, spinal, shoulder, toe, finger etc. The corrosion mechanisms that occur in temporary implants are crevice corrosion at shielded sites in screw/plate interface and beneath the heads of fixing screws and pitting corrosion of the implants made of SS [13, 14]. The main cause for the failure of the orthopaedic implants is wear, which in turn is found to accelerate the corrosion [15].

Studies on retrieved implants show that more than 90% of the failure of implants are due to pitting and crevice corrosion attack [16, 17]. These localized corrosion attacks and leaching of metallic ions from implants necessitate improvement in the corrosion resistance of the currently used type 316L SS by bulk alloying or modifying the surface [4].

There has been a constant attempt by engineers and scientists to improve the surface-related properties of biomaterials to reduce the failure of implants due to poor cell adhesion and leaching of ions due to wear and corrosion [18]. The various surface modification techniques used for bioimplants have been reviewed by Anil Kurela et al. [19] and Bauer et al. [3]. Preventing corrosion using inhibitors is not possible in an extremely sensitive and complex bio system and hence several surface passivation and coating methods have been adopted. The techniques such as chemical treatment, plasma ion implantation, plasma source ion implantation (PSII)), plasma electrolytic oxidation (PEO), laser melting (LSM), laser alloying (LSA), laser nitration, ion implantation, and physical vapor deposition (PVD) and also surface texturing are widely applied for surface engineering of SS. However, each of these methods also has some limitations.

III. SURFACE ENGINEERING

Mechanical properties of materials used for biomedical devices and components are the primary aspect for hard tissue replacements. They are the most important for establishing mechanical formation of implants. However, to achieve a high grade of compatibility of a material system with the host tissue, key factors are surface determined, such as biocompatibility and corrosion resistance. Indirectly, these surface factors effect mechanical behaviour such as stress shielding, wear debris or fatigue failure. Therefore major attention must be paid to the surface of a material system as its reaction with the host tissue is often crucial on success or failure of implantation. On the other hand, surface characteristics such as roughness, topography and chemistry play a pivotal role in specific cell responses such as attachment, migration, proliferation and differentiation of connective tissue progenitor cells. Consequently, surface modification can be a key technology to enhance the in vivo performance of biomaterials. Proper surface modification techniques not only retain the desired bulk attributes of biomedical materials, but also improve specific surface properties required by different clinical applications. The influence of surface roughness on the rate of osseointegration and biomechanical fixation of hard tissue implants has been identified as a key factor. Mainly surface topographies at the micron level were reported as important and several surface modification techniques operating at this length scale were developed [3].

The goal of surface engineering is not only to fit the demands of avoiding negative effects of implanted materials on the surrounding tissue but even more to enhance the interplay between the designed technical material and the living matter. There are pretty number of methods for improving biocompatibility of the 316 L SS, which can be classified as mechanical, chemical, heat treatment, electrochemical and coating technologies. A variety of surface treatments and coatings are commonly performed on medical implant materials to promote corrosion and wear resistance and biocompatibility.

3.1. Coating

Coating is a logical way to enhance surface-dominated properties, like resistance to corrosion, ion release or wear, without compromising the mechanical properties of the bulk [20]. The long-term performance of the coating/substrate system, however, may be challenged by the loss of the mechanical integrity of the coating because maximum stresses during use occur at the surface, hence the need to develop “hard yet tough” coatings when considering load-bearing engineering applications. In this context, the toughness of the coating is as important as, if not more important than, super hardness. Particularly, calcium phosphates are known for their bioactive properties and their increased bone binding effects. Therefore, calcium phosphate coatings, similar to the mineral phase of bone, have been extensively investigated as bioactive coatings on bioinert implant materials [21-23]. For example, metal implants have been coated with layers of calcium phosphates mainly composed of hydroxyapatite. While hydroxyapatite resembles in its chemical structure apatites, carbonate apatite comprises a chemical composition that is more close to the human bone. F.-H. Lin et al. [24] employed chemical method to establish and induce a bioactive HAp layer on the surface of 316L SS. When the metallic substrates treated with 10 M NaOH aqueous solution and subsequently heated at 600°C, a thin sodium chromium oxide layer was formed on the surfaces as the linking layer for HAp and 316L SS.

D. Gopi et al. [25] reported a successful electro deposition method for coating hydroxyapatite (HAp) onto surgical grade SS. Pure HAp coatings could be achieved and the coating resistivity was assessed by potentiodynamic polarization and impedance techniques which showed that HAp coatings deposited onto the borate passivated SS specimens possess maximum bioresistivity in Ringer’s solution. The coatings were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Atomic force microscopy (AFM). The results have showed that the borate passivation followed by HAp coating performed on 316L SS could enhance the longevity of the alloy in the simulated body solution (Ringer’s solution).

J. Tavares et al. [26] presented a novel plasma treatment involving the deposition of ethylene glycol plasma polymer-coated titanium nanoparticles on a 316L SS surface. The deposition of ethylene glycol plasma polymer-coated nanoparticles confers properties to the surface making it more biocompatible, which is beneficial in applications of SS 316L as a blood-contacting implant (e.g. vascular stents, heart valves). These properties include increased hydrophilicity and general corrosion resistance of the surface, and reduced substrate-dependent denaturation of adsorbed protein fibrinogen.

Methods such as physical vapour deposition coating (TiN, TiC), ion implantation (N^+), thermal treatments (nitriding and oxygen diffusion hardening), and laser alloying with TiC have been examined for improving wear. Ion implantation has been the most common treatment employed.

V. Muthukumaran et al. [27] AISI 316L SS implanted with two different ions: nitrogen and helium. The crystallographic orientation and surface morphology were studied using X-ray diffraction (XRD) and scanning electron microscope (SEM). The effects of ion implantation on the corrosion performance of AISI 316L SS was evaluated in 0.9% NaCl solution using electro chemical test both on the virgin and implanted samples. The subsequent Tafel analysis showed that the ion implanted specimens were more corrosion resistant when compared to the bare specimens. The results of the studies indicated that there was a significant improvement in both corrosion resistance and hardness of implanted samples.

In recent years, attention has also focused on the use of Nb and Ta as implant materials due to their outstanding biocompatibility, superior corrosion resistance and excellent fatigue properties. However, in the pure form, Nb is mechanically weak. This inadequacy in strength has excluded their use for the construction of load-bearing prosthetic materials, although strengthening can be achieved through the application of powder metallurgy techniques. An alternative method to benefit from the biocompatibility of Nb, without any sacrifice in overall component strength, is to deposit Nb on suitable substrate. Here the rationale assumes that the substrate provides the necessary mechanical properties associated with load-bearing implants, while the Nb coating provides enhanced biocompatibility and corrosion resistance [28, 29].

M. Omrani et al. [30] reported the results of TiN-ions implantation into the SS 316L samples as bipolar plates, Plasma Focus device operated with nitrogen gas for 10, 20, and 30 shots in order to improve the corrosion resistance and electrical conductivity of samples. The corrosion potential of the TiN coated samples increased compared to the bare SS 316L and corrosion currents decreased in TiN implanted samples. The thickness of coated layer which was obtained by cross sectional SEM was about 19 nm.

Polymer coatings can be used for fabrication of protective coatings on medical devices too. One of the polymers used today for medical devices is parylene (poly-para-xylylene) due to its excellent biocompatibility and possibility to form a thin, continuous and inert film [31]. Pre-treatment with the organic silane A174 prior to parylene coating is the recommended surface preparation. Basically, silane is used as an adhesion promoter owing to its intermediate character and thus can serve as an electrostatic glue between inorganic (metal surface) and organic (parylene coating) interfaces [32]. The corrosion resistance of a two-layer polymer (silane+parylene) coating, on implant SS was investigated by microscopic observations and electrochemical measurements. Long term exposure tests in Hank's solution revealed that the coating can be successfully used for corrosion protection. However, the addition of H_2O_2, simulating the inflammatory response of human body environment causes a dramatic destruction of the protective coating [33].

Nanostructured films were deposited on conductive substrates (SS foils and graphite) and exhibited a fibrous, crack free and porous microstructure with pore size in the range 10–100 nm. It was suggested that the porous structure of manganese dioxide deposits was beneficial for ionic conductivity, whereas CNT could provide improved electronic conductivity MnO_2/CNT composite deposits obtained by electrophoretic co-deposition (deposition voltage 15 V) from a sodium alginate solution [34].

Y. Liu et al. [35] evaluated **s**ilver **n**anoparticle/**p**oly(DL-lactic-co-glycolic acid) (PLGA) coated 316L stainless **s**teel **a**lloy (SNPSA) as a potential antimicrobial implant material. From a materials and device development perspective, SNPSA exhibited strong bactericidal and osteoinductive properties that make it a promising pharmaceutical material in orthopedic surgery. Their results indicated that silver nanoparticle/PLGA coating is a practical process that is non-toxic, easy to operate, and free of silver nanoparticle aggregation too. In addition, the results revealed that the antibacterial and osteoinductive activities of SNPSA are silver-proportion-dependent, raising the interest in increasing the silver proportion of the coating in future investigations.

Novel biomaterial surfaces with antibacterial Ag agents and a wear-resistant S-phase have been generated on SS by duplex plasma silvering–nitriding techniques for application to load-bearing and other medical devices. A silver and nitrogen alloyed duplex surface system was developed for the first time by two-step plasma alloying: DG plasma silvering followed by active screen plasma nitriding. The Ag wass embedded in a hard substrate (Fe_4N and nitrogen S-phase). The surface roughness, hydrophilicity, surface free energy and N content were found to be increased by the duplex plasma process. The remaining presence of silver on the surface under a scratching was confirmed and the wear resistance of the Ag/N duplex alloyed surface was more than two orders magnitude higher than that of untreated 316LVM SS. Thus a duplex surface system that combines bacterial inhibitory and wear-resistant properties might provide long-term antibacterial function for load-bearing biomedical surfaces [36].

With a view to developing a smart coating combining both biocompatibility and corrosion resistance over bioimplants, polypyrrole/TiO_2 nanocomposite coatings were electrochemically synthesized by cyclic voltammetric technique on 316L SS in an aqueous solution of oxalic acid. The results showed that the nanocomposite coatings exhibited superior biocompatibility and enhanced corrosion protection performance over 316L SS than that of pure polypyrrole coatings [37].

C. Garcia et al. [38] experimented hybrid coatings such as hydroxyapetite, bioactive glass and glass ceramic particles on 316L stainless steel. After 10 days of immersion in SBF, the glass ceramic double layer coating has better corrosion resistance than after 24h. This likely indicates that the dissolution products are blocking effectively the electrochemical process at the pores and the defects of the coating, acting as a protective layer against corrosion and ion diffusion. The three kind of particles used, showed bioactive signals since they induced the formation of a HA film after some time of immersion in SBF. This reactivity depends on the particle size; the larger the size, the slower the reactivity of the particles containing coatings.

A. Balamurugan et al. [39] reported increase in corrosion resistance of titania coated on 316L stainless steel. Gel titania films can have a beneficial and desired effect on corrosion behavior of 316L SS and decrease the corrosion current density that is a distinct advantage for prevention of ion release. SEM, XRD, FT-IR results confirmed the uniform coating and presence of uniform coating. The corrosion kinetic parameters show a considerable increase in the corrosion resistance for the coated steel samples in comparison to the pristine steel substrates.

M.H. Fathi et al. [40] evaluated corrosion behavior of hydroxyapatite and titanium coatings on 316L stainless steel. The samples were coated using plasma spraying technique and physical vapour deposition. The coatings were tested using SEM, XRD, EDX for microstructure and morphology. The electrochemical potentiodynamic polarization was done to determine the corrosion behaviour. This double layer coating showed a positive effect on improvement of corrosion behaviour. The current densities were decreased for this double layer coating when compared to current densities of uncoated samples and HA coatings on 316L stainless steel.

IV. CONCLUSION

In recent years, surface modification and coating of AISI 316L stainless steel has been recognized as one of the main directions of implant material development and various methodologies and techniques have been tried. Among the most promising methods are surface coatings with multi-layered thin films, bioglass and silver coatings and biocompatible nano-composite layers. Different studies have pointed out that plasma electrolytic techniques, such as plasma electrolytic oxidation can potentially provide beneficial surface modifications to a range of steels, but further research are needed to introduce this procedure from research to an application level.

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